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Role of Thiosulfate in NO_2 Absorption in Aqueous Sulfite Solutions

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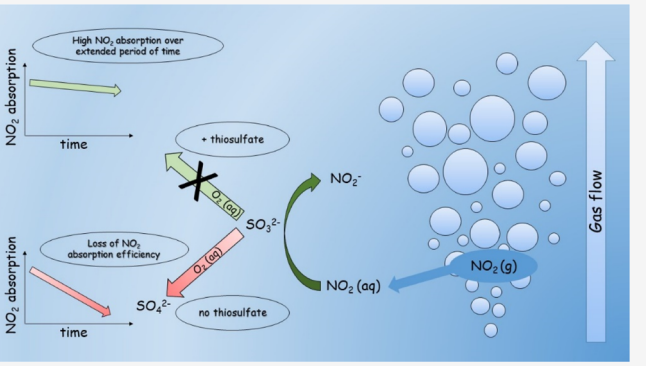
ABSTRACT: NO_x emissions continues to be a major challenge in order to reduce the environmental impact of thermal conversion of non-recyclable waste and fuels with high nitrogen contents. Oxidation of NO to NO_2 followed by absorption of NO_2 in aqueous solutions with sulfur compounds as additives has recently gained more attention in order to reduce NO_x emissions from flue gases. One major challenge in NO_2 absorption is the high consumption of sulfite, requiring sulfite oxidation inhibitors such as thiosulfate. The present study clarifies the chemistry and consumption of thiosulfate in wet scrubbing of NO_2 with buffered solutions under well-controlled conditions at neutral pH at 25 °C. Absorption rates for the reaction of thiosulfate and NO_2 in the scrubber were determined, and the ability of thiosulfate to inhibit the sulfite oxidation was investigated and quantified. With 1 mM thiosulfate (no sulfite) in the scrubber solution, the NO_2 absorption rate increased by 30% as compared to pure water and by 160% with 100 mM thiosulfate. The absorption rate increased with time in the presence of oxygen. With 1 mM sulfite (no thiosulfate), the initial NO_2 absorption rate increased by 200% as compared to pure water. However, the absorption rate decreases significantly after short periods of time due to the high consumption of sulfite through undesired oxidation by O_2. In tests with sulfite and thiosulfate as an oxidation inhibitor, high removal efficiencies could be maintained over extended periods of time. With a 10 mM sulfite solution, 1 mM thiosulfate decreased the sulfite oxidation rate from 130 to 31 $mg{\cdot}L^{-1}{\cdot}min^{-1}$, and 2 mM thiosulfate decreased the rate to 16 $mg{\cdot}L^{-1}{\cdot}min^{-1}$. For the investigated conditions, the consumption of thiosulfate did not change significantly when higher sulfite concentrations were used. The results of the study demonstrate high NO_2 absorption rates for low concentrations of sulfite and thiosulfate at neutral pH.



1. INTRODUCTION

NO_2 absorption in aqueous sulfite solutions has recently gained more attention in order to reduce NO_x emissions from thermal conversion of non-recyclable waste and fuels with high nitrogen contents.[1−4] The NO_x in flue gases consists mostly of NO. Due to the low solubility of NO in water, NO is oxidized to NO_2 which has a higher solubility in water.[5,6] NO_2 reacts with water forming nitrite and nitrate (see RR1).[7] In order to further improve NO_2 absorption rates, additives such as sulfite can be used.[8−10] The sulfite concentration, the oxygen concentration, and the pH of the scrubber solution influence the NO_2 absorption rate.[11−13] The reaction between sulfite and NO_2 is believed to take place close to the surface of the liquid via charge transfer, forming nitrite (NO_2^-) and a sulfite radical ($SO_3^{\bullet-}$) (see RR2).[14]

$$2NO_2(aq) + H_2O(l) \rightarrow NO_2^- + NO_3^- + 2H^+ \quad (R1)$$

$$NO_2(aq) + SO_3^{2-} \rightarrow NO_2^- + SO_3^{\bullet-} \quad (R2)$$

The sulfite radical can undergo a radical chain reaction (see RR3, RR4, RR5, and RR6) which results in a high consumption of sulfite in the presence of oxygen. In this chain reaction, $SO_5^{\bullet-}$ and SO_4^- radicals are formed oxidizing sulfite to sulfate. The kinetics of the sulfite oxidation by oxygen has been studied by Lian et al.[15] The influence of sulfite concentration and $NO_2(g)$ concentration on the sulfite oxidation rate has been investigated showing that the oxidation rate increases with increased sulfite concentrations.[11,13]

$$SO_3^{\bullet-} + O_2(aq) \rightarrow SO_5^{\bullet-} \quad (R3)$$

$$SO_5^{\bullet-} + SO_3^{2-} \rightarrow SO_4^{\bullet-} + SO_4^{2-} \quad (R4)$$

$$SO_3^{2-} + SO_4^{\bullet-} \rightarrow SO_3^{\bullet-} + SO_4^{2-} \quad (R5)$$

$$2SO_3^{\bullet-} \rightarrow S_2O_6^{2-} \quad (R6)$$

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Thiosulfate can be used as a sulfite oxidation inhibitor to reduce the consumption rate of sulfite in the NO_2 absorption process.[16,17] Thiosulfate acts as a radical scavenger and terminates the chain reaction (see RR7 and RR8). Besides this, thiosulfate can also react with NO_2, similarly to the reaction between sulfite and NO_2, forming nitrite and another radical (see RR9).

$$SO_5^{\bullet-} + S_2O_3^{2-} \rightarrow SO_5^{2-} + S_2O_3^{\bullet-} \quad (R7)$$

$$SO_5^{2-} + SO_3^{2-} \rightarrow 2SO_4^{2-} \quad (R8)$$

$$NO_2(aq) + S_2O_3^{2-} \rightarrow NO_2^{-} + S_2O_3^{\bullet-} \quad (R9)$$

The role and chemistry of thiosulfate in NO_2 absorption have only been investigated to a limited extent.[9,13] Sapkota et al. investigated the kinetics of the NO_2-catalyzed sulfite oxidation at low NO_2 concentrations (2−10 ppm) and sulfite concentrations of around 40 and 25 mM or 100 mM thiosulfate at pH 9.[13] In their tests with 40 mM sulfite and 25 or 100 mM thiosulfate, the sulfite oxidation rate was reduced by 1 order of magnitude, while a further increase in the thiosulfate concentrations (from 25 to 100 mM thiosulfate) only showed minor improvements. The use of even lower thiosulfate/sulfite ratios under neutral pH has not been investigated previously, which is the aim of the present work. For industrial applications, it is crucial to understand the details of the absorption process with thiosulfate and sulfite in order to minimize the consumption of chemicals and thereby reduce the production of waste products.

The present study investigates the role of thiosulfate in NO_2 absorption in aqueous sulfite solutions. The reactions between thiosulfate and NO_2 and O_2 are investigated to understand the overall contribution of thiosulfate on the NO_2 absorption. In a second step, the role of thiosulfate as a sulfite oxidation inhibitor is investigated. Sulfite oxidation rates in the presence of thiosulfate are determined, as well as the consumption of thiosulfate when used as a sulfite oxidation inhibitor. To understand the thiosulfate and sulfite consumption rates is of great importance in order to minimize the usage of additives for NO_2 absorption, while maintaining a high NO_2 absorption efficiency.

2. EXPERIMENTAL SECTION

The setup used for the NO_2 absorption experiments is shown in Figure 1. The gases used in the experiments were mixed before entering a gas washing bottle in which the gas bubbled through a magnetically stirred absorption solution (50 mL) at room temperature. The NO_2 was purchased from Air Products (200 ppm NO_2, N_2 as balance gas). After passing through the absorption solution, the gas passed a SCC-K catalyst from ABB to reduce all NO_2 to NO. The NO was then quantified using a chemiluminescence detector from Teledyne, model 200EM. The total gas flow rate of 2.3 NL/min was controlled with EL-FLOW mass flow meters from Bronkhorst. The inlet gas concentration was either 50 ppm NO_2 without oxygen or 50 ppm + 5% O_2 with nitrogen as the carrier gas.

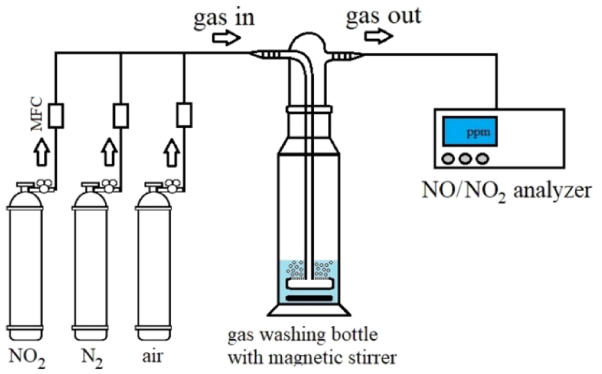

Figure 1. Experimental setup for NO_2 absorption experiments; MFC = mass flow controller.

Absorption tests with only thiosulfate in the absorption solution were performed with thiosulfate concentrations between 0 and 100 mM. The sodium thiosulfate (anhydrous, ≥98%) was purchased from Riedel-de Haën. For the absorption tests with both sulfite and thiosulfate, absorption solutions containing 2−10 mM sulfite and 0−5 mM thiosulfate were used. The sodium sulfite (anhydrous, ≥98%) was purchased from Sigma-Aldrich. The solutions were buffered with a phosphate buffer ($NaHPO_4{\cdot}2H_2O$ + KH_2PO_4) to maintain stable conditions around pH 7. Ion chromatography was performed for selected absorption experiments to follow the consumption of thiosulfate. For the quantification of thiosulfate, a Metrosep A SUPP 4 column from Metrohm was used with a carbonate/bicarbonate eluent.

3. RESULTS AND DISCUSSION

3.1. NO_2 Absorption with Thiosulfate. Figure 2 shows NO_2 concentrations for the experiments with 0−100 mM thiosulfate (a) or 0−20 mM sulfite (b) (reproduced from[11]) in the scrubber solution. The corresponding apparent absorption rates are presented in Table 1 (absorption rates marked with * are estimated values for comparison with data from[11]). Without thiosulfate, that is, pure water, the NO_2 concentration decreased from the initial 50 to 44 ppm. In the experiment with 1 mM thiosulfate, the NO_2 concentration decreased to 42 ppm, that is, the absorption rate increased by 30%. Increasing the thiosulfate concentration from 1 to 2 mM had no observable effect on the NO_2 absorption. With 10 or 100 mM, the NO_2 concentration decreased to 39 or 35 ppm, respectively.

Comparing the NO_2 absorption rates from tests with thiosulfate to the tests with sulfite, it is clear that sulfite has a much stronger effect on the NO_2 absorption rates than thiosulfate, which is in agreement with earlier findings in literature.[9,18] The apparent reaction rates for the sulfite solutions with 1, 2, or 5 mM concentration are about 2.5−3 times higher as compared to the corresponding thiosulfate solutions. Various reactions might occur simultaneously (NO_2 either reacting with sulfite/thiosulfate or water), hence only apparent reactions rates are given to describe the observed phenomena in our scrubber system. However, ion chromatography analysis of selected tests indicate that NO_2 mainly reacts with thiosulfate and sulfite as only nitrite was found as an absorption product (compare RR2 and RR9).

Figure 3 shows NO_2 concentrations for absorption experiments with 2 mM thiosulfate (no sulfite) with and without O_2(g) in the inlet gas, and Table 2 lists the thiosulfate concentrations in the absorption solution before and after the corresponding experiments. Without oxygen, the NO_2 concentration decreased from the initial 50 ppm to around 40 ppm and remained almost constant during the 30 min period of the experiment. A slight increase of the NO_2 concentration could be observed as the experiment proceeded.

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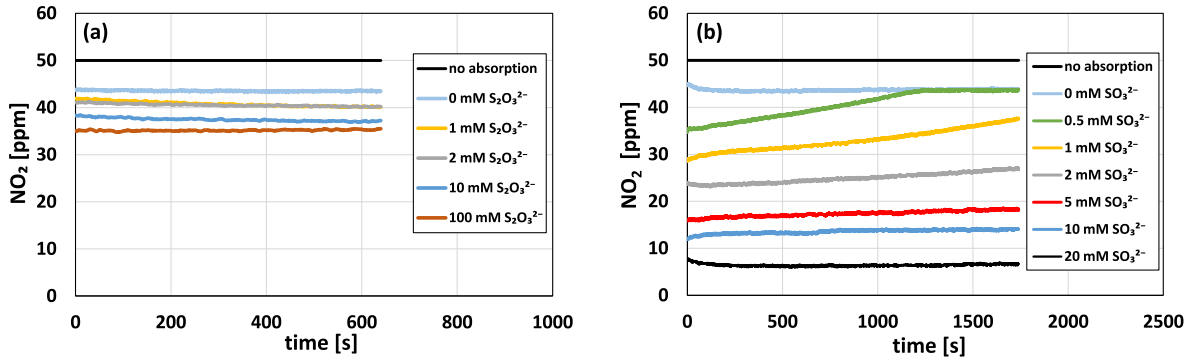

Figure 2. NO_2 concentrations for absorption experiments with (a) 0−100 mM thiosulfate and (b) 0−20 mM sulfite (reproduced from[11]); inlet gas 50 ppm NO_2 (rest N_2, no oxygen).

Table 1. Apparent Reaction Rates for Reaction of NO_2 with Thiosulfate or Sulfite Solutions; 50 ppm NO_2, No Oxygen[a]

additive concn [mM]	NO_2 abs. rate (thiosulfate) [mol•dm^{-3}·s^{-1}]	NO_2 abs. rate (sulfite) [mol•dm^{-3}·s^{-1}]11
0	1.82×10^{-7}	1.88×10^{-7}
0.5	2.23×10^{-7}*	4.23×10^{-7}
1	2.37×10^{-7}	5.95×10^{-7}
2	2.72×10^{-7}	7.45×10^{-7}
5	3.10×10^{-7}*	9.46×10^{-7}
10	3.50×10^{-7}	1.05×10^{-6}
20	3.93×10^{-7}*	1.25×10^{-6}
100	4.68×10^{-7}	n.i.

[a]*Estimated, n.i. = not investigated.

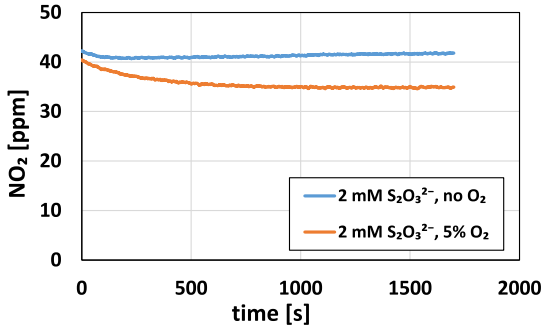

Figure 3. NO_2 concentrations for absorption experiments with 2 mM $S_2O_3^{2-}$, 50 ppm NO_2 with or without 5% O_2.

Table 2. Thiosulfate Consumption Determined by Ion Chromatography

gas inlet conc.	SO_3^{2-} [mM]	$S_2O_3^{2-}$ [mM] initial conc.	$S_2O_3^{2-}$ [mM] after 30 min	$S_2O_3^{2-}$ consumed [%]
50 ppm NO_2		2.08	1.96	5.8
50 ppm NO_2 + 5% O_2		2.10	1.74	17.1

This is likely due to the consumption of thiosulfate by the absorption reaction with NO_2 (compare RR9). In the 30 min test without oxygen, around 6% of the thiosulfate was consumed.

In the presence of oxygen, the thiosulfate consumption increased and also the NO_2 absorption efficiency increased. Initially the NO_2 decreased to 40 ppm, and a further decrease of the NO_2 concentration over time was observed. After around 700 s, the NO_2 concentration decreased to 35 ppm and remained at this level. One possible explanation for this observation might be the partial oxidation of thiosulfate to sulfite. The oxidation of thiosulfate has been described as a very slow reaction and the final oxidation product is sulfate,[16,19] which does not react with NO_2. However, sulfite might be formed as an intermediate in the oxidation of thiosulfate, which is then reacting with NO_2. Due to the much higher reaction rate for the reaction with sulfite as compared to thiosulfate, a small amount of thiosulfate oxidized to sulfite could explain the improved NO_2 absorption efficiency. As only thiosulfate and sulfate were present in the scrubber solution after the experiment, it is likely that sulfite is consumed rapidly after its formation, which could also explain why the NO_2 concentration in Figure 3 eventually becomes constant, that is, the absorption rate is constant and the rate is limited by the oxidation of thiosulfate to sulfite. Another possibility could be the formation of sulfite by decomposition of thiosulfate. This has previously only been described for acidic solutions at room temperature.[20] The formation of sulfide from decomposition of thiosulfate[21] could also be a possible explanation for the increased absorption as sulfide reacts rapidly with NO_2,[22] but this would likely lead to H_2S formation at the investigated pH, which was not the case in our experiments.

3.2. NO_2 Absorption with Thiosulfate and Sulfite.

Figure 4 shows the NO_2 concentrations for experiments with 2 or 5 mM thiosulfate and 2, 5, or 10 mM sulfite. The initial NO_2 concentrations for the experiments with same sulfite concentration but different thiosulfate concentration are identical. Also, when comparing the initial NO_2 concentrations to the corresponding tests without thiosulfate in Figure 2b, it can be seen that the initial NO_2 concentrations are identical. Hence, it can be concluded that thiosulfate has no relevant influence on the NO_2 absorption under the investigated conditions in the presence of sulfite. However, thiosulfate has a positive effect as a sacrificial agent on maintaining the absorption efficiency of sulfite over an extended period of time. The increase of the NO_2 concentration over time, that is, the loss of absorption efficiency, was more rapid in the case with 2 mM thiosulfate as compared to 5 mM thiosulfate. With 10 mM sulfite and 2 mM thiosulfate, 76% of the NO_2 is absorbed initially. The absorption efficiency decreased to 60% after 10 min in the case with 2 mM thiosulfate, while it was still at 70% with 5 mM thiosulfate.

In our previous work,[11] we determined oxidation rates for sulfite (oxidation by O_2, excluding oxidation by NO_2) based on multiple absorption tests with and without O_2. An example of

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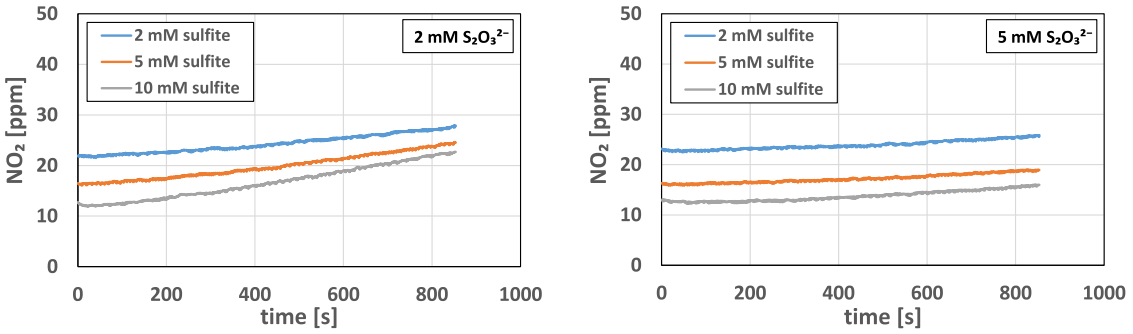

Figure 4. NO_2 concentrations for absorption experiments with 2−10 mM sulfite and 2 or 5 mM thiosulfate; input 50 ppm NO_2 + 5% O_2 (rest N_2).

the sulfite oxidation rate (excluding oxidation by NO_2) with 2 mM sulfite and 1 mM thiosulfate is presented in Figure 5.

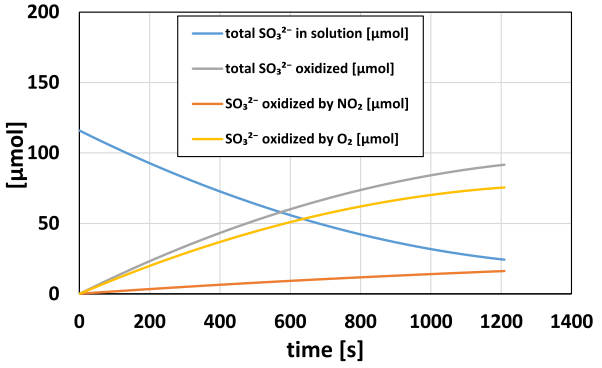

Figure 5. Total amount of sulfite as a function of time (blue line) and amount of consumed sulfite: total consumption (gray), consumed by O_2 (yellow), and consumed by NO_2 (red); test with 2 mM sulfite and 1 mM thiosulfate, input gas 50 ppm NO_2 + 5% O_2 (rest N_2).

Using this approach, the sulfite concentration at each point of time is determined based on the NO_2 absorption efficiency. The amount of sulfite oxidized by NO_2 is then calculated based on the NO_2 absorption up to this point, and the stoichiometric ratio according to RR2. RR1 has been shown to be negligible at sufficient high sulfite concentrations and based on the above results, it is assumed that the reactions of thiosulfate with NO_2 can be neglected for the overall reaction as well with sufficient high sulfite concentrations. The difference between the amount of sulfite oxidized by NO_2 and the total amount of oxidized sulfite is considered to be the amount of sulfite that has been oxidized due to the presence of oxygen through the above described mechanisms (RR3, RR4, RR5, and RR6).

The results for those sulfite oxidation rates based on the above describe approach are shown in Figure 6. Oxidation rates have been determined for 2, 5, and 10 mM sulfite with 0, 1, 2, or 5 mM thiosulfate. Without thiosulfate, sulfite oxidation rates were high and increased with increasing sulfite concentration, which is in agreement to previous studies.[11,13] With 2 mM sulfite, the oxidation rate was around 40 and 130 $mg{\cdot}L^{-1}{\cdot}min^{-1}$ with 10 mM sulfite. With 1 mM thiosulfate, the oxidation rate decreased notably for all sulfite concentrations, 9 $mg{\cdot}L^{-1}{\cdot}min^{-1}$ for 2 mM sulfite and 31 $mg{\cdot}L^{-1}{\cdot}min^{-1}$ for 10 mM sulfite, respectively. A further increase in the thiosulfate concentration above 2 mM showed only little reduction of the oxidation rate, as it is already low at this point for all cases.

Figure 7 compares NO_2 concentrations from absorption experiments with 10 mM sulfite and various thiosulfate

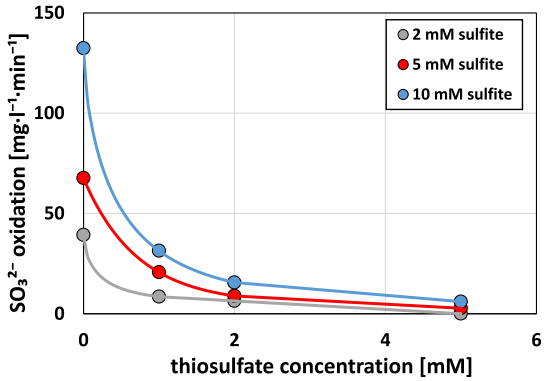

Figure 6. Sulfite oxidation rates (oxidation by O_2; oxidation by NO_2 excluded) vs thiosulfate concentration for 50 ppm NO_2 + 5% O_2 (rest N_2).

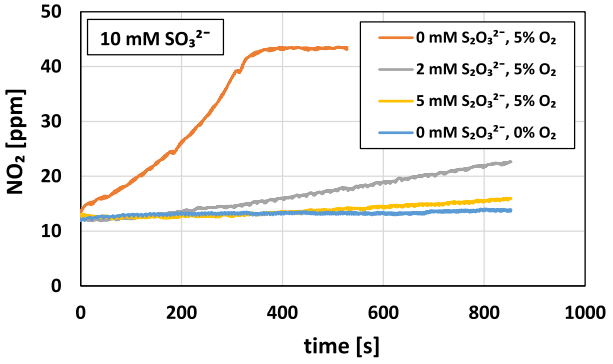

Figure 7. Comparison of NO_2 absorption experiments with 10 mM sulfite and various thiosulfate concentrations with and without oxygen; inlet gas 50 ppm NO_2 or 50 ppm NO_2 + 5% O_2 (rest N_2).

concentrations with and without oxygen in the inlet gas (red line for 0 mM $S_2O_3^{2-}$, 5% O_2 and blue line for 0 mM $S_2O_3^{2-}$, 0% O_2 reproduced from[11]). This figure illustrates the effect of thiosulfate on the improved NO_2 absorption over extended periods of time. With 2 mM thiosulfate and 5% O_2, the absorption still decreases with time. With 5 mM thiosulfate and 5% O_2, the absorption is almost the same over the investigated period of time as compared to 0 mM thiosulfate and 0% O_2. This indicates that it is possible to inhibit the sulfite oxidation to such an extent that the absorption almost works equally well and long in the presence of oxygen as compared to the absorption without oxygen in the inlet gas when thiosulfate is used as an oxidation inhibitor.

Table 3 presents thiosulfate concentrations from an additional absorption test with 2 or 5 mM sulfite and 2 mM

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Table 3. Thiosulfate Consumption Determined by Ion Chromatography

gas inlet concn	SO_3^{2-} [mM]	$S_2O_3^{2-}$ [mM] initial concn	$S_2O_3^{2-}$ [mM] after 30 min	$S_2O_3^{2-}$ consumed [%]
50 ppm NO_2 + 5% O_2,	2	2.00	1.24	38.0
50 ppm NO_2 + 5% O_2,	5	2.04	1.14	44.1

thiosulfate and 50 ppm NO_2 + 5% O_2 in the inlet gas. The time of the experiment was 30 min, and the thiosulfate concentrations were measured before and after the tests. Interestingly, the consumption of the thiosulfate did not increase significantly when more sulfite is present in the solution. In the test with 2 mM sulfite, around 38% of the thiosulfate was consumed in 30 min, while 44% of the thiosulfate was consumed in the case with 5 mM sulfite. Based on the obtained data, it cannot be clarified to which extent thiosulfate is consumed by oxygen or reaction products from the sulfite oxidation mechanism. The higher sulfite oxidation rates with higher sulfite concentrations may be explained by a higher concentration of sulfite radicals which accelerate the chain mechanism described in RR3, RR4, RR5, and RR6. Based on the suggested mechanism, a higher thiosulfate consumption could be expected for higher sulfite concentrations as more radicals are available for reaction with thiosulfate according to RR7. This, however, was not observed in the experiments. Also, according to RR8, the SO_5^{2-} ion formed in RR7 should still be able to oxidize sulfite to sulfate. In this case, however, sulfite should be consumed at a higher rate than what is observed. Based on our results, it may be concluded that the current understanding about the sulfite oxidation inhibition with thiosulfate requires further research.

4. CONCLUSIONS

The present study investigated the role of thiosulfate in wet scrubbing of NO_2 with aqueous sulfite solutions under buffered conditions. Absorption rates for the reaction of thiosulfate and NO_2 in the scrubber were determined, and the ability of thiosulfate to inhibit the sulfite oxidation was investigated. In addition, NO_2 absorption with only thiosulfate was investigated.

With 1 mM thiosulfate (no sulfite) in the scrubber solution, the NO_2 absorption rate increased by 30% as compared to pure water, and by 160% with 100 mM thiosulfate. With 1 mM sulfite (no thiosulfate), the NO_2 absorption rate increased by 200% as compare to pure water. Interestingly, in tests with thiosulfate (no sulfite) and oxygen, the NO_2 absorption rates improved with time. This effect has previously not been observed to our knowledge and may have a strong influence of future industrial NO_2 absorption processes.

Tests with both sulfite and thiosulfate as an oxidation inhibitor resulted in high removal efficiencies that could be maintained over extended periods of time. With small concentrations of thiosulfate, the sulfite oxidation rates decreased significantly. For a 10 mM sulfite solution, 1 mM thiosulfate decreased the oxidation rate by 75%, and with 2 mM thiosulfate by 88%, respectively.

For the investigated conditions, the consumption of thiosulfate when used as a sulfite oxidation inhibitor did not change significantly when higher sulfite concentrations were used. For a 2 mM sulfite solution and 2 mM thiosulfate, 38% of the thiosulfate was consumed after 30 min, while 44% was consumed in the corresponding test with 5 mM sulfite. The results demonstrate high NO_2 absorption rates for low concentrations of sulfite and thiosulfate at neutral pH.

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Notes

The authors declare no competing financial interest.

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