



## Study on NO<sub>2</sub> absorption by ascorbic acid and various chemicals<sup>\*</sup>

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**Abstract:** Study on NO<sub>2</sub> absorption aimed at seeking a better NO<sub>2</sub> absorption chemical at pH 4.5~7.0 for application to existing wet flue gas desulfurization (FGD). The results from the double-stirred reactor indicated that ascorbic acid has very high absorption rate at this pH range. The rate constant of ascorbic acid reaction with NO<sub>2</sub> (0~1000×10<sup>-6</sup> mol/mol) is about 3.54×10<sup>6</sup> mol/(L·s) at pH 5.4~6.5 at 55 °C.

**Key words:** NO<sub>2</sub>, Absorption, Rate constant, Ascorbic acid

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### INTRODUCTION

Nitrogen oxide (NO<sub>x</sub>) is one of the main air pollutants found in the flue gases from chemical and power plants belching acid rain and photochemical smog. Over 90 percent of all man-made nitrogen oxides that enter our atmosphere are produced by the combustion of various fuels. Compared with the advanced stage of SO<sub>2</sub> gas removal technologies development, the removal of NO<sub>x</sub> gases is still in the initial stages of development as roughly 90 to 95 percent of NO<sub>x</sub> emitted in combustion processes appears in the form of NO which is comparatively inactive and insoluble. To reduce the generation and emission of NO<sub>x</sub> to the atmosphere, it is necessary to use low nitrogen fuel, low NO<sub>x</sub> burners and implement more stringent air pollutant emission standards, it is necessary to setup and operate NO<sub>x</sub> control devices for further reduction of pollutions. Some processes have been dis-

cussed, such as SCR (selective catalytic reduction), SNCR (selective non-catalytic reduction), NSCR (non-selective catalytic reduction) and adsorption. Wet FGD (flue gas desulfurization) scrubbers are very efficient to remove SO<sub>2</sub> from flue gas, but cannot remove NO because of its low solubility in aqueous solution. Research efforts to modify existing wet FGD processes for simultaneous control of SO<sub>2</sub> and NO<sub>x</sub> emissions led to several new approaches to enhance NO<sub>x</sub> absorption in scrubbing liquors.

One promising approach to simultaneously remove SO<sub>2</sub> and NO<sub>x</sub> from flue gas is the combination of NO oxidation to NO<sub>2</sub> and conventional wet scrubbing. The possible NO oxidants include KMnO<sub>4</sub> (Kobayashi *et al.*, 1977), hydrogen peroxide (Thomas and Vandescheren, 1998), NaCl<sub>2</sub>O (Chien and Chu, 2000), P<sub>4</sub> (Chang and Lee, 1992), etc. The NO oxidation product, NO<sub>2</sub>, can be absorbed by several chemical reagents, although most chemical reagents for NO<sub>2</sub> absorption are effective only at high pH range. In this work, our research is aimed at finding a better NO<sub>2</sub> absorption chemical effective at pH 4.5~7.0, which is the application pH range for existing popular wet limestone/lime FGD.

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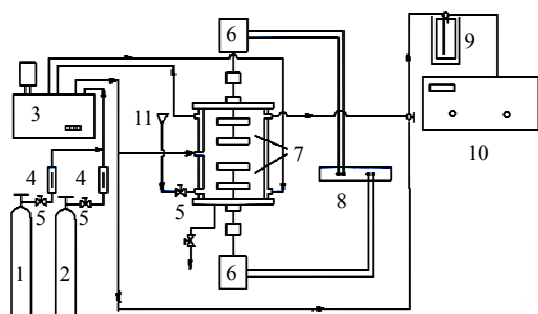
## EXPERIMENTAL DETAILS

### Chemicals

L-ascorbic acid (99%), thiourea (99%), 2,4-pentanedione (99%), 2,3-pentanedione (97%), barbituric acid (99%), oxalic acid (98%), glyoxal (40 wt%), di(ethylene glycol) (99%), were all obtained from Shanghai Chemical Reagent Co., China and used without further purification. The gases used included 5.0% NO<sub>2</sub> in N<sub>2</sub> and 99.99% N<sub>2</sub>. All other chemicals were analytical grade reagents.

### Apparatus and procedure

Experiments on NO<sub>2</sub> absorption were carried out in a highly characterized double-stirred reactor with a planar gas-liquid interface, which was mentioned in our previous papers (Shi *et al.*, 1996; 1997). The double-stirred reactor had a gas-liquid interface that was planar to a close approximation. The reactor was 80 mm in diameter and equipped with four vertical baffles and two stirring blades. A water jacket of the reactor is used to maintain the desired temperature by circulating water from a constant temperature water bath. The reactor had continuous gas flow rate of 1000 ml/min. Five percent (V/V) of NO<sub>2</sub> was diluted by carrier nitrogen gas. The inlet concentration of NO<sub>2</sub> in this experiment ranged from 0~1000×10<sup>-6</sup> mol/mol. All the experiments were conducted with liquid stirring speed of 150 r/min and gas stirring speed of 900 r/min. The experimental setup includes a flue gas simulation system, a double-stirred reactor, and analysis system shown in Fig.1.



**Fig.1** Experimental setup for measurement of NO absorption

1, 2: NO<sub>2</sub>, N<sub>2</sub> cylinder; 3: Attenuator; 4: Gas flowmeters; 5: Gas/liquid control valve; 6: Driving motors; 7: Stirred cell reactor; 8: Stirring speed controller; 9: Cold trap; 10: Gas analyzer; 11: Entrance of liquid

The liquid phase was a deionized water solution of chemical reagents. The solution pH was adjusted by adding small amounts of concentrated NaOH or H<sub>2</sub>SO<sub>4</sub>. The volume of the aqueous solution in the reactor was always 310 ml. For the case of SO<sub>3</sub><sup>2-</sup> solution preparation, the deionized water was boiled for 10 min to remove the dissolved oxygen, then cooled down no oxygen atmosphere. All the experiments were performed at 55 °C (normal temperature of conventional wet FGD) in stirring reactor and operated in batch mode. The gas film mass transfer coefficient of the apparatus ( $K_{\text{GNO}_2}$ ) was  $2.04 \times 10^{-5}$  kmol/(m<sup>2</sup>·s) and the liquid-side mass transfer coefficient ( $K_{\text{KNO}_2}$ ) was  $3.96 \times 10^{-6}$  kmol/(m<sup>2</sup>·s) (Shi *et al.*, 1996).

The inlet and outlet gas concentration of NO<sub>2</sub> were measured with a chemiluminescent NO<sub>x</sub> analyzer with independent outputs for NO, NO<sub>2</sub>, and NO<sub>x</sub>. A cold trap was used to remove moisture before the gas entered the analyzers. During the experiments, NO<sub>2</sub> and NO<sub>x</sub> in the simulated flue gas were examined.

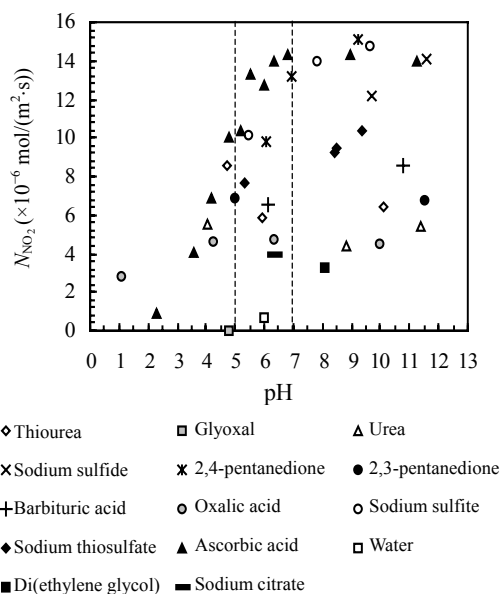
## RESULTS AND DISCUSSION

### Comparison of NO<sub>2</sub> absorption rate by various chemical reagents

To search for ideal chemical to absorb and reduce NO<sub>2</sub>, numerous chemicals were tested in the stirring reactor. The NO<sub>2</sub> absorption rates of various chemicals, including thiourea, urea, sodium sulfide, 2,4-pentanedione, 2,3-pentanedione, barbituric acid, oxalic acid, sodium sulfite, sodium thiosulfate, L-ascorbic acid, glyoxal, di(ethylene glycol) and water, were determined with different pH. The results of comparison of the rate of NO<sub>2</sub> absorption into these chemical reagents with various pH values are depicted in Fig.2.

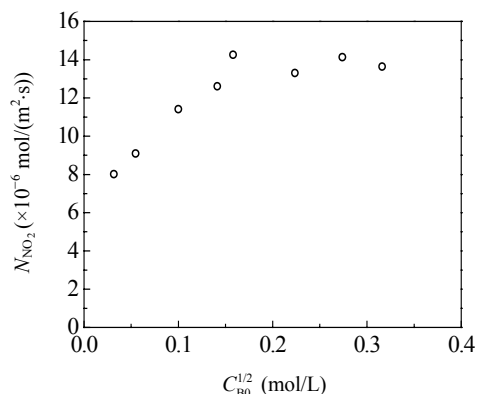
### Effect of ascorbic acid concentration on the absorption rate

Fig.3 shows the effect of the square root of ascorbic acid concentration on the absorption rate. The absorption rate increases linearly increasing ascorbic acid concentration ( $C_{\text{B0}}$ ) from 0~25 mmol/L. On the basis of mass transfer model with chemical reaction, there should be a linear relationship between



**Fig.2 Effect of the aqueous solution pH on the rate of NO<sub>2</sub> absorption by various chemicals**

Gas flowrate: 1000 ml/min; NO:  $500 \times 10^{-6}$  mol/mol;  $C_{B0}$ : 0.05 mol/L;  $T$ : 55 °C



**Fig.3 Effect of ascorbic acid concentration on the absorption rate**

$T$ : 55 °C; pH: 5.4~6.0; NO:  $500 \times 10^{-3}$  mol/mol; Gas flow rate: 1000 ml/min

NO<sub>2</sub> absorption rate and the square root of the ascorbic acid concentration in a second order reaction (first order with respect to ascorbic acid and first order with respect to NO<sub>2</sub>). The prediction was confirmed in the range of low concentration of ascorbic acid, 0~25 mmol/L. When concentration was higher than 25 mmol/L, the absorption rates remained almost steady at  $1.4 \times 10^{-5}$  mol/(m<sup>2</sup>·s), which probably indicated that the reaction was a fast gas-liquid surface reduction during the concentration range.

### Chemical and physical properties of NO<sub>2</sub>

The kinetics and chemistry of NO<sub>2</sub> absorption into aqueous solution is complicated. Schwartz (1983) reviewed the chemical equilibria in detail, including the Henry's law (solubility) equilibria of the reactive oxides NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub>, etc. Henry's coefficient,  $H_{NO_2}$ , and the rate of the second-order hydrolysis reaction,  $k_2$ , are two key parameters required for characterizing heterogeneous process involving NO<sub>2</sub> (g). However, even after numerous studies, uncertainty still exists in the values of these two parameters. Literature values range from  $7 \times 10^{-8}$  to  $2 \times 10^{-7}$  mol/(L·Pa) for  $H_{NO_2}$ , and from  $10^7$  to  $10^8$  mol/(L·s) for  $k_2$  at 25 °C. These uncertainties are mainly due to the complexity of NO<sub>2</sub> aqueous interaction.

In our research, the diffusion coefficient of dissolved NO<sub>2</sub> ( $D_{NO_2}$ ) was taken to be  $3.28 \times 10^{-9}$  m<sup>2</sup>/s (Shen and Rochelle, 1998; Wilke and Chang, 1955) at 55 °C. Henry's coefficient of NO<sub>2</sub>,  $H_{NO_2}$ , was taken to be  $1.4 \times 10^{-7}$  mol/(L·Pa) at 25 °C in recent research results of Cheung *et al.* (2000). No existing data on  $H_{NO_2}$  at 55 °C was found a way must be found to estimate it.

The solubility of gases decreases with increasing temperature. According to the relation of Henry's coefficient and the temperature,  $H_{NO_2}$  at 55 °C could be estimated by the following Clausius-Clapeyron equation (Manahan, 1999):

$$\text{Log}(C_2/C_1) = (\Delta H/2.303R) \times (1/T_1 - 1/T_2), \quad (1)$$

where  $C_1$  and  $C_2$  denote the gas concentration in water at absolute temperatures of  $T_1$  and  $T_2$ , respectively;  $\Delta H$  is the heat of solution; and  $R$  is the gas constant. The value of  $R$  is 8.314 J/(K·mol), which gives  $\Delta H$  units of J/mol. However, due to the complexity and uncertainty of  $\Delta H$ , we have to take the data from Cheung *et al.* (2000),  $H_{NO_2} = 1.4 \times 10^{-7}$  mol/(L·Pa) at 20 °C and  $2.3 \times 10^{-7}$  mol/(L·Pa) at 0 °C, and the Clausius-Clapeyron equation to extrapolate Henry's constant at temperature of 55 °C. Henry's constant of NO<sub>2</sub> at 55 °C is estimated to be  $6.8 \times 10^{-8}$  mol/(L·Pa) by the above means.

### Estimate of NO<sub>2</sub> reaction rate constant

According to Danckwerts theory (Danckwerts, 1970), in fast pseudo- $m$ -order reaction, there is linear relationship between the absorption rate and square root of the ascorbic acid concentration if  $C_{B0}$  the concentration of ascorbic acid in the bulk liquid, is much larger than the NO<sub>2</sub> concentration at the interface, that is:  $N_A \propto C_{B0}$ . To a close approximation, the absorption rate for a pseudo- $m$ th order reaction is given by

$$N_A = \sqrt{2k_{m+1}DC_i^{m+1}C_{B0} / (m+1)}, \quad (2)$$

where  $D$  is the diffusivity in liquid phase, m<sup>2</sup>/s;  $m$  is the reaction order;  $N$  is the absorbing rate;  $k$  is the rate constant; A is dissolved gas (NO<sub>2</sub>); B is the liquid-phase reactant;  $i$  is the gas-liquid interface and 0 is initial value.

Fig.3 shows a linear relationship between the absorption rate and square root of the ascorbic acid concentration of 0~25 mmol/L, which verifies that the

value of  $m$  in Eq.(2) should be 1.0. Hence, this absorption is the fast pseudo-first order reaction when the ascorbic acid concentration is 0~25 mmol/L. The reaction rate constants between NO<sub>2</sub> and ascorbic acid can be obtained from Eq.(2) using the experimental data and the above estimated chemical and physical parameters. The calculating results on reaction rate constants are shown in Table 1. The rate constant of ascorbic acid reaction with NO<sub>2</sub> is about  $3.54 \times 10^6$  mol/(L·s) at pH 5.4~6.5 at 55 °C.

The chemistry of NO<sub>2</sub> absorption into aqueous phase of SO<sub>3</sub><sup>2-</sup> or other reagents is complicated. The reduction of NO<sub>2</sub> was found to be first order with respect to SO<sub>3</sub><sup>2-</sup> and first order with respect to NO<sub>2</sub> by Takeuchi *et al.*(1977). Shen and Rochelle (1998) indicated that the reactions between NO<sub>2</sub> and sulfite (SO<sub>3</sub><sup>2-</sup>), bisulfite (HSO<sub>3</sub><sup>2-</sup>) and thiosulfate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) were first order in NO<sub>2</sub> concentration. Their rate constants at 55 °C in this work and in other reports are also listed in Table 1.

Table 1 Values of NO<sub>2</sub> reaction rate constant,  $k_2$

Reagent	Investigator	$k_2$ , mol/(L·s)
Ascorbic acid (pH 5.4~6.5)	This work	$3.54 \times 10^6$
SO <sub>3</sub> <sup>2-</sup> /HSO <sub>3</sub> <sup>2-</sup> (pH 5.4~6.5)	This work	$1.05 \times 10^6$
Sodium thiosulfate (pH 5.4~6.5)	This work	$3.37 \times 10^5$
SO <sub>3</sub> <sup>2-</sup>	Shen and Rochelle (1998)	$1.12 \times 10^6$
HSO <sub>3</sub> <sup>2-</sup>	Shen and Rochelle (1998)	$2.8 \times 10^4$
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	Shen and Rochelle (1998)	$5.4 \times 10^3$
SO <sub>3</sub> <sup>2-</sup>	Takeuchi <i>et al.</i> (1977)	$6.6 \times 10^5$

### CONCLUSION

The results from the double-stirred reactor indicated that ascorbic acid has very high absorption rate at the wet limestone/lime FGD pH 5.0~7.0, the order of NO<sub>2</sub> absorption rate is as follows, ascorbic acid>2.4-pentanedione>SO<sub>3</sub><sup>2-</sup>/HSO<sub>3</sub><sup>2-</sup>>S<sub>2</sub>O<sub>3</sub><sup>2-</sup>>2.3-pentanedione>barbituric acid>thiourea>oxalic acid>glyoxal>citrate>H<sub>2</sub>O. The calculated results on reaction rate constant of ascorbic acid reaction with NO<sub>2</sub> is about  $3.54 \times 10^6$  mol/(L·s) at for pH 5.4~6.5 at 55 °C.

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