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Journal

Energy and fuels, 5(2)

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Littlejohn, D.
Chang, S.-G.

Publication Date

1990-10-01



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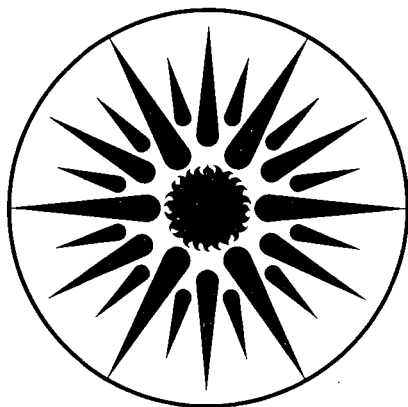
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D. Littlejohn and S.-G. Chang

October 1990



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Modeling of the Chemistry of Wet Limestone FGD Systems

David Littlejohn and Shih-Ger Chang*

Lawrence Berkeley Laboratory
Applied Science Division
1 Cyclotron Road
Berkeley, California 94720

This work was supported by the Assistant Secretary for Fossil Energy, Office of Coal Utilization Systems, U.S. Department of Energy under Contract No. DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, PA.

* Author to whom correspondence should be addressed.

Abstract

The chemistry of wet limestone flue gas desulfurization (FGD) systems is complicated by the interaction of dissolved SO_2 and dissolved nitrogen oxides. A substantial number of nitrogen-sulfur compounds can be formed from the reactions of sulfite and bisulfite ions with nitrogen oxyanions. A computer model is used to simulate the kinetics and to determine the effect of scrubber operating conditions on the production of nitrogen-sulfur compounds. With increasingly stringent regulations covering solid and liquid waste disposal, it is important to minimize undesirable byproducts in FGD systems. The modeling is also used to study the effect of scrubber conditions on the production of N_2O (nitrous oxide). Emission of N_2O into the atmosphere is undesirable because it has both significant ozone depletion potential and global warming potential.

Introduction

A number of wet limestone flue gas desulfurization (FGD) systems are capable of efficiently removing SO_2 from flue gas. Absorption of significant amounts of NO_x by the FGD systems can complicate the aqueous chemistry due to the interaction of sulfur oxyanions with nitrogen oxyanions¹. Some of the reactions that may occur are illustrated in Figure 1. The nitrogen-sulfur (N-S) compounds produced include HADS, ATS, HAMS, ADS, sulfamic acid, and NHAS ². NHAS will readily hydrolyze to produce nitrous oxide (N_2O). N_2O emissions to the atmosphere are of interest because it is an important greenhouse gas and has significant global warming potential. The major loss process for N_2O , once in the atmosphere, is photolysis in the stratosphere. The photolysis of N_2O produces $\text{N}_2 + \text{O}$, and the oxygen atom can react with ozone. Consequently, N_2O has a significant ozone depletion potential as well. Due to the potential environmental impacts associated with N_2O , it could face restrictions to atmospheric emissions in the future.

The other nitrogen-sulfur compounds are fairly stable in solution under suitable conditions and could build up to significant concentrations in scrubbing liquors. This is particularly true in the case of limestone FGD systems modified to enhance NO_x removal. One approach for NO_x removal is based on the addition of Fe(II)edta or other agents to enhance the solubility of NO . Another approach is to oxidize NO to more soluble NO_2 , as in the case of the Phosnox process developed at Lawrence Berkeley Laboratory^{3,4}.

The nitrogen-sulfur compounds such as HADS, HAMS, ATS, and ADS are fairly soluble in solution and, if discharged in wastewater from the FGD scrubbing liquor, could require additional treatment prior to release. If the compounds are co-precipitated out of the scrubbing liquor with the calcium solids, the solid could face disposal restrictions due to possible leaching of N-S compounds. In advanced limestone FGD systems, it is desirable to recover gypsum from the scrubbing liquor for commercial use. In such a case, the gypsum must have a minimum of contaminants in it.

It would be advantageous to determine the scrubber operating conditions in which production of the N-S compounds and N_2O are minimized. It would also be of value to develop techniques to convert the N-S compounds to innocuous materials, either as solids or in solution.

There are a large number of reactions occurring in scrubbing liquors in which both sulfur oxyanions (SO_2aq , HSO_3^- , SO_3^{2-} , $\text{S}_2\text{O}_5^{2-}$, SO_4^{2-}) and nitrogen oxyanions (HNO_2 , NO_2^- , NO_3^-) are present¹. Additionally, there are a number of physical processes involved with the chemistry (absorption, evaporation, dissolution, precipitation). These processes are not currently explicitly included in our computer model. Models of FGD systems must be capable of simulating the chemical kinetics and other processes that influence solution chemistry.

Experimental Section

Exact expressions for calculating the change in concentrations with time of reacting chemical species can only be obtained for the simplest reaction systems. Methods such as the steady-state approximation allow estimates of concentration vs time to be made of more complex reaction systems where conditions are not changing rapidly. However, such methods are unsuitable for modeling the chemistry in FGD scrubbing liquors.

Work in the 1970's by Whitten^{5,6} and others led to the development of matrix-based computer codes to simulate chemical kinetic systems in the gas phase. The processes were based on converting the expressions for a system of chemical reactions into a series of ordinary differential equations. A computer routine to integrate a system of ordinary differential equations that was developed by Gear⁷ and modified by Hindmarsh⁸ of Lawrence Livermore National Laboratory was the basis of most kinetic modeling codes that were developed. The integrating package based on the Gear routine has subsequently been improved to increase its operating efficiency⁹. The program used in this study is based on the improved Gear package. It has been adapted for solution kinetics from programs for kinetic modeling routines used for air pollution studies. The package runs on a Macintosh computer with a Fortran 77 compiler. It can model a reaction system with up to 89 species and 200 reactions. The routine has been tested by using a reaction set involving a series of equilibria, the results of which can be predicted.

The reactions used in the model are shown in Table 1. These reactions have been reviewed in reference 1 and can be broken down into gas absorption, NO_x and SO_x interconversions, production and interconversion of nitrogen-sulfur (N-S) compounds, and decomposition of N-S compounds. The modeling routine was used to simulate two basic types of wet limestone FGD systems. In the first type of system, the limestone slurry is sprayed into the flue gas stream with a contact time of 3 seconds. The scrubbing liquor then goes to a hold tank for 300 seconds for sulfite/bisulfite (S(IV)) oxidation and CaSO_4 precipitation. The slurry is recharged with limestone and returned to the absorber. Several variations of the basic limestone FGD system were studied, including systems with metal chelates to enhance NO solubility, and with gas-phase oxidation of NO to NO_2 .

The second type of system investigated is based on the Chiyoda CT-121 process. Flue gas is bubbled through the scrubbing liquor, along with supplementary oxidizing air. The scrubbing liquor is in continuous contact with the flue gas. Precipitated CaSO_4 is continuously removed and CaCO_3 is continuously added to maintain a suitable fraction of the slurry as solid.

The systems were modeled to determine the fraction of absorbed nitrogen oxides that are converted to N-S compounds and N_2O . The conditions of the modeled scrubbing liquor that were varied include bulk pH, temperature, and L/G. The effect of the rate of oxidation of S(IV) was also studied.

Additional reactions that occur in this system were not included if their rates are sufficiently slow as to not significantly affect the chemistry. The first 11 reactions listed are equilibria between species in the system. These include gas-liquid equilibria as well as interconversion of dissolved species. There are several reactions for conversion of absorbed NO_x into nitrogen oxyanions. The majority of the reactions involve formation and interconversion of nitrogen-sulfur compounds. Some of the reaction rates have some dependence on ionic strength, pressure and mass transfer. These variables are not currently included in the program, so the rates were adjusted as appropriate before entering them into the program.

The S(IV) oxidation reaction has been studied extensively, but is still not well understood. A number of free radicals appear to be involved in the oxidation process. Trace quantities of a number of species can catalyze or inhibit the reaction, including species such as transition metal ions and organic compounds. The studies have not provided a clear dependence on dissolved oxygen concentration. Laboratory studies of S(IV) solutions without solids and with small, well-defined impurity concentrations show faster oxidation at high pH conditions, whereas S(IV) in scrubbing liquors is oxidized more quickly at low pH. Given the uncertainty associated with the rate of the reaction, an empirically derived value for the first-order oxidation rate constant of S(IV) was used in the simulations. The effect of this rate constant on the chemistry was investigated as part of this study.

The simulations were done by starting with realistic concentrations of a number of species and doing simulations of cycling the scrubbing liquor through the absorber. The program was run through enough cycles to obtain consistent concentration changes per cycle. All the simulations were done with flue gas containing 2500 ppm SO_2 , 400 ppm NO, and 40 ppm NO_2 . The scrubbing liquor used in the simulations contained 10% (by weight) $CaCO_3$, 1% (by weight) $CaSO_4$, 0.1M SO_4^{2-} , and 0.03M S(IV). All simulations were done using co-current flow conditions at pH 5.5, 50°C, and a L/G=60, except where noted.

Results and Discussion

Since this study focuses on the nitrogen-containing species in flue gas scrubbing liquor, the primary concern is the fate of the absorbed NO_x . Dissolved NO will react primarily with SO_3^{2-} or HSO_3^- to form NHAS¹⁰. The NHAS hydrolyzes into N_2O and SO_4^{2-} . If oxidizable metal ions such as Fe(II) are present, NHAS can react with them to form N_2O

and sulfite ion¹¹. Consequently, NO dissolved by the scrubbing liquid will primarily form N₂O. Dissolved NO₂ is quickly converted into nitrite and nitrate ions^{12,13}. NO₃⁻ is fairly unreactive under typical scrubbing liquor conditions, and will build up in the scrubbing liquor unless it is removed. Most of the dissolved NO₂ is initially converted to NO₂⁻. The presence of S(IV) at a concentration of about .03M causes most of the NO₂(aq) to react via reaction 14 rather than reaction 13. If no S(IV) is present, the NO₂ absorption decreases from about 90% to about 15%. The main loss mechanism for nitrite ion is reaction with bisulfite ion to form the N-S compounds (Figure 1). Oxidation by oxygen is a fairly slow process.

The fraction of NO_x absorbed into solution vs time for a number of nitrogenous species is shown in Figure 2 for a scrubbing liquor at pH 5.5 and 50°C with L/G=60. The N-S compounds formed under these conditions are primarily HADS and HAMS, and NHAS, which decomposes to N₂O. HAMS is fairly stable under these conditions and will tend to build up in solution. HAMS hydrolyzes either under very acidic conditions¹⁴ or under alkaline conditions¹⁵. If bisulfite ion is present in large concentrations, HADS and HAMS will be converted to ATS and ADS. Since bisulfite ion concentrations are generally fairly low in conventional scrubbing liquors, ATS and ADS concentrations are considerably lower than the concentrations of HADS and HAMS.

The effect of temperature on scrubber chemistry is shown in Figure 3. The nitrogen-containing product distribution at the end of 300 seconds in the hold tank is illustrated. The conversion of NO₂⁻ to HADS and HAMS is faster at higher temperatures. Since an empirical value of the S(IV) oxidation rate was used, no temperature dependence for this process was included. However, if the S(IV) oxidation has a temperature dependence similar to the S(IV) + NO₂⁻ reaction, the formation of N-S compounds will not increase so rapidly. The hydrolysis of HADS to HAMS would still show an increase similar to that shown in the figure due to the increased HADS hydrolysis rate. The increase in rate constants more than offsets the decrease in solubility of NO and NO₂ with temperature.

The acidity of the solution influences the distribution of the forms of the sulfur oxyanions and nitrogen oxyanions, as well as the solubility of CaSO₃ and many of the N-S compound hydrolysis reactions. In the model, the pH dependent rates were adjusted to simulate the chemistry over the range of pH 4.5 to 6.5. The results are shown in Figure 4 for the product distribution at the end of 300 seconds in the hold tank. There is much higher conversion of NO₂⁻ to N-S compounds at low pH conditions, primarily due to the higher fraction of S(IV) in the form of HSO₃⁻. As would be expected for this pH range, there is little effect of pH on NO_x absorption. Under more acidic conditions, NO_x and SO₂ removal

efficiency would decrease. There is very little pH effect on the production of N_2O . High pH conditions inhibit N-S compound formation, but do little to affect N_2O production.

The effect of the liquid-to-gas ratio was also studied using the scrubber chemistry model. With conditions of $T=50^\circ C$, $pH=5.5$, and flue gas with 2500 ppm SO_2 , 400 ppm NO , and 40 ppm NO_2 , the L/G was varied from 45:1 to 75:1 (gal/min:1000 cfm). The simulations indicated that the main effect of varying the L/G was to vary the concentrations of the species in solution, as might be expected. A slightly larger fraction of the absorbed NO_x was converted to N-S compounds at lower L/G, since the concentrations of NO_2^- and HSO_3^- are slightly higher at these conditions.

Due to the complexities of the oxidation of HSO_3^- and SO_3^{2-} discussed above, an empirically established value was used for k_{12} , the S(IV) oxidation reaction. In scrubbing systems, some control of S(IV) oxidation may be obtained by adding or removing transition metal ions, adding supplementary air to provide more oxygen, adding oxidation inhibitors such as $S_2O_3^{2-}$, and controlling pH. Simulations were carried out to observe the effect of the oxidation rate variation on the chemistry. Values for k_{12} of .005, .05, .5 and 5.0 seconds^{-1} were used for the first order oxidation rate of S(IV). Figure 5 shows the effect of S(IV) oxidation rate on nitrogen-containing species at the end of 300 seconds in the hold tank. Rapid oxidation of S(IV) reduces both the concentration of S(IV) species and the time for interaction of aqueous nitrogen oxides with S(IV), so there is a large decrease in the formation of N-S compounds. N_2O production is only slightly affected by the S(IV) oxidation rate. Increasing the S(IV) oxidation rate causes a small decrease in the NO_x removal efficiency by reducing the concentrations of S(IV) available to react with the absorbed NO_x .

There are a number of FGD processes under development besides the standard limestone FGD system. We have done a limited number of simulations on some other systems to compare with the simulations discussed above. We considered the system with enhanced NO solubility where an agent is added to the scrubbing liquor to absorb NO, such as a metal chelate. Since agents such as Fe(II)edta do affect the solution chemistry, additional reactions were added to simulate the reactions of Fe(II)edtaNO with S(IV) to produce HADS and N_2O ^{11,16}. There is some uncertainty in the rates of these reactions, since they are relatively difficult to measure.

Another modification considered is the oxidation of NO to more-soluble NO_2 in the gas phase, as with the Phosnox process. Simulations were also done for a counter-current flow absorber, in which the sprayed droplets of scrubbing liquor flow in an opposing direction to the flow of the flue gas. Most of the simulations were done with a co-current

flow arrangement. Other simulations were made of a scrubbing liquor without calcium, such as a sodium carbonate system, and the Chiyoda CT-121 process.

In the Chiyoda CT-121 process, the flue gas passes through the limestone scrubbing liquor, rather than spraying the liquor through the flue gas. Since the scrubbing liquor is constantly exposed to the flue gas it can be considered to have a 100% duty cycle, compared to the approximately 1% duty cycle in a conventional absorber - hold tank FGD system (3 sec exposure to flue gas, 300 sec total cycle time). It is difficult to directly compare the amount of NO_x absorbed by the Chiyoda process to that of a conventional FGD system due to the differences in absorber geometry, gas-liquid contact, duty cycle, L/G ratio and S(IV) oxidation rate. We can compare the fraction of absorbed NO_x converted into NO_2^- , NO_3^- , N_2O , and N-S compounds. A comparison of a conventional FGD system with systems in which NO is oxidized to NO_2 , and NO solubility is enhanced and the Chiyoda process is shown in Figure 6. The simulations were carried out with the scrubbing liquor at 50°C, pH 5.5 and L/G = 60 for all the processes except the Chiyoda process, which does not have a comparable L/G ratio. The system with enhanced NO solubility produces the largest quantity of N_2O of the systems compared, as might be expected. In systems using metal chelates to enhance NO solubility, the metal ions and, in some cases, the chelating agent, interact with the aqueous-phase NO_x chemistry to alter the reaction products substantially. Also, several antioxidants are under study for these systems to stabilize the Fe(II) ion and these agents may also shift the nitrogen product distribution substantially. The metal chelate chemistry could not be precisely duplicated in the model used here because some of the reactions are not thoroughly understood and many of the rate constants are not well established. However, the product distribution predicted by the model is similar to that measured experimentally.¹¹

The simulation of the scrubbing system in which most of the NO is oxidized to NO_2 in the gas phase (as with the Phosnox system) produces essentially no N_2O , as might be expected. Since considerable amounts of NO_2^- are produced, N-S compound formation is relatively high. The rates for reactions of dissolved NO_2 in solution have not been well studied at typical scrubber temperatures, and are not well-defined even at room temperature conditions. These rates are the major source of uncertainty in the simulation of this system. More extensive measurements of the reactions and the temperature dependence of the rates are needed to improve the modeling results.

The simulation of the Chiyoda system generated somewhat lower concentrations of N-S compounds than the other systems. This is primarily due to the forced oxidation of S(IV), which is incorporated into the system design. The rapid oxidation of the S(IV) reduces its availability for reaction with dissolved NO_x species. A larger value of k_{12} (0.5)

was used in the simulation of the Chiyoda process than was used in the simulations of the other processes ($k_{12} = 0.05$). Operation at conditions with a lower pH would be likely to increase N-S compound production, however. As discussed above, more rapid oxidation of S(IV) species also significantly reduces N-S compound production in conventional FGD systems.

The fractions of gaseous SO_2 , NO , and NO_2 absorbed in the simulations of the different scrubbing systems are listed in Table 2. In general, the fractions of the gases absorbed are quite similar. The exception is the fraction of NO absorbed by scrubbing liquor with an additive to enhance the solubility of NO .

The effect of limestone on the scrubbing liquor chemistry was studied by comparing simulations done with and without Ca^{2+} present. In terms of N_2O and N-S compound production, there were few substantial differences between the simulations done with calcium and those done without calcium. This was a result of the dissolved S(IV) concentrations being similar in the two conditions. If FGD systems without limestone have higher S(IV) concentrations than their limestone-based counterparts, then more N-S compound production would be expected.

In summary, the simulations of scrubbing liquor chemistry provide quantitative results of the effects of scrubber conditions on the production of nitrogen-containing products. The accuracy of the calculations are limited by current knowledge of the solution kinetics of the reactive species in scrubbing liquor and by the ability to model heterogeneous processes (such as dissolution and formation of solid particles) and free radical processes. Without a kinetic model, it is very difficult to predict the quantities of N_2O and N-S compounds that will be formed in scrubbing liquors.

The results of our simulations indicate that lower temperatures minimize production of both N_2O and nitrogen-sulfur compounds. Maintaining the scrubbing liquor above pH 5.5 will help minimize N-S compound formation. Solution pH has little effect on N_2O formation. Rapid oxidation of S(IV) to sulfate not only minimizes CaSO_3 formation, but reduces the rates of the dissolved NO_x with S(IV) reactions that produce N-S compounds. At these conditions, the Chiyoda CT-121 process appears to be capable of reducing NO_x conversion to N-S compounds. The Phosnox process should be capable of nearly eliminating N_2O production. Systems which enhance NO solubility may have problems with N_2O formation, although the metal chelate system used can exert strong influence on the solution chemistry. All of the metal chelate chemistry was not included in the simulation because it depends on the specific metal ion - chelate compounds combination used, and many of the reactions involved are not well understood. Some antioxidants have been proposed for use with metal chelate systems, which would further complicate the solution kinetics.

This investigation indicates a number of areas in which additional research is needed. A better understanding of NO_2 aqueous chemistry is needed, especially for the reactions involved with the conversion of $\text{NO}_2(\text{aq})$ to NO_2^- and NO_3^- . The S(IV) oxidation process is still poorly understood. A number of free radicals may be involved in the aqueous sulfur oxyanion chemistry and their role needs to be better defined.

Further studies of N-S compound chemistry are needed. Trace metal ions, organic compounds, and other species influence the decomposition of $\text{S}_2\text{O}_7^{2-}$ and peroxymonosulfuric acid (Caro's acid). The hydrolysis reactions of the N-S compounds may show similar dependence on trace species. Techniques for removing N-S compounds from solution, such as thermal decomposition, precipitation, or oxidation need further study. Also, efficient techniques need to be developed for removing NO_2^- and NO_3^- from scrubbing liquor.

This work was supported by the Assistant Secretary for Fossil Energy, Office of Coal Utilization Systems, U.S. Department of Energy under Contract No. DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, PA.

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2. The abbreviations are for the following chemical names: HADS - hydroxyamido-disulfonate, or hydroxyimidodisulfate; HAMS - hydroxyamidomonosulfonate, or hydroxysulfamate; ATS - aminetrisulfonate, or nitridotrisulfate; ADS - amine-disulfonate, or imidodisulfate, NHAS - N-nitrosohydroxylamine-N-sulfonate. The last name listed after each abbreviation is that currently accepted as correct.
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Table 1

Reactions Used in Modeling Scrubber Chemistry

1. $\text{SO}_2(\text{gas}) = \text{SO}_2(\text{aq})$
2. $\text{NO}(\text{gas}) = \text{NO}(\text{aq})$
3. $\text{NO}_2(\text{gas}) = \text{NO}_2(\text{aq})$
4. $\text{SO}_2(\text{aq}) = \text{HSO}_3^- + \text{H}^+$
5. $\text{HSO}_3^- = \text{SO}_3^{2-} + \text{H}^+$
6. $\text{HNO}_2 = \text{NO}_2^- + \text{H}^+$
7. $\text{HAMS} = \text{HAMS}^- + \text{H}^+$
8. $\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}$
9. $\text{CaSO}_3 = \text{Ca}^{2+} + \text{SO}_3^{2-}$
10. $\text{CaSO}_4 = \text{Ca}^{2+} + \text{SO}_4^{2-}$
11. $\text{NO}(\text{aq}) + \text{NO}_2(\text{aq}) + \text{H}_2\text{O} = \text{HNO}_2 + \text{HNO}_2$
12. $\text{S(IV)} + .5\text{O}_2 \rightarrow \text{SO}_4^{2-}$
13. $2\text{NO}_2(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{NO}_3^-$
14. $\text{NO}_2(\text{aq}) + \text{HSO}_3^- \rightarrow \text{NO}_2^- + \text{H}^+ + \text{SO}_3^-$
15. $\text{NO}_2(\text{aq}) + \text{SO}_3^{2-} \rightarrow \text{NO}_2^- + \text{SO}_3^-$
16. $\text{SO}_3^- + \text{SO}_3^- \rightarrow \text{S}_2\text{O}_6^{2-}$
17. $\text{NO}(\text{aq}) + \text{HSO}_3^- \rightarrow (\text{ONSO}_3)^{2-} + \text{H}^+$
18. $\text{NO}(\text{aq}) + \text{SO}_3^{2-} \rightarrow (\text{ONSO}_3)^{2-}$
19. $\text{NO}(\text{aq}) + (\text{ONSO}_3)^{2-} \rightarrow \text{NHAS}$
20. $\text{NHAS} \rightarrow \text{N}_2\text{O} + \text{SO}_4^{2-}$
21. $\text{NO}_2^- + \text{HSO}_3^- + \text{H}^+ \rightarrow \text{ONSO}_3\text{H} + \text{OH}^-$
22. $\text{HSO}_3^- + \text{ONSO}_3\text{H} \rightarrow \text{HADS}$
23. $\text{HADS} \rightarrow \text{HAMS} + \text{SO}_4^{2-} + \text{H}^+$
24. $\text{HAMS} \rightarrow \text{NH}_3\text{OH}^+ + \text{SO}_4^{2-}$
25. $\text{HADS} + \text{HSO}_3^- \rightarrow \text{ATS}$

26. $\text{HADS} + \text{HSO}_3^- \rightarrow \text{ADS} + \text{SO}_4^{2-} + \text{H}^+$
27. $\text{ATS} \rightarrow \text{ADS} + \text{SO}_4^{2-} + \text{H}^+$
28. $\text{ADS} \rightarrow \text{H}_2\text{NSO}_3^- + \text{SO}_4^{2-} + \text{H}^+$
29. $\text{HAMS} + \text{HSO}_3^- \rightarrow \text{ADS}$
30. $\text{HAMS} + \text{HSO}_3^- \rightarrow \text{H}_2\text{NSO}_3^- + \text{SO}_4^{2-} + \text{H}^+$
31. $\text{NH}_3\text{OH}^+ + \text{SO}_2(\text{aq}) \rightarrow \text{H}_2\text{NSO}_3^- + 2\text{H}^+$
32. $\text{HAMS}^- \rightarrow \text{ONOO}^- + \text{HSO}_3^-$
33. $\text{ONOO}^- + \text{HAMS} \rightarrow \text{NO}_2^- + (\text{ONSO}_3)^{2-}$
34. $(\text{ONSO}_3)^{2-} + \text{HAMS}^- \rightarrow \text{NHAS} + \text{SO}_3^{2-}$
35. $\text{HAMS}^- \rightarrow \text{SO}_3^{2-} + \text{HNO}$
36. $\text{HNO} + \text{HNO} \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$

Table 2

Fraction Absorbed by Scrubbing System

Method	SO ₂	NO	NO ₂
co-current	.91	.02	.91
counter-current	.95	.02	.93
NO oxidation	.91	.02	.91
enhanced NO sol.	.91	.47	.91
Chiyoda	.90	.02	.90

Figure Captions

- Figure 1. Reactions involving nitrogen-sulfur compounds.
- Figure 2. Modeled concentration vs time of species in scrubbing liquor.
- Figure 3. Effect of temperature on nitrogen-containing products.
- Figure 4. Effect of solution pH on reaction products.
- Figure 5. Effect of S(IV) oxidation rate on scrubber products.
- Figure 6. Comparison of products generated by different scrubber processes.

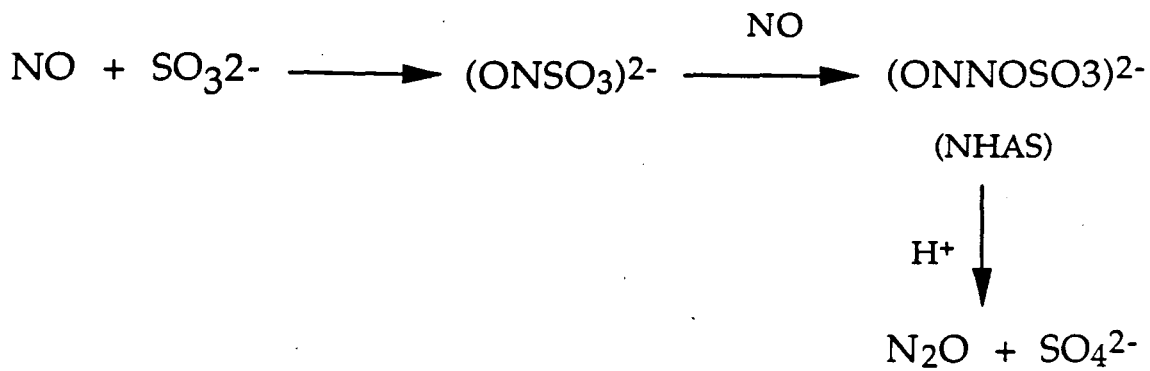
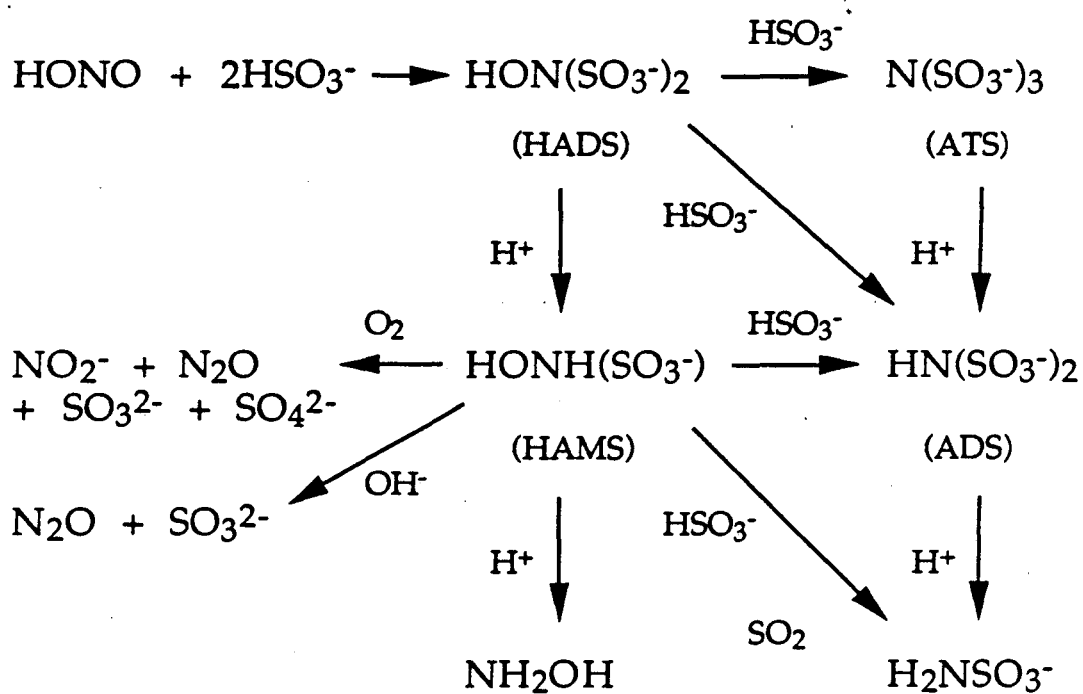


Figure 1

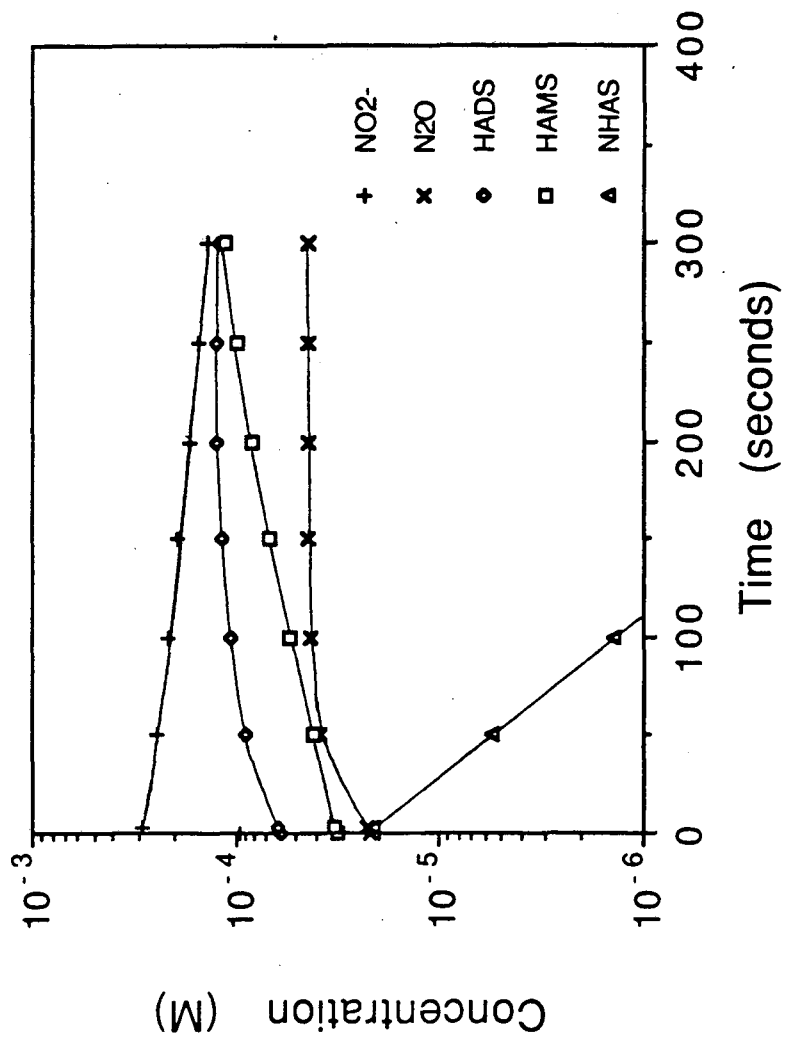


Figure 2

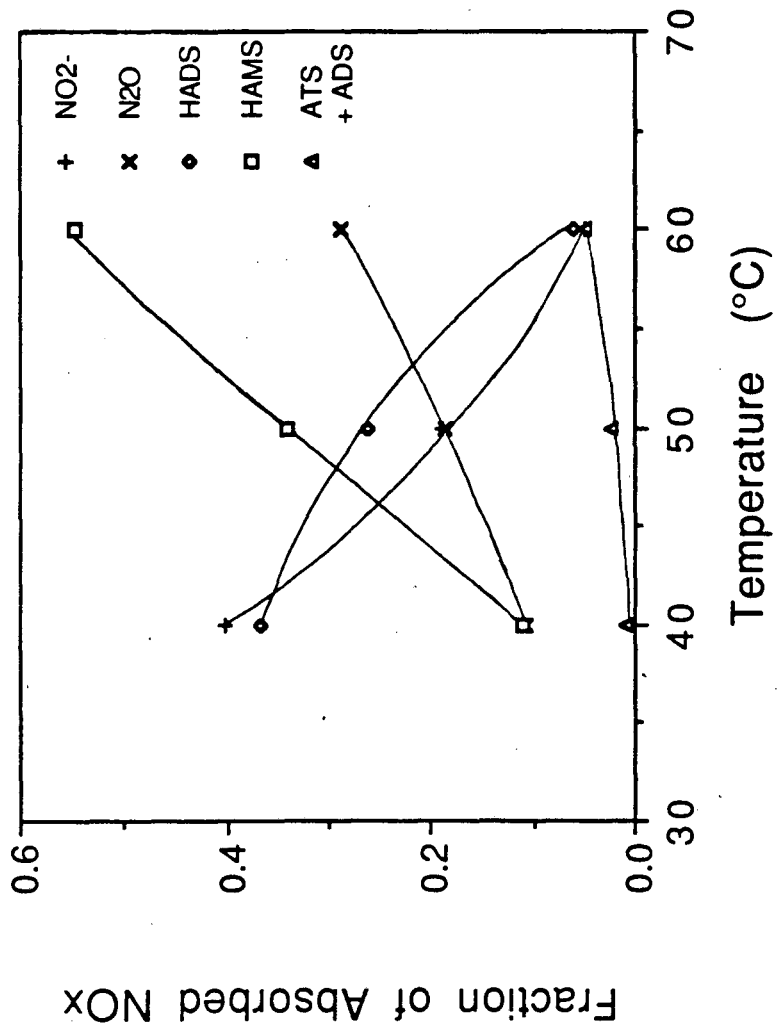


Figure 3

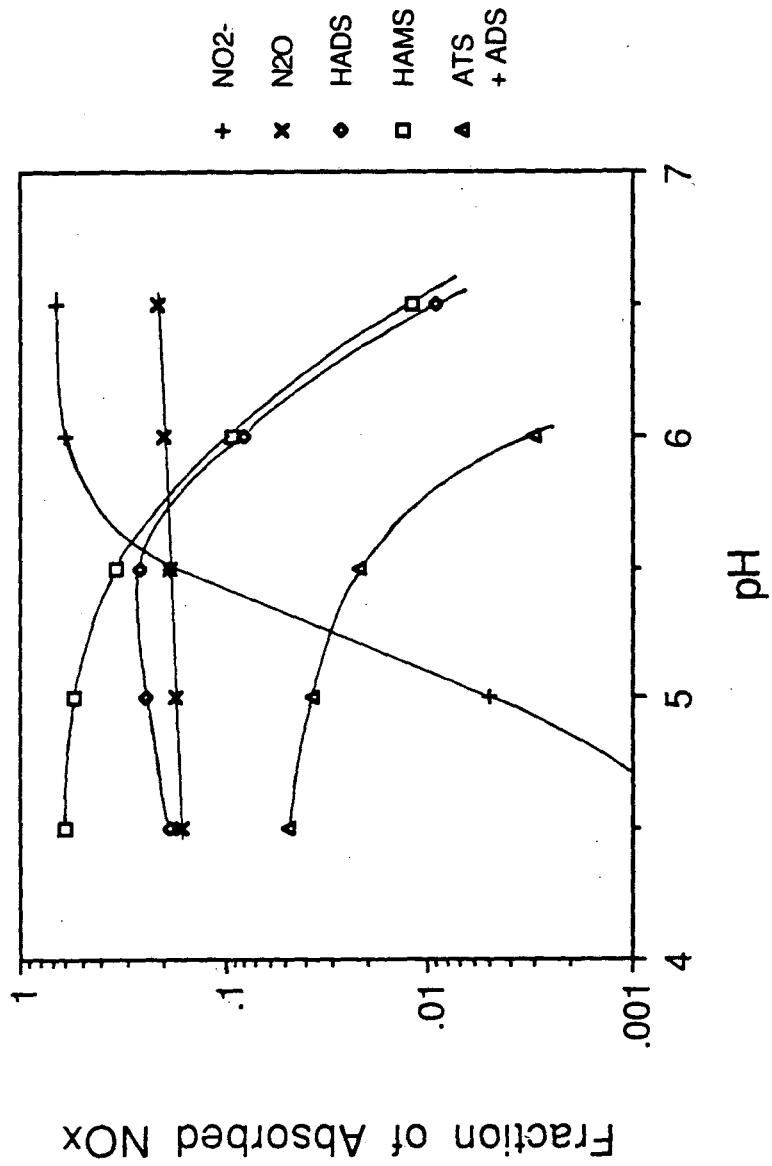


Figure 4

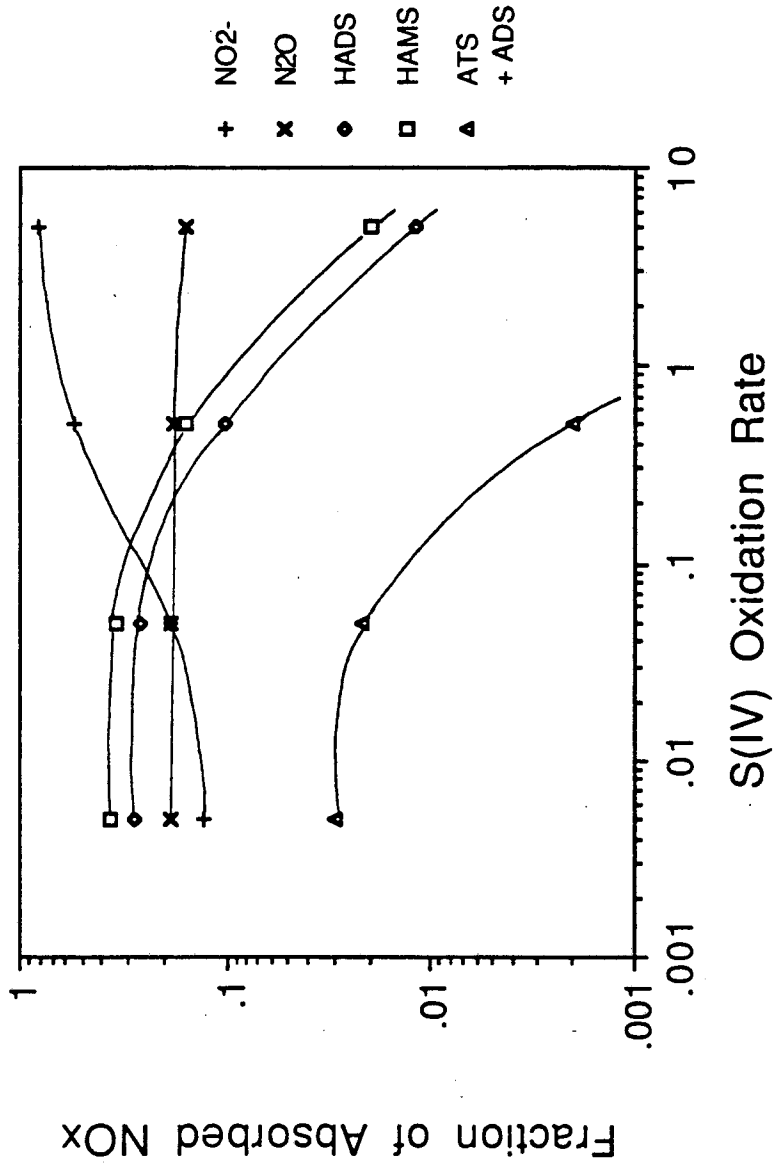


Figure 5

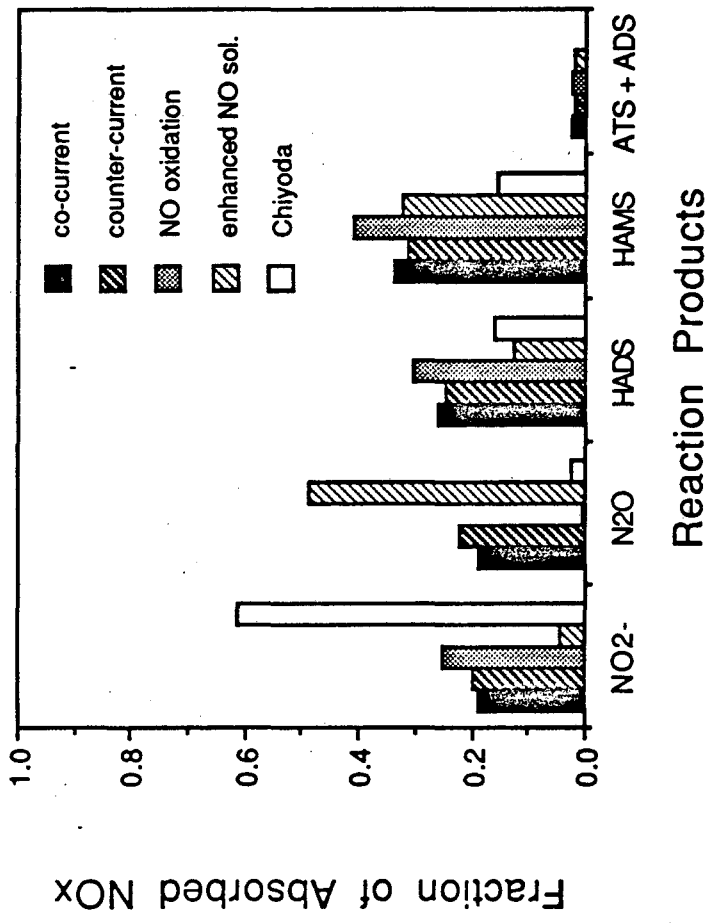


Figure 6

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720