Conf-770909--3

BNWL-SA-6370

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WET REMOVAL OF SULFUR COMPOUNDS FROM THE ATMOSPHERE^(a)

Prepared for Presentation at the International Symposium on Sulfur in the Atmosphere, September 7-14, 1977, Dubrovnik, Yugoslavia, and to be submitted for publication in Atmospheric Environment.

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June 1977

(a) This paper is based on work performed under Energy Research and Development Administration Contract EY-76-C-06-1830.

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WET REMOVAL OF SULFUR COMPOUNDS FROM THE ATMOSPHERE

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ABSTRACT

Wet removal of sulfur dioxide and sulfate from the atmosphere constitutes an important component of the global sulfur balance. Sulfur deposition in the northern hemisphere is increasing with fossil fuel utilization, and has been related with severe impact on soils and surface waters in specific instances. The majority of sulfur in rainfall occurs as sulfate, although dissolved sulfur dioxide (sulfite) can contribute significantly under many conditions.

This paper presents a brief overview of our current capability to calculate sulfur scavenging rates. The general wet removal process can be decomposed into several individual pathways. These include direct sulfur dioxide scavenging, direct sulfate scavenging, and combined scavenging and chemical reaction. Modeling approaches for these pathways are discussed, and pertinent research areas for improvement of our present modeling capability are recommended.

INTRODUCTION

The Importance of Sulfur Compounds in Precipitation

Sulfur occurs in the atmosphere in a number of different compounds and oxidation states, the most important of which are gaseous sulfur dioxide (S IV) and particulate sulfate (S VI). Because of this abundance and also because of their generally high solubility in water, these compounds have a profound influence on precipitation chemistry, their wet removal constituting an important component of the global sulfur balance.

Although it is likely that other oxidation states of sulfur play significant atmospheric roles, their direct wet removal is expected to be comparatively unimportant. Budgetary considerations (cf. Junge (1960)) and indirect measurements (Hitchcock (1976)), for example, suggest that naturally emitted sulfur in the -II oxidation state (hydrogen sulfide, mercaptans, organic sulfides) may be an important component of the atmospheric sulfur balance. The observed low concentrations of these substances, however, imply that they are rapidly oxidized to other compounds in the atmosphere. Moreover, their limited solubilities render them of only marginal interest insofar as precipitation chemistry is concerned. Similarly, elemental sulfur (oxidation state 0) occurs in the atmosphere at concentrations that are much lower than those observed to be typical of the compounds in higher oxidation states. From these considerations it may be concluded that scavenging of sulfur dioxide and sulfate aerosol constitute the predominant pathways for wet removal of sulfur from the atmosphere, and the emphasis of this paper will focus on these two classes of compounds accordingly.

Some idea of the significance of sulfur removal by wet processes can be obtained by considering the several material-balance studies that have been published over the past three

decades (Conway (1943), Eriksson (1959), Junge (1960), Robinson and Robbins (1968) Kellogg, et al. (1972), Friend (1973), Bolin and Charleson (1976) and Rasmussen, et al. (1974)). While these have by no means been in total agreement, there is rather general accord that the global input of sulfur to the atmosphere is of the order of $1-2 \times 10^{11}$ kilograms sulfur per year. Combining this with an estimated tropospheric volume of 3×10^{18} cubic meters suggests that, if wet and dry removal processes did not exist, the sulfur concentration would increase by about 70 micrograms per cubic meter per year. This may be compared with the current United States annual standard for SO_2 , which is 40 micrograms per cubic meter (expressed as S).

Because of difficulties in obtaining precise measurements of dry deposition rates the relative importance of dry and wet deposition of sulfur compounds is rather uncertain. The budget studies cited above estimate that fifty to ninety percent of the atmospheric sulfur burden is removed by wet processes. While the higher of these estimates were based on radioactive fallout measurements and can be expected to overestimate the wet component for near-surface sources, there seems little doubt that precipitation scavenging constitutes an important, perhaps dominant mechanism for sulfur removal.

As a consequence of its effective nature as an atmospheric cleansing agent, precipitation scavenging is also of concern with regard to the delivery of sulfur compounds to surface ecosystems. Adverse effects to soils, forests, and fisheries in several parts of Europe and North America have been extensively documented, and while there is continuing conjecture over specific effects and mechanisms, there appears to be little doubt at present that such negative impacts can be severe under specific circumstances. Many of these detrimental effects can be associated directly with the tendency of dissolved sulfur compounds to displace the acid-base chemistry of precipitation,

resulting in significant increases in hydrogen-ion concentration. Indeed, dissolved sulfate often is the primary contributor to the acidity of rain (cf. Granat (1972), Likens (1976)). Depending upon the buffering capacity of specific soils and surface waters, corresponding increases in acidity can be induced in these media, often with severe detrimental results.

The Distribution of Sulfur Compounds in Precipitation

Sulfur compounds have been measured in samples collected on a variety of precipitation chemistry networks over the past three decades. These networks have focused primarily on the measurement of sulfate, which is undoubtedly the most abundant sulfur-containing specie present in precipitation under most circumstances. Typical concentrations of sulfate in precipitation range from ten to one hundred micromoles per liter, with much higher values occurring in specific samples on occasion.

Sulfate concentrations in precipitation in general tend to increase in regions downwind of areas of large sulfur emission; they also have been shown to increase with time during the last two decades in both North America and Northern Europe. Nisbet (1975), for example, has utilized United States network data to indicate that a 60-65 percent increase in sulfate content of precipitation has occurred during the ten-year period between 1955 and 1965. Although his results indicate a partial leveling off subsequent to 1966, the concentrations appear to be resuming their upward trend at the present time. Sulfur concentrations in rain are estimated to increase by another forty percent by 1980, if current trends continue.

Comparatively little is known with regard to the abundance of sulfite (IV oxidation state) in precipitation. This species tends to oxidize in solution and generally occurs at concentration levels lower than those characteristic of sulfate. Because

of sample preservation problems, reliable measurements of sulfite levels in rain are more difficult to obtain, and most of the usable data in this regard has come from short-term measurement programs where special sample-preservation practices were implemented. Sulfite levels in rain tend to show an inverse relationship with rain acidity and thus with sulfate content. Typical sulfite levels range between zero and twenty micromoles per liter, with higher values occurring under conditions of high ambient sulfur dioxide concentration. A recent analysis for the northeastern United States (Hales, Dana and Glover (1977)) has suggested that from ten to thirty percent of the sulfur in rain approaching the surface exists in the form of sulfite ion.

Objectives

In view of the above aspects of sulfur deposition by wet processes it appears important to possess the capability to calculate the wet deposition rates of sulfur compounds on the basis of source and rainfall information. This capability is valuable for estimating the spatial distribution of sulfate concentrations in both air and precipitation; even more importantly, however, such calculations are essential for predicting the long-term effects of increased industrialization and energy production. Such a capability can be visualized as one component of a comprehensive model to predict the combined effects of transport, deposition, and conversion on the fate of atmospheric sulfur compounds (cf. Bolin and Persson (1975)).

Unfortunately, a totally satisfactory method for calculating scavenging rates does not exist at the present time. In reflection of the multiple pathways for sulfur removal, scavenging calculations tend to be multifaceted with some aspects well understood and others remaining at relatively unsatisfactory

stages of development. Accordingly, the objectives of this paper are to examine the most important of these pathways, to indicate in rather uncomplex terms the (currently) best ways for describing them mathematically, and to describe specific areas where research is needed to upgrade the calculational techniques to a more satisfactory level. A general description of scavenging pathways is given in the next section, followed by detailed discussions of individual mechanisms.

GENERAL SCAVENGING PATHWAYS

Because of the variety of mechanisms contributing to wet removal of sulfur compounds, it is appropriate at this point to examine the pathways for their delivery from the atmosphere to the ground. These are shown in a general fashion in Figure 1, which depicts the atmospheric interactions between SO_2 gas, sulfate aerosol, and precipitation.

As indicated by the figure, gas-phase SO_2 (as well as other sulfur-containing gases) can become absorbed by precipitation and delivered directly to the surface (Steps 1-3-5). Alternatively, absorbed SO_2 may react to form sulfate (Step 3-5) and subsequently approach the surface via Step 4-6. SO_2 also may be converted to sulfate in the gas phase (Step 1-2) and then may be assimilated, along with existing sulfate aerosol, by precipitation and delivered to the surface (Steps 2-4-6).

The above sequences describe the major pathways for wet removal of sulfur compounds. Reverse processes are of course possible, and can contribute significantly to scavenging behavior under appropriate atmospheric conditions. SO_2 may, for example, desorb from precipitation back into the gas phase; and sulfate aerosol may be regenerated via droplet evaporation. Reverse reactions to form reduced sulfur compounds from sulfate, while possible, are unfavored thermodynamically, and can be

considered inconsequential in the atmosphere.* Also depending upon conditions, SO_2 and other sulfur-containing gases may desorb from the surface back into the gas phase. In addition, sulfate aerosol may be resuspended from the surface to the atmosphere. A notable example of this latter effect is the input of sulfate to the atmosphere by the evaporation of sea spray, a mechanism which is thought to account for a significant fraction of the atmospheric sulfur burden.

Two major aspects of this brief discussion concerning scavenging pathways should be emphasized. The first of these is the suggestion that scavenging processes generally occur in a rather dynamic fashion, where a given sulfur atom may undergo several cycles of pathways before deposition. Obviously this complicates calculations of the scavenging process. The second important point is the indication that processes 1-3-5, 2-4-6, 1-2-4-6, and 1-3-4-6 constitute the major pathways for sulfur compound removal. These will be examined individually in the following sections of this paper.

PATHWAY 1-3-5: DIRECT SO_2 SCAVENGING

Because of sulfur dioxide's properties as a gas, its direct scavenging can be calculated in a manner that tends to be much more simple and reliable than corresponding calculations involving sulfate. This relative simplicity occurs for several reasons. First, gas-scavenging calculations do not involve size-distributed aerosol systems. This advantage is doubly beneficial because, in addition to being much less cumbersome mathematically, gas-scavenging calculations do not require dealing with the uncertainties usually encountered in specifying size spectra of aerosol systems.

* This is not always the case in surface waters and soils, however, where reducing conditions often prevail.

A second simplifying feature of SO₂ scavenging calculations arises from the relatively high diffusivity of this gaseous material. This property permits one to neglect a number of rather complicated transport mechanisms, and allows reliable estimation of interphase transport by physical analogy.

Finally, direct SO₂ scavenging calculations tend to be simpler than corresponding calculations for sulfate because of reversible absorption. Since SO₂ readily absorbs and desorbs from precipitation, its aqueous phase concentration tends to reflect only the gas phase concentrations experienced during its recent history. This usually makes definition of the total concentration history of the hydrometeor unnecessary, and often is an overwhelming simplifying feature in associated calculations.

Basic Gas Scavenging Theory

A general theory of gas scavenging has been presented elsewhere (Hales, 1972). The basic precept of this development is that gas molecules may absorb or desorb from an individual hydrometeor depending upon the direction of the concentration "driving-force" between the hydrometeor and its surroundings. For spherical raindrops this behavior may be expressed by a material balance for pollutant within a hydrometeor;

$$\frac{dc_x}{dz} = \frac{3K_y}{v_z a c} (c_y - H'c_x) \quad (1)$$

where

$\frac{dc_x}{dz}$ = change of dissolved gas concentration in hydrometeor with height above ground.

K_y = mass-transfer coefficient for interchange of gas between droplet and its surroundings.

a = hydrometeor radius,

$v_z = \frac{dz}{dt}$ = vertical velocity of hydrometeor,

c = total gas-phase concentration (nominally 1/22,400 moles/ml),

y, x = subscripts denoting gas and aqueous phase, respectively,

and

H' = solubility parameter.

When the distribution of SO_2 between the gaseous and aqueous phases is in equilibrium, then

$$c_y = H' c_x \quad (2)$$

Inspection of (1) reveals that there will be no net interphase exchange under such circumstances.

Scavenging of gases can be calculated in a relatively straightforward manner using Equation (1), provided physical- or "pseudophysical"-absorption is the dominant uptake mechanism*, and the spatial distribution of the gas-phase concentration is known. The usual procedure is to discretize the raindrop size

*In this and the following discussion, we will use the convenient chemical engineering concept of "pseudophysical absorption." By this we mean that a reactive gas such as sulfur dioxide has absorption behavior somewhat similar to that of a non-reactive gas, and can be treated in roughly the same manner mathematically. This is acceptable whenever the significant chemical reactions involved in the absorption process are reversible and occur rapidly compared to the purely physical steps. The dissociation reactions

are very rapid and satisfy these conditions.

spectrum and integrate (1) over the fall path of the raindrop to the ground. Combining repeated calculations of this type for separate drop-size ranges leads to the delivery rate of scavenged material to the surface.

Computer codes currently exist to perform this integration for Gaussian (Dana, et al., 1973) and step-function plumes (Adamowicz and Hill, 1977). Under simplified conditions of vertical rainfall and linearized solubility behavior, these situations may be integrated analytically. The results are (cf. Hales, et al., 1973)

1) Gaussian Plume:

$$c_x(x,y,o,a) = - \frac{Q F \xi}{2\sqrt{2\pi} \sigma_y \bar{u}} \exp \left(- \frac{y^2}{2\sigma_y^2} + \frac{\sigma_z^2 \zeta^2}{2} \right) \left\{ \exp(\zeta h) \left[1 - \operatorname{erf} \left(\frac{-\sigma_z^2 \zeta - h}{\sigma_z \sqrt{2}} \right) \right] + \exp(-\zeta h) \left[1 - \operatorname{erf} \left(\frac{-\sigma_z^2 \zeta + h}{\sigma_z \sqrt{2}} \right) \right] \right\} \quad (3)$$

2) Step-Function Plume:

$$c_x(x,y,o,a) = S_n \frac{\xi}{\zeta} F(e^{\zeta b} - e^{\zeta d}) \quad (4)$$

Here

$c_x(x,y,o,a)$ = ground-level aqueous-phase concentrations of pollutant in a raindrop of radius a at a point x,y beneath the plume,

Q = source strength (moles/unit time) of the plume,

F = plume depletion factor (taken as unity for SO₂ plumes close to the source),

σ_y, σ_z = Gaussian plume dispersion parameters

$\bar{u}$ = wind speed

h = virtual emission height

$$\zeta = \frac{3K_y H'}{c v_z a}$$

$$\xi = \frac{3K_y}{v_z a}$$

and S_n = step function

= 0 for $b < z < d$

= c_y/c for $b < z > d$

Mass-transfer coefficients for use in the above equations depend upon mixing in both the gas and liquid phases. For moderately soluble gases such as SO₂, however, it is acceptable to approximate mixing behavior by assuming that the majority of transport resistance is in the gas phase. This permits calculation of K_y using the Froessling equation (Bird et al. (1960)),

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3}, \quad (5)$$

where

$$Sh = \frac{2K_y a}{D_{Ay} c_y} = \text{Sherwood number},$$

$$Re = \frac{-2av_z}{\nu} = \text{Reynolds number},$$

and

$$Sc = \frac{\nu}{D_{Ay}} = \text{Schmidt number}.$$

Here D_{Ay} and v denote the diffusivities of mass and momentum in the gas phase.

Solubility of sulfur dioxide in water varies as a function of concentration, temperature, and acidity of the hydrometeors. This can be expressed in the combined form* (cf. Hales and Sutter (1973))

$$c_x = \frac{1}{H'} c_y = \frac{c_y}{H} + \frac{-[H_3O^+]_{ex} + \sqrt{[H_3O^+]_{ex}^2 + 4K_1 c_y/H}}{2} \quad (6)$$

where $[H_3O^+]_{ex}$ denotes the concentration, in moles per liter, of hydrogen ion donated by sources other than dissolved sulfur dioxide. Under most conditions it is reasonable to approximate $[H_3O^+]_{ex}$ by equating it to the total free hydrogen ion concentration, that is,

$$[H_3O^+]_{ex} \approx 10^{-pH} \quad (7)$$

The temperature-dependent parameters K_1 and H have been given by Johnstone and Leppla (1934), and are presented in Table 1.

The above discussion presents a reasonably reliable and simple approach for calculating direct SO_2 scavenging in the locality of sources (cf. Hales, Wolf and Dana (1973), Hutcheson and Hall (1974)), and similar techniques can be utilized for additional gaseous pollutants if desired. For small hydrometeors or for larger distances from the source, however, the approach

* This equation is based on the assumption that sequestering of dissolved sulfur dioxide by foreign contaminants such as trace metals and organics is negligible. Our experience indicates this assumption to be generally a valid approximation for both clean and polluted atmospheres, although recently some highly interesting arguments to the contrary have been advanced by Eatough (1977).

Table 1. Values of the Parameters K_1 and H

<u>Temperature</u> °C	<u>K_1</u> moles/l	<u>H</u> Dimensionless
0	0.0232	0.0136
10	0.0184	0.0196
18	0.0154	0.0270
25	0.0130	0.0332
35	0.0105	0.0445
50	0.0076	0.0673

is even simpler. This is made possible by the fact that, if the gas-phase concentration varies sufficiently slowly in the vicinity of a hydrometeor, the aqueous-phase concentration should approach equilibrium with its gas-phase surroundings; in short, it should be given by Equation (2).

The above circumstances are known as equilibrium-scavenging conditions. Equilibrium scavenging prevails whenever the relaxation time for uptake by the hydrometeors is small in comparison with the rate of change in gas-phase concentration. Equilibrium is favored by small drop sizes, small changes in gas-phase concentration with height, and low solubilities. Utilizing elementary mass-transfer considerations these conditions can be combined conveniently into a single dimensionless criterion. For general source conditions this is given by (cf. Hales (1972))

$$\frac{-3K_y H' c_y \left| \frac{dc_y}{dz} \right|_{\text{ground level}}}{c v_z a \left| \frac{dc_y}{dz} \right|_{\text{max}}} \gg 1, \quad (8)$$

which reduces to

$$\frac{-3K_y H' \sigma_z e^{1/2}}{c v_z a \exp(h^2/2\sigma_z^2)} \gg 1 \quad (8a)$$

for the special case of a Gaussian, point-source plume. Here $\left| \frac{d c_y}{d z} \right|_{\max}$ is the absolute value of the vertical concentration gradient experienced by the falling drop.

Experience has indicated (Dana, et al., (1973)) that equilibrium scavenging conditions are satisfied whenever the values of these groups are greater than about 15; for SO₂ plumes from tall stacks this suggests that equilibrium scavenging should prevail beyond about twenty stack heights downwind. This extremely fortunate circumstance allows the calculation of SO₂ delivery to regional areas simply on the basis of gas-phase concentrations, rain rates, and solubility. As mentioned previously such an exercise recently has been completed by Hales, Dana and Glover (1977) for the northeastern United States.

Insofar as comprehensive regional models of sulfur pollution are concerned, it appears totally acceptable to incorporate the equilibrium scavenging expression (Equation 2) as a means of calculating the direct SO₂ scavenging component. For local plumes expressions such as (3) or the available computer codes (Dana, et al. (1973)) should be applied. If repeated calculations are to be made, the computer codes (which are more elaborate but require only small execution times) are recommended to avoid the tedium of hand calculation.

In summary it is apparent that the calculation of direct SO₂ scavenging is reasonably well in hand, and little further research is needed in this general area. As mentioned earlier, the question of sulfite sequestering in solution was disregarded in this development; if this does occur to an appreciable extent then this paper's results should be reviewed accordingly.

Further research in this specific area should be conducted to

evaluate this effect; if it is found to be significant the developments described in this paper should be restructured to reflect such behavior. Because of the generally favorable comparison between field calculations and measurements, however, the chances of any real changes in the calculational procedure in reflection of this effect appear to be small.

A second specific area where more information is needed is that of SO_2 concentrations in regional precipitation. As mentioned previously, such data are practically nonexistent at present and are badly needed to evaluate the real role of direct SO_2 scavenging in regional and global sulfur balances.

Finally, a cautionary note with regard to SO_2 scavenging calculations should be emphasized: One should never attempt to apply "irreversible" or washout-coefficient theory to describe the scavenging of SO_2 . Use of this approach in the past has resulted in the calculation of scavenging rates several orders of magnitude higher than the appropriate values; for most modeling applications it is far better simply to ignore SO_2 washout altogether than to make this conceptual error. Fortunately, the rather simple techniques described in this section makes this choice unnecessary, and provide a comparatively reliable method for assessing SO_2 concentrations in rain.

PATHWAY 2-4-6: DIRECT SULFATE SCAVENGING

Material Balances: Generalized Computational Approach

As stated in the previous section, the direct scavenging of sulfate aerosol is usually difficult to describe mathematically, both because it involves distributed particle-size systems and because it typically requires integrations over longer time periods of the hydrometeor's history.

In spite of these differences, however, these calculations share a fair degree of commonality with those for gas scavenging. The aqueous-phase material-balance Equation (1), describing transport of pollutant to a hydrometeor, can be expressed for the aerosol case as

$$\frac{dc_x}{dz} = \frac{3K_y}{v_z} \frac{1}{a} c_y \quad (1a)$$

where the absence of the c_x term on the right reflects the irreversible nature of particulate scavenging. In principle, (1a) may be integrated over the raindrop's trajectory in a manner similar to that applied for gas scavenging; and indeed this may be completed in a straightforward fashion under conditions when c_y is well defined (cf. Engelmann (1968)). The fact that c_y (and also the mass-transfer coefficient K_y) are usually unknown, however, leads to the typically low confidence levels that often characterize aerosol scavenging calculations.

The spatial and temporal distributions of sulfate aerosol can be described in terms of a microscopic material balance for the gas phase, given by the form (cf. Hidy (1973), Hales (1972), (1976))

$$\frac{\partial c_y}{\partial t} = - \nabla \cdot c_y \vec{v} - w + r_y \quad (9)$$

Here the time rate of change of pollutant concentration in a differential volume element of space is equated to the sum of contributions from divergence, scavenging, and reaction terms: $\vec{v}$ represents the velocity vector of airborne pollutant and $-w$ accounts for its removal by scavenging. In physical terms w is the amount of pollutant transferred from the gas phase to the aqueous phase per unit volume per unit time, at a point x, y, z in space. It is related to the local scavenging coefficient

by the form

$$w = \Lambda c_y \quad (10)$$

Equation (10) may be considered a definition of the scavenging coefficient.

Under specific conditions Equation (9) reduces to simple forms commonly encountered in published scavenging calculations. For a nonreactive aerosol in a well-mixed volume, for example,

$$\frac{\partial c_y}{\partial t} = \frac{dc_y}{dt} = -w = -\Lambda c_y \quad (9a)$$

It is important to note that, in contrast to Equation (10), special forms such as (9a) should not be considered as general definitions of Λ . Failure to recognize this fact has led to severe errors in several previous scavenging analyses.

A general procedure for direct sulfate scavenging analysis using Equation (9) can be stated as follows:

1. Obtain transport information to define velocity vector $\vec{v}(x,y,z,t)$ in Equation (9). This information may be in the form of measured wind and diffusion data, or it may be generated as output of previous modeling calculations.
2. Obtain quantitative information regarding Λ and (if necessary) r_y .
3. Solve (9), subject to appropriate initial and boundary conditions, to obtain $c_y(x,y,z,t)$. Such solutions may be numerical, or (if possible) analytical in nature.
4. If concentration data in the aqueous phase are required, obtain solutions to (1a) corresponding to the computed

values of c_y . This involves decomposition of the overall scavenging coefficient for application to specific drop sizes.

This algorithm is rather unsatisfying in a pragmatic sense, because it gives very little specific guidance in the performance of actual scavenging calculations. In view of the diversity of situations occurring in the atmosphere, however, it is impossible to provide a more definitive treatment without loss of generality. Obviously, a great deal of meteorological judgment must be exercised in applying this procedure to obtain calculations of scavenging rates. Observance of this general procedure is extremely important, however, because it provides a systematic approach that helps to avoid many of the conceptual pitfalls that have plagued some previous attempts of scavenging calculation.

Examples where the above procedure has been applied to obtain scavenging rates for relatively simple situations are abundant (cf. Engelmann (1968)). This algorithm has been applied as well for more complex systems, involving detailed numerical analyses. Key examples of this type of application are the convective-storm scavenging model by Hane (1974) and the frontal-storm scavenging model of Kreitzberg (1977).

Microphysical Attachment Mechanisms

The variety of mechanisms leading to the transport of aerosol to the aqueous phase (and thus contributing to the magnitude of Λ) is a subject of continuing conjecture (cf. Hidy (1973)). The individual mechanisms most commonly thought to contribute to the interphase transport process are:

- impaction
- interception

- diffusion (Brownian motion)
 - turbulent transport
 - nucleation
 - thermo- and diffusiophoresis
- and
- electrical effects.

The first four of these mechanisms depend primarily upon size and density of the aerosol particles, and thus can be expected to be similar for aerosols of similar size and mass distributions, regardless of their chemical composition. Thermophoresis and electrical effects may be expected to depend upon chemical composition to some extent, owing to their respective dependence on thermal conductivity and dielectric constant. Nucleation is extremely composition dependent, and can be expected to be a highly effective transport mechanism for hygroscopic materials such as sulfuric acid and its common salts.

The relative significance of the various attachment mechanisms can be expected to vary markedly as a function of meteorological circumstances, and accordingly it is convenient to classify the present discussion according to whether transport is occurring within a condensing cloud or in areas populated by large falling raindrops with relatively few cloud particles.

The latter case has been reviewed by Slinn (1974), who has concluded that - given a fixed aerosol size distribution - the primary interphase transport mechanisms are impaction, interception, and diffusion. Slinn has proceeded to formulate expressions for scavenging efficiency based on these mechanisms; for an aerosol particle of radius a and raindrop of radius R the corresponding efficiencies are as follows:

$$\text{Impaction: } \left[\frac{S - 1/12}{S + 7/12} \right]^{3/2}$$

Interception: $s \frac{a}{R}$

Brownian diffusion: $0.65 \times 10^{-12} \left[\frac{10^{-7}}{a^2 R^2} + \frac{1}{a^{4/3} R} \right]$

where S is the Stokes parameter, given by

$$S = \frac{-2}{9} \frac{a^2}{R} \frac{v_z}{v} \frac{\rho_p}{\rho_a} \quad (11)$$

and ρ_p/ρ_a is the density ratio of the aerosol particle and air. Total capture efficiencies $E(a,R)$ can be estimated by summing the above contributions. These then can be integrated over the raindrop and aerosol size distributions (provided these are known) to obtain the appropriate scavenging coefficient (Dana and Hales (1975)), as follows:

$$\Lambda = \pi \int_0^\infty \int_0^\infty R^2 E(a,R) F(R) f(a) dR da \quad (12)$$

Here F and f are probability-density functions for the size distributions of raindrops and aerosol particles, respectively.

Example integrations of (12) for log-normally distributed spectra have been completed by Dana and Hales (1975), leading to plots of Λ versus geometric mean particle size as shown in Figure 2. This figure pertains to particular meteorological circumstances and care should be exercised in its application to individual situations. Its primary importance in the present context is its indication of how seriously in error one can be by applying inappropriate particle statistics to scavenging calculations. Consider, for example, the calculation of the washout coefficient of an aerosol with a 0.1 geometric mean particle radius and geometric standard deviation of $\sigma_g = 2.5$.

As a first approximation one might be tempted to assume the aerosol can be characterized by a homogeneous ($\sigma_y = 1$) ensemble of particles having the indicated geometric mean radius. As can be seen from Figure 2, such an assumption would lead to an estimate that is almost three orders of magnitude low.

This propensity for error is compounded by our present lack of knowledge with regard to the size-distribution spectra of atmospheric sulfate. Aside from knowing relatively little concerning the size spectra of sulfate aerosols under low relative-humidity conditions, their state under humidities approaching saturation is almost totally uncertain. Given the significant nucleating capability of sulfate aerosol it seems reasonable to assume that the dominant pathway for below-cloud scavenging is first for the particles to grow by condensation of water, and subsequently be removed (with a correspondingly modified efficiency) by the mechanisms discussed. Some interesting evidence in support of this contention is given by Radke, et al. (1974).

Adding the nucleation step to the scavenging pathway introduces the rather distasteful prospect of dealing with joint distributions of condensation droplet size and sulfate concentration. Much additional research remains to be completed in this area before reliable scavenging calculations can be achieved.

Insofar as scavenging within condensing clouds is concerned, similar mechanisms prevail. Here, however, one should expect nucleation processes to become more dominant (cf. Hidy (1973)), especially for sulfate particles, which can be expected to compete effectively for cloud water with other types of aerosols. Attempts have been made to account rigorously for all in-cloud attachment mechanisms (cf. Dingle and Lee (1973)); these have tended to be so complex, however, as to discourage widespread

application. In reflection of this complexity a number of gross parameterizations have been suggested. Slinn (1974), for example, has reasoned that interphase transport efficiencies in many cloud systems should approach unity, and that subsequent delivery of scavenged material to the surface depends primarily upon the clouds ability to loose its liquid water by precipitation. Combining these ideas with further simplifying assumptions, Slinn suggests that the expression

$$\bar{\Lambda} = \frac{J}{2 R_m} \quad , \quad (13)$$

where J is the rainfall rate and R_m is the mean raindrop size at ground level, provides a reasonable approximation to the mean scavenging coefficient.

Similar types of rough approximations of this type have been developed elsewhere; a particularly noteworthy example is the scavenging-ratio concept of Engelmann (1971), which is based upon an integral material balance over a storm system, and provides a convenient rule-of-thumb for estimating pollutant concentrations in precipitation on the basis of their corresponding values in air.

On the basis of this discussion one can conclude that direct sulfate-scavenging calculations are not at a satisfactory state of development at the present time. Although there are several factors contributing to this situation, it seems apparent that the most severe deficiency is our lack of knowledge regarding the character of sulfate-containing aerosols. Specifically, additional research emphasis should be focused on the following areas:

- size distributions of sulfate-containing aerosols
- composition versus size relationships for sulfate-containing aerosols

and nucleating abilities of sulfate-containing aerosols; i.e., aerosol size versus relative humidity.

Once adequate knowledge in these particular areas has been obtained, our capability to predict direct sulfate scavenging can be expected to advance significantly.

PATHWAYS 1-2-4-6 AND 1-3-4-6:
SULFUR DIOXIDE REMOVAL BY THE COMBINED
EFFECTS OF SCAVENGING AND CHEMICAL REACTION

Since the preponderance of anthropogenic sulfur emitted to the atmosphere is released in the form of sulfur dioxide, and since the majority of sulfur in precipitation occurs as sulfate, it is logical to presume that pathways 1-2-4-6 and 1-3-4-6 in Figure 1 constitute the most important routes for atmospheric sulfur removal. Conversion to sulfate by dry processes (or wet processes followed by droplet evaporation) with subsequent wet removal is simply the previously-discussed pathway 2-4-6, preceded by chemical reaction. Gas-phase reactions of sulfur dioxide have been considered in several recent reviews (Granat (1975), Harrison, et al. (1976), Levy, et al. (1976)) and are discussed at length elsewhere in this volume. Accordingly, these will not be considered here, other than to note their significance as steps in the overall removal process.

Aqueous-phase oxidation of sulfur dioxide is considered at length in the above citations as well. This phenomenon is more intrinsically associated with the wet-removal process, however, and accordingly deserves some brief mention here. In considering the net oxidation of sulfur dioxide, it is important to bear in mind the proportions of the gas typically distributed between the gaseous and aqueous phases. Under comparatively unpolluted conditions equilibrium concentrations in the aqueous

phase (cf. Equation 2) often are of the order of 10^4 times those in the gas phase; and combining this with a typical cloud-water content of 1 gram per cubic meter suggests that about one percent of the total sulfur dioxide loading can exist in the aqueous phase. This implies that even under relatively favorable conditions bulk reactions in the aqueous phase must be moderately rapid if they are to account for a significant portion of the total conversion to sulfate.

Oxidation of sulfur dioxide in pure aqueous solution in the presence of oxygen atmospheres was investigated by Fuller and Crist (1941), who demonstrated that although oxidation definitely does occur under these circumstances, its rate is normally too slow to be significant as an atmospheric process. These and numerous subsequent authors (cf. Levy, et al. (1976)) have investigated the effects of added trace materials as promoters for this reaction both in bulk and dispersed aqueous phases. Ammonia has received special attention in this regard because of its rather ubiquitous presence in the atmosphere, and because of its noted effectiveness in increasing the solubility of sulfur dioxide. Other trace materials investigated as promoters include copper, manganese, lead, vanadium, sodium, cobalt, and iron. The role of dissolved ozone as an oxidant also has been examined.

While these studies generally have supported the idea that aqueous-phase conversion can account for a significant fraction of total sulfate formation, they have not come to any real consensus with regard to reaction mechanism(s); nor have they provided rate expressions that can be employed with confidence in scavenging calculations. Considerable divergence of opinion exists, for example, with regard to the true influences of temperature, hydrogen-ion concentration, and sulfur-dioxide concentration on the conversion process. These laboratory

studies have been complimented by some limited investigations of sulfur dioxide oxidation in actual rain samples (Hales, Dana and Glover (1977)). Sulfur dioxide in these samples was observed to decay slowly at temperatures in the vicinity of the freezing point, and to become rapid at temperatures approaching 20°C. Aside from providing a semiquantitative indicator, however, these measurements cannot be considered to be of any large benefit to the general problem of modeling wet-removal processes.

If reliable parameterizations of aqueous-phase conversion rates were available, then incorporating them into a description of the scavenging process could be conducted in a relatively straightforward manner. One fortunate circumstance in this respect is the fact that, in cloud environments, at least, the chemical reaction step is rate limiting, and one can use (2) as a steady-state approximation to describe the aqueous-phase sulfur dioxide concentration. A criterion for chemical-reaction limited scavenging has been derived previously (Hales (1972)) as

$$\frac{a k_1 c}{3 K_y H'} \ll 1 \quad (14)$$

and (8) satisfied,

where k_1 is a pseudofirst-order rate constant for the reaction process. Applying (14) for the case of sulfur dioxide suggests reaction-limited conditions prevail in clouds for reactions having half-times of the order of a few seconds or more.

Reaction-limited conditions may not prevail in the case of rain scavenging, especially in situations involving local plumes where (8) is unsatisfied. Even under these conditions, however, scavenging can be calculated in a rather straightforward manner

using extensions of gas-scavenging theory. The computer codes described by Adamowitz and Hill (1977) and by Dana, et al. (1976) are key examples of such applications.

In conclusion it can be stated that the primary research need in this area is that of obtaining reliable parameterizations of aqueous-phase conversion rates. Because of the relative simplicity involved in composing serviceable scavenging models with simultaneous mass transfer and chemical reaction, future laboratory measurements in this area should be conducted with bulk, rather than dispersed aqueous systems. The latter type of experiment (water-aerosol systems, supported droplets, etc.) contributes nothing additional to the elucidation of the major problem, and usually involves considerable unnecessary experimental difficulty.

It seems apparent that much research remains to be completed in the reaction-rate measurement and parameterization area. Once this is brought to a satisfactory stage, however, a substantially improved basis for sulfate scavenging calculations can be expected to evolve.

ACKNOWLEDGMENTS

This work was completed under support of the Division of Biomedical and Environmental Research of the U.S. Energy Research and Development Administration. The author expresses his sincere appreciation to this agency for their support.

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Figure 1: General Schematic of Pathways for Wet Removal of Atmospheric Sulfur Compounds.

Figure 2: Washout Coefficients* for Size-Distributed Aerosols of Geometric Mean Diameters a_g and Standard Deviations σ_g for a Typical Rain Spectrum.

* Normalized to unit rainfall rate, J.