LABORATORY MEASUREMENT OF SULFUR DIOXIDE DEPOSITION VELOCITIES

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ABSTRACT

Measurements of sulfur dioxide deposition velocities have been carried out in the laboratory with the use of a cylindrical flow reaction. Analysis of data from these experiments was performed with models that specifically account for diffusive transport in the system. Consequently, the resulting deposition velocities were independent of diffusion processes and represented the maximum removal rates that would be encountered in the environment under turbulent atmospheric conditions. The measured values ranged from 0.04 cm/sec for asphalt to 2.5 cm/sec for cement, and were independent of sulfur dioxide and oxygen concentrations as well as relative humidity and total pressure.

Prolonged exposure to sulfur dioxide eventually destroyed the ability of the various solids to remove this species. Overall capacities increased significantly at moderate relative humidities, yielding values of 0.4 to 2.8 grams of sulfur dioxide per square meter of solid in moist systems. Several experiments indicated that the reactivity of a solid subjected to prolonged sulfur dioxide exposures could be restored by washing the surface with distilled water or exposing the spent solid to ammonia. Some implications of these findings relative to the environment are discussed.

CONTENTS

ACKNOWLEDGMENTS

SECTION 1

INTRODUCTION

Deposition velocities of pollutant gases are used extensively in calculating atmospheric budgets for these species (1-2). Both field and laboratory measurements of these quantities have been made. Field measurements are generally carried out by one of two methods for determination of deposition velocities. The first involves simultaneous measurements of wind velocity, temperature, and pollutant gas concentration profiles above the surface (3-7). The vertical atmospheric diffusity $K(z)$ is estimated from the former two quantities, and the deposition velocities V_g are calculated from

$$F = -K(z) \frac{dc}{dz} = V_g c \qquad (1)$$

relating the downward flux (F) of the pollutant gas to $K(z)$ and the concentration gradient. The concentration c is measured at some fixed height above (but near) the surface.

The second method, which is also used extensively in the laboratory, is based on total uptake of sulfur dioxide (8-12) and sulfur-35 dioxide labelled sulfur dioxide is frequently used (13-19). In the latter case, the total uptake of sulfur-35 dioxide is measured as well as its concentration just above the surface. The deposition velocity is then readily calculated from Equation (1). In some cases, flow systems are also used for laboratory measurements (20-24).

Measured deposition velocities typically range from a few tenths of a centimeter per second or less to several centimeters per second (18). Substantial variations in the magnitude of the deposition velocity determined at a given field site or for a given material in the laboratory are common (3,4,5,7). These variations may be partly related to surface changes that are dependent on environmental conditions. For example, sulfur dioxide uptake by leaves is largely controlled by the stomata (25). The opening and closing of the stomata depend on a number of environmental factors, e.g., daylight, relative humidity, and season. In the laboratory, deposition velocities, in many cases, represent values that are limited by mass transport to the surface. Questions then arise concerning the limits of deposition velocities imposed by physical and chemical processes related to the actual removal of the pollutant gas at the surface.

In this report, a method is presented for laboratory measurement of deposition velocities independent of mass transport phenomena together with experimental results for sulfur dioxide removal on several environmental

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surfaces. The values obtained in this manner represent the maximum deposition velocities that would be encountered in the open atmosphere, particularly when turbulent mixing is sufficiently high to remove mass transport limitations.

SECTION 2

EXPERIMENTAL

APPARATUS

A block diagram of the apparatus used in these experiments is shown in Figure 1. This system, which is basically a cylindrical flow reactor, is similar to systems previously described by Hedgpeth et al. (27), and by Stewart and Judeikis (28). The major difference between the present system and those previously described is the method of analyzing gases flowing through the reactor. Additional changes consisted of replacing system components that were found to be reactive toward sulfur dioxide. Virtually all components in the final version of the modified system consisted of pyrex glass, 316 stainless steel, and teflon-coated aluminum.

In the system shown in Figure 1, a carrier gas stream was initially split into two streams; one of the streams passed through a humidifier, where it was saturated with water vapor. The two streams were subsequently recombined. (The ratio of flow rates of the split streams determined the relative (humidity of the carrier gas.) The carrier gas stream was then mixed with a small amount of nitrogen that contained traces of sulfur dioxide and the mixture was fed into the cylindrical flow reactor (2.5 cm radius) that contained a concentric pyrex cylinder (2.1 cm radius) coated with the solid of interest. (The choice of a cylinder for a substrate was not unique, and other geometries, such as parallel plates, could have been used.) The latter cylinder was coated by preparing a slurry of the solid of interest, coating the blank pyrex cylinder (outside the reactor), and permitting the coating to air dry and then to dry overnight in a vacuum in the tubular reactor.

Reaction of sulfur dioxide with the coated walls led to a concentration gradient for sulfur dioxide along the axial (as well as radial) directions. (In the absence of a solid coating, there was no change in the sulfur dioxide concentration on passage through the reactor.) In order to measure the axial concentration gradient, the gas mixture in the reaction chamber was sampled by means of a set of small probes (connected through a 16-port rotary valve to mass spectrometer) whose intakes were centered along the axis of the coated cylinder. The probes were nominally 0.15 cm outer diameter and 0.08 cm inner diameter. Flow through the sampling system was sufficiently slow so that the flow pattern in the reaction chamber was not disturbed, but yet it was sufficiently fast so that transit time through the sampling system was minimal ($\sim$ 3 to 4 sec).
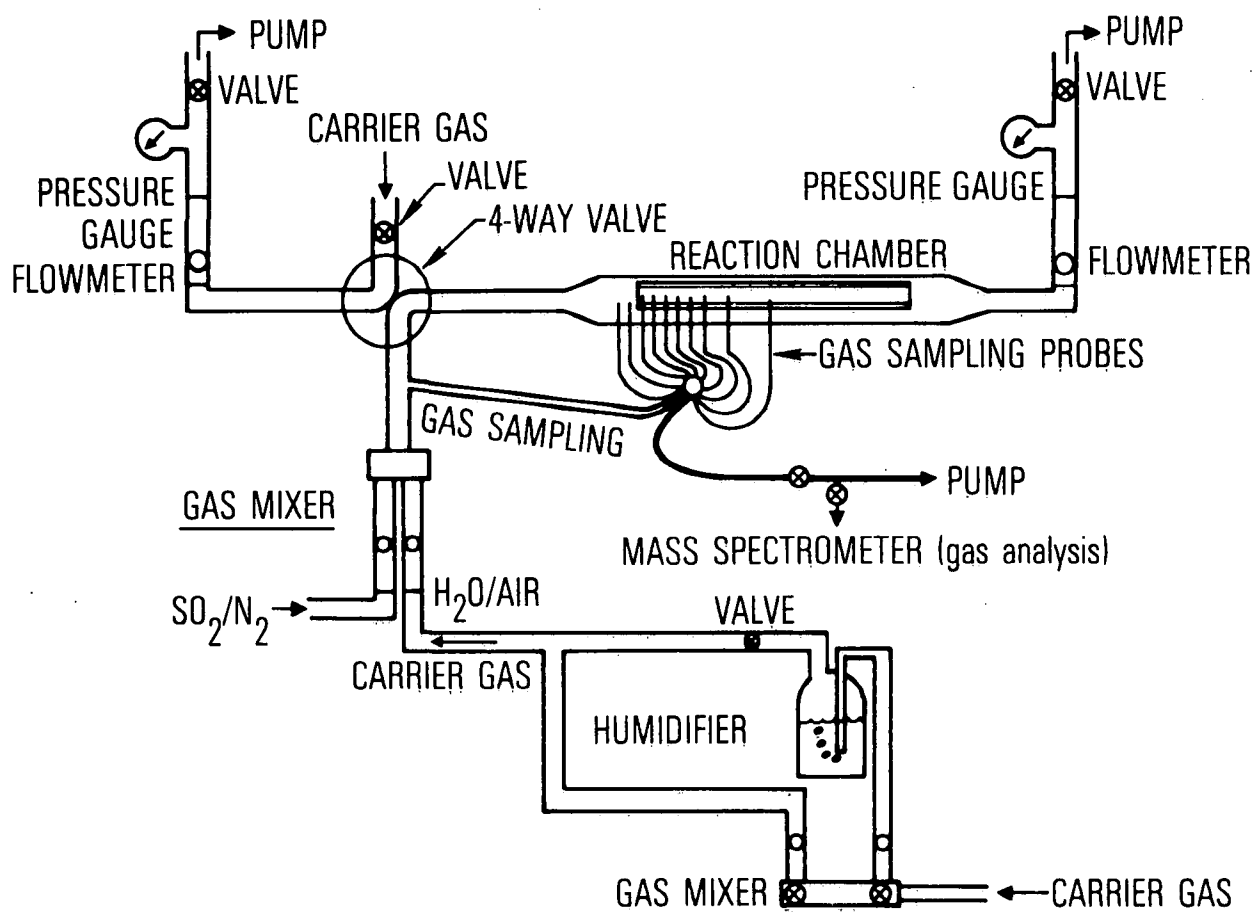
Figure 1. Block diagram of cylindrical reactor with sampling probes.

Typical operating conditions used were pressures of 10 to 700 Torr[1], flow velocities of 1 to 30 cm^3/sec (average linear velocities of 0.05 to 1.5 cm/sec), and ambient temperatures (Reynolds numbers < 50). Sub-ambient pressures were frequently required in order to measure non-diffusion-limited deposition velocities. (This point is discussed in more detail in the following sections.) Flow rates were selected to give a sufficiently high axial sulfur dioxide concentration gradient in order to permit accurate measurements of this quantity.

Gases sampled through the probes were analyzed by using a mass spectrometer. The sensitivity of the mass spectrometer for sulfur dioxide detection was ∿ 0.3 ppm. Consequently, experiments were conducted with initial sulfur dioxide concentrations of ≥ 3 ppm. In addition, high concentrations of oxygen in the reaction mixture tended to oxidize the filaments in the mass spectrometer. For this reason, oxygen concentrations were limited to ∿ 10% or less.

MATERIALS

Solids investigated in this study included commerical formulations of cement, ready mix cement (cement with sand and gravel), asphalt, and exterior stucco. In the cases of cement and exterior stucco, samples from two different sources of each material were used. Other materials studied were soil samples of sandy loam and adobe clay taken from the Los Angeles area. These materials were generally sifted through a screen to eliminate particles >1 mm in diameter. Water-based slurries of these materials were used in preparing the coated pyrex cylinders (except for asphalt, where a trichloroethylene slurry was used). Consequently, the cement, ready mix cement, and exterior stucco were cured during the process of preparing the coatings. Surface roughnesses were typically ≤ ∿1 mm.

Gases used were reagent grade gases obtained from Matheson and were used as received. Two specially prepared mixtures were used for sulfur dioxide and oxygen in order to obtain the desired concentrations of these gases in the reaction mixture. These were 1000 ppm SO_2 in N_2 and 20% O_2 in N_2. In addition, distilled water was used for humidifying gas mixtures.

DATA ANALYSIS

Mass transport in a cylindrical flow tube, under conditions of nonturbulent flow and at steady state, has been described by Walker (29), and Stewart and Judeikis (28) (and their cited references) as:

$$D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial x^2}\right) - V_x \frac{\partial c}{\partial x} = 0 \qquad (2)$$

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[1] To convert from Torr to newton/meter^2, multiply by 1.333 22 E + 02.

subject to the boundary conditions

$$c = c_0 \text{ at } r, x = 0$$

$$\frac{\partial c}{\partial r} = 0 \text{ at } r = 0, x$$

and

$$-D \frac{\partial c}{\partial r} = \phi k_r c \text{ at } r = R, x > 0. \tag{3}$$

$$k_r = (R T/2\pi M)^{\frac{1}{2}} \tag{4}$$

where
- r = radial coordinate
- x = axial coordinate
- c = concentration of the reacting species
- c_0 = initial concentration
- D = diffusion coefficient of the reacting gas in the mixture
- V_x = linear gas flow velocity in the axial direction
- k_r = molecular velocity of the reacting species in the radial direction
- R = cylinder radius
- $k_r c$ = the gas-solid collision frequency
- ϕ = reactivity, the fraction of collisions that lead to removal of the reacting species from the gas phase*
- R = the gas constant
- T = the absolute temperature
- M = the molecular weight of the diffusing gas

In this report, binary diffusion coefficients are calculated for sulfur dioxide in nitrogen by using expressions given by Present (30). The presence of oxygen or water vapor in the reaction mixture would lead to diffusion coefficients slightly different than the calculated values. The uncertainties that arise from these differences are less than those from other sources. Equation (3) expresses the condition that the diffusion of the reacting species to the walls is equal to its removal by heterogeneous reaction. (Actually, c', the concentration at one mean free path away from

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*For first-order or pseudo-first-order processes, it can be shown that ϕ is actually composed of a collection of constants, including the sticking coefficient, as well as the rate constants for adsorption, desorption, and surface reaction (32).

the walls, should be used in Equation (3) in place of c (31, 32). However, except for $\phi \simeq 1$, the two are essentially equal.)

The deposition velocity V_g is related to ϕ, as is shown by comparing Equations (1) and (3). Equating the right sides of these equations yields

$$V_g = \phi k_r. \tag{5}$$

Thus, the deposition velocity over a given material can be obtained from laboratory determinations of ϕ values. Note also that the depostion velocities determined in this manner correspond to values at one mean free path above the surface.

Solution of Equation (2) is generally accomplished by making several simplifying assumptions. One is the assumption of plug flow (V_x = constant). The solution in this case is (28,29)

$$\frac{c}{c_0} = \sum_{i=1}^{\infty} \frac{2J_0 \alpha_i \frac{r}{R}}{\alpha_i \left(1 + \delta^2 \alpha_i^2\right) J_1(\alpha_i)} e^{\beta_i x} \tag{6}$$

where $J_0(\alpha_i r/R)$ and $J_1(\alpha_i)$ are Bessel functions of the first kind,

$$\delta = \frac{D}{Rk_c \phi} \tag{7}$$

$$\beta_i = \frac{V_x}{2D} \left\{ 1 - \sqrt{1 + \frac{D \alpha_i}{RV_x}^2} \right\} \tag{8}$$

and α_i is the ith root of

$$J_0(\alpha_i) = \delta \alpha_i J_1(\alpha_i). \tag{9}$$

For laminar flow, expressed as

$$V_x = 2V_{average}(1 - r^2/R^2), \tag{10}$$

solutions to Equation (2) have been obtained (for equivalent heat transfer problems by Sideman, Luss, and Peck (33) and their cited references) where axial diffusion can be neglected ($D_\sigma^2 c/_\sigma X^2 \approx 0$). (Criteria necessary for this assumption were delineated in an analogous heat transfer problem by Singh (34). In general, the conditions for which these solutions apply in this study are of limited use in the determination of value for ϕ because reactions tend to become diffusion-limited under experimental conditions where axial diffusion can be neglected, particularly for high reactivities. Examples of this are illustrated below. Consequently, numerical solutions of Equation (2), with laminar flow, were required for the cases of interest here. These were obtained by using a modification of the method of finite differences (35).

The geometry of the present system is such that laminar flow is not fully developed at the entry to the coated cylinder. This generally presents no problem, however, because, under most experimental conditions, either the plug or laminar flow models adequately describe the experimental results and yield ϕ values that agree to within a few to 20%. (Values derived from the plug flow model are <u>always</u> lower than those derived from the laminar flow model.)

The major discrepancy between ϕ values derived from the two models occurs at high pressures ($\sim$ 700 Torr) and high reactivities ($\phi > 10^{-4}$). Under these conditions, sulfur dioxide removal tends to become diffusion-limited. Although these conditions are avoided in most experiments (see Section 3), they do provide an opportunity to distinguish between the two models (since the solutions become independent of ϕ). In such cases, generally, sulfur dioxide concentration gradients calculated from the plug flow model are more consistent with experimentally measured values. Consequently, the plug flow model was used for the analysis of data reported here. As noted earlier, any deviations from this model would result in slightly higher values (by as much as 20%) for ϕ (or V_g) than are reported in Section 3.

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SECTION 3

RESULTS

Values of ϕ derived from a number of measurements of sulfur dioxide removal over various solids are given in Table 1 together with deposition velocities calculated from Equation (5) for a temperature of 25°C.[2] The values given represent averages from 3 to 6 experiments on each material investigated. In the cases of cement and exterior stucco, data on the material from different sources are reported individually.

TABLE 1. EXPERIMENTAL RESULTS FOR SO_2 REMOVAL

Material	ϕ	V_g, cm/sec
Cement-I[a]	3.2×10^{-4}	2.5
Ready mix cement[a]	2.6×10^{-4}	2.0
Exterior stucco-I[a]	2.3×10^{-4}	1.8
Cement-II[a]	2.0×10^{-4}	1.6
Exterior stucco-II[a]	1.1×10^{-4}	0.86
Adobe clay soil	8.4×10^{-5}	0.66
Sandy loam soil	8.3×10^{-5}	0.65
Asphalt	5.1×10^{-6}	0.04

[a]Cured

Values determined from consecutive measurements of sulfur dioxide concentration gradients on a given sample usually agreed to within 20 to 30%. Variations in ϕ values from sample to sample of the same material (for an equivalent sulfur dioxide exposure) were comparable. Overall, the

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[2] To convert from °C to °K, add 273.15.

$t_k = t_c + 273.15$

probable errors for the values given in Table 1 are about 30%.

The values reported in Table 1 were generally found to be independent of sulfur dioxide concentrations over variations of one to two orders of magnitude. (The minimum partial pressure of sulfur dioxide used in these experiments was $\sim$ 0.15 m Torr.) Representative data illustrating this point for exterior stucco-I are shown in column A of Table 2. (Here, as in the other data in Table 2, these comparisons were made in sequential runs on the same sample of a given material in order to minimize uncertainties that arise from sample to sample variations.) Thus, sulfur dioxide removal over these solids follows first-order kinetics.

We also examined reactivities as a function of oxygen concentration and relative humidity and found ϕ to be independent of these parameters to within experimental error. Representative results from these experiments over ready-mix cement and sandy loam soil are given in Table 2, columns B and C, respectively. For oxygen, problems with oxidation of the mass spectrometer filaments limited us to the use of oxygen concentrations $\leq \sim$ 10%. However, even with these limitations, the oxygen concentration exceeded that of sulfur dioxide by factors ranging from $\sim 10^3$ to 10^4 (except, of course, for experiments conducted in the absence of oxygen).

For materials with reactivities of $\sim 10^{-4}$ or greater, measurements made at atmospheric pressure yielded sulfur dioxide concentration gradients near the diffusion-limited value. Moreover, ϕ values derived from such measurements were subject to large uncertainties. The reason for this is illustrated in Figure 2A, which shows concentration profiles that were calculated for different values of ϕ at 1 atm total pressure.[3] It is shown that a reactivity $\geq 10^{-3}$ results in a diffusion-limited sulfur dioxide concentration gradient, whereas the gradient for $\phi = 10^{-4}$ ϕ differs by only 10% from the diffusion-limited gradient.

Consequently, experimental conditions were altered for those materials with reactivities near 10^{-4}. Although, in principle, several parameters could be varied, in practice, the most sensitive and easiest to vary was the total pressure. The effects of reducing the total pressure can be seen by comparing Figures 2A and 2B. In the latter case (for 0.1 atm total pressure), the concentration gradients differ by approximately a factor of two for reactivities of 10^{-3} and 10^{-4}.

Since sub-ambient pressures were frequently used in these experiments, the effects of total pressure on measured reactivities were studied. In general, ϕ values were found to be independent of total pressure, to within experimental uncertainties, for pressures ranging from $\sim$ 50 to 500 Torr. This is illustrated in Table 2, column D, for sulfur dioxide removal over sandy loam soil.

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[3] To convert from atmosphere to newton/meter^2, multiply by 1.013 250* E + 05.

TABLE 2. REACTIVITIES AS A FUNCTION OF SO_2 AND O_2 CONCENTRATIONS, RELATIVE HUMIDITY, AND TOTAL PRESSURE

Parameter Varied	Material	Pressure, Torr			RH^c	ϕ
		Total	O_2	$SO_2 \cdot 10^3$		
A. SO_2 concentration	Exterior stucco-I[b]	55	2.6	1.1	28	2.4×10^{-4}
		55	2.6	13.2	28	2.2×10^{-4}
B. O_2 concentration	Ready mix cement[b]	58	0.0	1.6	57	2.0×10^{-4}
		58	6.2	1.6	57	2.4×10^{-4}
C. Relative humidity	Sandy loam soil	100	4.4	3.7	0	6.1×10^{-5}
		100	4.3	4.2	100	5.9×10^{-5}
D. Total pressure	Sandy loam soil	50	0.0	4.2	50	8.3×10^{-5}
		400	0.0	4.8	50	7.4×10^{-5}

[a]Flow rates were nominally 10 cm^3/sec.
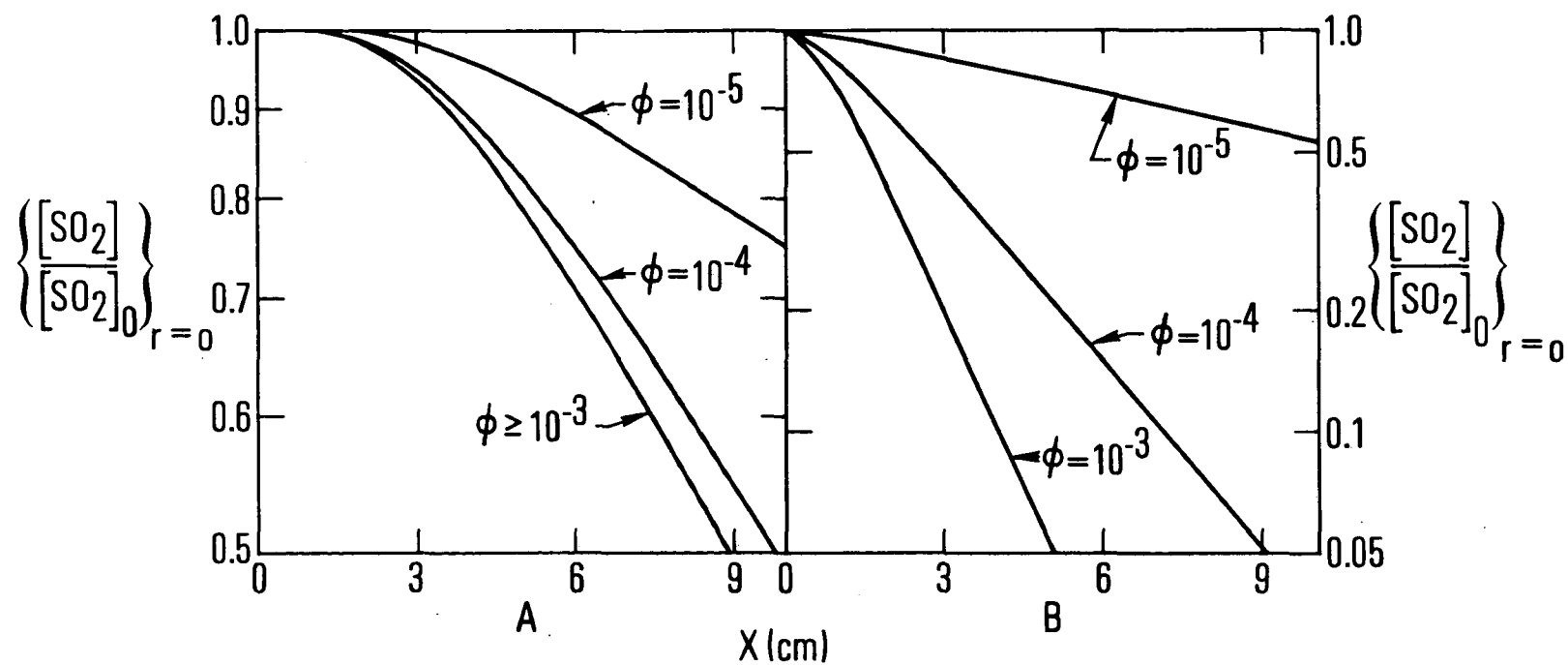
[b]Cured

[c]Relative Humidity %

Figure 2. Calculated SO_2 concentration gradients. Gradients calculated for total pressures of 1.0 (A) and 0.1 (B) atm. In both cases, R = 2.1 cm, T = 25°C, and V_x = 1 cm/sec.
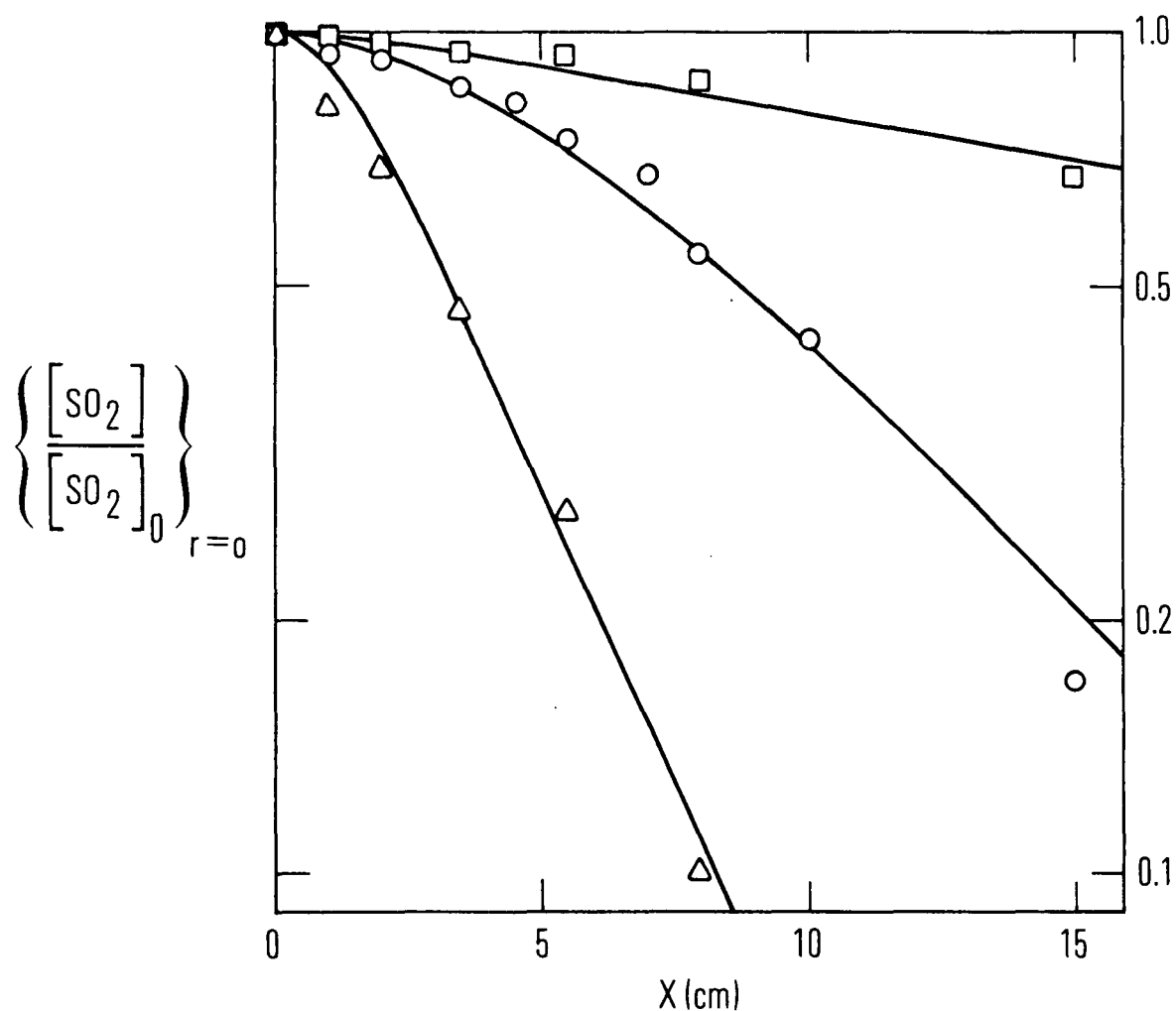
Figure 3. Measured SO_2 concentration gradients as a function of time (SO_2 exposure). Experimental parameters for SO_2 removal over adobe clay soil: P(total) = 300 Torr; $P(O_2)$ = 19 Torr; $P(SO_2)$ = 22 m Torr; T = 24°C; V_x = 0.5 cm/sec. Gradients after exposure to SO_2 of 3.6 min ($\triangle$), 2.7 hr (O), and 7.7 hr ($\square$), or 0.009, 0.39, and 1.1 g SO_2/m^2 of solid surface, respectively. Data points are from experimental measurements. Solid curves are calculated for $\phi = 1.0 \times 10^{-4}$ ($\triangle$), 1.2×10^{-5} (O), and 2.2×10^{-6} ($\square$).

We also attempted to analyze solids after reaction for sulfate formed. Wet chemical methods were used. These efforts were largely unsuccessful because of interferences by various species present in the unexposed samples. However, in a related study (to be reported on later) on sulfur dioxide by metal oxides and other materials, wet chemical and photoelectron spectroscopy methods indicate a near quantitative conversion of sulfur dioxide to sulfate. (Similar results were found by Seim (9) after exposing various soils to sulfur dioxide.)

The reactivities and deposition velocities reported above are for sulfur dioxide removal over freshly prepared coatings. With time (sulfur dioxide exposure), these reactivities diminish as the capacity to remove sulfur dioxide is expended. This poisoning effect is shown in Figure 3 for adobe clay soil. In general, this type of behavior was noted with all of the solids investigated in this study.

The capacities for sulfur dioxide removal can be determined from experiments such as that illustrated in Figure 3. Values obtained for several of the solids listed in Table 1 (the adobe clay and sandy loam soils ready-mix cement, and exterior stucco-I) range from 0.04 to 0.6 grams of sulfur dioxide per square meter of solid surface for dry reaction mixtures, and 0.4 to 2.8 grams of sulfur dioxide per square meter of solid surface for humidified reaction mixtures (50 to 95% relative humidity). Typically, capacities were a factor of 3 to 10 higher for humidified reaction mixtures compared with dry mixtures. A sufficient number of experiments to measure capacities were not conducted to determine if the absolute value of the relative humidity affects capacities. The limited data available, however, indicate that the capacity for sulfur dioxide removal from humidified reaction mixtures does not depend on relative humidity so long as the latter is $\geq \sim$ 30 to 40%. Other than the relative humidity, parameters such as the sulfur dioxide oxygen concentrations and the total pressure did not appear to have any significant effect on capacities for sulfur dioxide.

Although the experimental results indicate only a limited capacity for sulfur dioxide removal by the ground-level surfaces examined here, several possibilities exist for continued removal in the open atmosphere. For example, rain could wash away soluble sulfates (or other products), which would rejuvenate the surfaces for further sulfur dioxide uptake (8). Several authors (18,24) have suggested that sulfur dioxide removal may be pH-limited, e.g., sulfuric acid being formed from sulfur dioxide taken up by the surface, with the reaction gradually decreasing as the acid concentration builds up. Interaction with atmospheric ammonia could diminish such an effect. Of course, sulfates are nutrients for plant growth, and sulfates formed on soils could be removed by this process.

In order to examine these possibilities, several additional experiments were carried out. In one experiment, a sample of ready mix cement was exposed to sulfur dioxide at 95% relative humidity until the capacity of this material for sulfur dioxide removal was completely expended. (It was generally found that sulfur dioxide removal was an irreversible process. Thus, termination of sulfur dioxide exposures and evacuation of solid samples did not result in any desorption of sulfur dioxide restoration of the ability of

the solid to remove sulfur dioxide). The coated cylinder was then removed
from the reactor, and the coating was rinsed with distilled water and allowed
to air dry. The coated cylinder was then replaced into the reactor, dried
overnight in vacuum, and subsequently re-exposed to sulfur dioxide at 95%
relative humidity. Experimental measurements indicated a complete restora-
tion of the ability of ready-mix cement to remove sulfur dioxide.

In another experiment, adobe clay soil was exposed to sulfur dioxide in
a dry reaction mixture until completely poisoned. The gas mixture was then
humidified (95% relative humidity). The result was a complete restoration of
the reactivity toward sulfur dioxide removal.

The effects of ammonia were investigated in an experiment with a sample
sandy loam soil. The sample was exposed to sulfur dioxide (95% relative
humidity) until completely poisoned. The sulfur dioxide exposure was then
terminated, and the sample was exposed to ammonia (the total ammonia ex-
posure was only ∿ 20% of the sulfur dioxide exposure required to initially
poison the sample). After exposure to ammonia, the system was purged with
nitrogen and then re-exposed to sulfur dioxide. The result, again, was a
complete restoration of the activity of the sandy loam soil toward sulfur
dioxide.

SECTION 4

DISCUSSION

In the analysis of data obtained from these experiments, we specifically account for transport-related phenomena. Thus, the deposition velocities given in Table 1 represent values that are limited only by the adsorption and chemical processes leading to sulfur dioxide removal from the gas phase. These values, then, represent the maximum deposition velocities that would be encountered over the materials listed in Table 1 under turbulent atmospheric conditions.

Experimentally, for materials with reactivities $> 10^{-4}$, such as exterior stucco or cement, it was necessary to conduct experiments at sub-ambient pressures in order to obtain non-diffusion-limited reactivities. Although such conditions deviate from the ambient atmosphere, the results are more applicable than those that would be obtained from experiments conducted at atmospheric pressures. The reason for this is that diffusivities for sulfur dioxide in our experiments, which were conducted under nonturbulent conditions, are $\sim 10^3$ to 10^5 (37,38). Thus, a process that would be diffusion-limited in our laboratory experiments would not be likely to be limited by transport to the surface in the open atmosphere, but rather by the adsorption and chemical processes responsible for uptake.

An added feature of the type of experiment reported here is the ability to measure changes in deposition velocities with time (sulfur dioxide exposure). In a number of measurements reported in the literature, materials are exposed for a fixed period of time and determined total sulfur dioxide uptake. Such measurements can only give an average value for the deposition velocity, the magnitude of which depends on the degree of poisoning of the solid under study.

It is instructive to compare our results with other data reported in the literature for related materials. In a study conducted on seven European soils in a system in which a fan was used to mix the air above the soil, Payrisset and Beilke (24) reported deposition velocities of 0.19 to 0.60 cm/sec. They also observed first-order kinetics for sulfur dioxide removal and evidence of poisoning and measured a slight dependence of removal rates on relative humidity. In an additional study on five soils from the midwestern United States, Seim (9) measured average deposition velocities of 0.2 cm/sec. He also reported that deposition velocities were relatively independent of sulfur dioxide concentrations (first-order kinetics) and moisture levels.

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Measurements of deposition velocities over building materials, notably limestone, have been reported in the literature (8,13,21). Reported values range from 0.03 to 0.3 cm/sec, which is considerably lower than the values we found for cements and stuccos. However, Braun and Wilson (8) measured the sulfur content of limestone exposed to atmospheric sulfur dioxide to be 2.4 to 2.6 g/m^2, which compares favorably with the higher capacities for sulfur dioxide we have measured, in humidified reaction mixtures.

Several interesting possibilities are suggested from the deposition velocities and capacities for sulfur dioxide uptake measured here and in other laboratories. If we assume an average deposition velocity of 1 cm/sec and an atmospheric sulfur dioxide concentration of 0.1 ppm, from Equation (1), a deposition rate of 2.6×10^{-6} g/m^2 sec can be calculated. If we further assume a capacity of 2.5 grams of sulfur dioxide per square meter of solid surface, we conclude that the ability of a solid surface to remove sulfur dioxide from the atmosphere will be expended in 11 days, in the absence of any processes such as precipitation that might act to rejuvenate the surface activity for sulfur dioxide removal. In an urban area such as Los Angeles, where midsummer precipitation is negligible, this could lead to higher sulfur dioxide concentrations than would otherwise be experienced. Of course, this type of calculation and conclusion is greatly oversimplified for a number of reasons.

Other variables, such as surface roughness, total areas, and source strengths, enter into application of the data in Table 1 to the environment. Generally, our samples had surface roughnesses $\leq \sim 1$ mm. Surface roughnesses in the environment are usually greater than this, in some cases by large factors. Thus, in the environment, the actual surface area available for uptake could be significantly greater than that available in our reactor. Of course, vegetation would have a very high ratio of actual to ground-level surface areas.

In addition, several possibilities for rejuvenating poisoned surfaces were indicated above. The few experiments conducted during this study to explore these possibilities supported those suggestions. Thus, in the open atmosphere, uptake of sulfur dioxide might be determined by the balance of rates of surface poisoning and rejunvenation of the active surface.

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16. ABSTRACT

Measurements of sulfur dioxide deposition velocities have been carried out in the laboratory with the use of a cylindrical flow reaction. Analysis of data from these experiments was performed with models that specifically account for diffusive transport in the system. Consequently, the resulting deposition velocities were independent of diffusion processes and represented the maximum removal rates that would be encountered in the environment under turbulent atmospheric conditions. The measured values ranged from 0.04 cm/sec for asphalt to 2.5 cm/sec for cement, and were independent of sulfur dioxide and oxygen concentrations as well as relative humidity and total pressure. Prolonged exposure to sulfur dioxide eventually destroyed the ability of the various solids to remove this species. Overall capacities increased significantly at moderate relative humidities, yielding values of 0.4 to 2.8 grams of sulfur dioxide per square meter of solid in moist systems. Several experiments indicated that the reactivity of a solid subjected to prolonged sulfur dioxide exposures could be restored by washing the surface with distilled water or exposing the spent solid to ammonia. Some implications of these findings relative to the environment are discussed.

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