Simultaneous Removal of NO and SO_2 by Absorption into Aqueous Mixed Solutions

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Currently, nitric oxide and sulfur dioxide emitted from stationary combustion facilities have been removed separately by selective catalytic reduction processes and wet scrubbing processes. There is no practical process successful for simultaneous removal of NO and SO_2. Since scrubbing solutions for wet NO removal also remove SO_2, wet scrubbing processes are potential candidates for simultaneous NO and SO_2 removal. For instance, by use of liquid-phase reaction sequences in which both dissolved NO and SO_2 participate, simultaneous removal of both the gases can be achieved effectively in a single step or equipment. Aqueous solutions of Na_2SO_3 with added Fe(II)EDTA (ferrous ion coordinated to ethylenediaminetetraacetic acid) seem to be promising absorbents to fulfill such a possibility. To establish the procedure for inevitable regeneration or treatment of spent adsorbent, it is necessary to clarify the whole scheme of the liquid phase complicated reactions.

In our previous work (Sada et al., 1984, 1986), the pathways of the liquid-phase reactions were completed and presented in the form of a map. The degree of removal of NO was found to depend on the concentration of Fe(II), which was determined from a balance of oxidation and reduction rates of iron. The removal of NO during simultaneous absorption of NO and SO_2 could be predicted from corresponding experimental results for absorption of only NO into an absorbent of the same pH value. Regarding reaction kinetics, the reduction of Fe(III) to Fe(II) by HSO_3^- with coexisting EDTA, the oxidation of Fe(II) to Fe(III) by NO in the presence of Na_2SO_3, and the oxidation of Fe(II)EDTA by dissolved oxygen were investigated (Sada et al., 1986, 1987).

In view of the results of our earlier fundamental work cited above, there are two important considerations that emerge in the simultaneous NO and SO_2 removal process:

1. To keep the level of the concentration of Fe(II) as high as possible and for this purpose, to reduce a portion of the effluent stream by sulfite at the boiling temperature in the outer loop of the absorber
2. to control the pH of the absorvent.

The former is required from the experimental result that the degree of NO removal mainly depends on the concentration of Fe(II). The latter is necessary because of the pH of the absorbent is decreased by simultaneously absorbed SO_2.

In the present work, the process flow diagram for simultaneous removal of NO and SO_2 by absorption into an aqueous solution of Na_2SO_3 with added Fe(II)EDTA was first proposed on the basis of our earlier fundamental work. Secondly, to put this simultaneous removal process into practical application, long-term absorption tests and the regeneration of (simulated) spent liquor by reduction at its boiling temperature were undertaken.

Background of Simltaneous NO and SO_2 Removal Process

The wet scrubbing method generally has a significant disadvantage of inevitable waste-liquor treatment, so that the process should incorporate a regeneration or treatment step of spent liquor. To do this, it is necessary to clarify the whole scheme of the liquid-phase reactions. The pathways of the liquid-phase reactions accompanying absorption of NO and SO_2 into an aqueous solution of Na_2SO_3 with added Fe(II)EDTA chelate have been studied previously (Sada et al., 1984, 1986). The mechanisms of production of N–S compounds, oxidation of Fe(II) to Fe(III) by NO in the presence of Na_2SO_3, and production of gaseous N_2O were clarified, and the pathways of the liquid-phase reactions were presented in the form of a map. It has been shown that the degree of NO removal mainly depends on the concentration of Fe(II). The influence of the coexistence of SO_2 is reflected only by the decrease in pH of the absorbent due to the reaction of SO_2 with sulfite. The degree of removal of NO during simultaneous NO and SO_2 absorption can be interpreted by the corresponding experimental results during absorption of only NO at the same pH value.

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The reaction kinetics for reduction of Fe(III) to Fe(II) by sulfite with coexisting EDTA, oxidation of Fe(II) to Fe(III) by NO in the presence of Na_2SO_3, and oxidation of Fe(II)EDTA by dissolved oxygen were established (Sada et al., 1986, 1987). The reduction of Fe(III) by sulfite,

$$\mathrm{Fe(III)EDTA^- + HSO_3^- \rightarrow Fe(II)EDTA^{2-} + \tfrac{1}{2}S_2O_6^{2-} + H^+} \quad (a)$$

was found to be first order in both Fe(III)EDTA and HSO_3^-, respectively, and minus first order in Fe(II)EDTA. The apparent oxidation by NO in the presence of Na_2SO_3,

$$\mathrm{2Fe(II)EDTA(NO)^{2-} + SO_3^{2-} \rightarrow 2Fe(II)EDTA^{2-} + SO_3(NO)_2^{2-} \rightarrow 2Fe(III)EDTA^- + N_2O_2^{2-} + SO_3^{2-}} \quad (b)$$

was found to be first order in both Fe(II)EDTA(NO) and Na_2SO_3, and minus first order in Fe(III)EDTA. The oxidation reaction of Fe(II)EDTA by dissolved oxygen,

$$\mathrm{4Fe(II)EDTA^{2-} + O_2 + 2H_2O \rightarrow 4Fe(III)EDTA^- + 4OH^-} \quad (c)$$

was first order in dissolved oxygen, and about half-order in Fe(II)EDTA. This oxidation was suppressed as much as about 30% by adding 20% EDTA in excess.

In view of the experimental evidence mentioned above, the process flow for simultaneous NO and SO_2 removal by an aqueous solution of Na_2SO_3 with added Fe(II)EDTA can be schematically drawn as in Figure 1. The important points in this process are to keep the concentration of Fe(II) as high as possible and to control the pH value of the absorbent.

Experimental Method

Reduction of Fe(III)EDTA by sulfite at boiling temperature

To maintain the degree of removal of NO at a high level, it is necessary to keep the concentration of Fe(II) in the absorbent as high as possible. In the schematic flow diagram for the simultaneous NO and SO_2 removal process depicted in Figure 1, some portion of the absorbent is taken out of the absorber and regenerated by reduction at a boiling temperature in the regeneration loop. It should be confirmed whether the reduction rate equation presented for reaction temperatures ranging from 20 to 60°C does or does not hold at the boiling point. The experimental apparatus and procedures, which are similar to those in our earlier work (Sada et al., 1986), are described briefly in the following.

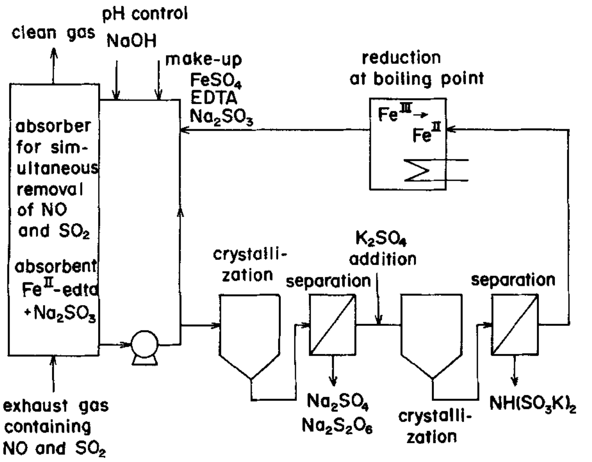

Figure 1. Flow diagram for simultaneous NO and SO_2 absorption process into aqueous mixed solutions of Fe(II)EDTA and Na_2SO_3.

The reactor is a bubble column equipped with a porous ball bubbler as a gas sparger; the diameter of sintered glass particles is 0.1 mm, the ball diameter is 10 mm. The reactor was charged with aqueous $FeCl_3$ solution and aqueous EDTA solution through which N_2 was passed at a flow rate of about 30 cm³/s. The volume of reactant solution was 1,000 cm³. A reaction was caused by adding aqueous Na_2SO_3 solution. The initial concentration of Fe(III)EDTA was 0.03 molar (M), the initial pH was varied from 6 to 8, and the initial concentration of Na_2SO_3 was varied from 0.05 to 0.25 M. The reaction was followed by sampling a desired amount of reaction liquid periodically and determining the concentration of Fe(II) by 1,10-phenanthroline colorimetry.

Long-term absorption test

The absorption of lean NO at 1,000 ppm was carried out at 50°C for 3 h, with coexisting 5% O_2, simulating practical flue gases. The absorber used was a bubble column, similar to the one used in Fe(III) reduction runs. The absorbent was an aqueous mixed solution of 0.01 M $FeSO_4$, 0.011 M EDTA · 2NA (disodium salt of EDTA), and 0.25 M Na_2SO_3. The chelate solution of Fe(II)EDTA was prepared by adding 10% EDTA in excess. This is because the oxidation rate of Fe(II)EDTA by dissolved oxygen was empirically found to be suppressed by about 30% by adding 10% EDTA in excess (Sada et al., 1987). The bubble column reactor was operated continuously with respect to the gas phase and batchwise with respect to the liquid phase. The total gas flow rate was kept constant at 31.7 cm³ (STP)/s. The reactant liquid volume free of gas bubbles was 1,000 cm³. The concentration of NO in the influent gas stream and the concentration of Fe(II) in the absorbent in the course of absorption were measured. The concentration of NO was determined by means of a Yanaco UO-1 UV derivative spectrophotometer analyzer.

Subsequently, some absorption tests were run over a fairly long time. NO at about 760 ppm in the first 105 min and successively as high as 4,000 ppm was absorbed for 20 h to realize a lowering of absorbent capacity due to accumulation of N–S products. The total gas flow rate was maintained at 30 cm³ (STP)/s. The initial concentrations of Fe(II)EDTA and Na_2SO_3 were 0.01 and 0.25 M, respectively. Also, the chelate solution of Fe(II)EDTA was prepared by adding 10% EDTA in excess. The initial pH value was 7.0, and in the course of absorption, the pH value was adjusted at the same value by adding NaOH solution. The concentrations of such reaction products as $HON(SO_3)_2^{2-}$, $N(SO_3)_3^{3-}$, $NH(SO_3)_2^{2-}$ and $S_2O_6^{2-}$, and Fe(II) were determined by chemical analyses and 1,10-phenanthroline colorimetry, respectively. The schematic diagram for determination of such compounds has been shown in a previous article (Sada et al., 1984).

Simultaneous absorption of NO and SO_2 in the presence of O_2

According to our previous work (Sada et al., 1984), the effect of coexisting SO_2 on the degree of removal of NO had been found to occur only through a decrease in pH of the absorbent resulting from dissolution of SO_2. It should be confirmed whether or not this experimental finding is also valid in the presence of O_2. Some experiments were made on simultaneous absorption of NO and SO_2 into a batch of aqueous mixed solution of 0.01 M Fe(II)EDTA and 0.25 M Na_2SO_3 in the presence of 6.2% O_2 at 50°C for 3 h. The initial values of pH were above and below 7. The concentrations of NO and SO_2 in the influent stream were fixed at 1,000 and 1,500 ppm, respectively, and the total gas flow rate was maintained at 30 cm^3 (STP)/s.

Results and Discussion

Reduction of Fe(III)EDTA by sulfite at boiling temperature

It has been reported that the rate of reaction between Fe(III)EDTA and Na_2SO_3 in aqueous solutions can be expressed as first order with respect to both Fe(III)EDTA and HSO_3^- concentrations and minus first order with respect to Fe(II)EDTA concentration (Sato et al., 1978; Sada et al., 1978):

$$-\frac{d[\mathrm{Fe(III)EDTA^-}]}{dt} = k_2\frac{[\mathrm{Fe(III)EDTA^-}][\mathrm{HSO_3^-}]}{[\mathrm{Fe(II)EDTA^{2-}}]} = \frac{k_2}{1+K_2/[\mathrm{H^+}]}\frac{[\mathrm{Fe(III)EDTA^-}][\mathrm{Na_2SO_3}]}{[\mathrm{Fe(II)EDTA^{2-}}]} \quad (1)$$

or

$$-\frac{d(a_0-x)}{dt} = \frac{k_2}{1+K_2/[\mathrm{H^+}]}\frac{(a_0-x)(b_0-x)}{x} \quad (2)$$

where K_2 denotes the second dissociation constant of sulfurous acid (= $[H^+][SO_3^{2-}]/[HSO_3^-]$). Integration of Eq. 2 results in

$$\frac{a_0 \ln(a_0-x) - b_0 \ln(b_0-x)}{a_0-b_0} = \frac{k_2 t}{1+K_2/[\mathrm{H^+}]} + \frac{a_0 \ln a_0 - b_0 \ln b_0}{a_0-b_0} \quad (3)$$

On the basis of an integral form of the rate equation, the experimental data are represented in Figures 2 and 3 as a plot of the lefthand member of Eq. 3 vs. reaction time. Such plots essentially give straight lines. The reaction rate constant, k_2, can be calculated from the slope of the straight line. The calculated reaction rate constants at the boiling temperature (about 102°C) are plotted against $1/T$ in Figure 4 along with those at

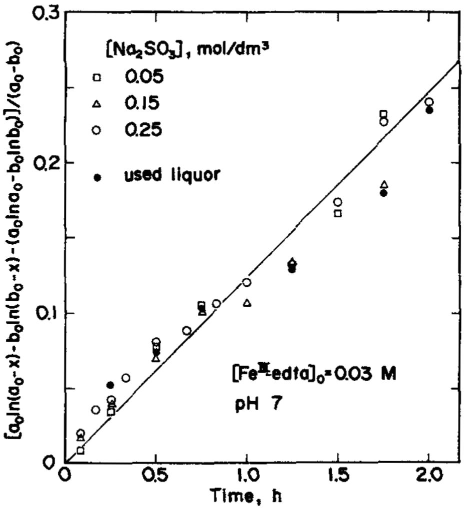

Figure 3. Test of Eq. 3 for Fe(III)EDTA reduction at boiling temperature.

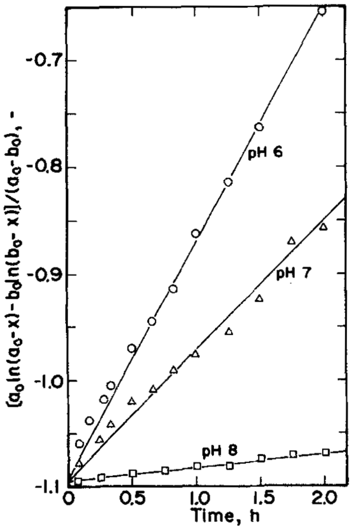

Figure 2. Test of Eq. 3 for reduction of Fe(III)EDTA by Na_2SO_3 at boiling temperature.

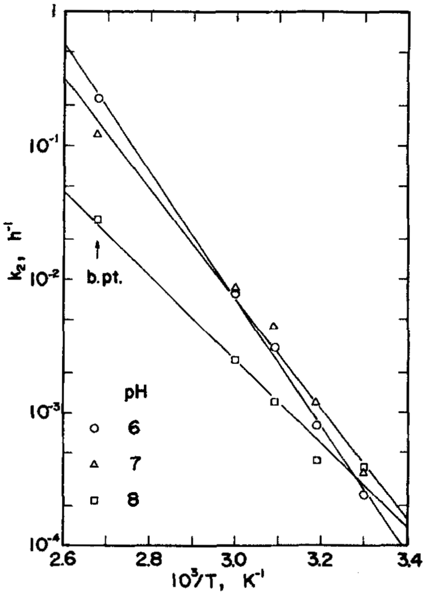

Figure 4. Arrhenius plot of reduction rate constant k_2.

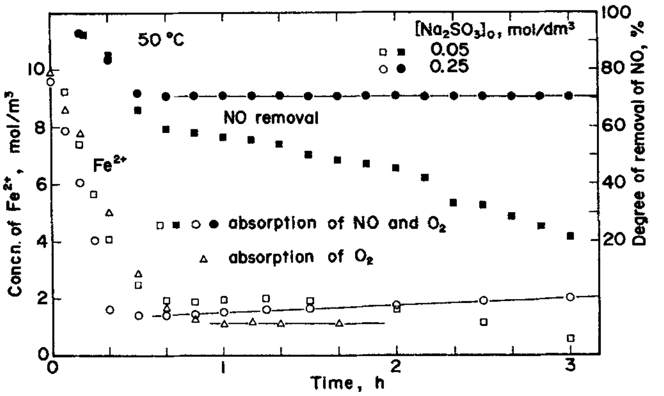

Figure 5. Time changes of degree of removal of NO and concentration of Fe^{2+} in the presence of O_2.

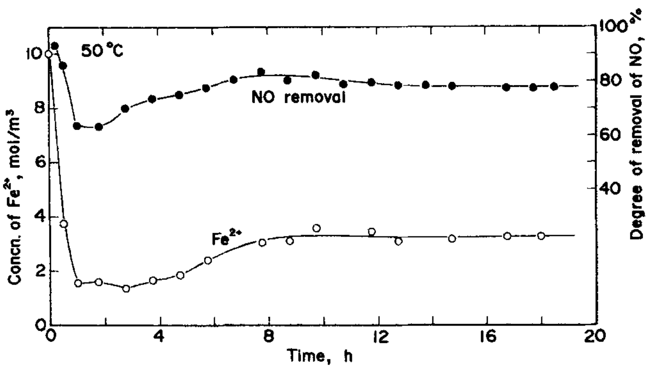

Figure 6. Long-term removal of NO in the presence of O_2.

different temperatures (Sada et al., 1986). A good linear relationship could be drawn between these two factors. Even at the boiling temperature, the reaction rate equation, Eq. 1, is found to be valid. The filled circles in Figure 3 represent the data for reduction of the spent liquor at the boiling point. The spent liquor here means an aqueous absorbent resulting after 1,000 ppm NO diluted with N_2 passed through a 1,000 cm^3 aqueous solution of 0.03 M Fe(II)EDTA and 0.25 M Na_2SO_3 at the total gas flow rate of 60 cm^3/s for 3 h. The filled circles fall close to the straight line. Accordingly, the reduction kinetic law also holds for reduction of spent absorbent.

Long-term absorption test

The experimental results on the time dependence of the degree of removal of NO and the concentration of Fe(II) are shown in Figure 5. It is shown that the concentration of Fe(II) is maintained at the level of about 20% of the initial value or slightly increased when 0.25 M Na_2SO_3 is loaded, and the degree of removal of NO is kept constant at a high level of about 70%. It is also apparent that the oxidation of Fe(III)EDTA by NO in the presence of Na_2SO_3 has been promoted by increasing the sulfite concentration. But it should be noted that the concentration of Fe(II) after simultaneous NO and SO_2 absorption for 1 h or more, is higher than that after single absorption of O_2 for the same time period. It implies that the oxidation of Fe(II)EDTA by dissolved oxygen is suppressed by coexisting NO. This fact is interpreted as follows: The Fe(II)EDTA chelate in the presence of dissolved NO exists as the chelates both with and without coordination with NO. According to Eq. 1, the reduction of Fe(III)EDTA is minus first order with respect to Fe(II)EDTA. If the Fe(II)EDTA chelate participating in the reduction is only the chelate without any coordination with NO, then it follows that the reduction rate is enhanced by the presence of NO.

The time dependences of the degree of removal of NO and the concentration of Fe(II) for 20 h absorption are shown in Figure 6. The time dependences of the concentrations of liquid-phase products are plotted in Figure 7. The degree of removal of NO is mutually related to the concentration of Fe(II), as would be expected. It should be emphasized that both the degree of NO removal and the Fe(II) concentration were kept constant at 76% and 0.0034 mol/dm^3, respectively, after 10 h had passed. This fact, along with that depicted in Figure 5, implies that the process can be continuously operated at a realistic level of NO removal. The concentration of the main product, $HON(SO_3)_2^{2-}$, keeps a constant value of 0.03 mol/dm^3. The other N-S com-

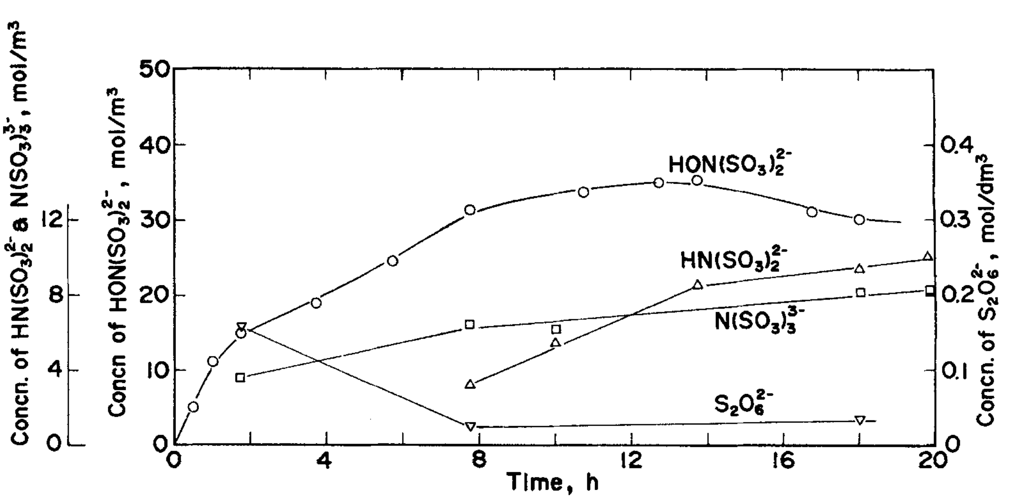

Figure 7. Time changes of concentrations of liquid-phase species for long-term removal of NO in the presence of O_2.

Table 1. Concentrations of Liquid-Phase Species Before and After Reduction of Spent Liquor

Species	Conc., mol/dm^3 Before	Conc., mol/dm^3 After*
$HON(SO_3)_2^{2-}$	0.0300	0.0050
$N(SO_3)_3^{3-}$	0.0094	0
$HN(SO_3)_2^{2-}$	0.0081	0.0324
$S_2O_6^{2-}$	0.0342	0.0147
SO_4^{2-}	0.300	0.487
Fe^{2+}	0.00342	0.00664

*Reduction at boiling temp. for 2 h

pounds, $N(SO_3)_3^{3-}$ and $HN(SO_3)_2^{2-}$, gradually increase. $S_2O_6^{2-}$, which is produced by reduction of Fe(III) by sulfite, exists only in a much lower concentration level, as would be expected. This may be because a large portion of the compound is oxidized by dissolved oxygen to form SO_4^{2-}.

To confirm the effectiveness of the reduction of spent liquor at the boiling temperature, the spent absorbent was reduced at the boiling point for 2 h. The liquid-phase compositions before and after reduction are listed in Table 1. It is shown that the concentration of Fe(II) increases from 0.034 to 0.066 mol/dm^3 and the final reaction product, $HN(SO_3)_2^{2-}$, increases from 0.0081 to 0.032 mol/dm^3. The mass balances in SO_3^{2-} and SO_4^{2-}, however, do not hold. This may be because the liquid absorbent is oxidized by air at the boiling temperature.

In summary, the pathways of the liquid-phase reactions accompanying the absorption of NO and SO_2 in the presence of O_2 can also be described in the map presented in an earlier article (Sada et al., 1986), but further, the following two reactions are possible:

1. $S_2O_6^{2-}$ is oxidized to SO_4^{2-}
2. $H_2N_2O_2$ (or $HN_2O_2^-$) and $N_2O_2^{2-}$ react with HSO_3^- to produce $HON(SO_3)_2^{2-}$

Reaction 2 is plausible if the nitrogen mass balance in earlier stages of the absorption depicted in Figure 7 is considered. Considering these, the reaction map can be drawn as in Figure 8.

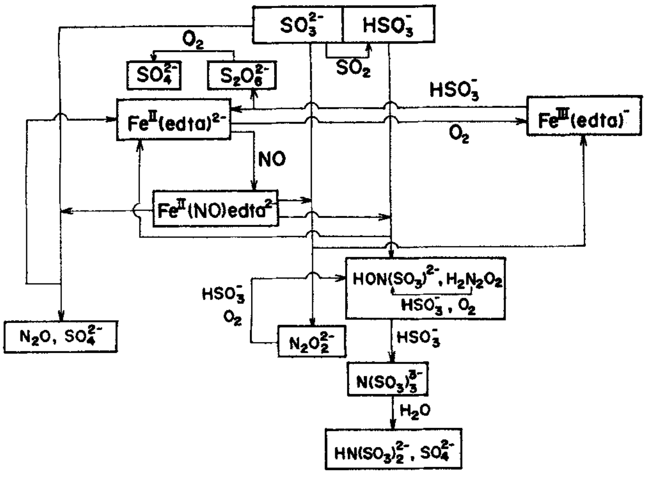

Figure 8. Pathways of liquid-phase reactions accompanying simultaneous absorption of NO and SO_2 into aqueous solutions of Na_2SO_3 with added Fe(II)EDTA in the presence of O_2.

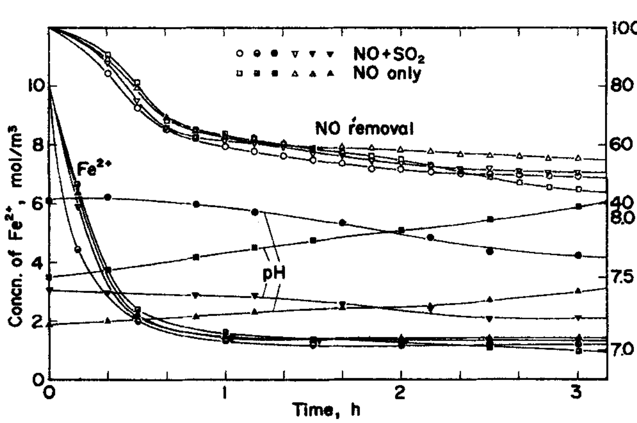

Figure 9. Time dependences of degree of removal of NO, concentration of Fe^{2+}, and pH during single NO and simultaneous NO and SO_2 absorptions in the presence of O_2 above pH 7.

Simultaneous absorption of NO and SO_2 in the presence of O_2

Typical examples of the time dependences of the degree of removal of NO, the concentration of Fe(II), and the pH value of the solution for simultaneous absorption are shown in Figures 9 and 10, along with those for single absorption of NO. It should be emphasized that in each run the degree of removal of SO_2 was higher than 95%. The degrees of NO removal for simultaneous absorption as shown in Figure 9 are found to be very close to those for single absorption at the same pH values. Below pH 7, the time dependences of the degree of NO removal for simultaneous absorption are found to agree well with those for single absorption, as depicted in Figure 10. When SO_2 coexists, HSO_3^-, which functions as reducing agent for Fe(III)EDTA, is formed by reaction of dissolved SO_2 with SO_3^{2-}. Accordingly, the amount of sulfite make-up can be considerably reduced,

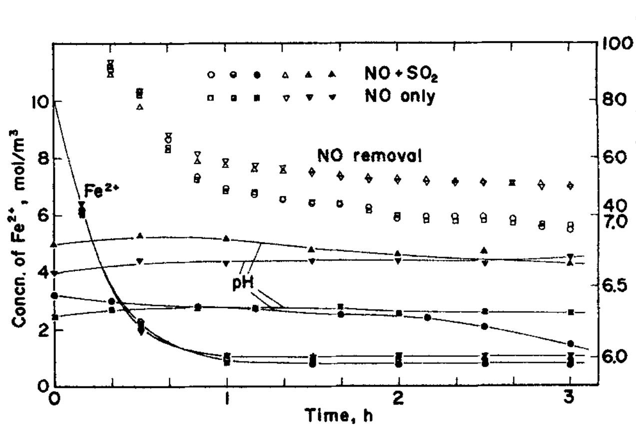

Figure 10. Time dependences of degree of removal of NO, concentration of Fe^{2+}, and pH during single NO and simultaneous NO and SO_2 absorptions in the presence of O_2 below pH 7.

although pH control through NaOH addition is inevitably imposed.

Conclusions

The rate for reduction of Fe(III) by sulfite with coexisting EDTA at the boiling temperature can be expressed as first order with respect to the concentration of Fe(III)EDTA and HSO_3^- and minus first order with respect to the concentration of Fe(II)EDTA, which is the same form as that at temperatures of 20–60°C. The degree of removal of NO can be maintained at a high value over a long time period even with coexisting SO_2 and O_2, as long as the concentration of sulfite is kept constant at 0.2–0.25 molar or more. The dithionate formed by reduction of Fe(III)EDTA with sulfite was found to be oxidized by dissolved oxygen and converted to sulfate. Such findings would be directly useful to put the proposed simultaneous NO and SO_2 removal process into practical application.

Notation

a_0 = initial concentration of Fe(III)EDTA, mol/dm^3
b_0 = initial concentration of Na_2SO_3, mol/dm^3
K_2 = second dissociation constant of sulfurous acid, mol/dm^3
k_2 = reaction rate constant in Eq. 1, s^{-1}
T = reaction temperature, K
t = reaction time, s or h
x = concentration of Fe(II) in the course of reduction of Fe(III)EDTA by sulfite, mol/dm^3

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