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Minimizing Solvent Oxidation with NO₂ Prescrubbing

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Abstract

A novel method to remove nitrogen dioxide (NO₂) from the flue gas of coal-fired power plants with CO₂ capture has been advanced for commercial implementation. The technology leverages the equipment and chemistry in an existing (sulfur dioxide) SO₂ polishing scrubber upstream of the main CO₂ capture unit to remove the NO₂, preventing degradation of the CO₂ capture solvent and formation of nitrosamines. The report focuses on further evaluation of the chemical additives and operating conditions associated with the NO₂ removal process to define conditions for commercial scale testing and deployment. Experimental work systematically evaluated a series of potential additives to minimize the oxidation of sulfite in a representative SO₂ pre-scrubber solution. The additive combinations and concentrations were varied alongside important process conditions such as temperature, oxygen concentration, and metals present in solution to mimic the conditions expected in a commercial system. Important results of the parametric experimental work include identifying a new, potent sulfite oxidation inhibitor, revealing the importance of combining inhibitors with metal chelating agents, validation of a low-cost additive process, and development of a new semi-empirical model to represent mechanisms associated with sulfite oxidation. In addition, the experimental work revealed the impact of operating at higher temperatures (representative of a field test unit), which will guide the selection and concentration of additives as well. Techno-economic analysis identified potential net savings as large as \$1.30/tonne CO₂ captured and quantified the potential benefit of low cost additive options actively being pursued by the development team. Finally, the experimental results and engineering analysis supported the development of a detailed field testing plan and protocol to evaluate the technology at near-commercial scale. The field test preparation included development of procedures to introduce chemical additives to an existing SO₂ polishing unit and identification of representative flue gas conditions based on a review of existing plants. These activities will have direct bearing on operation and design of commercial units.

1 Background

Coal is used to generate approximately 40% of the electricity in the United States, with historical capacity numbers approaching 60% of total electricity generation. A variety of market, environmental, and regulatory factors play a role in determining the mix of fuels used in electricity generation. In the case of coal, environmental considerations have been an important part of competing with other fossil fuels (e.g., natural gas) and alternative sources of energy (wind, nuclear, hydropower, etc.). Maximizing the value of coal as a fuel requires balancing the need for reliable, low-cost electricity with management of the associated environmental impact of coal use.

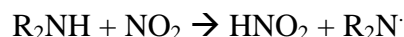
Coal-fired power plants have made significant progress in reducing emissions of sulfur dioxide (SO₂), nitrogen oxides (NO_x), particulate matter (PM), and recently mercury (Hg), since the passage of the Clean Air Act. Future regulations may require carbon capture on any new coal-fired power plant. To prepare for upcoming regulations, significant research and development is currently being pursued for new technologies to capture carbon from flue gas streams produced by coal-fired electric generating power plants.

Solvent-based technologies appear to be a viable option for large-scale carbon capture from coal-fired utilities. The United States Department of Energy (DOE) is currently supporting multiple small- and large-scale R&D projects to demonstrate the technical and economic feasibility of carbon capture using a variety of solvent technologies, but many of these solvent systems have similar challenges external to advances made to reduce both the capital cost and the regeneration energy penalty. These challenges include oxidation and degradation of the solvents, which increase the costs and environmental impact of the capture process. The focus of this paper and associated research is to address some of these solvent management challenges for amine-based CO₂ capture solvents.

1.1 Introduction

A significant operating cost of post-combustion CO₂ capture with amine scrubbing is solvent degradation and loss of amine scrubbing efficiency, including solvent oxidation. Solvent oxidation of amine solvents by SO_x in flue gas is well-documented. Most modern coal-fired power plants are equipped with flue gas desulfurization (FGD) systems, which reduce the concentration of SO_x to approximately 40 ppmv (DOE/NETL 2013). This concentration of SO_x can still generate a significant amount of sulfate heat-stable salts in the amine circulation loop and contribute to aerosol formation in the CO₂ absorber, so it is recommended to use an alkaline pre-scrubber to reduce SO_x in the amine capture system to 1 ppmv or less.

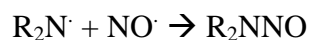
Typical coal-fired boiler flue gas contains nitrogen oxides (NO_x) composed of NO and NO₂ that ultimately reach the SO₂ polishing unit. While the bulk of the NO_x is in the form of NO, NO does not readily absorb in amine solvents (Fine 2015). NO₂ does absorb readily into amine solutions and poses the larger risk to the CO₂ capture process. Research conducted at The University of Texas (UT) has indicated that NO₂ absorbs into amine solvents to ultimately oxidize the amine and generate nitrosamine (Fine, 2015). In practice, very little NO₂ is removed in the SO₂ polisher and eventually reaches the CO₂ absorber. Effectively all of the NO₂ is absorbed into the amine solution as nitrite, forming an amine radical in the process.



The amine free radical may then react with itself or oxygen to stoichiometrically oxidize the amine.



In addition, the amine free radical can react with nitric oxide (NO) in the high-temperature portion of the capture process to produce nitrosamine or other oxidation products (Fine 2015):

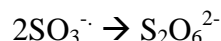
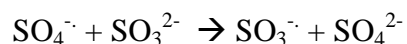
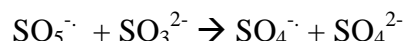
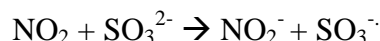


The nitrosamine accumulates in the solvent until it decomposes to oxidation products and N₂O at the highest operating temperatures within the stripper. It is hypothesized that 1 mole of NO₂ in the inlet flue gas will oxidize 2 to 4 moles of amine within the CO₂ capture system (Fine 2015).

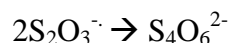
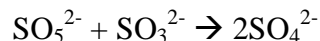
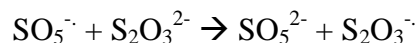
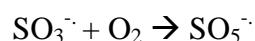
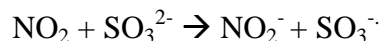
In addition to the economic challenges regarding the oxidation of the solvent, nitrosamines also pose a significant environmental concern. Many nitrosamine compounds are considered carcinogenic to humans at low concentrations. Additionally, nitrosamine accumulation in the solvent will be a problem for spills and for waste solvent handling and disposal and may be present in cleaned flue gas emissions from the absorber (Maree, Nepstad and de Koeijer 2013).

As CO₂ capture is implemented, advances need to be made in order to increase the economic feasibility of the amine capture process by reducing reclaiming and solvent makeup costs, and to mitigate additional environmental risks associated with the solvent capture process through the formation of nitrosamines and other solvent oxidation products. The University of Texas (UT) has determined that it is economically attractive to remove NO₂ in the sulfur dioxide (SO₂) pre-scrubber by adding sodium thiosulfate (Na₂S₂O₃)/ethylenediaminetetracetic acid (EDTA) or a tertiary amine to the caustic (NaOH) scrubbing liquor.

In the case of NO₂ absorption by sulfite solutions, oxidation of the sulfite can significantly limit the viability of the process. NO₂ absorption produces sulfite radical species, which can react with oxygen to generate additional free radicals. In this way, each mole of NO₂ absorbed can generate many moles of sulfite radical. These radicals eventually are oxidized to sulfate or terminated in a reaction with another free radical. This reaction mechanism is outlined by Nash (1979) and Huie and Neta (1984).



Thiosulfate provides an additional termination step, which can slow the rate of sulfite oxidation. After the same absorption and free radical formation steps, thiosulfate can create a new termination pathway. Equations below are outlined by Owens (1984).



This chemistry provided the basis for initial experimental work at UT that demonstrated the viability of the NO₂ absorption process (Fine 2015). Minimal equipment modification is required for an existing pre-scrubber to accomplish NO_x scrubbing and therefore near-zero additional capital costs are required

to implement this solution. While the use of sodium thiosulfate could potentially be cost prohibitive at certain operating conditions, particularly at low SO₂ concentrations in the flue gas (e.g., low sulfite production rates), alternate inhibitors and additive pathways are evaluated in this work.

Absorption rates of NO₂ in tertiary amines are also very fast (Fine 2015). Only 10 to 20 mM tertiary amine is required to provide 90% NO₂ removal at typical packing heights in an SO₂ pre-scrubber. Therefore, an inexpensive amine such as triethanolamine (TEA) could be sacrificed in the SO₂ pre-scrubber, thus avoiding nitrosamine formation and the more expensive loss of the main amine in the capture system.

With funding from the U.S. Department of Energy (DOE), UT conducted additional bench-scale experiments to further quantify the use of thiosulfate, EDTA, tertiary amines, and other proprietary additives in an SO₂ pre-scrubber to remove NO₂. The experimental and analytical methods (including a batch reactor) were based off of the methods used by Fine at UT.

Trimeric then used the data from the UT experiments, along with a thorough literature review, to develop a pilot field test and sampling plan in conjunction with the National Carbon Capture Center. An initial phase of pilot-scale field testing was completed by UT in the summer of 2017.

Finally, Trimeric used the bench-scale data collected by UT to conduct a preliminary concept engineering design and cost analysis. This engineering work demonstrates that such an approach could be implemented at a full-scale using commercially available chemicals and equipment, in a cost effective way, while managing any safety and environmental issues. Furthermore, no fatal flaws were identified during the course of this engineering analysis.

2 Experimental Section

The primary focus of the bench-scale research in this work was to perform experiments that simultaneously quantified the effect of pre-scrubber additives on sulfite oxidation and NO₂ absorption in a bench scale reactor apparatus that is described in detail in subsequent sections.

2.1 Methods/Test Plan

Operating conditions and additive concentrations were selected to prepare for the conditions at the pilot test site. The National Carbon Capture Center (NCCC), operating at the Alabama Power E.C. Gaston power generation facility, has an SO₂ polisher that treats a slipstream of flue gas from a full-scale coal-fired boiler and flue gas desulfurization (FGD) unit. This host site provides representative conditions to test the commercial application of the technology.

Table 1: Experimental Parameters for Oxidation Reactor Tests

Parameter	Value	Comments
Inlet NO ₂ Concentration (ppmv)	1.5 - 5	2 ppm reflects target concentration for field testing
Temperature (°C)	25 - 55	Higher T represents process conditions expected at pilot and commercial scale
Sulfite Concentration (mmol/kg)	4 - 50	15 mmol/kg reflects target concentration for 90% NO ₂ removal in field test unit
Thiosulfate Concentration (mmol/kg)	0 - 200	200 mmol/kg identified as point of diminishing returns on thiosulfate. Operate field test at this "maximum" value to test effectiveness of thiosulfate-based oxidation

		inhibition system.
Metals Concentration (mmol/kg)	0.1 - 0.5	Guided by separate metal solubility experiments. See Section 3.
EDTA Concentration (mmol/kg)	0.02 - 1	Low level of EDTA for both sets of experiments confirmed as important to chelate background levels of dissolved metal in solution.
Tertiary Amine Concentration (mmol/kg)	N/A	Range of conditions omitted to protect proprietary information
pH	9.5	The field SO ₂ Polisher is expected to operate in a range between 8.5 and 9. See discussion below.
Total Gas Rate (SLPM)	2.1	Experimental parameter only.

Additional proprietary additives and inhibitors were developed during the bench-scale testing. General results for proprietary additives will be discussed in this report.

2.1.1 Laboratory Apparatus

A High Gas Flow apparatus (HGF, Figure 1) is used to conduct experiments demonstrating NO₂-catalyzed sulfite oxidation. Dry air exits a mass flow controller and passes through a temperature controlled water saturator to maintain water balance in the HGF. CO₂ and dilute NO₂ is then directly mixed with the hydrated air stream. The resulting gas stream is sparged directly into the bottom of the HGF through 350 mL of the experimental absorbing solution. A constant operating temperature within the HGF apparatus is maintained via an oil bath circulating fluid through the jacket of the reactor.

The gas stream is sparged through the solution, and the effluent gas stream from the HGF is analyzed using the Thermo Scientific model 42i trace level NO_x analyzer before being exhausted back to the fume hood. A vacuum pump pulls the exhaust gas through the analyzer. The gas stream can also be bypassed around the HGF and diluted with air before entering the NO_x analyzer to evaluate the feed NO₂ concentrations.

Liquid samples are taken from a sample port at the bottom of the HGF at regular intervals and analyzed for sulfite and sulfate concentration using anion chromatography.

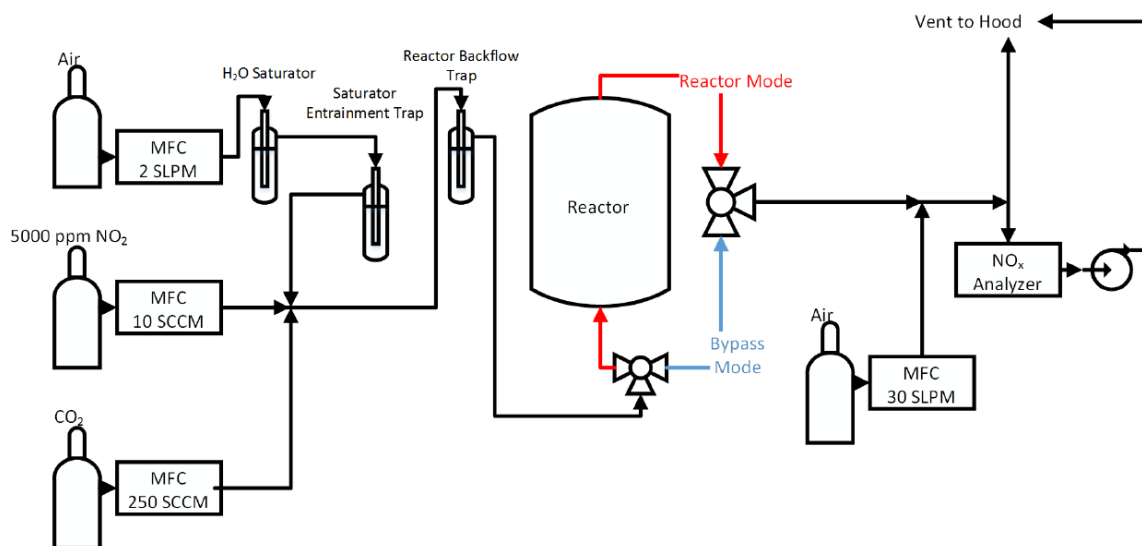


Figure 1: High Gas Flow Apparatus

2.1.2 Test Procedure

Each experiment starts with the preparation of 400 mL of synthetic absorbing solution (350 mL for the reactor, 50 mL for pre-rinse). The following additives may be included in the solution preparation:

- Sodium Sulfite
- Sodium Thiosulfate
- Sodium Carbonate
- Sodium Bicarbonate
- Ferrous Sulfate (Iron source to simulate the effect of catalytic oxidation)
- EDTA
- Tertiary Amine
- Deionized Water

The sodium carbonate and bicarbonate are added in roughly a 3:1 ratio to simulate a solution in equilibrium with the CO₂ in the gas stream as estimated from literature VLE data (Hilliard 2008) and a solution pH of approximately 9.5.

The solution is stirred for 60 to 90 minutes before the experiment. The high gas flow apparatus is then rinsed with deionized water and 50 mL of sulfite solution prior to every experiment. The apparatus is then charged with the remaining 350 mL of solution.

2.1.3 Experiment and Sampling

The experiment begins with the gas flow in bypass mode (see Figure 1) to measure the initial NO₂ concentration in the gas stream. The valve is then turned to “reactor” mode to initiate the absorption-oxidation experiment. The effluent gas from the reactor is measured continuously during the experiment to quantify outlet NO₂ concentration. Liquid samples are collected every 6-10 minutes. The sample collection starts by switching the apparatus to bypass mode so a liquid sample can be removed by pipette from the sampling port near the bottom of the reactor. The sample is immediately preserved via the addition of formaldehyde to convert the sulfite to methylsulfonic acid (MSA). Two dilution steps are performed to prepare the sample for ion chromatography.

Experiment time can range from 45 minutes to 2 hours depending on the rate of oxidation. Longer experiments are required when oxidation is strongly inhibited to allow sufficient accumulation of oxidation products.

2.1.4 Analytical Methods

The gas leaving the HGF apparatus (or in bypass mode to measure the inlet concentration) is sent continuously to the Thermo Scientific model 42i trace level NO_x analyzer. The liquid samples from the HGF are analyzed using ion chromatography. Anion chromatography is used to quantify formate, nitrite, sulfate, sulfite, and thiosulfate concentrations with a Dionex ICS-3000 anion chromatograph with an IonPac AS15 column. In the case of sulfate, sulfite, and thiosulfate, the sample must be preserved because sulfite is oxidatively unstable at room temperatures.

2.2 Experimental Results

The experimental test results are summarized in Table 2. Please note that in the first three experiments in the table, the NO_x analyzer was not functioning properly, so NO₂ absorption could not be measured.

Table 2: High Gas Flow NO₂-Catalyzed Sulfite Oxidation Experimental Results

Test	Sulfite Conc.	Thiosulfate Conc.	Amine Conc.	EDTA Conc.	Fe ²⁺ Conc.	T	O ₂	NO ₂ inlet conc.	NO ₂ outlet conc.	k ^{ox} * 10 ³	NO ₂ absorption rate * 10 ⁶	F-value (SO ₃ ox/ NO ₂ abs)	
	mmol/kg	mmol/kg	mmol/kg	mmol/kg	mmol/kg	°C	Vol%	ppm	ppm	min ⁻¹	mol/kg/min	mol/mol	
Low T Vary Sulfite	1 (Base)	47	100	0	0.02	0	25	21	5	unk	3.2	1.07 ¹	108
	2	23	100	0	0.02	0	25	21	5	unk	2	1.05 ¹	55
	3	7.4	100	0	0.02	0	25	21	5	unk	3.8	0.96 ¹	19
	4	6	100	0	0.02	0	25	21	4.87	1.11	1.5	0.9	10
	5 (Base)	43.6	100	0	0.02	0	25	21	5.67	1.19	2.4	1	115
	FINE (Base)	40	100	0	0.02	0	20	21	5	0	3.4	3.6	37.9
High T Vary SO ₃ ²⁻ , NO ₂ , S ₂ O ₃ ²⁻	6	39.3	100	0	0.02	0	53	21	5.35	2.8	5.5	0.6	296
	7	4.2	100	0	0.02	0	55	21	5.01	3.01	5.1	0.5	38
	8	10.4	100	0	0.02	0	55	21	5.8	2.88	7.6	0.7	89
	9	13.8	200	0	0.02	0	55	21	1.71	1.21	3.3	0.1	328
	10	16.5	200	0	0.02	0	55	21	5.86	3.4	5.2	0.6	126
Metals	11	12.1	200	0	0.02	0.5	53	21	3.95	1.72	5.2	0.5	102
	12	14.1	200	0	0.02	0.1	54	21	2.12	1.53	3.9	0.1	402
	13	16.4	200	0	1	0.5	52	21	2.21	0.92	3.7	0.3	200
	14	14.6	200	0	0.2	0.1	52	21	1.67	0.78	3	0.2	177

¹ For the first three experiments, NO₂ absorption measurements were not obtained due to problems with the NO_x analyzer. The absorption rates were calculated from a model that will be discussed later in this section. The F-value is derived from this calculated absorption rate.

Table 2: High Gas Flow NO₂-Catalyzed Sulfite Oxidation Experimental Results (Continued)

Test	Sulfite Conc.	Thiosulfate Conc.	Amine Conc.	EDTA Conc.	Fe ²⁺ Conc.	T	O ₂	NO ₂ inlet conc.	NO ₂ outlet conc.	k _{ox} * 10 ³	NO ₂ absorption rate * 10 ⁶	F-value (SO ₃ ox/ NO ₂ abs)	
	mmol/kg	mmol/kg	mmol/kg	mmol/kg	mmol/kg	°C	vol %	ppm	ppm	min ⁻¹	mol/kg/min	mol/mol	
Oxygen	15	13.6	200	0	0.02	0	52	8	2.02	0.52	2.2	0.3	88
	16	16.6	200	0	0.02	0	52	4	2	1.46	1.1	0.1	121
	17	15.4	200	0	0	0	52	4	2	1.15	7	0.2	530
Tertiary Amine	18	17.3	0	20	0.02	0	52	21	2	0.1	0.4	0.5	17
	19	15.2	0	20	0.02	0	25	21	2	1.6	0.3	0.1	65
No Inhibitor	24	16.2	0	0	0.02	0	53	21	2	1.4	22.7	0.2	980

The series of parametric tests in the experimental results in Table 2 will be discussed below, followed the regression of an empirical model to explain the effects of experimental parameters over the entire dataset.

2.2.1 Explanation of Measured Results Variables

Three measured results are quantified and presented in Table 2: first-order sulfite oxidation rate constant (k_{ox}), NO₂ absorption rate, and the F-value (defined by Fine as the ratio of moles of sulfite oxidized per mole of NO₂ absorbed). Absolute absorption or oxidation rates can be misleading due to underlying experimental conditions, so the F-value was defined as a convenient metric to indicate the effectiveness of an additive in limiting the oxidation for every mole of NO₂ absorbed. Therefore, lower F-values are indicative of more effective additives/inhibitors. A full theoretical background for these processes is not within the scope of this paper – details are available in the literature (Fine 2015) (Shen 1997).

2.2.2 Comparison to Previous Work (Fine 2015) (Tests 1 and 5)

The baseline experiments associated with tests 1 through 5 attempted to duplicate the operating conditions of Fine (with the exception of slightly higher temperature, 25°C vs. 20°C). When comparing the results to Fine, the measured oxidation rates (k_{ox}) are lower in the most recent experiments, though Case 1 is similar to the results of Fine.

Despite the lower oxidation rate, the F-value in Table 2 is significantly higher for Case 5 than the comparable Fine baseline experiment. One explanation is that the NO₂ absorption rate is lower in the current experiments due to the lower overall gas rate to the HGF (2.1 vs. 7.5 SLPM). However, even accounting for this difference, the relative catalytic effect of NO₂ appears to be higher in the current experiments than in Fine's previous work at these base case conditions.

One potential source of error in the experiments is the measurement of NO₂ absorption. As noted by Fine, and experienced again throughout this experimental work, the NO_x analyzer is very sensitive to the presence of water. The gas in this experiment is saturated to water, and in the high temperature experiments in particular, this presents a risk for condensation in the reactor outlet. Removing the water (via desiccant or other method) risks removing NO₂ in the gas phase as well via absorption, providing an alternate path for error in the absorption measurements. Therefore, the F-values calculated in this work

are subject to the limitations of the NO₂ absorption measurements, and the oxidation rates will provide a better representation of the effect of changing experimental conditions. The absorption measurements will be discussed in a subsequent section. An alternate drying method has been identified (membrane-based dryer) that will selectively remove water from the gas-phase, limiting the risk of condensation and absorption. This approach will be used in future work.

2.2.3 *Effect of Thiosulfate (Test 8 vs. Test 10)*

Fine previously established that thiosulfate at low concentrations (25 mmol/kg) significantly inhibited oxidation, and concentrations of 100 mmol/kg provided the expected additional benefit (~2x reduction in the sulfite oxidation rate). As noted in the discussion of the test matrix development, one bench-scale test objective was to establish if there is a point of diminishing returns associated with the addition of thiosulfate, and apply that condition to field testing to provide a margin for potentially higher rates of oxidation in field systems (presence of metals or other contaminants, loss of additives via blowdown, etc.).

Experiments 8 and 10 in Table 2 provide nearly identical experimental conditions with thiosulfate concentration increasing from 100 to 200 mmol/kg. As the oxidation rate indicates (k_{ox}), doubling the thiosulfate concentration leads to a 1.4x reduction in the oxidation rate. This is consistent with the square root dependence of oxidation on thiosulfate concentration. Thus, even at the higher value of thiosulfate concentration, the inhibitor effect appears to still be following the expected mechanism.

2.2.4 *Effect of Metals and EDTA (Tests 11-14)*

Tests 11 and 12 directly examined the effect of metals in the presence of low baseline levels of EDTA. As the results indicate, the addition of 5 times as much iron (0.5 vs. 0.1 mmol/kg) did increase the oxidation rate by 33%. This result indicates that the additional iron must be soluble to some degree in solution to catalyze oxidation – it has been hypothesized that EDTA may be providing the mechanism to solubilize additional iron by chelating iron present in solution. Furthermore, while the oxidation rate increases, it is not as large as the increase in metals concentration might indicate. This may indicate that a solubility limit is reached or that EDTA is effectively limiting the impact of metals.

2.2.5 *EDTA vs. Oxidation Inhibitors (Test 16 vs. 17, Test 22 vs. 23, Test 24)*

A series of experiments were run to isolate the effect of EDTA (reducing oxidation by chelating metals) from the effect of the oxidation inhibitors (terminating oxidation chain reactions).

Test 16 vs. Test 17: Thiosulfate vs. EDTA

Experiments 16 and 17 are identical with the exception that one test uses a baseline concentration of EDTA, while the other experiment is performed in the absence of EDTA. Experiment 16 pairs a high thiosulfate concentration known to be effective in limiting oxidation (200 mmol/kg) with a baseline level of EDTA (0.02 mmol/kg). Test 17 removes the EDTA. Results indicate that the sulfite oxidation rate increases by a factor of 7 when the EDTA is removed, and even small amounts of EDTA are effective at limiting catalytic effects of trace levels of metal which can lead to significant oxidation regardless of the presence of oxidation inhibitors.

Test 22 vs. Test 23: Proprietary Inhibitor vs. EDTA

Tests 22 and 23 are similar to Tests 16 and 17, with the addition of a proprietary inhibitor. The detailed experimental conditions and results are not presented here, but general results will be addressed. Removing EDTA causes the oxidation rate to increase by a factor of 18 over the test conducted with the proprietary inhibitor and EDTA, indicating the mechanism of EDTA is not dependent on the type of inhibitor present. These measured oxidation rates reinforce that the presence of EDTA is important to manage oxidation.

Test 24: EDTA without Inhibitor

The final experiment tested EDTA without the presence of an oxidation inhibitor. The oxidation rate in this case was the highest measured in this work. This result indicates that EDTA and oxidation inhibitors are acting on two largely independent mechanisms that catalyze oxidation of sulfite, with both mechanisms being relevant in the conditions of the SO₂ pre-scrubber. The oxidation inhibitors are likely following the thiosulfate free-radical termination mechanism associated with the absorption of NO₂ (see Equations 1.6 – 1.8). The EDTA is likely acting on the metal catalysis of the sulfite –oxygen reaction in solution to oxidize the solvent. Therefore, in order for the NO₂ removal technology to be effective, both EDTA and an oxidation inhibitor are required. Additional experiments may evaluate the final composition of the solution, including byproducts and the inhibitors, to try to develop a deeper understanding of these mechanisms.

2.2.6 Effect of Oxygen Concentration (Test 9 vs. Tests 15 and 16)

Tests 9, 15, and 16 were all operated at similar conditions with decreasing concentrations of oxygen in the inlet synthetic flue gas (21 vol%, 8 vol%, and 4 vol%, respectively). The high oxygen case (21%) represents a “worst-case” or accelerated oxidation scenario, while 4-5% oxygen is more representative of a flue gas stream from a coal-fired boiler. Previous work by Fine hypothesized that oxygen concentrations would only be relevant at low concentrations (< 5%) due to depletion of oxygen in the boundary layer impacting the bulk solution oxidation. However, results indicate that the oxidation rate drops proportionally with the oxygen concentration over the entire range of the experiments. Therefore, it is important to account for the effect of oxygen when modeling or predicting the performance of the process.

2.3 Modeling Experimental Results

Two sets of modeling activities were developed as part of the experimental analysis. First, an NO₂ absorption model that Fine validated at low temperatures (20°C) was modified with an Arrhenius temperature term to see if the absorption measurements at higher temperatures in this work could be effectively predicted by accounting for temperature dependence.

The second activity developed a general empirical model for oxidation rates using the theoretical basis for oxidation mechanisms (Shen 1997) to guide selection of parameters for the model. This oxidation model served as the basis for the subsequent techno-economic analysis in Section 4 and generalized the effect of the different parameters tested in the experimental work.

2.3.1 NO₂ Absorption Rate Temperature Dependence

The NO₂ absorption rate data in these experiments is limited by the concerns regarding water entering the NO_x analyzer at higher temperatures as outlined above. However, the early experimental data after the initial repair of the analyzer (following Test 3) is the most reliable before the analyzer performance began to degrade towards the end of the test matrix. This dataset includes a transition from 25°C to 55°C, allowing an opportunity to test the effect of temperature. Fine previously developed a model for ambient temperature and anticipated that the NO₂ absorption rate would not show a temperature dependence based on analysis by Shen (Shen 1997). However, he was unable to independently corroborate this, and simply used the model at higher temperatures where he could not take measurements. The equation below adds a temperature dependent term to his original model:

$$N_{NO_2} = \frac{(1 - e^{-N_{OG}})[NO_2]_{FEED} V}{m_{Solution}} * \exp\left[\frac{E_A}{R} * \left(\frac{1}{T_{REF}} - \frac{1}{T_{ACTUAL}}\right)\right]$$

Where:

- N_{OG} = Number of gas phase transfer units;
- V = Molar flow of feed gas to apparatus;
- m_{solution} = Mass of solution in HGF;
- T_{REF} = 298.15 K.

The term for the number of gas phase transfer units (N_{OG}) contains a regression parameter to fit absorption rate data (Fine 2015). This term was not manipulated in this work – only the temperature dependence (E_A) was regressed. Experiments 4 through 10 were included in the regression in an effort to avoid the later data that faced analyzer issues. The results are depicted in Figure 2.

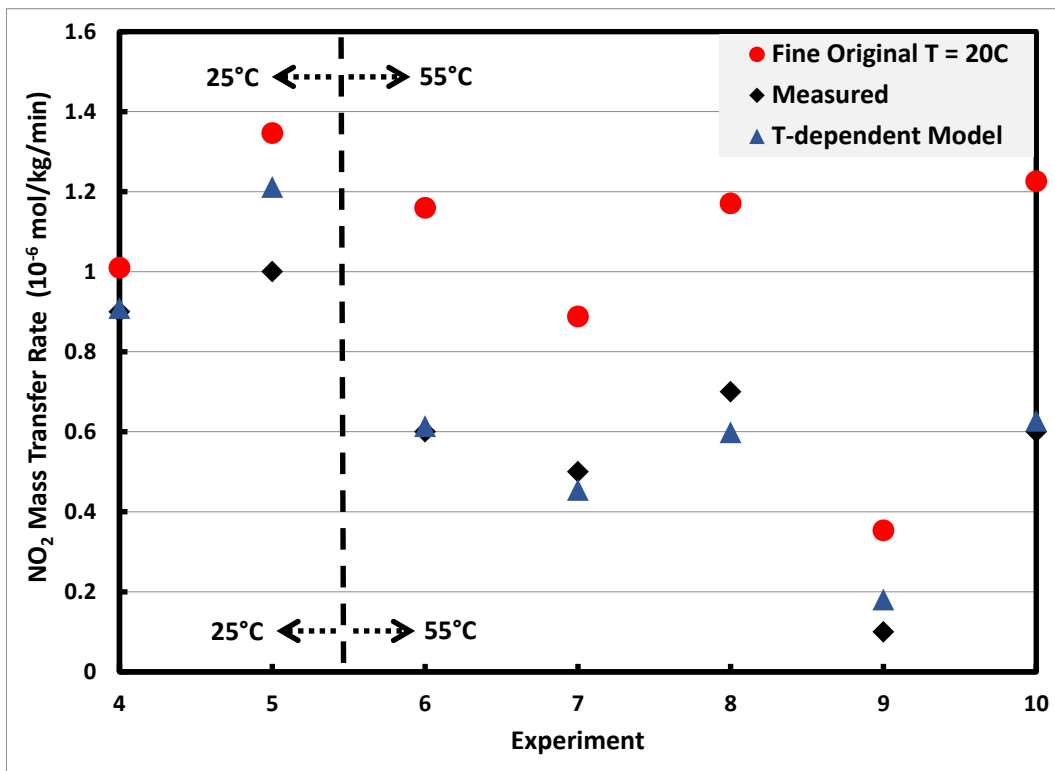


Figure 2: Temperature-Corrected NO₂ Absorption Rate predictions for the HGF apparatus

An activation energy of -15.3 kJ/mol was used to fit the data, indicating that increases in temperature reduce the NO₂ absorption following Equation 3.3. The figure illustrates this effect, as Fine's original model generally over-predicts the mass transfer rate for these cases, particularly the 55°C cases. The new temperature dependent model shows good agreement with measured data.

2.3.2 Generalized Model for Sulfite Oxidation in the Presence of Inhibitors

A power-law empirical model was regressed using the sulfite oxidation rate data (k_{ox}) collected in this work in addition to data from Fine's work to create a database of 25 experiments for the regression. Experiments conducted with metals added, without EDTA or an inhibitor, and with tertiary amine were all excluded. The metals experiments were excluded because the mechanism is unlikely to be captured by the generic model. The general form of the model is as follows:

$$k_{OX} = C_1 \left(\frac{y_{NO_2, Feed} [1 - \exp(-N_{OG})]}{y_{NO_2, REF}} \right)^{X_1} \left(\frac{[SO_3^{2-}]}{[SO_3^{2-}]_{REF}} \right)^{X_2} \left(\frac{[S_2O_3^{2-}]}{[S_2O_3^{2-}]_{REF}} \right)^{X_3} \left(\frac{[O_2]}{[O_2]_{REF}} \right)^{X_4} \exp \left[\frac{E_A}{R} * \left(\frac{1}{T_{REF}} - \frac{1}{T_{ACTUAL}} \right) \right]$$

Where:

k_{OX} = Rate of sulfite oxidation (min⁻¹)

C1, x1, x2, x3, x4, E_A = regressed parameters;

y_{NO2} = NO₂ in feed (ppm);

The equation represents the different contributors to the oxidation rate: nitrite concentration, sulfite concentration, thiosulfate concentration, oxygen concentration and a term to account for temperature dependence embedded in rate constants, diffusion coefficients, and Henry's constants. The results of the regression for thiosulfate are summarized in Table 3.

Table 3: Regression parameters for oxidation rate model

	Regressed Model	Theoretical (Shen)
C1	7.30	N/A
Ea (kJ/mol)	23.8	N/A
X1 (Nitrite)	0.55	0.5
X2 (Sulfite)	-0.05	0
X3 (Thiosulfate)	-0.39	-0.5
X4 (O ₂)	0.18	0.5

The regression results for the full data set are compared to the expected theoretical dependence. Interestingly, the general power law form captures the theoretical dependence of the model well. Only thiosulfate and oxygen dependence deviate significantly from theory. For each of these parameters, the sensitivity to the parameter may vary depending on the range over which the variable is tested. For example, Fine indicated that most of his data above 5% oxygen was insensitive to oxygen concentration, but was expected to be much more sensitive below that range (Fine 2015).

The predictions of the full model regression for thiosulfate are compared to the measured oxidation rates in Figure 3.

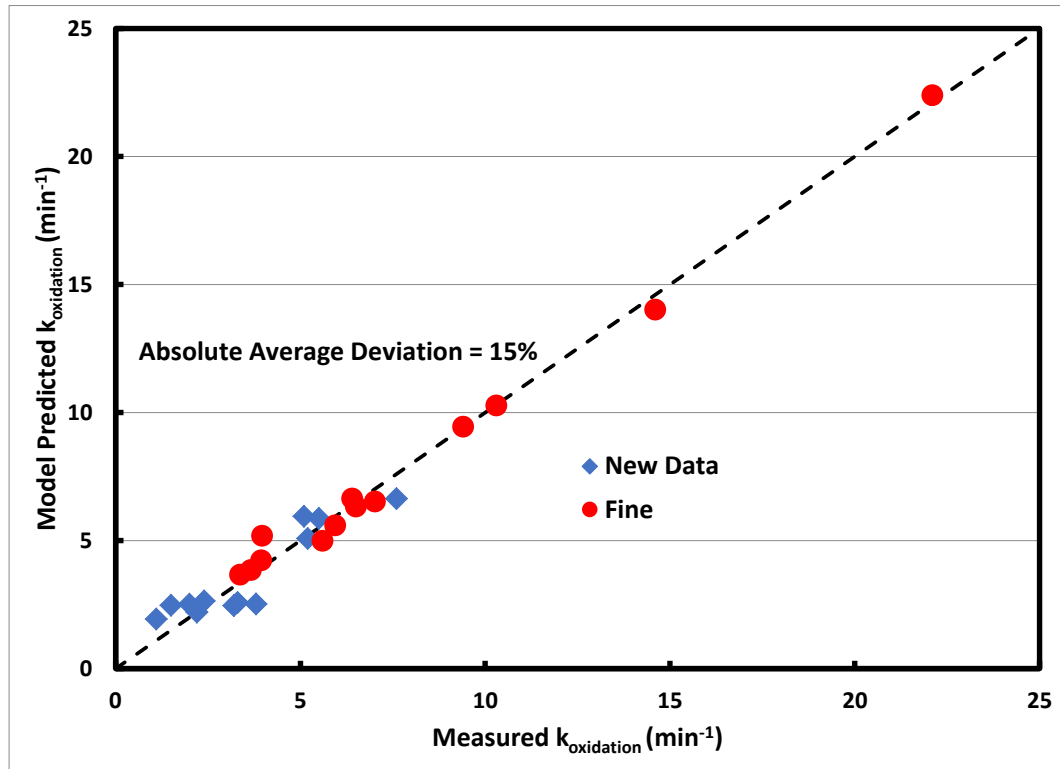


Figure 3: Model-Predicted vs. Experimental Oxidation Rates

Figure 3 illustrates that the model does a good job of predicting the oxidation rates for both data sets over the wide range of conditions and rates tested.

While the model appears to provide a strong fit of the data and the interpretation relative to theory provides some insight, the limited data and large number of parameters necessitates caution if the model is used for significant extrapolation. The model will be used for conditions that fall largely within the range of values in the experimental analysis as the experiments were designed to represent conditions applied in the field. Therefore, the model should be adequate for use in the techno-economic analysis to derive concentrations of additives such as thiosulfate.

3 Field Test

The pre-scrubbing system at the NCCC consists of a packed column, buffer tank, and a pump that recirculates the sodium hydroxide solution from the buffer tank to the packed column. A slipstream of flue gas exiting the FGD from the main power generation facility flows through the pre-scrubber, which uses dilute caustic solution to remove a majority of the remaining SO_2 from the flue gas. The dilute caustic solution, stored in a buffer tank, is pumped through the pre-scrubber using a recirculation pump. Concentrated sodium sulfate solution from the SO_2 pre-scrubber is blown down to wastewater neutralization, while the cooled flue gas exits the pre-scrubber to a flue gas blower. The pre-scrubber equipment specifications and operating conditions are summarized in Table 4.

Table 4: National Carbon Capture Center Pilot Scale SO₂ Pre-Scrubber

Packing Type	MP202Y	
Packing Height	20	ft
Diameter	29.25	in.
Specific Area	200	m ² /m ³
Operating Temperature	55	°C
Operating Pressure	101	kPa
Buffer Tank Volume	1420	gallons
Liquid Recirculation Rate	15	gpm
Gas Rate	8,000 – 12,000	lb/hr
SO ₂ in Feed Gas	30 - 40	ppmv
NO ₂ in Feed Gas	0.5 - 1	ppmv

The pre-scrubber is operated in a semi-batch mode: 50 wt% caustic is added in batches as the pH approaches ~8 to keep the operating pH in the 8-9 range and to maintain a concentration of approximately 10 wt% NaOH in the pre-scrubber.

The UT-Trimeric project team also modified the pilot unit for direct injection of NO₂ into the flue gas stream upstream of the SO₂ pre-scrubber. This provided the ability to vary the NO₂ over a wide range of conditions.

The field test plan objectives are broadly summarized as follows:

- Vary NO₂ feed concentration
 - Installed NO₂ injection system to raise inlet NO₂ up to 5 ppmv
- Vary additive combinations and concentrations
 - Semi-batch operation = additive concentrations vary with time (reaction, dilution)
- Analyze liquid samples
 - Quantify oxidation rates
 - Waste stream characterization/disposition

3.1 Results

At the time of the development of this paper, the field testing at NCCC was in progress. The results in this paper should be treated as preliminary results with additional data and analysis expected after completion of the field testing.

The experiments at NCCC thus far have demonstrated the effectiveness of the thiosulfate inhibitor system. After initial addition of thiosulfate, the sulfite concentration in the pre-scrubbing system accumulated to approach a steady state value, validating the performance of the thiosulfate as an inhibitor. Figure 4 indicates that NO₂ removal above 95% was achieved with 85 to 90% removal consistently attained. The field testing also validated liquid sampling methods, the injection of NO₂ into the flue gas, gas-phase NO₂ measurements, and batch operation and control of the pre-scrubbing system.

Additional testing will confirm the consumption of the additives (primarily thiosulfate) with time and evaluate the performance of the system as the concentrations of the key components vary (including the effect of batch addition of caustic solution to change the pH of the solution).

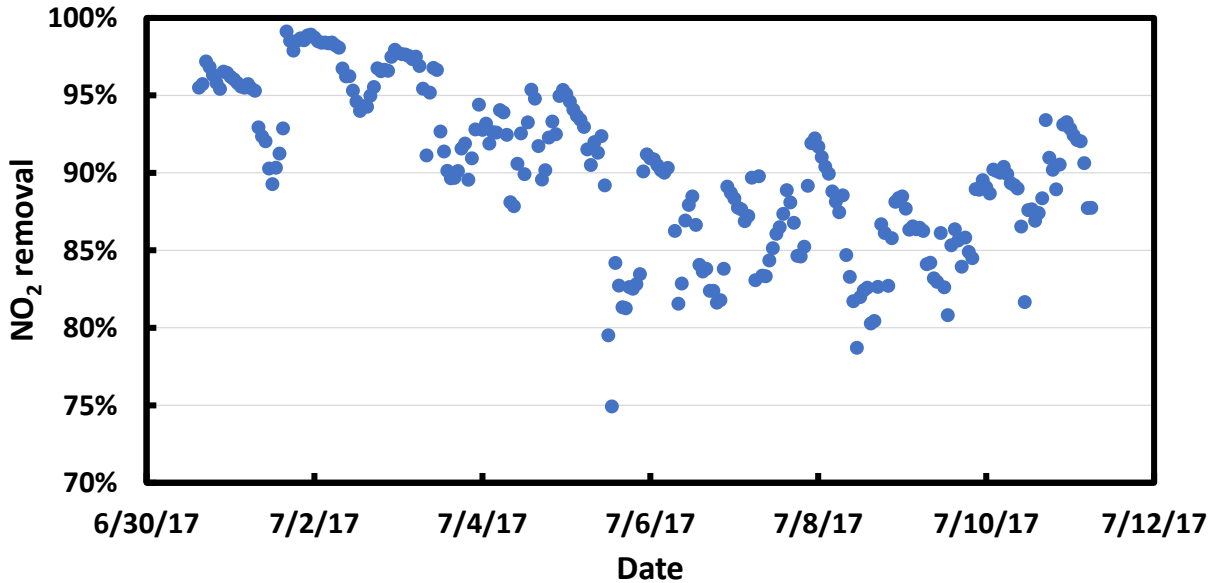


Figure 4: Experimental Field Tests NO₂ Removal Results

4 Techno-Economic Analysis

This portion of the paper will focus on the conceptual design and evaluation of a commercial scale system based on the data and findings of experiments, literature review, and field test preparation.

4.1 Conceptual Process Design

Figure 5 depicts the SO₂ polisher, where the additives are used to facilitate the concurrent absorption of NO₂, in relation to the direct contact cooler (DCC) and the absorber unit in the main CO₂ capture process.

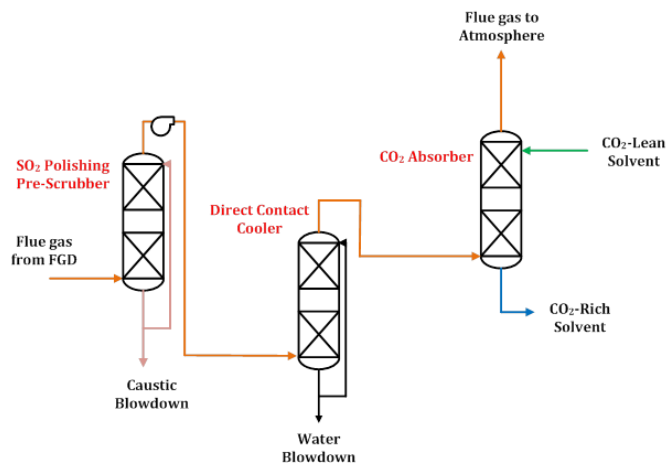


Figure 5: Process Flow Diagram

The process flow diagram illustrates an important design choice for the process. While integrating the SO₂ polisher and DCC might appear desirable from a capital cost standpoint (elimination of a column), the dual-column design is important for the chemical consumption of the SO₂ polisher. The blowdown rate (or equivalently, chemical make-up rate) in the individual SO₂ polisher is nominally dictated by the

solubility limit of sodium sulfate that accumulates as SO_2 is absorbed. If the DCC is integrated, the purge rate will be set at a much higher level to remove the water that is condensed from gas in the DCC to maintain the water balance in the unit (and prevent dilution). This effect is even more important when NO_2 removal is integrated into the polishing scrubber. The primary cost of the NO_2 removal process is the chemical additives that are used. If purge rates are artificially high to remove water, the economics of the NO_2 removal will suffer.

Furthermore, combining the unit operations effectively increases the volume of waste solution that must be handled from the process. In the independent columns, a comparatively smaller, concentrated waste stream leaves the SO_2 polisher, while a large volume of process quality water leaves the direct contact cooler for potential re-use elsewhere in the CO_2 capture process or at the utility host site.

The sequence of the columns is also important. The experimental results in Section 3 indicate that higher operating temperatures reduce NO_2 absorption and increase sulfite oxidation. This would seem to incentivize moving the DCC upstream of the polishing scrubber to reduce the temperature of the feed gas. However, the issue of isolating waste streams arises again. The direct contact cooler now sees flue gas with higher levels of contaminants - in addition to the NO_2 and SO_2 , impurities such as metals that may be removed in the SO_2 polisher instead accumulate in the water leaving the DCC. In addition, the introduction of SO_2 into the DCC creates a corrosive environment, necessitating the use of more expensive materials of construction. Therefore, the specific arrangement and function of the unit operations upstream of the capture unit are important to maximizing the viability of the NO_2 removal process and reducing the volume of waste for the capture process as a whole.

The basic equipment requirements for the NO_2 removal process are satisfied by an existing SO_2 polisher unit – the addition of specific chemical additives to the existing polisher is the basis of the technology. At most, a small storage tank or chemical tote might be required if chemicals cannot be introduced directly into the SO_2 polisher buffer tank. The assumption in the subsequent economic analysis will be that no additional capital costs are incurred as part of the process implementation. However, the economics of the process can be improved at specific operating conditions (e.g., low SO_2 content flue gas, which results in lower steady-state sulfite concentration in solution) by adding incremental packing to the column over what is nominally required for SO_2 removal (Fine 2015). In those specific cases, the initial design of the column must include the costs of additional packing.

Finally, the inlet NO_2 concentration to the SO_2 polisher is an important aspect in determining performance and cost savings potential of the NO_2 scrubbing technology. Coal-fired power plants may have a variety of emissions technologies upstream of the SO_2 polisher associated with the CO_2 capture unit that impact the NO_2 concentration. As a rule of thumb, NO_2 is up to ~5% of the total NO_x leaving a boiler. In some large international markets, where coal-fired plants do not have NO_x restrictions (e.g., Australia, China), the total NO_x concentrations may range from 100 – 700 ppm depending on the specific conditions at the site (type of coal, boiler, age, etc.) [e.g., (Cousins, et al. 2012)]. This corresponds to NO_2 concentrations as high as 35 ppm.

For the U.S. market, which is the initial focus of this work, there are restrictions on NO_x emissions via the Clean Air Act and Clean Air Act Amendments. A detailed review and analysis conducted in 2005 evaluated the technology response of coal-fired power facilities to tightening NO_x regulations (Srivastava, et al. 2005). The results of their evaluation indicated a wide range of NO_2 concentrations reflecting, in part, underlying variations such as the type of coal or age of the facility as well as the technology approach used to control NO_x . However, their results indicated NO_2 levels generally below 15 ppmv with plants with SCR installed providing the lowest NO_2 levels.

4.2 Methods

The approach to evaluate the economic viability of the NO₂ removal technology in this work relies on a baseline CO₂ capture plant cost assessment for a process utilizing piperazine (PZ) and a custom reclaiming model/solvent degradation model developed for amine solvents such as PZ monoethanolamine (MEA), and a blend of methyldiethanolamine (MDEA) and PZ. While this analysis focuses on PZ, the technology will have value for amine solvents in general – previous research has shown that all classes of amines (primary, secondary and tertiary) will absorb NO₂ and form degradation products as a result (Fine 2015). The benefit of the technology will scale to some level with the cost of the amine itself (more expensive solvents will yield a larger benefit). In addition, the level of nitrosamine formation (which varies greatly across amines) may provide additional incentive. In general, applying the NO₂ removal technology enhances the ability to select amines based on performance in the main capture system rather than being constrained by degradation or environmental/safety considerations.

The CO₂ capture techno-economic evaluation of PZ included a bottom up cost assessment of all of the equipment, chemicals, and operating costs associated with a capture process, including a baseline value for the cost of a thermal reclaimer. The approach mirrored the one used in the Cost and Performance Baseline Document produced by National Energy Technology Laboratory within the U.S. Department of Energy and provided the cost scaling factors to roll up the installed equipment cost into the impact on total plant costs (National Energy Technology Laboratory 2010). The SO₂ polisher, which is relevant for the modeling of the NO₂ absorption process, was included but was not specified in detail. Therefore, the NCCC pre-scrubber test unit was used to define equipment specifications such as packing height and type, while the diameter was scaled up to the commercial flow rates in the PZ cost analysis. The relevant baseline conditions and assumptions from the PZ analysis and SO₂ polisher are summarized in Table 5 and Table 6.

Table 5: Baseline Assumptions for Techno-Economic Analysis

Total equivalent electrical capacity	723	MWe
Flue Gas Flow Rate	25.7	kmol/s
NO ₂ Concentration (ppmv)	1 - 5	ppmv
SO ₂ Concentration (ppmv)	10 - 300	ppmv
CO ₂ Capture Rate (@ 90% capture, 100% Capacity Factor)	4,339,178	tonne/yr
Capacity Factor	85%	

Table 6: SO₂ Polisher Information

Packing Type	Sulzer MP202Y	
Height of Packing	6.1	m
Diameter of Column	17	m
Specific Area of Packing (ap)	200	m ² /m ³
Operating Temperature	55	°C
Operating Pressure	101.325	kPa

The cost savings from removing the NO₂ upstream of the capture unit are directly associated with the amine solvent reclaimer and solvent losses. Removing NO₂ upstream results in a lower reclaimer flow rate, which should reduce the size of the reclaimer and associated capital costs and reduce the amine losses associated with reclaiming. In addition, the reduced nitrosation/degradation of the solvent further reduces amine losses. The combination of these savings is the gross economic benefit of removing the NO₂ upstream of the capture unit before accounting for costs of the process.

4.2.1 Cost of NO₂ removal process

The cost associated with the removal of NO₂ is the consumption of the additives associated with the process. In this analysis, it was assumed that the baseline SO₂ polisher installed for the capture process (Table 6) was not modified to implement the NO₂ scrubbing process. This is the most desirable scenario as the process can leverage existing capital investment.

The NO₂ removed was defined by the packing characteristics in Table 6 and by the concentration of sulfite or amine (when the amine is used as a scavenger). With the packing in the column fixed by the existing SO₂ polisher design, the only way to reach 90% removal is to vary the sulfite or tertiary amine concentration. Once this concentration is defined, in the case of the sulfite system, the balance between oxidation of sulfite and absorption of SO₂ defines the concentration of inhibitor required. At steady state, the oxidation (sulfite destruction) rate will be equal to the SO₂ absorption (sulfite production) rate. This allows direct calculation of the inhibitor concentration at steady state.

4.3 Results of Techno-Economic Analysis

The methods to calculate the savings generated by NO₂ removal and costs associated with additives were used to evaluate the economic viability of the NO₂ removal process. Figure 6 presents the net cost savings of applying the NO₂ removal technology as a function of the NO₂ and SO₂ concentration in the flue gas the thiosulfate inhibitor system.

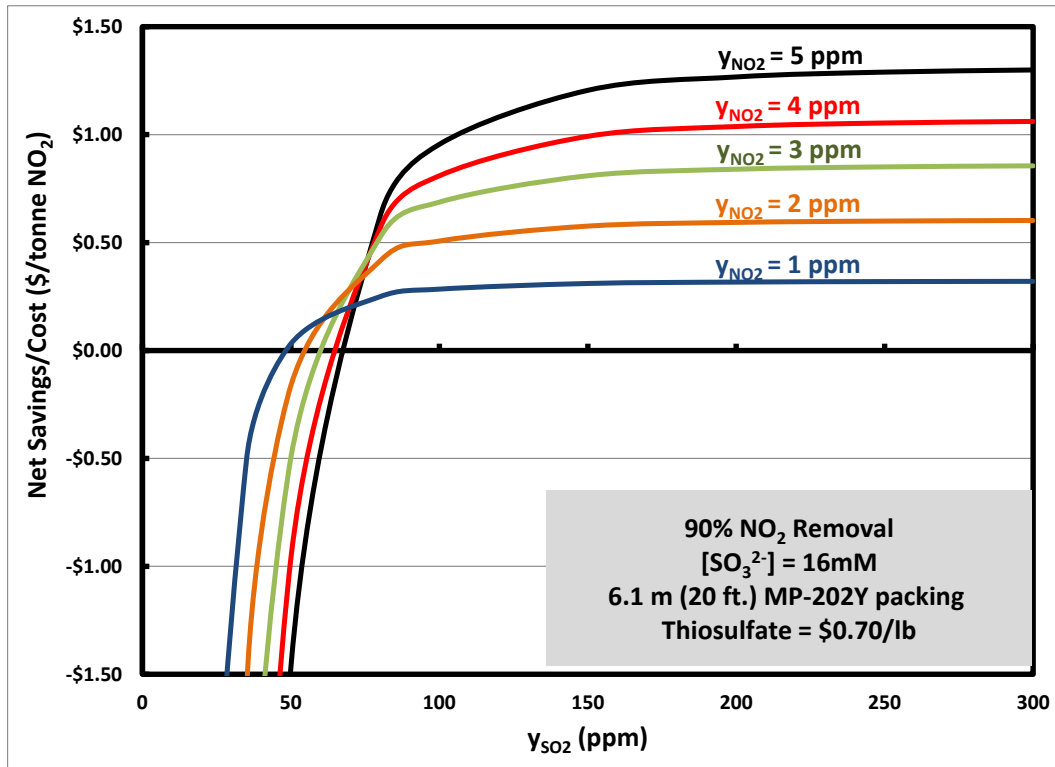


Figure 6: Net Savings of NO₂ removal using thiosulfate as an inhibitor

The figure illustrates several important points:

- As expected, increasing SO₂ concentrations in the flue gas improve the economics significantly by replenishing any sulfite that is oxidized. While the purge rate also increases, the reduced concentration of inhibitors in the purge more than offsets the increased flow.
- Increasing NO₂ has two effects. Low NO₂ concentrations reduce the rate of oxidation – this is apparent in the preceding figure as lower NO₂ concentrations “break-even” at lower levels of SO₂ – less sulfite needs to be made up due to lower oxidation rates. However, the lower NO₂ limits the maximum cost savings that can be achieved as the impact of NO₂ on the main capture process is reduced at lower NO₂ concentrations.
- The figure appears to reach an asymptote as a function of SO₂ concentration for each NO₂ concentration. This reflects an approach to the maximum cost savings.
- The approach to this asymptote, or maximum savings, represents the effectiveness of the specific inhibitor.

To evaluate the impact of alternative additive formulations, the results for the proprietary inhibitor identified in this work is compared to thiosulfate for specific operating conditions in Figure 7.

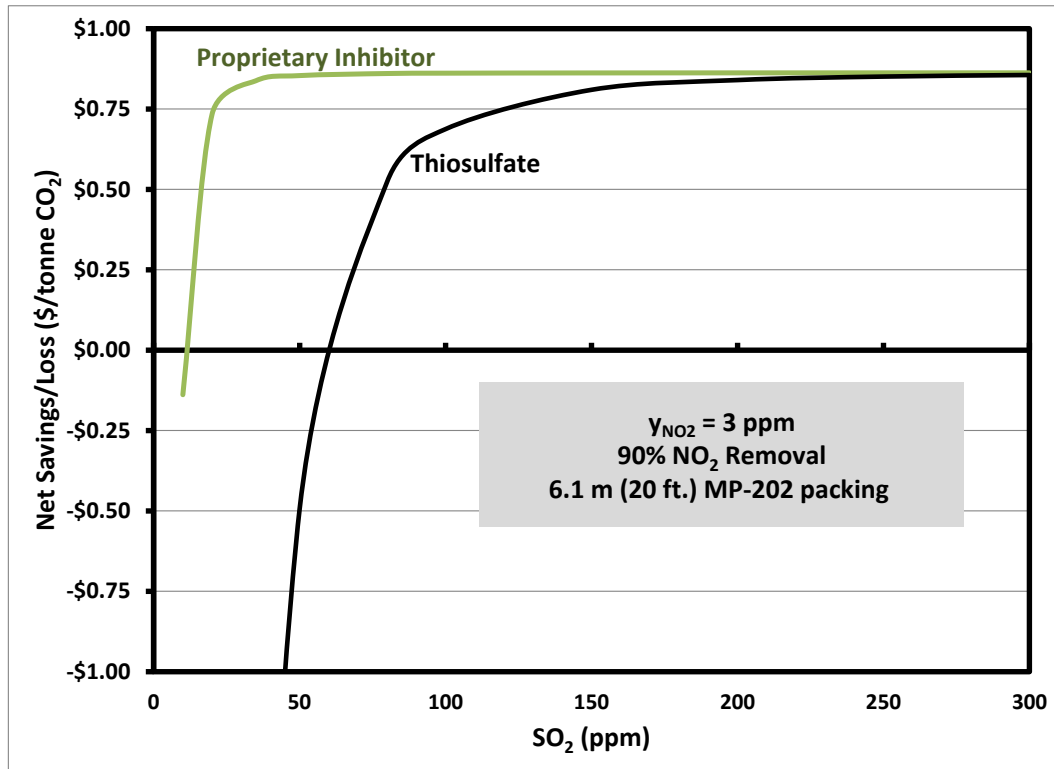


Figure 7: Net Savings of NO₂ removal: Thiosulfate vs. proprioritary inhibitor

As the figure indicates, the proprietary inhibitor expands the economically attractive operating window (i.e., lower SO₂ concentrations) and generates larger costs savings compared to the baseline thiosulfate technology across the range of conditions in the figure. The result sin the figure highlight one of several options developed by the team to improve the economics and performance of the NO₂ removal technology compared to the thiosulfate system.

5 Conclusions

The experimental evaluation, field testing, and techno-economic evaluation of the novel NO₂ removal technology accomplished several important goals of the research:

- Experimental data were obtained which provide the necessary proof-of-concept required to demonstrate the effectiveness of the technology. Specifically, the team identified concentrations and combinations of additives required to minimize sulfite oxidation across a wide range of representative operating conditions.
- A greater understanding of the complex relationships between the operating conditions and the effectiveness of the technology has been obtained.
- Optimal additives and potential solutions to manage secondary impacts of the technology were identified (e.g., sending pre-scrubber blowdown to the FGD unit).
- Specific operating conditions were analyzed to guide field testing and to develop knowledge for commercial-scale operation (e.g., transient behavior of the pre-scrubbing system during start-up and for semi-batch operation). Expected operating conditions at commercial sites were analyzed to guide further testing and optimization (e.g., review of expected NO₂ concentration reaching the pre-scrubber).

- A techno-economic evaluation of the entire CO₂ capture process with the PZ solvent and a reclaiming model to predict the effects of degradation were leveraged to evaluate the total cost savings for 90% removal of NO₂ at feed concentrations of 1 – 5 ppm NO₂. The range of potential savings \$0.30 to \$1.30.

In summary, the absorption of NO₂ with sulfite plus oxidation inhibitors has proven to be viable at bench scale and field scale. Multiple routes to low-cost chemical additives, including novel inhibitors, have been identified to enhance the probability of adoption at commercial scale. The technology has garnered interest across the value chain of solvent suppliers, CO₂ capture technology suppliers, and utility owners and operators and there are plans for the field and laboratory work to continue with industry support moving forward.

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Minimizing Solvent Oxidation with NO₂ Pre-Scrubbing

*2017 Carbon Management Technology Conference
July 18, 2017*

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Trimeric Corporation

- Background on Trimeric
 - Providing technical services to industry
 - Process engineering, chemical engineering, R&D
 - **Specialized**.... in process/chemical engineering
 - **Diversified**.... across multiple industries
- Trimeric's Resources
 - Regular Staff
 - Senior Associates
- Selected Clients
 - Oil & Gas Production, Oil Refining, Silicon Processing, R&D/Govt, Other (Petrochemicals, Food, etc.)



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Overview



- Background and Objectives
- Solvent Oxidation
- NO₂ Pre-Scrubbing
- Laboratory Testing
- Techno-Economic Engineering Evaluation
- Pilot Plant Testing
- Summary

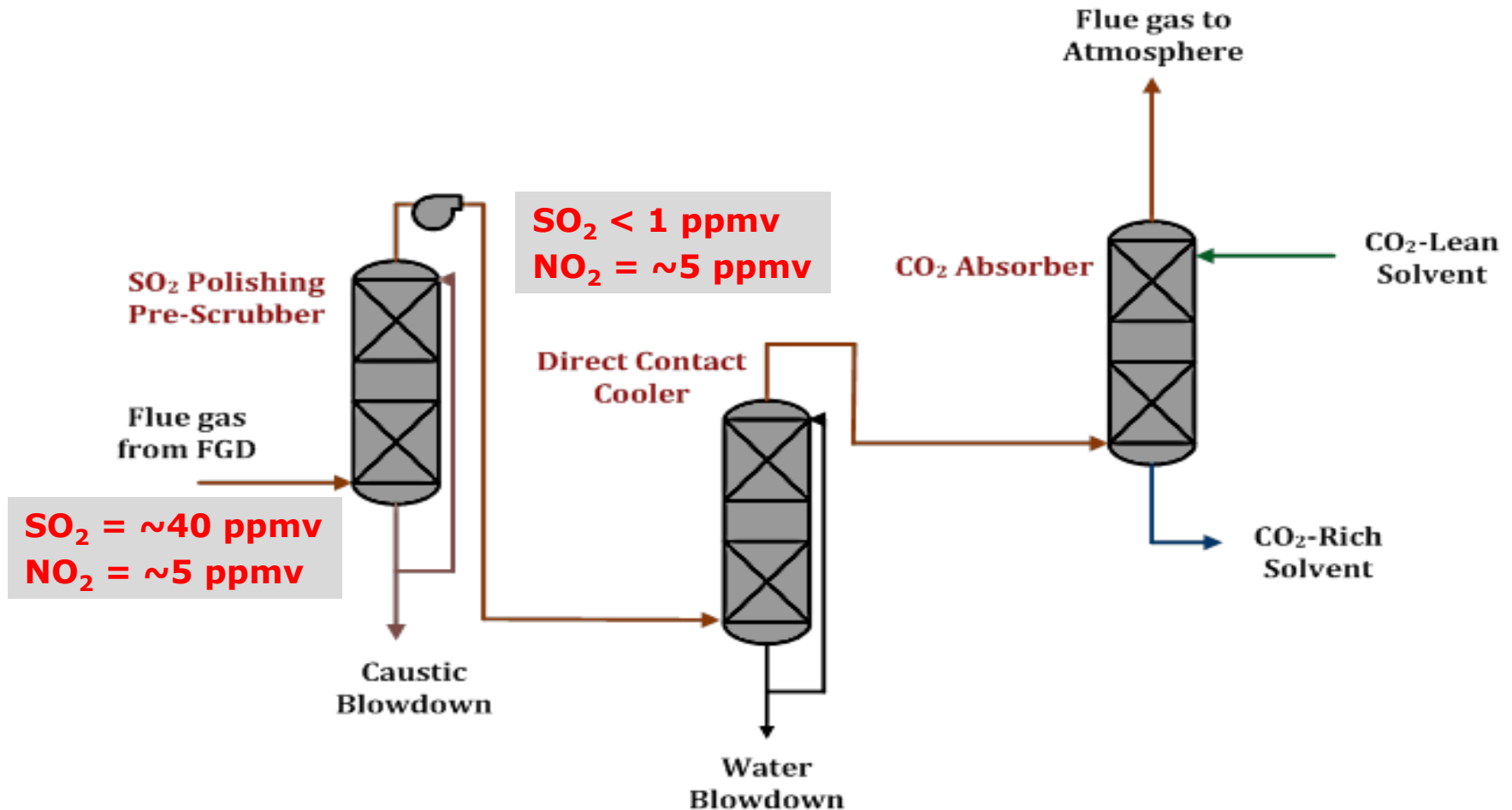


Background and Objectives

- DOE SBIR FY16 Phase I Release 2: Carbon Capture System Improvements
 - Aerosols, Reclamation, Oxidation
- Amine-based solvents = Ready for Deployment
- Flue gas contaminants oxidize amines (↑ costs)
- **R&D needed to reduce costs/risks of amine-based capture**



CO₂ Capture Pre-Treatment



Solvent Oxidation Risk

- Pre-scrubbing *does not* address NO₂ (1 – 10 ppmv)



- Nitrosamines = potential environmental/health risk
- 1 mole of NO₂ may oxidize 2 – 4 mols amine¹ = \$
- **Opportunity: Integrate NO₂ removal into SO₂ pre-treatment**

1: Fine, 2015



NO₂ Pre-Scrubbing Concept

- NO₂ absorbs in sulfite solutions²(SO₂ polisher)
 - Issue: Sulfite is rapidly consumed by oxidation
 - **Solution: Introduce oxidation inhibitors to reduce sulfite oxidation rate**
- No new unit operations required
- Commercially available additives:
 - Thiosulfate (Oxidation Inhibitor)
 - Tertiary Amines (Scavenger)

2: Shen, 1997



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Technology Status

- UT: Initial proof of concept at bench scale¹

- UT/Trimeric: Path to commercialization³:
 - Extended laboratory testing with multiple additives
 - Techno-economic engineering evaluation
 - Pilot test experimental design
 - Pilot-Scale field testing (currently in progress at NCCC)

- Collaboration with U.S. DOE and industrial partners

1: Fine, 2015

3: Funding provided via Phase I SBIR Award from U.S. Department of Energy



Laboratory Testing: Methods

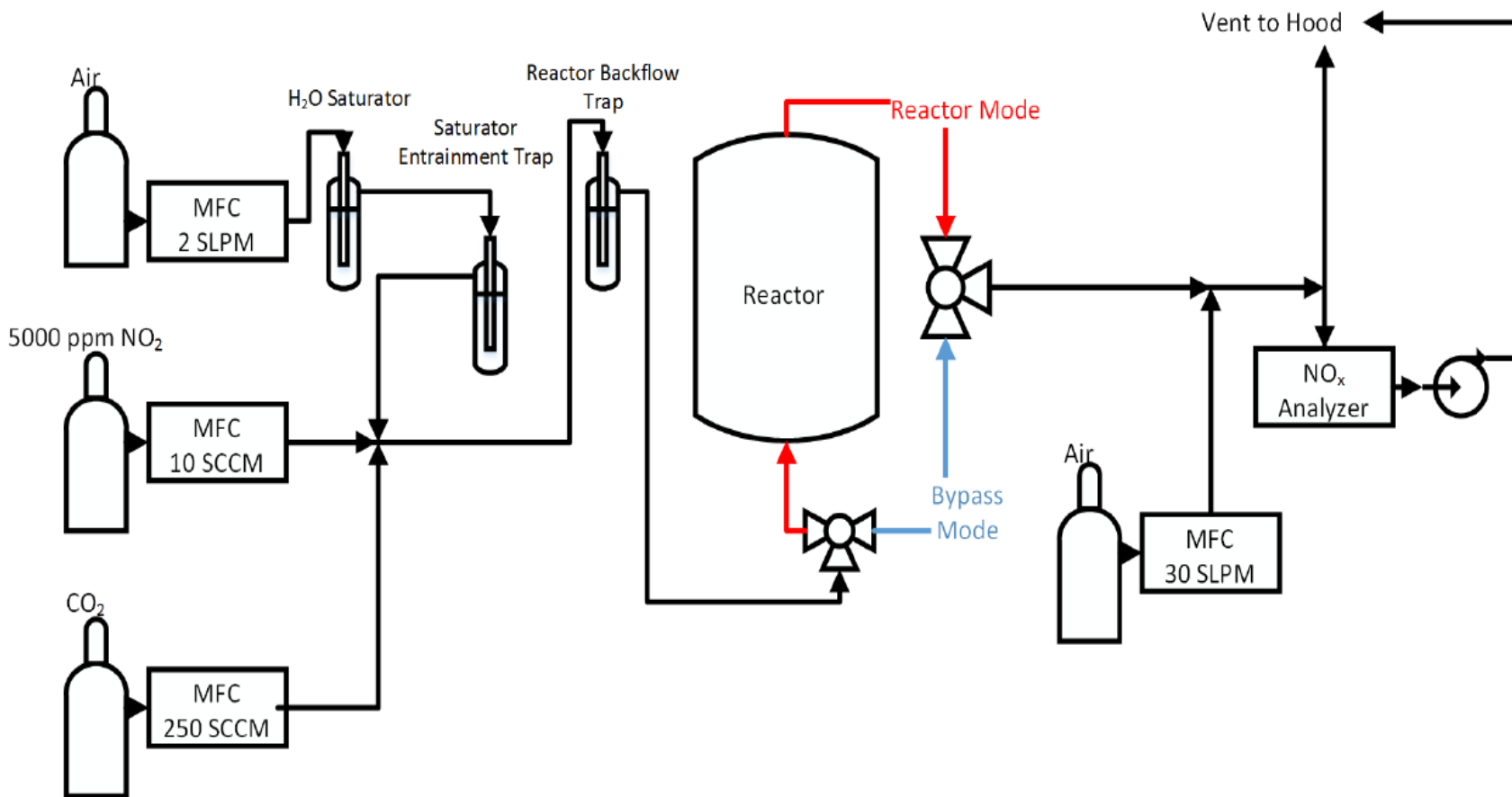
- High Gas Flow Apparatus (UT): Batch gas-sparged reactor (see next slide)

- Measure as a function of time:
 - NO₂ absorbed
 - Sulfite concentration in liquid
 - Sulfite oxidation inhibitor concentration in liquid

- Goal: Quantify normalized ratio of sulfite oxidation per mole of NO₂ absorbed as a function of process conditions



Laboratory Testing: Apparatus



Laboratory Testing: Test Parameters

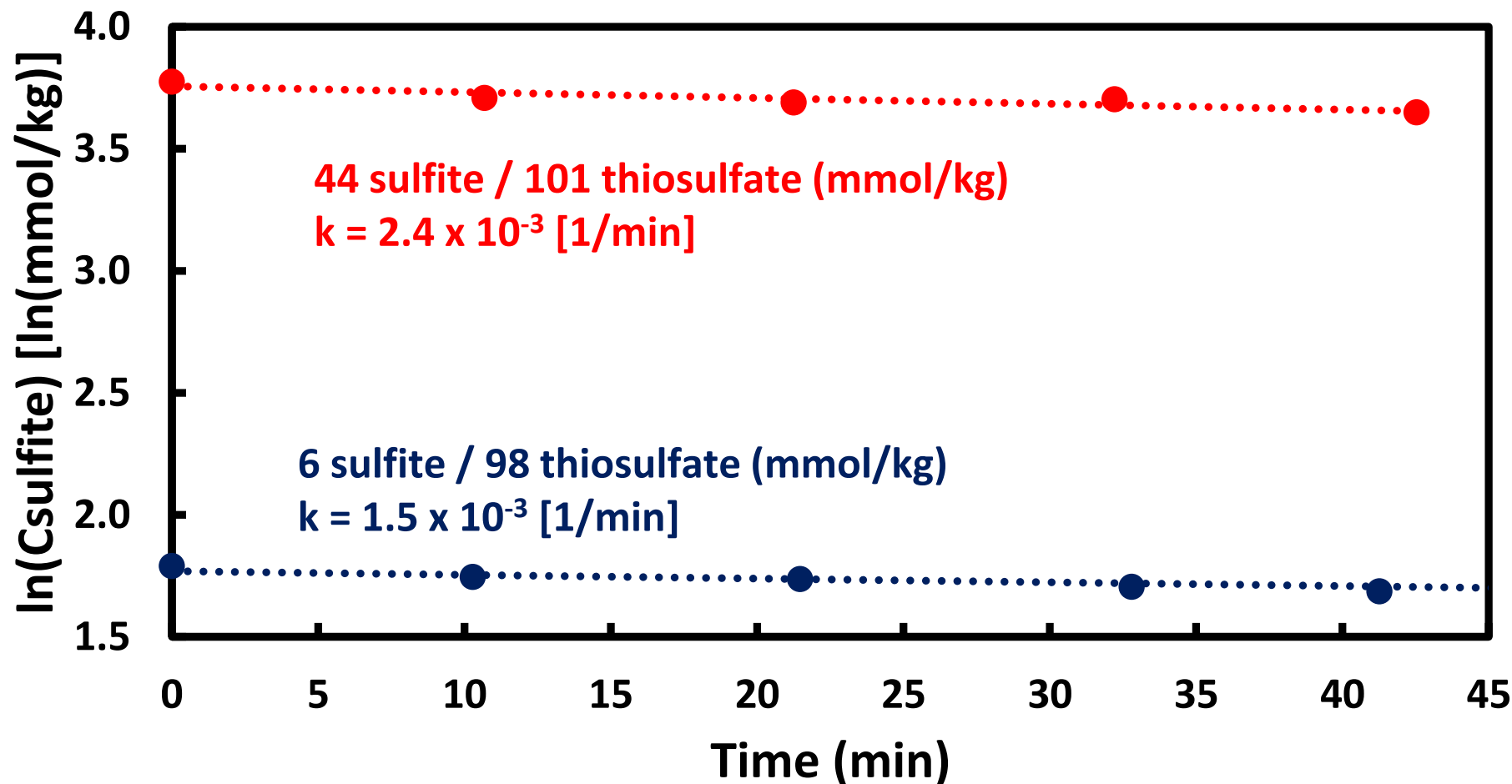
Parameter	Units	Value
NO₂ Concentration	ppmv	1-5
Temperature	°C	25-55
Sulfite Concentration	mmol/kg	4-50
Thiosulfate Concentration	mmol/kg	0-200
Tertiary Amine Concentration	mmol/kg	5-200
Metals Concentration	mmol/kg	0.1-0.5
EDTA Concentration	mmol/kg	0.02-1

1: Metals may be present in flue gas and catalyze oxidation

2: EDTA (Ethylenediaminetetraacetic acid) chelates metals to inhibit oxidation



Laboratory Testing: Example Results



Laboratory Testing: Summary of Key Results

- Validated theoretical inhibition effect of thiosulfate
- Demonstrated the effectiveness of EDTA:
 - Small amounts of EDTA important to chelate trace background metals
 - EDTA effect separate from oxidation inhibitor
- Identified new inhibitor (proprietary)
 - Oxidation rates $\sim 10x$ lower than comparable thiosulfate
- Demonstrated low-cost pathway to introduce inhibitor into scrubbing solution (proprietary)



Techno-Economic Engineering Analysis

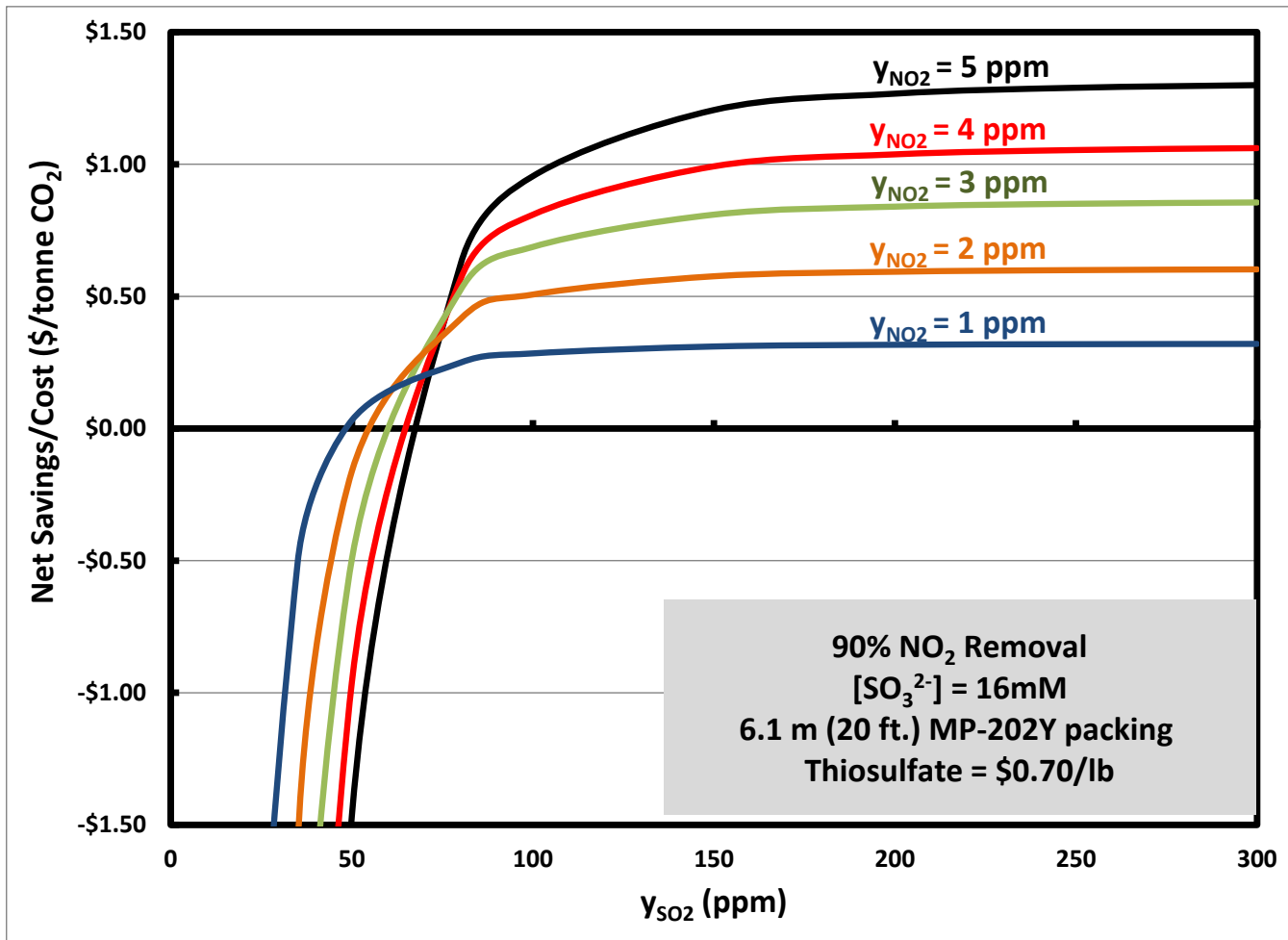
- Developed empirical model for sulfite oxidation, NO₂ absorption¹
- Performed steady-state modeling of SO₂ polisher:
 - Estimate inhibitor make-up rates
 - Estimate NO₂ removal percentage
 - Estimate steady-state sulfite concentration in solution
- Used internal solvent degradation model² to:
 - Estimate reduction in solvent losses and solvent makeup (operating costs)
 - Estimate reduction of solvent reclaiming system (capital costs)
- **Estimate cost/savings of NO₂ pre-scrubbing as function of operating conditions**

1: Absorption rate data from Fine, 2015

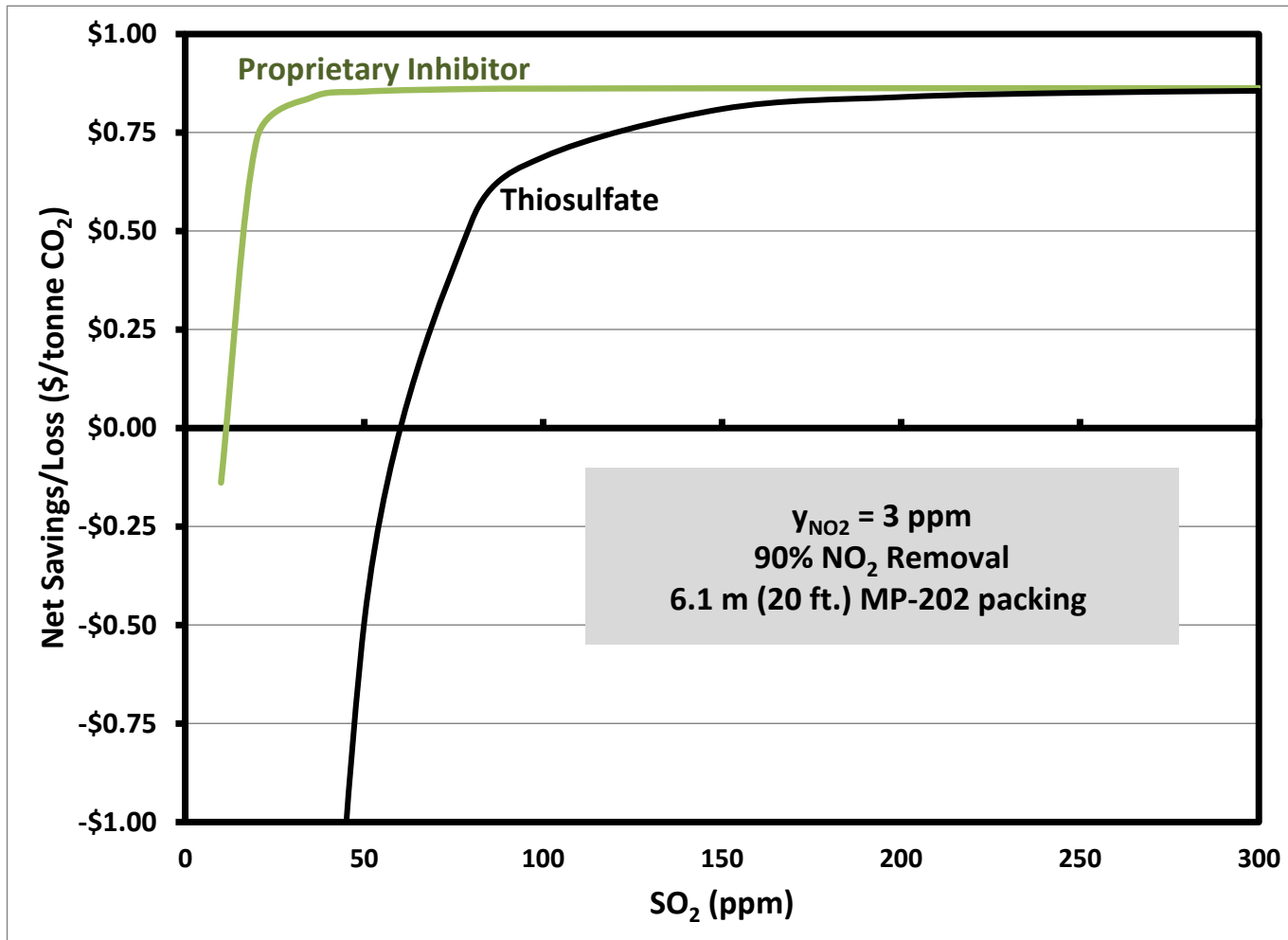
2: Developed by Trimeric and UT



Techno-Economic Analysis: Results for Base Case System



Techno-Economic Analysis: Benefits of Improved Additive



Techno-Economic Analysis: Results

- Savings > \$1 /tonne of CO₂ are possible
 - Up to \$5MM in annual savings
- Alternatives to thiosulfate expand envelope of acceptable operating conditions
 - Low cost inhibitor sources
 - Proprietary inhibitor (stronger inhibitor = reduced make-up)
- Combination of additives allow cost-savings across entire range of conditions (NO₂ = 1–5 ppm, SO₂ = 10–300 ppm)



Pilot Testing

- Pilot Bay 3 Pre-Scrubber at National Carbon Capture Center (NCCC)
 - Actual power plant flue gas (slip-stream)

Column Packed Height	20	ft
Column Diameter	29.25	in.
Operating Temperature	55	°C
Liquid Recirculation Rate	15	gpm
Gas Rate	8,000 – 12,000	lb/hr
SO₂ in Feed Gas	30 - 40	ppmv
NO₂ in Feed Gas	~0.4	ppmv



Pilot Testing: Test Plan

- Vary NO₂ feed concentration
 - Installed NO₂ injection system to raise inlet NO₂ up to 5 ppmv
- Vary additive combinations and concentrations
 - Semi-batch operation = additive concentrations vary with time (reaction, dilution)
- Analyze liquid samples
 - Quantify oxidation rates

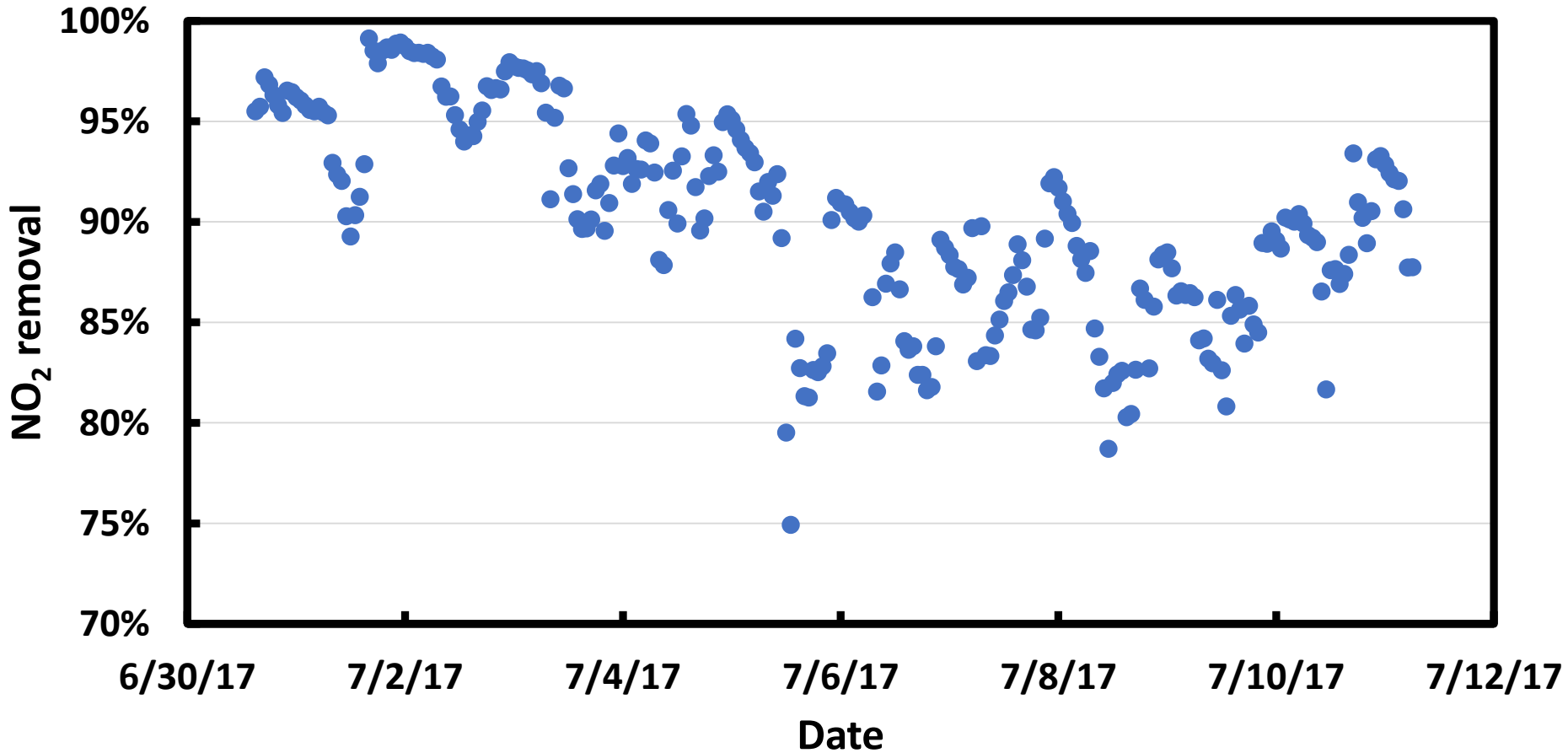


Pilot Testing: Preliminary Results

- Demonstrated effectiveness of thiosulfate
 - Sulfite concentrations ↑ time when thiosulfate is present
- Achieved NO₂ removal from 80% to 99%
- Validated liquid sampling methods, NO₂ injection and measurement, and batch operation and control of pre-scrubbing system
- Testing on-going at NCCC



Pilot Testing: NO₂ Removal



Summary

- Absorption of NO₂ with sulfite + oxidation inhibitors validated at bench and field scale
- Multiple routes to low-cost chemical additives identified at bench-scale
 - Novel inhibitors identified
- No new unit operations required
- Potential net savings > \$1/tonne CO₂ captured
- Accelerated path to commercialization



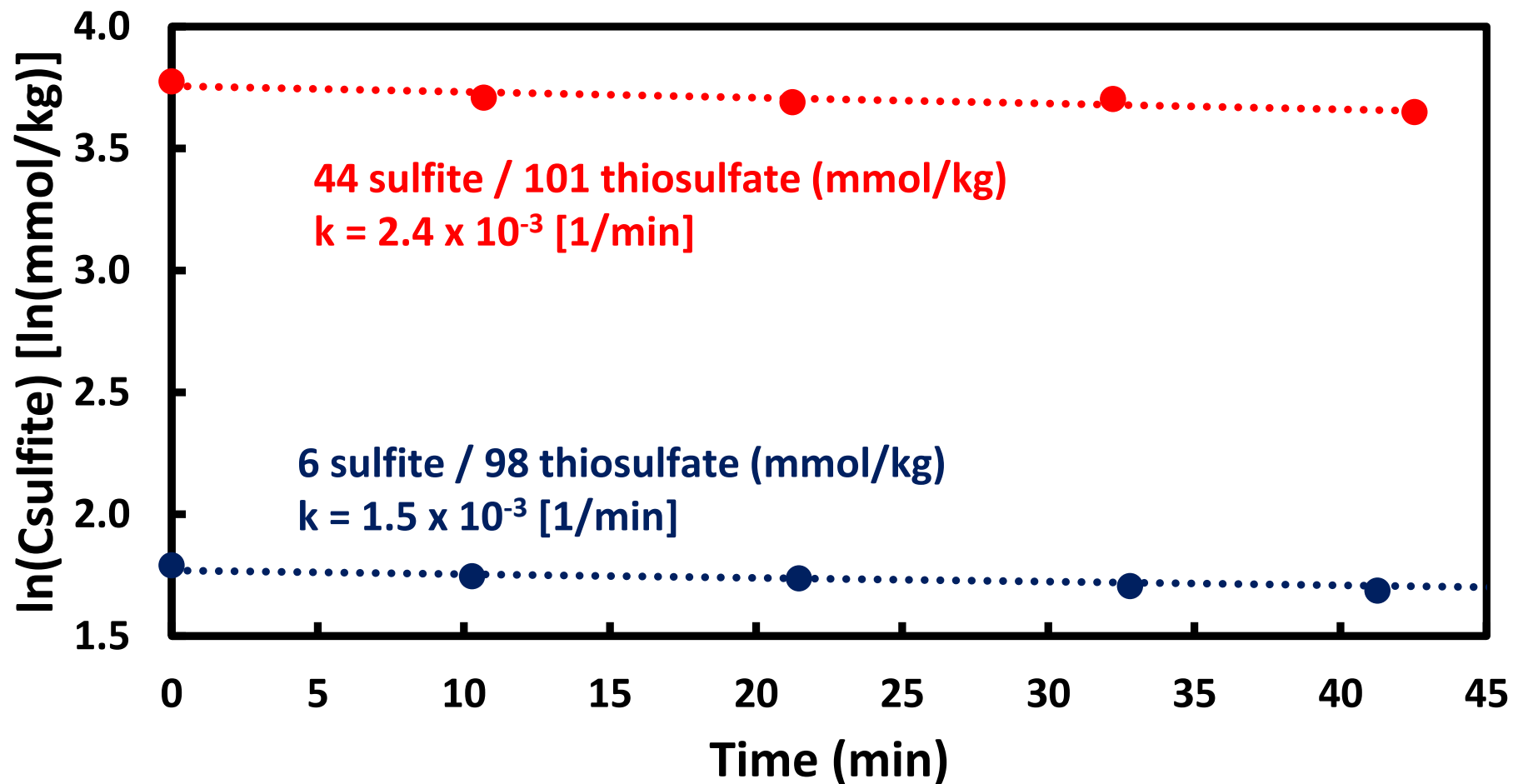
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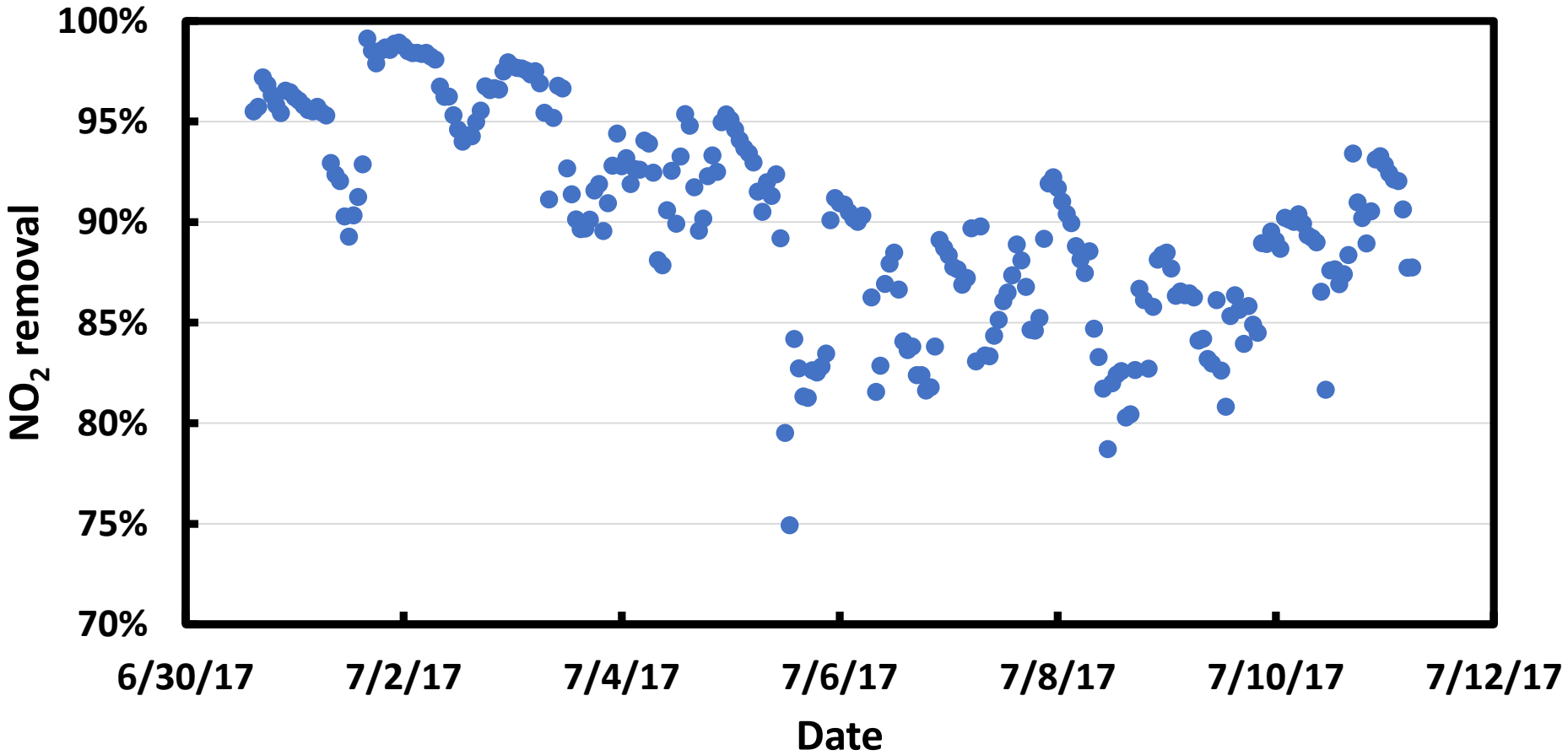
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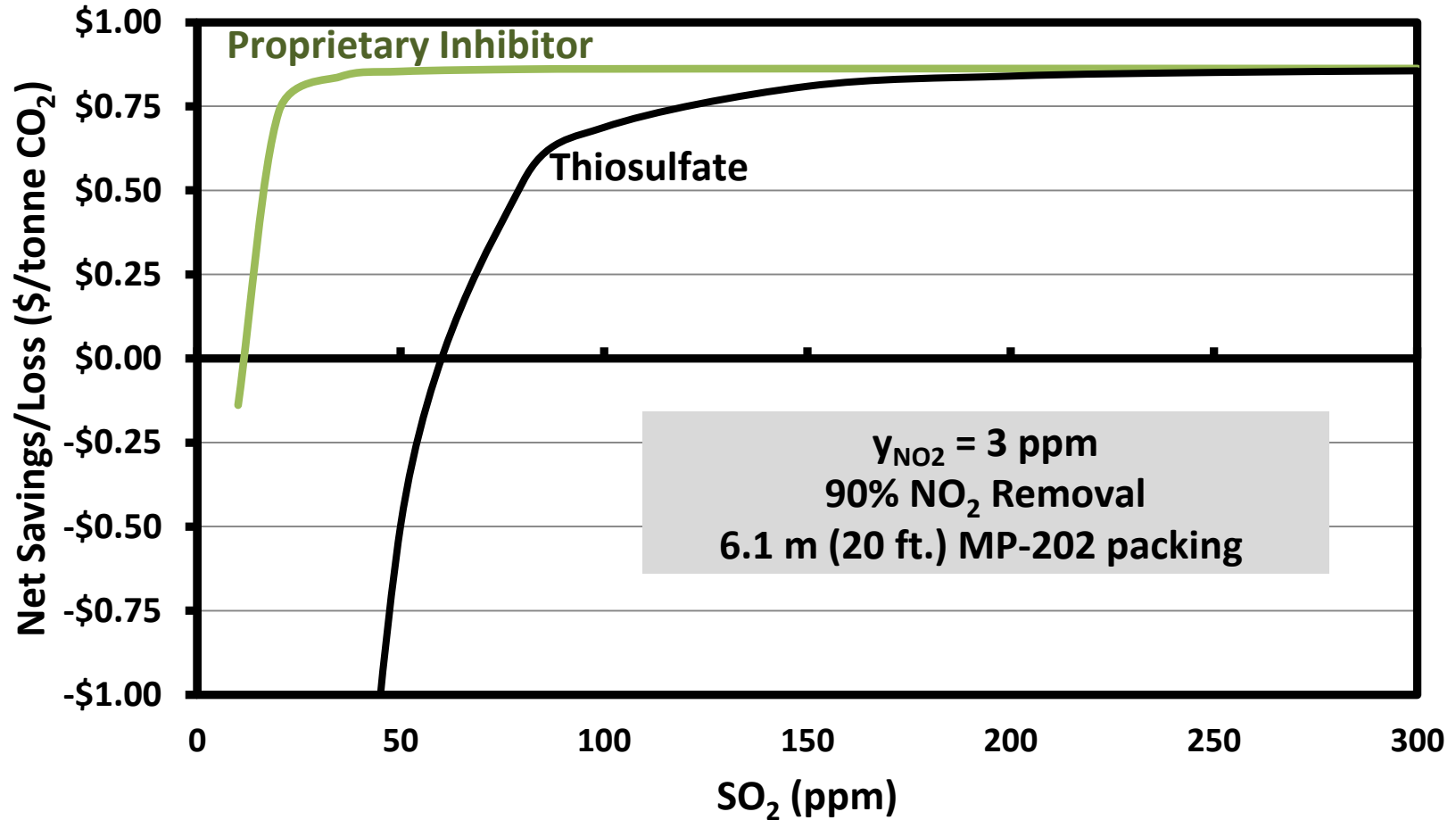
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