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Publication Date
1990-04-01

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April 1990
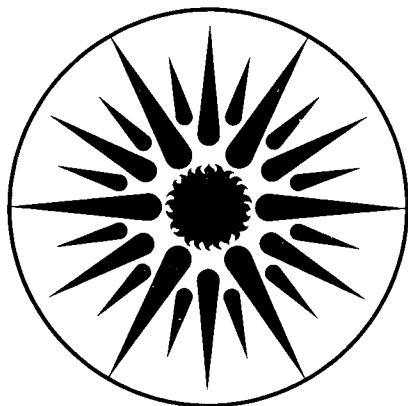
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COMPUTER MODELING OF THE CHEMISTRY OF AQUEOUS SCRUBBER SYSTEMS

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Abstract

The chemistry occurring in aqueous flue gas scrubbing solutions can be quite complicated, due to the large number of chemical species present and the many physical processes involved. These include gas absorption into solution, gas and solution kinetics involving both nitrogen oxides and sulfur oxides, oxidation and hydrolysis reactions in solution, and liquid-solid interactions. Simple models that neglect the solution kinetics which can occur in scrubbers cannot be expected to accurately model aqueous-based scrubber chemistry. We have developed a computer model which incorporates the aqueous solution kinetics of nitrogen oxyanions, sulfur oxyanions, nitrogen-sulfur compounds, and other species. The model can be adapted to predict the chemistry in a wide range of aqueous-based scrubber systems. It can be used to study the effect of changes in the operating conditions of the scrubbers. The results of the model can be compared with experimental observations to determine how well the chemistry of the solutions is understood.

Introduction

A good understanding of the chemistry occurring in wet flue gas scrubbing systems is inportant. The chemistry will influence the NO_x and SO_2 removal and the product distribution, as well as factors such as scaling. A large number of compounds can be formed in scrubber solutions.[1] The compounds present depend, in part, on the type of scrubber chemistry utilized. Nitrogen-sulfur compounds will form under neutral to acidic conditions when both nitrite ion and bisulfite ion are present in significant quantities.[1] The term nitrogen-sulfur compound is used to collectively refer to hydroxyimidodisulfate (HADS), hydroxysulfamic acid (HAMS), nitridotrisulfate (ATS), imidodisulfate (ADS), sulfamate, and hydroxylamine. The compounds have been observed in a number of wet scrubber solutions.[2,3] These compounds can interfere with the recovery of desirable byproducts from scrubber solutions. They will also build up in scrubber solutions and must eventually be treated or removed.

To develop an understanding of the solution chemistry of wet scrubbers, a chemical kinetic computer modeling program has been developed. It allows simulation of the known reactions occurring in solution and calculation of reaction rates and concentration of aqueous species.

The Model

Exact equations for calculating the concentrations of species involved in chemical reactions can only be established for the simplest reaction systems. Approximations, such as the steady-state approximation, permit estimation of concentrations and rates of reaction in more complicated chemical systems under suitable conditions, provided that the system is not too complicated. A different approach is required to accurately calculate concentrations and rates in complex reaction systems, particularly where conditions are rapidly changing.

In the 1970's, work by Whitten[4] and others led to the development of matrix-based computer calculations to simulate complicated chemical kinetic systems. The system of chemical reactions is converted into a series of ordinary differential equations . A method to integrate a sytem of ordinary differential equations was developed by Gear[5] and modified by Hindmarsh[6] at Lawrence Livermore National Laboratory. This routine is the basis for most chemical kinetic modeling schemes. The program performing the Gear routine has subsequently been modified to handle sparse matrices and improve its operating efficiency.[7] This version of the Gear routine is the basis of the chemical kinetic modeling program used in this work. It is similar to modeling routines that have been used to simulate air pollution chemistry for a number of years.[8]

Results and Discussion

The chemistry of the nitrogen-sulfur compounds in solution has been studied extensively for many years, and is, for the most part, reasonably well understood. The rate constants for the reactions involving nitrogen-sulfur compounds, along with those for other important reactions, are incorporated into the computer model. The initial conditions for the calculation are also included as input. These include temperature or temperture vs time profile, initial concentration of species, pH and length of time of the calculation. The program generates a list of reaction rates vs time and concentration vs time for all species included in the calculation. In this way, we can explore the effect of variables such as temperature, pH, concentrations, and additives on the scrubber chemistry.

The chemical reaction database used as input into the model is listed in Table 1. Depending on conditions, some of the reactions are unimportant and are not included in the calculation to reduce the processing time. Tests are performed to ensure the absence of a reaction does not significantly alter the results of the calculation. Updated or additional reaction rate constants can be incorporated into the database as new measurements become available.

Examples of the calculations are shown in Figure 1 and Figure 2. Figure 1 illustrates the effect of pH on the generation and interconversion of nitrogen-sulfur compounds. Calculations were done at pHs of 3, 5 and 7 at a temperature of 40°C for a batch reactor exposed to concentrations of SO_2 = 2000 ppm, NO = 450 ppm and NO_2 = 50 ppm. Increasing the solution pH significantly increases the total concentration of nitrogen-sulfur compounds and favors ATS and ADS as products. Figure 2 illustrates the effect of temperature on the system of nitrogen-sulfur compounds. Calculations were done at temperatures of 20°C (68°F), 40°C (104°F), and 60°C (140°F) at a pH of 5 for a batch reactor exposed to concentrations of SO_2 = 2000 ppm, NO = 450 ppm, and NO_2 = 50 ppm. Increasing the solution temperature also increases the total concentration of nitrogen-sulfur compounds. Higher temperatures increase the concentrations of ATS and ADS relative to HADS and HAMS.

These calculations illustrate what can be studied using the computer model. The influence of a number of scrubbing system parameters can be investigated relatively rapidly. The model does require accurate information on kinetics, gas concen-trations, and solubilities for all compounds that have a significant influence on the chemistry to provide realistic results.

The chemical kinetics modeling program is still under development to increase its versatility. We are in the process of incorporating precipitation processes in the model to simulate the formation of solids. This will allow more accurate investigation of some scrubber chemistries, such as lime/limestone-based scrubbing systems. Measurement of the solubilities of the nitrogen-sulfur compounds is currently in progress,[9] and the results of this study will be incorporated into the model.

The model is also being developed to incorporate the effects of ionic strength and activities of the ions in solution on the reactions used. Scrubbing solutions are generally at conditions that are far from those of ideal solutions. By incorporating ionic strength and ionic interactions into the model, we should be able to obtain more accurate simulation of the chemistry of scrubbing solutions.

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Table 1

Chemical Reactions Related to Aqueous Scrubber Chemistry

Reaction			k,K or H[a]	E$_{act}$[b]
1. $SO_2(gas)$	<=>	$SO_2(aq)$	1.24	
2. $NO(gas)$	<=>	$NO(aq)$	.0019	
3. $NO_2(gas)$	<=>	$NO_2(aq)$	.007	
4. $CO_2(gas)$	<=>	$CO_2(aq)$	.034	
5. $HNO_2(gas)$	<=>	$HNO_2(aq)$	60	
6. $NO + NO_2 + H_2O$ (gas)	<=>	$HNO_2 + HNO_2$	5.3×10^{-2}	
7. $SO_2(aq)$	<=>	$HSO_3^- + H^+$	1.5×10^{-2}	
8. $CO_2(aq)$	<=>	$HCO_3^- + H^+$	4.3×10^{-7}	
9. HSO_3^-	<=>	$SO_3^{2-} + H^+$	1.2×10^{-7}	
10. $HNO_2(aq)$	<=>	$NO_2^- + H^+$	5.8×10^{-4}	
11. HSO_4^-	<=>	$SO_4^{2-} + H^+$	1.2×10^{-2}	
12. $HSO_3^- + HSO_3^-$	<=>	$S_2O_5^{2-} + H_2O$	6.5×10^{-2}	
13 $NO(aq) + NO_2(aq)$	—>	$HNO_2(aq) + HNO_2(aq)$	1.6×10^8	
14. $HNO_2(aq) + HNO_2(aq)$	—>	$NO(aq) + NO_2(aq)$	14	
15 $H^+ + HNO_2(aq)$	—>	$NO^+ + H_2O$	4.08×10^2	11.5
16. $HNO_2 + HSO_3^-$	—>	$ONSO_3^- + H_2O$	2.43	12.1
17 $NO^+ + HSO_3^-$	—>	$ONSO_3^- + H^+$	c	
18. $ONSO_3^- + HSO_3^-$	—>	$HON(SO_3)_2^{2-}$	c	
19 $HON(SO_3)_2^{2-} + H^+$	—>	$HONHSO_3^- + H^+ + HSO_4^-$	2.1×10^{11}	17.6
20 $HON(SO_3)_2^{2-}$	—>	$HONHSO_3^- + HSO_4^-$	1.67×10^{11}	23.0
21.$HONHSO_3^- + H^+$	—>	$NH_2OH + H^+ + HSO_4^-$	6.2×10^{12}	26.3
22. $HON(SO_3)_2^{2-} + HSO_3^-$	—>	$N(SO_3)_3^{3-} + H_2O$	3.4×10^{10}	19.2
23. $N(SO_3)_3^{3-} + H^+$	—>	$HN(SO_3)_2^{2-} + HSO_4^-$	1.5×10^{13}	16.5
24. $HN(SO_3)_2^{2-} + H^+$	—>	$H_2NSO_3^- + HSO_4^-$	2.54×10^{14}	23.5
25. $HON(SO_3)_2^{2-} + HSO_3^-$	.—>	$HN(SO_3)_2^{2-} + HSO_4^-$	1.5×10^{10}	19.0
26. $HONHSO_3^- + HSO_3^-$	—>	$HN(SO_3)_2^{2-} + H_2O$	1.4×10^{13}	24.5
27. $HONHSO_3^- + HSO_3^-$	—>	$H_2NSO_3^- + HSO_4^-$	6.0×10^{12}	24.5
28 $NH_2OH + SO_2(aq)$	—>	$H_2NSO_3^- + H_2O + H^+$	1.74×10^{11}	13.4
29. $NH_2OH + SO_2(aq)$	—>	$NH_4^+ + HSO_4^-$	1.06×10^2	3.0

Table 1
(continued)

30. $H_2NSO_3 + HNO_2$	$\longrightarrow$	$HSO_4^- + H_2O$	1.13×10^2	11.3
31. $NO(aq) + HSO_3^-$	$\longrightarrow$	$^-ONSO_3^- + H^+$	2.6×10^{14}	17.6
32. $NO(aq) + SO_3^{2-}$	$\longrightarrow$	$^-ONSO_3^-$	3.2×10^{10}	10.6
33. $NO(aq) + {}^-ONSO_3^-$	$\longrightarrow$	$^-ON(NO)SO_3^-$	c	
34. $^-NO(NO)SO_3^-$	$\longrightarrow$	$N_2O + SO_4^{2-}$	1.55×10^{-3}	
35. $NO_2(aq) + NO_2(aq)$	$\longrightarrow$	$HNO_2(aq) + NO_3^- + H^+$	8.4×10^7	
36. $HSO_3^- + 2NO_2(aq)$	$\longrightarrow$	$2NO_2^- + 3H^+ + SO_4^{2-}$	1.2×10^7	

a. k in units of $M^{-1} sec^{-1}$ or sec^{-1}; K in units of M; H in units of $M\ atm^{-1}$

b. In units of $kcal\ mol^{-1}$

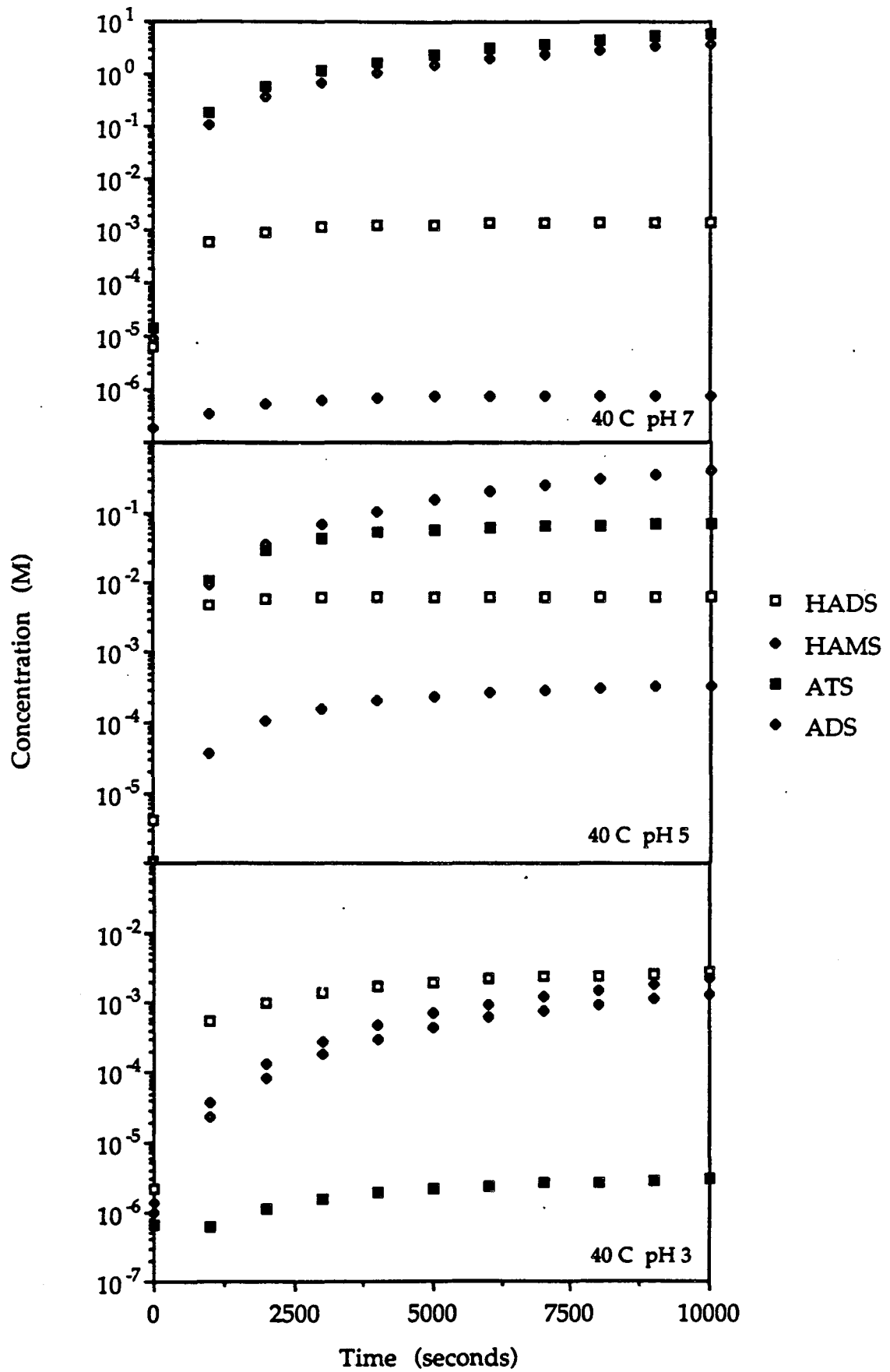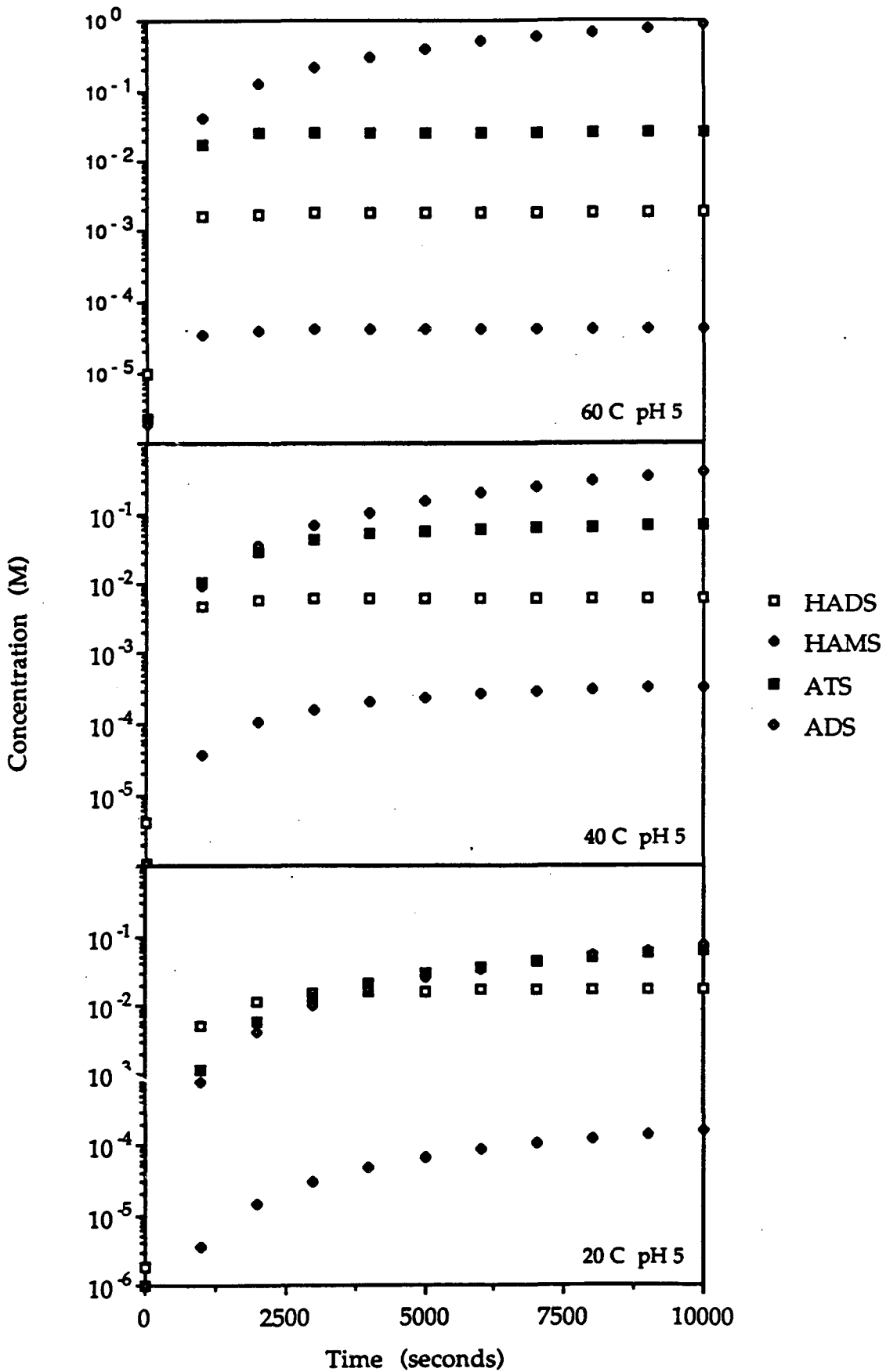c. reactions 17,18 and 33 are assumed to be fast.

Figure 1

Figure 2

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