

# Pilot plant NO<sub>2</sub> Removal with Aqueous Solutions of Sodium Sulfite

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October 31, 2017

## ***Abstract***

UT-Austin and Trimeric performed testing for removal of NO<sub>2</sub> in order to reduce effects on the downstream CO<sub>2</sub> capture system, including solvent losses for amine-based systems. In addition, the application addresses a specific technical problem of how to reducing nitrosamine accumulation in the solvent system and reducing solvent oxidation. The presence of nitrosamines, coupled with increased solvent makeup rates, increases the cost for capturing CO<sub>2</sub> and is an environmental concern. The process involved the use of a low-cost additive, thiosulfate, in an existing SO<sub>2</sub> pre-scrubber upstream of the PC4's Pilot Bay 3.

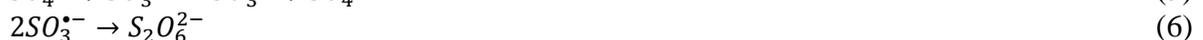
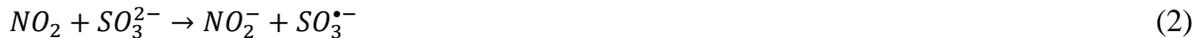
Sulfite and thiosulfate were added to a 1400-gal sulfur dioxide (SO<sub>2</sub>) polishing scrubber operating at pH 7.5 to 9 with 9,000 lb/hr flue gas containing up to 5 ppm NO<sub>2</sub> and 40 ppm SO<sub>2</sub> over a two-month test campaign. NO<sub>2</sub> removal varied from 70% to 98% throughout the course of the test campaign. NO<sub>2</sub> removal was highly dependent on basicity, with a 1-unit increase in pH improving NO<sub>2</sub> removal by 8%. 90% NO<sub>2</sub> removal was achieved with a minimum concentration of 50 millimoles per liter (mM) of thiosulfate in the scrubbing solution, which correlates to a concentration of 25 mM of sulfite in the scrubbing solution.

## ***Introduction***

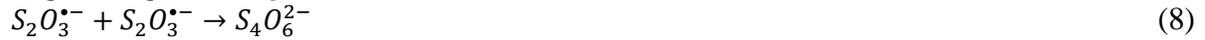
NO<sub>2</sub> in flue gas will react with aqueous amine to form nitrosamines, causing solvent degradation in CO<sub>2</sub> capture systems (Fine, 2015). Selective catalytic reduction reduces total NO<sub>x</sub>, but limestone slurry scrubbing does not remove the residual NO<sub>2</sub>. Within the slurry scrubber, SO<sub>2</sub> is absorbed and forms SO<sub>3</sub><sup>2-</sup> (Equation 1).



The reaction of NO<sub>2</sub> with sulfite generates sulfite radicals (Equation 2), which react with oxygen to generate additional sulfite radicals (Equation 3). The sulfite radicals eventually oxidize to sulfate or dithionate ions (Equations 4–6). This reaction mechanism was determined by Nash (1979) and Huie and Neta (1984).



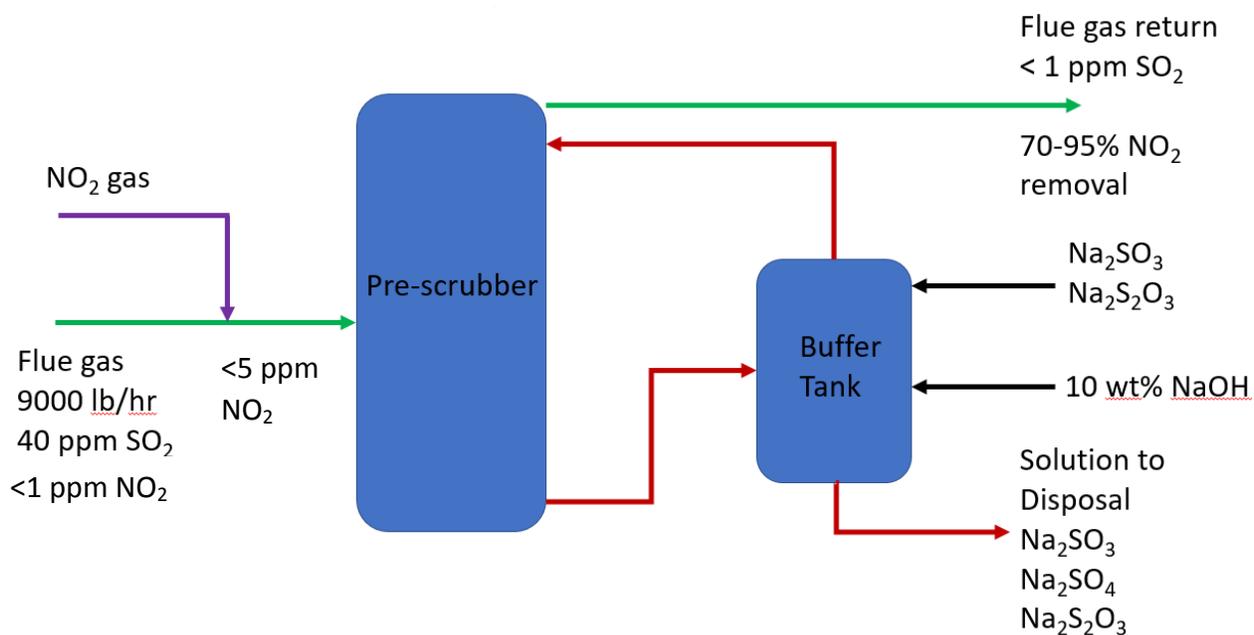
Due to the free radical oxidation, multiple moles of sulfite are oxidized for every mole of NO<sub>2</sub> absorbed. To reduce sulfite oxidation, thiosulfate can terminate the free radical reaction as shown by Owens (1984).



The objective of this work was to study sulfite oxidation rates with SO<sub>2</sub> scrubbing by Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> to determine the feasibility of thiosulfate-inhibited sulfite absorption of NO<sub>2</sub> at the pilot-scale. An ideal NO<sub>2</sub> removal process must remove at least 90% of NO<sub>2</sub> by maintaining a useful concentration of sulfite.

### ***Experimental***

A diagram of the pilot-scale test equipment is shown in Figure 1. The experiments were completed using a 1400-gal prescrubber tank containing water and 10 wt % NaOH fed with flue gas from a coal-fired power plant. The pH was maintained between 7.5 and 9 by adding NaOH when the pH dropped below 8. Flue gas containing 40 ppm SO<sub>2</sub> and <1 ppm NO<sub>2</sub> was fed at about 9000 lb/hr. The SO<sub>2</sub> was converted to sulfite and sulfate, with 99% SO<sub>2</sub> removal. Solvent was circulated from the prescrubber to a buffer tank at a rate of 1500 lb/hr. Water condensation from the flue gas increased total tank level over the campaign, diluting the added thiosulfate. The level was initially reduced to 30% when adding sulfite, thiosulfate, and EDTA, then allowed to increase to 80%. From there the level was maintained between 60 and 80% by draining excess solution. After running for one week with 0–1 ppm NO<sub>2</sub>, concentrated NO<sub>2</sub> was added to the flue gas to increase the concentration to 3–5 ppm NO<sub>2</sub>.



**Figure 1: Process Flow Diagram of Scrubbing Test Equipment**

Sodium sulfite, sodium thiosulfate pentahydrate, and EDTA were purchased from Fischer Scientific. All solid chemicals were dissolved in water before adding to the buffer tank. The supplemental NO<sub>2</sub> flowrate was maintained by a valve rather than a controller, which maintained a constant flow of NO<sub>2</sub> based on average gas flowrate rather than a specific concentration.

After measuring initial concentrations of the prescrubber solvent, chemicals were added to increase the sulfite to 22 mmol/kg, thiosulfate to 120 mmol/kg, and EDTA to 0.02 mmol/kg. After running for a week, the thiosulfate concentration was further increased to 230 mmol/kg.

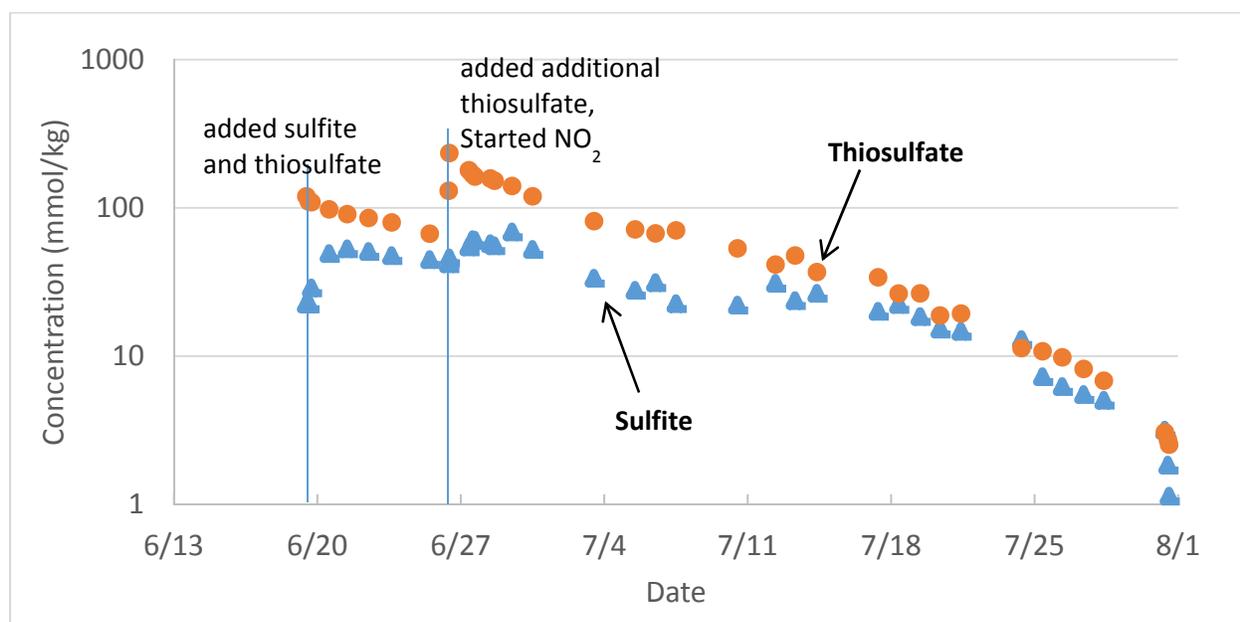
At fixed points during the campaign liquid samples were collected from the tank. Samples of 10 g were immediately mixed with 2 g of 35 wt % formaldehyde to react sulfite to form methylsulfonic acid, which does not oxidize like sulfite at room temperature. The samples were shipped to Austin for further analysis. Liquid samples were diluted 30x with distilled water and analyzed by anion chromatography to determine the rate of sulfite oxidation.

### ***Safety***

Because NO<sub>2</sub> exposure can cause respiratory damage and skin corrosion, care was taken to avoid exposure to NO<sub>2</sub> gas. The supplemental NO<sub>2</sub> gas cylinder was stored in a gas cabinet operated at a negative pressure, with multiple NO<sub>2</sub> sensors around the cabinet to detect any leaks. All personnel were required to wear personal NO<sub>2</sub> sensors as an extra precaution. All personnel wore hard hats, safety glasses, steel-toed boots, and reflective vests for general plant safety.

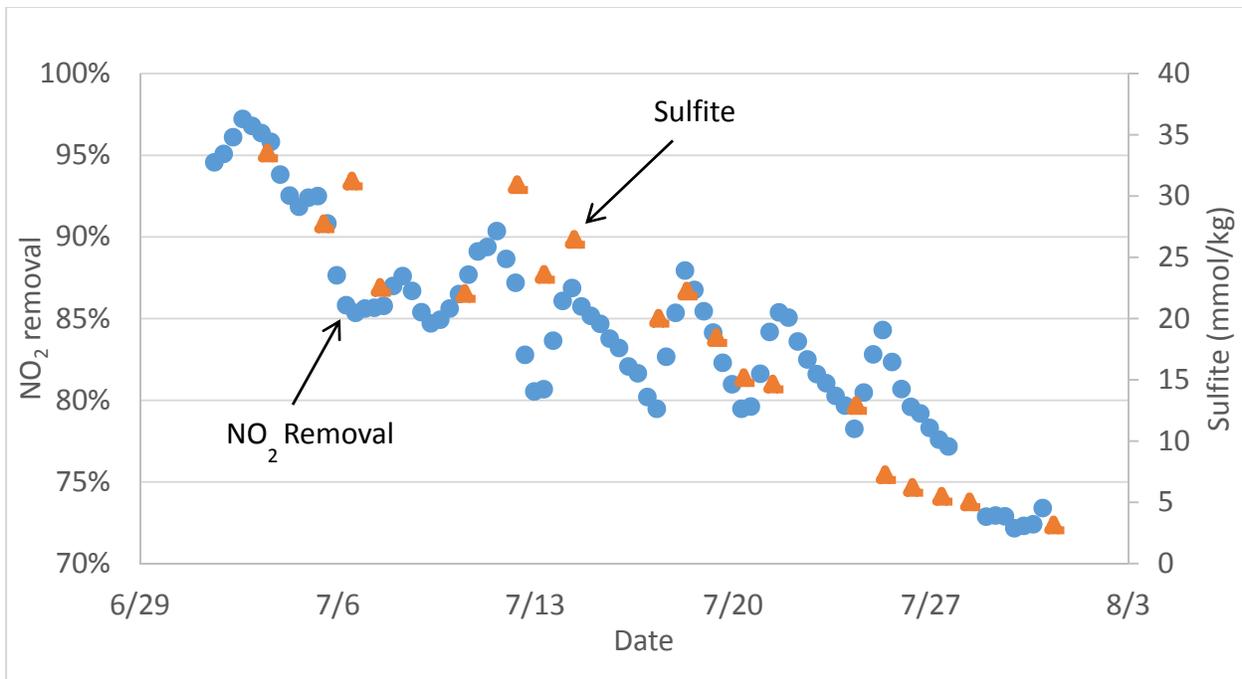
## Results

Figure 2 shows the concentration of sulfite and thiosulfate in the buffer tank during the campaign. After the initial addition of sulfite, thiosulfate, and EDTA with no  $\text{NO}_2$  flow, sulfite concentration was 22 mmol/kg and thiosulfate was 120 mmol/kg. During the first few days, the sulfite concentration increased significantly to 53 mmol/kg, showing that thiosulfate effectively reduced oxidation. As the thiosulfate dipped below 90 mmol/kg, the sulfite reached steady state at 45 mmol/kg. Beginning in week 2, the  $\text{NO}_2$  was increased to 5 ppm and the thiosulfate was increased to 230 mmol/kg. With these changes, the sulfite concentration increased further and reached steady state. From weeks 2–6, sulfite loss was first order with respect to sulfite, with a rate constant of  $k = 3.0 \text{ hr}^{-1}$ . This rate is an order of magnitude slower than previous bench-scale experiments, which produced rate constants of 50–400  $\text{hr}^{-1}$ . This is due to the constant feed of 40 ppm  $\text{SO}_2$  in the pilot-scale testing, compared to the fixed solvent volume in the bench-scale apparatus. Modifying the bench-scale apparatus to provide a constant feed of sulfite and intermittent bleed of sulfate may provide similar conditions for additional testing. On the final day of the experiment, the remaining supplemental  $\text{NO}_2$  was fed to the scrubber, rapidly oxidizing the remaining sulfite and thiosulfate.



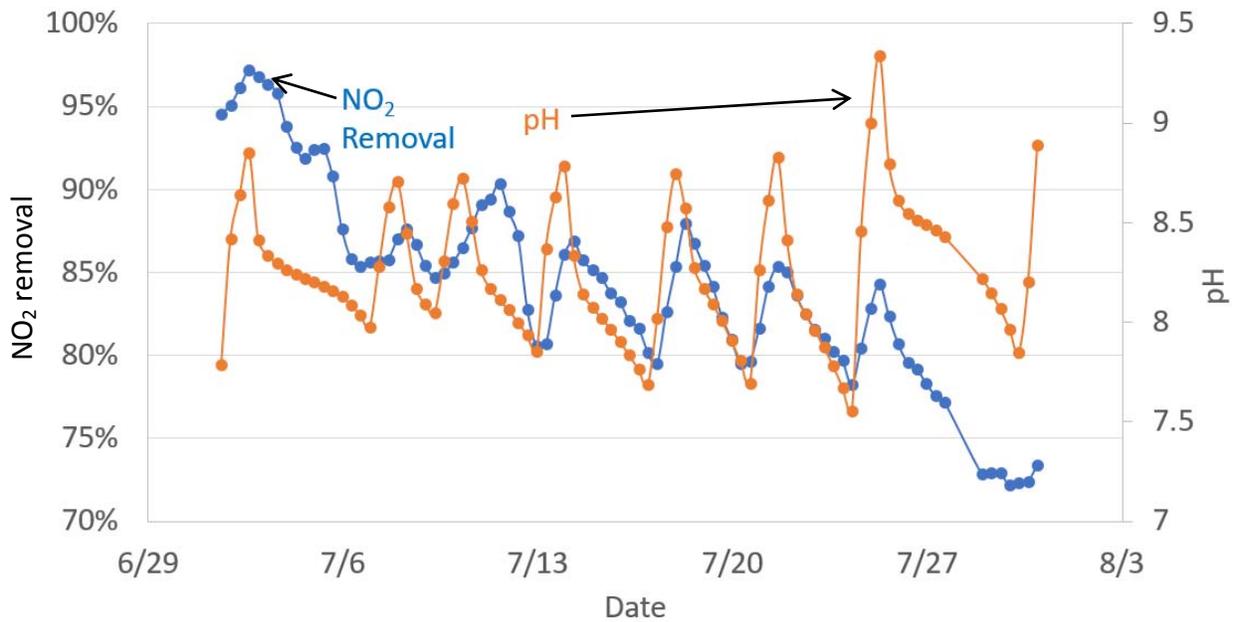
**Figure 2: Sulfite and thiosulfate oxidation due to  $\text{NO}_2$ . 9000 lb/hr flue gas, 40 ppm  $\text{SO}_2$ ,  $\leq 5$  ppm  $\text{NO}_2$ , 5–7%  $\text{O}_2$ .**

Figure 3 shows the  $\text{NO}_2$  removal and sulfite after  $\text{NO}_2$  was increased to 5 ppm. The total  $\text{NO}_2$  removal was initially 95–98% using 35 mmol/kg sulfite. Over the following days, the removal decreased a minimum of 72%. As the thiosulfate becomes further diluted, sulfite oxidation outpaces sulfite production and total sulfite decreases. Only 3 mmol sulfite/kg is sufficient to remove over 70% of the  $\text{NO}_2$ , and 25 mmol/kg of sulfite is needed to remove 90%. Additionally, the  $\text{NO}_2$  removal is cyclical with multiple peaks and valleys, which will be discussed further in Figure 4. Further research is needed at lower sulfite to remove 50–70% of  $\text{NO}_2$ .



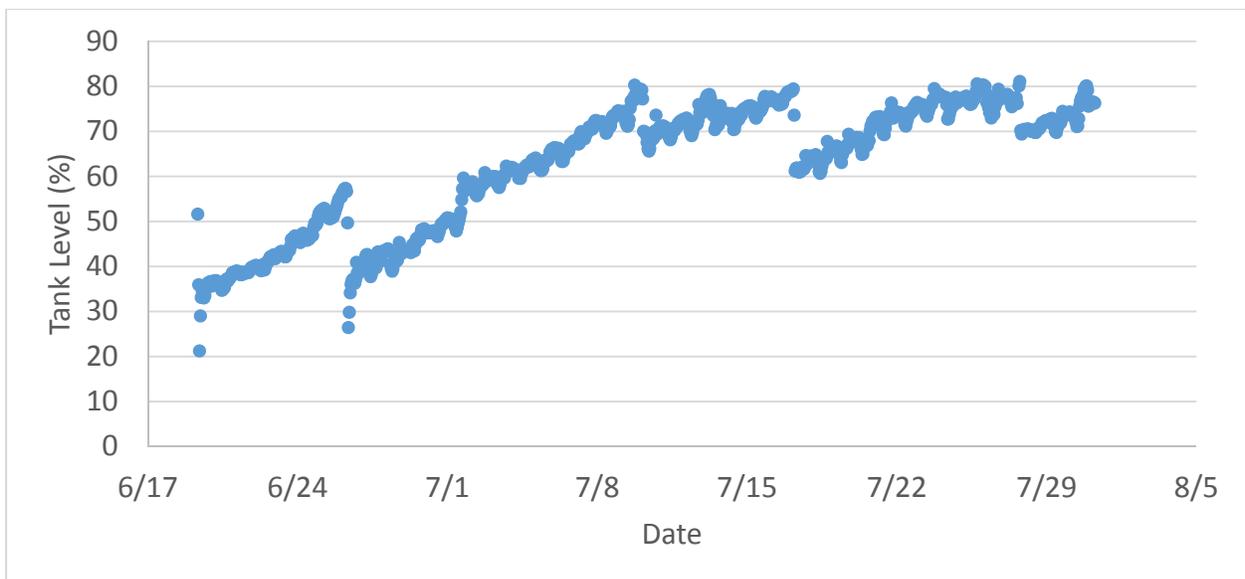
**Figure 3: NO<sub>2</sub> removal decreases as sulfite oxidizes to sulfate, 5 ppm NO<sub>2</sub>, 3–35 mmol/kg sulfite.**

Figure 4 again shows the NO<sub>2</sub> removal compared to pH. There is a strong effect of pH on NO<sub>2</sub> removal, with increases in pH immediately preceding increases in removal. A pH change of 1.5 points provides an increase in removal of 5–8%, regardless of the sulfite concentration. This has two possible causes: a change in the bisulfite/sulfite ratio and a change in the sulfite oxidation rate. Bisulfite is an order of magnitude slower than sulfite at removing NO<sub>2</sub>, so an increase in pH may reduce the bisulfite/sulfite ratio and effectively increase the concentration of sulfite. In addition, the increased pH may reduce the sulfite oxidation rate in the liquid film, providing more NO<sub>2</sub> removal even if the bulk sulfite is reduced.



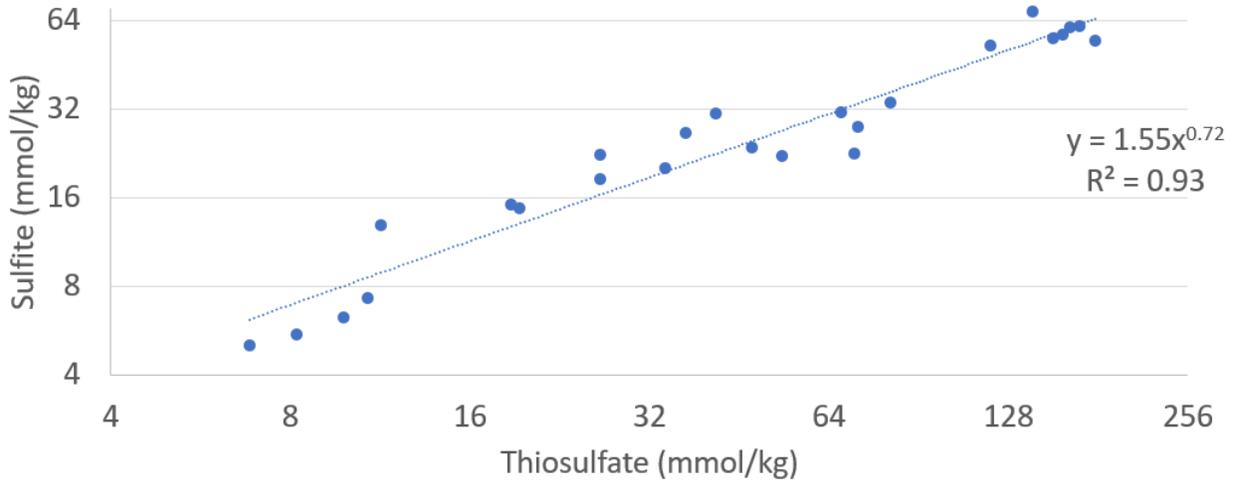
**Figure 4: NO<sub>2</sub> removal cyclical behavior is highly correlated to cyclical pH changes**

Figure 5 shows the tank level (%), including startup and maintenance phases. The tank level was reduced to 30% each time thiosulfate was added, followed by a slow increase of 2–4% per day. After reaching 80% of capacity at the end of week 3, the level was maintained between 60 and 80% by intermittent dumps of solution. Small spikes in the tank level were due to additions of NaOH when the pH decreased below 7.5. The intermittent dumps provided the only control on the concentration of sulfate, which otherwise accumulated in the prescrubber tank.



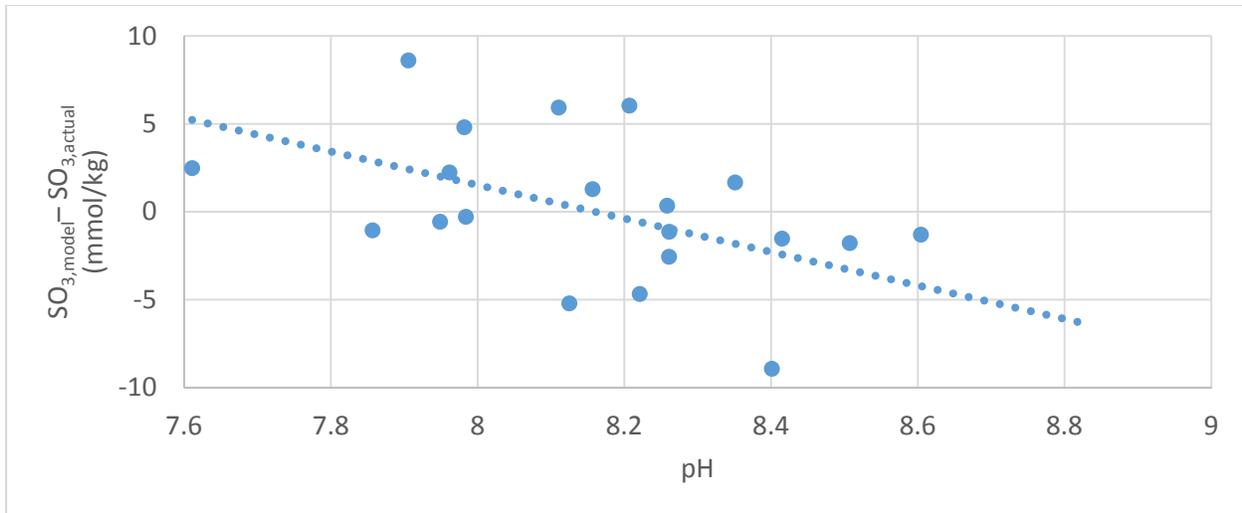
**Figure 5: Prescrubber tank level increase and maintenance**

Figure 6 shows sulfite vs thiosulfate with supplemental NO<sub>2</sub> added. With a flue gas containing 40 ppm SO<sub>2</sub> and 5 ppm NO<sub>2</sub>, there is a power law correlation between the thiosulfate concentration and the resulting sulfite that can be maintained. If the thiosulfate is doubled, sulfite increases by 1.6. The correlation was developed between 5 and 180 mmol/kg of thiosulfate. The effects of increased gas flow on sulfite are mixed, as increased NO<sub>2</sub> reduces prescrubber performance but increased SO<sub>2</sub> produces additional sulfite. Ideally, the sulfite concentration can be controlled by adding thiosulfate. However, if condensation occurs then thiosulfate must be added frequently to maintain performance.



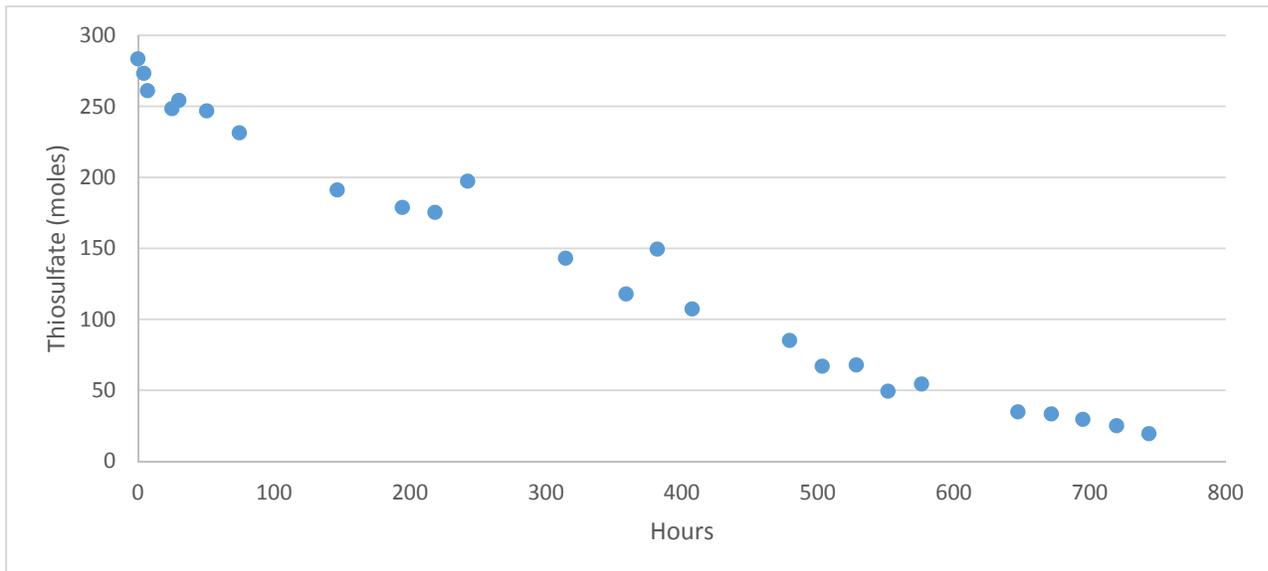
**Figure 6: Sulfite maintained by addition of thiosulfate, 9000 lb/hr flue gas, 40 ppm SO<sub>2</sub>, 5 ppm NO<sub>2</sub>.**

Figure 6 shows the residuals of the thiosulfate-sulfite model linearly correlated with pH. The model is based on an average pH of 8.2 in the prescrubber, but the actual pH varies from 7.5–9. At low pH, the model overestimates the concentration of sulfite, and underestimates at high pH. This suggests the rate of sulfite oxidation is reduced at high pH, and therefore higher sulfite can be maintained by increasing pH with no increase in thiosulfate.



**Figure 7: Sulfite model residuals overestimate sulfite production at less basic conditions.**

Figure 8 shows the total moles of thiosulfate after the second addition over 750 hours. A total of 260 moles of thiosulfate were lost during this period, 60 moles due to disposal of solution to maintain tank level, for an average of 0.27 mol thiosulfate / hr lost due to oxidation. The dominant mechanism for thiosulfate loss during testing was due to oxidation and reaction, and not via blowdown to maintain tank level. Given a flue gas rate of 9,000 lb/hr, 5 ppm  $NO_2$  and 12%  $CO_2$ , the total thiosulfate replenishment required is 0.4 mol thiosulfate / mol  $NO_2$ , or  $2 * 10^{-5}$  mol thiosulfate / mol  $CO_2$ . Assuming a cost of \$0.70 / lb of sodium thiosulfate, the thiosulfate replenishment cost is \$0.18 / MT  $CO_2$ .



**Figure 8: Thiosulfate loss due to both oxidation and solution disposal.**

## ***Conclusions***

The addition of thiosulfate was successful in inhibiting sulfite oxidation and removing over 90% of the NO<sub>2</sub> from flue gas. 98% NO<sub>2</sub> removal was initially achieved, decreasing to 85% as sulfite decreased from 60 mmol/kg to 20 mmol/kg. A minimum pH of 8.5 increases NO<sub>2</sub> removal by up to 8% compared to a minimum pH of 7.5. High thiosulfate allowed for the increased production of sulfite from the inlet SO<sub>2</sub>, and as thiosulfate decreased the sulfite steady-state concentration decreased simultaneously. Based on 40 ppm SO<sub>2</sub> and 5 ppm NO<sub>2</sub> contained in the flue gas, 50 mmol/kg thiosulfate can maintain a sulfite concentration of 25 mmol/kg, which is sufficient to remove 90% of NO<sub>2</sub>.

## ***Acknowledgements***

This work was done as a collaboration with Trimeric Corporation as part of a Small Business Innovation Research (SBIR) grant from the Department of Energy. We thank our colleagues at NCCC who provided their expertise that greatly benefited this campaign, with special thanks to John Carroll, Graham Bingham, and Cindy Dillard for their time and effort.

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