

DEVELOPMENT OF PROCESS TO SIMULTANEOUSLY SCRUB NO₂ AND SO₂ FROM COAL-FIRED FLUE GAS

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INTRODUCTION

The CombiNO_x process is being developed to provide a low-cost method of controlling the NO_x emissions of coal-fired utility boilers to very low levels. This process incorporates a family of NO_x reduction technologies including staged combustion, Advanced Reburning (i.e. reburning combined with selective non-catalytic reduction) and methanol injection to convert NO to NO₂ which can then be removed by wet scrubbing. While individually these technologies are limited in their NO_x reducing capabilities, in combination they are capable of reducing NO_x emissions to extremely low levels at a fraction of the cost of selective catalytic reduction.

The methanol injection step, however, is subject to the limitation that one must have a scrubber that will remove NO₂. The removal of SO₂ and NO₂ by sodium-based wet scrubbers is a well-established technology, but the majority of wet scrubbers currently in use are calcium based. Accordingly, this study was undertaken to determine whether or not the chemistry which occurs in calcium based scrubbers could be modified to allow removal of NO₂ as well as SO₂.

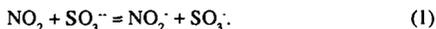
Bench-scale experiments were performed in conjunction with chemical computational modeling to evaluate the effect of scrubbing solution composition on SO₂ and NO₂ scrubbing efficiency. In addition, potential by-products were identified. Finally, larger pilot-scale tests were performed with a packed tower scrubber to address scale-up issues and confirm the bench-scale results.

BENCH-SCALE STUDIES

The bench-scale NO₂ scrubbing apparatus is displayed in Figure 1. A simulated flue gas containing variable amounts of NO₂ and SO₂ was flowed through a constant temperature, 80 cubic centimeter, bubbler containing the scrubbing solution to be evaluated. After passing through the "scrubber", the gas was analyzed for O₂, NO_x, N₂O, and SO₂ to determine removal efficiencies.

Figure 2 graphically summarizes the bench-scale results. The numbers symbolize various cases that were performed while varying slurry composition, the lines show the resulting performance as a

function of time. A $\text{Ca}(\text{OH})_2$ solution (2 percent $\text{Ca}(\text{OH})_2$ by weight) achieved 99+ percent SO_2 reduction, indicating that the scrubber provides good mass transfer. However, only 50 percent of the NO_2 was removed. Reference 1 indicates that the crucial reaction for NO_2 scrubbing is:



With pure $\text{Ca}(\text{OH})_2$ solution, the necessary sulfite ion (SO_3^{2-}) tends to precipitate out as calcium sulfite, instead of reacting, as desired, with NO_2 .

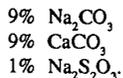
Since sodium sulfite (Na_2SO_3) can provide the necessary sulfite ions for NO_2 absorption, a 2 percent solution was evaluated. 99+ percent SO_2 and 89 percent NO_2 capture was obtained initially, however, this performance decreased after approximately 2 minutes of run time. After these 2 minutes, SO_2 reduction became negative and NO_2 reduction dropped to 17%. SO_2 is captured via the reaction



and NO_2 via reaction (1). Unfortunately, the SO_3^- generated by NO_2 removal is a chain carrier in the oxidation of sulfite and bisulfite ions to sulfate and bisulfate ions. Oxidation of the bisulfite ion to the bisulfate ion acidifies the solution, forcing SO_2 back into the gas phase.

Adding $\text{Ca}(\text{OH})_2$ to the Na_2SO_3 scrubbing solution eliminates the problem of SO_2 rejection by keeping the solution basic, however the NO_2 capture remains poor and short lived. Replacing the highly soluble $\text{Ca}(\text{OH})_2$ with very low solubility CaCO_3 increases the concentration of sulfite ion that stays in solution. This improves NO_2 absorption, but the sulfite ion quickly oxidizes to sulfate, hampering NO_2 removal. Experiments were conducted under conditions which inhibited the oxidation of sulfite to sulfate (i.e. decreasing reaction temperature and/or flue gas oxygen content). Even though these conditions can not be applied to a real application, they did show that if sulfite ion stays in solution, NO_2 capture improves and can be sustained for a longer period of time.

Sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) has been proposed as a method of inhibiting the oxidation of sulfite to sulfate (2). We found that by adding this compound to the scrubbing solution (1% by weight), 95% NO_2 capture was achieved and this capture was sustained for the duration of the test. Based on these results, the recommended slurry solution to achieve 99+ percent SO_2 and 95 percent NO_2 at bench-scale level is:



This scrubbing mixture was studied computationally using the mechanism of Chang et al. (1). For the batch experiments, the reaction was found to proceed in three stages. During the first stage, carbonate ion concentration falls while the concentrations of sulfate, bisulfate and sulfite ion increase. This first stage ends when the ratio of carbonate to sulfite ion becomes so low that calcium carbonate starts to dissolve while calcium sulfite precipitates. During the second stage, the ratio of the concentrations of carbonate and sulfite ion are constant and the pH remains fairly steady. The

concentration of sulfate ion increases until calcium sulfate starts to precipitate. The second stage ends when the calcium carbonate is exhausted. When this happens the pH begins to rise until it reaches a level at which SO_2 absorption fails and scrubbing solution is spent.

The model predicts that NO_2 capture will remain effective through these three stages of the process, but the fate of absorbed NO_2 changes. During the first and second stages nearly all of the absorbed NO_2 will be present as nitrite ion, with only trace amounts of the complex nitrogen sulfur ions being formed. During the third stage, however, the nitrite ion is converted to complex nitrogen sulfur ions, chiefly the aminetrisulfonate ion. Near the end of the third stage the aminetrisulfonate ions are hydrolyzed to sulfate ion and sulfamic acid.

While the model contains reactions which are capable of forming N_2O and nitrate ions, these reactions are only significant at very low pH. During the bench-scale experiments samples were taken of the bubbler's exhaust and, consistent with the models predictions, no significant N_2O production was observed. Measurements were also made with EM Quant test strips on spent scrubbing solution. As one would expect from the model, nitrite ion was found in fresh solution but not in solution which had been allowed to age. Nitrate ions were not detected in the spent solution.

PILOT-SCALE STUDIES

Scale-up effects were investigated in two different pilot-scale facilities corresponding nominally to heat inputs of 2 MMBtu/hr and 10 MMBtu/hr. The small pilot-scale scrubber tests were performed by Research Cottrell using the facility illustrated in Figure 3. The small pilot-scale scrubber consists of a propane combustor, absorber tower, absorber feed tank, analytical train, and solid disposal system. To simulate a coal-fired flue gas, variable amounts of SO_2 and NO_2 were doped into the exhaust upstream of the absorber tower. At the absorber tower exit, NO_x , SO_2 , CO , and O_2 were measured. The absorber tower is a vertical, stainless steel, 16 inch diameter tube, approximately 20 feet in height. The simulated flue gas enters the tower from the bottom, travels through five sections to the top, and exits to the gas sample conditioning systems and analyzers. The first two sections can be packed with a light packing material to provide improved gas/liquid contact. Sections of the tower may also be removed, if desired, to reduce absorber tower residence time. The scrubber slurry is continually being mixed with dry limestone, sodium salts, and water in the absorber feed tank. From the 200-gallon feed tank, the slurry is pumped to the top of the absorber tower and dispensed in counter flow to the flue gas with a single slurry nozzle. The slurry solution is drained by gravity from the bottom of the tower back to the feed tank.

The first tests were performed to verify that SO_2 removal was possible on the pilot-scale scrubber. For a 6 percent limestone slurry, flue gas flow rates were varied between 127 - 140 cfm, and slurry flow rates were maintained at 12 gpm. Up to 99 percent SO_2 removal was obtained indicating satisfactory mass transfer.

Simultaneous scrubbing of NO_2 and SO_2 was evaluated using scrubbing salts consisting of 49.5 percent CaCO_3 , 49.5 percent Na_2CO_3 , 1 percent $\text{Na}_2\text{S}_2\text{O}_3$. Note this is approximately 1/5 of the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ utilized in the bench-scale tests. During this test series, the following parameters were varied: liquid/gas ratio (liquid flow and gas flow were independently varied),

concentration of sodium carbonate in slurry, concentration of sodium thiosulfate in slurry, and initial NO_2 concentration. NO_2 removal efficiency ranged between 65 and 90 percent while maintaining 97 - 99 percent SO_2 removal.

The ratio of slurry flow rate to flue gas flow rate is defined as the liquid to gas ratio (L/G), and is expressed here in units of (gallons of slurry)/(1000 cubic feet of gas). The slurry flow and gas flow were varied independently of one another. Figure 4 summarizes the effects of L/G ratio on NO_2 scrubbing efficiency. As would be expected, a larger L/G ratio results in higher NO_2 removal. Even though not depicted in the figure, data indicate that gas flow rate has a larger affect on the NO_2 scrubbing efficiency than slurry flow rate. By decreasing the gas flow rate by a small fraction (from 135 to 115 cfm), efficiency increased from 77 to 84 percent. However, when the slurry flow rate was nearly doubled (11.4 to 20 gpm), the efficiency only increased by approximately the same amount, 77 to 85 percent.

Experiments were performed to determine the effect of initial NO_2 concentration on NO_2 scrubbing efficiency. Slurry flow rate remained approximately constant as inlet NO_2 concentration was varied by adjusting the doping gas flow rate. Results are displayed in Figure 5. The general trend shows that scrubbing effectiveness drops as initial NO_2 concentrations increase.

The effect of Na_2CO_3 concentration on NO_2 and SO_2 scrubbing efficiency was evaluated by diluting the scrubbing solution by a factor of two, while continuing to add limestone to maintain pH and ion concentration. Figure 6 shows that even though scrubbing efficiency was initially hampered by the dilution that occurs 200 minutes into the test, with time the NO_2 removal efficiency rose again to approximately the same level as before the dilution. Even after diluting the slurry a second time, the NO_2 scrubbing efficiency returned to almost the original value. These data indicate that NO_2 removal efficiency is not sensitive to Na_2CO_3 concentration in this range.

The effect of sodium thiosulfate concentration was tested by adding an additional 3.8 mmol of sodium thiosulfate per liter of solution. As expected, NO_2 removal efficiency jumped from 65 percent to 89-90 percent within 15 minutes, and SO_2 removal efficiency remained at 99+ percent. The thiosulfate inhibits oxidation of sulfite to sulfate, sustaining the presence of sufficient sulfite ions for NO_2 capture.

Throughout the experiments discussed above, scrubbing solution composition measurements were periodically taken. In general, these observations were consistent with the model and the assumption that the scrubber was operating in the second stage (see previous discussion). The model is, however, limited in its ability to account for sulfite ion oxidation, therefore, not surprisingly, sulfite to sulfate conversion was much higher than predicted. The small pilot-scale studies also show nitrate ion as a major product, contradicting both model's prediction and the bench-scale results.

A single test was performed in EER's large pilot-scale facility. The large pilot-scale scrubber facility consists of a simple spray tower with a pad-type demister. The spray tower is 6 ft in diameter and 16 ft high, with an array of 16 spray nozzles. Natural gas combustion products were doped with NO_2 to a concentration of 74 ppm. SO_2 was not added. The test was conducted at an L/G ratio of approximately 30 gal/1000 acf and the scrubbing solution was 9 percent CaCO_3 /9 percent NaOH /1

percent $\text{Na}_2\text{S}_2\text{O}_3$. The test results are also shown in Figure 4. Much higher NO_2 removal was achieved than was expected based on the small pilot-scale results. This may have been due to the much higher concentration of sodium thiosulfate used in the large pilot-scale test. However, additional tests are necessary to validate this hypothesis. The results do indicate that high NO_2 removal efficiencies can be achieved even with a relatively primitive scrubbing system operating at L/G ratios similar to that of large commercial scrubbers.

DISCUSSION

The primary goal of this research, demonstration of efficient NO_2 and SO_2 scrubbing in a calcium based wet limestone scrubber, has been achieved. Two important questions, however, remain with respect to the disposability of the products produced by this modified scrubber. First, there is the question of whether or not using sodium compounds in the scrubbing solution will result in unacceptable sodium contamination of the calcium sulfate/sulfite product. Since wet scrubbers require considerable amounts of makeup water, it is theoretically possible to solve this problem by washing the calcium sulfate/sulfite with the makeup water, but this option would require an engineering design study which has not been done.

The second question of disposability regards the formation of nitrate ion seen in the pilot-scale experiments. This ion formation was not detected during bench-scale or computer modeling studies. One possible explanation for this discrepancy is that as the scrubbing liquid passes downward through the absorber tower, it reaches a point at which its ability to absorb SO_2 is completely exhausted. This low pH condition was not considered in the modeling study, yet it may be responsible for the increase in nitrate concentration. Mechanisms within the computer model do, in fact, show nitrate ion formation at low pH levels.

While the possible formation of nitrate ion will require further research, there are a number of ways in which this problem might be solved. Adjustment of scrubbing conditions so that the solution is prevented from over-reacting may prevent nitrate formation. Alternatively, if nitrate forms by oxidation of nitrite ion, the removal of nitrite ion by reaction with $\text{NH}_2\text{SO}_3\text{H}$ may prevent nitrate formation, or, all else failing, nitrate ion could be removed by selective reduction with scrap aluminum (3). In a brief study the authors found that this method works quite well with shredded soda cans as the source of aluminum.

ACKNOWLEDGMENTS

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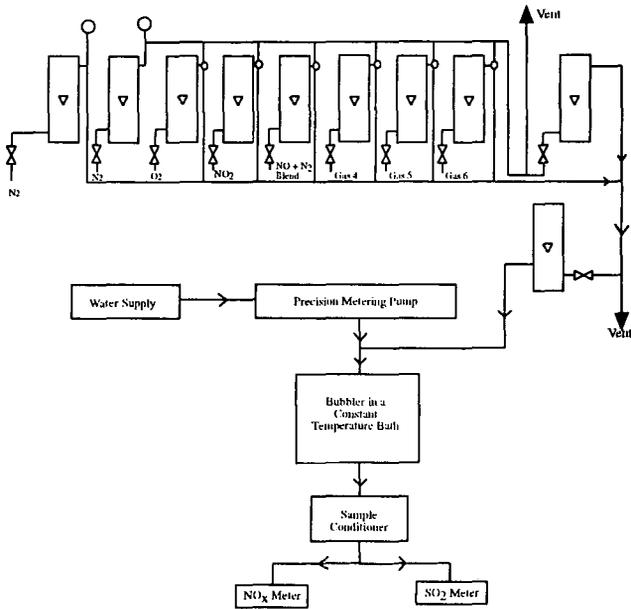


Figure 1. Experimental set-up for NO_2/SO_2 scrubbing experiments.

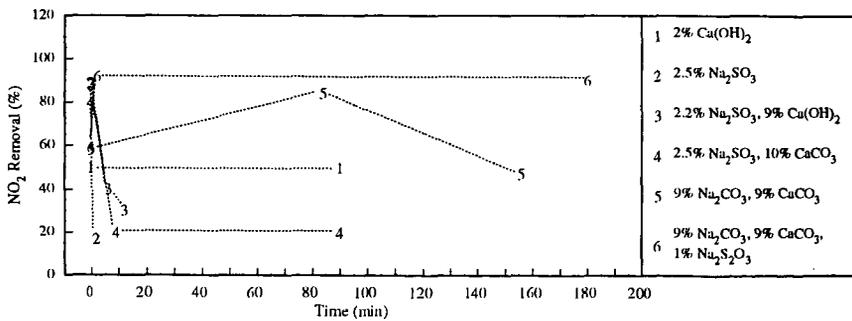


Figure 2. Bench-scale scrubbing studies results.

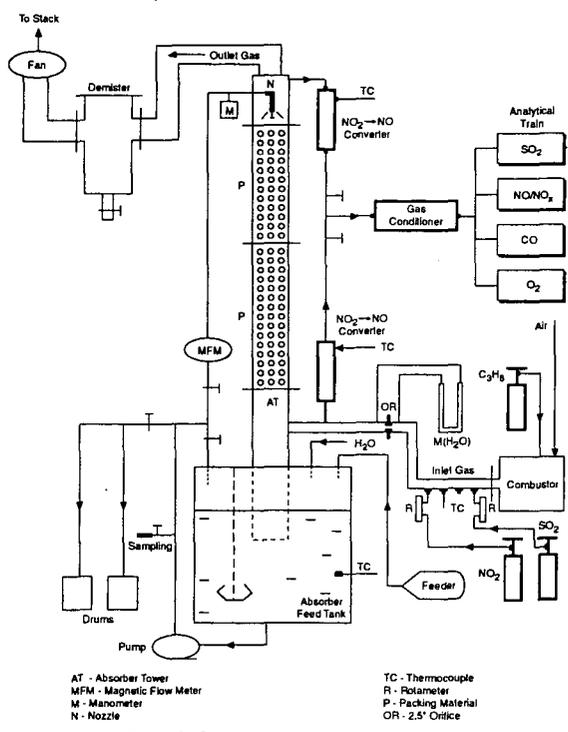


Figure 3. Schematic of the pilot-scale scrubber.

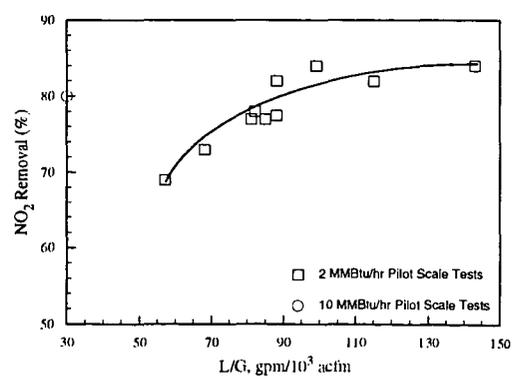


Figure 4. Effect of liquid to gas ratio on NO₂ removal.

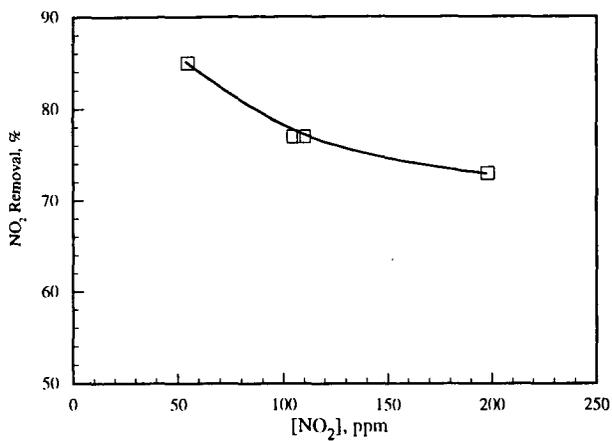


Figure 5. Effect of initial NO₂ concentration on NO₂ removal.

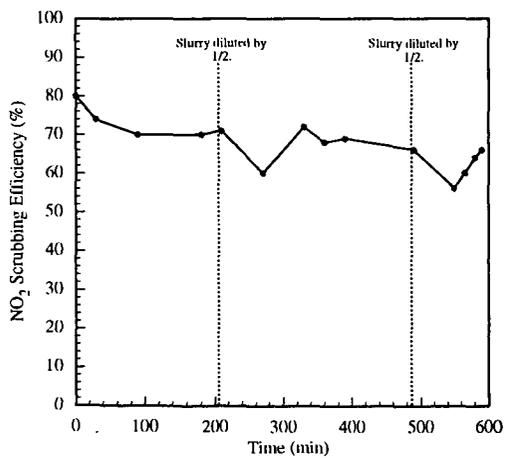


Figure 6. Effect of Na₂CO₃ dilution on NO₂ scrubbing performance.