Air Oxidation of Aqueous Ferrous Sulfate Solution in the Alkaline Region

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The air oxidation of an aqueous $FeSO_4$ solution was studied in an alkaline region by blowing air from a horizontal nozzle into the solution. The pH value of the solution was maintained at ca. 10 by adding Na_2CO_3 in the solution. No catalytic action of Cu^{2+} ion was observed. The rate of oxidation was not virtually affected by the temperature, but increased with the rise of the flow rate of air. A zero order rate equation was found. From the presumption that the reaction is composed of the sequential steps of dissolution of gaseous oxygen at the surface of rising air bubbles and the oxidation of Fe^{2+} ion and $Fe(OH)_2$ precipitate by the dissolved oxygen, it was revealed that the rate determining step of the overall reaction is the step of oxygen dissolution. From the rate constant of the rate equation, the liquid-film mass transfer coefficient of dissolved oxygen in the liquid boundary layer at the bubble surface was estimated, and it was fairly well coincident with the directly measured values. The rise of the rate of oxidation with the flow rate of air stream was interpreted in terms of the increase in the surface area of rising air bubbles.

1. Introduction

Many gas-liquid reactions have been employed in the pyro- and hydrometallurgical processes. These reactions are often carried out by blowing gas bubbles in the liquid phase. It is clear that chemical reactions and mass transfer of gaseous components occur at the surface of rising gas bubbles. When the overall rate is affected by the chemical reactions or the mass transfer of the gaseous components at the gas-liquid interface, it is thought that the surface area of the rising gas bubbles is closely correlated with the overall rate of the reaction.

The air oxidation of ferrous sulfate in an alkaline solution was studied in the present work. This reaction is often carried out in industries by bubbling air through a nozzle placed in the solution. The air oxidation of ferrous salts is known as the important process in hydrometallurgy: it is used for the regeneration of Fe^{3+} ion in the spent solution from the leaching process[1] and for the purification of pregnant solution containing Fe^{2+} ion by separating it as the solid ferric hydroxide precipitate.[2],[3] The former reaction is conducted in acidic solutions, whereas the latter reaction is carried out in weakly acidic, neutral and alkaline solutions at pH values higher than about 4.[4]
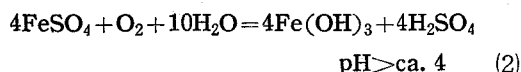
It is clear that the reaction schems of these two reactions are different. The overall reactions may be written as

$$4FeSO_4 + O_2 + 2H_2SO_4 = 2Fe_2(SO_4)_3 + 2H_2O$$
$$pH < ca. 4 \quad (1)$$

and

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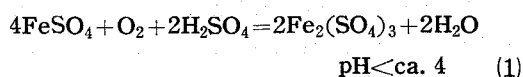
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$$4FeSO_4 + O_2 + 10H_2O = 4Fe(OH)_3 + 4H_2SO_4$$
$$pH > ca.\ 4 \qquad (2)$$

respectively. As seen from these equations, acid is consumed and the pH value of the solution rises along with the progress of the former reaction, and acid is formed and pH is lowered in the latter reaction.

When the process of mass transfer of oxygen gas across the gas-liquid interface at the bubble surface is considered, the overall reaction (2) is rewritten as the following sequential steps:

$$O_2 = \underline{O_2} \qquad (3)$$

and

$$4FeSO_4 + \underline{O_2} + 10H_2O = 4Fe(OH)_3 + 4H_2SO_4 \quad (4)$$
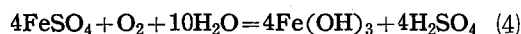
where $\underline{O_2}$ represents the dissolved oxygen in the solution. It is noted that the rate of dissolution of oxygen gas is affected by the hydrodynamic conditions of air bubbling, whereas the rate of reaction (4) is not affected because of its homogeneous character.

It is known from the literature[5] that the overall rate of the air oxidation of Fe^{2+} ion is proportional to the squared Fe^{2+} ion concentration in the region of pH below 1,[6],[7] and it is proportional to the concentration of Fe^{2+} ion and to the second power of the concentration of OH^- ion in the region of pH between 4 and 7.5.[2],[8]~[10] It was reported,[11] on the other hand, regarding the air oxidation in the alkaline solution that the overall rate is independent of the amount of hydroxide present in the reaction vessel. It is also expected in the alkaline solution that the rate of oxidation is much higher than the rate of gaseous oxygen at the bubble surface.

Although the air oxidation of Fe^{2+} ion in acidic and neutral solutions were extensively studied by the previous workers, the studies in the alkaline solutions were very few[11],[12]

presumably because of its relatively higher rate of oxidation, even though the air oxidation of ferrous salts in alkaline solution is widely employed in industries for the recycling and disposal of water from mines and plants.

It was intended in the present work to study the kinetics of air oxidation of ferrous sulfate in an alkaline solution of pH at about 10. The major interest in the present work was to study the hydrodynamic effects of air bubbles on the progress of air oxidation in the alkaline solution. In addition, the catalytic effect of $CuSO_4$ in the solution and the effect of solution temperature on the rate of oxidation were also investigated.

2. Experimental

The experimental arrangement in the present work is schematically illustrated in Fig. 1. Air is sent from a baby compressor to a capillary flowmeter and a humidifier. The humidified air is blown into the solution through a horizontal nozzle which is placed in the reaction vessel.
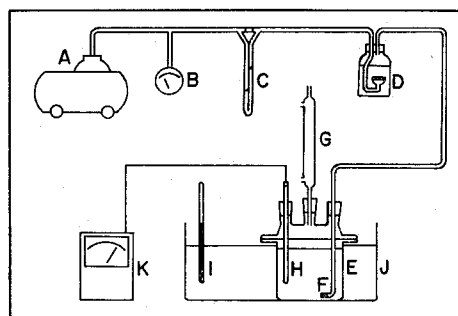

Fig. 1 Experimental arrangement
(A) Compressor, (B) Manometer, (C) Capillary flowmeter, (D) Humidifier, (E) Reaction vessel, (F) Nozzle, (G) Reflux condenser, (H) Glass electrode, (I) Thermometer, (J) Water bath, (K) pH meter

The capillary flowmeters provided with three glass capillaries of different inner diameter were used. They were calibrated against a soap-film flowmeter. The humidifier serves for elevating the moisture content in the air

stream by passing fine air bubbles through water column from a porous glass plate. It was observed in a preliminary test in which a combination of the humidifier and the reflux condenser was used that the variation of water volume in the reaction vessel was very small at 50°C before and after the air bubbling for 2 hours.

The reaction vessel was a 1000 ml-cylindrical glass flask provided with a glass lid with five holes and was placed in a thermostat. The inner dimension of the flask was 114 mm in inner diameter and 125 mm in height.

Through the holes of the glass lid, a nozzle, a combined glass electrode and a reflux condenser were installed, respectively. A horizontal glass nozzle of 1 mm in inner diameter was used for bubbling the air stream in the solution. Its dimension is shown Fig. 2. The pH value of the solution was continuously measured with a Hitachi-Horiba pH-meter of type 42-A.
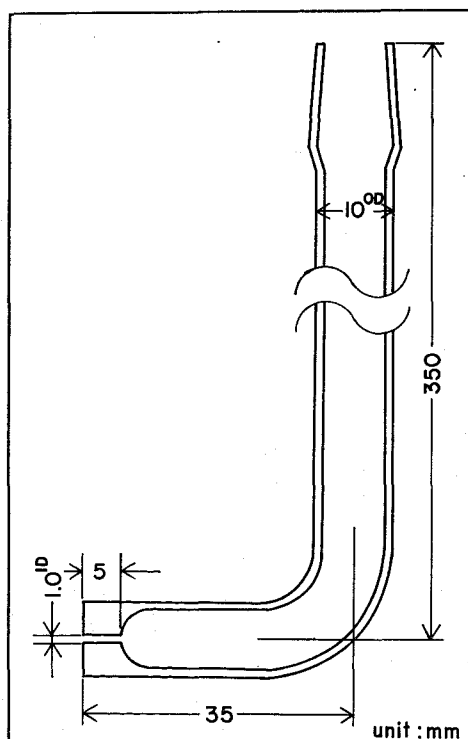

Fig. 2　Nozzle

Analytical reagent grade $FeSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$ and Na_2CO_3 were used. The dissolved oxygen in the deionized water was removed by bubbling nitrogen gas for 2 hours. By mixing the stock solutions of 0.1M $FeSO_4$ and 0.5M Na_2CO_3, the test solutions of the prescribed composition were made up. A small amount of H_2SO_4 was added to the 0.1M $FeSO_4$ stock solution, and the pH value was maintained at about 2 during the preservation to prevent the oxidation of Fe^{2+} ion. The composition of the test solution was 0.01M $FeSO_4$ and 0.05M Na_2CO_3. As a catalyst for the oxidation, $CuSO_4$ was added in several runs. Due to the presence of Na_2CO_3 as a buffer, the test solution was maintained at about 10.2 during the course of the oxidation.

Before the start of the experiment, the interior of the reaction vessel was purged with nitrogen gas and the test solution was gently poured from a 1000 ml-measuring flask. After the solution temperature was attained at the experimental temperature, nitrogen gas was bubbled and an aliquot of the solution was withdrawn and placed in 1:4 H_2SO_4 solution. Then nitrogen gas was switched to the air stream of the predetermined flow rate, and the air oxidation was started. At the appropriate time intervals, aliquots of the solution were pipetted and placed in 1:4 H_2SO_4 solution to quench the reaction. Colloidal hydroxide was dissolved by heating the acid solution, and the concentration of Fe^{2+} ion in these aliquots was determined by titrating it against a standard 0.01M $KMnO_4$ solution.

In the first place, the catalytic effect of $CuSO_4$ was studied. The test solutions containing 0.01M $FeSO_4$, 0.05M Na_2CO_3 and 0, 0.002 and 0.004M $CuSO_4$, respectively, were prepared, and the air oxidation was conducted at 20°C. The flow rate of the air stream was maintained at the Reynolds number of 1000 which is defined

as

$$Re = \frac{d_0 \, \bar{u} \, \rho_g}{\mu_g} \qquad (5)$$

Where d_0 represents the inner diameter of the nozzle, and $\bar{u}$, ρ_g and μ_g are the mean linear velocity of the air stream in the nozzle, the density and viscosity of air, respectively.

The results are shown in Fig. 3. As seen in this figure, no significant catalytic effect of $CuSO_4$ was observed except for the final stage of the oxidation. It was reported[2] that the increase in the rate of air oxidation due to the presence of Cu^{2+} ion in the solution was relatively small and the rate was attained to a saturated value at a fairly low concentration of Cu^{2+} ion in the neutral solutions of pH at about 7, through the catalytic action of Cu^{2+} ion was evident in the acidic solutions.
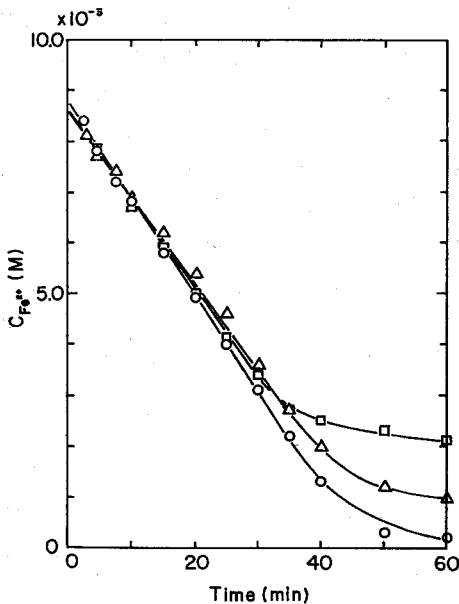

Fig. 3 Effect of Cu^{2+} ion concentration on the rate of
reaction (20°C, Re = 1000)
—○— : 0   M $CuSO_4$
—△— : 0.002M $CuSO_4$
—□— : 0.004M $CuSO_4$

The effect of temperature on the reaction rate was examined in the test solutions of 0.01M

$FeSO_4$ and 0.05M Na_2CO_3 without $CuSO_4$. At the temperature of 20°C, 35°C and 50°C, air was bubbled at the Reynolds number of 1000. The experimental results are summarized in Fig. 4. It is seen in this figure that the rate of oxidation of Fe^{2+} ion is independent of temperature. At the final stage of the reaction, the oxidation seemed to be retarded at 50°C presumably because of the formation of magnetite precipitate.[12]
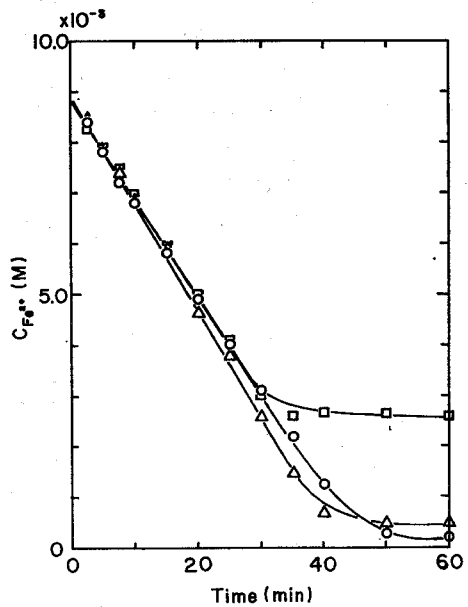

Fig. 4 Effect of temperature on the rate of reaction
(Re = 1000)
—○— : 20°C
—△— : 35°C
—□— : 50°C

It is also seen in Fig. 3 and 4 that the total concentration of Fe^{2+} ion and $Fe(OH)_2$, C_{Fe}^{2+}, linearly decreases along with the elapsed time. This means that the overall rate of air oxidation in the alkaline solution is represented by a zero order rate equation with regard to C_{Fe}^{2+} except for the final stage : the rate constants were directly obtained from the slopes of these straight lines. They are 3.14×10^{-6}, 3.50×10^{-6} and 3.22×10^{-6} mol / l·s at 20°, 35° and 50°C, respectively. It has been reported,[2],[9] on the

other hand, that the rate of oxidation of Fe^{2+} ion in the solutions of pH 4 to 7.5 was proportional to the concentration of Fe^{2+} ion and the activation energy was about 3 Kcal/mol. These differences in the air oxidation of Fe^{2+} ion regarding the rate equation and the activation energy in weakly acidic and neutral solutions and in alkaline solution is thought to be due to the diffference in the reaction mechanism in these solutions.

In order to pursue the effect of the flow rate of air stream, the solutions containing 0.01 M $FeSO_4$ and 0.05M. Na_2CO_3 were oxidized at 20°C with the air stream of various flow rates. The results are summarized in Fig. 5. The Reynolds number was varied from 250 to 10000.
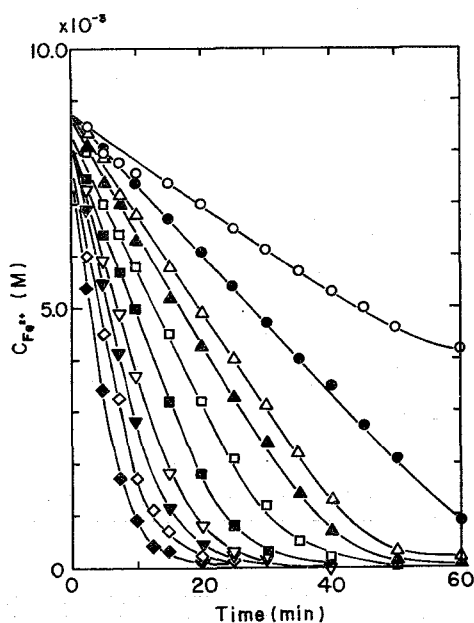

Fig. 5 Effect of Reynolds number on the rate of reaction (20°C)
- —○— : Re=   250
- —●— : Re=   500
- —△— : Re= 1000
- —▲— : Re= 1500
- —□— : Re= 2000
- —■— : Re= 3000
- —▽— : Re= 4000
- —▼— : Re= 6000
- —◇— : Re= 8000
- —◆— : Re=10000

It is evident from this figure that the rate of oxidation increases along with the rise of the Reynolds number. Presuming that the rate of this reaction is of the zero order with regard to $C_{Fe^{2+}}$, the rate constants were calculated from the slopes, and they were plotted against the Reynolds number in Fig.6. When this relationship of the rate constant versus the Reynolds number in the alkaline solution is compared with that in the weakly acidic solution,[13] it was found that the rate constant increased with the Reynolds number in the alkaline solution whereas it was maintained constant at higher Reynolds number in the weakly acidic solution. This difference in the rate constant upon the Reynolds number in these solutions may also be attributed to the difference in the rate determining step of the reaction.

3. Discussion

As already described, the air oxidation of ferrous sulfate in aqueous solution is composed of the sequential steps of
1.　the dissolution of oxygen gas at the surface of air bubbles and
2.　the oxidation of Fe^{2+} ion (and $Fe(OH)_2$ precipitate) by the dissolved oxygen in the solution
which were shown as Eq. (3) and (4), respectively. It is evident in the alkaline solution that ferrous sulfate is hydrolyzed according to

$$FeSO_4 + 2H_2O = Fe(OH)_2 + H_2SO_4 \qquad (6)$$
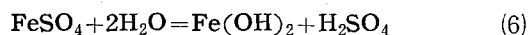
It may be reasonable to presume that the hydolysis is in equilibrium, and Fe^{2+} ion and the suspended $Fe(OH)_2$ precipitate are oxidized by the dissolved oxygen in the solution.

The dissolution of oxygen gas at the gas-liquid interface may be composed of
1.　the mass transfer of oxygen gas in the gas boundry film within the bubbles,

2. the dissolution of oxygen gas at the bubble surface, and

3. the mass transfer of dissolved oxygen in the liquid boundary film adjacent to the bubbles.

It may be a reasonable presumption that the step 3 is the rate determining step of the reaction (3). It is also appropriate to assume that the reaction (4) is irreversible because of the formation of solid ferric hydroxide precipitate and that the rate of the forward reaction is proportional to the product of $C_{Fe^{2+}}$ and C_{O2}. Then the rate equations regarding the reactions (3) and (4) may be written as

$$-\frac{dC_{Fe^{2+}}}{d\theta} = kC_{Fe^{2+}}C_{O2} \tag{7}$$

$$\frac{dC_{O2}}{d\theta} = k'_L(C^e_{O2} - C_{O2}) - \frac{k}{4}C_{Fe^{2+}}C_{O2} \tag{8}$$

where

$$k'_L = \frac{S}{V}k_L \tag{9}$$

In these equations, the symbols k, k_L, S, V and θ represent the rate constant of the forward reaction of Eq. (4), the liquid-film mass transfer coefficient of dissolved oxygen, the surface area of the rising air bubbles, the volume of the solution and time, respectively. The superscript "e" denotes the saturated value.

When it is assumed that Eq. (3) is the rate determining step in the air oxidation, C_{O2} is presumed to be unvaried and it is far lower than the saturated value of C^e_{O2}. Then

$$\frac{dC_{O2}}{d\theta} \doteqdot 0 \quad \text{and} \quad C_{O2} \ll C^e_{O2} \tag{10}$$

Substitution of Eq. (10) into Eq. (7) and (8) yields

$$-\frac{dC_{Fe^{2+}}}{d\theta} = 4k'_L C^e_{O2} \tag{11}$$

This is the zero order rate equation.

It is seen from Eq. (9) and (11) that the rate of air oxidation is proportional to the surface area of rising air bubbles and the liquid-film mass transfer coefficient of dissolved oxygen at the surface of rising air bubbles. Onogi[14] obtained the k_L' value in the dissolution of gaseous oxygen in water by measuring the concentration of dissolved oxygen with a platinum electrode covered with a polymer film. The obtained k'_L values were also plotted against the Reynolds number in Fig. 6. By comparing these two k'_L-curves in Fig. 6, it is evident that both relationships are extremely similar. The value of C^e_{O2} is 0.000276M at 20°C.[15] This value was substituted into Eq. (11), and the k'_L value of $2.9 \times 10^{-3} (s^{-1})$ was obtained from Fig. 6 at the Reynolds number of 1000. This value agreed well with $2.2 \times 10^{-3} (s^{-1})$ obtained by Onogi.[14]
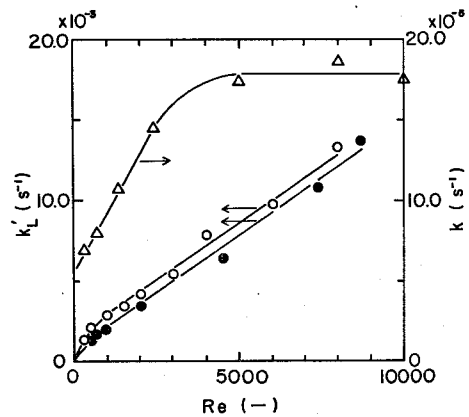

Fig. 6 Rate constant versus Reynolds number
—O— : this work
—△— : weakly acidic solution[13]
—●— : dissolution of O_2 gas in water[14]

As described earlier, it was reported regarding the air oxidation of Fe^{2+} ion in weakly acdic and neutral solutions that the rate of reaction is proportional to the concentration of Fe^{2+} ion. It was already shown in Fig. 6 that the rate constant becomes unvaried at higher Reynolds numbers. Assuming that the reaction (4) is the rate determining step of the air oxidation of Fe^{2+} ion, we can write that $C_{O2} = C^e_{O2}$. Then Eq. (8) is rewritten as

$$-\frac{dC_{Fe^{2+}}}{d\theta} = kC_{Fe^{2+}}C^e_{O_2} \qquad (12)$$

which is the first order rate equation regarding the concentration of Fe^{2+} ion. It may be said from this presumption of chemical reaction control that the oxidation of Fe^{2+} ion is catalyzed by Cu^{2+} ion in the solution and that the rate constant becomes unvaried at higher Reynolds number.

4. Summary

The air oxidation of ferrous sulfate in an alkaline solution containing 0.01M $FeSO_4$ and 0.05M Na_2CO_3 was studied in the present work. Air was blown a horizontal glass nozzle of 1 mm in inner diameter into the solution. The pH value of the solution was maintained at 10.2 during the oxidation due to the buffer action of Na_2CO_3.

The rate of oxidation was not accelerated by the presence of Cu^{2+} ion in the solution which is known as a potent catalyst in the acidic solutions. Furthermore, the rate of oxidation was not affected by the temperature between 20°C and 50°C The only one factor which influences the rate of oxidation found in this work was the flow rate of air stream: the rate increases with the rise of the flow rate of air.

It was also found that a rate equation of zero order regarding $C_{Fe^{2+}}$ holds with the air oxidation in the alkaline solution, which is different from the first order rate equation in the air oxidation in weakly acidic and neutral solutions. Taking into account a presumption that the overall reaction is composed of the sequential steps of dissolution of gaseous oxygen at the surface of rising bubbles and the oxidation of Fe^{2+} ion and $Fe(OH)_2$ precipitate by the dissolved oxygen, it is a reasonable thought that the rate determining step of the air oxidation of Fe^{2+} ion in the alkaline solution is the former step of oxygen dissolution, whereas the latter step of oxidation in the solution determines the overall rate in the solutions of lower pH values.

From this thought, a rate equation of zero order was derived, and the liquid-film mass transfer coefficient of dissolved oxygen at the surface of rising air bubbles was estimated from the obtained rate constant. The estimated values of the mass transfer coefficient coincided fairly well with the directly measured ones.

Furthermore, the variation of the overall reaction with the Reynolds number in the weakly acidic solution and in the alkaline solution were compared. It may be said that the former rate constant is unvaried at higher Reynolds numbers of the chemical reaction control and that latter increases with the Reynolds number due to the increase of surface area of the rising air bubbles.

Acknowledgements

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