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Absorption of NO_2 into Na_2S solution in a stirred tank reactor*

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Abstract: To understand the absorption mechanism of nitrogen dioxide into a sodium sulfide solution, a stirred tank reactor with a plane gas-liquid interface was used to measure the chemical absorption rate of diluted nitrogen dioxide into sodium sulfide solution. The absorption rates under various experimental conditions were measured and the effects of experimental conditions on nitrogen dioxide absorption rate were discussed. The results show that, in the range of this study, nitrogen dioxide absorption rate increases with increasing sodium sulfide concentration, nitrogen dioxide inlet concentration, and flue gas flow rate, but decreases with increasing reaction temperature and oxygen content in flue gas.

Key words: Nitrogen dioxide, Gas-liquid reaction, Kinetics, Absorption
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INTRODUCTION

SO_2 and NO_x emissions from coal-fired power plants play an important role during the formation of acid rain. The removal of these pollutants is of great importance to achieve ambient air quality goals. At present, each contaminant is removed by a different air pollution control device, such as wet flue gas desulfurization (WFGD) scrubbers and selective catalytic reduction (SCR) reactors. Both of these are expensive and have large space requirements. As we all know, the existing WFGD scrubbers cannot remove NO, the main component of NO_x present in typical coal-fired flue gas (Pereira and Amiridis, 1995), because of its low solubility in water (Shen and Rochelle, 1998). In recent years, removal of NO from flue gas by its oxidation to more reactive NO_2 followed by absorption in existing scrubbers for flue gas desulfurization proved to be a prospective method. In this process, NO is oxidized to NO_2 by various oxidants, such as $NaClO_2$, $KMnO_4$, ClO_2, O_3, before absorption (Chien and Chu, 2000; Chu *et al*., 2001; Mok and Lee, 2006; Deshwal *et al*., 2008).

Kobayashi *et al*.(1977) and Kaczur (1996) found that Na_2S solution is an effective aqueous reagent for the absorption of NO_2. This process has been developed and put into commercial application (Kaczur 1996). Shen and Rochelle (1999) measured the absorption rates of NO_2 into aqueous sulfide in a highly characterized stirred cell contactor at 55 °C and found that NO_2 absorption initiated sulfide oxidation in the presence of oxygen. But the experiments were performed in the pH range of 8.8~13.1, which is far from the application pH range of typical limestone-gypsum WFGD system. In addition, the effects of experimental conditions, such as Na_2S concentration, reaction temperature, NO_2 inlet concentration, were, however, not examined and therefore the absorption mechanism of NO_2 into Na_2S solution is still not completely clear.

The process of NO_2 absorption into Na_2S solution can be expressed as follows (Mok and Lee, 2006; Yamamoto *et al*., 2002):

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Diffusion of NO_2 through the gas film:

$$NO_2\ (g) \leftrightarrow NO_2\ (aq); \tag{1}$$

S^{2-} is oxidized to SO_4^{2-} by NO_2 (aq):

$$S^{2-}+2NO_2\ (aq) \rightarrow SO_4^{2-}+N_2; \tag{2}$$

The net reaction can be written as follows:

$$2NO_2\ (g)+N_2S \rightarrow Na_2SO_4+N_2\ (g); \tag{3}$$

When O_2 is present in the flue gas, Na_2S would react with O_2 as follows:

$$Na_2S+2O_2 \rightarrow Na_2SO_4. \tag{4}$$

The reaction between NO_2 and Na_2S solution is a complicated heterogeneous reaction. In this paper, an experimental study on the absorption of low concentration of NO_2 into Na_2S solution in a stirred tank reactor was preformed. The absorption rates under various experimental conditions were measured and their effects on NO_2 absorption rate have been discussed.

EXPERIMENTAL

The experiments were performed in a stirred reactor with a plane gas-liquid interface, as shown in Fig.1. The reactor was a cylinder vessel of 100 mm inner diameter and 160 mm height, equipped inside with 4 baffles of 10 mm width. The total volume of the reactor was 1.257 L, of which 557 ml and 700 ml were the typical gas and liquid volumes, respectively. Three 4-blade impellers were mounted on the same rod; the upper and the bottom ones were used for mixing the gas and the liquid, respectively, at the same speed. And the middle larger one was floating on the solution to sweep the interface between gas phase and liquid phase. The area of the gas-liquid interface was 78.54 cm^2. The absorption experiment was conducted at atmospheric pressure. The simulated flue gas was prepared by pure N_2, pure O_2 and 3763 mg/m^3 NO_2 (balanced with N_2) purchased from New Century Gas Co., China. And their flow rates were controlled by three mass flow controllers (MFC, Qixinghuachuang Co., China) to the required concentration, then the simulated flue gas was mixed adequately in the mixing box before fed into the reactor. The flow rate of the simulated flue gas was kept at a desired value. The liquid temperature was controlled to the desired temperature within ±0.2 °C through a water bath. At the start of the experiment, a solution containing Na_2S purchased from Hangzhou Guohua Chemical Engineering Co., Ltd. was freshly prepared and fed into the reactor. The solution pH was continuously monitored with a Mettler Delta 320 pH electrode (Shanghai) inserted into the liquid. A continuous flue gas analyzer (Rosemount Analytical NGA2000, Emerson Process Management Co., Ltd., Germany) was used to analyze the concentration of NO_x in the outlet flue gas stream.

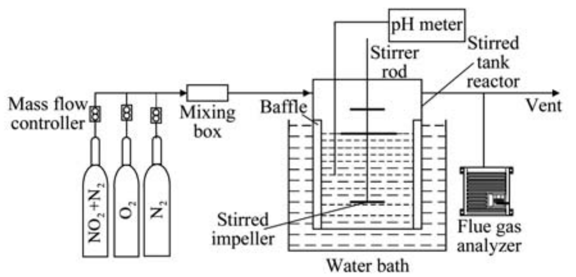

Fig.1 Schematic of the experimental apparatus

In this experiment, either the gas or the liquid phase in the stirred tank is under the condition of complete mixing flow. After a preliminary test was performed, the inlet and outlet gas samples were analyzed for all other experiments at 10 min because that the absorption rate of the system remained stable after 7~8 min, thus the absorption rate of NO_2 can be expressed by (Levenspiel and Godfrey, 1974):

$$-N_{NO_2}=\frac{v_G P}{RTS}\left[\left(\frac{p_{NO_2}}{p_I}\right)_{in}-\left(\frac{p_{NO_2}}{p_I}\right)_{out}\right], \tag{5}$$

where N_{NO_2} is the absorption rate of NO_2, mol/(m^2·s); v_G is the gas volume flow rate, m^3/s; P is the total pressure, Pa; R is the gas constant, J/(mol·K); T is the temperature, K; S is the interfacial area, m^2; p_{NO_2} is the partial pressure of NO_2, Pa; p_I is the partial pressure of inert component, Pa.

RESULTS AND DISCUSSION

Effect of Na_2S concentration on NO_2 absorption rate

Some experiments were performed to investigate the effect of Na_2S concentration on NO_2 absorption rate. It is obvious from Fig.2 that higher Na_2S concentration is favorable to the absorption of NO_2. According to Eq.(2), when NO_2 is absorbed by Na_2S solution, S^{2-} is oxidized to SO_4^{2-} and NO_2 is reduced to N_2. As a result, when the concentration of Na_2S solution increases at a constant NO_2 inlet concentration, more Na_2S is provided for the consumption in the process of NO_2 absorption. Thus the absorption rate of NO_2 increases with increasing Na_2S concentration.

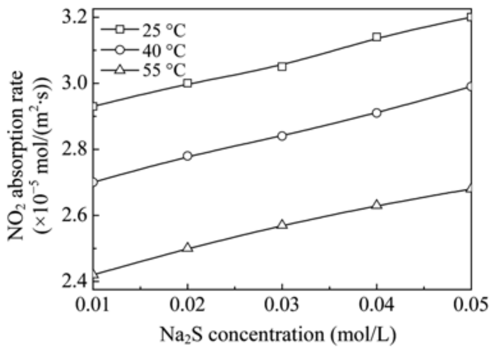

Fig.2 Effect of Na_2S concentration on NO_2 absorption rate. NO_2 inlet concentration: 342 mg/m^3; stirred speed: 200 r/min; flue gas flow rate: 2 L/min; O_2 content: 0

Effect of NO_2 inlet concentration on its absorption rate

Effect of NO_2 inlet concentration on its absorption rate is shown in Fig.3. Fig.3 shows that NO_2 absorption rate increases with its inlet concentration. Shen (1990) reported that during the process of NO_2 absorption into Na_2S solution, the liquid phase mass transfer resistance is very little compared with gas phase mass transfer resistance. Thus the absorption process is controlled by gas phase mass transfer. The driving force for gas phase mass transfer would increase with the increase of NO_2 concentration. Therefore the absorption process of NO_2 is enhanced. Shen and Rochelle (1990) also found that the rate of NO_2 absorption increases with increasing concentrations of HS^- and gas phase NO_2.

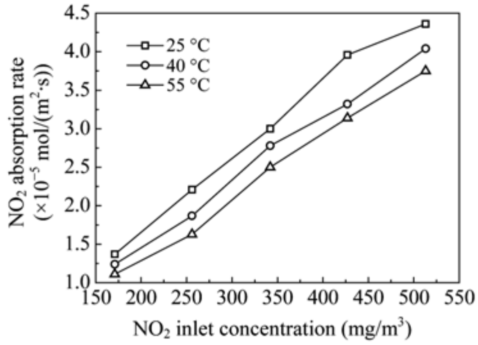

Fig.3 Effect of NO_2 inlet concentration on its absorption rate. Flow gas flow rate: 2 L/min; stirred speed: 200 r/min; Na_2S concentration: 0.02 mol/L; O_2 content: 0

Effect of O_2 content in flue gas on NO_2 absorption rate

Fig.4 displays the effect of O_2 content in flue gas on NO_2 absorption rate. It is found that the presence of O_2 in flue gas can inhibit the absorption, which is consistent with the findings of Shen and Rochelle (1999). Under most solution pH conditions, when Na_2S is dissolve in water, nearly the whole S^{2-} would hydrolyze as follows (Stahl and Jordan, 1987):

$$S^{2-}+H_2O\rightarrow HS^{-}+OH^{-}. \qquad (6)$$

The equilibrium constant is very large (Giggenbach, 1974), thus S^{2-} in solution exists almost exclusively in the form of HS^-. And NO_2 is absorbed through the reaction between NO_2 (aq) and HS^-:

$$NO_2\ (aq)+HS^{-}\rightarrow NO_2^{-}+HS.\cdot \qquad (7)$$

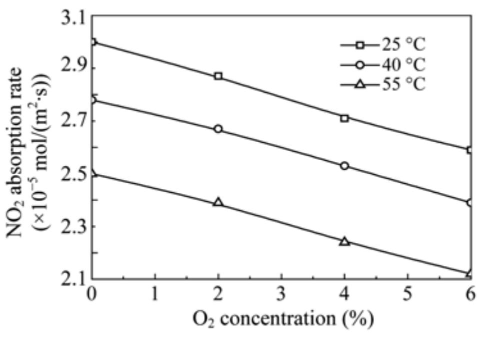

Fig.4 Effect of O_2 content on NO_2 absorption rate. Flow gas flow rate: 2 L/min; stirred speed 200 r/min; Na_2S concentration: 0.02 mol/L; NO_2 inlet concentration: 342 mg/m^3

When O_2 is present, it would react with the free radicals produced by NO_2 reaction with HS^-, and $S_2O_3^{2-}$ is the main oxidation product. As a result, the absorption rate of NO_2 decreases. The similar effect was observed by Kuhn *et al*.(1983).

Effect of flue gas flow rate on NO_2 absorption rate

Fig.5 shows the measurements of NO_2 absorption rate into Na_2S solution over a range of flue gas flow rates. It is observed that the absorption rate increases with increasing flue gas flow rate. This confirms that the absorption process of NO_2 in this study is gas film controlled.

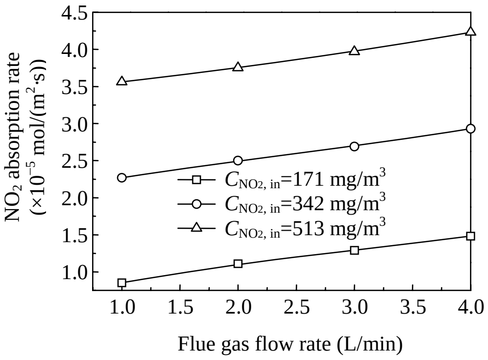

Fig.5 Effect of flue gas flow rate on NO_2 absorption rate. Reaction temperature: 55 °C; stirred speed: 200 r/min; Na_2S concentration: 0.02 mol/L; O_2 content: 0

Effect of reaction temperature on NO_2 absorption rate

To study the dependence of the rate of NO_2 absorption on reaction temperature, the experimental runs were made at 25, 40 and 55 °C, respectively. Fig.6 shows the effect of reaction temperature on NO_2 absorption rate into Na_2S solution. It is indicated that NO_2 absorption rate decreases with increasing reaction temperature. Such an effect may be attributed to the decreased solubility of NO_2 in the liquid at higher temperature. In addition, lower temperature is favorable to the formation of N_2O_4, the dimer of NO_2, which is of higher solubility than NO_2 at a lower temperature (Takeuchi *et al*., 1977). The standard enthalpy change of reaction Eq.(3) can be obtained by the following equation:

$$\Delta H_{298}^{\theta} = v_i \Delta H_{298,i}^{\theta}, \quad (8)$$

where v_i is the stoichiometry of reactant i or product i in reaction Eq.(3); $\Delta H_{298,i}^{\theta}$ is the standard enthalpy of formation of i, which can be obtained from Dean (2003). The standard enthalpy change of reaction Eq.(3) is −239.06 kJ/mol, a negative value. Thus reaction Eq.(3) is an exothermic reaction; increasing reaction temperature is unfavorable to the formation of products.

However, with the increasing Na_2S concentration, the decreased solubility caused by temperature rise can be offset by the increase in reaction rate at higher temperature.

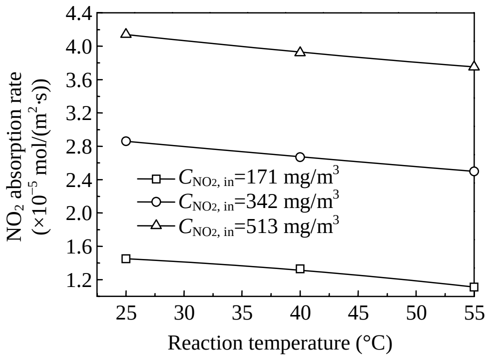

Fig.6 Effect of reaction temperature on NO_2 absorption rate. Flow gas flow rate: 2 L/min; stirred speed: 200 r/min; Na_2S concentration: 0.02 mol/L; O_2 content: 0

CONCLUSION

The absorption of dilute NO_2 in a stirred tank reactor with Na_2S solution was carried out. The results show that the absorption of NO_2 into Na_2S solution in the range of this study is gas film controlled. Under the conditions in this study, NO_2 absorption rate increases with increasing Na_2S concentration, NO_2 inlet concentration and flue gas flow rate, but decreases with increasing reaction temperature and O_2 content in flue gas.

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