3422 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3422—3426 (1972) [Vol. 45, No. 11

Conditions Favorable for the Formation of γ-FeOOH by Aerial Oxidation in an Acidic Suspension of Iron Metal Powder

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(Received December 2, 1971)

Dilute solutions of ferrous sulfate, sulfuric acid, hydrochloric acid, nitric acid and acetic acid in which iron powders are dispersed have been oxidized at below 80°C by blowing air into them. The resulting precipitates have been examined by means of X-ray diffraction, chemical analysis and optical and electron microscopy. When the iron powder is well dispersed, γ-FeOOH is formed with or without α-FeOOH, α-Fe_2O_3, or Fe_3O_4. The mode of formation depends on such factors as particle size, amount of iron powder, kind of anion present and temperature. Particle size greatly influences the formation of γ-FeOOH in the sulfate system, but not in the other systems.

Clarification of conditions for the formation of ferric oxyhydrate (FeOOH) would be significant with respect to the theory of mechanism of corrosion of iron. Ferric oxyhydrate has four modifications: α-, β-, γ-, and δ-forms. The first three are nonferromagnetic[1–3] and the last is ferromagnetic.[4,5] By dehydration of γ-FeOOH, which is isomorphous with boehmite γ-AlOOH, ferromagnetic ferric oxide γ-Fe_2O_3 is formed.[6,7] This drew the attention of many chemists who investigated conditions favorable for its formation. γ-FeOOH can be obtained by slow oxidation of a suspension of ferrous compound precipitated by adding alkali to excess ferrous salt solution under certain conditions.[8–10] By oxidation γ-FeOOH is always formed *via* a dark green compound called green rust I or II. Presence of the green rust has been considered to be indispensable for the formation of γ-FeOOH. However, we have found that γ-FeOOH can also be formed directly from aqueous solutions of ferrous salt ($FeBr_2$ or a mixture of $FeCl_2$ and excess NaI solutions).[11] In order to clarify the mechanism of formation of γ-FeOOH more systematical experiments are needed.

In the present paper experimental conditions favorable for the formation of γ-FeOOH in acidic suspensions of iron powder are given.

Experimental

Materials. Chemical reagents of analytical grade were used. Crushed electrolytic iron powders of 270, 240, 140, 117, 104, 74, 61, and 43μ in particle size were prepared by use of 50, 60, 100, 120, 150, 200, 250, and 325 mesh sieves, respectively. Air for stirring and oxidizing the solution containing iron powder was passed through washing vessels containing KOH solution to remove dust and organic elements.

Apparatus. An ordinary reaction vessel was found to be unsuitable, since with such a vessel the rate of precipitate formation is very low because of aggregation of the iron particles. For the sake of uniform stirring and oxidation we used a hard glass vessel 7 cm in internal diameter and 80 cm in height as shown in Fig. 1. The vessel is composed of a cylindrical tube A, a perforated plate B 0.1 cm in thickness with small holes of 0.1 cm in diameter arranged at equal distances of about 0.8 cm, and a gas holder C. The vessel is closed with a rubber D into which are inserted a temperature regulator E, a thermometer F, a quartz tube containing nichrome heater G and a water condenser H. The temperature regulator consists of a spiral bimetal dipped in oil in a glass tube.

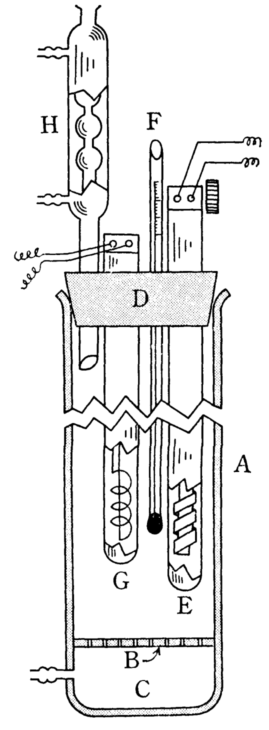

Fig. 1. Schema of reaction vessel
A: Cylindrical tube, B: Perforated plate, C: Gas holder, D: Rubber stopper, E: Thermoregulator, F: Thermometer, G: Heater, H: Condenser.

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Procedure. Compressed air was bubbled into the vessel from the bottom through the perforated plate at a rate of 100 *l*/hr by operating a cock. One liter of each acidic solution was poured into the vessel from the top, but it was scarcely observed to fall into the gas holder. The iron powder was poured into the solution and the air flow rate was increased to a certain degree. The solution in which the iron powder was dispersed was quickly heated by the nichrome heater and kept at a certain temperature. After being separated from the remaining iron particles by decantation, the precipitate was filtered, washed with water, and then dried at about 105°C. pH measurements were carried out with a Horiba electrode pH meter.

Identification. The sample thus prepared were examined by means of chemical analysis and X-ray diffraction using Fe$K\alpha$ radiation, and observed under optical and electron microscopes. The content of γ-FeOOH (R) was determined from the equation $R=I_\gamma/I_\gamma+I_\alpha$, where I_γ and I_α are the relative intensities of the X-ray diffraction lines of γ-EeOOH (d(020)6.32 Å) and α-FeOOH (d(110) 4.21 Å), respectively.

Results and Discussion

Precipitation in Sulfate Suspensions. Experiments were carried out by use of the iron powder with size distributions: 140—104=1.0, 104—74=8.4, 74—61=10.4, 61—43=15.8, below 43μ=64.4 wt%. Air was blown at the rate of 650 *l*/hr for 10 hr into 0.5M-$FeSO_4$ and 0.2M-$FeSO_4$ solutions containing 20 g (0.36 mol) of the iron powder. These suspensions were kept at 70°C. 0.2M-H_2SO_4 solution containing 31 g (0.56 mol) of the iron powder was also subjected to the same treatment. These sulfate suspensions changed gradually from grayish black to brownish yellow, as the reaction proceeded. In order to know the relation between the pH of the suspensions and the remaining iron particles, a part of each suspension (about 50 m*l*) was taken out for examination during the course of oxidation. The pH values are plotted against time in the logarithmic scale in Fig. 2. The pH value increased to about 7 by addition of the iron powder to the solution, and then decreased to about 4. It remained at about 4 while the iron powder was present in the solution. When the iron powder disappeared completely, the pH dropped to below 3. It is believed that precipitation takes place when the iron powder is dissolved and the ferrous ions are oxidized as follows.

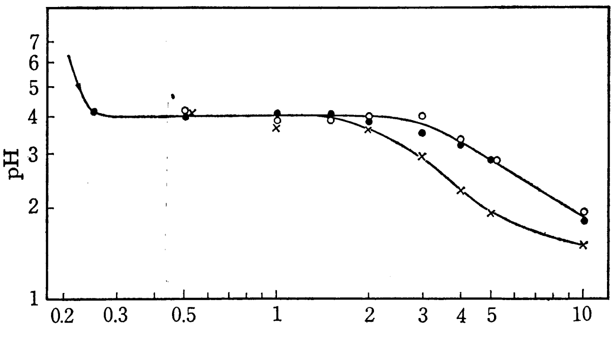


Fig. 2. pH of suspension at various time intervals: × =0.5M-$FeSO_4$, ○=0.2M-$FeSO_4$, ●=0.2M-H_2SO_4 as the starting solution.

$$2Fe(metal) + 4H^+ = 2Fe^{2+} + 2H_2(gas)$$

$$2Fe^{2+} + 3H_2O + \frac{1}{2}O_2 = 2FeOOH + 4H^+$$

When the iron powder is uniformly dispersed, the ferrous ions consumed by oxidation to form a precipitate are replenished by neutralization between the acid formed and the iron powder. This might be the reason that the pH remained at about 4. The solubility products of iron hydroxides are: $(Fe^{2+})(OH)^2=10^{-14}$ and $(Fe^{3+})(OH)^3=10^{-36}$. In these suspensions, no ferrous precipitate can exist but ferric ions which are to be precipitated.

The samples thus obtained (Found: Fe_2O_3 87.5—88.6 wt%, Calcd for $Fe_2O_3 \cdot H_2O$, Fe_2O_3 89.9 wt%) were mixtures of α-FeOOH and γ-FeOOH. Their γ-FeOOH content R progressively increased to about 0.3 in the samples prepared from 0.5M-$FeSO_4$ (sample A), 0.2M-$FeSO_4$ (B) and 0.2M-H_2SO_4 (C) which were the starting solutions. Optical micrographs of these samples show that acicular particles are present with granular ones (Fig. 3). Their shapes and sizes depend on the concentration of ferrous ions in the starting solution. Electron micrographs of typical particles are given in Fig. 4 (D) and (E) and that of twin particles observed by carbon replica method in Fig. 4 (F). Very elongated and big bur-like particles can be seen together with X-, Y-, and tablet-shaped ones. According to electron microdiffraction, the very elongated particles were γ-FeOOH and the other ones α-FeOOH. The X- and Y- shaped ones as well as the big bur-like ones did not overlap one another. The former had a re-entrant angle of about 60°,

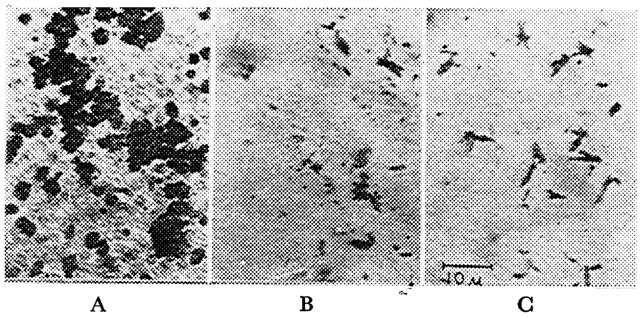


Fig. 3. Optical microscope photographs of FeOOH particles: A=0.5M-$FeSO_4$, B=0.2M-$FeSO_4$, C=0.2M-H_2SO_4 used as the starting solution.

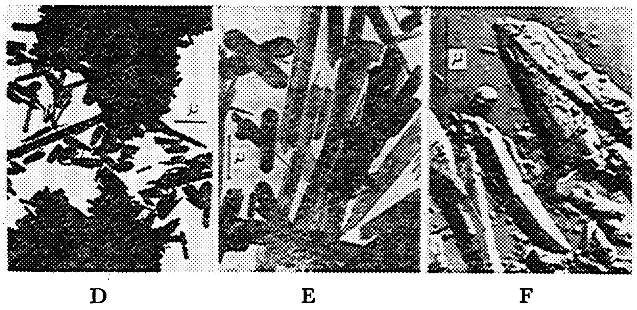


Fig. 4. Electron micrographs of typical shapes of particles prepared from the sulfate suspension.

In order to find the favorable conditions for the formation of γ-FeOOH, experiments were carried out by use of the same iron powder. Oxidation was continued for 6 hr under various conditions, such as the flow rate of air blown, concentration of sulfuric acid, amount of the iron powder added and reaction temperature.

Table 1. Iron compounds formed by oxidation of iron powder ($<140\,\mu$) present in sulfuric acid solutions under various conditions

Reaction conditions				
Composition (mol/l)		Temp. (°C)	Flow rate (l/hr)	Iron compounds[a)]
SO_4^{2-}	Fe			
0.20	0.57	70	100	α-H
0.20	0.57	70	350	α-H$\gg\gamma$-H
0.20	0.57	70	500	α-H$>\gamma$-H
0.20	0.57	70	650	α-H$\approx\gamma$-H
0.20	0.57	80	650	α-H
0.20	0.57	70	650	α-H$\approx\gamma$-H
0.20	0.57	60	650	α-H$\approx\gamma$-H
0.20	0.57	50	650	α-H$>\gamma$-H
0.16	0.57	70	650	α-H$\approx\gamma$-H
0.07	0.57	70	650	α-H$>\gamma$-H
0.00	0.57	70	650	α-H$\approx Fe_3O_4$
0.20	0.92	70	650	α-H
0.20	1.62	70	650	α-H
0.20	3.27	70	650	α-H

a) Abbreviations: α-H=α-FeOOH, γ-H=γ-FeOOH.

The results are summarized in Table 1. With the increase of air flow rate the iron powder becomes more uniformly dispersed, the formation of γ-FeOOH being accelerated. In water the rate of precipitation was very slow and the oxidation product contained not γ-FeOOH but a mixture of α-FeOOH and Fe_3O_4 (or γ-Fe_2O_3). The formation of γ-FeOOH depends strongly on the amount of iron powder, γ-FeOOH being always formed together with α-FeOOH.

In order to examine the effects of particle size and amount of iron powder experiments were carried out as follows. Four iron powders with different particle sizes (270—240 μ, 140—117 μ, 74—61 μ, and below 43 μ) were used and different amounts of each iron powder were added to 0.2M-H_2SO_4 solutions. The suspensions were oxidized for 8 hr at 65°C by blowing air into them at 1000 l/hr.

The γ-FeOOH contents R for different iron particle sizes are plotted against the amount of iron powder in Fig. 5. After 8 hr, the solutions to which 80 g (1.43 mol/l) and 200 g (3.58 mol/l) of the iron powder with 117—140 μ in particle size and 20 g or more of the iron powder with 240—270 μ had been added, had a pH of about 4 and still retained the iron powder. For a given amount of iron powder the larger the particle size, the higher the R, the maximum of R on each curve depending on particle size. This indicates that the particle size of iron powder is more effective for γ-FeOOH formation than its total surface area which is the product of its amount and particle size at the initial stage of oxidation.

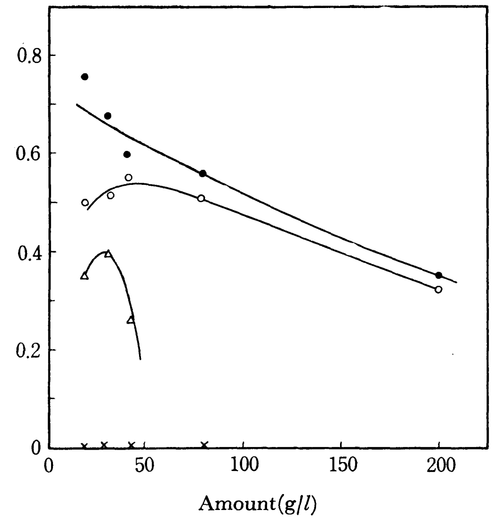


Fig. 5. Effects of the size and amount of the iron powder on the γ-FeOOH content R.
●: 270—240 μ, ○: 140—117 μ, △: 74—61 μ, × : —43 μ

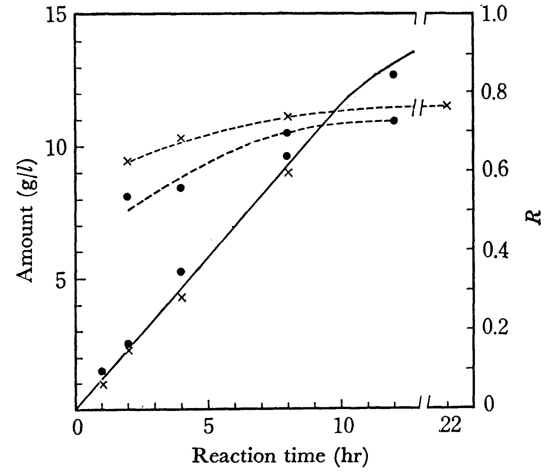


Fig. 6. Amount of precipitates formed and R(γ-FeOOH content) at various periods. Iron powder with particle size of 240—270 μ, 20 g= ×, 40 g=●. ——: Amount, ----: R

In order to increase R, the following experiments were carried out. 0.35 mol (20 g) and 0.70 mol of iron powder (240—270 μ) were added to 0.2M-H_2SO_4 solution. The suspensions were oxidized at 65°C for different periods by blowing air into them at a rate of 1500 l/hr. The amount of precipitate formed and R are plotted against time in Fig. 6. Neither depends strongly on the amount of iron powder added and R hardly varies with time.

Precipitation in Other Suspensions. Since a single phase of γ-FeOOH was hardly formed in the sulfate suspensions, experiments were carried out with hydrochloric, nitric and acetic acids in order to examine the effect of anions on the formation of γ-FeOOH.

33 g (0.675 mol/l) of iron powder (104—140 μ) was added to each of the solutions 0.25M-HCl, CH_3COOH and HNO_3. The suspensions were oxidized at 40, 55, 70, and 80°C for 8 hr by blowing air at the rate 1000 l/hr. When the iron powder was added to the acetic acid solution, foaming occurred so heavily that at first

Table 2. Iron compounds formed by oxidation of iron powder (140—104 μ) in chloride, nitrate and acetate solutions (0.25 M in acid) at various temperatures

Temp. (°C)	Chloride	Nitrate	Acetate
40	γ-H>α-H	α-H>γ-H>Sp	α-H
55	γ-H>α-H	γ-H>α-H>Sp	γ-H>α-H
70	γ-H≫α-H	α-H≈Sp>γ-H ≈α-O	γ-H≫α-H
80	γ-H>α-H ≈α-O	α-H≈α-O>γ-H ≈Sp	α-O>γ-H

α-H=α-FeOOH, γ-H=γ-FeOOH, $\alpha\text{-O}=\alpha\text{-Fe}_2\text{O}_3$, $\text{Sp}=\text{Fe}_3\text{O}_4$ or $\gamma\text{-Fe}_2\text{O}_3$.

air had to be jetted from the top of the vessel into the suspension to subdue the farm. No iron particles remained in the chloride suspensions oxidized at 70 and 80°C, and the acetate suspensions oxidized at 55, 70, and 80°C. The pH of the chloride suspensions remained at about 4 while iron particles were present, whereas the pH of the acetate suspensions was about 4 regardless of the presence of iron particles. In the nitrate suspensions oxidized at temperatures between 40 and 80°C, iron particles were present. The remaining iron particles in the nitrate suspensions oxidized at 70 and 80°C were coated with black material (probably Fe_3O_4), the rate of precipitation being slow. The kinds of precipitates obtained from each suspension at various temperatures are given in Table 2. γ-FeOOH is formed below 70°C together with α-FeOOH in the chloride and acetate suspensions. $\alpha\text{-Fe}_2\text{O}_3$ begins to be formed at 70°C in the nitrate suspension and is formed with other precipitates in all the suspensions at 80°C.

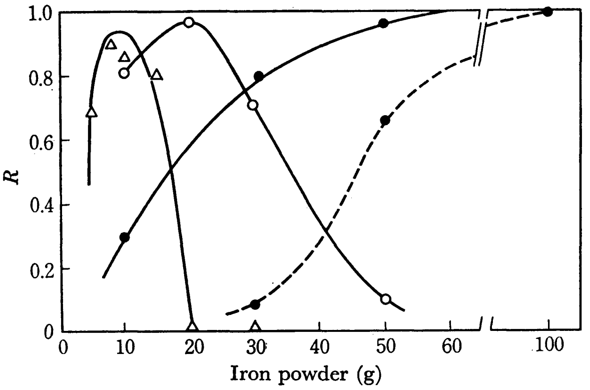


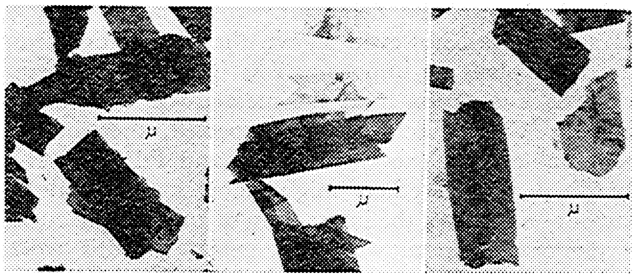
Fig. 7. Effects of the particle size and amount of iron powders added to acetate solution (0.5 *l*) on *R*: △=<43 μ, ●=117—140 μ, ○=240—270 μ.
Solid curves: at 70°C, air flow rate 1500 *l*/hr,
Dotted curve: at 55°C, 1000 *l*/hr.

In order to examine the effect of the air flow rate on *R* at temperatures where $\alpha\text{-Fe}_2\text{O}_3$ is hardly formed, the same suspensions were oxidized for 8 hr at different air flow rates between 500 and 1500 *l*/hr at 70°C for the chloride and acetate and at 55°C for the nitrate. The *R* value for acetate increased with the increase of air flow rate. It reached 1.0 at the rate of 1500 *l*/hr. The *R* values for the other suspensions did not depend strongly on the air flow rate. It was about 0.8 for the chloride and 0.4 for the nitrate.

The effects of the particle size and the amount of iron powder on *R* were examined. Three kinds of iron powders with different particle sizes (<43, 117—140 and 240—270 μ) were added to acidic solutions containing 0.25M-acid, their amounts being between 10 and 200 g (0.358 and 3.58 mol/*l*), and each suspension was oxidized at 70°C for 6 hr by blowing air into it at 1500 *l*/hr. Of the three suspensions the total volume of the acetate suspension decreased to 1/2 liter, since foaming became heavier with the increase of surface area of the iron powder. With the acetate suspension, *R* depends on both the amount and particle size of the iron powder (Fig. 7). It increases with the increase or decrease in the amount of iron powder, depending on the particle size, *viz.*, it depends on the total surface area of the iron powder present at the initial stage. The surface area favorable for the formation of γ-FeOOH changes with reaction condition as can be seen by the dotted curve in Fig. 7 (reaction temperature: 55°C, air flow rate: 1000 *l*/hr, the other conditions the same as above). When the suspensions containing more than 30 g (0.54 mol/*l*) of iron powder with particle size of below 43 μ was oxidized at 70°C, fine particles of Fe_3O_4 (about 0.1 μ) were formed.

Table 3. Conditions favorable for the formation of γ-FeOOH from 0.25N-acid solutions containing iron powder
(air flow rate=1500 *l*/hr, time=6 hr)

	Acid	Iron powder		Temp. (°C)	γ-FeOOH content *R*
		size (μ)	amount (mol/*l*)		
No. 1	CH_3COOH	104—140	1.75	70	1.00
No. 2	HCl	104—140	1.75	70	0.97
No. 3	HNO_3	74—61	2.53	55	1.00



(No. 1) (No. 2) (No. 3)

Fig. 8. Electron micrographs of γ-FeOOH particles formed in acetate (No. 1), chloride (No. 2) and nitrate suspensions (No. 3) as in Table 3.

The effects of particle size and amount of iron powder on *R* for chloride and nitrate were less marked than for acetate suspension. γ-FeOOH was obtained in the chloride and nitrate suspensions under proper conditions, iron particles remaining. Fine particles of Fe_3O_4 (about 0.1 μ) were also formed in the surface layer of iron particles in nitrate suspension containing more than 30 g of the iron powder (<43 μ) and in chloride suspension containing more than 60 g of iron powder (<43 μ). The conditions favorable for the formation of γ-FeOOH are summarized in Table 3 and electron micrographs of the γ-FeOOH particles separated from the remaining iron particles are shown in Fig. 8. The γ-FeOOH particles evidently differ from the very elongated ones prepared from sulfate.

The presence of green rust has been considered to be indispensable for γ-FeOOH formation, and it has been suggested that γ-FeOOH is formed by its surface oxidation. However, the shape of γ-FeOOH particles (acicular) prepared *via* the green rust does not resemble that of the particles of green rust (hexagonal plate-like). γ-FeOOH can also be formed by oxidizing ferrous salt solutions or suspensions of iron powder not *via* the green rust. It is thus proposed that γ-FeOOH may be formed not by surface oxidation of the green rust but by oxidation of hydroxo iron (II) complex formed by dissolution of either the green rust or iron powder.