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Published in: Industrial & Engineering Chemistry Research

DOI: 10.1021/acs.iecr.3c03205

Published: 13/12/2023

Document Version Final published version

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Link to publication

*Please cite the original version:* Schmid, D., Hupa, M., Paavola, M., & Karlström, O. (2023). NO2 Absorption in Aqueous Solutions with Phenolic Additives: Hydroquinone and 4Methylaminophenol Sulfate. *Industrial & Engineering Chemistry Research*, *62*(49), 21007-21012. https://doi.org/10.1021/acs.iecr.3c03205

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Article

# NO<sub>2</sub> Absorption in Aqueous Solutions with Phenolic Additives: Hydroquinone and 4-Methylaminophenol Sulfate

Daniel Schmid,\* Mikko Hupa, Mikko Paavola, and Oskar Karlström



**ABSTRACT:** NO<sub>2</sub> absorption has recently gained attention as a promising alternative to conventional NO<sub>x</sub> reduction methods. One key challenge in NO<sub>2</sub> absorption is that high amounts of additives are required to maintain satisfactory absorption efficiency. The present study investigates the absorption of NO<sub>2</sub> from flue gases in aqueous solutions with low concentrations of phenolic additives. Absorption tests with hydroquinone and 4-methylaminophenol sulfate were performed in a laboratory-scale absorption system with test gases containing 0 or 5% O<sub>2</sub> (N<sub>2</sub> as a balance gas) and 50, 100, or 150 ppm of NO<sub>2</sub>, representing typical flue gas conditions in a range of industrial processes. The results show that NO<sub>2</sub> was absorbed efficiently with small concentrations of 4-methylaminophenol sulfate, both with 0 or 5% O<sub>2</sub> in the test gas.



Hydroquinone also enhanced NO<sub>2</sub> absorption but to a lesser degree than 4-methylaminophenol sulfate. Interestingly, the presence of  $O_2$  did not influence the consumption of the phenolic additives, in contrast to commonly used additives such as sulfite that require oxidation inhibitors such as thiosulfate. With a 2 mM solution of 4-methylaminophenol sulfate, more than 90% of the incoming NO<sub>2</sub> was absorbed. Thus, NO<sub>2</sub> absorption with 4-methylaminopheno sulfate appears to be able to remove NO<sub>x</sub> emissions from flue gases with high efficiency.

# 1. INTRODUCTION

NO<sub>2</sub> absorption in wet scrubbing systems is an effective method to reduce NO<sub>x</sub> emissions from industrial combustion flue gases and other industrial processes.<sup>1-3</sup> NO<sub>2</sub> absorption has several advantages as compared to conventional methods, e.g., selective catalytic reduction (SCR) is not suitable for flue gases with impurities, and selective non catalytic reduction (SNCR) is also sensitive to both impurities and may give rise to ammonia slip. In the combustion flue gases, the majority of  $NO_x$  is in the form of NO. Due to its low water solubility, NO is oxidized to NO<sub>2</sub> to enable absorption in aqueous solutions, as NO<sub>2</sub> has a higher water solubility.<sup>4,5</sup> In spite of the higher water solubility of NO2, additives are needed to achieve reasonable absorption rates. Sulfite is commonly used as an additive for converting  $NO_2(aq)$  to nitrite  $(NO_2^{-})$  and improving NO<sub>2</sub> absorption rates.<sup>6</sup> In a recent laboratory absorption study with 50 ppm of  $NO_2$  and 0%  $O_2$  in the incoming gas, the NO<sub>2</sub> concentration was reduced to 25 ppm with 2 mM sulfite in the solution and to 10 ppm of NO<sub>2</sub> with 10 mM sulfite in the solution. Sulfite is consumed following the reaction<sup>7</sup>

$$2NO_2(aq) + SO_3^{2-} + H_2O \rightarrow 2NO_2^{-} + SO_4^{2-} + 2H^+$$

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© XXXX The Authors. Published by American Chemical Society In the presence of oxygen, the following  $NO_2$ - and  $O_2$ induced radical chain mechanism for sulfite oxidation has been suggested<sup>8,9</sup>

$$NO_2 + SO_3^{2-} \rightarrow NO_2^{-} + SO_3^{-}$$
(2)

$$SO_3^- + O_2(aq) \rightarrow SO_5^-$$
 (3)

$$SO_5^- + SO_3^{2-} \to SO_4^- + SO_4^{2-}$$
 (4)

$$SO_3^{2-} + SO_4^{-} \to SO_3^{-} + SO_4^{2-}$$
 (5)

$$2SO_3^- \to S_2O_6^2 \tag{6}$$

The oxidation of sulfite to sulfate reduces the NO<sub>2</sub> absorption rate, requiring either additional sulfite or a sulfite oxidation inhibitor to maintain a high NO<sub>2</sub> absorption rate. One recently studied sulfite oxidation inhibitor is thiosulfate  $(S_2O_3^{-2})^{.10,11}$ . Thiosulfate is a radical scavenger and terminates

Received:	September 11, 2023
Revised:	November 17, 2023
Accepted:	November 20, 2023

(1)

the chain reaction of sulfite oxidation. Some studies proposed that the chain reaction is terminated by the reaction of thiosulfate with the  $SO_5$ <sup>--</sup> radical,<sup>6,9</sup> whereas others proposed that it is terminated by a reaction with the  $SO_3$ <sup>--</sup> radical.<sup>12,13</sup> Other radical scavengers that have shown to reduce the sulfite oxidation rate are, e.g., ascorbic acid,<sup>14</sup> alcohols,<sup>15</sup> and hydroquinone.<sup>16</sup>

Besides their ability to reduce sulfite oxidation, substituted phenols can also react directly with NO2. The reactions between phenols and NO<sub>2</sub> have been of interest due to their importance in atmospheric chemistry.<sup>17-19</sup> Aromatic hydrocarbons represent a significant part of nonmethane hydrocarbons in the atmosphere.<sup>20</sup> In gas-phase reactions,  $NO_2$  may react with phenols to form HNO<sub>3</sub>, NO, and nitrophenols.<sup>17</sup> In the liquid phase, the solvent influences the reaction products.<sup>21,22</sup> In order to understand the reactions of NO<sub>2</sub> in aqueous solutions containing phenolic compounds, Ammann et al. investigated hydroxy- and methoxy-substituted phenols in a wetted-wall reactor to obtain rate-constants for the NO2 uptake under conditions relevant for atmospheric chemistry.<sup>2</sup> Rate constants for other substituted phenols with NO<sub>2</sub> have also been determined using pulse radiolysis.<sup>24,25</sup> The reaction between phenolic compounds and NO<sub>2</sub> is initiated by a charge transfer from the phenolic compound (ArOH or ArO- in the deprotonated form) to  $NO_2^{19,2}$ 

 $NO_2 + ArOH \rightarrow HONO + ArO$  (7)

$$NO_2 + ArO^- \rightarrow NO_2^- + ArO^- \tag{8}$$

The ArO<sup>•</sup> radical can react further with NO<sub>2</sub> to produce several reaction products. A mechanistic study by Coombes and Diggle observed the formation of 2-nitro-4-methylphenol and 6-nitrocyclohexa-2,4-dien-1-on from the reaction of 4methylphenol with NO<sub>2</sub>.<sup>22</sup> The reactivity of the phenolic compound toward NO<sub>2</sub> is influenced by the substituents. A theoretical study about the influence of various substituents in different positions of the phenol has been performed by Shenghur et al.<sup>19</sup>

In a recent study, we investigated thiosulfate as an oxidation inhibitor in aqueous sulfite solutions in a laboratory-scale NO<sub>2</sub> absorption system.<sup>10</sup> While absorption solutions containing sulfite and thiosulfate show good performance in NO2 absorption, the consumption of additives is still relatively high. To further increase the efficiency and decrease the environmental impact of the NO<sub>x</sub> removal processes via NO<sub>2</sub> absorption, the consumption of additives should be further reduced. This may be achieved either by finding additives that decrease sulfite oxidation more efficiently than thiosulfate or by finding additives that react efficiently with NO<sub>2</sub> and are not consumed by oxygen in the flue gas. The present study investigates two phenolic additives, hydroquinone and 4methylaminophenol sulfate, and their potential for usage in NO2 absorption under industrially relevant conditions in comparison to the previously studied additives sulfite and thiosulfate.

# 2. EXPERIMENTAL SECTION

Figure 1 shows the experimental setup used for the  $NO_2$  absorption experiments (a more detailed description can be found elsewhere<sup>8,10</sup>).  $NO_2$  was mixed with air and nitrogen to obtain a gas mixture containing 50, 100, or 150 ppm of  $NO_2$  and 5 vol %  $O_2$ , with  $N_2$  as a balance gas. These  $NO_2$  concentrations represent typical flue gas conditions of



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Figure 1. Experimental setup for laboratory-scale  $NO_2$  absorption experiments; MFC = mass flow controller.

industrial processes. The total flow of the gas was 2.3 NL/ min. The gas was bubbled through a gas washing bottle at room temperature. The gas washing bottle contained 50 mL of absorption liquid in all tests. At the bottom of the bottle, where the gas came in contact with the liquid, a porous glass sinter provided a high surface area for good contact between the gas and the absorption liquid. The absorption solution was magnetically stirred to avoid concentration gradients within the solution. The NO<sub>2</sub> concentration in the off-gas of the absorption system was continuously analyzed. In the first step, the NO<sub>2</sub> was reduced to NO on an SCC-K catalyst from ABB. The NO was then quantified with a chemiluminescence analyzer from Teledyne, model 200EM.

Absorption tests were done with 5%  $O_2$  and 50–150 ppm NO<sub>2</sub> at pH 8 with sulfite; sulfite and thiosulfate; sulfite and hydroquinone; and sulfite and 4-methylaminophenol sulfate. In these tests, the sulfite, thiosulfate, and hydroquinone concentrations were 2 mM; the 4-methylaminophenol sulfate concentration was 1 mM (1 mol of 4-methylaminophenol sulfate contains 2 mol of the phenolic compound). In addition, tests were done with solutions containing only hydroquinone or 4-methylaminophenol sulfate at pH 5–8. The solutions were buffered with phosphate buffer (NaHPO<sub>4</sub>·2H<sub>2</sub>O + KH<sub>2</sub>PO<sub>4</sub>). The chemical structures of hydroquinone and 4-methylaminophenol sulfate



Figure 2. Chemical structures of hydroquinone and 4-methylaminophenol sulfate.

(also known commercially as Metol) is a chemical derived from hydroquinone and methylamine.<sup>26</sup> The hydroquinone (99% purity) was purchased from Sigma-Aldrich, and the 4methylaminophenol sulfate (98% purity) was purchased from Acros Organics.

Hydroquinone and 4-methylaminophenol sulfate are commercially available solid chemicals with recommended storage temperatures of 15-25 °C. 4-Methylaminophenol sulfate needs to be stored protected from light, as it slowly decomposes under the influence of light. Both chemicals dissolve rapidly in water, and the investigated solutions were prepared right before the experiment.

Absorption tests with 4-methylaminophenol sulfate and hydroquinone caused increased foam formation in the absorption solution when the experiments were run for a longer period of time. To ensure the reproducibility and accuracy of the reported experiments, experiments were run only for shorter periods of time during which no or only little foam was formed.

# 3. RESULTS

Figure 3 presents results from  $NO_2$  absorption tests (5%  $O_2$ ) in water with sulfite; sulfite and thiosulfate; sulfite and



**Figure 3.** NO<sub>2</sub> concentrations from absorption tests with 2 mM sulfite with no additive or addition of 2 mM thiosulfate, 2 mM hydroquinone, or 1 mM 4-methylaminophenol sulfate at pH 8; 50 ppm of NO<sub>2</sub> inlet concentration shown as dotted line (5%  $O_2$ ,  $N_2$  as balance gas).

hydroquinone; and sulfite and 4-methylaminophenol sulfate. In the case with only sulfite, around 40% of the  $NO_2$  was absorbed initially. The  $NO_2$  absorption rate decreased rapidly, and after less than 200 s, all of the sulfite had been consumed. At this point, the  $NO_2$  absorption rate corresponded to that of pure water.<sup>8</sup> With sulfite and thiosulfate in the solution, a similar absorption efficiency was observed initially in the experiment compared to the experiment with only sulfite. However, the decrease in the  $NO_2$  absorption rate was slower, i.e., a higher absorption rate was maintained during the experiment. After 1500 s, the absorption efficiency was still 30%. The test with sulfite and hydroquinone gave similar results as compared to those with sulfite and thiosulfate. The

initial absorption rate was slightly higher with hydroquinone, but the absorption rate decreased at similar rates, and the NO<sub>2</sub> absorption was 30% after 1500 s. With 4-methylaminophenol sulfate, almost 80% of NO<sub>2</sub> was initially absorbed. The absorption rate remained almost constant during the time of the experiment. An absorption efficiency of 75% was observed even after 1500 s in this case. The high absorption efficiency with 4-methylaminophenol sulfate indicates a strong interaction between the additive and NO<sub>2</sub>.

To understand the higher NO<sub>2</sub> with the phenolic additives, hydroquinone and 4-methylaminophenol sulfate were investigated separately on their reactions with NO2. The results for the absorption tests with only hydroquinone or 4-methylaminophenol sulfate (no sulfite) are presented in Figure 4. In these tests, 2 mM of the respective phenolic compounds was dissolved at pH 5, 6, 7, and 8. Generally, the NO<sub>2</sub> absorption was significantly higher when using 4-methylaminophenol sulfate as compared to hydroquinone. The pH had a strong effect on the absorption efficiency as well. At pH 8, around 90% of the NO<sub>2</sub> was absorbed with the 4-methylaminophenol sulfate solution, while with hydroquinone only 25% of the NO<sub>2</sub> was absorbed. In the tests at a lower pH, lower NO<sub>2</sub> absorption was observed for both additives. At pH 5, the NO<sub>2</sub> absorption efficiency was around 45% with 4-methylaminophenol sulfate and 18% with hydroquinone. The difference in the reactivity toward NO2 may be explained by the reaction mechanism and the influence of the different substituents on the phenol. As discussed in the introduction part, phenols may interact with NO<sub>2</sub> via a charge transfer or a hydrogen transfer, depending on if the -OH group is protonated (ArOH) or deprotonated (ArO<sup>-</sup>). Nitrite is formed as a product in this reaction (compare reactions 7 and 8). The phenoxide anions are thereby much more reactive, which explains the observed pH dependency of the NO<sub>2</sub> absorption. At a higher pH, a higher fraction of the phenolic compound is present in the deprotonated form. These observations are in agreement with earlier studies.<sup>23</sup> The role of the substituents on phenol in this reaction is to stabilize the aromatic radical. The reactivity of phenols is higher when a more stable radical is formed. This may explain why the NO<sub>2</sub> absorption is more effective with 4methylaminophenol sulfate as compared to hydroquinone. The -NHCH<sub>3</sub> group is a better electron donor than the -OH group in the para-position, which is in agreement with results from earlier studies on the effects of substituents on the reactivity of phenols.<sup>19,25</sup>

Figure 5 shows the  $NO_2$  concentrations from absorption tests with various concentrations of 4-methylaminophenol between 0 and 2 mM at pH 8.0 mM represents the absorption



**Figure 4.** NO<sub>2</sub> concentrations from absorption experiments with 1 mM 4-methylaminophenol sulfate (a) and 2 mM hydroquinone (b) solutions at pH 5–8; 50 ppm of NO<sub>2</sub> inlet concentration shown as dotted line (5%  $O_2$ ,  $N_2$  as the balance gas).



Figure 5. NO<sub>2</sub> concentrations from absorption experiments with 0-2 mM 4-methylaminophenol sulfate solution (pH 8); 50 ppm of NO<sub>2</sub> inlet concentration shown as dotted line (5% of the O<sub>2</sub>, N<sub>2</sub> as the balance gas).

with pure water (+buffer). With only water, the NO<sub>2</sub> concentration decreased from 50 ppm to around 43 ppm, corresponding to an absorption efficiency of 15%. With 0.25 mM 4-methylaminopheno sulfate, the  $NO_2$  concentration decreased initially to 22 ppm, i.e., almost 60% of the NO<sub>2</sub> was absorbed. After around 300 s, the NO<sub>2</sub> concentration started to increase until it remained constant at around 800 s. At 800 s, the NO<sub>2</sub> absorption is similar to the NO<sub>2</sub> absorption in pure water, and it can be assumed that most of the 4methylaminophenol sulfate has been consumed, and absorption reactions occur mainly with water. In the test with 0.5 mM 4-methylaminophenol sulfate, similar observations were made. Initially the NO<sub>2</sub> concentration decreased to 13 ppm and slowly increased after around 500 s. However, even after 800 s, the absorption was still higher than 60%. In the tests with 1 or 2 mM 4-methylaminophenol sulfate, NO<sub>2</sub> concentrations decreased from 10 or 5 ppm to 5 or 0 ppm, respectively. The slight decrease in the NO<sub>2</sub> concentration might be explained by the formation of a foam in the scrubber solution, which might have some effect on the absorption process. The foam formation was also the reason why experiments with higher additive concentrations were not run until all of the additive was consumed. From the experiments with 0.25 and 0.5 mM, it was estimated that it would take around 6000 s until all additive is consumed in the 2 mM solution. With the increasing foam formation, however, it was not possible to achieve reliable results for such long experiments.

Ion chromatography was used to quantify the reaction products nitrite and nitrate in the solutions after the tests with 0-2 mM 4-methylaminophenol sulfate. Table 1 shows results from these tests. The amount of absorbed NO<sub>2</sub> (in  $\mu$ mol) has been calculated from the results shown in Figure 5. Nitrite was the only reaction product of NO<sub>2</sub> that could be identified in

Table 1. Amount of Absorbed NO<sub>2</sub> and Nitrite Found in Solution after Experiments with 0-2 mM 4-Methylaminophenol Sulfate Solution (pH 8); 50 ppm of NO<sub>2</sub> Inlet, 15 min Test

additive conc. [mM]	additive total [µmol]	NO <sub>2</sub> input [µmol]	$NO_2$ absorbed [ $\mu$ mol]	found as nitrite (NO <sub>2</sub> <sup>-</sup> ) [µmol]
0.25	25	66	29	38
0.5	50	66	47	53
1	100	66	57	61
2	200	66	63	69

the scrubber solutions, and no nitrate was found. Under the investigated conditions, nitrite solutions are stable for long periods of time, so the transformation of nitrate would not be expected when only nitrite is initially formed during NO<sub>2</sub> absorption.<sup>27</sup> Within the uncertainty of the measurements of around 10%, the amount of formed nitrite corresponds well to the amount of absorbed NO<sub>2</sub>, indicating that this is the main reaction product from the NO<sub>2</sub> absorption. The ion chromatograms and standard curve for nitrite can be found in Figures S1 and S2 in the Supporting Information, and the ion chromatogram for the test solutions with 4-methylaminophenol sulfate after the absorption tests can be found in Figure S3 in the Supporting Information.

Since the amount of nitrite found in the product solution corresponds well with the amount of absorbed NO<sub>2</sub>, it seems that no or only little NO<sub>2</sub> is reacting with the amine in 4-methylaminophenol sulfate. Amines (R<sub>2</sub>NH) can also react with NO<sub>2</sub> when nitrogen oxides are absorbed into aqueous amines.<sup>28–30</sup> When amines react with NO<sub>2</sub>, a radical (R<sub>2</sub>N<sup>•</sup>) is formed, which can react further with NO<sub>2</sub>.<sup>30</sup> In this case, however, a lot of absorbed NO<sub>2</sub> should be bound to the additives and not be present in the solution. This supports that the amine is not the reactive group under the investigated conditions.

Figure 6 shows the NO<sub>2</sub> absorption as a function of the NO<sub>2</sub> inlet concentration. The gas inlet concentrations were 50, 100, or 150 ppm of NO<sub>2</sub>, and the absorption solution contained 2 mM 4-methylaminophenol sulfate. At the lowest concentration, a high absorption efficiency could be maintained for almost 1500 s before the level of NO<sub>2</sub> slowly started to increase. With 100 ppm of NO<sub>2</sub>, the NO<sub>2</sub> concentration increased after 700 s and with 150 ppm of NO<sub>2</sub> after 400 s. The results indicate that the absorption efficiency is not affected by the NO<sub>2</sub> inlet concentration. With all inlet concentrations, 50, 100, and 150 ppm, the absorption efficiency was the same. In addition, when the reactive additive was consumed and the NO<sub>2</sub> concentration reached a constant level at a higher concentration, the absorption efficiency was the same for different NO<sub>2</sub> inlet concentrations.

To investigate the influence of oxygen on the  $NO_2$  absorption with 4-methylaminophenol sulfate, a 30 min test with and without oxygen in the test gas was performed. The results for this test are listed in Figure 7. Similar to the results in Figure 5, a decrease from initial  $NO_2$  was observed. This is likely due to the formation of a foam on the absorption liquid that might have an influence on the absorption efficiency. The foam formation was observed both with and without oxygen in the test gas. In both cases, the  $NO_2$  initially dropped to around 10 ppm and decreased to less than 2 ppm after 1000 s and less than 1 ppm after 1500 s. Interestingly, the  $NO_2$  absorption was almost identical in both cases, with and without oxygen in the test gas.

Based on the above presented results, it can be stated that phenolic additives can be a highly efficient additive for  $NO_2$ absorption, especially with activating substituents. To evaluate the overall performance, however, costs of chemicals, safety issues, and waste treatment need to be considered as well. While 4-methylaminophenol sulfate has a higher price per ton as compared to conventionally used sulfite and thiosulfate, the much lower consumption and higher performance of this additive may still compensate for this. Concerning recovery of chemicals, neither the phenolic additives nor the sulfurous additives can be recovered for reuse in the process. Both

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Figure 6.  $NO_2$  concentrations (a) and  $NO_2$  absorption (b) from the absorption experiment with 1 mM 4-methylaminophenol sulfate solution (pH 8) and 50–150 ppm of  $NO_2$  inlet concentration (inlet concentrations marked with dotted lines).



Figure 7. NO<sub>2</sub> concentrations from absorption experiment with 1 mM 4-methylaminophenol sulfate solution (pH 8) without or with 5% O<sub>2</sub>; 50 ppm of NO<sub>2</sub> inlet (balance gas N<sub>2</sub>).

hydroquinone and 4-methylaminophenol sulfate are harmful chemicals that are toxic to aquatic life and must therefore not be released into the environment. Wastewater treatment may include, e.g., treatment with UV-light and peroxide.<sup>31</sup> Reaction products from the absorption process also need to be removed from the wastewater. The formation of different products in the wastewater is strongly dependent on the conditions of the process, since, e.g., the reactions of nitrite with other chemicals depend on the pH of the wastewater.<sup>27</sup> Further research is needed to better understand possible reactions in the wastewater.

## 4. CONCLUSIONS

The present study investigated sulfurous and phenolic additives for the absorption of  $NO_2$  into aqueous solution for  $NO_x$  removal from flue gases. The sulfurous additives sulfite and thiosulfate were compared to the phenolic additives hydroquinone and 4-methylaminophenol sulfate.

Sulfite can effectively absorb  $NO_2$  from the flue gas but is rapidly consumed in the presence of oxygen. The addition of thiosulfate, which acts as a sulfite oxidation inhibitor, significantly reduces sulfite consumption and enables  $NO_2$ absorption with sulfite over extended periods of time. Hydroquinone had a similar effect to thiosulfate when added to a sulfite solution. However, increased  $NO_2$  absorption with hydroquinone addition to the sulfite solution indicated that hydroquinone itself is interacting with  $NO_2$ . The addition of 4methylaminophenol sulfate enhanced the  $NO_2$  even more when it was added to the sulfite solution.

To investigate the interactions between the phenolic additives and  $NO_2$ , experiments were also performed without the presence of sulfite in the solution. Solutions containing 1 mM hydroquinone absorbed around 20-25% of the  $NO_2$  in

the test gas, depending on the pH. The same amount of 4methylaminophenol sulfate absorbed 50% of the incoming NO<sub>2</sub> at pH 5 and 80% at pH 8. When the concentration was increased to 2 mM, the NO<sub>2</sub> concentration was reduced from 50 to almost 0 ppm. Thus, it is concluded that 4methylaminophenol sulfate has an exceptional capacity to improve NO<sub>2</sub> absorption and potentially even entirely eliminate NO<sub>x</sub> from flue gas. Interestingly, the oxygen concentration in the test gas had no influence on the NO<sub>2</sub> absorption with 4-methylaminophenol sulfate, which is a great advantage in industrial processes. It eliminates the need for additional additives, which are required when, e.g., using sulfite solutions that need a sulfite oxidation inhibitor.

Further studies are needed to clarify the reaction mechanisms in detail and to understand the fate of reaction products in the absorption liquid. Due to the harmfulness of the phenolic additives, safety issues need to be addressed in future studies as well. However, wastewater treatment is also required when using conventional sulfurous additives.

## ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.3c03205.

Ion chromatograms for the solutions from the  $NO_2$  absorption tests with 4-methylaminophenol sulfate and standard solutions used for quantification (PDF)

### AUTHOR INFORMATION

#### **Corresponding Author**

Daniel Schmid – High-Temperature Processes and Materials, Faculty of Science and Engineering, Åbo Akademi University, Turku 20500, Finland; orcid.org/0000-0002-7786-7134; Email: dschmid@abo.fi

#### Authors

- Mikko Hupa High-Temperature Processes and Materials, Faculty of Science and Engineering, Åbo Akademi University, Turku 20500, Finland
- Mikko Paavola Valmet Technologies Oy, Tampere 33900, Finland
- Oskar Karlström High-Temperature Processes and Materials, Faculty of Science and Engineering, Åbo Akademi University, Turku 20500, Finland; Industrial Engineering and Management, Department of Mechanical and Materials Engineering, University of Turku, Turku 20500, Finland

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.iecr.3c03205

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This study was financed by the Academy of Finland finances project "Chemical challenges in gasification of biomass waste" (321598 and 328952).

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