

Absorption of NO₂ by Sodium Sulfite Solution Adding Ethanol in High Oxygen Concentration

P Wang¹, L N Wu^{1*}, L Cui¹ and T Fan²

¹National Engineering Lab for Coal-fired Pollutants Emission Reduction, Shandong University, Jinan 250061, China

²Shengli Youtian Kangbei Shiyou Gongcheng Zhuangbei Limited company, DongYing 257000 China

Corresponding author and e-mail: L N Wu, 201512938@mail.sdu.edu.cn

Abstract. In order to achieve effective removal of NO₂ by sodium sulfite solution with a high oxygen concentration, an additive was explored in this study. Flue gas was oxidized by ozone and was then absorbed by sodium sulfite solution adding ethanol into with a high oxygen concentration. Research showed that sodium sulfite solution, with the addition of ethanol, was an effective absorbent in high oxygen concentrations. Influencing factors such as the type of additive, added ethanol concentration, absorption temperature, absorption product, and enrichment of ion (NO₂⁻ and NO₃⁻), were investigated during the absorption process of the NO₂ by sodium sulfite solution. The optimal additive was ethanol in the removal of NO₂ by sodium sulfite solution. In regard to the absorption product, NO₂⁻ and NO₃⁻ were reaction products, which decreased absorption efficiency of NO₂. Furthermore, increase of ethanol concentration in sodium sulfite solution could counteract adverse effects of ion during the absorption of the NO₂.

1. Introduction

A large number of pollutants are produced in the production of steel, which have caused serious environmental problems. Flue gas pollutants produced by sintering processes account for 55% of these pollutants, [1] which are from unstable, hyperoxic (15%), [2] low temperature (150 °C) flue gas. A draft of advice for emission standards from EPD of China was issued, in which NO_x emission concentration was modified from 300 mg/m³ to 100 mg/m³. At present, denitrification technology mainly includes SCR, SNCR, and activated carbon adsorption and ozone oxidation wet absorption combined with ozone oxidation [3] which are easily adapted and developed.

Wet absorption combined with oxidation technology consists of two parts: namely oxidation and absorption. This technology has been studied by scholars at home and abroad. Researched showed that the main product of oxide of NO by ozone is NO₂. [4] Wet absorption is mainly aimed at NO₂ whose solubility is much greater than that of NO. Zhuang [5] reported that pH had a significant influence on the absorption of SO₂ and NO₂ in alkali solution. When pH is higher than 6, NO₂ absorption efficiency could reach 80%. Guo et al. [6] determined that (NH₄)₂SO₃ formed in ammonia desulphurization was the effective component of denitrification. The process of denitrification is actually that of oxidation-reduction between SO₃²⁻ and NO₂. Sun [7] et al. found that MgO was an

effective NO₂ absorbent. Improvement of pH and MgO concentration promoted NO₂ absorption efficiency. Chen L et al. used Na₂SO₃ as an NO₂ absorbent whose concentration had a significant influence on NO₂ absorption efficiency. In this research the ratio of liquid to gas became a dominant factor of NO₂ absorption. NO₂ absorption efficiency is 90% when the liquid to gas ratio equaled to 4, while the efficiency is 55% when ratio is 1.8. [8]

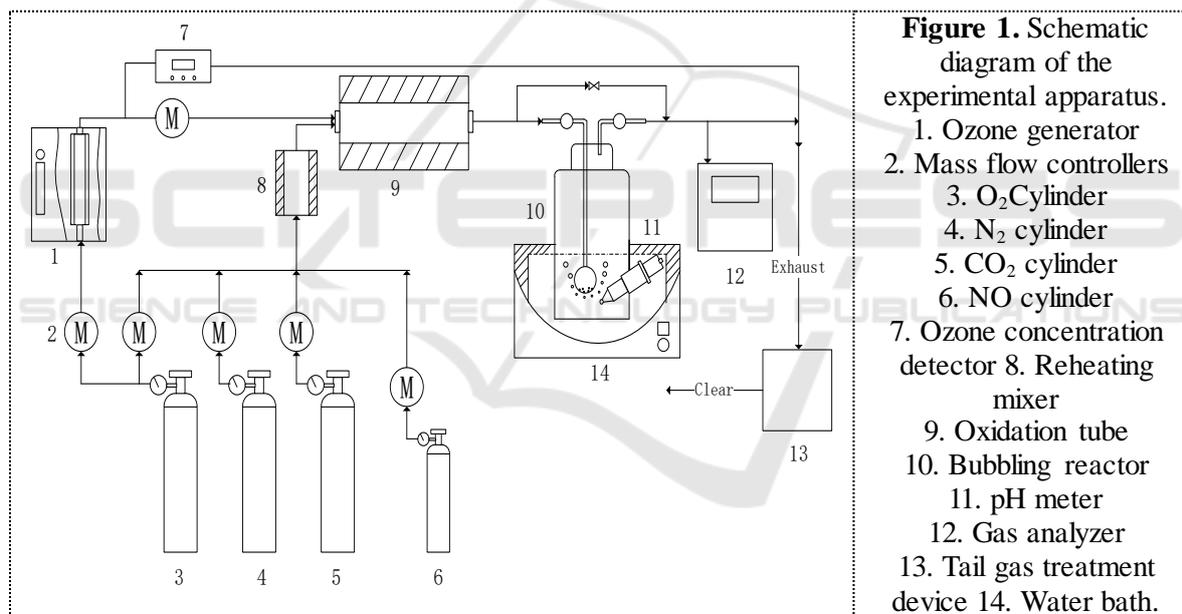
Tang [9] et al. reported that Na₂SO₃ and CaSO₃ were effective absorbents. The absorption efficiency and consumption of Na₂SO₃ was much greater than those of CaSO₃. These studies had indicated that SO₃²⁻ played an important role in the absorption of NO₂.

In previous researches oxygen concentration of flue gas was lower (6%) which was not in accordance with characteristics of sintering flue gas. In this paper exploratory research on absorption of NO₂ by sodium sulfite adding ethanol in high oxygen concentration (15%) was investigated.

2. Experimental section

2.1. Experimental System.

A schematic diagram of the experimental setup for the bubble column reactor absorption of NO₂ generated in oxidation part was shown in Figure 1. The experimental system is divided into three parts namely, gas phase oxidation, bubble column reactor absorption and gas detection.



The flue gas in the laboratory came from the gas cylinder (CO₂, N₂, O₂, NO) controlled by mass flow controllers. The initial concentration was set to be 4%, 15% and 200mg/m³ for CO₂, O₂, and NO respectively. The simulated flue gas was mixed and preheated in a preheating mixer at a temperature of 150 °C. Then, flue gas was oxidized by O₃ produced by an O₃ generator at a temperature of 150 °C. NO₂ in the oxidized flue gas was absorbed by bubbling reactor containing 100ml solution. The initial and outlet concentrations of NO₂ in the bubbling reactor were quantitatively analyzed by a gas analyzer.

2.2. Removal efficiency

In this study we use the same amount of ozone as that of NO. We only focused on the removal of NO₂. The concentrations of the imported and exported gas of bubbling reactor were measured by

bypass lines. NO₂ removal efficiency of the bubbling reactor was calculated using the following equation:

$$\text{NO}_2 \text{ removal efficiency (\%)} = \frac{C_{\text{NO}_2,\text{in}} - C_{\text{NO}_2,\text{out}}}{C_{\text{NO}_2,\text{in}}} \times 100$$

Where C_{NO₂,in} is the inlet NO₂ concentration of the bubbling reactor and C_{NO₂,out} is the outlet NO₂ concentration of the bubbling reactor.

3. Results and discussion

3.1. Selection of additives

According to previous studies, it was found that adding reductive substances to sodium sulfite solution can inhibit the oxidation of sulfite. [10] Other reports indicated that alcohols are optimal for the preservation and oxidation inhibition of sodium sulfite solutions. [11] In this study, we used alcohols as additives in sodium sulfite solution to explore their promotion of the absorption of NO₂. While the MR of O₃ and NO were controlled at 1, 0.01mol C₂H₅OH ,0.01mol H₂C₂O₄,0.01mol (CH₂OH)₂ and 0.01mol (CH₃)₂CHOH were added respectively into 100ml of 3.6g/L Na₂SO₃ solution whose pH were adjusted to around 9.5 by NaOH. The temperature of the water bath was set to 55 °C.

The absorption efficiency of NO₂ with different additives in Na₂SO₃ solution are shown in Figure 2. The additives increased NO₂ absorptive capacity of sodium sulfite solution by varying degrees. Compared with oxalic acid, alcohol additive had a synergistic effect on initial NO₂ absorption efficiency. With the prolongation of reaction time, the synergistic effect of oxalate was prominent. The synergistic effect of NO₂ absorption was more efficient than that of ethylene glycol or propanol. NO₂ absorption with the addition of ethanol was much higher than that of the other additives, regardless of the initial NO₂ absorption rate or the NO₂ absorption capacity of the sodium sulfite solution. The removal efficiency of NO₂ increased from 60% to 70%. The effective duration increased from 7min to 32min . As an additive of sodium sulfite solution, ethanol had a great significant synergistic effect on the absorption of NO₂ with a high oxygen concentration (15%).

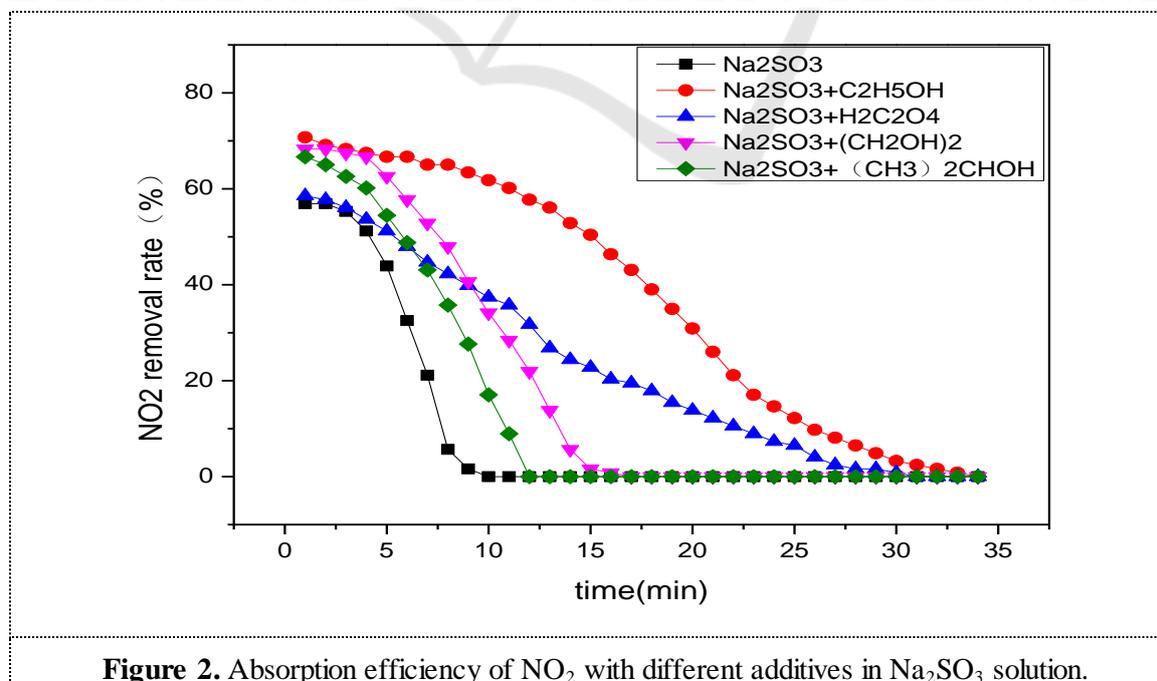


Figure 2. Absorption efficiency of NO₂ with different additives in Na₂SO₃ solution.

3.2. The effect of the concentration of ethanol on the absorption of NO₂ in Na₂SO₃ solution

While MR of O₃ and NO were controlled at 1, 0.005mol C₂H₅OH, 0.01mol C₂H₅OH, 0.02mol C₂H₅OH were added respectively into 100ml of 3.6g/L Na₂SO₃ solutions. The effect of the concentration of ethanol on the absorption of NO₂ in Na₂SO₃ solution is shown in the figure 3.

The increase of ethanol concentration in the absorption solution enhanced the absorptive capacity of NO₂. The removal efficiency of NO₂ increased from 50% to 80% when ethanol concentration increased from 0 to 0.2mol/L. Meanwhile the effective duration increased from 7min to 32min.

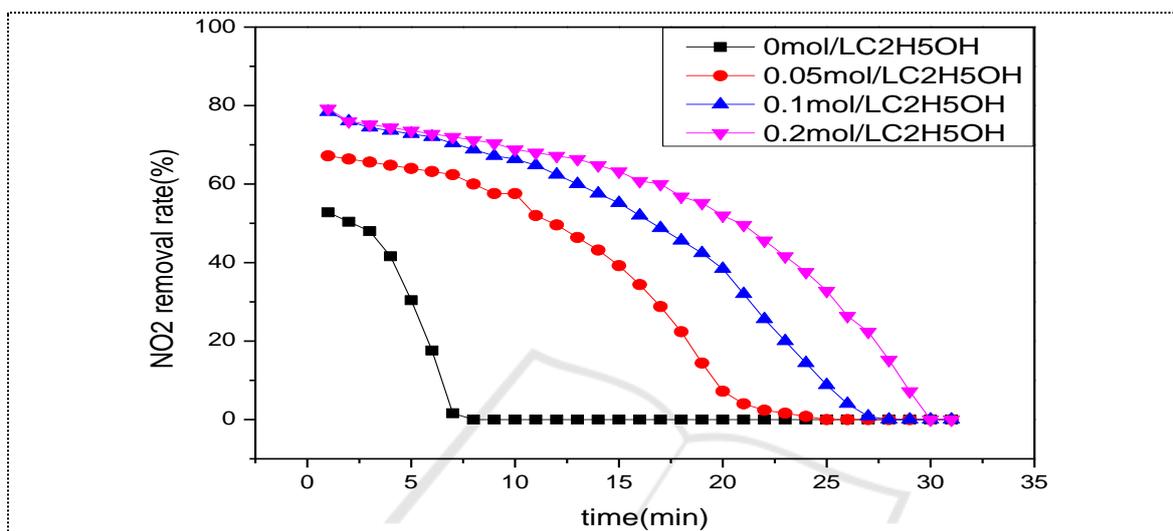


Figure 3. The effect of the concentration of ethanol on the absorption of NO₂ in Na₂SO₃ solution.

3.3. The effect of temperature on absorption of NO₂

While MR of O₃ and NO was controlled at 1, the water bath was set at 35 °C, 55 °C and 75 °C. Then, 100ml of 3.6g/L Na₂SO₃ solution was added to 0.01mol/L C₂H₅OH, and the absorption of NO₂ was investigated. As shown in Figure 4, the reaction temperature of the liquid phase had little effect on the absorption of NO₂.

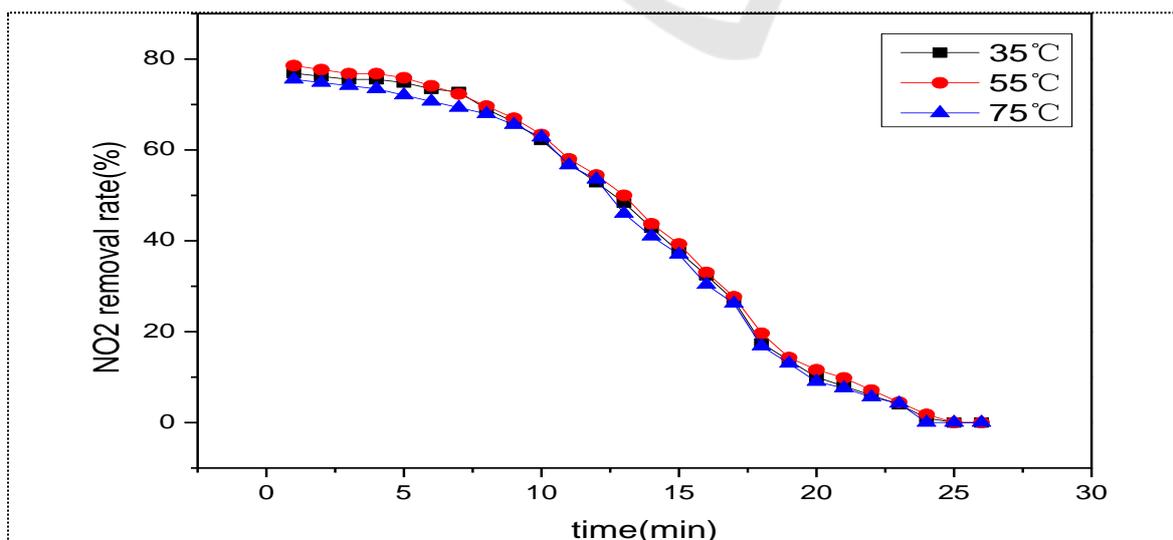


Figure 4. The effect of temperature on absorption of NO₂.

3.4. Ions in the absorption solutions

While MR of O_3 and NO were controlled at 1, 0.01mol C_2H_5OH were added into 100ml of 3.6g/L Na_2SO_3 solution. The temperature of water bath was set at $55\text{ }^\circ\text{C}$. The reaction time was controlled respectively at 5min, 10min, 15min, 25min. NO_3^- and NO_2^- in reaction solutions were measured by using Ion chromatograph. The concentrations of ions in the absorption solutions are shown in picture 5.

In the absorption of NO_2 , NO_2^- was the main product of oxidation-reduction reaction in the solution. The concentration of NO_3^- in the solution was only 10mg/L. This shows that the direct product of the reaction between NO_2 and SO_3^{2-} in the solution was NO_2^- . The results were the same as that of previous studies [12] in Which Na_2SO_3 solution absorbed NO_2 without additives. The addition of ethanol to sodium sulfite did not change the product of its absorption of NO_2 . A small amount of NO_3^- in the solution is produced by the hydrolysis of NO_2 .

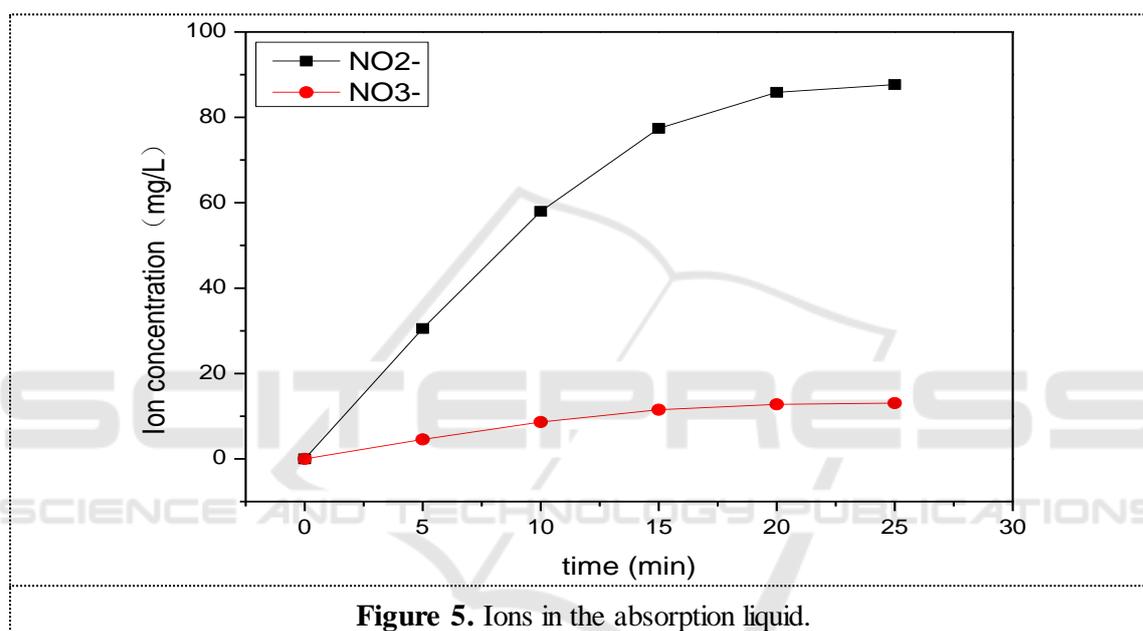


Figure 5. Ions in the absorption liquid.

3.5. The effect of ion enrichment on absorption of NO_2

According to ion detection, it was found that NO_3^- and NO_2^- are the products in the process of NO_2 absorption. When these two ions are enriched in solution, they might have an adverse effect on NO_2 absorption. $NaNO_3$ and $NaNO_2$ of different quality were added respectively into 100ml of 3.6g/L Na_2SO_3 , 0.1mol/L C_2H_5OH . Effect of ion enrichment on absorption of NO_2 in absorbent was shown in the Figure 6 and Figure 7.

The addition of NO_3^- caused a slight decrease in the initial absorption rate of NO_2 but did not change the effective time for the solution to absorb NO_2 . The addition of NO_2^- had a significant impact on the absorption of NO_2 including initial absorption rate of NO_2 and the effective duration. These results showed that NO_2^- was a direct product of the absorption of NO_2 .

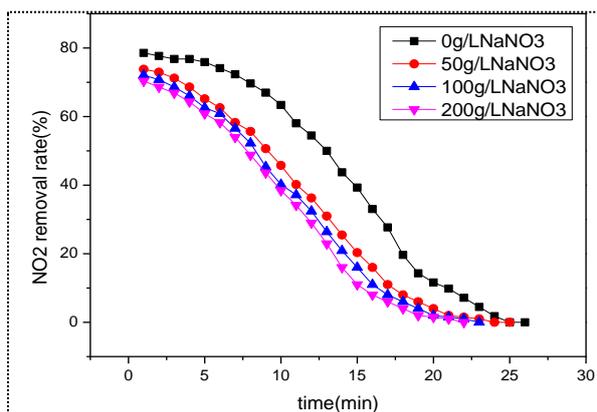


Figure 6. Effect of NO₃⁻ enrichment on NO₂ absorption.

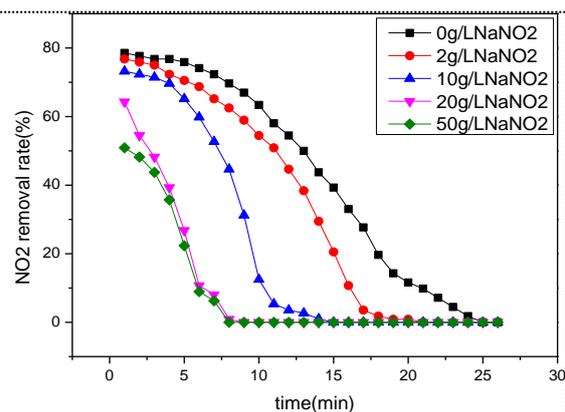


Figure 7. Effect of NO₂⁻ enrichment on NO₂ absorption.

Increasing the concentration of ethanol in the solution was found to counteract the effect of ion enrichment on NO₂ absorption. As shown in Figure 8. NO₂ absorption capacity of 10g/L NaNO₃, 10g/L NaNO₂ and 3.6g/L Na₂SO₃ solution added into 0.015mol C₂H₅OH reached equal levels to that of 3.6g/L Na₂SO₃ and 0.1mol/L C₂H₅OH solution. This showed that increasing the concentration of ethanol could cancel the effect of ion enrichment on NO₂ absorption

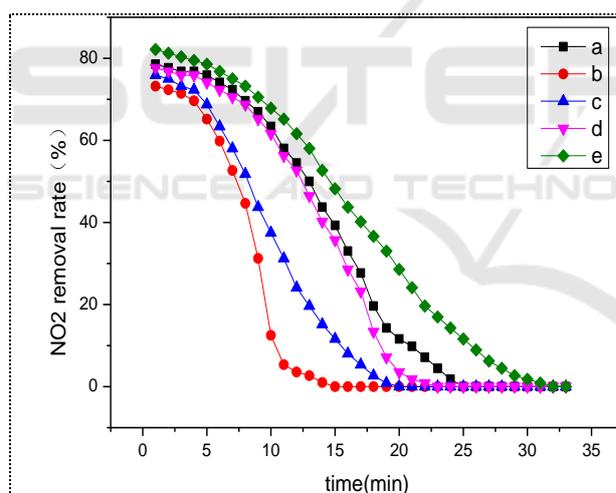


Figure 8. Cancellation of the effect of ion enrichment on NO₂ absorption.

- 0.1mol/L C₂H₅OH
- 10g/L NaNO₃ + 10g/L NaNO₂ + 0.05mol/L C₂H₅OH
- 10g/L NaNO₃ + 10g/L NaNO₂ + 0.1mol/L C₂H₅OH
- 10g/L NaNO₃ + 10g/L NaNO₂ + 0.15mol/L C₂H₅OH
- 10g/L NaNO₃ + 10g/L NaNO₂ + 0.2mol/L C₂H₅OH

4. Conclusions

This study researched that sodium sulfite solution with added ethanol was an effective absorbent in high oxygen concentration. The increase in ethanol concentration in absorption solution enhanced its NO₂ absorptive capacity. In the process of NO₂ absorption, the reaction temperature of the liquid phase had little effect on the absorption of NO₂. NO₂⁻ was a direct product of the process of NO₂ absorption. The addition of ethanol to sodium sulfite did not change the product of its absorption of NO₂. Increasing the concentration of ethanol could cancel the effect of ion enrichment on NO₂ absorption

Acknowledgement

The authors gratefully acknowledge the support from the National Key R&D Program of China (2017YFB0603202), the Key R&D Program of Shandong Province (2016CYJS10B02), and the Fundamental Research Funds of Shandong University (2017JC012)

References

- [1] Zou Z S and Wang C 2007 *China J. Iron & Steel* 42 8 17
- [2] Luo H B 2016 *J. Chemical Fertilizer Design* 54 2 40
- [3] Chen G, Gao J, Gao J and et al 2010 *China J. Industrial & Engineering Chemistry Research* 49 23
- [4] Mok Y S and Lee H J 2006 *Korea J. Fuel Processing Technology* 87 7 591
- [5] Zhuang Z, Sun C, Zhao N and et al 2016 *China J. Journal of Chemical Technology & Biotechnology* 91 4 994
- [6] Guo S, Lv L, Jia Z and et al 2015 *China J. Chemical Industry & Chemical Engineering Quarterly* 21 00 29
- [7] Sun C, Zhao N, Wang H and et al 2015 *China J. Energy & Fuels* 29 5
- [8] Chen L, Lin J W and Yang C L 2002 *Taiwan J. Environmental Progress & Sustainable Energy* 21 4 225
- [9] Tang N, Liu Y, Wang H and et al 2010 *China J. Chemical Engineering Journal* 160 1 145
- [10] Chen L, Lin K F and Yang C L 2011 *Taiwan J. Environmental Progress & Sustainable Energy* 30 4 632.
- [11] Wang L D, Ma Y L, Hao J M and et al 2009 *China J. Industrial & Engineering Chemistry Research* 48 9 4307
- [12] Takeuchi H and Yamanaka Y 1978 *Japan J. Industrial & Engineering Chemistry Process Design & Development* 17 17 389