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The Oxidation of Iron(II) Sulfate with Sulfur Dioxide and Oxygen Mixtures

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The oxidation of iron(II) sulfate with SO_2/O_2 (sulfur dioxide and oxygen mixtures) was carried out using an air-lift percolator in the temperature range of 25—50 °C and over the pH range of 0—3. Under conditions in which sulfur dioxide is immediately oxidized, the rate of the oxidation of iron(II) is proportional to the flow rate of sulfur dioxide and independent of the flow rate and partial pressure of oxygen, and the concentration of iron(II). The molar ratio of Fe^{2+} oxidized/SO_2 oxidized is 1.3—2 in the pH range of 0.5—2.0. A free-radical chain reaction in which HSO_5^- oxidizes iron(II) is proposed as the reaction mechanism.

Although the oxidation of iron(II) with oxygen according to Eq. (1):

$$Fe^{2+} + 1/4\,O_2 + 1/2\,H_2O \longrightarrow Fe^{3+} + OH^-, \tag{1}$$

is thermodynamically possible, practical rates of oxidation are so slow in acidic solutions that the oxidation is frequently performed with the aid of manganese dioxide, hydrogen peroxide, pressurized oxygen, iron-oxidizing bacteria, *etc.* Recently, it was reported that, although sulfur dioxide by itself reduces iron(III) to iron(II), a mixture of sulfur dioxide with oxygen oxidizes iron(II) to iron(III).[1,2] It was suggested that this reaction might be used for the separation of iron from a zinc-containing solution,[1] the selective recovery of zinc and copper from iron-containing lead slags,[3] and the leaching of metal-sulfide concentrates.[2] However, no systematic study of this reaction has yet been made, and the details are not clear. In the present study, a series of tests was carried out to investigate specifically the oxidation behavior of iron(II) with SO_2/O_2 in acidic solutions.

Experimental

Materials. All the chemicals were of an analytical reagent grade and were used without further purification.

Apparatus and Procedure. The apparatus used for the oxidation study is shown diagramatically in Fig. 1. In each test, 400 cm³ of redistilled water was transferred to a Pyrex-glass air-lift percolator ($50\,\mathrm{mm}^{\phi} \times 650\,\mathrm{mm}^{H}$) fitted with an unglazed pottery gas-ditributor plate. After the removal of the dissolved oxygen by passing nitrogen gas through for 20 min, a known quantity of iron(II) sulfate, sodium perchlorate, and 10 mol/dm³ perchloric acid were added to adjust the concentration of iron(II), the ionic strength, and the pH, and then SO_2/O_2 was introduced to start the reaction. The pH of the solution was maintained at a preselected value by the addition of a 0.5 mol/dm³ sodium hydroxide solution by means of a peristaltic pump; the temperature was maintained at a set temperature ±0.5 °C by circulating temperature-controlled water through the jacket.

Unless otherwise stated, the general experimental conditions used were: temperature, 25 °C; pH, 1.7; ionic strength, 1.0 mol/dm³; flow rate of oxygen, 200 cm³/min; flow rate of sulfur dioxide, 5 cm³/min; initial iron(II) concentration, 0.08 mol/dm³.

Analysis. The concentration of iron(II) was determined by the modified 1,10-phenanthroline method proposed previously.[4] The concentration of sulfurous acid was determined iodimetrically after the addition of an acidified sodium cyclo-hexaphosphate solution to mask the iron(II) and iron(III), while the sulfate and dithionate concentrations were estimated gravimetrically as barium sulfate. The concentration of sulfur dioxide in the outlet gas was determined by the back-titration of the excess iodine with a sodium thiosulfate solution after the absorption of the sulfur dioxide in the iodine solution for 15 min.

Results and Discussion

Oxidation of Iron(II) with Oxygen. Experiments were conducted at two different temperatures, 25 and 50 °C, in the presence of 0.02 mol/dm³ of different foreign substrates. The results of these tests are shown in Fig. 2. The oxidation of iron(II) with oxygen at both temperatures was very slow. However, in the presence of ethylenediaminetetraacetic acid (EDTA=H_4edta) and sodium triphosphate, the oxidation proceeded rapidly until the amount of resulting iron(III) reached about 0.02 mol/dm³, the rates then fell, and the reaction stopped essentially. Copper(II) sulfate, known as a catalyst for iron(II) oxidation with oxygen,[5,6] increased the reaction rate, but the catalytic effect was substantially less than that seen with the complex-forming species, EDTA and triphosphate. On the other hand, the addition of catechol ($C_6H_4(OH)_2$) show-

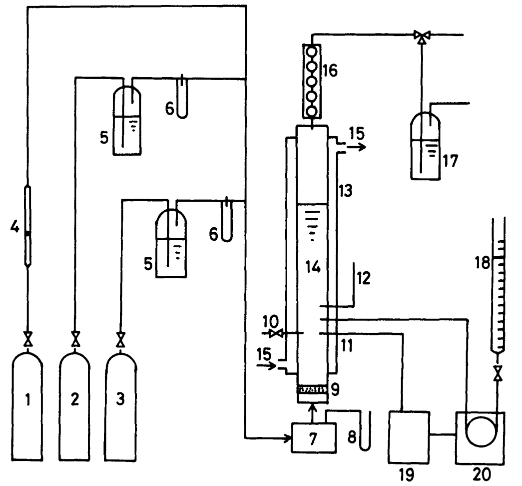

Fig. 1. Schematic diagram of the equipment used.
1. Sulfur dioxide cylinder, 2. Oxygen cylinder, 3. Nitrogen cylinder, 4. Flow meter, 5. Presaturater (H_2O), 6. Orifice, 7. Gas chamber, 8. Manometer, 9. Unglazed pottery plate, 10. Sample tap, 11. pH electrode, 12. Thermometer, 13. Water jacket, 14. Reaction solution, 15. Constant temperature water, 16. Condenser, 17. Iodine solution, 18. Sodium hydroxide solution, 19. pH controller, 20. Peristaltic pump.

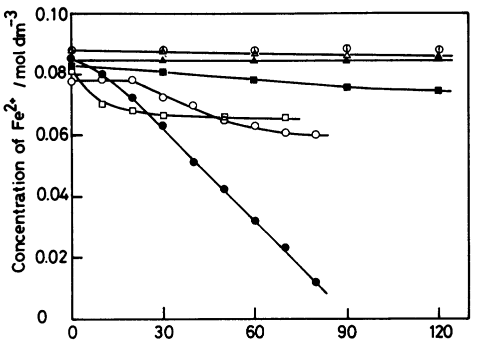

Fig. 2. Oxidation of iron(II) with oxygen in the presence of different foreign substrates.
■: 0.02 mol/dm³ $CuSO_4$, ○: 0.02 mol/dm³ $Na_5P_3O_{10}$, □: 0.02 mol/dm³ EDTA-2Na, ⦶: 0.02 mol/dm³ $C_6H_4(OH)_2$, ●: SO_2 was introduced at a rate of 5 cm³-NTP/min, △ ▲: None, Temperature (°C)---- ○, ●, □, ▲, ⦶: 25, ■, △: 50.

ed no effect. These results indicated that the increase in the oxidation rate with EDTA and triphosphate was probably due to the reduction in redox potentials. The redox potentials of the metal ion and metal-complex ion couples are related through Eq. (2):

$$E^\circ_{ML} = E^\circ_M + \frac{RT}{nF}\ln\frac{K_{M(R)L}}{K_{M(O)L}}, \tag{2}$$

where E°_M and E°_{ML} are the standard redox potentials of metal aquaions and metal-complex ions, and where $K_{M(R)L}$ and $K_{M(O)L}$ are the stability constants of the reduced form and the oxidized form of metal-complex ions respectively. If $K_{M(O)L}$ is larger than $K_{M(R)L}$, E°_{ML} is smaller than E°_M, and the metal-complex ion is thermodynamically less stable than the aquaion under oxidizing conditions. Such an effect was in accord with the test results. When iron was complexed with EDTA and triphosphate ligands with large values of $K_{M(O)L}$, the oxidation rate of iron(II) was increased, whereas the rate was not affected in the presence of catechol, which has a smaller value. The fall-off in the reaction rate observed in the presence of EDTA and triphosphate (Fig. 2) seemed to be due to the consumption of the complex-forming species:[7]

$$Fe^{3+} + edta^{4-} = Fe(edta)^-, \tag{3}$$

$$Fe^{3+} + H_2P_3O_{10}{}^{3-} = FeH_2P_3O_{10}, \tag{4}$$

$$Fe^{3+} + H_3P_3O_{10}{}^{2-} = FeH_3P_3O_{10}{}^+. \tag{5}$$

When sulfur dioxide was introduced together with oxygen, iron(II) was rapidly oxidized at a constant rate. In addition, more than 99% of the sulfur dioxide introduced was converted in the solution to be oxidized to sulfate. The yield of dithionate was less than 1%, so that the reaction of iron(III) and hydrogen sulfite shown as Eq. (6)[8—10] was not significant under the reaction conditions used.

$$2Fe^{3+} + 2HSO_3{}^- \longrightarrow 2Fe^{2+} + S_2O_6{}^{2-} + 2H^+, \tag{6}$$

Therefore, the reactions occurring in the presence of SO_2 may be represented by Eqs. (1), (7), and (8):

$$SO_2 + H_2O = HSO_3{}^- + H^+, \tag{7}$$

$$HSO_3{}^- + 1/2\,O_2 \longrightarrow SO_4{}^{2-} + H^+. \tag{8}$$

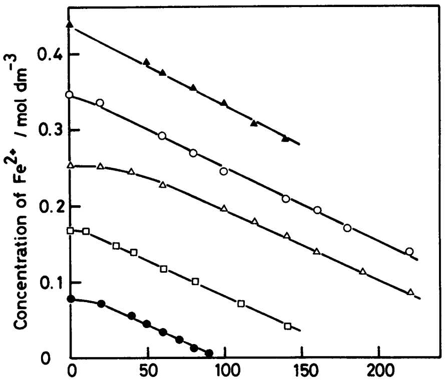

Fig. 3. Oxidation of different concentration of iron(II) with SO_2/O_2 at 50 °C.
Solution pH: 0.9.

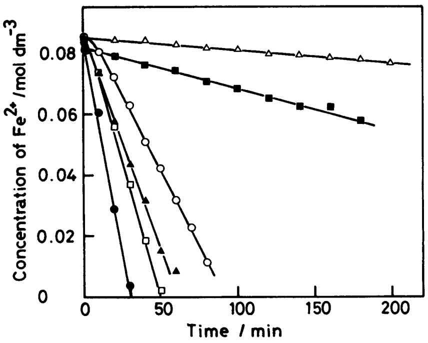

Fig. 4. Oxidation of iron(II) with SO_2/O_2 at different flow rate of sulfur dioxide.
Flow rate of sulfur dioxide (cm³-NTP/min)----△: 0.39, ■: 0.77, ○: 5.0, ▲: 10, □: 15, ●: 20.

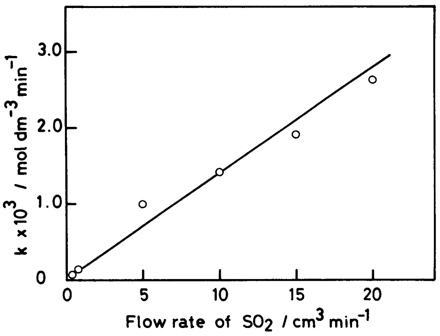

Fig. 5. Rate of oxidation as a function of sulfur dioxide flow rate.

Oxidation of Different Concentrations of Iron(II) with SO_2/O_2. A series of experiments was conducted in which the initial concentration of iron(II) was varied from 0.08 to 0.44 mol/dm³. As is shown in Fig. 3, the plots of the concentration of iron(II) *versus* the time were all linear, with the same gradient. The reaction rate, therefore, was zeroth-order with respect to the iron(II) concentration. The lag period found in all experiments seems to be attributable to the time necessary for the sulfur dioxide to get to the solution from the cylinder rather than to some induction period.

In addition, a constant rate of oxidation was found even when the oxygen-flow rate and the partial pressure were varied over the ranges of 100—300 cm³-NTP/min and 0.14—0.98 atm respectively. The mass transfer of oxygen, therefore, does not control the reaction under these experimental conditions.

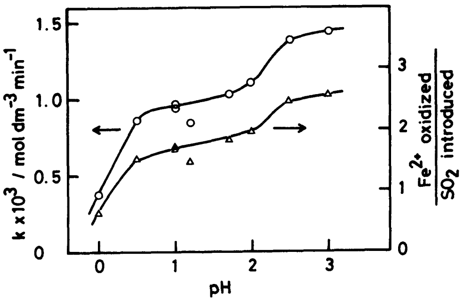

Fig. 6. Oxidation of iron(II) with SO_2/O_2 at different solution pH.

Oxidation of Iron(II) with SO_2/O_2 at Different Flow Rates of SO_2. The effect of changes in the flow rate of sulfur dioxide on the rate of oxidation of iron(II) is shown in Figs. 4 and 5. It is significant to note that the rate of oxidation increased linearly with the flow rate of sulfur dioxide over the range of 0.38—20 cm^3-NTP/min. The average value of the molar ratio of Fe^{2+} oxidized/SO_2 oxidized, calculated from the slope of the straight line shown in Fig. 5, is 1.3.

Oxidation of Iron(II) with SO_2/O_2 at Different Solution pHs. A series of oxidation experiments was carried out in which the solution pH was varied from 0 to 3.0. The results, shown in Fig. 6, indicated that there was no significant pH effect in the pH range of 0.5—2.0 with values of 1.3—2.0 for the molar ratio of Fe^{2+} oxidized/SO_2 introduced. However, the oxidation rate decreased dramatically below pH 0.5 and increased appreciably above pH 2.5. Since a significant amount of SO_2 was detected in the outlet gas at low-pH experiments, the reduction in the rate at low pHs may be due to the decreases in the solubility of sulfur dioxide[11] and in the oxidation rate of sulfurous acid with oxygen.[12,13] On the other hand, the rate increase at higher pHs seems to be attributable to the reduction of the oxidation potential of iron by the formation of a complex between iron and the hydroxide ions, as shown in Eqs. (9)—(14):[14]

$$Fe^{2+} + OH^- = FeOH^+, \tag{9}$$

$$Fe^{2+} + 2OH^- = Fe(OH)_2, \tag{10}$$

$$Fe^{3+} + OH^- \overset{K_I}{=} FeOH^{2+} \qquad pK_I = 11.1, \tag{11}$$

$$Fe^{3+} + 2OH^- \overset{K_{II}}{=} Fe(OH)_2{}^+ \qquad pK_{II} = 21.69, \tag{12}$$

$$2Fe^{3+} + 2OH^- \overset{K_d}{=} Fe_2(OH)_2{}^{4+} \qquad pK_d = 25.10, \tag{13}$$

$$Fe^{3+} + 3OH^- \overset{K_{sp}}{=} Fe(OH)_3 \qquad pK_{sp} = 37.20, \tag{14}$$

It has been reported that the reactive species of iron(II) with oxygen is Fe^{2+} in an acidic solution but $FeOH^+$ above a pH of about 3.[15] Further, the main iron(III) species above pH 2.5 is insoluble $Fe(OH)_3$; under these conditions, iron(II) becomes more easily oxidized.[15] Therefore, the direct oxidation of iron(II) with oxygen also proceeds at high pHs.

Oxidation of Iron(II) with SO_2/O_2 in the Presence of Different Foreign Substrates. A series of experiments was conducted in which different foreign substrates were added. Specifically, EDTA, sodium triphosphate, copper(II) sulfate, and catechol were used as these materials, all were known as accelrators or inhibitors for the oxidation of iron(II) and sulfite with oxygen, as shown in Table 1. Since the same reaction behavior was observed when the concentration of additives were changed from 0.01 to 0.03 mol/dm^3, the results of the tests using 0.02 mol/dm^3 of additives are given in Figs. 7 and 8. There was no noticeable influence on the reaction rate with the addition of copper(II) sulfate. In the presence of catechol, the oxidation did not proceed at all. On the other hand, EDTA and sodium triphosphate showed a limited inhibition; that is, the inhibition continued until the amount of iron(III) formed rose to about 0.02 mol/dm^3, but thereafter the rate was constant. When those results are compared with those shown in Fig. 2, it can be said that, while inhibition persists, the rates of oxidation in the presence of EDTA and triphosphate were

TABLE 1. CHARACTERIZATION OF ADDITIVES

Reaction	Acceleration	Inhibition
Oxidation of Fe^{2+} with O_2	EDTA $Na_3P_3O_{10}$ $CuSO_4$	$C_6H_4(OH)_2$
Oxidation of HSO_3^- with O_2	$CuSO_4$	EDTA $Na_5P_3O_{10}$ $C_6H_4(OH)_2$

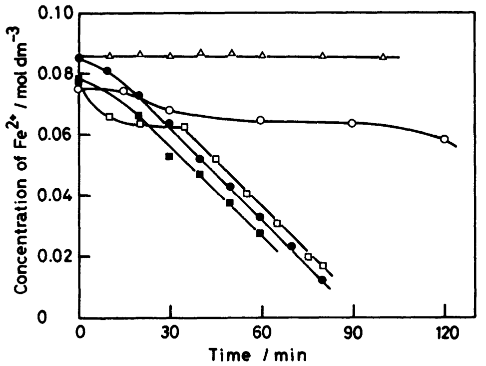

Fig. 7. Oxidation of iron(II) with SO_2/O_2 in the presence of different foreign substrates.
△: 0.02 mol/dm^3 $C_6H_4(OH)_2$, ■: 0.02 mol/dm^3 $CuSO_4$, ○: 0.02 mol/dm^3 $Na_5P_3O_{10}$, □: 0.02 mol/dm^3 EDTA-2Na, ●: None.

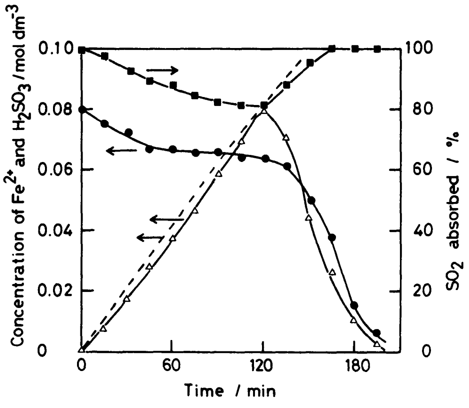

Fig. 8. Oxidation of iron(II) with SO_2/O_2 in the presence of 0.02 mol/dm^3 $Na_5P_3O_{10}$.
●: Fe^{2+}, △: H_2SO_3 found, ----: SO_2 absorbed (Calculated using analytical results of sulfur dioxide concentration in outlet gas).

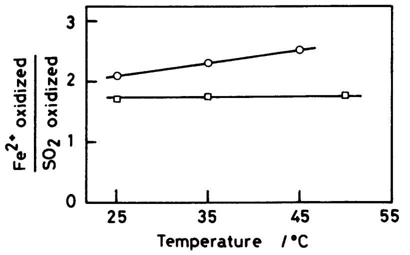

Fig. 9. Effect of temperature on the oxidation of iron(II) with SO_2/O_2.
□: pH 1.0, ○: pH 2.0.

almost the same as those found when oxygen alone was used with those compounds. It is of interest to note that the oxidation of sulfite did not proceed during this inhibition period, but that afterwards sulfurous acid and iron(II) both were rapidly oxidized (Fig. 8). It is considered, therefore, that complex-forming species, such as EDTA, triphosphate, and catechol, inhibit the oxidation of sulfurous acid with oxygen by masking iron(III), which acts as an oxidation catalyst. Such a process is known to inhibit sulfite oxidation.[16] It is also considered that some reactive intermediate produced in the reaction of sulfurous acid and oxygen plays a significant role in the oxidation of iron(II) to iron(III). The anions of HSO_5^-[17] and SO_5^{2-}[18] have, in fact, been postulated as intermediates in the oxidation of sulfite with oxygen, and SO_5^{2-} is known to be a strong oxidant in alkaline media.[19]

Oxidation of Iron(II) with SO_2/O_2 at Various Temperatures. The effect on the oxidation of the temperature over the 25—50 °C range at two different pHs, pH 1.0 and pH 2.0, is shown in Fig. 9. The Fe^{2+} oxidized/SO_2 oxidized molar ratio increased slightly with the increase in the temperature at pH 2.0, but there was no appreciable temperature effect at pH 1.0. The results obtained at pH 1.0 are not inconsistent with the idea that iron(II) is oxidized by an intermediate produced in the oxidation of sulfurous acid with oxygen. On the other hand, the results obtained at pH 2.0 showed that the direct oxidation of iron(II) with oxygen also occurred at higher temperatures.

General Discussion

The experimental results presented above have shown that; (a) the rate of the oxidation of iron(II) with SO_2/O_2 mixtures is independent of the concentrations of oxygen and iron(II), but is directly proportional to the amount of sulfurous acid oxidized; (b) the effects of changes in the pH and the temperature on the reaction rate are not significant; (c) the value of the Fe^{2+} oxidized/SO_2 oxidized molar ratio is 1.3—2.0; (d) some reactive intermediate produced in the reaction of sulfurous acid and oxygen plays a significant role in the oxidation of iron(II), and (e) the reaction between iron(III) and hydrogen sulfite does not occur under the reaction conditions used.

There have been many studies of the oxidation of sulfite with oxygen, and the free-radical-chain reactions shown by Eq. (A), proposed by Bäckstrom,[18] are the accepted oxidation mechanism for diluted sulfite solutions in the neutral and alkaline regions:

$$\left.\begin{aligned}
&SO_3^{2-} + Cu^{2+} \longrightarrow \cdot SO_3^- + Cu^+, \\
&\cdot SO_3^- + O_2 \longrightarrow \cdot SO_5^-, \\
&\cdot SO_5^- + SO_3^{2-} \longrightarrow \cdot SO_3^- + SO_5^{2-}, \\
&SO_5^{2-} + SO_3^{2-} \longrightarrow 2SO_4^{2-} + O_2, \\
&2\cdot SO_5^- \longrightarrow 2SO_4^{2-} + O_2.
\end{aligned}\right\} \qquad \text{(A)}$$

On the other hand, Schroeter has postulated the anion of HSO_5^- as an intermediate in the oxidation of a sulfite solution.[16] Since the tetravalent sulfur exists as $SO_2 \cdot H_2O$ and HSO_3^- below pH 4.5,[15] the postulation of HSO_5^- as an oxidation intermediate seems reasonable. Therefore, the following mechanism containing free-radical-chain reactions similar to that proposed for sulfite oxidation by Bäckstrom[18] was considered to be in reasonable agreement with the reaction results:

Equilibria:

$$SO_2 + H_2O \overset{K_1}{=} HSO_3^- + H^+, \qquad (7)$$

$$Fe^{2+} + HSO_3^- \overset{K_2}{=} FeHSO_3^+, \qquad (15)$$

$$Fe^{3+} + HSO_3^- \overset{K_3}{=} FeSO_3^+ + H^+. \qquad (16)$$

Initiation:

$$FeHSO_3^+ + 1/4\,O_2 \xrightarrow{k_1} FeSO_3^+ + 1/2\,H_2O, \qquad (17)$$

$$FeSO_3^+ \xrightarrow{k_2} \cdot SO_3^- + Fe^{2+}. \qquad (18)$$

Propagation:

$$\cdot SO_3^- + O_2 \xrightarrow{k_3} \cdot SO_5^-, \qquad (19)$$

$$\cdot SO_5^- + HSO_3^- \xrightarrow{k_4} HSO_5^- + \cdot SO_3^-. \qquad (20)$$

Termination:

$$HSO_5^- + HSO_3^- \xrightarrow{k_5} 2SO_4^{2-} + 2H^+, \qquad (21)$$

$$HSO_5^- + 2Fe^{2+} + H^+ \xrightarrow{k_6} SO_4^{2-} + 2Fe^{3+} + H_2O, \qquad (22)$$

$$\cdot SO_5^- + \cdot SO_5^- \xrightarrow{\text{slow}} 2SO_4^{2-} + O_2. \qquad (23)$$

The derived Fe^{2+} oxidized/SO_2 oxidized molar ratio based on this postulated mechanism is:

$$\frac{d[Fe^{3+}]/dt}{d[SO_4^{2-}]/dt} = \frac{2k_6[Fe^{2+}]^2[H^+]}{2k_5[HSO_3^-]+k_6[Fe^{2+}]^2[H^+]}$$

which would approach 2, since $2k_5[HSO_3^-]$ should be very small; this value is in agreement with the experimentally determined values of between 1.3—2.0 at pH 0.5—2.0. The assumption of a small value for $2k_5[HSO_3^-]$ seems reasonable because the sulfur dioxide introduced into the solution is immediately oxidized under the experimental conditions used. If the effect of the concentration of HSO_3^- on the oxidation of iron(II) could be investigated, it should be quite useful in confirming the propriety of this oxidation mechanism. However, it is important to remember that, in the presence of appreciable amounts of sulfurous acid, iron(III) reacts with HSO_3^- to form dithionate according to Eq. (6). In order to prevent this side reaction, the oxidaiton with SO_2/O_2 needs to be conducted in the absence of hydrogen sulfite ions in high concentrations at all time. Further, this mechanism may also elucidate the strong oxidation power of SO_2/O_2 mixtures that was shown for the leaching of ZnS.[2]

References

1) K. N. Subramanian and D. B. W. Yawney, British Patent 1494564 (1977).

2) W. A. Robert and I. G. Matthew, *Proc. Australas. Inst. Min. Met.*, **No. 280**, 41 (1981).

3) T. Sato and F. Lawson, *Hydrometallurgy*, **11**, 371 (1983).

4) T. Sato, *Ryusan to Kogyo*, **32**, 1 (1979).

5) R. E. Huffman and N. Davidson, *J. Am. Chem. Soc.*, **78**, 4836 (1956).

6) C. T. Mathews and R. G. Robins, *Proc. Australas. Inst. Min. Met.*, **No. 242**, 47 (1972).

7) L. G. Sillen, "Stability Constants of Metal Ion Complexes," Chem. Soc. Burlington House, London (1964), p. 116.

8) W. C. E. Higginson and J. W. Marshall, *J. Chem. Soc.*, 447 (1973).

9) D. W. Carlyle and D. F. Zeck, Jr., *Inorg. Chem.*, **12**, 2973 (1973).

10) T. Sato, T. Shimizu, and T. Okabe, *Nippon Kagaku Kaishi*, 361 (1978).

11) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions (Oxidation Potentials)," 2nd Ed., Prentice Hall (1952), p. 74.

12) T. Sato and T. Okabe, *Nippon Kagaku Kaishi*, 1124 (1977).

13) R. J. Meyer, "Gmelins Handbook of Inorganic Chemistry," 8th Ed., Verlag Chemie, Weinheim, Germany, Vol. 9 (1965), p. 1454.

14) K. B. Yatsimirskii and V. P. Vasil'ev, "Instability Constants of Complex Compounds," Pergamon Press (1960), p. 113.

15) M. Nagayama, "Oxidation of Iron(II) Ion in Aqueous Solution with Oxygen," Symposium on the Characteristics of Waste Water and Its Treatment, Sendai, Japan (1973), p. 38.

16) A. Huss, Jr., P. K. Lim, and C. A. Eckert, *J. Phys. Chem.*, **86**, 4224 (1982).

17) L. C. Schroeter, "Sulfur Dioxide," Pergamon Press, New York (1966), p. 44.

18) L. C. Bäckstrom, *Z. Phys. Chem.*, **B25**, 122 (1934).

19) V. A. Etell, M. A. Mosiu, and E. A. Devuyst, *Hydrometallurgy*, **4**, 247 (1979).