

Article

The Chemical Behaviors of Nitrogen Dioxide Absorption in Sulfite Solution

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Abstract: The simultaneous removal of nitrogen oxides (NO_x) and sulfur dioxide (SO_2) by absorption is considered to be one of the most promising technologies for flue gas treatment, and sulfite is the main component of the absorption solution. To understand the chemical behaviors of the NO_2 absorption in sulfite solution, the absorption time dependences of concentrations of nitrogen and sulfur compositions in both gas phase and liquid phases were investigated by flue gas analyzer, Ion chromatography (IC), Gas chromatography (GC), and Fourier transform infrared spectrometry (FTIR) methods using a bubbling reactor. The mass equilibrium of the N and S compositions were also studied. The results indicate that sulfite concentration plays a vital role in NO_2 absorption. The main absorption products are NO_3^- and NO_2^- , and NO_2^- can be converted into NO_3^- in the presence of oxygen. Besides, about 4% to 9% by-products of S compositions are formed, and 4% to 11% by-products of N compositions such as NO , N_2 , N_2O_5 , N_2O , and HNO_3 in the gas phase were detected in the emissions from the bubbling reactor. On the basis of N and S compositions, a possible pathway of NO_2 absorption in sulfite solution was proposed.

Keywords: absorption; nitrogen oxides; sulfite solution; chemical behaviors; product analysis

1. Introduction

As major poisonous air pollutants, nitrogen oxides (NO_x) and sulfur dioxide (SO_2) from the fossil fuel combustion are key contributors to acid deposition, photochemical smog and hazy weather, and bring out a great harm to the environment and human health [1]. NO_x and SO_2 removal technologies, therefore, have been the research focus of air pollution control in recent decades. It is well known that the commonly practiced technologies of removing NO_x , such as low NO_x burners, selective non-catalytic reduction (SNCR), and selective catalytic reduction (SCR), have been widely developed and used. SO_2 emissions have also been effectively controlled by wet flue gas desulfurization (WFGD), circulated fluid bed flue gas desulfurization (CFB-FGD), and so on. Although the combination of the commonly practiced de- NO_x and de- SO_2 processes can meet the limitations of SO_2 and NO_x emissions stipulated by environmental legislation, traditional NO_x and SO_2 removal technologies in a stepwise manner have some drawbacks, such as the requirement for large construction site, high capital investment, and high operation costs. Thus, the emerging technologies for the simultaneous removal of NO_x and SO_2 are to be extensively developed [2,3].

The integrated oxidation-absorption process using chemical reagents for simultaneous removal of NO_x and SO_2 is considered as a cost-effective and environmental friendly technology for flue gas treatment and has gained increasing interest [4]. However, nitric oxide (NO), accounting for more than 95% of NO_x in typical flue gas, is almost insoluble and low active. Thus, NO has to be oxidized into soluble nitrogen dioxide (NO_2) at the first step. Recently, a few studies related to the NO oxidation have been reported [5–12], including gas phase catalytic oxidation, ozone oxidation, corona discharge

oxidation, and liquid oxidation. After oxidation, the soluble NO_2 can be further removed with SO_2 in the subsequent absorption process [13]. Till now, the NO_2 absorption process using chemical reagents have widely been studied to develop the industrial scale process. Many absorbents such as $\text{Ca}(\text{OH})_2$, CaCO_3 , Na_2SO_3 , $(\text{NH}_4)_2\text{SO}_3$, and CaSO_3 have been tested and the reaction mechanism have been probed [1,14–22]. Among them, sulfite solutions have been considered as a cost-effective absorbent because of their high removal efficiency, their desulphurization byproduct characteristics, and their capacity of simultaneous removal of mercury and chlorine [23–25]. However, NO_2 and SO_2 absorption into sulfite absorbents involves complex chemical behaviors. Consequently, and the chemical behavior of absorption has not been widely generalized up to now. Furthermore, there are few reports on the analysis of the gas products from the NO_2 and SO_2 absorption in absorbents. Thus it is absolutely necessary to further understand the chemical behaviors of the absorption process to promote NO_2 and SO_2 removal by adsorption.

In this study, Na_2SO_3 solution was selected as sulfite absorbent. The time-dependences of concentrations of main nitrogen and sulfur (N and S) compositions in both gas phase and liquid phase were investigated by flue gas analyzer, Ion chromatography (IC), Gas chromatography (GC) and Fourier transform infrared spectrometry (FTIR). The mass equilibrium of the N and S compositions of NO_2 absorption into absorbent through mass balance calculation were also carried out. Moreover, a possible reaction pathway of NO_2 removal was proposed.

2. Experimental Section

2.1. Experimental Setup

A scheme of the experimental setup is shown in Figure 1. It consists of a reaction gas feeding unit, an absorption reactor, and a set of gas analytical instruments. A stirred bubbling device with an effective volume of 5 L (150 mm inner diameter and 300 mm in height) was used as the absorption reactor. A mechanical agitator provided continuous stirring at a speed of 105 rpm. The temperature of the reactor was maintained with the help of a thermostatic water bath. A condenser was used to cool and dehydrate the outlet flue gas and reduce the influence of H_2O on products analysis.

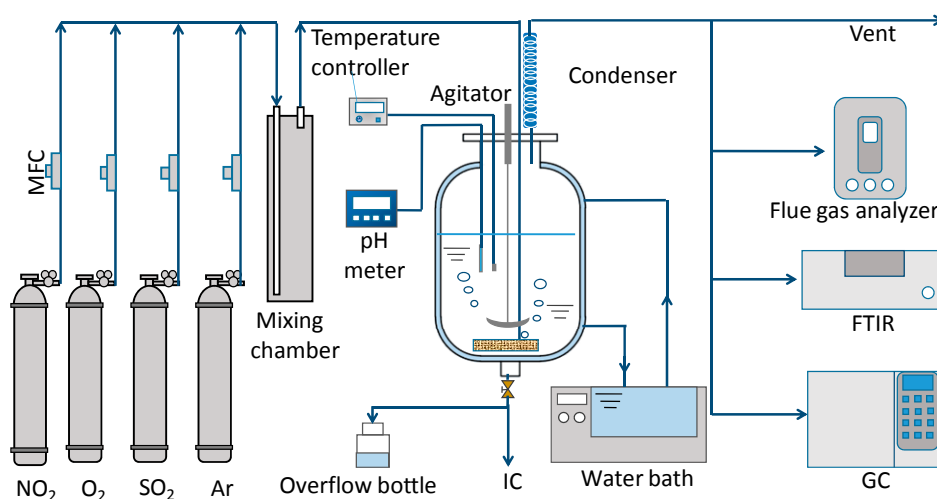


Figure 1. Schematic diagram of the experimental setup. MFC: Mass flow controller; IC: Ion chromatography; FTIR: Fourier transform infrared spectrometry; GC: Gas chromatography.

2.2. Experimental Methods

All experiments were performed at atmospheric pressure and the temperature of 325 ± 5 K. The simulated flue gas, which was supposed to be outlet flue gas after NO oxidation, was simulated by mixing proper amount of NO_2 , O_2 , SO_2 , and Ar from compressed gas cylinders. The basic simulated

flue gas compositions were 260 ppm NO₂, 300 ppm SO₂, 6% O₂ and Ar. The gas flow rate was adjusted by mass flow controller (MFC), and the four gas streams with a total flow rate of 4 L min^{−1} were completely mixed in a mixing chamber before being fed into the absorption reactor. The volume of Na₂SO₃ solution (0.02 M) stored in the stirred bubbling device was 2 L. pH of absorption solution was maintained at 6–7 by adding 1 M HCl or 1 M NaOH solution. The liquid samples at different times for IC analysis were attained from the sampling port. Qualitative analysis of liquid phase (NH₄⁺, NO₃[−], NO₂[−], and SO₄^{2−}) was carried out by ion chromatography (IC, Metrohm 792, Herisau, Switzerland). The concentrations of NO₂, NO, SO₂, and O₂ in the tail gas were monitored by a flue gas analyzer (Testo350-pro, Schwarzwald, Germany). Sulfite ions (SO₃^{2−}) in the liquid phase were measured by an iodometric titration method. N₂ formed in the absorption reaction was monitored using gas chromatography (GC, Agilent 7890, Santa Clara, CA, USA) with a Thermal conductivity detector (TCD, Agilent, Santa Clara, CA, USA), and 5 Å molecular sieve chromatographic column (Agilent, Santa Clara, CA, USA), and the temperature of column oven and detector were 40 and 180 °C, respectively. Other N compositions of outlet gas were analyzed by Fourier transform infrared spectrometry (FTIR, Nicolet 6700, Waltham, MA, USA) equipped with a high-sensitivity mercury cadmium telluride detectors (MCT, Nicolet, Waltham, MA, USA) cooled by liquid nitrogen. The outlet gas stream passed through a 2.5 L gas cell, which had optical path length of 10 m, accordingly averaged spectra after 32 scans at 4 cm^{−1} resolution were collected in the 3000–650 cm^{−1} ranges.

In the current system, inlet NO₂, SO₂ concentrations, and initial sulfite concentration were previously set, without other sources of nitrogen and sulfur compositions. The molar quantity of N and S compositions in a closed loop system from absorption reaction could be calculated by graphical integration during a fixed period, and the theoretical values in this loop-locked system were expressed as follows:

$$TN_t = \int_0^t \frac{Q(C_0 - C_t) \times 10^{-6}}{V_m} dt \quad (1)$$

$$TS_t = \int_0^t \frac{Q(C_0 - C_t) \times 10^{-6}}{V_m} dt + 0.04 \quad (2)$$

where TN_t and TS_t are the total molar quantity of N and S compositions absorbed into reaction system during t absorption time (mol). C_0 and C_t are inlet and outlet concentrations of NO₂ or SO₂ (ppm), respectively. Q is the total flow rate of the flue gas (L min^{−1}). V_m is the molar volume of NO₂ or SO₂ in 325 K (L mol^{−1}), and t is the absorption time (min). Meanwhile, 0.04 in Equation (2) is the original molar quantity of SO₃^{2−} in stirred bubbling device (mol).

3. Results and Discussion

3.1. Quantitative Analysis of N and S Compositions in Gaseous and Liquid Phases

In order to analyze the distribution of N and S compositions in closed loop reaction system, the dependence of outlet NO₂ and SO₂ concentrations with the absorption time were investigated, and the results are shown in Figure 2. Due to the high sulfite concentration, both NO₂ and SO₂ were not detected in the outlet flue gas during the initial absorption period of about 200 min, which suggests that nearly all of NO₂ and SO₂ are absorbed. The outlet NO₂ and SO₂ concentrations rapidly increase from 210 min to 230 min and are almost unchanged after 230 min. It is clear that the absorption equilibrium is established after a certain absorption time. These results also show that the reaction between NO₂ and sulfite may be mainly controlled by diffusion in the initial reaction period, which is due to the sulfite concentration makes reaction rate is much faster than the diffusion rate [22,26]. Figure 2 also shows that NO, as one of the absorption products, has similar time dependence to NO₂ and SO₂ concentrations. It was found that hardly any NO was detected during initial absorption period of about 200 min. NO concentration gradually increases from about 210 min to 230 min and almost keeps unchanged after 230 min. This can be explained as follows: in the initial absorption period, NO₂ can oxidize sulfite solutions directly (R1). However, with the depletion of sulfite solutions,

NO_2 absorption in H_2O (R2) occurs, and HNO_2 may be formed. Generally, HNO_2 is unstable in its liquid phase and can decompose into NO as R3 [22,27].

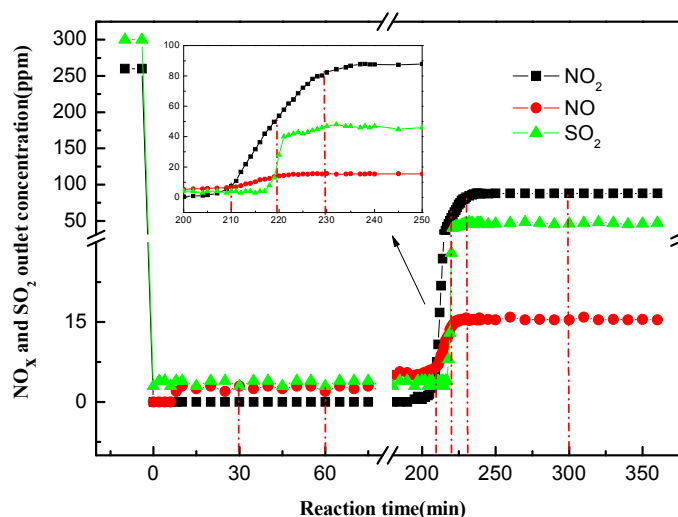
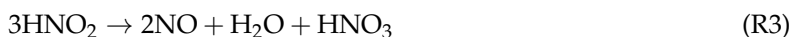


Figure 2. The dependence of outlet NO_2 , SO_2 , and NO concentrations with the absorption time.

NO_3^- , NO_2^- , SO_3^{2-} , and SO_4^{2-} , which are main reactants or products of liquid phase, are synchronously analyzed by IC at the absorption times of 30 min, 60 min, 210 min, 220 min, 230 min and 300 min to better understand the chemical behaviors of NO_2 and SO_2 absorption in sulfite solution. As shown in Figure 3, NO_3^- , NO_2^- , and SO_4^{2-} concentrations in absorption solution increase as the absorption proceeds. Compared with NO_2^- , more NO_3^- was formed at the same absorption time, which can be ascribed to the oxidation of NO_2^- and the decomposition of unstable HNO_2 [22,28]. After the absorption time of about 300 min, NO_2^- concentration is almost unchanged although NO_3^- ions still increase, which is attributed to the fact that nitrite ions are further oxidized into nitrate ions.

Figure 3 also shows that the sulfite concentration gradually decreases as the absorption proceeds and are almost unavailable after 220 min, which results in a sharp decrease of NO_2 absorption performance. It indicates that sulfite concentration is closely related with the performance of the removal of NO_2 , which agrees well with the findings shown in Figure 2. The sulfite is consumed because of its reaction with NO_2 or O_2 . For NO_2 absorption in sulfite solution, the sulfate is formed through the reaction between NO_2 or O_2 and sulfite (R1) [29].

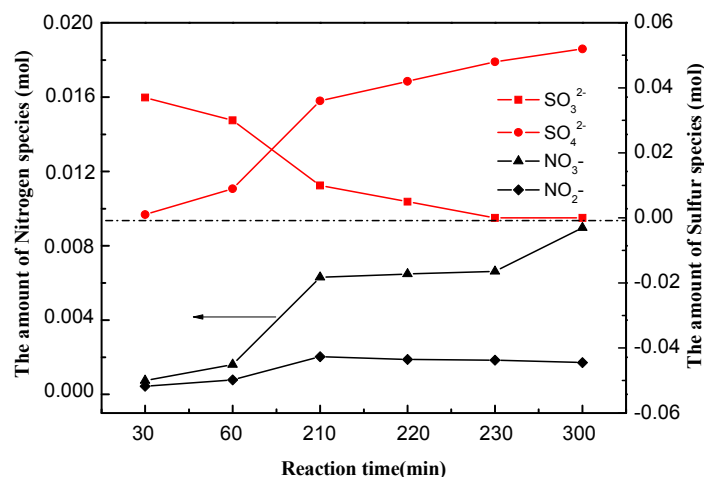


Figure 3. The dependence of SO_3^{2-} , SO_4^{2-} , NO_3^- , and NO_2^- contents with the reaction time.

3.2. Equilibrium Analysis of N and S Compositions

Figures 4 and 5 present the N and S equilibrium of NO_2 and SO_2 absorption in sulfite solution, respectively. It can be seen from Figure 4 that the sum of NO_3^- and NO_2^- ions in the absorption solution is lower than the calculated TN_t for almost all the reaction times, which suggests that other N compositions of about 4% to 11%, are formed in the absorption process. Some researchers have confirmed the existence of other N compositions. Siddiqi et al. [30] studied the effect of nitrogen dioxide on the absorption of sulfur dioxide in wet flue gas cleaning processes and pointed out that nitrogen–sulfur compounds could be formed and further decomposed into gaseous products in the co-existence condition of NO_2 and SO_2 absorption process. Yan, et al. [31] also reported that the reaction of sulfite with NO could produce N_2 . However, few quantitative researches about gas phase products have been previously reported. In addition, Figure 4 also shows that the amount of other N compositions is almost kept constant before 210 min, and then decreases as the absorption proceeds, which means that sulfite plays a dominant role in the formation of other N compositions. These results are consistent with the dependence of NO_2 removal (Figure 2) and SO_3^{2-} amount (Figure 3) with the reaction time.

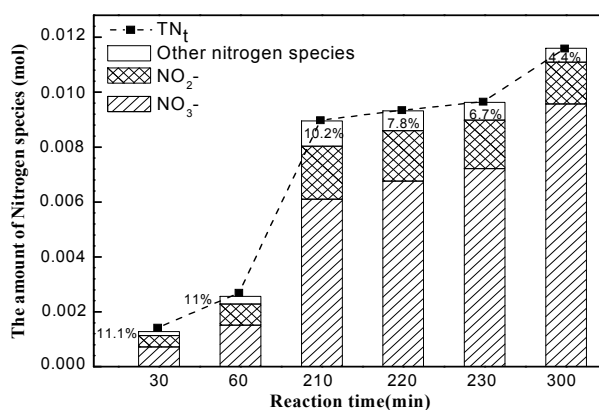


Figure 4. The equilibrium analysis of N compositions for NO_2 absorption in sulfite solution.

Similarly, the calculated TS_t is also more than the sum of detected SO_3^{2-} and SO_4^{2-} , as shown in Figure 5. Other S compositions besides SO_3^{2-} and SO_4^{2-} account for about 4% to 9% in the reaction system. Besides the above-mentioned nitrogen–sulfur compounds, Chen et al. [32] and Zhuang et al. [32,33] thought that the sulfite radicals could be formed by the reaction between NO_2 and

sulfite, the sulfite radicals could undergo either recombination or reaction with oxygen. By comparing Figure 4 with Figure 5, it can be seen that the amount of other S compositions is much lower than that of other N compositions, which suggests that not all other S compositions participate in the formation of other N compositions.

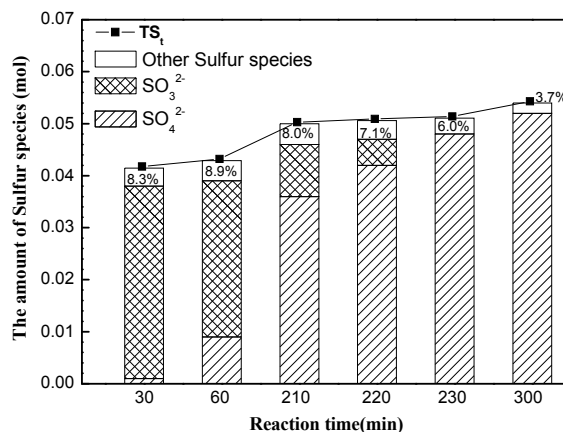
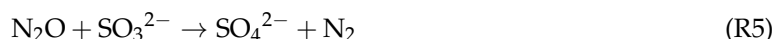
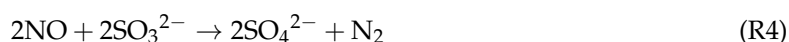


Figure 5. The equilibrium analysis of S compositions for SO₂ absorption in sulfite solution.

3.3. Qualitative Analysis of N Compositions

Besides NO₂, NO, NO₂[−], and NO₃[−], the nitrous products such as N₂O, N₂O₃, N₂O₅, and N₂, can form during the NO₂ absorption into sulfite solution [10,30]. IC, GC, and FTIR were used to detect these products in this study. Figures 6 and 7 present the GC and FTIR spectra of the gaseous products, respectively.

It can be seen from Figure 6 that the gaseous N₂ is formed mainly in the initial absorption period, declines as the absorption proceeds, and finally disappears after 230 min. N₂ formation can be explained by the following reactions [31],



The sulfite plays an important role in N₂ formation according to Reactions (4) and (5). Thus N₂ concentration decrease is due to the fact that sulfite concentration in reaction system gradually declines and finally disappears. Although N₂ concentration cannot contribute to the equilibrium analysis of nitrogen, the observed declining tendency of N₂ peaks with the absorption time indicates that N₂ is one of other nitrogen compositions.

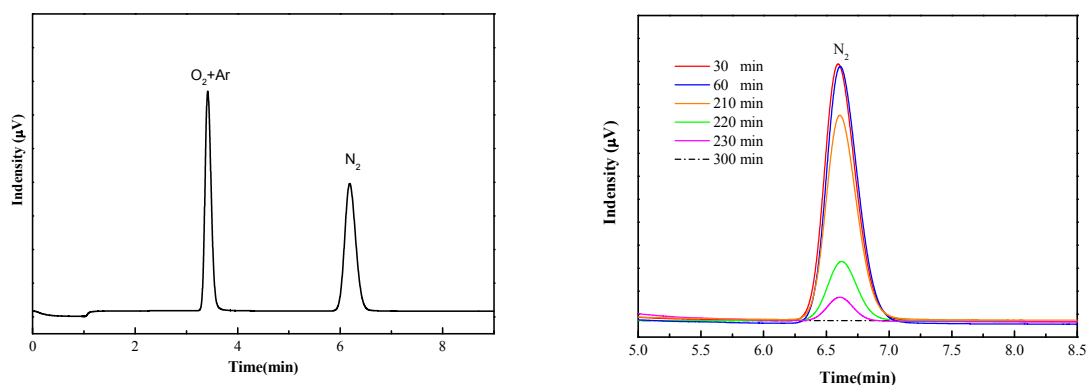


Figure 6. GC spectra of gaseous N-products during NO₂ absorption.

Based on the FTIR analysis, the effect of absorption time on the gaseous N-product distribution can be seen, as shown in Figure 7. Six distinct absorbance peaks are observed at 2930 cm^{-1} , 2287 cm^{-1} , 1720 cm^{-1} , 1600 cm^{-1} , 1326 cm^{-1} , and 887 cm^{-1} , and the bands are assigned to NO_2 , N_2O , N_2O_5 , NO_2 , HNO_3 , and HNO_3 , respectively [34]. In the initial absorption period, the intensities of bands at 2287 cm^{-1} , 1720 cm^{-1} , 1326 cm^{-1} , and 887 cm^{-1} almost keep unchanged, which shows that N_2O , N_2O_5 , and HNO_3 as gaseous products are continuously generated from the absorption reactions. Then the amounts of N_2O , N_2O_5 , and HNO_3 rapidly decrease after the absorption time of about 210 min and finally disappear after about 230 min, which indicates that the absorption equilibrium is established, and no sufficient sulfite is used to react with NO_2 to produce gaseous N_2O , N_2O_5 , and HNO_3 . These results are consistent with the equilibrium analysis of sulfur compositions (see Figure 5). In fact, not all sulfite would be converted to sulfate ions, nitrogen–sulfur compounds, and sulfite radical may exist in reaction system. In addition, the occurrence of N_2O_5 is due to the reaction between NO_2 and O_2 in gas phase, or the decomposition of nitrogen–sulfur compounds. Furthermore, the gaseous HNO_3 is not only attributed to the fact that HNO_3 in absorption liquid enters gas phase, but also that gas phase reaction happens, which can be described by the following Reaction (6):



Figure 7 also shows that the peak at 1600 cm^{-1} , assigned to NO_2 , gradually increases and the peak at 1900 cm^{-1} , assigned to NO , gradually decreases after the absorption time of about 210 min. The results are also in accordance with those of gas phase composition analysis by flue gas analyzer (Testo350-pro, Germany), as shown in Figure 2.

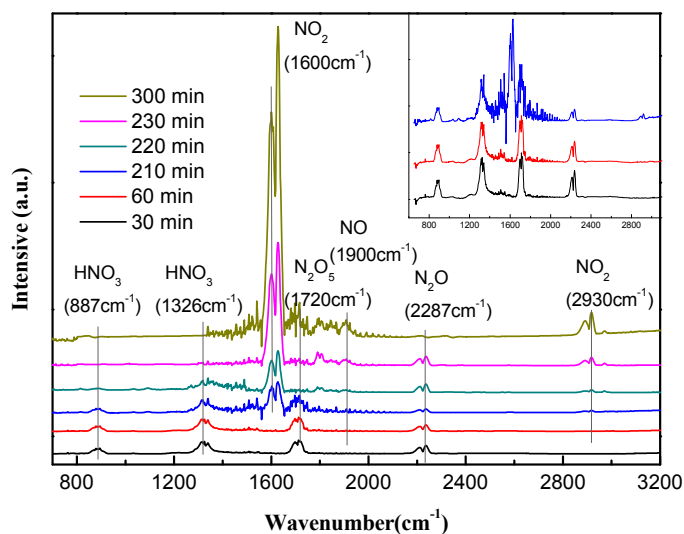


Figure 7. FTIR spectra of the gaseous N-products during NO_2 absorption.

Figure 8 shows the distribution of nitrogen products for NO_2 absorption into sulfite solution, based on mass balance for a typical inlet gas with 260 ppm NO_2 , as the sole N source. Because NO_2 is hardly detected in the outlet flue gas of the reactor before 60 min, NO_2 absorbed into the liquid phase is 2.56 mmol during initial absorption time of 60 min. NO_3^- and NO_2^- concentrations in the absorption solution, based on IC results, are 1.511 and 0.766 mmol, respectively. Because both NH_3 and NH_4^+ have not been found by FTIR and IC, the other N compositions is calculated as 0.283 mmol according to mass balance, account for 11% of the total N compositions, and the calculated values of other N compositions content are in good agreement with the experimental values.

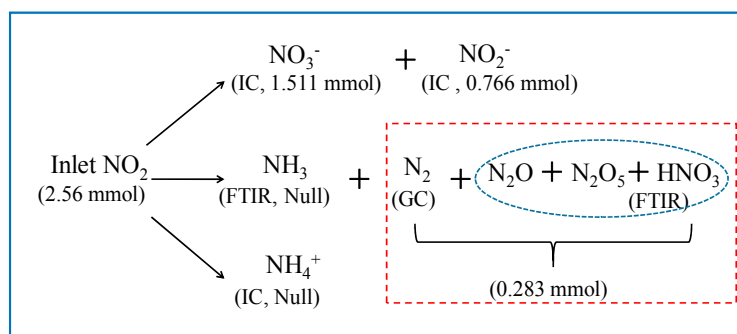


Figure 8. The nitrogen balance of NO_2 absorption in sulfite solution.

3.4. NO_2 Absorption Pathway

According to the above-mentioned analyses, a possible NO_2 absorption pathway can be proposed, as depicted in Figure 9.

The main reactants in the gas phase include NO_2 , SO_2 , and O_2 . The sole N source in the inlet flue gas is NO_2 . When NO_2 laden gas contacts with sulfite solution, the transfer of the NO_2 into absorption solution occurs, meanwhile, reactions take place in the liquid phase, and the main products of NO_2 absorption in flue gas are NO_3^- and NO_2^- , especially NO_3^- in absorption solution dramatically increases due to the absorption of NO_2 and the oxidation of NO_2^- . HNO_3 is considered to involve gas and liquid states existing in reaction system, and the gaseous HNO_3 in outlet flue gas is from both HNO_3 escape in absorption solution and the reaction between NO_2 and H_2O in the gas phase. HNO_2 may be produced by NO_2^- combining with H^+ , and HNO_2 is unstable in liquid phase and easily decomposes, which leads to HNO_3 formation and NO release. As NO increasing, a homogeneous reaction of NO and NO_2 results in an increase of the N_2O_3 to a smaller extent, the NO or N_2O_3 can react with SO_3^{2-} to form hydroxylamine-disulfonate (HADS), which is a precursor of numerous N-S compounds. In addition, the existence of SO_2 in the gas phase is in favor of the sulfite and bisulfate formation, and HNO_2 can also react with HSO_3^- to form HADS. The intermediate products of N-S compounds finally decompose to N_2O_5 , N_2O , and N_2 in gas phase.

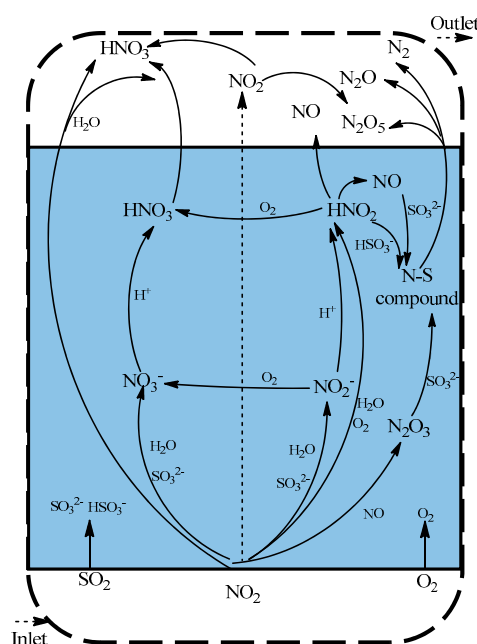


Figure 9. A possible NO_2 absorption pathway.

4. Conclusions

A series of experiments were performed to study the chemical behaviors for the NO₂ and SO₂ absorption in sulfite solution, and a possible NO₂ absorption pathway was proposed. The main findings can be summarized as follows: The performance of NO₂ absorption is closely related with sulfite concentration. The main N and S compounds generated in the NO₂ absorption process are NO₃[−], NO₂[−], and SO₄^{2−}. Moreover the NO₃[−], NO₂[−], and SO₄^{2−} concentrations change with absorption times. Besides, about 4% to 9% by-products of S compositions are formed, and 4% to 11% by-products of N compositions, such as NO, N₂, N₂O₅, N₂O, and HNO₃ in gas phase, were detected in the emissions. Meanwhile, N₂, N₂O₅, and N₂O could be ascribed to the decomposition of sulfur–nitrogen compounds as intermediate products exited from the redox reaction between sulfite solutions and NO₂.

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Author Contributions: Tianle Zhu conceived and designed the experiments; Ye Sun performed the experiments; Ye Sun, Xiaowei Hong, Xiaoyan Guo and Deyuan Xie analyzed the data; Ye Sun and Tianle Zhu wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Adewuyi, Y.G.; Sakyi, N.Y. Simultaneous Absorption and Oxidation of Nitric Oxide and Sulfur Dioxide by Aqueous Solutions of Sodium Persulfate Activated by Temperature. *Ind. Eng. Chem. Res.* **2013**, *52*, 11702–11711. [[CrossRef](#)]
- Guo, R.T.; Hao, J.K.; Pan, W.G.; Yu, Y.L. Liquid Phase Oxidation and Absorption of NO from Flue Gas: A Review. *Sep. Sci. Technol.* **2015**, *50*, 310–321. [[CrossRef](#)]
- Sun, Y.X.; Zwolinska, E.; Chmielewski, A.G. Abatement Technologies for High Concentrations of NO_x and SO₂ Removal from Exhaust Gases: A Review. *Crit. Rev. Environ. Sci. Technol.* **2016**, *46*, 119–142. [[CrossRef](#)]
- Zhao, Y.; Hao, R.L.; Qi, M. Integrative Process of Preoxidation and Absorption for Simultaneous Removal of SO₂, NO and Hg⁰. *Chem. Eng. J.* **2015**, *269*, 159–167. [[CrossRef](#)]
- Deshwal, B.R.; Lee, S.H.; Jung, J.H.; Shon, B.H.; Lee, H.K. Study on the Removal of NO_x from Simulated Flue Gas Using Acidic NaClO₂ Solution. *J. Environ. Sci. China* **2008**, *20*, 33–38. [[CrossRef](#)]
- Jin, D.-S.; Deshwal, B.-R.; Park, Y.-S.; Lee, H.-K. Simultaneous Removal of SO₂ and NO by Wet Scrubbing Using Aqueous Chlorine Dioxide Solution. *J. Hazard. Mater.* **2006**, *135*, 412–417. [[CrossRef](#)] [[PubMed](#)]
- Fang, P.; Cen, C.-P.; Wang, X.-M.; Tang, Z.-J.; Tang, Z.-X.; Chen, D.-S. Simultaneous Removal of SO₂, NO and Hg⁰ by Wet Scrubbing Using Urea + KMnO₄ Solution. *Fuel Process. Technol.* **2013**, *106*, 645–653. [[CrossRef](#)]
- Liu, Y.; Zhang, J.; Sheng, C.; Zhang, Y.; Zhao, L. Simultaneous Removal of NO and SO₂ from Coal-fired Flue Gas by UV/H₂O₂ Advanced Oxidation Process. *Chem. Eng. J.* **2010**, *162*, 1006–1011. [[CrossRef](#)]
- Yoon, H.J.; Park, H.W.; Park, D.W. Simultaneous Oxidation and Absorption of NO_x and SO₂ in an Integrated O₃ Oxidation/Wet Atomizing System. *Energy Fuel* **2016**, *30*, 3289–3297. [[CrossRef](#)]
- Wang, M.; Sun, Y.; Zhu, T. Removal of NO_x, SO₂, and Hg From Simulated Flue Gas by Plasma-Absorption Hybrid System. *IEEE Trans. Plasma Sci.* **2013**, *41*, 312–318. [[CrossRef](#)]
- Van Eynde, E.; Lenaerts, B.; Tytgat, T.; Blust, R.; Lenaerts, S. Valorization of Flue Gas by Combining Photocatalytic Gas Pretreatment with Microalgae Production. *Environ. Sci. Technol.* **2016**, *50*, 2538–2545. [[CrossRef](#)] [[PubMed](#)]
- Adewuyi, Y.G.; Khan, M.A. Nitric Oxide Removal by Combined Persulfate and Ferrous-Edta Reaction Systems. *Chem. Eng. J.* **2015**, *281*, 575–587. [[CrossRef](#)]
- Krzyzynska, R.; Hutson, N.D. Effect of Solution pH on SO₂, NO_x, and Hg Removal from Simulated Coal Combustion Flue Gas in an Oxidant-enhanced Wet Scrubber. *J. Air Waste Manag. Assoc.* **2012**, *62*, 212–220. [[CrossRef](#)] [[PubMed](#)]
- Komiyama, H.; Inoue, H. Absorption of Nitrogen Oxides into Water. *Chem. Eng. Sci.* **1980**, *35*, 154–161. [[CrossRef](#)]

15. Thomas, D.; Vanderschuren, J. Analysis and Prediction of the Liquid Phase Composition for the Absorption of Nitrogen Oxides into Aqueous Solutions. *Sep. Purif. Technol.* **1999**, *18*, 37–45. [[CrossRef](#)]
16. Hüpen, B.; Kenig, E.Y. Rigorous Modelling of Absorption in Tray and Packed Columns. *Chem. Eng. Sci.* **2005**, *60*, 6462–6471. [[CrossRef](#)]
17. Hu, G.; Sun, Z.; Gao, H. Novel Process of Simultaneous Removal of SO₂ and NO₂ by Sodium Humate Solution. *Environ. Sci. Technol.* **2010**, *44*, 6712–6717. [[CrossRef](#)] [[PubMed](#)]
18. Sun, W.-Y.; Wang, Q.-Y.; Ding, S.-L.; Su, S.-J.; Jiang, W.-J.; Zhu, E.-G. Reaction Mechanism of NO_x Removal from Flue Gas with Pyrolusite Slurry. *Sep. Purif. Technol.* **2013**, *118*, 576–582.
19. Guo, Q.; Sun, T.; Wang, Y.; He, Y.; Jia, J. Spray Absorption and Electrochemical Reduction of Nitrogen Oxides from Flue Gas. *Environ. Sci. Technol.* **2013**, *47*, 9514–9522. [[CrossRef](#)] [[PubMed](#)]
20. Gao, X.; Guo, R.-T.; Ding, H.-L.; Luo, Z.-Y.; Cen, K.-F. Absorption of NO₂ into Na₂S Solution in a Stirred Tank Reactor. *J. Zhejiang Univ. Sci. A* **2009**, *10*, 434–438. [[CrossRef](#)]
21. Guo, Q.; He, Y.; Sun, T.; Wang, Y.; Jia, J. Simultaneous Removal of NO_x and SO₂ from Flue Gas Using Combined Na₂SO₃ Assisted Electrochemical Reduction and Direct Electrochemical Reduction. *J. Hazard. Mater.* **2014**, *276*, 371–376. [[CrossRef](#)] [[PubMed](#)]
22. Gao, X.; Du, Z.; Ding, H.-L.; Wu, Z.-L.; Lu, H.; Luo, Z.-Y.; Cen, K.-F. Effect of Gas-liquid Phase Compositions on NO₂ and NO Absorption into Ammonium-sulfite and Bisulfite Solutions. *Fuel Process. Technol.* **2011**, *92*, 1506–1512. [[CrossRef](#)]
23. Roy, S.; Rochelle, G. Simultaneous Absorption of Chlorine and Mercury in Sulfite Solutions. *Chem. Eng. Sci.* **2004**, *59*, 1309–1323. [[CrossRef](#)]
24. Rochelle, G.T. Chlorine Absorption in Sulfite Solutions. *Sep. Sci. Technol.* **2005**, *39*, 3057–3077.
25. Shibukawa, T.; Ohira, Y.; Obata, E. Absorption of Nitrogen Dioxide by Sodium Sulfite Solution. *Kagaku Kogaku Ronbun* **2008**, *34*, 438–443. [[CrossRef](#)]
26. Gao, X.; Du, Z.; Ding, H.-L.; Wu, Z.-L.; Lu, H.; Luo, Z.-Y.; Cen, K.-F. Kinetics of NO_x Absorption into (NH₄)₂SO₃ Solution in an Ammonia-Based Wet Flue Gas Desulfurization Process. *Energy Fuel* **2010**, *24*, 5876–5882. [[CrossRef](#)]
27. Zheng, C.; Xu, C.; Zhang, Y.; Zhang, J.; Gao, X.; Luo, Z.; Cen, K. Nitrogen Oxide Absorption and Nitrite/nitrate Formation in Limestone Slurry for WFGD System. *Appl. Energy* **2014**, *129*, 187–194. [[CrossRef](#)]
28. Shen, C.H.; Rochelle, G.T. Nitrogen Dioxide Absorption and Sulfite Oxidation in Aqueous Sulfite. *Environ. Sci. Technol.* **1998**, *32*, 1994–2003. [[CrossRef](#)]
29. Tang, N.; Liu, Y.; Wang, H.; Xiao, L.; Wu, Z. Enhanced Absorption Process of NO₂ in CaSO₃ Slurry by the Addition of MgSO₄. *Chem. Eng. J.* **2010**, *160*, 145–149. [[CrossRef](#)]
30. Siddiqi, M.A.; Petersen, J.; Lucas, K. A Study of the Effect of Nitrogen Dioxide on the Absorption of Sulfur Dioxide in Wet Flue Gas Cleaning Processes. *Ind. Eng. Chem. Res.* **2001**, *40*, 2116–2127. [[CrossRef](#)]
31. Yan, B.; Yang, J.H.; Guo, M.; Zhu, S.J.; Yu, W.J.; Ma, S.C. Experimental Study on Fe(II)Cit Enhanced Absorption of NO in (NH₄)₂SO₃ Solution. *J. Ind. Eng. Chem.* **2015**, *21*, 476–482. [[CrossRef](#)]
32. Chen, L.; Lin, J.W.; Yang, C.L. Absorption of NO₂ in a Packed Tower with Na₂SO₃ Aqueous Solution. *Environ. Prog.* **2002**, *21*, 225–230. [[CrossRef](#)]
33. Zhuang, Z.K.; Sun, C.L.; Zhao, N.; Wang, H.Q.; Wu, Z.B. Numerical Simulation of NO₂ Absorption Using Sodium Sulfite in a Spray Tower. *J. Chem. Technol. Biotechnol.* **2016**, *91*, 994–1003. [[CrossRef](#)]
34. Sun, C.; Zhao, N.; Zhuang, Z.; Wang, H.; Liu, Y.; Weng, X.; Wu, Z. Mechanisms and Reaction Pathways for Simultaneous Oxidation of NO_x and SO₂ by Ozone Determined by in situ IR Measurements. *J. Hazard. Mater.* **2014**, *274*, 376–383. [[CrossRef](#)] [[PubMed](#)]

