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# Combined $NO_x/SO_2$ Control with Dry Sorbents

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# COMBINED $NO_x/SO_2$ CONTROL WITH DRY SORBENTS

## INTRODUCTION

The use of dry sorbents in flue-gas cleanup (FGC) systems has become increasingly important with the emergence of spray-dryer systems, the renewed interest in furnace injection of sorbents (LIMB), and the ongoing development of numerous duct-injection technologies. In general, the sorbents used in these processes are designed solely for the removal of sulfur dioxide ($SO_2$), but there could be clear advantages for systems capable of also removing nitrogen oxides ($NO_x$). This is particularly true in light of the growing concerns over $NO_x$ emissions in connection with acid deposition, and the possibility of new, more stringent requirements for control of $NO_x$ from stationary sources.

Argonne National Laboratory (ANL) has been conducting research on combined $NO_x/SO_2$ control systems for the U.S. Department of Energy (DOE) since 1981. Recently, the research program has been focused on spray-dryer-based FGC systems and has involved research on $NO_x$ removal enhancement through chemical additives and modified process conditions. Tests have been conducted in a laboratory-scale spray dryer at ANL[1], an intermediate-scale system at the Pittsburgh Energy Technology Center[2], and Argonne's commercial-scale spray-dryer/fabric-filter system[3]. In addition, the performance of dry sorbent/additive combinations under a variety of conditions has been studied at ANL using a laboratory-scale fixed-bed reactor. The experimental conditions were selected to model the post air-preheater environment for a boiler firing high-sulfur coal, and to specifically address conditions expected in the fabric filter portion of a spray dryer or duct injection system.

In the remainder of this paper, we describe the fixed-bed experimental facility and the results of both statistically designed and parametric experiment series conducted using a lime ($Ca(OH)_2$) sorbent and a variety of additives. While considerable research is still required to fully understand the removal reaction mechanisms involved, a number of significant factors affecting removals are identified and evaluated. These include both individual variables and a number of interactions between process variables.

## RESEARCH APPROACH

The fixed-bed reactor system and the experiment program were designed to rapidly screen, on a consistent basis, a variety of chemical additives and process modifications. The latter included flue-gas/sorbent temperature and flue-gas composition ($NO_2$ and moisture concentrations). The additives included compounds known to be effective in wet scrubbers (e.g., Fe(II)EDTA), sodium-based compounds such as NaOH (based in part on results reported by Niro Atomizer[4]), and chloride-containing compounds (NaCl and $CaCl_2$) that might affect sorbent moisture content. Following the initial screening in a fractional factorial experiment design, the three most active additives (NaOH, NaCl, and $NaHSO_3$) were tested further in follow-on experiments using a full-factorial design to better evaluate the effects of interactions between the experimental variables. Lastly, the same three additives were tested in a series of parametric experiments where the $SO_2$ concentration in the flue gas was varied.

### Experimental Apparatus

The equipment used in these experiments was divided into five separate subsystems -- the flue-gas blending and feed system, the flue-gas analyzer system, the fixed-bed reactor system, the data acquisition system, and the laboratory exhaust system. A diagram of the system is shown in Figure 1.

The flue-gas blending and feed system used cylinders of pure gases and "house" air to produce a controlled gas composition representative of flue gas from high-sulfur coal combustion. A metering system enabled the operator to easily change the composition of key gases such as $SO_2$ and $NO_2$ as needed for specific experiments. The air and nitrogen streams were metered into a humidifier, which was maintained at a controlled temperature to govern the moisture content of the resulting, saturated gas stream. Carbon dioxide was used as a carrier gas for the NO and $NO_2$ pollutant feeds. The $CO_2/NO/NO_2$ stream was added to the humidified air/$N_2$ stream at the humidifier exit. The $SO_2$ stream was piped separately and added downstream of the $CO_2$ addition point to insure thorough dilution of the NO and $NO_2$ before contacting them with the $SO_2$. In order to prevent condensation and premature scrubbing of the pollutant gases, the feed stream was heat-traced from the humidifier exit to the fixed-bed reactor and flue-gas analyzer systems.

The flue-gas analyzer system consisted of a sample-conditioning section to remove water vapor; individual gas analyzers for $CO_2$, $O_2$, $SO_2$, and $NO_x/NO$; and a six-point recorder. Both flue-gas feed and reactor effluent samples were delivered to the analyzer system in heat-traced Teflon® tubing maintained at or above 90°C to prevent condensation. At the analyzers, each sample stream first passed through a trap submerged in a wet-ice bath to remove excess moisture. It then passed through in-line filters and permeation driers before being analyzed. During an experiment, the data acquisition system controlled system operation by switching between the feed and the effluent streams and between the $NO_x$ and NO modes of the $NO_x$ analyzer. The sample sequence and timing was programmed into the computer and involved taking a pair of feed samples (one $NO_x$ and one NO determination) followed by three pairs of effluent samples. The difference between the $NO_x$ and NO determinations was taken to be the $NO_2$ concentration. The analyzer system was calibrated immediately before starting an experiment and then rechecked following each experiment.

The fixed-bed reactor system consisted of a flue-gas preheater, a heated enclosure, and the reactor itself. For safety, these components were all located in a hood connected to the laboratory exhaust system. The preheater was placed immediately ahead of the reactor and was used to raise the temperature of the flue gasses to the desired experimental conditions, since gases leaving the feed system were only heated to 70°C to maintain them above their dew point. To maintain the fixed-bed reactor at a uniform temperature, a heated enclosure was constructed using 18 in. diameter ceramic pipe insulation. This enclosure was fitted with three heating elements, a recirculation fan, an internal frame which supported the fixed-bed reactor, thermocouples, and temperature-limit switches for safety. The reactor used in these experiments was a 12.5 cm diameter Andersen air-sampling filter holder, which was used without modification to support a fixed bed of sorbent/additive. The holder was assembled with a Whatman glass-microfiber filter covering the fritted disk. Two gram moles of sorbent/additive were poured into the assembled filter holder and smoothed into a uniform, level surface (typically about 2 cm thick) by tapping on the side of the holder. Following the pretreatment step, described below, the furnace was opened to visually examine the fixed-bed. Any "cracks" which might have developed in the sorbent layer were eliminated by further tapping on the side of the filter holder.

The main gas flow from the reactor was purged to the laboratory exhaust system, which was designed to isolate the laboratory from the airspace of the rest of the building. The exhaust rate provided more than 10 air changes per hour in the laboratory itself, minimizing the exposure of occupants to any toxic gas leaks.

The laboratory data acquisition system included a 60-channel data logger, a mini-computer, a terminal, and a 1200-baud modem. The data logger scanned thermocouples and analog DC voltages from the flue-gas analyzer system, gas flowmeter, and pressure sensors at 10 sec intervals. These data were passed to the mini-computer which either averaged successive scans or discarded them depending of the status of the stream and $NO_x$/NO mode switching. The averaged data was stored on a floppy disk that became the permanent record of each experiment. The primary data analysis was done on Argonne's central, main-frame computer, which performed a simple material balance to determine removals of the pollutant species and prepared graphical displays of these results.

**Sorbent Preparation**

Several different approaches for applying chemical additives to the base sorbent ($Ca(OH)_2$) were evaluated early in the program on the basis of ability to produce a homogeneous sorbent/additive mixture containing the target amount of additive. The procedure selected used a concentrated solution of the additive in distilled water and called for spraying this solution over thin layers of the solid sorbent. The layers were then thoroughly mixed and dried overnight in a vacuum oven. These solids were then ground to less than 200 mesh and transferred to the reactor for an experiment.

The amount of powder transferred to the reactor was calculated to keep the total chemical equivalence of the cations (calcium plus additive cation) constant and equivalent to that of two gram moles of pure $Ca(OH)_2$. When an experiment called for untreated sorbent (0.0 mole % additive), reagent grade $Ca(OH)_2$ was sieved through a 200-mesh screen and loaded directly into the reactor. This was previously shown to give results equivalent to treatment of $Ca(OH)_2$ with pure water followed by drying and grinding.

Finally, the sorbent/additive powder was pretreated before the actual experiment by passing humidified nitrogen (dewpoint 70°C) through the reactor for two hours to attain an equilibrium moisture content. Following the pretreatment the furnace was opened to inspect the sorbent bed. Any cracks that had developed in the bed during the pretreatment were noted and eliminated by tapping on the side of the reactor. The reactor was blanketed with dry nitrogen until beginning the $NO_x/SO_2$ removal experiment.

**Experimental Design**

The additive screening and follow-on experiments used statistical designs in four variables. These were the additive type/concentration, moisture concentration in the flue gas, sorbent temperature, and $NO_2$ concentration in the flue gas. The additive screening experiments used a fractional factorial design (substituting the $NO_2$ effect for the third-order interaction between the first three variables), while a full-factorial design was used for the follow-on experiments by expanding the original screening experiment series. Additive-free experiments were performed as control experiments for each of the different additives. The flue-gas compositions and experimental conditions are shown in Table I.

Additives studied in the screening experiments fell into three groups. The first included compounds that had been shown to be effective in promoting $NO_x$ removal in wet scrubbers[5]. These included aluminum sulfate, aluminum sulfate/citric acid, and ferrous ethylenediaminetetraacetic acid (Fe(II)EDTA). The second group were sodium-based compounds selected because earlier work, including large-scale tests by Niro Atomizer, had shown sodium hydroxide to be effective in spray dryers for enhancing $NO_x$

removal[4]. This group included sodium hydroxide, sodium chloride, sodium bisulfite, and sodium sulfite. The third group contained compounds incorporating chloride ions. It overlapped with the second since it included sodium chloride as well as calcium chloride. These compounds were chosen because they could affect the moisture content of the powder and some spray drying research had indicated that such compounds improved spray-dryer removal efficiencies[6]. For the follow-on experiments, sodium hydroxide, sodium chloride, and sodium bisulfite were selected for more detailed evaluation. These experiments used the same set of conditions shown in Table I.

The $SO_2$ parametric experiments used flue-gas compositions ranging from 0 to 3000 ppm of $SO_2$ with 50 ppm $NO_2$ (500 ppm total $NO_x$), 15.0% water vapor by volume, and a reactor temperature of 65°C. These appeared to be the most favorable conditions for simultaneous $NO_x/SO_2$ removal based upon the results of the follow-on experiments. From a process perspective, these conditions would be fairly typical of the filtration environment in a spray-dryer/fabric-filter system. The sorbent/additive combinations selected for this phase of the study were pure $Ca(OH)_2$, $Ca(OH)_2/NaCl$, $Ca(OH)_2/NaHSO_3$, and $Ca(OH)_2/NaOH$. The first two additives were substituted at a 10 mole % level while the NaOH substitution was 20 mole %. The larger value for NaOH was used to make the conditions more comparable to those used in Argonne's large-scale spray-dryer tests.

## RESULTS

The primary result of each experiment was a plot of removal versus time for the principal pollutant species. A typical example is shown in Figure 2, which compares results for NO removal from three of the early experiments used to develop the sorbent/additive pretreatment procedures. The monotonically decreasing removals throughout each 2 hr experiment shown in Figure 2 are characteristic of all of the experiments run in the fixed-bed apparatus. In order to make numerical comparisons between experiments, the removals were interpolated for 5, 10, and 30 minutes after the start of the experiments. These values were then used to determine the effects of the experimental variables by processing the combined results of each data set using Yates's Algorithm.

Figure 2 also illustrates the important role of moisture in enhancing sorbent removal activity. As the moisture content in the pretreatment gas stream increased, the NO removal increased dramatically. Moisture had a similar effect on $NO_x$ and $SO_2$ removals. Higher moisture levels were not studied because of experimental system limitations.

### Additive Screening Experiments

The relative performances of all nine of the additives are compared in Table II for $NO_x$, NO, and $SO_2$ removals. The numerical value used to rank each additive is the difference between the mean removal percentage (at the time of interest) for the four experiments where the additive was used and the four experiments where no additive was used. Thus, a positive value represents an enhancement of removal by that particular additive over the removal observed for the unmodified $Ca(OH)_2$. A negative value indicates that the additive in question actually depressed the removal. These values are arranged in decreasing order of enhancement across Table II with the first column showing the mean values of the control experiments.

For example, the first additive entry under total $NO_x$ removal at 5 minutes indicates that the four experiments with NaOH (10 mole %) gave the greatest

enhancement over the control experiments by boosting total $NO_x$ removal 19.78 percentage points (from 28.7% up to 48.5%). On the other hand, both the chloride-containing additives actually depressed total $NO_x$ removal. At 10 minutes, NaOH (10 mole %) continued to be substantially better than the second best additive and was surpassed only slightly at 30 minutes by Fe(II)EDTA, which had steadily increased its relative performance over the course of the experiments. Also note how far NaCl rose in these rankings (from 8 to 5 to 3), whereas $CaCl_2$ remained in last place. The very poor performance of NaOH (20 mole %) was another surprise in this comparison. Its enhancement was virtually negligible throughout the course of these experiments. The contrast with respect to the very good performance of the NaOH (10 mole %) suggests that there might be an optimum additive concentration, at least for this species.

Sodium hydroxide (10 mole %) also was the best additive for increasing NO removal at 5 and 10 minutes but dropped to a very close second place at 30 minutes. Note that again NaCl steadily improved in relative performance throughout the course of the experiments and was ranked higher at all times for NO removal than it was for $NO_x$. The performance of Fe(II)EDTA also seemed to improve again, but the trend was not as clear as for total $NO_x$. The performance of $CaCl_2$ was again very poor, as it and several additives, including NaOH (20 mole %) gave a depression of the NO removal. In general the NO removal enhancements were smaller than those for total $NO_x$. This is because NO to $NO_2$ oxidation gave baseline NO removals that were greater than the total $NO_x$ removals and because the additives changed the extent of NO oxidation. While NO oxidation contributes to "nitrogen oxide" removal, the NO is only converted into another species, $NO_2$, which is counted among the "total $NO_x$".

While NaOH (10 mole %) also performed very well for $SO_2$ removal enhancement, it was only second at 5 and 10 minutes to the combination of aluminum and citric acid. However, at 30 minutes NaOH was the best performer with $NaHSO_3$ a close second and Al/CIT third. The high $NaHSO_3$ ranking later in the experiments is very interesting in that it was clearly the worst performer at 5 minutes. Aluminum sulfate also performed fairly well as did NaCl. The Fe(II)EDTA additive, which had been selected for its previously demonstrated performance in aqueous systems for NO removal, was somewhat of a surprise with substantial enhancement of $SO_2$ removal at both 5 and 10 minutes before dropping off dramatically at 30 minutes. Once again, $CaCl_2$ and NaOH (20 mole %) both showed little or negative effectiveness.

**Follow-on Experiments**

Analysis of the fractional factorial screening experiments indicated that a number of interactions or "cross effects" between the variables had significant influences on the removals. Therefore, additional experiments were run to expand the data set to a full factorial design for three of the most effective additives (NaOH, NaCl, and $NaHSO_3$). The results of those follow-on experiments are shown in Figures 3, 4, and 5, which give the relative values of each of the fifteen effects. The effects are grouped by the order (number of variables) of the effects -- first, second, third, and fourth order (note this is not the sequence generated by the Yates's Algorithm). Furthermore, the individual bars are coded to indicate the relative significance of the effects. The criteria for this ranking of the effects come from an analysis of variance performed on the fit of the model selected to describe the actual data . A variable was deemed to be significant when its inclusion in the simple linear model resulted in an increased "F-Value" together with a decreased probability that the fit of the model could be a random result and a value less than 0.10 for the probability that the effect of the variable itself was a random event. The probability of the effects (being random) was also used to assign a relative significance to each effect. An effect with a probability of 0.001 or less was

defined to be "most important" while one with a probability greater than 0.001 but less than or equal to 0.01 was "more important". Effects with probability values greater than 0.01 but less than or equal to 0.05 were rated as "important", while those with probabilities less than or equal to 0.1 down to 0.05 received a "less important" rating. Effects with probability values greater than 0.01 were defined to be "unimportant".

Figure 3 compares the effects for total $NO_x$ removal at the 5 minute point of the experiments. The figure legend shows the shading pattern used to indicate the relative significance of the effects while the notation across the bottom of the figure identifies the variables contributing to the individual effects. "Additive" (A) represents the presence of the additive in the sorbent. "Humidity" (H) represents higher moisture concentrations in the flue gas (15% vs. 7.5%). "R Temp" (T) represents increased temperature in the fixed bed (95°C vs. 65°C) and "$NO_2$ Conc" (C) represents increased $NO_2$ levels in the flue gas (50 ppm vs. 0 ppm). Looking at the figure from left to right, the first group of four effects are the first order effects with the additive effect first as indicated by the 'A' directly beneath the bar. The second group of effects are the six (combination of four variables taken two at a time) second-order effects. Each of the second-order effects is identified by a pair of letters underneath the bar. The four third-order effects (combination of four variables taken three at a time) and the single fourth-order effect complete the set.

The NaCl additive effect was vanishingly small, which indicates that it was ineffective in directly promoting $NO_x$ removal at that point (5 min) in the experiments. On the other hand, the additive effects for $NaHSO_3$ and NaOH were significant and showed an enhancement of $NO_x$ removal, but neither was very strong. The effect of humidity was significant and had a negative impact on $NO_x$ removal for NaCl and NaOH but again neither effect was very strong. The humidity effect in the $NaHSO_3$ dataset was negligible. Likewise, the temperature effect for $NaHSO_3$ was virtually zero but significant and major for both NaCl ("most important") and NaOH ("more important"). The effect of $NO_2$ concentration was "unimportant" for all three additives.

The different performances (between additives) of the non-additive first-order effects, as well as the second- and third-order effects that did not involve additives, is an indication that these additives modify the base sorbent in some fairly fundamental fashion and probably do so through more than one mechanism. This point will be emphasized as the additive comparison proceeds through the NO and $SO_2$ removal data.

The second-order effects on $NO_x$ removal showed some pronounced differences between the additives. The effect of "AxH" was significant only for $NaHSO_3$ and showed a minor enhancement of $NO_x$ removal. The "AxT" effect was dramatically different for NaCl and $NaHSO_3$. In both cases it was a "more important" effect but had opposite results for $NO_x$ removal. The effect of "HxC" was positive for $NO_x$ removal for $NaHSO_3$ and NaOH, while "TxC" had a negative effect on $NO_x$ removal for all three additives. This variable showed the most consistent performance for the three additives. Sodium bisulfite had two significant third-order effects, "AxHxT" and "AxTxC", which were "unimportant" for the other two additives. However, for NaCl the "AxHxC" effect showed a "most important", negative impact on $NO_x$ removal. Meanwhile, NaOH had an "important", negative effect from "HxTxC", the only non-additive, third-order effect. The single fourth-order variable was insignificant at 5 minutes in all cases.

A similar comparison is presented in Figure 4 for the removal of NO. While there are some similarities with the total $NO_x$ removal effects, the most striking difference is the contribution of $NO_2$ concentration to the removal of NO for all three additives. Once again, the additive effect for NaCl at this point in the experiments was fairly weak

and was rated as "unimportant". However, both $NaHSO_3$ and NaOH gave a relatively weak, "less important" contribution to NO removal, which was similar to the situation for total $NO_x$ removal. Humidity had a negative effect for all three additives but was significant only for NaOH. The temperature effect was "most important" for NaCl, "unimportant" for $NaHSO_3$, and "important" for NaOH. This is also similar to its effects on total $NO_x$ removal.

For the second-order effects, NO removal shows the same difference in the effects of "AxT" between NaCl and NaOH. Furthermore, all three additives had the same negative impact on NO removal by "TxC" as for total $NO_x$ removal. However, here the effects were not as significant for both $NaHSO_3$ and NaOH. Positive effects were attributed to "HxC", but it was significant only for NaOH. In the case of NaCl, "AxC" contributed to NO removal but not to total $NO_x$ removal. For the third-order effects, "AxHxT" was significant and negative for total $NO_x$ removal only in the case of $NaHSO_3$, while it appears to have been significant in depressing NO removal for all three additives. Otherwise, the pattern of third-order effects is the same for removing both NO and $NO_x$. Only for NaOH did the fourth-order effect appear to be significant where it was "less important" in decreasing the NO removal.

The comparison of the 5 minute additive effects for $SO_2$ removal, presented in Figure 5, shows pronounced differences between the additives. Except for "AxHxT" ("less important"), the significant effects for NaCl are all "most important", while there were no variables ranked as "most important" for the other two additives. The additive effect contributed to improved $SO_2$ removal for both NaCl and NaOH, but for NaOH the effect was only "important". Not surprisingly, the effect of humidity was to increase $SO_2$ removal, but this was significant only for NaCl and $NaHSO_3$. However, the temperature effect was a surprise. It was negative for $NaHSO_3$ but strongly positive for NaCl. The $NO_2$ concentration effect was negative in all cases, but was significant only for NaCl.

The two second-order effects for NaCl which indicated enhanced $SO_2$ removal were opposite to the corresponding effects for $NaHSO_3$ and NaOH. In the case of "AxT", the value of the $NaHSO_3$ effect was negative and rated "more important". For "TxC", the effect in the NaOH dataset was negative and rated "important". The NaOH dataset also indicated that "AxC" and "HxC" were "important" in increasing $SO_2$ removal. Among the third-order effects, "AxTxC" gave increased $SO_2$ removal for NaCl and was, by far, the largest and most important effect. For NaOH, the effect of "HxTxC" was found to be "important" in depressing $SO_2$ removal. In this case the fourth-order effect was significant by promoting $SO_2$ removal for NaCl and $NaHSO_3$.

Similar results have been obtained for the data at both 10 and 30 minutes, although some changes are evident corresponding to the trends observed in the fractional factorial experiments.

### $SO_2$ Parametric Experiments

Previous ANL results for aqueous scrubber chemistries indicated that the $SO_2$ concentration in the flue gas had a positive effect on $NO_x$ and NO removals. Other work also suggested that there was a critical $SO_2$ to $NO_x$ ratio for $NO_x$ removal. Since the statistically designed experiments all used a single level of $SO_2$ (3000 ppm), the parametric experiments were designed to determine whether or not the influence of $SO_2$ extended to powdered sorbents, to further define additive effects, and to test the critical ratio concept.

In general, the effect of $SO_2$ concentration on $NO_x$ removal was positive, but it was also different for the three additives as shown in Figure 6. Sodium bisulfite showed the greatest improvement in $NO_x$ removal over the unmodified $Ca(OH)_2$ sorbent and also showed a pronounced dependency upon the $SO_2$ concentration. The $NO_x$ removals for NaOH were also better than for the unmodified $Ca(OH)_2$, but the NaCl results were more scattered with respect to the $Ca(OH)_2$ baseline and actually showed worse $NO_x$ removal at 3000 ppm $SO_2$.

The NO removals followed a similar pattern, as shown in Figure 7. Again the $NaHSO_3$ gave the greatest increase over unmodified $Ca(OH)_2$ with NaOH being only slightly less active. Results for both the NaCl and the unmodified $Ca(OH)_2$ sorbent appear to have a maximum NO removal at 2000 ppm $SO_2$ with the NaCl results essentially equivalent to those for the unmodified sorbent.

Conversely, the $SO_2$ removals decreased with increasing $SO_2$ concentration, although this trend appeared to level out above 2000 ppm $SO_2$. However, the additive effects on $SO_2$ removal were practically random. There simply does not appear to have been a consistent pattern of either $SO_2$ removal enhancement or depression.

## CONCLUSIONS

The additive screening experiments showed that the removal activity of $Ca(OH)_2$ for total $NO_x$, NO, and $SO_2$ could be increased substantially by a wide variety of additives, and that the relative performance of some of the additives was strongly affected by the duration of exposure to the flue gas. Several additives changed the rate of oxidation of NO to $NO_2$ and the oxidation rate depended on the "exposure" time in ways that were quite different for different additives. For example, NaOH (10 mole %) showed increasing oxidation with time as did NaCl, while it remained about constant for Fe(II)EDTA. The contrast between the effects of 10 and 20 mole % NaOH performance suggests that the additive concentrations could be optimized.

Much of the improvement in performance observed with additives could be attributed to enhancement of the beneficial effects of non-additive variables. This could be observed through the strong correlations between the effects of non-additive variables and particular additives.

All three of the additives studied in the follow-on experiments exhibited improved NO and $SO_2$ removals and, to a lesser degree, improved $NO_x$ removals. The differences in the NO and $NO_x$ removals was again caused by the different impacts the additives had on NO oxidation. Sodium chloride strongly promoted oxidation initially and maintained higher NO removal than total $NO_x$ removal throughout the experiments. Sodium bisulfite showed better selectivity for total $NO_x$ removal but did not completely supress the oxidation of NO. These results also showed very strong correlations between the effects of the non-additive variables and their interactions with the additives.

The correlation of effects seen in both groups of experiments suggests the existence of a fundamental mechanism for modifying sorbents to achieve higher chemical activities for emission control applications. This modification probably occurs during the pretreatment and involves changes in the equilibrium between the modified sorbents and gas-phase moisture such as discussed by Karlson[6].

From a very limited analysis of ionic interactions, the separate effects of $Na^+$, $Cl^-$, and their interaction indicates that more attention should be devoted to the cation/anion pairs as a means of directing the removal mechanism(s) toward total $NO_x$ removal and

away from NO oxidation. The $Na^+$ effect slightly favored NO oxidation, but the interaction effect greatly increased NO oxidation.

Other research in the ANL program has utilized a laboratory spray-dryer system. Results from the investigation of additives and modified process conditions in that system are reported in Reference 1. Consideration of those results together with the ones reported here leads to the following conclusions regarding additives.

- Additives are capable of increasing the $NO_x$ and $SO_2$ removals of calcium-based sorbents in both spray-dryer and filtration-type environmental control technologies.

- The best additives for $NO_x$ removal (of those studied thus far) in spray-dryer applications are sodium chloride, calcium chloride, and sodium bisulfite.

- The best additives for $NO_x$ removal in filtration applications are sodium chloride, sodium bisulfite, sodium hydroxide, Fe(II)EDTA, aluminum sulfate, and a mixture of aluminum sulfate and citric acid.

- Calcium chloride, sodium chloride, sodium hydroxide, and sodium bisulfite all enhanced spray dryer $SO_2$ removals.

- Sodium hydroxide, a mixture of aluminum sulfate and citric acid, sodium chloride, and aluminum sulfate all increased $SO_2$ removals in the fixed bed (filtration applications), but the enhancements were significantly less than those seen in the spray dryer.

Several different $NO_x$ removal mechanisms appear to be operating in these two different types of systems as indicated by the effects of the non-additive variables.

- The removal of $NO_x$ was strongly promoted by higher $NO_2$ levels in the spray dryer.

- The effect of $NO_2$ on $NO_x$ removal in the fixed-bed reactor was much weaker than for the spray dryer and tended to promote NO oxidation to $NO_2$ instead.

- In the spray dryer, the additive enhancement of $NO_x$ removal disappeared as temperature increased and the activity of additive-free calcium hydroxide for $NO_x$ removal increased sharply.

- The $NO_x$ removal in the fixed-bed experiments increased with increasing temperature for sodium chloride and sodium hydroxide, but not for sodium bisulfite.

- The $SO_2$ removal decreased dramatically for all additives as the spray dryer temperature increased.

- In the case of sodium chloride in the fixed-bed reactor, higher temperatures improved $SO_2$ removal.

The decreased spray dryer $SO_2$ removal with increasing temperature either with or without the additives is consistent with a decrease in drying time for the slurry droplets. The removal mechanism for $SO_2$ inside a spray-dryer is reasonably well understood, but the reaction mechanism(s) for $NO_x$/NO removal in a spray-dryer and in a

filtration system are poorly understood and appear to be extremely complicated. Indications from the data presented here are that several $NO_x$/NO removal mechanisms may exist which could be the basis for the development of new environmental control processes. Additional research is needed to identify and fully characterized those mechanisms. Some of the differences observed between the fixed-bed and the spray-dryer experiments suggests that trade-offs between the drying and the filtration steps will need to be carefully evaluated in the design of any combined $NO_x/SO_2$ control technology based on a spray-dryer/fabric-filter system.

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5. C.D. Livengood, P.S. Farber, and J.B.L. Harkness, "Combined $NO_x/SO_2$ Removal for High Sulfur Coal," Fourth Symposium on Integrated Environmental Control, Washington, D.C. (March 1988).

6. H. T. Karlson, et al., "Activated Wet-Dry Scrubbing of $SO_2$," JAPCA 33:23 (1983).

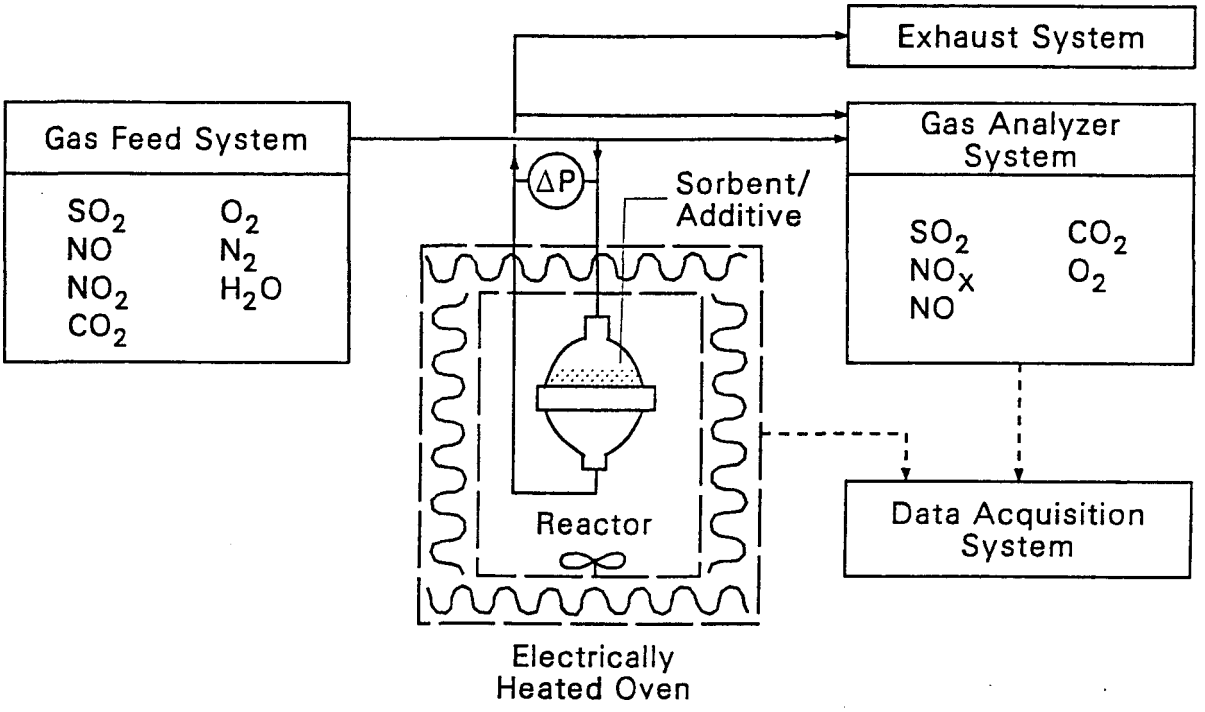


Figure 1 Flowsheet for the Fixed-Bed Experimental System

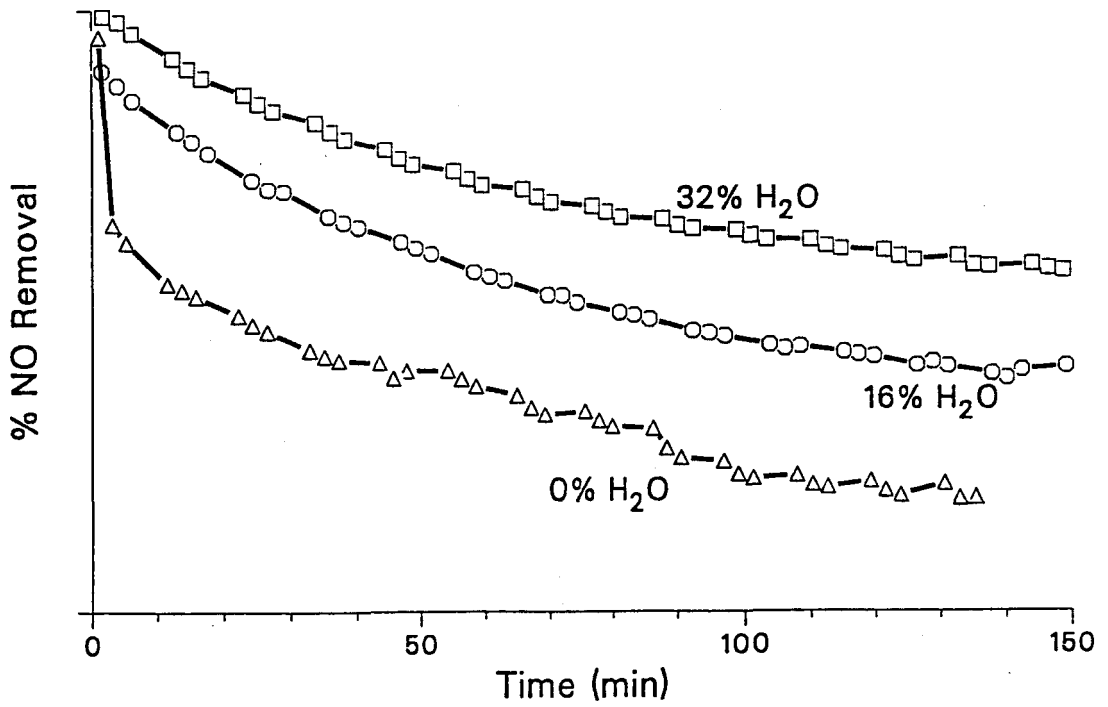


Figure 2 Typical Fixed-Bed Removal Profiles for Different Levels of Humidity Pretreatment

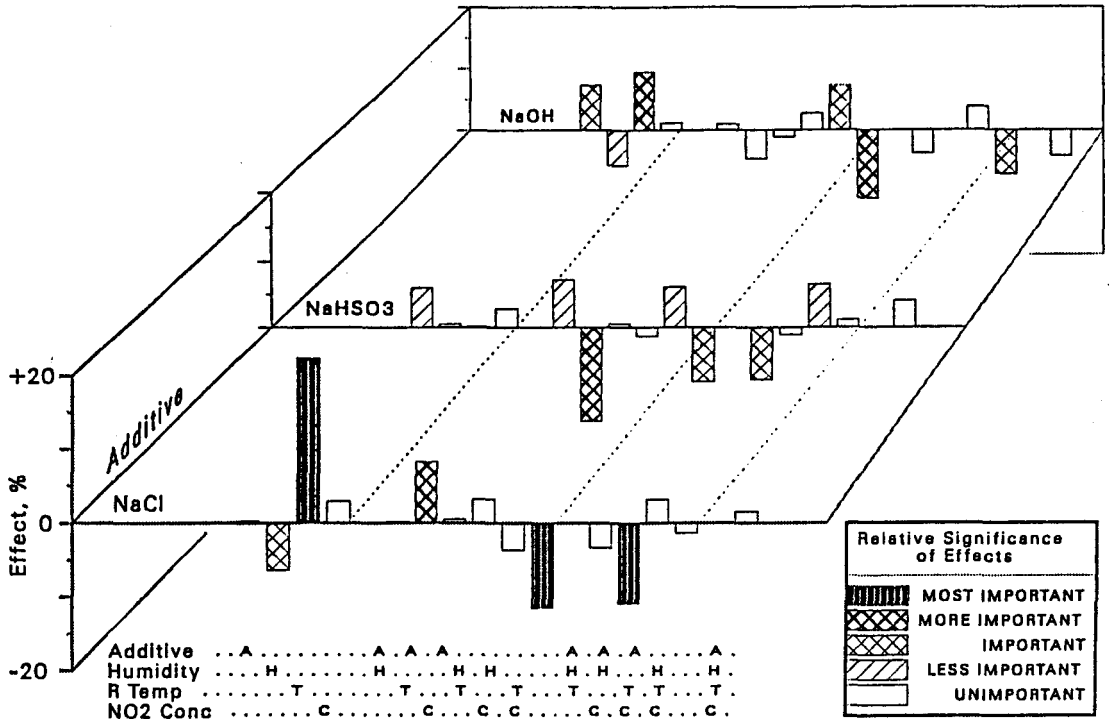


Figure 3 Comparison of Effects on $NO_x$ Removal

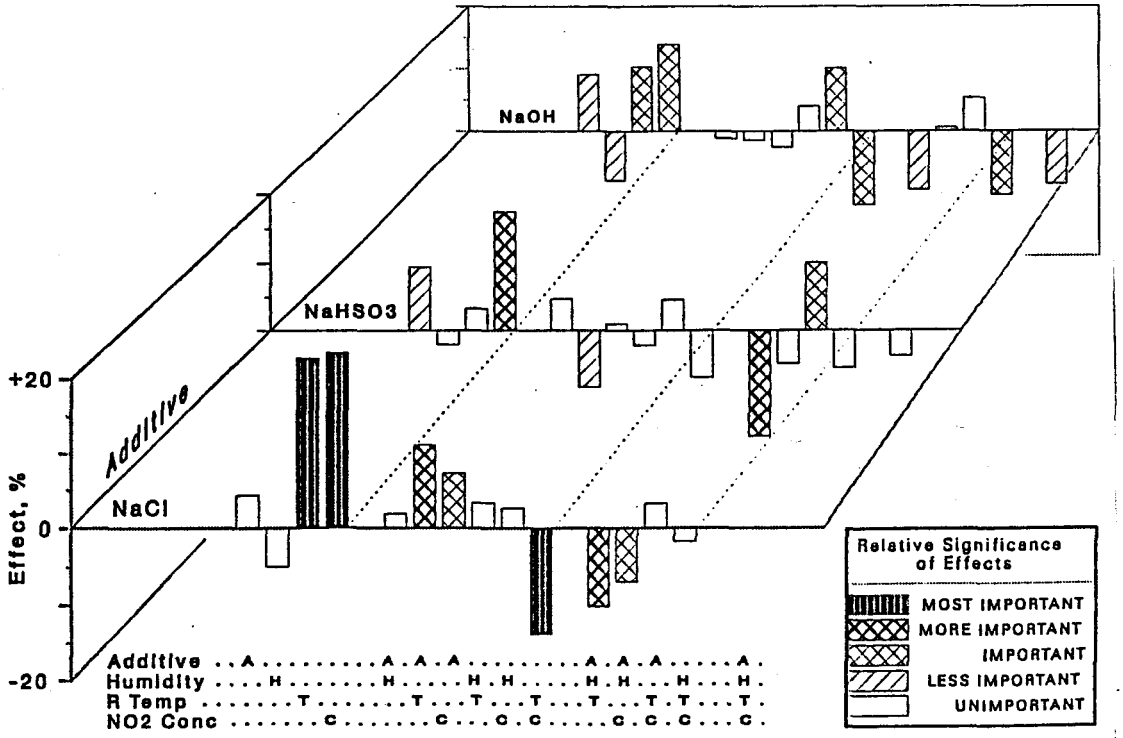


Figure 4 Comparison of Effects on NO Removal

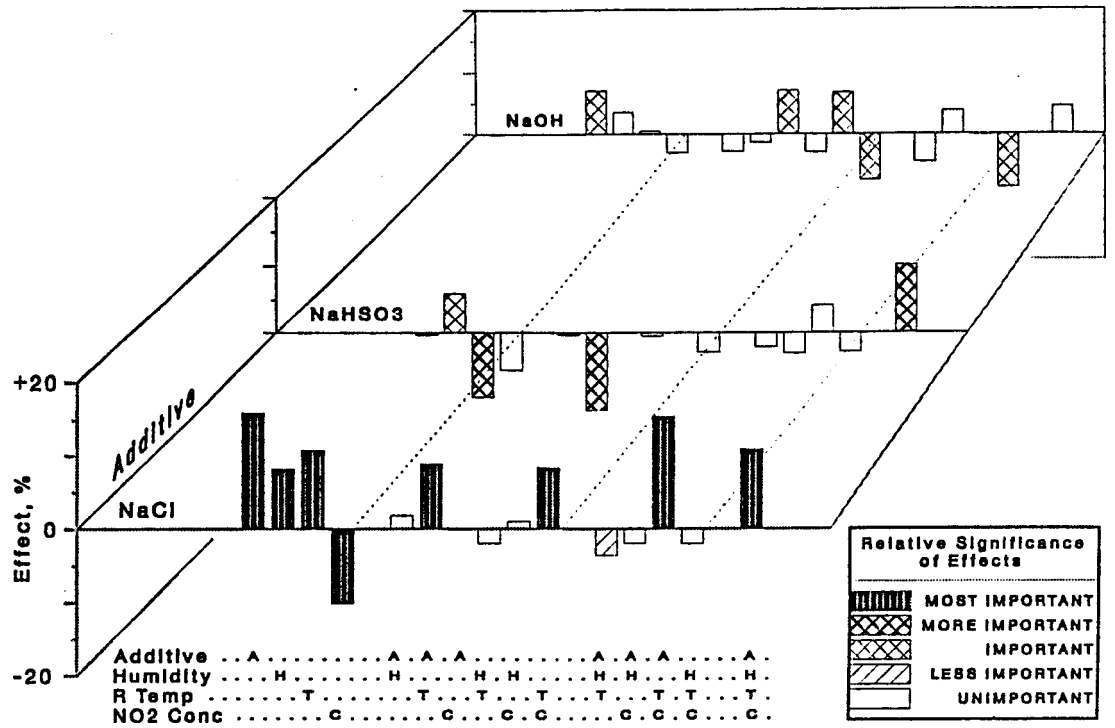


Figure 5 Comparison of Effects on $SO_2$ Removal

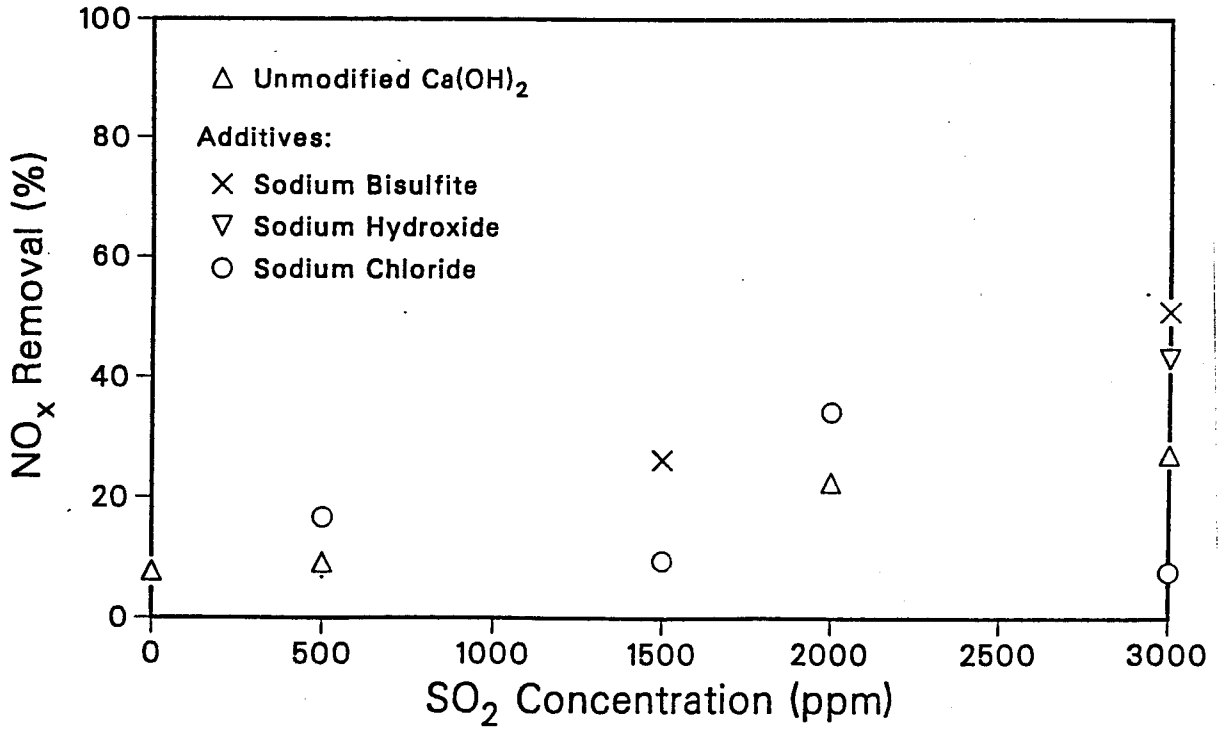


Figure 6 Effects of $SO_2$ and Additives on $NO_x$ Removal

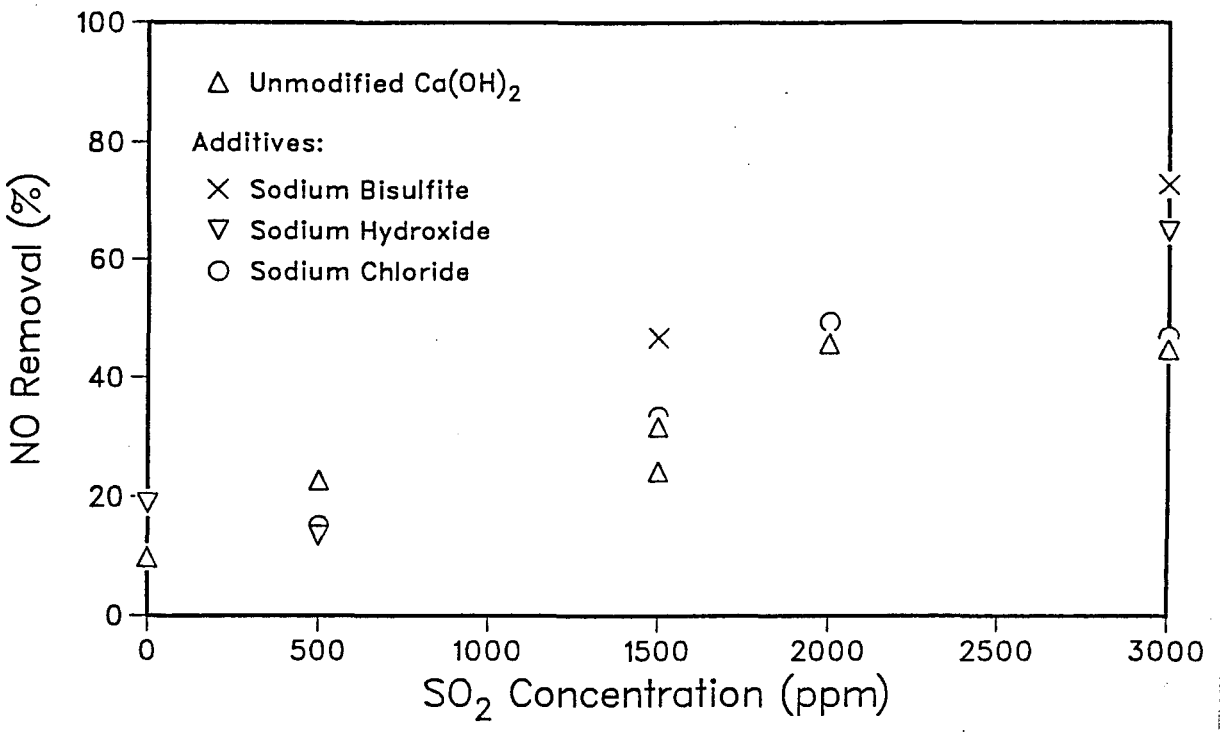


Figure 7 Effects of $SO_2$ and Additives on NO Removal

Table I Fixed-bed experimental program.

| Parameter | Values |
|---|---|
| FGD Sorbent | Lime -- $Ca(OH)_2$ |
| Additives | NaOH, NaCl, $NaHSO_3$<br>Fe(II)EDTA, $Na_2SO_3$, $Al_2(SO_4)_3$<br>Al/Citrate, $CaCl_2$ |
| Additive Concentration | 0 or 10 mole % (plus 20 mole % for NaOH) |
| Temperature | 65°C or 95°C |
| Flue-Gas Moisture | 7.5 or 15% by volume |
| Flue-Gas Composition (dry basis): | |
| $SO_2$ | 3000 ppm |
| NO | 450 or 500 ppm |
| $NO_2$ | 50 or 0 ppm |
| $O_2$ | 5.4% |
| $CO_2$ | 14.5% |
| $N_2$ | Balance |

Table II Additive performance in screening experiments.

| Exper. Time (min) | Control Avg. Removal (%) | Additive/Removal Enhancement (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $NO_x$ Removal | | | | | | | | |
| 5 | 28.7 | NaOH 10% +19.78 | $NaSO_3$ +10.30 | Fe(II)EDTA +8.70 | $Al_2(SO_4)_3$ +7.42 | $NaHSO_3$ +7.12 | Al/CIT +4.48 | NaOH 20% +0.20 | NaCl -1.06 | $CaCl_2$ -1.66 |
| 10 | 24.16 | NaOH 10% +19.24 | Fe(II)EDTA +8.66 | $NaSO_3$ +8.46 | $NaHSO_3$ +7.26 | NaCl +5.48 | $Al_2(SO_4)_3$ +4.82 | Al/CIT +4.26 | NaOH 20% -1.46 | $CaCl_2$ -3.30 |
| 30 | 17.40 | Fe(II)EDTA +10.56 | NaOH 10% +10.14 | NaCl +9.52 | $Al_2(SO_4)_3$ +9.00 | $NaHSO_3$ +7.86 | $NaSO_3$ +6.98 | Al/CIT +3.70 | NaOH 20% +1.74 | $CaCl_2$ -3.10 |
| | | NO Removal | | | | | | | | |
| 5 | 39.22 | NaOH 10% +14.24 | $NaHSO_3$ +3.54 | NaCl +2.68 | $Al_2(SO_4)_3$ +2.20 | Fe(II)EDTA +1.56 | NaOH 20% -1.24 | $NaSO_3$ -2.24 | Al/CIT -10.74 | $CaCl_2$ -13.74 |
| 10 | 30.92 | NaOH 10% +15.62 | NaCl +11.28 | Fe(II)EDTA +5.90 | $NaHSO_3$ +5.00 | $Al_2(SO_4)_3$ +3.48 | $NaSO_3$ +0.08 | NaOH 20% -1.52 | Al/CIT -4.80 | $CaCl_2$ -10.78 |
| 30 | 20.44 | NaCl +16.08 | NaOH 10% +15.94 | $Al_2(SO_4)_3$ +12.4 | Fe(II)EDTA +10.10 | $NaHSO_3$ +6.60 | $NaSO_3$ +1.44 | NaOH 20% +1.16 | Al/CIT -1.26 | $CaCl_2$ -5.42 |
| | | SO2 Removal | | | | | | | | |
| 5 | 37.62 | Al/CIT +18.94 | NaOH 10% +18.50 | $Al_2(SO_4)_3$ +16.40 | NaCl +12.48 | Fe(II)EDTA +8.76 | $NaSO_3$ +8.16 | $CaCl_2$ -0.20 | NaOH 20% -1.40 | $NaHSO_3$ -4.70 |
| 10 | 28.13 | Al/CIT +21.34 | NaOH 10% +19.60 | $Al_2(SO_4)_3$ +17.22 | NaCl +17.04 | Fe(II)EDTA +13.30 | $NaSO_3$ +10.70 | $NaHSO_3$ +7.24 | $CaCl_2$ -0.30 | NaOH 20% -0.58 |
| 30 | 23.97 | NaOH 10% +18.98 | $NaHSO_3$ +16.36 | Al/CIT +14.90 | $Al_2(SO_4)_3$ +14.42 | NaCl +10.88 | $NaSO_3$ +6.80 | $CaCl_2$ +5.28 | Fe(II)EDTA +3.08 | NaOH 20% -0.04 |