Conditions for the Formation of Fe_3O_4 by the Air Oxidation of $Fe(OH)_2$ Suspensions.

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The optimum conditions were studied for the formation of Fe_3O_4 by the air oxidation of $Fe(OH)_2$. The suspensions obtained by mixing NaOH and $FeSO_4$ solutions in various values of $R(=2NaOH/FeSO_4)$ were subjected to oxidation with air at various temperatures. The oxidation products were then examined by X-ray powder diffraction, chemical analysis, electron microscopic observation, and BET surface-area determination. Fe_3O_4 is formed at higher temperatures than is FeOOH. The temperature of formation becomes low as R approaches 1.0. In neutral suspensions ($R<1$), Fe_3O_4 is formed *via* green rust II or a mixture of green rust II and $Fe(OH)_2$. By further oxidation, the Fe_3O_4 formed gradually changes to γ-Fe_2O_3. A mixture of α-FeOOH and either $NaFe_3(OH)_6(SO_4)_2$ or α-Fe_2O_3 is formed as the final oxidation product. In alkaline suspensions ($R>1$), Fe_3O_4 is formed directly. The morphology and ferrous-ion content of Fe_3O_4 powder change considerably with the presence of green rust II before the formation of Fe_3O_4. It is suggested that Fe_3O_4 is formed near the surface of the particles of $Fe(OH)_2$ and green rust II by the coprecipitation of ferrous ions with ferric hydroxo-complexes.

The formation of iron oxides and oxyhydroxides, such as α-Fe_2O_3, γ-Fe_2O_3, Fe_3O_4, α-FeOOH, β-FeOOH, γ-FeOOH, and δ-FeOOH, has thus far been achieved by means of wet methods, such as the hydrolysis and oxidation of iron salt solutions. α-FeOOH, β-FeOOH, and α-Fe_2O_3 have been obtained by the hydrolysis of ferric salts.[1-7] A mechanism of hydrolysis was suggested on the basis of the spectrophotometric and magnetic properties of the ferric complexes present in the solution prior to the formation of precipitates.[8]

δ-FeOOH is formed when $Fe(OH)_2$ is oxidized rapidly in an alkaline solution by the addition of hydrogen peroxide.[9,10] If oxidation is carried out slowly by passing air into a suspension obtained by mixing ferrous salt and alkaline solutions, α-FeOOH, γ-FeOOH or Fe_3O_4, or a mixture of them is obtained according to the pH, the temperature, and the kind of anion present.[11-15] Feitknecht proposed the following mechanism:[16] (1) γ-FeOOH, δ-FeOOH, and γ-Fe_2O_3 are formed by the surface oxidation of green rust, $Fe(OH)_2$, and Fe_3O_4 particles respectively. (2) The formation of α-FeOOH proceeds in a liquid phase of suspension. (3) The formation of Fe_3O_4 takes place by the surface oxidation of the green rust particles in a neutral suspension medium. The formation can also take place in a liquid phase of alkaline suspension. From crystallochemical considerations, Bernal *et al.* suggested that the reaction of solid phase proceeds topotaxially in the particles of intermediate oxidation products.[17]

These theories hold except for the formation of γ-FeOOH and Fe_3O_4. The presence of green rust is not indispensable for the formation of γ-FeOOH.[18-20] In this paper, the conditions and the mechanism of the formation of Fe_3O_4 will be given.

Experimental

Material. Chemical reagents of an analytical grade were used. The air for stirring and oxidation was bubbled through washing vessels containing a KOH solution to remove carbon oxides and dust. Distilled water into which nitrogen had been bubbled at the boiling point for 2 hr to remove any dissolved oxygen was used.

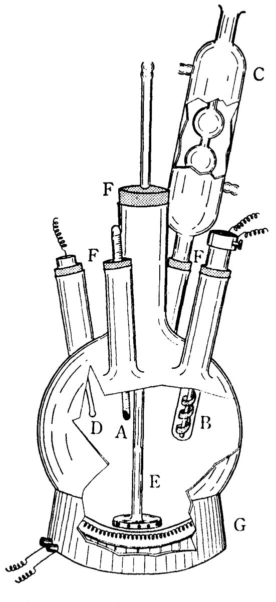


Fig. 1. The reaction vessel.
A: Thermometer, B: Temperature regulator, C: Reflux condenser, D: Electrode for self-recording pH meter, E: Glass tube, F: Rubber stopper, G: Electrical heater.

Apparatus. Figure 1 shows the reaction vessel specially constructed for the air-oxidation experiments. A spherical flask with a capacity of about 4 l is fitted with five inlet necks. A glass tube (E) with a flat end having eight holes (0.1 cm in diameter) at equal intervals is kept in contact with the bottom of the flask. The temperature regulator (B) consists of a spiral bimetal strip dipped in oil in a glass tube. Since the $Fe(OH)_2$ suspension in the flask is thoroughly stirred with air, a small portion (50—100 ml) taken out of the suspension can be considered to be an appropriate sample.

Procedure. The suspensions of $Fe(OH)_2$ were prepared by adding various amounts of a NaOH solution to 1 l of 0.72 M-$FeSO_4$ in each flask, the total volume of each suspension then being made 3 l with water. The suspensions in the flasks were quickly heated to the desired temperatures. Nitrogen was passed through the suspension from the eight holes at a rate of 1 l/min to prevent bumping and oxidation. When the suspension reached the desired temperature, compressed air was passed through in place of nitrogen. The temperature was kept constant during the course of oxidation.

The oxidation conditions were confined as follows: a) The $R(=2NaOH/FeSO_4)$ molar ratio was kept at 0.1—4.0. b) Air was passed through at a rate of 200 l/hr. c) Oxidation was carried out at temperatures between 5 and 85 °C. The oxidation product was collected on filter paper, washed with water, and then dried at about 50 °C under reduced pressure.

Analysis of the Oxidation Product. The amounts of ferrous and ferric ions were determined by chemical analysis. The ferrous-ion content was determined by means of $KMnO_4$ titration after the sample had been dissolved in dilute H_2SO_4 by heating under a nitrogen atmosphere. The total iron content was determined by the gravimetry of the precipitate obtained from the solution prepared by the dissolution of the sample in a mixture of dilute HNO_3 and HCl solutions by heating.

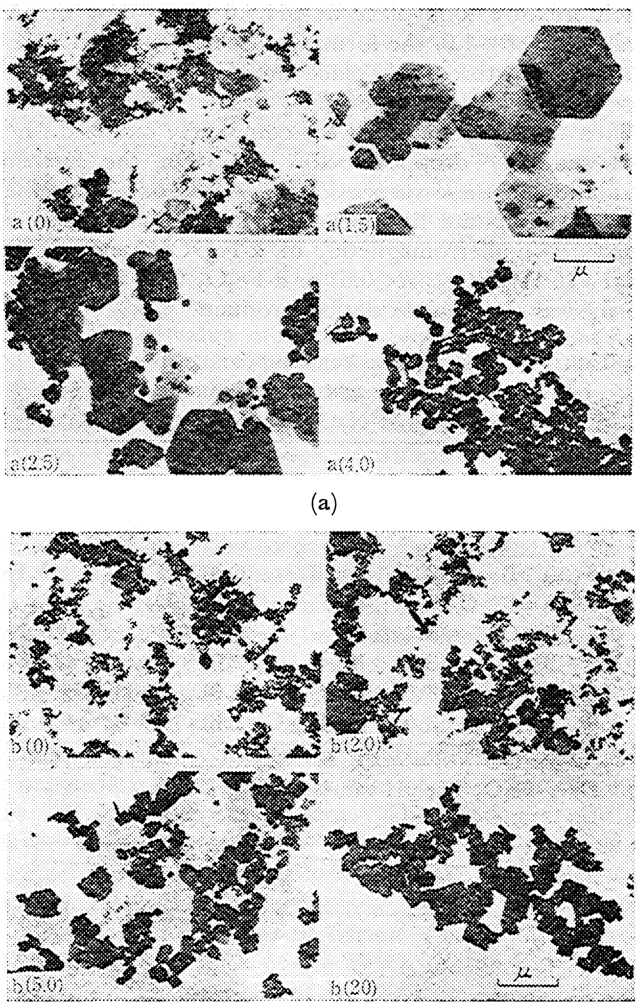
The samples were examined by means of X-ray diffraction using FeKα radiation. By means of electron microscopic examination, it was found that FeOOH particles are needle-like, while Fe_3O_4 particles are spherical, cubic, and octahedral. The presence of a small amount of FeOOH was detected by electron-microscopic examination. For the sake of confirmation, the samples found by X-ray analysis to consist only of Fe_3O_4 were subjected to electron-microscopic examination. When $Fe(OH)_2$ and green rust remained in the suspension, the wet precipitate obtained by filtration was also subjected to those examinations. In order to prevent oxidation during X-ray analysis, the wet precipitate was sealed with cellophane tape.

The mean particle size of the samples was estimated from their surface area as measured by the BET method using nitrogen gas.

Results and Discussion

Formation of Fe_3O_4. Precipitates were formed when NaOH and $FeSO_4$ solutions were mixed: (a) When the amount of NaOH was insufficient ($R<1$), the resulting whitish suspension was neutral (pH 7—9). The precipitate was usually amorphous, but the precipitate in the suspension with $R<0.6$ changed to a crystalline precipitate of ferrous basic sulfate when subjected to aging in an inert gas.[21] (b) When excess NaOH ($R>1$) was added, the suspension became alkaline (pH>10) enough to give a white precipitate. The precipitate in (b) consisted of fine crystal particles of $Fe(OH)_2$, the size of which increased with the NaOH concentration.

The black ferromagnetic precipitate (Fe_3O_4) was formed by the oxidation of the suspension at higher temperatures than was the yellowish brown and non-ferromagnetic precipitate (FeOOH). The process of the Fe_3O_4 formation in (a) differs from that in (b). Electron-micrographs of the precipitates formed at 70 °C in the course of oxidation, corresponding to the R values of 0.5 and 2.0, are shown in Figs. 2(a) and (b) respectively. After 90 min, a whitish precipitate (Fig. 2(a(0)) was oxidized; thereafter it turned dark green. It consists of hexagonal particles (a(1.5)), the pH of the suspension being reduced from 7.2 to 6.5.* About 40% of the total iron ions were ferric ions in the precipitate, and its X-ray diffraction data agreed with those of green rust II (hexagonal crystal unit cell, a 3.17 and c 10.7 Å).[17] The precipitate of Fe_3O_4 began to be formed at pH 6.5. After 4 hr, green rust II was transformed into Fe_3O_4 and a small amount of α-FeOOH, the former being spherical and the latter needle-like (Fig. 2(a(4.0)), the pH being suddenly reduced from 6 to 3.7. On the other hand, distinct octahedral and cubic particles of Fe_3O_4 were obtained directly from the alkaline suspension of $Fe(OH)_2$(b (0), (2), (5), and (20), Fig. 2). The appreciable difference in particle shape between the precipitates of $Fe(OH)_2$ and green rust II, and the precipitate of Fe_3O_4 indicates that the formation of Fe_3O_4 does not take place by the surface oxidation of the particles of $Fe(OH)_2$ and green rust II.



(a)

(b)

Fig. 2. Electron micrographs of the precipitates during the course of oxidation at 70 °C. (a) $R=0.5$; (0) amorphous, (1.5) green rust II, (2.5) green rust II> Fe_3O_4, (4.0) $Fe_3O_4 \gg \alpha$-FeOOH. (b) $R=2.0$; (0) $Fe(OH)_2$, (2.0) and (5.0) mixtures of $Fe(OH)_2$ and Fe_3O_4, (20) Fe_3O_4.

Number in parentheses indicates the time of oxidation in hr.

In the case where $R<0.6$, all the whitish precipitate turned to green rust II, irrespective of the oxidation temperature. The formation of Fe_3O_4 or FeOOH, or

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* When the suspension was not stirred, its pH decreased to about 5.

their mixture took place at pH 6.0±0.5. For the R values of 0.6—1.0, the formation of Fe_3O_4 or FeOOH, or their mixture took place at pH 7—9 due to the presence of colloidal $Fe(OH)_2$ besides green rust II. When these precipitates were completely oxidized, the pH suddenly dropped below 4.5. On the further oxidation of these suspensions at 70 °C or above, the Fe_3O_4 precipitate disappeared very gradually, and a mixture (nonferromagnetic) of α-FeOOH and either $NaFe_3(OH)_6(SO_4)_2$($R<0.6$) or α-Fe_2O_3($0.6<R<1$) was formed as the final oxidation product.

Table 1. Precipitates formed during the course of oxidation of the suspension containing 0.24 M–$FeSO_4$ and 0.48 M–NaOH at 40, 70, and 85 °C

Oxidation time (hr)	40 °C		70 °C		85 °C	
5	A>B	(8.5)	A≈B	(6.4)	B	(4.1)
8	A≈B>C	(8.4)	B	(3.6)	B	
25	B>C	(4.1)	B	(3.3)	B	(3.1)
150	B>C	(3.7)	B≫C	(2.9)	B≫D	(2.6)
300	B>C	(3.6)	B≫C>D	(2.9)	B≈D≫C	
750	B>C	(3.5)	B≈D>C	(2.8)	D≫C	(2.6)

A=$Fe(OH)_2$ B=Fe_3O_4 or γ-Fe_2O_3 C=α-FeOOH D=α-Fe_2O_3 The pH values are in brackets.

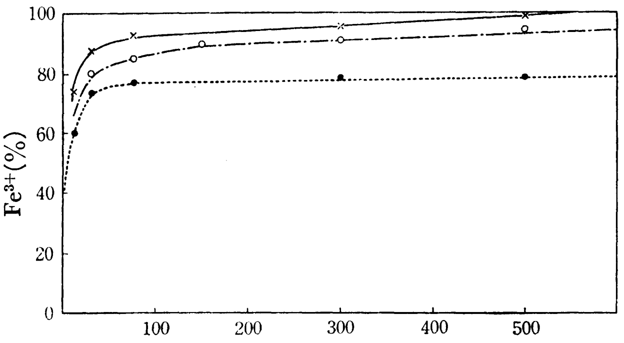

Fig. 3. Change in the ferric ion content of the suspension given in Table 1 with time. Temperature of oxidation: 40 ···●···, 70 ○—○ and 85 °C ×—×.

In order to study the formation and the decomposition of Fe_3O_4, the suspension with $R=1.0$ was oxidized at 40, 70, and 85 °C for a very long time. Table 1 shows the precipitates present in the suspension, together with the pH values at different times. The ferric-ion contents of the suspension are plotted against the time in Fig. 3. When the pH remained in the 7—9 range, the rate of oxidation was great because of the presence of $Fe(OH)_2$. When the precipitate of $Fe(OH)_2$ was completely oxidized to Fe_3O_4 or a mixture of Fe_3O_4 and α-FeOOH, the pH dropped below 4.5 and the changes in pH and ferric-ion content became very slow. By oxidation at 40 °C, a small amount of α-FeOOH is formed in addition to Fe_3O_4, the composition of the precipitate being nearly independent of the oxidation time. Fe_3O_4 is gradually oxidized to γ-Fe_2O_3 at 70 and 85 °C, since the surface oxidation of the Fe_3O_4 particles takes place topotaxially. The black color remained unchanged until the ferrous-ion content decreased to about 10% of the total iron ions. Electron-micrographs of the precipitates during the course of oxidation at 70 and 85 °C are given in Fig. 4. Electron microdiffraction showed that the X-, Y-, and I-shaped particles were all α-FeOOH. The spherical particles below 0.2 μm in size were of the spinel type (a solid solution of γ-Fe_2O_3 and Fe_3O_4), and the bigger ones, α-Fe_2O_3. This indicates that α-FeOOH and α-Fe_2O_3 are formed on the further oxidation of the particles (the solid solution) in an acidic solution. This might result from the hydrolysis of the ferric hydroxo-complexes formed by the dissolution of the precipitate of γ-Fe_2O_3, which is unstable in an acidic solution.

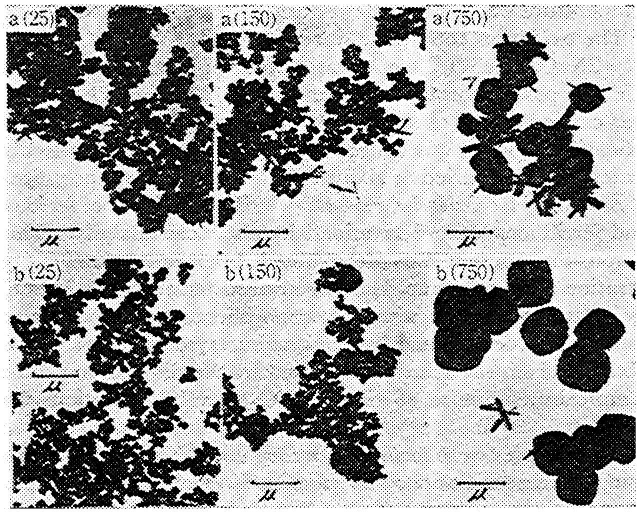

Fig. 4. Electron micrographs of the precipitates during the course of oxidation at 70 (a) and 85 °C (b). Number in parentheses indicates the time of oxidation in hr.

A kinetic study of the aerial oxidation of mixtures of $FeSO_4$ and NaOH solutions was made by Miyamoto.[22] He found that the oxidation of the suspensions proceeds in proportion to the time, irrespective of the R values. This could be explained by considering the fact that oxidation takes place in the liquid phase and not in the solid phase. In the present experiments, the ferric-ion content in the suspension increased in proportion to the oxidation time until 70% or more of the total precipitates of $Fe(OH)_2$ or green rust II had been transformed into Fe_3O_4 (or FeOOH). At a given temperature, the smaller the concentration of excess NaOH, the greater the acceleration of oxidation, in line with Miyamoto's result. The concentration of $FeSO_4$ in the neutral suspensions with $R<0.8$ slightly influenced the oxidation rate, which increased as R approached 1.0.

If the solid-phase reaction is predominant, the increase in the ferric-ion content in the suspension must be apporoximately represented by the parabolic law because the oxidation rate decreases with the increase in the thickness of the Fe_3O_4 layer on the particles of $Fe(OH)_2$ and green rust II. The fact that the oxidation of the suspension proceeds in proportion to the time indicates that the formation of Fe_3O_4 takes place in liquid phases of alkaline and neutral suspensions. The suspension medium is saturated with respect to $Fe(OH)_2$ or green rust II. When air was bubbled into the suspension, the ferrous ions in the suspension medium react with the dissolved oxygen, thus giving rise to the formation of a ferric hydroxo-complex (polynuclear complex). When the suspension is well stirred by bubbling air, the ferrous ion consumed by oxidation is incessantly supplied by the dissolution of the precipitates of $Fe(OH)_2$ and green rust II in the suspension medium. If bubbling is carried out at a constant rate, the oxidation might proceed in proportion to the time since the rate of the dissolution of oxygen is constant. The rate of oxidation is determined by the rate of the dissolution of oxygen or the precipitates of $Fe(OH)_2$ and green rust II into the suspension medium.

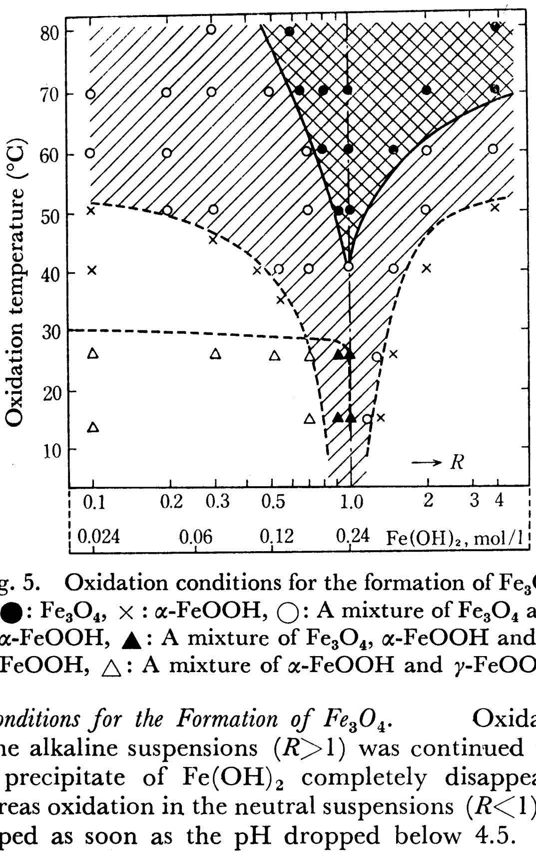

Fig. 5. Oxidation conditions for the formation of Fe_3O_4. ●: Fe_3O_4, ×: α-FeOOH, ○: A mixture of Fe_3O_4 and α-FeOOH, ▲: A mixture of Fe_3O_4, α-FeOOH and γ-FeOOH, △: A mixture of α-FeOOH and γ-FeOOH.

Conditions for the Formation of Fe_3O_4. Oxidation in the alkaline suspensions ($R>1$) was continued until the precipitate of $Fe(OH)_2$ completely disappeared, whereas oxidation in the neutral suspensions ($R<1$) was stopped as soon as the pH dropped below 4.5. The formation of precipitates is shown in Fig. 5 in terms of the temperature (ordinate) and the R value (abscissa). For the R values up to 1.0, the amount of ferrous precipitates such as $Fe(OH)_2$, formed by the addition of the NaOH solution to the $FeSO_4$ solution increases with the increase in R. The amount of ferrous precipitate in the starting suspension as calculated from the R value, is also indicated in terms of $Fe(OH)_2$ on the other abscissa. We see that the temperature at which Fe_3O_4 is formed is lowered as R approaches 1.0. Only Fe_3O_4 is formed in the upper triangular region, but FeOOH is also formed in the lower region. The influence of R on the Fe_3O_4 formation is almost symmetrical with respect to the line with $R=1.0$.

Either Fe_3O_4 or FeOOH, or their mixture, is formed in the suspension of the same value of R, depending on the oxidation temperature. Such a variety in the product formation may be due to the difference in the pH in the suspension. From the measurements of the hydrolysis constants of ferrous ions, it is generally considered that the $FeOH^-$ ion** is in equilibrium with the Fe^{2+} ion** in a neutral suspension medium or with $HFeO_2^-$ ion** in an alkaline suspension medium[23,24] and that the saturated solution of only $Fe(OH)_2$, in which most ferrous ions are present as $FeOH^+$ ions, has a pH value of 9.3 or 9.4.[25] Each particle of $Fe(OH)_2$ or green rust II in the suspension might be surrounded by a thick and dense layer of $FeOH^+$ ions. The R value most favorable for the formation of Fe_3O_4 was 1.0. The starting suspensions with the R of 1.0 had a pH of 9—10. The pH value in the layer of $FeOH^+$ ion can also be taken as 9—10.

The Fe_3O_4 particles are considered to be formed and to grow on (or in) the layer with pH 9—10 by the slow coprecipitation of $FeOH^+$ with ferric hydroxo-complexes formed by oxidation. Some of the particles of Fe_3O_4 might migrate outside the layer with pH 9—10 and be gradually oxidized to γ-Fe_2O_3. On the other hand, FeOOH may be formed outside the layer by the hydrolysis of the ferric hydroxo-complexes. Favorable conditions for the formation of Fe_3O_4 include an increase in the surface area and volume of the layer (roughly given by the product of the thickness and the total surface area of the particles of green rust II and $Fe(OH)_2$ in the suspension). The thickness of the layer might increase with the temperature, so that a temperature rise is favorable for the formation of Fe_3O_4.

Morphology and Ferrous-ion Content of the Fe_3O_4 *Powders.* Electron-micrographs of the Fe_3O_4 powders are given in Fig. 6. The particles of the Fe_3O_4 powders obtained in the neutral suspensions (A–D) are spherical and cubic (the needle-like particles are α-FeOOH); those in the alkaline suspensions (E and F) are cubic, octahedral, and orthorhombic. The mean particle size of the Fe_3O_4 powders obtained in the neutral suspensions,

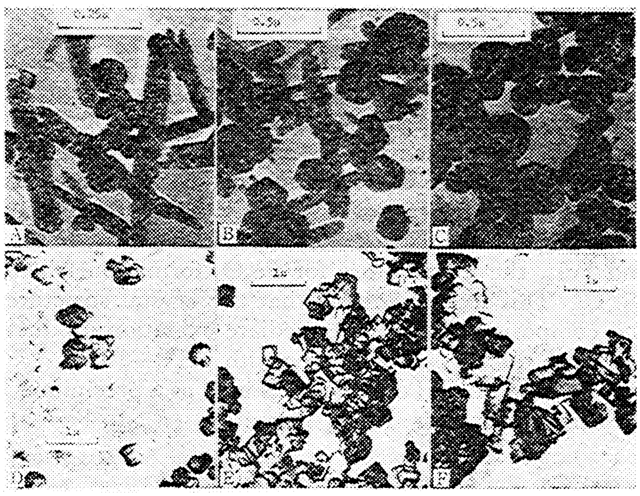

Fig. 6. Electron-micrographs of Fe_3O_4 precipitates formed by the oxidation of the suspensions at 70 °C with R values 0.1 (A), 0.3(B), 0.8(C), 1.0(D), 2.0(E) and 4.0(F). D, E and F were observed by the carbon replica method.

** H_2O ligands are omitted.

under the conditions where only Fe_3O_4 is formed, was found to be below 0.1 μm. The ferrous-ion content of the powders was less than 25% of the total iron ions, decreasing with the rise in the temperature and with the decrease in R. On the other hand, the mean particle size of the Fe_3O_4 powders in the alkaline suspensions was found to increase remarkably with the rise in the temperature and the R value, their ferrous-ion contents being about 30%. The absence of green rust II before the formation of Fe_3O_4 does not hinder the growth of Fe_3O_4 particles.

It is known that the rate of oxidation of Fe_3O_4 particles in an aqueous solution changes with the pH, the temperature, the particle size, *etc.* Oxidation may take place upon the dissolution of the ferrous ions in Fe_3O_4 particles into the aqueous solution or upon the adsorption of the oxygen atom on the Fe_3O_4 particles. In either case, the iron ions should diffuse toward the surface of Fe_3O_4 particles, thus causing oxidation. Since the oxidation of Fe_3O_4 particles takes place topotaxially, and since its rate depends on the surface area, the ferrous-ion content in each particle of Fe_3O_4 in the suspension is determined by its size. The fact that non-stoichiometric Fe_3O_4 (ferrous ion content$<$ 33.3%) was obtained in the present work might be a result of the particle-size distribution in the powder.

Additional Remarks on the Conditions for Fe_3O_4 Formation. *a)*: An air-flow rate greater or less than 100—400 l/hr was unfavorable for Fe_3O_4 formation. This indicates that the rate of movement of the particles of green rust II and $Fe(OH)_2$ in suspension affects the total surface area of the $FeOH^+$ layer with pH 9—10. When the flow rate is too small, the surface area of the layer with pH 9—10 diminishes as a result of a coagulation of the particles of $Fe(OH)_2$ and green rust II. When it is too great, the surface area of the layer with pH 9—10 diminishes as a result of the reduction of the thickness of the layer.

b): An increase in the concentrations of all ferrous ions in the starting suspension was favorable for Fe_3O_4 formation.

c): The use of $FeCl_2$, $FeBr_2$, or FeI_2 instead of $FeSO_4$ facilitated the formation of Fe_3O_4 or γ-FeOOH in the neutral suspension. The precipitate of Fe_3O_4 was formed *via* green rust I (not green rust II). The temperature for Fe_3O_4 formation could be lowered as compared with the case of $R<1$ in Fig. 5. For example, when suspensions with $R=0.5$ contained $FeCl_2$, $FeBr_2$, and FeI_2, the temperature for Fe_3O_4 formation fell to 25 °C. This might indicate that the crystal structure and composition of the intermediate oxidation product affect the thickness of the layer with pH 9—10.

d): When LiOH or KOH was used as a precipitant, the temperature for Fe_3O_4 formation ($R>1$, Fig. 5) became lower in the former and rose in the latter.

When a small amount of divalent metal ions (M^{2+}), such as Mg^{2+}, Mn^{2+}, and Co^{2+} ions, existed in the starting suspension, a ferromagnetic precipitate of $M_xFe_{3-x}O_4$ was obtained on slow oxidation. The conditions for $M_xFe_{3-x}O_4$ formation were similar to those for Fe_3O_4 formation, the amount of divalent metal ion in the precipitate depending on the pH.

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