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Sulfur dioxide uptake and oxidation in sea-salt aerosol

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Abstract. Measurements of SO₂ and O₃ uptake by sea-salt and NaCl aerosol were made in a 600 m³ environmental chamber by measuring the rate of SO₂ and O₃ depletion during nebulization of seawater and NaCl solutions. The experiments were carried out with starting relative humidity between 80% and 92%, with SO₂ concentrations between 35 and 60 ppb, and ozone concentrations between 0 and 110 ppb. For NaCl, no SO₂ or O₃ uptake was observed. For sea-salt aerosol, uptake in the range of 0.21 and 1.2 millimoles of S per liter of (nebulized) seawater was observed. Surprisingly, no O₃ uptake was observed even though the residence time of the aerosol in the chamber was long compared to the time required for the predicted S(IV)-O₃ reaction to occur. Several S(IV) oxidation schemes are considered to explain these observations. The Cl-catalyzed aerobic mechanism as formulated by *Zhang and Millero* [1991] from empirical data best explains our observations. The Cl-catalyzed S(IV) reaction decreases rapidly with decreasing pH, making it important only at pH > ~5.5. This rapid decrease with pH explains why SO₂ uptake was not observed in the NaCl aerosol and observed at a level approaching the sea-salt alkalinity in the case of sea-salt aerosol.

1. Introduction

The possible roles which sulfate-containing particles play in both the direct and indirect climate forcing make it imperative that the sinks of SO₂, the distribution of sulfate between various gas-to-particle conversion mechanisms, and the partitioning of sulfate on various sizes be understood. It is well known that marine boundary layer (MBL) aerosol contains sulfate in excess of that found in bulk seawater. This excess is referred to as non-sea-salt (nss) sulfate. Typical values of nss-sulfate lie in the range from 0.15 to 0.65 µg m⁻³ [Fitzgerald, 1991]. Since there is no known mechanism for enriching sulfate during aerosol formation, the nss-sulfate is assumed to be of atmospheric origin. In the atmosphere, SO₂ can be converted to sulfate either heterogeneously on aerosol and cloud particles or homogeneously in the gas-phase with subsequent condensation onto particulates.

The amount of SO₂ absorbed into liquid particles is highly pH-dependent. As the pH increases, an ever larger fraction of the absorbed SO₂ is in the form of bisulfite and sulfite ions resulting in a dramatic increase of the effective Henry's law constant [e.g., Martin, 1984; Seinfeld and Pandis, 1998]. The oxidation of dissolved SO₂ (as S(IV)) has been widely studied, especially in connection with cloud and acid rain

chemistry. A number of different mechanisms have been investigated, including oxidation by O₂, metal and chloride-catalyzed oxidation by O₂, oxidation by O₃, H₂O₂, and NO_x, and oxidation in the presence of NH₃ which can neutralize the sulfuric acid formed by oxidation of S(IV). Most experiments have shown the importance of dissolved H₂O₂ at pH < 5 and dissolved O₃ at pH > 5, as reviewed by *Seinfeld and Pandis* [1998].

Sievering et al. [1991, 1992] estimated the contribution of heterogeneous sulfur conversion in sea-salt particles during the Coordinated Air-Sea Experiment (CASE) of the Western Atlantic Ocean Experiment (WATOX) sampling program and attributed the nss sulfate to oxidation of S(IV) in sea-salt aerosol by ozone. Because of the rapidity of the O₃-S(IV) reaction at high pH, this mechanism is the prime suspect for initial sulfate formation in sea-salt aerosol. In a chemical modeling study, *Chameides and Stelson* [1992] found that (within the mechanisms included in the model) nearly all nss-sulfate could be attributed to O₃ oxidation of S(IV). This reaction proceeds rapidly until the alkalinity of the aerosol is expended and the aerosol pH drops below 6. Therefore the flux of alkalinity from the sea surface to the atmosphere in the MBL should be the controlling factor in the formation of nss-sulfate.

A number of studies [e.g., Keene et al., 1990; Huebert et al., 1996; Gurciullo et al., 1999] have found that nss-sulfate exceeds that which can be accounted for by O₃ oxidation proceeding only to the point where the sea-salt alkalinity is exhausted. *Clegg and Toumi* [1998] contend that early calculations overestimate the amount of nss-sulfate produced heterogeneously in aerosols and propose nss-sulfate formed during cloud processing is necessary to account for the observed nss-sulfate. In a recent paper, *Gurciullo et al.* [1999] estimate that 50 to 75% of nss-sulfate is formed heterogeneously in aerosols and the rest is formed during

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cloud processing. Others have also pointed out the importance of cloud processing in the formation of nss-sulfate [i.e., Hegg and Hobbs, 1982; Hoppel et al., 1986]. Sievering et al. [1999] suggest that the alkalinity of newly formed sea-salt aerosol may be greater than in bulk seawater since biogenic CaCO_3 skeletal fragments are known to concentrate in the surface microlayer water from which sea-salt aerosol are formed. This enhanced alkalinity could cause greater nss-sulfate from O_3 oxidation.

Keene et al. [1998] suggest that other soluble acidic gases in the MBL would also presumably titrate the sea-salt alkalinity diminishing the potential for S(IV) oxidation by ozone. They further suggest that an important alternative mechanism for S(IV) oxidation may be the one proposed by Vogt et al. [1996] where HOCl and HOBr are formed by an autocatalytic reaction cycle. Vogt et al. [1996] suggest that this mechanism can account for 60% of the S(IV) conversion in the aerosol phase (20% by HOBr and 40% by HOCl).

Surprisingly, we could find very few papers giving results of laboratory measurement of SO_2 uptake and conversion of S(IV) to S(VI) in authentic sea salt aerosols. Clarke and Williams [1983] and Clarke and Radojevic [1983, 1984] measured high conversion rates in bulk seawater and in sea-salt aerosol which they attributed to Cl-catalysis. Zhang and Millero [1991], in a more complete study, found high conversion rates at high pH values in bulk solutions of both NaCl and authentic seawater. Gund et al. [1991] measured SO_2 uptake in sea-salt aerosol and found the rate to be substantial and strongly dependent on the relative humidity (RH). Miller et al. [1987] found enhanced sulfate production in cloud droplets formed on NaCl and sea-salt particles; however, since cloud droplets are much more dilute than sea-salt aerosol, these results are not directly applicable to this study.

In the present paper the results of measurements of SO_2 uptake by NaCl in authentic sea-salt aerosol are presented and discussed. The experiments were part of the National Ocean Partnership Program (NOPP) Aerosol Processes Studies Experiment carried out in the Calspan 600 m^3 Environmental Chamber.

2. Experiment

The Calspan 600 m^3 chamber is 9.1 m in diameter and 9.1 m high with a 590 m^3 volume and surface area of 394 m^2 . The inside is covered with a Teflon coating except for windows of borosilicate glass (Pyrex TM) which cover the irradiation lamps. The lamps were not used in the experiments described in this paper. There is a large (1 m diameter), Teflon-coated variable-speed mixing fan to homogenize the chamber. The filtering system for the chamber incorporates absolute particulate filters which permits removal of essentially all particles (<1 condensation nucleus cm^{-3}). Impregnated charcoal filters enable removal of gaseous contaminants. The chamber is equipped with a wall-wetting ring located along the top circumference of the chamber. Deionized water is supplied to the ring by a high-pressure pump. More information on the chamber as it relates to the NOPP experiments is given by Hoppel et al. [1999]. Ozone and SO_2 were measured with Dasibi Model 1008 and Thermo Environmental Model 42S instruments having detection limits of 1.0 and 0.1 ppb, respectively.

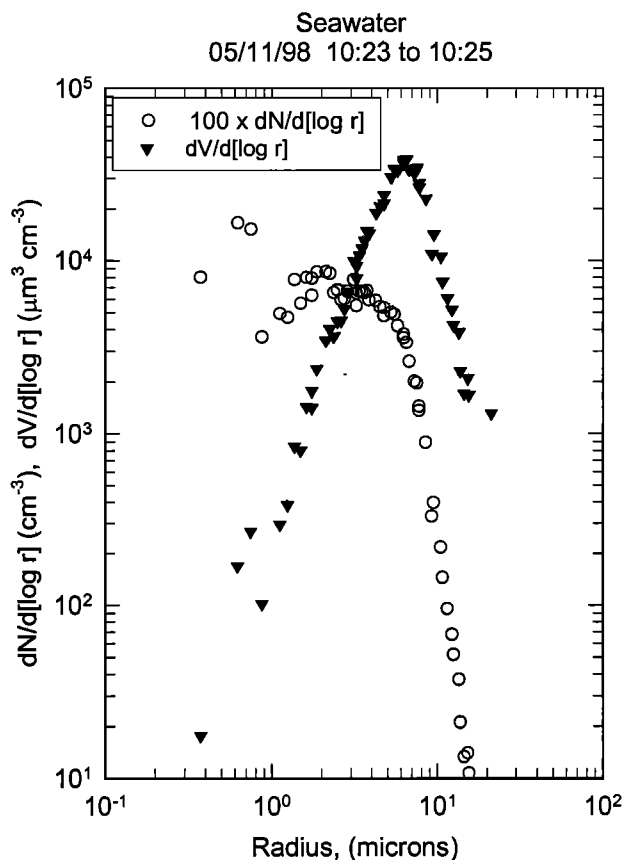


Figure 1. Logarithmic number and volume size distributions generated by nebulizing seawater.

The chamber is equipped with a Sowden Associates (Industrial Spray Products) PNEW-ATOM-1/4-JSS nebulizer in the top of the chamber capable of nebulizing solutions at rates of liters to tens of liters per hour (by changing nozzle inserts and air pressure). The nominal setting used during the experiments discussed here was about 1 L in 20 min at a gas pressure of about 25,600 Pa (35 psi). The gas used to nebulize the solution was research grade nitrogen from a cylinder. The logarithmic size distribution generated by the nebulizer operating under the prescribed conditions is shown in terms of the number and volume distributions in Figure 1.

The size distribution was measured with a Particle Measuring Systems, optical particle counter (PMS-OPC) Model CSASP-100-HV. These size distributions were measured during the chamber characterization experiments in May 1998 and not repeated during the main experiments in October 1998 for fear the large sea-salt load would damage the OPC. During the characterization experiments the heavy salt aerosol loading caused the aspiration fan in the OPC to seize up after a number of runs. Since the nebulization rate and air pressures were approximately the same for both deployments, the size distribution is assumed to be nearly the same during the October experiments as it was during the May experiment with the peak in the mass distribution at about 6 to 7 μm . It was also found during the characterization experiments that the size distribution was not very sensitive to the nebulization rate (for a given nozzle insert); a change in the nebulization rate by a factor of 2 made only a small change in the size distribution. The data shown in Figure 1

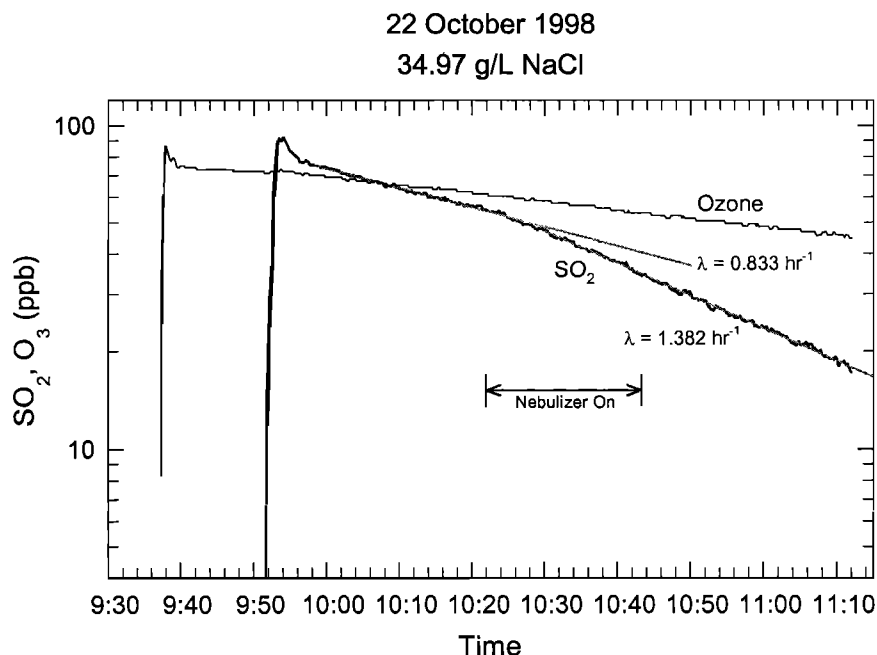


Figure 2. Uptake of SO_2 and O_3 during nebulization of NaCl solution.

are 2-min averages after 20 min of nebulization, and the relative humidity was 78%, whereas the starting relative humidities for the experiments shown later were 89% to 92%.

Before each run the chamber was filtered so that the background aerosol, ozone, and SO_2 concentrations were below the detection limits of the monitors. Ozone and SO_2 were then added to the chamber at about the 80 ppb level, and the wall loss for both O_3 and SO_2 were monitored for about 20 min. After sufficient data were acquired to establish wall loss, the nebulizer was turned on, and the SO_2 and ozone depletion was monitored until the SO_2 concentration reached about 20 ppb, at which time the nebulizer was turned off, and the wall loss after the nebulization was measured.

3. Experimental Results

Data were acquired for nebulization of (1) distilled water, (2) NaCl solution of 35 g L^{-1} (same salinity as the seawater), (3) seawater supplied by Sigma Chemical Co. listed as untreated, sterile, and taken from the Gulf of Mexico, and (4) untreated seawater supplied by the University of Delaware and taken from the Atlantic Ocean off the Delaware Coast. The seawater samples supplied by both Sigma and the University of Delaware were titrated with HCl at the Naval Research Laboratory (NRL) and found to have equivalence points of $2.45 \times 10^{-3} \text{ M}$ and $2.25 \pm 0.02 \times 10^{-3} \text{ M}$ (titration alkalinity), respectively, and pH values of 8.13 and

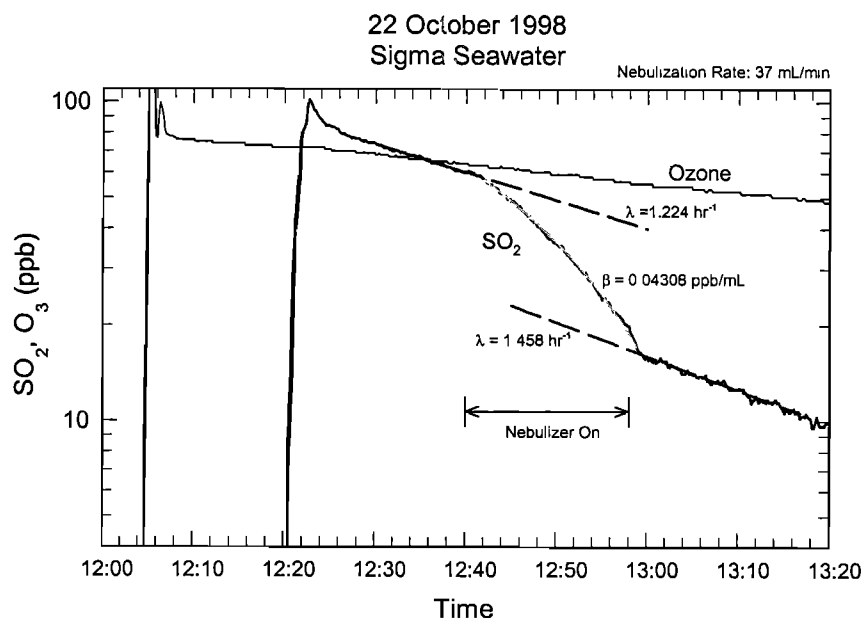


Figure 3. Uptake of SO_2 when Sigma-supplied seawater was nebulized into the chamber.

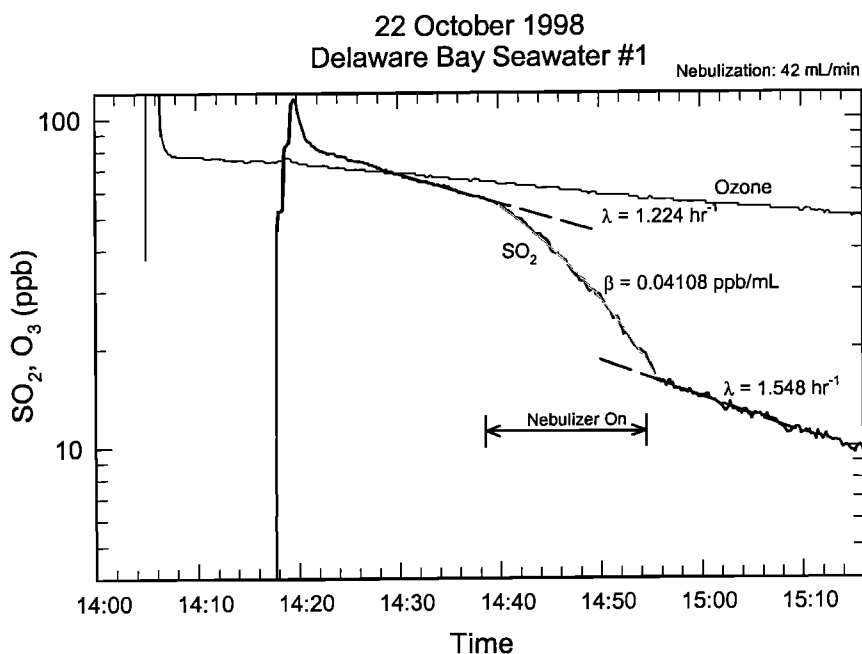


Figure 4. SO_2 uptake when seawater supplied by University of Delaware was nebulized.

8.12 ± 0.03 . These values are in excellent agreement with values given in the literature for seawater [Defant, 1961].

The data for the NaCl run, and one run each for Sigma and University of Delaware supplied seawater, are shown in Figures 2 through 4. The concentrations of SO_2 and ozone are shown as a function of time, and the arrow indicates the period when the nebulizer was on. The slope of the straight line gives the exponential decay constant λ for the wall loss. For the NaCl run there was a small change of slope of the SO_2 trace after nebulization started, and the new slope remained unchanged after the nebulization ceased, indicating either an increase in wall loss as the walls were contaminated with salt or a slow uptake of SO_2 due to a slow reaction of SO_2 with the NaCl aerosol in the chamber. The relative humidity prior to nebulization was 91%, and 95% at the end of nebulization. The slope prior to nebulization was characteristic of SO_2 wall loss in a clean chamber after the (Teflon-coated) walls have been washed down with deionized water and dried by overnight filtering. This NaCl run was the first experiment of the day on October 22 and the walls had been washed down the night before. For the subsequent runs on October 22 the walls were not washed down, but the chamber air was filtered to remove aerosol and gas-phase reactants prior to the next experiment. Notice that in the subsequent experiments shown in Figures 3 and 4, the starting SO_2 wall loss was about the same as that at the end of the NaCl run. For this reason, we interpret the change in slope during the NaCl run as due to an increase in wall loss and not a slow reaction in the NaCl aerosol residing in the chamber.

Figures 3 and 4 show similar plots for the enhanced uptake of SO_2 when Sigma and University of Delaware supplied seawater were nebulized in the chamber. Surprisingly, we observed no corresponding uptake of ozone as we had expected based upon the hypothesis that the $\text{S(IV)}\text{-O}_3$ reaction would occur in the highly alkaline sea-salt particles. To obtain the SO_2 uptake by the aerosols, as distinguished from

wall losses, it was assumed that the change in gas-phase SO_2 , denoted here as $\{\text{SO}_2\}(\text{ppb})$, can be written as

$$\frac{d\{\text{SO}_2\}}{dt} = -\lambda\{\text{SO}_2\} - \beta R, \quad (1)$$

where $\lambda(\text{s}^{-1})$ is the wall loss constant, $R(\text{L s}^{-1})$ is the nebulization rate, and $\beta(\text{ppb L}^{-1})$ is the aerosol uptake parameter. The solution to equation (1) is

$$\{\text{SO}_2\} = \{\text{SO}_2\}_0 \exp(-\lambda t) + \frac{\beta R}{\lambda} [\exp(-\lambda t) - 1], \quad (2)$$

where $\{\text{SO}_2\}_0$ is the initial SO_2 concentration at the start of nebulization and λ was taken as the mean value of λ prior to and after nebulization. β is then chosen to give the best fit to the data and is shown by the smooth curve through the data. The results for the two runs with Sigma and University of Delaware supplied seawater are given in Table 1. A second run with Delaware seawater, believed to be less accurate than the first run because the nebulization rate increased inexplicably during the run even though the nebulizer settings remained the same, is not included here. Increased dripping from the nozzle was reported by an observer. Because (1) these runs were similar to runs made during the chamber characterization experiments with respect to SO_2 uptake without observable ozone consumption, and (2) because of demands placed on the chamber by other parts of the NOPP project, no further runs were made during the October deployment. The SO_2 uptake for the data shown in Figures 3 and 4 is given in Table 1 (October 22 data) where the uptake is given in ppb per liter of seawater nebulized and in terms of moles of sulfur per liter of solution nebulized.

Aerosols were collected on Teflon filters for 1 min toward the end of the nebulization period. The filter sample was later dissolved in distilled deionized water, and the extract solution was analyzed by DIONEX DX500 Ion Chromatography

Table 1. Runs With Sigma and University of Delaware Supplied Seawater^a

Seawater Source	Date 1998	SO ₂ Concentration, ppb		Starting O ₃ Concentration, ppb	Starting RH, %	Uptake in Terms of Moles of S per Liter	SO ₂ Uptake (ppb per Liter of Seawater Nebulized)	Aerosol Sulfate on Filter, ppb		Nebulization Rate, mL min ⁻¹
		Start	End					Normalized	to 1 L	
Sigma	Oct. 22	60	16	63	92	0.0012	43.1	28.1	41.9	37
Delaware	Oct. 22	55	15	63	90	0.0011	41.1	27.1	40.1	42
Sigma	May 18	20	4	105	90	0.00021	7.2	NA	NA	110
Sigma	May 18	35	7	110	92	0.00036	12.8	NA	NA	91
Sigma	May 19	35	8	2	80	0.00054	19.1	NA	NA	88
Sigma	May 19	37	8.5	1	82	0.00051	18.3	NA	NA	84

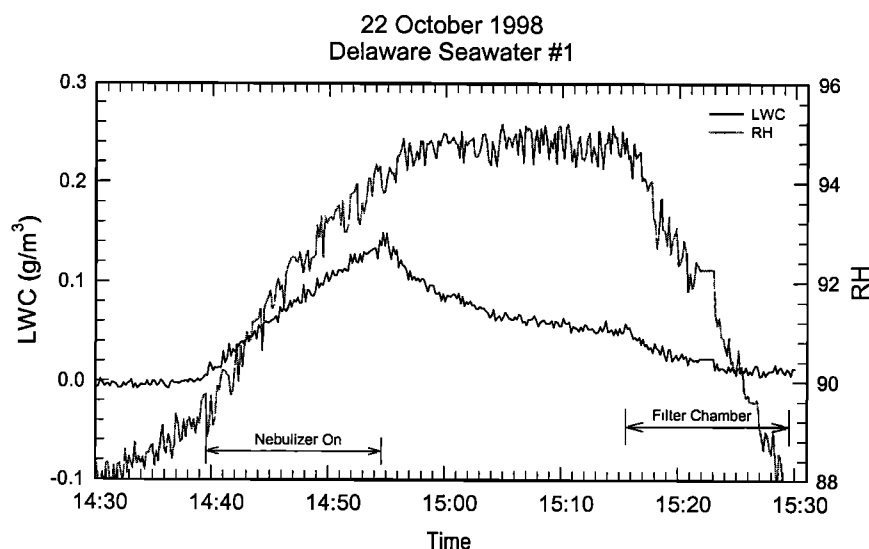
^aNA, not available.

System to determine the mass concentration of sulfate and chloride in the aerosol. The extract solution was also analyzed by Inductive Coupled Plasma - Atomic Emission Spectrometer to determine the concentration of cations, including sodium, calcium, and magnesium. Assuming the ratio of sodium to sea-salt sulfate were the same in the seawater as in the nebulized aerosol, we were able to calculate the mass concentration of nss-sulfate in the aerosol. The nss-sulfate mass concentration was also converted to SO₂ concentration (ppbv) to compare with the observed SO₂ uptake. Considering the uncertainty of sulfate and sodium measurement being 10%, the results show all of nss-sulfate was from the oxidation of SO₂ in both the Sigma and Delaware water cases.

During the chamber characterization experiments in May of 1998 a larger number of nebulization experiments were carried out as we tested and adjusted the nebulizer flow. Tests using triply distilled water during the May experiments showed no observable uptake of SO₂ and no observable change in wall loss. Of course, with distilled water, the resulting aerosol load was very small since the aerosol particles resulting from evaporation of distilled water droplets are much smaller than for the case of solution droplets. During the May characterization experiments we were

puzzled by the lack of ozone uptake comparable to that of SO₂, as would be expected if the SO₂-O₃ reaction were occurring in sea-salt aerosol, so we varied the ozone concentrations from 5 times the concentration of SO₂ to zero in the chamber and found the SO₂ uptake by sea-salt aerosol similar to that shown in Figures 3 and 4 with no observable O₃ uptake regardless of the O₃ concentration. Unfortunately, there were no aerosol filter samples with which to confirm sulfate formation in the aerosol during the May deployment. Table 1 contains data on uptake of SO₂ during four runs in May. Only Sigma-supplied seawater was available during the May deployment. For more details, see *Hoppel et al.* [1999]. For the four runs during the May deployment shown in Table 1, the nebulization rate was about twice that used in the two October runs. For the October runs the uptake of SO₂ ceased less than a minute after nebulization ceased, almost within the response time of the instruments (see Figures 3 and 4). For the higher nebulization rate used during the four May runs shown in Table 1, it took about 2 min after nebulization ceased for the enhanced SO₂ loss rate to relax back to the wall loss rate. Consequently, the fit of the data to equation (2) was not quite as good for the May runs as that shown in Figures 3 and 4.

The lifetime of the particles in the chamber is an important

**Figure 5.** Trace of IR extinction and relative humidity during and after nebulization.

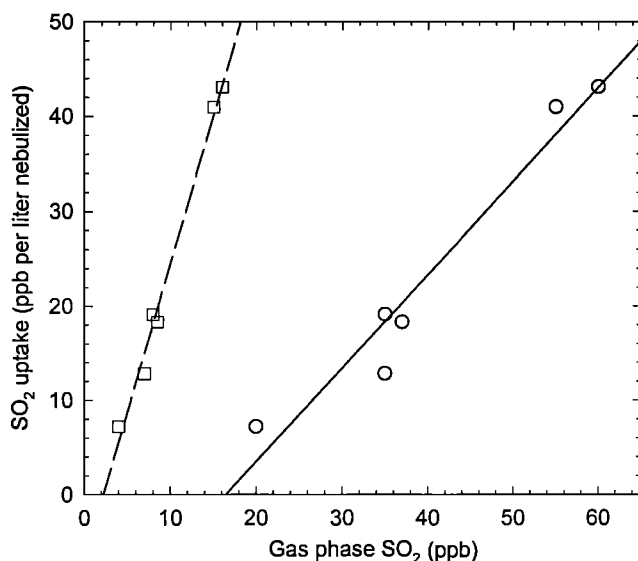


Figure 6. Total normalized SO_2 uptake as a function of beginning (circles) and ending (squares) SO_2 concentration.

parameter when considering possible reactions that may be occurring in the aerosol. The aerosol size distributions shown in Figure 1 are quite disperse with a peak in the mass-weighted size distribution at about 6 to 7 μm . The mixing fan was on during these experiments to keep the chamber thoroughly mixed. The larger particles will have shorter life times in the chamber due to higher inertial deposition rates. Figure 5 shows the trace of the infrared (IR) (11 μm wavelength) extinction as a function of time. The IR measurement is used to measure liquid water during cloud processing experiments and is plotted in terms of liquid water scale in Figure 5. Here we use it only to indicate the lifetime of the largest particles in the chamber. The increase in extinction is nearly linear during nebulization. After nebulization ceases, the decrease in extinction is initially more rapid, then slows gradually with increasing time. At 1320, filtering of the chamber is initiated causing a more rapid decay of particles and a very rapid decrease in relative humidity (dehumidifying coils in the filtering loop were also turned on). To get an estimate of the lifetime of the largest particles in the chamber, the initial rapid decay was fit to an exponential decay. The decay rate for the largest particles is 4.3 h^{-1} (14 min time constant). It is also clear that more than half the IR signal is due to particles with a resident time much longer than 15 min.

While no concerted effort was made to study the dependence of the SO_2 uptake on SO_2 concentration, there seems to be a significant dependence on the SO_2 concentration in the limited number of runs shown in Table 1. Figure 6 shows total normalized SO_2 uptake as a function of the SO_2 concentration at both the start and end of the nebulization period. As will be discussed shortly (in connection with Figure 8), about 50 ppb of SO_2 uptake (as S(IV)) would have been required to titrate the sea-salt alkalinity per liter of nebulized seawater.

4. Discussion

The above experiments employing aerosols generated from real seawater show a large uptake of SO_2 and sulfate

formation without uptake of ozone even though ozone was available. There was no comparable uptake of SO_2 in pure NaCl aerosol. NaCl makes up 78% of sea salt by weight.

4.1. Predicted Uptake of S(IV) in Seawater

It is well known [Martin, 1984] that the solubility of SO_2 in aqueous solutions is greatly influenced by the pH of the solution. The uptake of SO_2 as S(IV) for dilute solutions can be written as

$$[\text{S(IV)}] = H_S P_S + [\text{HSO}_3^-] + [\text{SO}_3^{2-}], \quad (3)$$

where

$$[\text{HSO}_3^-] = \frac{H_S K_1 P_S}{[H^+]} \quad (4)$$

$$[\text{SO}_3^{2-}] = \frac{H_S K_1 K_2 P_S}{[H^+]^2}, \quad (5)$$

where the brackets indicate concentration in M (moles L^{-1}), and H_S ($M \text{ atm}^{-1}$), K_1 (M), and K_2 (M) are Henry's constant and the first and second dissociation constants, respectively; P_S (atm) is the gas-phase SO_2 vapor pressure. The hydrogen ion concentration $[H^+]$ is determined by the ionic charge balance equation.

Seawater is a rather complicated ionic solution where inclusion of all ionic species which contribute to the alkalinity of the solution is difficult, and a complete mathematical treatment of the ionic behavior of seawater is beyond the scope of this paper. The effect of seawater alkalinity can be approximated by including the "titration alkalinity" in the ionic charge balance equation [Chameides and Stelson, 1992; Defant, 1961]. To estimate the ionic composition when the seawater solution is in equilibrium with the gas-phase SO_2 concentration, we have solved equations (3) to (5), together with the ionic charge balance equation, including a constant term for the titration alkalinity. The value of alkalinity used in the charge balance equation is $2.3 \times 10^{-3} M$ in keeping with the measured values given in the last section.

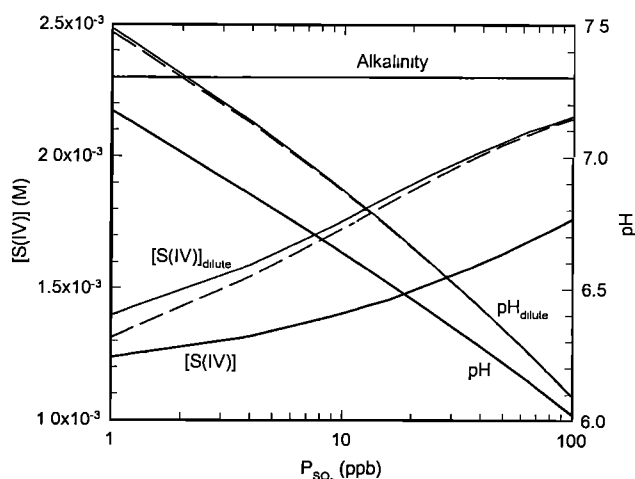


Figure 7. Estimated uptake of S(IV) in a solution with alkalinity of $2.3 \times 10^{-3} M$ and resulting pH of the solution as a function of gas-phase SO_2 . The dashed lines indicate the S(IV) concentration and pH when 350 ppm of CO_2 is included in the dilute approximation.

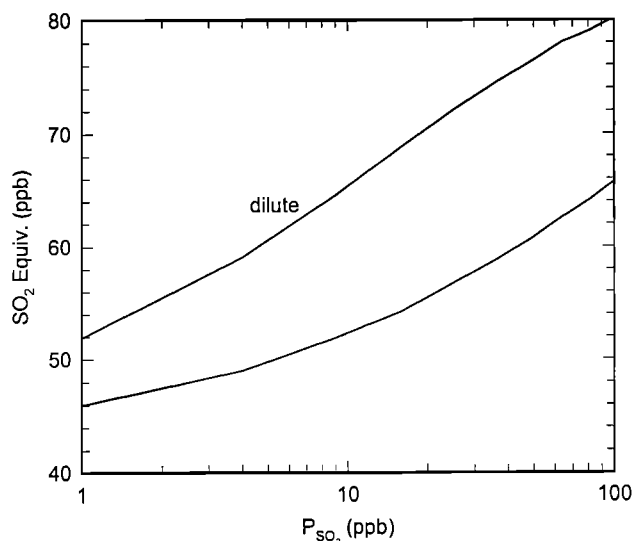


Figure 8. Equivalent amount of SO_2 (in ppb in the chamber) which must be supplied to bring 1 L of seawater into equilibrium as function of the gas-phase concentration.

The results of these calculations are shown in Figure 7 where $[\text{S(IV)}]$ and the pH of the solution at equilibrium are given on the ordinate as a function of the gas-phase concentration. The values calculated by the above equations are labeled “dilute” because we have used the dilute solution approximation. The concentrations of S(IV) uptake are in the millimolar range when sea-salt buffering is present. This can be contrasted with micromolar concentrations of S(IV) uptake in the absence of buffering. For example, Figure 7 indicates an uptake of about 1.4 millimoles for an SO_2 concentration of 10 ppb, whereas the uptake of S(IV) drops to about 11 micromoles when buffering is absent (concentrations cited are for the nondilute case). Because CO_2 is not removed by the chamber’s activated charcoal filtering system and will dissolve and contribute to acidity, we also included 350 ppm CO_2 in some of the runs. However, the addition of CO_2 to the system had only a small effect as shown by the lowering of $[\text{S(IV)}]$ indicated by the dashed lines in Figure 7.

In Figure 8, the above $[\text{S(IV)}]$ results have been translated to equivalent SO_2 uptake (in ppb) required to establish equilibrium at a given gas-phase SO_2 concentration, assuming that one liter of seawater is nebulized into the volume of the chamber. One liter of seawater dispersed in the chamber would require uptake of about 52 ppb of SO_2 in solution before equilibrium is reached with one ppb in the gas phase; an uptake of about 80 ppb would be required for 100 ppb SO_2 in the gas phase. This large uptake, even at low SO_2 concentrations, is required to titrate the seawater alkalinity and is shown by the horizontal line on Figure 7.

The dilute solution approximation can be relaxed by using the results of *Millero et al.* [1989], who measured the uptake of SO_2 as a function of ionic strength in NaCl solutions. Since sea salt is about 78% (by weight) NaCl, using the effect of NaCl ionic strength for S(IV) uptake should be a reasonable approximation for sea salt. Using the results of *Millero et al.* is equivalent to determining the activity coefficients as a function of ionic strength required for nondilute solutions calculations. The ionic strength of the aerosol in equilibrium at the relative humidity of the chamber

is greater than the ionic strength of seawater. We have determined the ionic strength of the aerosols by using the results of *Tang et al.* [1997], who measured the water uptake for sea-salt aerosol as a function of relative humidity. The result, when we include the effect of ionic strength for a chamber humidity of 90%, is also shown in Figures 7 and 8. Including the effect of ionic strength of the solution lowers the S(IV) uptake significantly, but does not change the big picture that the uptake of S(IV) is greatly enhanced by the alkalinity of sea salt.

If the experimentally determined uptake of SO_2 is 0.0012 moles of S(IV) per liter of nebulized seawater, as given in Table 1, we see that the observed value is close to the calculated value shown in Figure 7 (0.0014 M for 20 ppb), indicating that the predicted uptake of S(IV) could account for the observed uptake. While this comparison is interesting, it does not answer the question as to whether or not the S(IV) remains as S(IV) or has been converted to S(VI) within the aerosol.

4.2. Liquid-Phase Reactions for the Conversion of S(IV) to S(VI)

There has been a considerable amount of research done on the liquid-phase oxidation of S(IV) to S(VI) by different mechanisms over a range of pH values. Much of the research has been in connection with the problem of acid rain at low to moderate pH. In the case of clouds (not formed on sea-salt aerosol), S(IV) oxidation by O_3 and H_2O_2 are generally believed to be the most important processes, with the O_3 reaction dominant at high pH and the H_2O_2 reaction dominant at low pH. The number of studies and the certainty of the results are significantly reduced when looking at studies applicable at high pH and to alkaline solutions such as seawater. Because S(IV) oxidation by O_3 is known to proceed very rapidly at high pH, the O_3 oxidation mechanism has been the leading candidate for oxidation of S(IV) in sea-salt aerosol [*Sievering et al.*, 1992; *Chameides and Steltson*, 1992; *Keene et al.*, 1998]. Uncatalyzed aerobic reactions are usually dismissed as unimportant when compared to catalyzed aerobic reactions [*Seinfeld and Pandis*, 1998]. Because sea salt contains a large number of trace elements, catalytic reactions would be expected to play an important role. The two catalytic reactions known to be important in the aerobic oxidation of S(IV) are Fe^{3+} and Mn^{2+} . Of these two, Mn^{2+} is more important at low pH and Fe^{3+} at high pH [*Seinfeld and Pandis*, 1998]. A comprehensive review of transition metal-catalyzed oxidation reactions is given by *Brandt and Eldik* [1995]. The catalytic effect of Cl ions has also been observed and is discussed below in section 3.2.3.

4.2.1. SO_2 oxidation by O_3 . Since (1) the SO_2 - O_3 reaction has been well characterized and was suspected to be the dominant mechanism in the high pH sea-salt aerosol and (2) since the SO_2 - O_3 reaction turned out not to be important in our experiments, we look at the timescale of this reaction to see if the timescale of our experiment was such that we would expect the SO_2 - O_3 reaction to have occurred.

The liquid-phase oxidation rate of S(IV) by O_3 can be written as [*Hoffmann*, 1986]

$$\frac{d[\text{S(IV)}]}{dt} = (k_0 H_S P_S + k_1 [\text{HSO}_3^-] + k_2 [\text{SO}_3^{2-}]) H_0 P_0, \quad (6)$$

where k_0 , k_1 , and k_2 are the rate coefficients ($\text{M}^{-1} \text{s}^{-1}$) for each

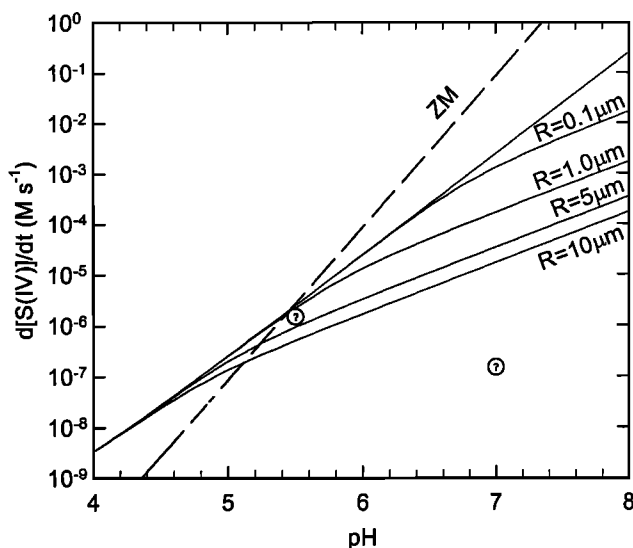


Figure 9. Bulk liquid-phase SO_2 - O_3 reaction rate (solid line). Also shown are transport limitations in particles of radius 0.1, 1, 5, and 10 μm radius. SO_2 and O_3 concentrations are 20 and 80 ppb, respectively. The circles are for Fe^{3+} catalyzed reaction; see text. The dashed line is the Cl-catalyzed rate given by equation (8).

of the S(IV) species and H_0 is Henry's constant for ozone. The equations for the sulfite and bisulfite ions are given by equations (4) and (5). The oxidation rate given by equation (6) is plotted in Figure 9 as a function of pH and is so fast above a pH of about 5 that it is transport-limited [Schwartz, 1988]. For the case of the SO_2 - O_3 reaction the transport limitation is primarily due to liquid phase transport of ozone [Schwartz, 1988], and is a strong function of particle radius. Figure 9 also shows the reduction in the S(IV) oxidation rate due to liquid-phase ozone transport in particles of 0.1, 1.0, 5.0, and 10 μm radius employing the method given by Schwartz and Freiberg [1981]. Since the accommodation coefficient of O_3 is only 5×10^{-4} [Tang and Lee, 1987], it was thought that the interfacial transport might also be important. Interfacial transport limitations are also included but found to be negligible compared to the aqueous-phase limitation.

Temporal plots of the S(IV)- O_3 reaction (integration of equation (6)) with and without liquid-phase transport limitation for O_3 are shown in Figure 10 where the charge balance includes the alkalinity, S(IV), and S(VI) ions as they are generated in the particle. The solution shown is for the case when the concentration of SO_2 is held constant at 20 ppb and the O_3 concentration is 80 ppb. For the transport-limited case the particle radius is taken to be 5 μm . With no transport limitations the sulfate is formed and the buffering used up in a few seconds. For the transport-limited case the sulfate formation requires times on the order of a couple of minutes, and the $[\text{H}^+]$ increase is delayed by the buffering. The total sulfate, [S(VI)], formed is approximately half the alkalinity. The factor of 2 results from the double charge of the sulfate ion. The initial alkalinity of the aerosol was almost 5 times greater than seawater because it was assumed to be in equilibrium with an ambient RH of 90%.

The time constant (~ 2 min) for the transport limited O_3 - SO_2 reaction in a 5 μm particle shown in Figure 10 is about an order of magnitude less than that for deposition of the

largest particles, estimated in section 2 to be about 15 min. Since we saw no decrease of O_3 in our experiments, we conclude that some other reaction was occurring at a faster rate, consuming the S(IV) and lowering the pH of the particle; otherwise, the O_3 reaction would have occurred and been reflected in a loss of O_3 .

4.2.2. Iron (Fe^{3+}) catalyzed aerobic reaction. The iron-catalyzed reaction of S(IV) to S(VI) is often cited as a likely candidate for oxidation of S(IV). Martin et al. [1991] have studied this reaction in detail in water. It is impossible to extend the results of their study to the buffered sea-salt aerosol case with any degree of confidence. The results of Martin et al. are stated to be valid only at ionic strengths less than $10^{-2} M$, whereas the ionic strength of sea-salt aerosol at 90% RH is more than 100 times greater. If we blindly insert the equilibrium S(IV) concentrations as given in Figure 7 (about $1.5 \times 10^{-3} M$) into the expressions given by Martin et al. for a pH between 5 and 7, we get the values given by the question mark symbol shown in Figure 9. The solubility of Fe^{3+} decreases with pH such that, for pH between 6 and 7, the solutions were saturated with respect to Fe^{3+} . For a pH of 7 the rate found by Martin et al. [1991] was the same as the control run with no added Fe^{3+} (presumably the uncatalyzed aerobic rate). The solubility of Fe^{3+} in seawater given by Millero [1998] is about 0.2 nM, 3 orders of magnitude below the concentrations used in the laboratory experiments and reflects the decreasing solubility of Fe^{3+} with increasing pH. Furthermore Martin et al. show that the Fe^{3+} catalyzed reaction is greatly inhibited at high pH by small amount of organic material. Seawater is known to contain organic material. Therefore, based on what is currently known about Fe^{3+} catalysis, it is not possible to attribute the S(VI) production to Fe^{3+} catalysis since the O_3 oxidation should have been much faster than the Fe^{3+} catalyzed rate.

4.2.3. Chloride ion catalysis. Experiments have shown an accelerating effect of chloride ions on S(IV) oxidation in the bulk solution [Clarke and Williams, 1983; Clarke and Radojevic, 1984, and Zhang and Millero, 1991]. Particularly

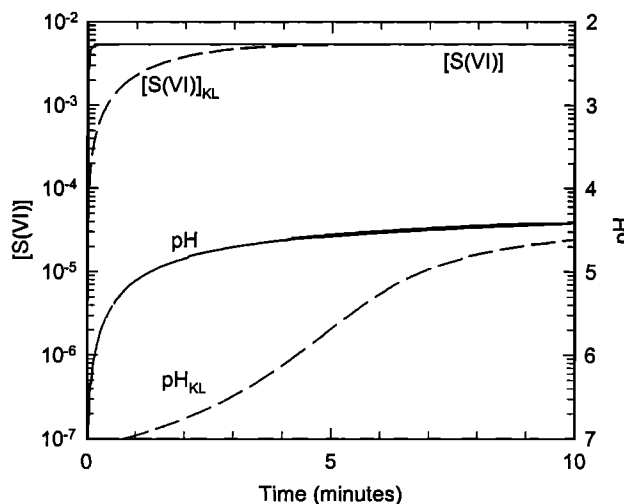


Figure 10. Temporal plot of S(VI) formation in a 5 μm sea-salt droplet in equilibrium at a relative humidity of 90% with gas-phase SO_2 and O_3 concentrations of 20 and 80 ppb, respectively. The dashed lines include liquid phase transport limitation of O_3 .

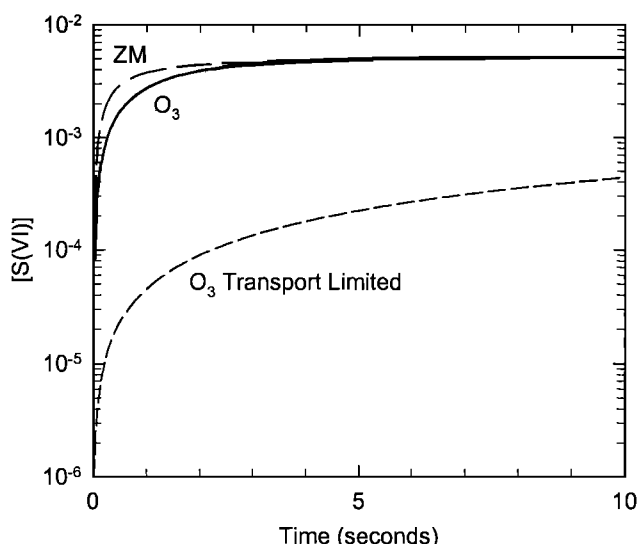


Figure 11. Calculated S(VI) formation in sea-salt aerosol by oxidation of S(IV) for the ZM mechanism (long-dashed line) and by ozone oxidation for cases where O_3 transport is included (dashed line) and excluded (solid line) over the first 10 s. The aerosol is assumed to be formed from seawater and in equilibrium at a relative humidity of 90%. The gas-phase SO_2 and O_3 concentrations are taken to be 20 and 80 ppb, respectively. For the transport-limited case the particles are assumed to be 5 μm in radius.

useful is the study of *Zhang and Millero* [1991] (hereafter referred to as ZM) who studied the rate of sulfite oxidation by O_2 in NaCl and bulk sea-water over a salinity range of 3.5 to 35. Unlike the aerosol case where sulfite is introduced into solution by SO_2 absorption, the sulfite of ZM was introduced into bulk solutions in concentrations of 5 to 10 μM as Na_2SO_3 . The rate of S(IV) oxidation was found to be represented well by the following equation:

$$-\frac{d[S(IV)]}{dt} = k[S(IV)]^2[O_2]^{0.5}. \quad (7)$$

The authors further suggest that the pH dependence of the equation can, reasonably well, be removed from the rate constant by writing the rate as

$$\frac{d[S(IV)]}{dt} = k''[HSO_3^-][SO_3^{2-}][O_2]^{0.5}, \quad (8)$$

where $\log(k'') = 6.17$.

This reaction rate is shown as a function of pH in Figure 9 by the dashed line where we have assumed the aerosol to be saturated with respect to oxygen. It is seen that the Cl-catalyzed rate is higher than the ozone oxidation rate at high pH, dropping below the ozone oxidation rate at a pH of approximately 5.5. The slope of three results from the $[H^+]^{-1}$ and $[H^+]^{-2}$ dependence of the bisulfite and sulfite ions, respectively. Not only is the Cl-catalyzed rate greater at high pH, but the transport limitations for S(IV) are much less severe than that of ozone which greatly limits the rate of S(IV) oxidation by ozone (as shown in Figure 9). Figure 11 shows the S(VI) formation predicted by equation (8) over the first 10 s as compared with the O_3 oxidation rate both with and without O_3 transport limitations. The solution for S(IV)

conversion by O_3 is shown in Figure 10 over a 10 min period. The Cl-catalyzed rate is faster initially at high pH but both eventually reach about the same final value which is largely determined by the alkalinity of the solution droplet. If we were to add the transport limitations for S(IV) for the Cl-catalyzed case, we would undoubtedly see some slowing of the reaction; however, the transport limitation for S(IV) is much less severe than that for ozone [Schwartz, 1988], making the Cl-catalyzed reaction the preferred rate at high pH.

It should be clear that the large S(IV) conversion predicted in both cases is due to the alkalinity of seawater. For the case of NaCl aerosol there is plenty of Cl to catalyze the reaction, but no buffering. For both mechanisms the reaction slows quickly with decreasing pH. Without the buffering to sustain the uptake of SO_2 , the amount of S(IV) required to lower the pH and turn off the reaction is very small, on the order of 10 μM whereas the amount of S(IV) required to expend the alkalinity of seawater is almost 3 orders of magnitude greater. This is why we were unable to detect uptake of SO_2 in our experiment with NaCl aerosol. Even though the Cl-catalyzed reaction may have been taking place in the NaCl aerosol, the reaction shuts down before a detectable amount of SO_2 was removed from the chamber.

In earlier studies, *Clarke and Radojevic* [1983, 1984] also observed the Cl-catalyzed reaction to be second order in S(IV) in bulk NaCl and seawater. In additional experiments with NaCl and sea-salt aerosol, *Clarke and Williams* [1983] and *Clarke and Radojevic* [1984] found more SO_2 uptake by NaCl aerosol than by sea-salt aerosol. This is in stark contrast to our observations which indicate that SO_2 uptake by NaCl aerosol was unobservable while SO_2 uptake by sea-salt aerosol approached the molar value of the sea-salt alkalinity. In the experiments of *Clarke and Williams* [1983] and *Clarke and Radojevic* [1984], much smaller aerosol were generated at the beginning of the experiment, and SO_2 was observed to decay over a period of an hour or two. Had there been SO_2 uptake of the magnitude observed by *Clarke and Williams* [1983] for either NaCl or sea-salt aerosol, it would have significantly exceeded that which we saw with sea-salt aerosol. Furthermore, SO_2 uptake began and ended within a minute of the start and finish of nebulization in our experiment. (As mentioned earlier, this is within the response time of our instrumentation.) *Sievering et al.* [1991] suggests that wall loss may have biased the results of *Clarke and Radojevic* [1984]. In our experiments the surface-to-volume ratio was more than an order of magnitude smaller, and we accounted for wall loss throughout the duration of the experiment.

We hasten to point out that the rate constants determined by ZM were for ionic strengths equal to or less than that of seawater, and for S(IV) concentrations the order of 10 μM . At the RH of the chamber the salinity of the aerosol was 3 to 5 times greater than that of seawater, and the S(IV) uptake was more than 2 orders of magnitude greater than 10 μM . A plot of the rate constant as a function of the square root of the ionic strength (Figure 3 of ZM) indicates a leveling off of the rate constant with increasing ionic strength and suggests that using the rate constant for seawater may be a reasonable approximation. Since there is an abundance of Cl ions, we would not expect the rate constant to be highly S(IV)-dependent. We further point out that even if the rate constant were 2 orders of magnitude less than shown in Figure 9 at pH greater than about 6.5, the ZM mechanism would still be

greater than the O_3 oxidation mechanism and none of the above conclusions would be significantly altered.

Zhang and Millero [1991] also found that Fe^{3+} and Fe^{2+} have a catalytic effect only before they hydrolyze to colloidal iron, and the addition of Mn^{2+} increased the rate of sulfite oxidation, indicating that the presence of trace elements in seawater could have additional effects on the oxidation rate.

5. Conclusions

Uptake of SO_2 by sea-salt aerosol generated by nebulizing authentic seawater into Calspan's 600 m³ environmental chamber ranged from about 7 to 44 ppb per liter of seawater nebulized (or 0.2 to 1.2 millimoles of S per liter of seawater nebulized). Since the measured titration alkalinity of seawater is 2.2 millimoles per liter, approximately 1.1 millimoles of sulfite or sulfate ions are required to titrate the alkalinity. For the two experiments carried out in October, filter samples of the aerosol taken at the end of nebulization were available and indicated the sulfur was present as sulfate on the filter at a level commensurate to the observed uptake of SO_2 . Since no particular care was taken to preserve the oxidation state of S during filter storage prior to analysis, we cannot exclude the possibility that the S(IV) was converted to S(VI) on the filter. However, given the rapidity of the Cl⁻-catalyzed reaction and the O_3 reaction with S(IV) discussed in the previous section, it seems likely that the reaction occurred in situ prior to collection of the aerosol.

These experiments were conducted with various levels of ozone added to the chamber. Unlike SO_2 , there was no observed uptake of ozone by the sea-salt aerosol, even though calculations indicate that the residence time (~20 min) of the aerosol in the chamber was sufficiently long for the S(IV) - O_3 reaction to have taken place. These calculations include the transport limitations due to liquid-phase and interface transport of ozone.

Of the mechanisms considered here, the Cl⁻-catalyzed aerobic reaction, as given by ZM, best accounts for our observations. The ZM mechanism is consistent with the following observations: (1) the absence of O_3 uptake during the experiments, (2) the absence of observable SO_2 uptake in NaCl aerosol, and (3) the amount of S(IV) uptake was comparable to, but less than, the alkalinity of the sea-salt aerosol. Not accounted for by our calculations using the ZM mechanism, is the dependence of SO_2 uptake on SO_2 concentration. One would expect that if the amount of S(IV) reacted depended only on the alkalinity, the SO_2 uptake would not depend on the SO_2 concentration, provided only that the SO_2 concentration was not expended. Figure 6 indicates a dependence of SO_2 uptake on the SO_2 concentration. The amount of SO_2 uptake is not only less than the alkalinity, but it is also less than the equilibrium uptake of S(IV) shown in Figure 7. However, at the highest SO_2 concentrations, the S(IV) uptake is approaching the value given by the alkalinity. As stated earlier, we have approximated the effect of sea-salt alkalinity in our calculations by entering the measured titration alkalinity as a constant value in the ionic charge balance equations, thus bypassing a comprehensive treatment of the complicated ionic composition of sea-salt aerosol. While this procedure should capture the essential features of SO_2 uptake resulting from the alkalinity, it obviously cannot represent the partitioning of all the ionic species as a function

of pH with a high degree of accuracy. A more comprehensive model of the ionic composition of sea-salt aerosol may be required to resolve the details of SO_2 uptake as a function of SO_2 concentration.

The lack of O_3 depletion during the chamber runs with sea-salt aerosol was surprising since we had approached the experiments with the prevailing bias that O_3 oxidation of S(IV) would be the dominant mechanism in alkaline sea-salt aerosol. Had we been aware of the study of ZM, our results could have been anticipated. While our calculations are only approximations, we believe they do elucidate the main features of what is physically occurring during S(IV) oxidation in sea-salt aerosol.

A logical extension of these results to MBL sea-salt aerosol would suggest that a substantial portion of the nss-sulfate found in sea-salt aerosol is due to Cl⁻-catalysis. The amount of the nss-sulfate which can be attributed to the ZM mechanism is approximately equal to the alkalinity of seawater (as adjusted for ambient RH). S(IV) oxidation by O_3 is probably negligible. S(VI) in excess of the sea-salt alkalinity is the result of other oxidation mechanisms which are more effective than the ZM mechanism at lower pH (pH < ~6).

Finally we wish to emphasize that our experiments were not designed to isolate the specific mechanism for S(IV) to S(VI) conversion in sea salt. While the ZM mechanism accounts for our observations better than other mechanisms known to us, our results do not eliminate the possibility that there may be other important catalytic mechanisms as yet unidentified which could also explain our observations.

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