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Lowering **A**bsorption process **U**ncertainty, risks
and **C**osts by predicting and controlling amine degradation

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Design of thiosulphate dosing system for the RWE pilot

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Executive summary

The oxidative degradation of amines can be connected to the presence and concentration of NO₂ in the flue gas, as it results in reactive species. A strategy for NO₂ removal based on thiosulfate dosing in the aqueous NaOH solution used in a standard SO₂ pre-scrubber has been developed by The University of Texas at Austin up to pilot scale (TRL5) at National Carbon Capture Center (NCCC). In LAUNCH, a number of degradation control technologies will be demonstrated at pilot scale at RWE (WP5), including thiosulfate dosing. For that, the design of the thiosulphate dosing system for the RWE pilot must be established. This design is discussed in the present document.

The initial design prescribed the addition of 120 mmol/kg of thiosulfate to the scrubbing liquid at RWE, while keeping the pH value at 7-8. When this design did not lead to any measurable NO₂ removal, the concentration of thiosulfate was increased, first to a range between 106 and 152 mmol/kg and then to 264 mmol/kg. The pH value was increased from 7.5 to 8.5 and finally to 9. However, again it was not possible to reduce the NO₂ concentration in the flue gas at the inlet of the CO₂ absorber. Actually, in contradiction to the expectations, the NO₂ concentration slightly increased from 5.5 - 6.5 mg/m³ to 6.5 – 8.0 mg/m³. A manual comparison measurement of the NO₂ concentration confirmed the NO₂ measurement.

A series of previously unplanned lab tests were conducted to confirm the principle. Freshly mixed sodium sulfite/thiosulfate solutions were shown to remove NO₂ from an artificial gas mixture. Also the circulating scrubbing liquid from the RWE plant was tested, and effectively removed NO₂.

Two hypothesis could explain the observations: 1) the NO₂ is removed in the spray scrubber at RWE, but is formed again within the flue gas path towards the absorber inlet, where the NO₂ sensor is, and therefore the removal cannot be detected; 2) there is not enough contact area in the spray scrubber. While lab tests seem to indicate the validity of the first hypothesis, both will be tested at the next NO₂ removal campaign at RWE.



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1 Introduction

The oxidative degradation of amines can be connected to the presence and concentration of NO₂ in the flue gas, as it results in reactive species [1]. NO₂ reacts with organic compounds leading to the formation of nitrous acid (HONO, which dissociates in alkaline solution to nitrite (NO₂⁻)) and highly reactive organic radicals which are transformed in consecutive reactions into the degradation products. The relevance of NO₂ as a degradation predictor is addressed in LAUNCH in WP1. A strategy for NO₂ removal based on thiosulfate dosing in the aqueous NaOH solution used in a standard SO₂ pre-scrubber has been developed by The University of Texas at Austin up to pilot scale (TRL5) at National Carbon Capture Center (NCCC) at Wilsonville, Alabama, USA [2], [3].

This technology for NO₂ removal takes advantage of already existing infrastructure in a CO₂ capture plant. The direct contact cooler (DCC) is normally also used to remove acidic components (SO_x) from the flue gas before it enters the CO₂ absorber. The DCC as pre-treatment column would allow to easily dose thiosulfate and if necessary sulfite (depending on the SO₂ concentration in the feed gas) into the scrubbing. However, due to the condensate formation caused by the temperature decrease of the flue gas in the DCC the consumption of thiosulfate is strongly depending on moisture content and temperature of the feed gas.

The alkaline scrubber solution in the DCC contains sulfite SO₃²⁻ (due to SO_x removal), the absorbed NO₂ reacts with sulfite via a free-radical mechanism and sulfite radicals (SO₃^{•-}) and nitrite ions (NO₂⁻) are formed. However, the sulfite radicals, in the presence of oxygen, promote the oxidation of sulfite to sulfate. As NO₂ will only react with sulfite (and not sulfate), the radicals inhibit the solutions' capacity to remove NO₂ from the flue gas. Free-radical scavengers such as thiosulfate (S₂O₃²⁻) can be added to the scrubbing fluid to inhibit sulfite oxidation.

The removal of NO₂ from the flue gas by thiosulfate dosing was investigated in laboratory tests and successfully demonstrated at pilot plant-scale [2], [3]. In a test at the NCCC with a two-column set-up (separate SO₂ scrubber and DCC), NO₂ removal rates of 90 to 95% could be achieved by sulfite and thiosulfate dosing. In that test campaign, the following parameter range was investigated:

- Sulfite addition: 0 - 70 mmol/kg
- Thiosulfate addition: 0 - 240 mmol/kg
- pH: above 8.5

In LAUNCH, a number of degradation control technologies will be demonstrated at pilot scale at RWE (WP5), including thiosulfate dosing. For that, the design of the thiosulphate dosing system for the RWE pilot must be established. This design is discussed in the present document.

2 Initial design of thiosulfate dosing system for the RWE pilot

The RWE capture pilot plant at Niederaussem is equipped with a DCC upstream the CO₂ absorber. This DCC also acts as a pre-treatment step, as NaOH is dosed into the circulating solution to remove SO_x (see Figure 1). This column could have been considered for testing the NO₂ removal technology by thiosulfate dosing. However, a large volume of water condenses in the DCC, and this would lead to a high loss of thiosulfate to the condensate drain. It should be noticed that the volume of condensate is a function of the water saturation in the flue gas prior to the DCC and of the temperature change, and this will vary from plant to plant.

Upstream the DCC, the RWE pilot is equipped with an “aerosol testing module”, which is a turbulent spray scrubber column (Figure 2). It was decided that this column is the preferred location in this pilot to test the NO₂ removing technology. The column normally operates by spraying water into the flue gas and a tray causes a turbulent gas-liquid zone downstream the tray. Pumps for dosing NaOH, sodium thiosulfate, and sodium sulfite aqueous solutions were sized and installed in the water circulation line.

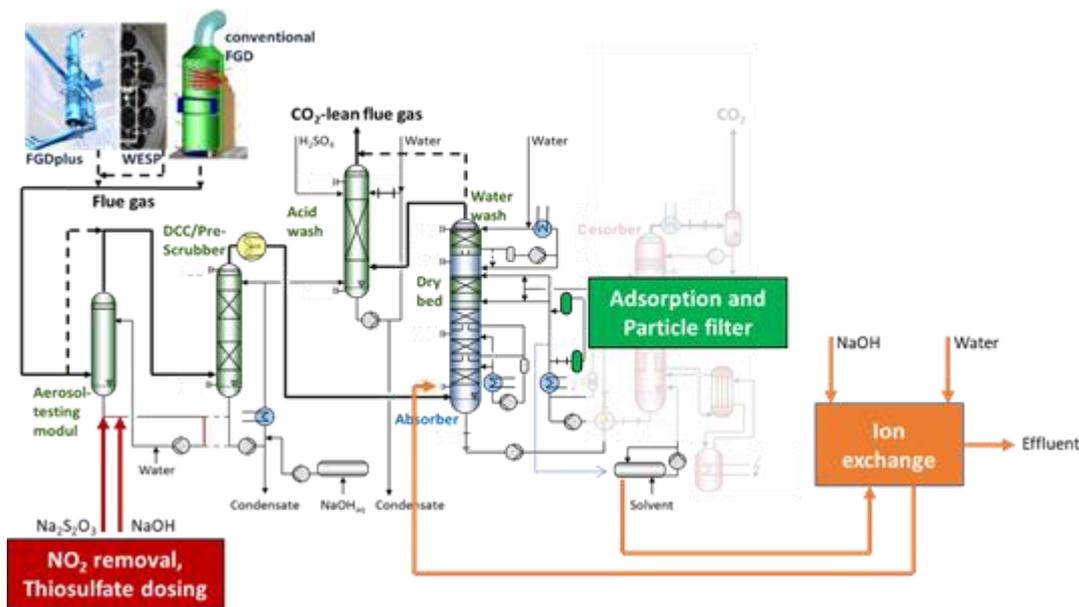


Figure 1. Process sketch of the RWE capture pilot and the solvent management technologies tested within LAUNCH: adsorptive removal of trace elements from the solvent with active carbon, removal of ionic trace elements from the solvent, and removal of NO₂ from flue gas



Figure 2. Turbulent spray scrubber used for the tests of NO₂ removal. left: before insulation, middle: after complete insulation right: observation window in the insulation

Previous results from the NCCC pilot runs suggested that approximately 50 mM thiosulfate in the circulating solvent would be needed to maintain 10 mM SO₃²⁻ while removing 100 ppm (262 mg/m³) of SO₂ and 2.5 ppm (4.7 mg/m³) of NO₂ from the flue gas in a DCC.

The NO₂ concentration in the RWE flue gas is typically between 5 – 10 mg/m³ (STP). The flue gas downstream a wet limestone desulphurization (FGD) is saturated with water (temperature approx. 64°C; SO₂ content of the flue gas before pre-treatment 60 - 160 mg/m³, dry (STP) (standard temperature and pressure: 273.15 K and 101.325 kPa; dry, 6% O₂ correction). Given the level of NO₂, a target concentration for thiosulfate in the scrubbing liquid was set at 120 mmol/kg. The target for the NaOH dosing system was to keep the pH value between 7 – 8 in the scrubbing liquid. This design was believed to be able to lead to NO₂ removal rate of approx. 90%. It should be mentioned that pH values below 7 could lead to thiosulfate disproportionation to H₂SO₃ and elemental sulfur, which could block the spray nozzle or pumps in the solution loop.

Sufficient surface between the gas and liquid phases is needed to achieve the targeted removal rate. The RWE spray scrubber has a bottom tray that can be used for the purpose of increasing the effective mass transfer area. Depending on the L/G ratio increase of the gas velocity (flowrate) can lead to turbulent solvent flow in the bottom section of the column. Figure 3 shows the pH in the scrubbing solution, the SO₂ content in the gas outlet of the spray column and the fan output. When the spray scrubber is operated as a turbulent spray scrubber - indicated by the higher fan output – SO₂ can be almost completely removed from the flue gas. This indicates that the turbulent flow creates enough mass transfer area for the SO₂ to be removed. While this does not necessarily translates in having enough area for achieving the desired 90% NO₂ removal, it shows that a reasonable mass transfer area is achieved. The turbulent regime is indicated by the fan output, but can also be visually confirmed (observation window in the insulation).

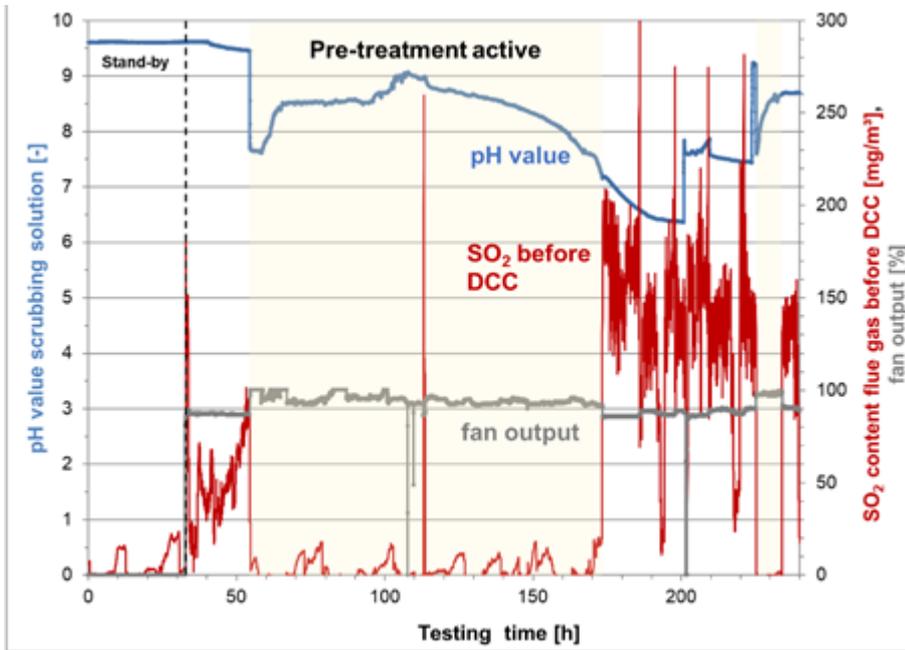


Figure 3. When the spray scrubber is operated in the turbulent regime - indicated by the higher fan output - SO₂ can be almost completely removed from the flue gas

3 Results and modifications to the design

The execution of the tests, according to the initial design described in chapter 2 took place within WP5. The results were presented in GHGT-15 and are being published in the International Journal of Greenhouse Gas Control [4]. Some of these results are also reported here, as they were not successful, and led to a second design.

For the measurement of the NO₂ concentration downstream the DCC at the inlet of the CO₂ absorber an UV spectrometer was used (SICK GMS 810-DEFOR, measuring range 0.0-50 mg/m³, accuracy approx. 0.5 mg/m³). As discussed, the target concentration of thiosulfate in the scrubbing liquid was 120 mmol/kg at a pH value between 7 – 8 in the scrubbing liquid to achieve an expected NO₂ removal rate of approx. 90%. The thiosulfate concentration was monitored off-line by an analyzer based on Raman spectroscopy and iodometric titration. The results of both methods coincided well. Also, by iodometric titration the sum of thiosulfate and sulfite concentration in the scrubbing solution was analyzed.

In the first tests, it was difficult to achieve the target concentration of thiosulfate as even a small temperature decrease of approx. 2°C of the flue gas in the flue gas duct and the spray scrubber caused a significant formation of condensate. To compensate this, the scrubber was completely insulated (Figure 2, right) and the dosing rate increased (by using of 50 wt% thiosulfate solution instead of 20 wt%). Although the condensate formation in the scrubber could be significantly reduced still a notable amount enters the scrubber via the feed gas duct.

The concentration of thiosulfate was adjusted in a first trial to a range between 106 and 152 mmol/kg and increased in a second test to 264 mmol/kg, see Figure 4. The pH value was increased from 7.5 to 8.5 and finally to 9. However, it was not possible in this configuration to reduce the NO₂ concentration in the flue gas at the inlet of the CO₂ absorber. Actually, in contradiction to the expectations, the NO₂ concentration slightly *increased* from 5.5 - 6.5 mg/m³ to 6.5 – 8.0 mg/m³. A manual comparison measurement of the NO₂ concentration confirmed the NO₂ measurement.

In discussions between RWE, UT and TNO, it was suggested that the presence of iron in the scrubbing solution could reduce the reaction rate between sulfite and NO₂ by increasing the oxidation rate to sulfate. However, the iron concentration in the scrubbing solution was determined to be very low (0,44 mg/l analysis with ICP-OES). Therefore, a catalytic effect of iron is not likely. The sulfite concentration (14 mmol/l) was lower than in the testing campaign at NCCC, where a typical concentration of 22 mmol/l was achieved. Therefore, in a following test, both thiosulfate and sulfite solutions have been dosed into the scrubbing solution, see Figure 5. However, although in this test a thiosulfate concentration of 175 mmol/kg and a sulfite concentration of 32 mmol/kg were achieved, again no NO₂ was removed from the flue gas.

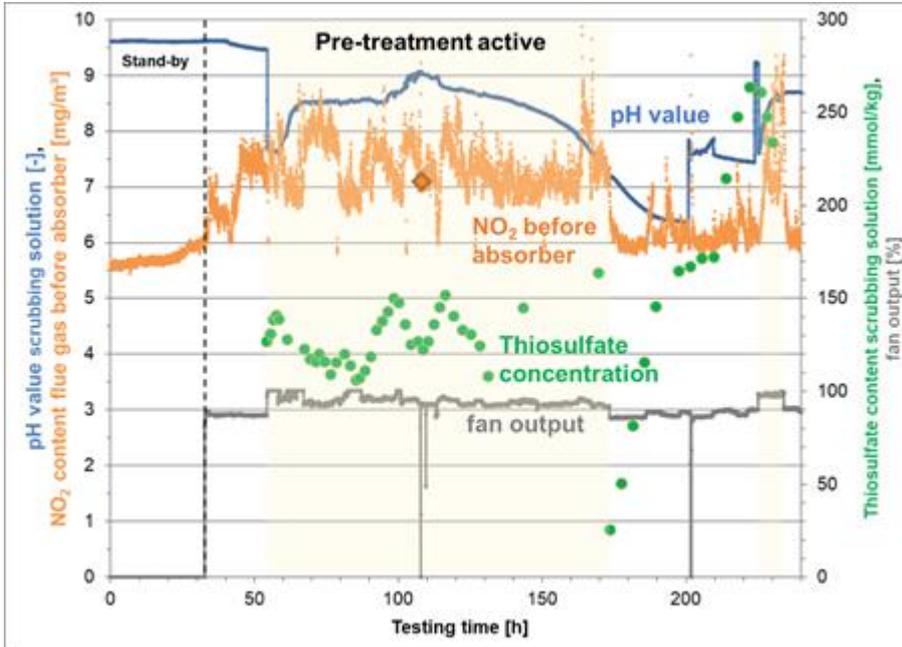


Figure 4. Although a thiosulfate concentration in the scrubbing solution of up of 264 mmol/kg was achieved, no NO₂ could be removed from the flue gas. The orange diamond shows the result of a comparison measurement which confirms the online measured NO₂ content of the flue gas upstream the CO₂ absorber

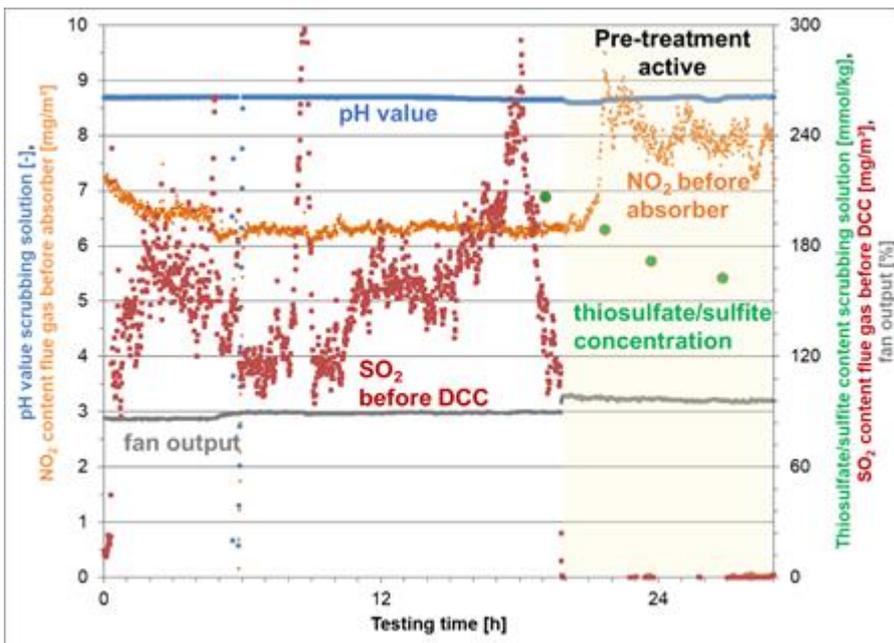


Figure 5. Although a thiosulfate concentration in the scrubbing solution of up of 175 mmol/kg and a sulfite concentration of 32 mmol/kg was achieved (the diagram shows the sum as result of the iodometric titration), no NO₂ could be removed from the flue gas

The reasons for this unexpected result are under examination. A possible explanation might be a fast formation of NO₂ (only 5% of the NO_x content in the feed gas) from NO (95% of the NO_x content) on the flue gas path from the pre-scrubber to the CO₂ absorber inlet (point in which the UV spectrometer is installed). While the equilibrium is completely shifted towards NO₂ at temperatures below 100°C, in detriment of NO, the kinetics rate at the oxygen content in the flue gas will determine the conversion. Another possibility is an insufficient surface for the NO₂ transfer from the gas phase into the scrubbing solution. To verify this hypothesis the pre-scrubber will be equipped with a high-performance packing (specific surface approx. 600 m²/m³) for additional. Additionally, further laboratory tests were performed in an attempt to explain the results from the pilot plant testing. These are discussed next.

4 Laboratory investigation of NO₂ from the flue gas by thiosulfate dosing

In an attempt to understand the results of the NO₂ removal tests performed at the RWE pilot, investigations were performed using a lab scale column, at TNO. For that purpose, a column of 8 cm internal diameter was used. Initially, the column was filled with 82 cm of Sulzer Mellapak 250X structured packing.

Artificial flue gas is generated by mixing air with a set amount of NO. The reaction between NO and the oxygen in the air is carried out at ambient temperature. The total flue gas flow rate is 2000 NI/min, which is kept constant throughout the experiments. The gas enters the bottom of the column and is contacted counter-currently with a liquid. The liquid is either DI water (baseline tests) or an aqueous sulfite solution to which thiosulfate and iron chloride is also added. The inlet liquid temperature is controlled at 25°C. At the outlet of the column, the gas composition is analyzed by an FTIR (Gasetm DX4000). In a control experiment, the NO_x levels were also determined using the Thermo Scientific™ Model 42i-HL High Level NO-NO₂-NO_x Analyzer. The NO₂ content in the gas as measured by both instruments showed excellent agreement. The connection lines are kept to a minimum length, so that the residence time of the gas in those lines (ca. 0.2 s) is negligible when compared to the residence time of the gas in the column (ca. 9 s).

4.1 Baseline tests

In the baseline tests, the gas is washed by water in the column. The gas analysis at the column outlet indicate the presence of considerable amounts of NO₂ in the gas (from 38% to 61% of the NO inlet, in mol basis). This indicates that, at low temperatures and with residence times of ca. ten seconds, substantial conversion of NO to NO₂ is observed. Since the current tests are performed with air, the oxygen partial pressure is considerably higher than that observed in flue gases. Nonetheless, the tests indicate that the hypothesis of conversion of NO to NO₂ in the flue gas path between the spray column outlet and the absorber inlet (where NO₂ is measured) cannot be ruled out.

Further tests will be conducted to investigate the kinetics rate as a function of oxygen content and temperature. It should be noted that the reaction between NO and O₂ to form NO₂ is already extensively studied in previous literature. The kinetics has been established for a wide range of concentrations and temperatures, and a good overview is given in [5]. Literature suggests that the rate of formation of NO₂ is a third order reaction, proportional to the concentration of O₂, and to the squared concentration of NO. However, this relationship does not explain the observation in this work. Moreover, given the kinetic constant suggested in literature for water-free systems ($k = 7000 \text{ L}^2 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$), the predicted conversions should have been negligible, between 0.1% and 1.1%.

Because of this discrepancy, additional baseline tests were performed by increasing the gas residence time from 9s to 20, 30 and 40s. These tests lead to NO conversions to NO₂ of 76%, 78% and 75%, respectively. The differences are within the expected error margin of the analyzer. These tests seem to indicate that equilibrium was achieved.

While the observations in this work indicate that the conversion of NO to NO₂ takes place in the operational range studied, these results are not supported by literature. The results were consistent amongst the tests performed and were confirmed by 2 analytical devices. Nevertheless, experimental errors cannot be discarded, and further investigation is needed to get a better interpretation of the observed phenomena. It could be possible that water plays a role in the reaction in the gas phase, or that water-based aerosol droplets containing nitrite are carried by the gas, and that this is analyzed as NO₂. In case the conversion is

confirmed to be substantial, the usefulness of proposed removal technology is questionable, unless the NO is mostly converted to NO₂ prior to the proposed washing step.

4.2 NO₂ removal tests

Right after a baseline test was conducted, the circulation liquid was changed from water to a sulfite solution. A total of 7 tests was conducted, and the main parameters and results are given in Table 1.

Table 1. Lab tests for NO₂ removal using sulfite solutions

	test 1	test 2	test 3	test 4	test 5	test 6	test 7
Circulating solution							
Na ₂ SO ₃ (mM)	30	15	15	15	15	15	as received from RWE
Na ₂ S ₂ O ₃ (mM)	200	100	100	100	100	100	
FeCl ₂ (mM)	10	5	0	5	5	5	
Column internals							
Column packing	yes	yes	yes	no	no	no	no
Spray nozzle	no	no	no	yes	yes	yes	yes
Bubble section	no	no	no	no	yes	no	no
Inlet gas							
NO inlet (mg/Nm ³)	275	237	255	261	267	26	38
Baseline results (inlet to column)							
NO + NO ₂ inlet (mol/s)	19.8	17.0	18.4	18.8	19.3	1.9	2.7
NO ₂ inlet (mol/s)	7.6	7.1	8.0	9.1	9.8	1.1	0.9
NO inlet (mol/s)	12.2	9.9	10.4	9.7	9.5	0.7	1.8
Results							
NO + NO ₂ outlet (mol/s)	10.6	9.8	9.0	15.3	13.2	0.8	1.9
NO ₂ absorbed (mol/s)	9.2	7.2	9.4	3.4	6.1	1.1	0.9
NO ₂ absorbed (mol%)	121%	101%	117%	38%	62%	94%	95%

Tests 1 to 5 were performed with high NO content, from of 237-275 mg/Nm³. Tests 6 and 7 were performed with lower NO content, 26 and 38 mg/Nm³, respectively.

Test 1 was conducted with a high concentration of sodium thiosulfate, with the column filled with packing. From the baseline results, the measured NO and NO₂ inlets to the column are given, in mol/s. The measured outlet NO + NO₂ flow is given, also in mol/s. The NO₂ absorption flow, in mol/s, is calculated as the difference between the sum of NO and NO₂ mols in the inlet and outlet of the column. In test 1, this is higher than the NO₂ inlet, leading to an absorption rate of 121%. This result is either caused by experimental



errors or is an indication that more NO is converted to NO₂ in the column when the sulfite solution is circulated (instead of water), which would indicate that the reverse reaction also plays a role. In test 2, the concentration of the circulating solution was halved, and the resulting NO₂ absorption was 101%. Test 3 is a variation of test 2, with no iron present in the solution. The resulting absorption rate was 117%.

In tests 4 to 7, the packing was removed from the column, and a spray nozzle was used to distribute the liquid. In test 4, which is otherwise comparable to test 2, the NO₂ absorption rate dropped to 38%. This is a clear indication that mass transfer limited the absorption. In test 5, the bottom of the column operates as a bubble column with 20 cm liquid height, which again led to higher mass transfer, with a resulting absorption rate of 62%. The configuration is test 5 and the closest to that of the RWE tests. The results of this investigation indicate that, while mass transfer plays an important role, it would be expected that at least some NO₂ would have been removed in the RWE column.

Test 6 is similar to test 4, but performed with a lower concentration of NO added to the air inlet. The resulting absorption rate was 94%. Finally, in test 7 the circulating liquid was the one used in the RWE pilot plant (a 20 l sample was collected after the tests and sent to TNO). The result is very comparable to that of test 6. Test 7 was a control test, to rule out the possibility that the solution circulated at the RWE pilot was unreactive towards NO₂.



5 Conclusions

The removal of NO₂ from the flue gas can be achieved by addition of thiosulfate to the circulating alkaline solution of a pre-scrubber of the capture pilot plant upstream the SO_x pre-scrubber/direct contact cooler. However, although a thiosulfate concentration of up to 175 mmol/kg and a sulfite concentration of 32 mmol/kg in the scrubbing fluid of RWE's turbulent spray column were achieved in tests campaigns, the NO₂ concentration at the entrance of the CO₂ absorber could not be reduced.

The lab tests performed with the sulfite/thiosulfate solution confirm that NO₂ absorption is technically feasible with the solution circulated at the RWE pilot (as well as freshly mixed solutions). The lab test results were not in good agreement with existing literature regarding the kinetics of NO₂ formation, and further investigation is on-going in order to evaluate the usefulness of the proposed process for NO₂ removal from flue gases.

The lab tests confirm that conversion of NO to NO₂ in flue gas path from the pre-scrubber to the CO₂ absorber inlet is possible. This could explain why no NO₂ removal is measured, and why the tests done at RWE seem to behave differently than those performed at NCCC.

Another possibility might be an insufficient surface for the NO₂ transfer from the gas phase into the scrubbing solution, although the mass transfer of SO₂ is sufficiently high under the test configuration to remove it from the flue gas. The pre-scrubber was equipped with a high-performance packing (specific surface approx. 600 m²/m³) to verify this hypothesis.

Further tests both at the lab and at the RWE pilot are planned to clarify the obtained results. These should be decisive to determine whether removing NO₂ from the flue gas is a reasonable approach, as the usefulness of the technology would be questionable in case the NO left in the flue gas would be rapidly converted back to NO₂.



6 References

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