

Removal of Atmospheric Pollutants

(4) Removal of NO by Aqueous Ferrous Sulfate Solutions

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大気汚染物質除去に関する研究

(4) FeSO₄水溶液による脱硝

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The kinetics of absorption of NO in aqueous FeSO₄ solutions were checked for wide operating conditions, i.e., for exposure times of 0.2-5000 s and NO concentrations of 100 ppm-99% by volum. For this purpose, three different types of absorbers, a wetted wall column, a quiescent liquid absorber, and a stirred tank absorber with a plain gas-liquid interface, were used. It was concluded that the chemical absorption process could be predicted satisfactorily by a theory of gas absorption with reversible reaction of the form of $A + B \rightleftharpoons E$ using existing information on reaction on kinetics and statics.

Introduction

The removal of NO emitted from stationary combustion facilities has recently been the target of intensive investigation. A number of wet scrubbing processes appropriate for the removal of NO have been developed and some of them are capable of removing another air-pollutant, SO₂, simultaneously. The wet scrubbing method, however, has a significant disadvantage of inevitable waste-liquor treatment. In view of this drawback, it appears that an aqueous solution of ferrous sulfate is a considerably promising absorbent because of easy regeneration. The kinetics of the reaction between NO and FeSO₄ in aqueous solutions have been studied by using the temperature-jump method (Kustin et al., 1966) and the chemical absorption method (Hikita et al., 1977). In fact, the concentration of NO in the flue gases emitted from fossil-fired sources is generally less than several hundred parts per million. Therefore, it is necessary to discuss the absorption mechanism of lean NO and point out the problem encountered in the lean gas absorption process from the standpoint of practical application.

The present work was undertaken to check the applicability of existing information on kinetics and

statics to the chemical absorption for wider operating conditions, i.e. for gas-liquid contact times of 0.2-5000 s and NO concentrations of 100 ppm-99% by volume.

Experimental Section

The chemical absorption has been carried out over a wide range of gas-liquid contact times using a wetted wall column and a quiescent liquid absorber. The contact time was varied from 0.2 to 0.9 s by changing the film height for the wetted wall column and from 600 to 5000 s for the quiescent liquid absorber, respectively. Some detailed description of the absorbers is given elsewhere (Sada et al., 1976). The gas phase was pure NO saturated with water vapor at the temperature of the experiment. The absorbents were aqueous FeSO₄ solutions of concentrations from 0.0525 to 0.145 M. In these solutions H₂SO₄ was added at a concentration of 0.17 M to suppress oxidation Fe²⁺ to Fe³⁺ in preparing the absorbent. In the wetted wall column experiment, 0.025 vol % of a surface active agent was also added to the absorbent to prevent rippling on the liquid film. Absorption rates in both absorbers were determined volumetrically (Sada et al., 1976).

The absorption of lean NO has been conducted in

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a stirred vessel with a plain gas-liquid interface. The concentration of NO in the gas phase was varied from 12% to 100 ppm by volume. The absorber was operated continuously with respect to the gas phase and batchwise with respect to the liquid phase. The vessel and the impellers in gas and liquid phases are sketched in Figure 1. The cylindrical absorption vessel was 8.0 cm i.d. with four symmetrically located baffles in the liquid phase. Two stirrers, driven by two separate motors, were used to agitate the gas and liquid phases. The liquid stirrer was a fan turbine with eight flat blades and was placed at half of the liquid depth. The gas stirrer was also a fan turbine with four flat blades mounted in the center of the gas phase. The stirring speeds of the liquid phase and gas phase stirrers were maintained at 162 and 500 rpm, respectively.

The solute gas NO was diluted by N₂, saturated with water vapor at the temperature of the apparatus, and fed into the absorber. The absorbents were aqueous FeSO₄ solutions ranging from 0.10 to 0.76 M. The absorbent contained 0.17 M H₂SO₄ as an anti-oxidation agent. The amount of liquid absorbent was 500 cm³. Concentrations of NO in the gas phase at the inlet and the outlet of the absorber were determined by either gas chromatography or UV spectrometry (Yanaco UO-1 derivative spectrophotometer). Absorption rates of NO were calculated from the difference between inlet and outlet concentrations and the total gas flow rate. All the experimental runs were performed at atmospheric pressure and at 25°C.

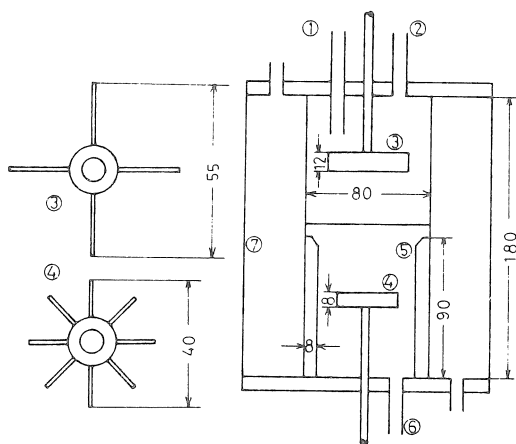
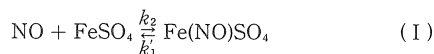


Fig. 1. Stirred vessel and impellers: 1, gas inlet; 2, gas outlet; 3, gas-phase stirrer; 4, liquid-phase stirrer; 5, baffle; 6, liquid inlet and outlet; 7, water jacket. Dimensions are given in millimeters.

Results and Discussion

Nitric oxide reacts reversibly with ferrous sulfate in aqueous solutions according to the reaction (Kustin

et al., 1966)



to form an unstable complex compound. The forward reaction is second order, i.e. first order in both NO and FeSO₄; the reverse reaction is first order in Fe(NO)SO₄ (Kustin et al., 1966).

The rate of absorption of NO into an aqueous FeSO₄ solution may be predicated by absorption theory for a reversible reaction of the form A + B ⇌ E.

In order to compare the results for the chemical absorption experiments with the theoretical predictions on the basis of film model or penetration model, it is necessary to know the values of physical solubility of NO and diffusivity of NO, Fe²⁺, and FeNO²⁺ in aqueous FeSO₄ solutions containing H₂SO₄.

Solubility and Diffusivity. The physical solubility of NO in aqueous FeSO₄ solutions containing H₂SO₄ was calculated from the correlation of the solubility in mixed electrolyte solutions (Onda et al., 1970b)

$$\log \frac{\alpha}{\alpha_w} = -(K_{s1}I_1 + K_{s2}I_2) \quad (1)$$

where K_{s1} and K_{s2} are the salting-out parameters for FeSO₄ and H₂SO₄ having ionic strengths I_1 and I_2 , respectively. The salting-out parameter depends on the ion and present and may be expressed by

$$K_s = x_g + x_a + x_c \quad (2)$$

The values of x for various species are available in the literature (Onda et al., 1970a; Sada et al., 1977): $x_g(\text{NO}) = -0.1825$, $x_a(\text{SO}_4^{2-}) = 0.3446$, $x_c(\text{Fe}^{2+}) = -0.0602$, and $x_c(\text{H}^+) = -0.1110$

The diffusivity of NO in aqueous FeSO₄ solutions containing H₂SO₄ also cannot be measured directly. Thus, the liquid-phase diffusivity of NO, D_A , was estimated from the following equation.

$$D_A/D_{Aw} = 1 - 0.122[\text{H}_2\text{SO}_4] - 0.291[\text{FeSO}_4] \quad (3)$$

Equation 3 is based on the correlation for diffusivity of carbon dioxide in aqueous electrolyte solution proposed by Onda et al. (1970c) and Sada et al. (1972)

$$D_w/D = 1 + 0.669B_1C + 0.412B_2C^2 \quad (4)$$

where B_1 and B_2 are constants obtained from viscosity data of the solution, e.g.

$$\mu = \mu_w(1 + B_1C + B_2C^2) \quad (5)$$

The numerical coefficients in eq 3 were estimated from the viscosity data. The value of D_{Aw} at 25°C is known (Wise and Houghton, 1968). The validity of eq 3 was checked by observed values of diffusivity of N₂O in aqueous FeSO₄ solutions containing H₂SO₄. The liquid-phase diffusivity of N₂O was measured by the laminar liquid-jet technique. The measured values agreed with eq 3 within 2% deviation as shown in Figure 2.

The effective diffusivity of FeNO²⁺ was not avail-

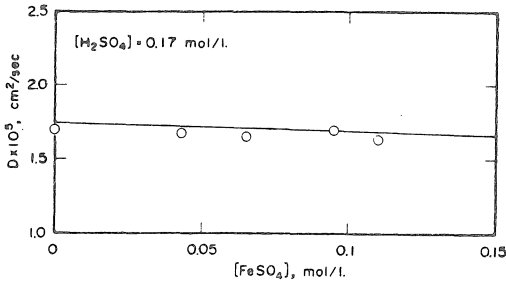


Fig. 2. Comparison of observed values of N_2O diffusivity in the liquid phase with predictions of eq 3 (solid line).

able in the literature; following Hikita et al. (1977), it was assumed to be equal to that of Fe^{2+} . The ratio of the effective diffusivity of Fe^{2+} to the liquid-phase diffusivity of NO , D_B/D_A , was assumed to be equal to that at infinite dilution. The effective diffusivity of Fe^{2+} at infinite dilution was estimated by the method of Vinograd and McBain (1941).

Chemical Absorption Using a Wetted Wall Column and a Quiescent Liquid Absorber. The experimental results for chemical absorption with a wetted wall column and a quiescent liquid absorber are shown in Figure 3 where the enhancement factor ϕ is plotted vs. the reaction-diffusion modulus \sqrt{M} . The values of the enhancement factor were calculated from the measured values of absorption rate N_A and exposure time t with estimates of C_{A1} and D_A as described above. In order to calculate the value of \sqrt{M} for each experimental run, the value of the forward reaction rate constant k_2 of reaction I is required. The value of k_2 was taken as $6.2 \times 10^5 L/mol s$ (Kustin et al., 1966). The solid lines represent the approximate penetration predictions proposed by Hikita et al. (1977) for gas absorption with reversible reaction of the form of $A + B \rightleftharpoons E$. In calculating the theoretical lines, the concentration of NO in the bulk of liquid was taken to be zero and the value of chemical equilibrium constant K of reaction I was taken as 450 L/mol reported by Kustin et al. (1966). A series of

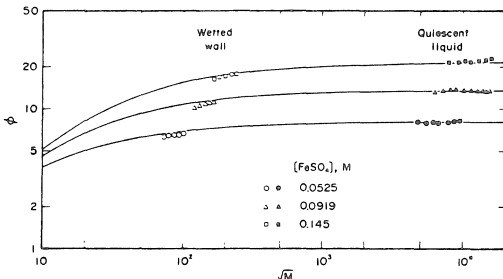


Fig. 3. Enhancement factor for absorption of pure NO in aqueous $FeSO_4$ solutions containing H_2SO_4 .

experimental points with both absorbers coincide with the solid lines. Experimental data from the quiescent liquid absorber with much longer exposure times fall on the theoretical predictions ϕ_∞ under an equilibrium reaction regime, approximately defined by (Hikita et al., 1977)

$$\phi_\infty = 1 + \frac{K\sqrt{D_E/D_A}C_{B0}}{1 + K\sqrt{D_E/D_B}C_{A1}} \quad (6)$$

Chemical Absorption Using a stirred Vessel with a Plain Gas-Liquid Interface. Experimental results with the stirred tank absorber were shown in Figure 4 as a plot of the absorption rate of NO , N_A , against

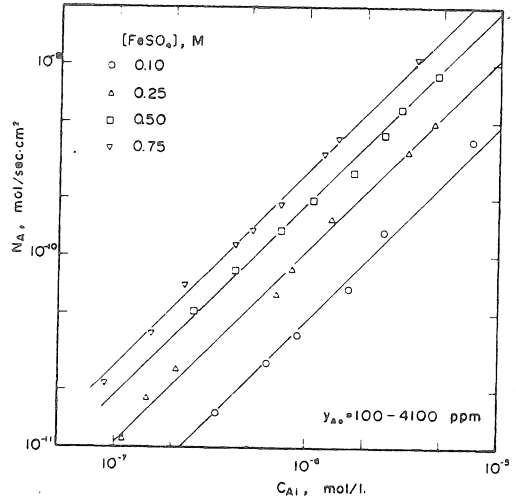


Fig. 4. Absorption of NO in aqueous $FeSO_4$ solutions containing H_2SO_4 using a stirred vessel with a plain gas-liquid interface ($y_{A0} = 100-4100$ ppm).

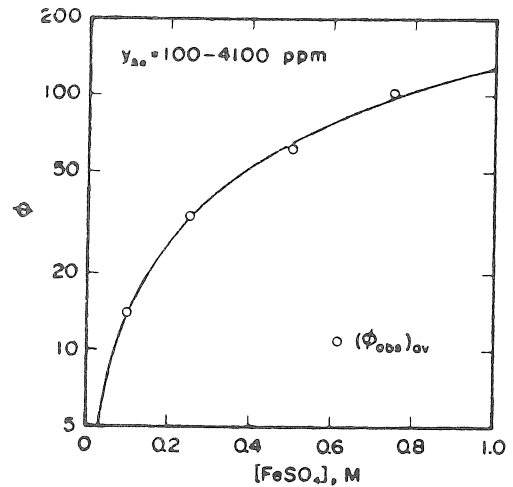


Fig. 5. Comparison of observed and predicted enhancement factor for absorption of NO into aqueous $FeSO_4$ solutions containing H_2SO_4 ($y_{A0} = 100-4100$ ppm).

the interfacial concentration of NO in the liquid phase, C_{A1} . In this case the concentration in the gas phase was varied from 100 to 4100 ppm. Figure 5 shows a comparison of the enhancement factors from experimental points with the film-theory predictions for gas absorption with equilibrium reaction of the form of $A + B \rightleftharpoons E$.

The values of the enhancement factor ϕ_{obs} were calculated from the measured values of absorption rate N_A with estimates of C_{A1} and the physical liquid-side mass transfer coefficient of NO, k_{LA}^* . In the present work, to estimate the value of k_{LA}^* , the rate of physical absorption of pure N_2O into water was measured using the same equipment; the liquid-side mass transfer coefficient k_L^* was determined under various liquid-phase stirring speeds n_L and correlated to n_L as $k_L^* = 9.89 \times 10^{-5} n_L^{0.65}$. The coefficient of NO, k_{LA}^* , was predicted by a correlation

$$k_{LA}^* = k_{L,NO_2-H_2O}^* (D_A/D_{N_2O-H_2O})^{2/3} \quad (7)$$

as in previous work (Sada et al., 1977 and Sada et al., 1978).

On the other hand, the solid curve represents the filmtheory solution of enhancement factor under an equilibrium reaction regime defined by

$$\phi_{\infty} = 1 + \frac{K(D_E/D_A)C_{B0}}{1 + K(D_E/D_B)C_{A1}} \quad (8)$$

Average values of the observed enhancement factor were in a good agreement with the solid curve.

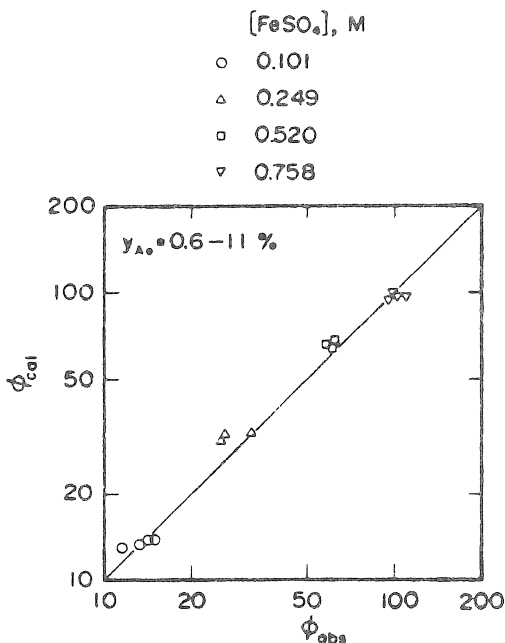


Fig. 6. Comparison of observed and predicted enhancement factors for the absorption of NO ($y_{A0} = 0.6-11\%$).

Figure 6 shows the comparison of the observed enhancement factor ϕ_{obs} with the enhancement factor ϕ_{cal} calculated by eq 8, when the gas-phase concentration of NO is varied from 0.6 to 11% by volume. The agreement between these two factors was also good. The absorption rate of lean NO with the stirred tank absorber was satisfactorily predicted by eq 8 using existing information on reaction statics.

Conclusion

The kinetics of absorption of NO in aqueous ferrous sulfate solutions were tested over an extended range of operating conditions, i.e., for exposure times of 0.2-5000 s and NO concentrations of 100 ppm-99% by volume. The chemical absorption process was satisfactorily predicted by the theory of gas absorption with reversible reaction of the form of $A + B \rightleftharpoons E$ using existing information on reaction kinetics and statics.

Nomenclature

- C concentration in the liquid phase, M
- D diffusivity in the liquid phase, cm^2/s
- I ionic strength of solution, g-ion/L
- K equilibrium constant of reaction I, L/mol
- k_2 second-order forward rate constant of reaction I, L/mol s
- k_1^* first-order reverse rate constant of reaction I, L/s
- k_L liquid-side mass transfer coefficient, cm/s
- K_s salting-out parameter, L/g-ion
- M reaction-diffusion modulus, $\pi k_2 C_{B0} t / 4$ for penetration theory and $k_2 C_{B0} D_A / (k_{LA}^*)^2$ for film theory
- N_A absorption rate of NO, mol/s cm^2
- n_L stirring speed in the liquid phase, rpm
- t exposure time, s
- x_g, x_a, x_c contribution of gas, anion and cation to K_s , respectively, L/g-ion
- y_A concentration of A in the gas phase, % or ppm

Greek Letters

- α Bunsen absorption coefficient, cm^3 of gas/ cm^3 of solution
- ϕ enhancement factor
- μ viscosity

Subscripts

- A absorbing gas A(NO)
- B liquid-phase reactant B(FeSO_4)
- E liquid-phase product E($\text{Fe}(\text{NO})\text{SO}_4$)
- i gas-liquid interface
- o outlet of absorber
- w water

- O initial value or value in the bulk of liquid
∞ with an instantaneous reaction

Superscript

- ° without reaction

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