

# Processes Limiting Oxidation of Sulfur Dioxide in Stack Plumes

Stephen E. Schwartz\* and Leonard Newman

Atmospheric Sciences Division, Department of Energy and Environment, Brookhaven National Laboratory, Upton, N.Y. 11973

■ A formalism is developed to treat chemical reactions in expanding stack plumes of arbitrary concentration profile to examine the effects of dilution and of oxidant or catalyst depletion upon SO<sub>2</sub> oxidation. The rate and extent of reaction are described in terms of an assumed mechanism and defined measurable properties of the concentration profile. The rate of plume expansion exerts a controlling influence upon reactions that are higher than first order in plume constituents. Quenching of reaction is exhibited at high expansion rates. For the concentration of a conservative tracer diminishing with time proportionately to  $t^{-n}$ , a  $p$ th-order reaction is quenched for  $n(p-1) > 1$  and unquenched for  $n(p-1) \leq 1$ . The meteorological stability classes that would lead to quenching of second- and third-order reactions are considered. Re-examination of SO<sub>2</sub> oxidation data obtained in studies of the Northport, N.Y., oil-fired plume confirms that the oxidation mechanism is higher than first order and strongly suggests second order. The data are consistent with this mechanism for a wide range of assumed catalyst/SO<sub>2</sub> ratios; it is thus established that no inference may be drawn concerning catalyst depletion. The implications of these new insights are considered relative to the design of plume experiments and to the understanding of SO<sub>2</sub> oxidation mechanisms in plumes and in the ambient atmosphere.

Because of the importance of atmospheric oxidation reactions of sulfur dioxide upon the ultimate fate of this atmospheric pollutant, in the last several years a number of experimental investigations and theoretical analyses of the rate of SO<sub>2</sub> oxidation in power plant and smelter plumes have been conducted. These studies have been motivated by the fact that localized point source emissions of SO<sub>2</sub> represent a substantial fraction of total SO<sub>2</sub> emissions, and by the opportunity afforded by stack plumes as localized, time-resolved "reactors" for the in situ study of the mechanism and rate of these oxidation reactions free from the influence of such uncontrolled laboratory variables as reactor walls. Despite nonuniform plume profiles and rapid dilution of plume constituents with distance, the extent of SO<sub>2</sub> oxidation in a plume may be determined by examination of the ratio of the integrated concentrations of SO<sub>2</sub> and sulfate.

An important feature of reactions in rapidly diluting plumes that are second or higher order in plume constituents is the fall-off in the oxidation rate as a function of distance or time due to the decreased concentration of the reagents with distance. Interpretations of the rate of oxidation of SO<sub>2</sub> in the plumes of the oil-fired Northport, N.Y., plant of the Long Island Lighting Co. (1) and of the Sudbury, Ontario, nickel smelting plant [data of Lusi and Wiebe (2), as interpreted by Forrest and Newman, (3)] have suggested a mechanism that is second order in plume constituents. This dependence has been inferred to represent the contribution of the SO<sub>2</sub> and catalytic particulate concentrations to the overall rate. Freiberg (4) also has discussed the effect of plume dilution upon the rates of higher-order reactions.

A second important feature of such is the possibility that rapid dilution may lead to quenching, i.e., that the reagent concentration may asymptotically approach a limit in excess of that dictated by equilibrium considerations. This possibility was suggested in the interpretation of the Northport data (1) and was noted as well by Freiberg (4) in a model calculation

based upon a mechanism that is third order in plume constituents.

A second process that might contribute to the decrease or possible cutoff of the rate of oxidation of SO<sub>2</sub> in plumes is the inhibition of oxidation by depletion as the reaction proceeds, of catalytic or oxidative species present in the plume. Such a process has been suggested to be responsible for the sharply curtailed rate of SO<sub>2</sub> oxidation observed in the early dilution of plumes from coal-fired electric generating plants (5, 6) and thus may play a role also in oil-fired and smelter plumes. However, this suggestion has not been quantitatively explored in previous studies, in which the analysis has been confined to the use of the simple rate expression:

$$\frac{\partial(\text{SO}_2)}{\partial t} = -k_2(\text{SO}_2)^2 \quad (1)$$

that describes the process as pseudo-second order.

In view of the continuing interest in SO<sub>2</sub> oxidation in plumes and of the implications of a limit to the ultimate extent of this oxidation, and in view also of questions that have been raised, e.g. (7), concerning the mathematical description of these processes, we consider here, in somewhat greater generality and detail than has been presented previously, the factors that govern the rate and extent of reactions in expanding plumes. We proceed to consider the effects of the two potential processes, dilution and oxidant or catalyst depletion, using the data of the Northport study to examine the degree to which the observed decrease in oxidation rate may be attributed to one or the other of these processes.

## General Formalism

In this section we develop equations that describe chemical reactions in an expanding plume, with specific reference to SO<sub>2</sub> oxidation. The treatment is general with respect both to order of reaction in species that dilute with the plume (taking SO<sub>2</sub> as a surrogate for all such species) and to the shape of the distribution of reactive species within the plume, since substantial insight may be developed even at this level of generality.

As is customary we consider the plume to be a steady state reactor. The time dependence of the amounts of the several species, and in turn of the rates of chemical reactions, is inferred from the distance to the stack  $x$  through the mean wind speed  $u$  as

$$t = x/u \quad (2)$$

where the time variable  $t$  represents the age subsequent to emission from the stack of the air parcel at distance  $x$ . As previously (1) we cast our equations in terms of  $f$ , the fraction of sulfur species at distance  $x$  that remains as SO<sub>2</sub>:

$$f = \frac{\int (\text{SO}_2) dA}{\int \{(\text{SO}_2) + (\text{SO}_4^{2-})\} dA} = \frac{\int (\text{SO}_2) dA}{\int (S) dA} \quad (3)$$

where (SO<sub>2</sub>) and (SO<sub>4</sub><sup>2-</sup>) denote the concentrations of SO<sub>2</sub> and sulfate, respectively, and where  $(S) = (\text{SO}_2) + (\text{SO}_4^{2-})$  denotes the total sulfur concentration. In Equation 3 the integrals are taken over the entire cross section of the plume  $dA = dydz$ . We introduce the square bracket notation

$$[S] = \int (S) dA \quad (4)$$

$[S]$  thus represents the number of moles of sulfur per unit extent of the plume in the direction of travel  $x$ ; we similarly

define  $[\text{SO}_2]$  and  $[\text{SO}_4^{2-}]$ . Under the assumption that the sum of the two sulfur species is conservative, i.e., that there is neither fallout of sulfate from the plume nor  $\text{SO}_2$  deposition, then  $[S]$  is constant and may be evaluated as the quotient of the emission rate of sulfur by the mean wind speed. In the square bracket notation

$$f = [\text{SO}_2]/[S] \quad (5)$$

Measurement of  $f$ , the ratio of integrated concentrations, may be achieved with aircraft-mounted integrating-type sampling equipment (1, 8).

The time rate of change in the amount of  $\text{SO}_2$  in the plume (per unit distance in the  $x$  direction) may be evaluated as

$$\begin{aligned} \frac{d[\text{SO}_2]}{dt} &= u \frac{d[\text{SO}_2]}{dx} = u \frac{d}{dx} \int (\text{SO}_2) dA \\ &= u \int \frac{\partial(\text{SO}_2)}{\partial t} \frac{dx}{dt} dA = \int \frac{\partial(\text{SO}_2)}{\partial t} dA \quad (6) \end{aligned}$$

Here,  $\partial(\text{SO}_2)/\partial t$  represents the rate of decrease in  $\text{SO}_2$  concentration due to chemical reaction, i.e., excluding the decrease due to dilution. For a reaction that is  $p$ th order in  $\text{SO}_2$ , or in other plume species that dilute as  $\text{SO}_2$ , we denote this rate as

$$\frac{\partial(\text{SO}_2)}{\partial t} = -k_p(\text{SO}_2)^p \quad (7)$$

Since  $[S]$  is constant,

$$\frac{d}{dt} \left\{ \frac{[\text{SO}_2]}{[S]} \right\} \equiv \frac{df}{dt} = -k_p[S]^{-1} \int (\text{SO}_2)^p dA \quad (8)$$

whence

$$\frac{df}{dt} = -k_p[S]^{p-1} f^p \frac{\int (\text{SO}_2)^p dA}{[\int (\text{SO}_2) dA]^p} \quad (9)$$

In Equation 9 we have used the definitions given in Equations 3–5. This expression for the rate of change of  $f$  is useful since all dependence upon dilution introduced by plume expansion is collected in the last factor. Since this quantity has units  $(\text{area})^{1-p}$ , it is convenient to denote

$$A_*^{p-1} = \frac{[\int (\text{SO}_2) dA]^p}{\int (\text{SO}_2)^p dA} \quad (10)$$

The effective plume area  $A_*$  may in principle be determined from plume  $\text{SO}_2$  concentration profiles obtained with real-time sampling apparatus. The ratio  $[S]/A_*$  has (Equation 4) units of concentration. Denoting

$$(S)_* = [S]/A_* \quad (11)$$

we may now write Equation 9 as

$$\frac{df}{dt} = -k_p(S)_*^{p-1} f^p \quad (12)$$

Equation 12 is formally identical with that employed in our previous work (1, 9), but does not require the previously employed assumption of uniform (top-hat) concentration profile. However, in this equation, which is derived from *arbitrary* concentration profile, the effective sulfur concentration  $(S)_*$  defined by Equations 10 and 11 is not an actual concentration that can be measured at a given point but rather is a mathematical construct that can be computed only from a known or assumed  $(\text{SO}_2)$  profile. Nevertheless, since  $(S)_*$  will decrease approximately as a conservative species as the effective area  $A_*$  of the plume increases, Equation 12 retains the salient feature of the previous work, viz., that for reactions that are second or higher order in plume species, the effective rate coefficient,  $k_p(S)_*^{p-1}$ , diminishes as the plume is diluted. In particular, the effective second-order rate coefficient  $k_2(S)_*$  exhibits a direct dependence upon plume expansion, whereas

the effective first-order rate coefficient  $k_1$  does not. This distinction between first- and higher-order processes has permitted the oxidation of  $\text{SO}_2$  to be ascribed to a second-order process both for the Northport oil-fired plume (1) and for the Sudbury nickel-smelter plume (3).

The differential rate equation in  $f$  (Equation 12) may be formally integrated by separation of variables

$$\int \frac{df}{f^p} = -k_p \int (S)_*^{p-1} dt \quad (13)$$

Evaluation of the integral in the right-hand side requires a determination of the time dependence of  $(S)_*$  or, alternatively, modeling  $(S)_*(t)$  to permit analytical integration.

A significant extension of Equations 12 or 13 may be achieved under the assumption that the  $\text{SO}_2$  concentration profile in the plume retains geometric similarity as the plume expands, i.e.,

$$(\text{SO}_2)(x, y, z) = (\text{SO}_2)_*(x) \chi \left( \frac{y - y_c}{\eta(x)}, \frac{z - z_c}{\zeta(x)} \right) \quad (14)$$

Here,  $\chi$  is a normalized distribution function,  $\int \chi d(y/\eta) d(z/\zeta) = 1$ , and  $\eta$  and  $\zeta$  are the scaling parameters of  $\chi$  in the  $y$  and  $z$  dimensions, respectively, e.g.,  $\sigma_y$  and  $\sigma_z$  for a gaussian distribution;  $y_c$  and  $z_c$  represent the plume centerline coordinates. This assumption may be expected to apply (10), provided that the rate of dilution greatly exceeds that of chemical reaction, as appears invariably to be the case for  $\text{SO}_2$  oxidation in stack plumes. With this assumption

$$(S)_* = \frac{[S]}{\eta \zeta} \Gamma^{1/p} \quad (15)$$

where

$$\Gamma = \int \chi^p d \left( \frac{y}{\eta} \right) d \left( \frac{z}{\zeta} \right) \quad (16)$$

is a numerical constant of order unity that depends on the shape function  $\chi$ . Equation 13 now becomes

$$\int \frac{df}{f^p} = -k_p \Gamma \int \left( \frac{[S]}{\eta \zeta} \right)^{p-1} dt \quad (17)$$

which is formally identical to Equation 13 since  $[S]/\eta \zeta$  has units of concentration. The similarity assumption thus permits, for an arbitrary, unspecified shape function, the analysis of the dependence of the reaction rate upon the order of reaction and upon dispersion parameters, as if this shape function were a uniform box, since the only effect of a non-uniform shape function  $\chi$  will be to alter the apparent rate coefficient by the constant factor  $\Gamma$ . We may thus proceed to use Equation 13 as if  $(S)_*$  were an actual, uniform concentration. This approach facilitates examination of the mechanism and order of plume reactions.

Equations similar to 17, but restricted to the gaussian shape function and to a specific third-order mechanism, have been presented by Freiberg (4) and by Lusi and Phillips (11). A similar equation for the time evolution of the concentration in a cloud emanating from an instantaneous, point-source release, expanding in three dimensions, was given by Friedlander and Seinfeld (10).

#### Effect of Plume Dispersion on Rate and Extent of Reaction

To introduce dispersion into Equation 13 or 17, it is convenient to model this process by the usual power-law expression for the concentration of a conservative species in an expanding plume

$$(S)_* \propto t^{-n} \quad (18)$$

It should be emphasized that a simple power-law expression such as Equation 18 is not expected to hold over the entire

extent of the plume, but that the effective dispersion index  $n$  may change with distance from the stack. This is considered in more detail below. Assuming for the moment that  $n$  is constant, we obtain, upon substituting Equation 18 into 13 and integrating, an analytical expression for  $f_t$ , the fraction of plume sulfur species remaining as  $\text{SO}_2$  at time  $t$ , for a reaction of order  $p > 1$ :

$$\frac{1}{f_t^r} - \frac{1}{f_0^r} = \begin{cases} k_p(S)_0 t_0^r \left( \frac{1}{nr-1} \right) \left[ 1 - \left( \frac{t_0}{t} \right)^{nr-1} \right], & nr \neq 1 \\ k_p(S)_0 t_0^r \ln \left( \frac{t}{t_0} \right), & nr = 1 \end{cases} \quad (19)$$

Here,  $t_0$  represents the plume age at an arbitrary initial time at which Equation 18 is applicable,  $(S)_0 = (S)_*$  at  $t_0$ , and  $r \equiv p - 1$ . The initial value  $f_0$  reflects the contributions both of primary sulfate emissions and of oxidation occurring in the plume prior to  $t_0$ . Equation 19 represents a generalization to arbitrary reaction order  $p$  of the equation we have employed previously in our analyses of  $\text{SO}_2$  plume oxidation data (i.e., Equation 16 of ref. 1). The adherence to the predictions of the model, for given reaction order  $p$  and dispersion index  $n$ , of a set of experimental measurements of  $f$  as a function of plume age  $t$  would be indicated by a linear fit of  $f^{1-p}$  to the power (or logarithm) of  $t$  indicated in the right-hand side (RHS) of Equation 19.

Despite the generality of the assumptions that have been made in the present derivation, we may nevertheless draw important conclusions from this treatment concerning the ultimate extent of  $\text{SO}_2$  oxidation in stack plumes. This is facilitated by considering the long-time limiting values of  $f$  that are indicated by Equation 19. For low values of the dispersion index  $n$  such that  $n(p-1) \leq 1$ , the RHS of Equation 19 increases without bound at long times; hence

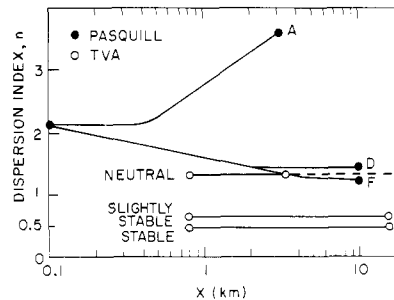
$$\lim_{t \rightarrow \infty} \frac{1}{f_t^r} = \infty, \quad n(p-1) \leq 1 \quad (20a)$$

Thus,  $f_\infty$  approaches zero, i.e., all of the  $\text{SO}_2$  in the plume is ultimately oxidized. On the other hand, for  $n(p-1) > 1$ , the RHS of Equation 19 approaches a finite limit,

$$\lim_{t \rightarrow \infty} \frac{1}{f_t^r} = \frac{1}{f_0^r} + k_p(S)_0 t_0^r \left( \frac{1}{nr-1} \right), \quad n(p-1) > 1 \quad (20b)$$

In this case, the long-time limit of  $f$  is not zero, but is a finite value between zero and one, i.e., for  $n(p-1) > 1$  the reaction is quenched by the expansion. The higher the order of reaction  $p$ , the lower is the value of the index of dispersion  $n$  that will lead to this dilution quenching. For a second-order reaction, dilution quenching will be manifested for the dispersion index  $n > 1$ ; for a third-order reaction,  $n > 1/2$  is sufficient to lead to quenching. This quenching phenomenon depends only on the order of reaction in plume constituents and on the index of dispersion and is independent of the details of the reaction mechanism.

It may be useful here to consider briefly the values of the dispersion index that may be expected for elevated buoyant plumes in various atmospheric stability classes. The subject of turbulent diffusion has been reviewed, for example, by Gifford (12), who emphasizes that no single power law, such as Equation 18, can be expected to fit diffusion data over all down wind ranges. Nevertheless, the approximate linearity over limited ranges of graphs of  $\log \sigma_y$  or  $\log \sigma_z$  vs.  $\log$  distance supports the utility of Equation 18. Within that approximation the summary of normalized axial concentration measurements ( $C$ ) for elevated releases presented by Isiltzer and Slade (13) is useful for estimating the dispersion index  $n$  appropriate for the several atmospheric stability classes. Values of  $n$  derived from Figure 4.6 of that paper as



**Figure 1.** Values of dispersion index  $n$  derived by Equation 19 from plots of normalized centerline plume concentrations of Isiltzer and Slade (13)

A, D, F: Pasquill stability classes. TVA-neutral curve extrapolated beyond 3.2 km. Quenching of second-order reactions expected for values of  $n > 1$ , and of third-order reactions for values of  $n > 1/2$

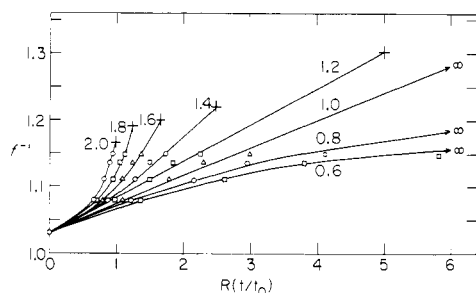
$$n = - \frac{d \log (C)}{d \log x} \quad (21)$$

are shown in Figure 1 for the TVA curves for centerline concentration of stack plumes. Also shown are values of  $n$  derived from the Pasquill curves. Briggs (14) has described the rise  $\Delta h$  of buoyant plumes as proportional to  $t^{2/3}$  and has pointed out as well the proportionality between plume depth and plume rise. Assuming an equivalent rate of expansion in the crosswind dimension leads to  $n = 4/3$ , identical to the TVA-neutral value in Figure 1.

From estimates of the dispersion index  $n$  derived from these several sources, it appears that quenching may be unequivocally predicted for second- and third-order reactions under unstable and neutral conditions, and for third-order reactions even under slightly stable conditions. For slightly stable and stable conditions the considerable variance between the several values of  $n$  encompasses the critical values of this parameter and thus precludes an a priori prediction of whether or not quenching of second-order reactions will occur. However, it would appear that the dispersion indicated by the Pasquill curves for slightly stable and stable conditions may be substantially overestimated (13), since these curves reflect enhanced dispersion characteristic of low altitude release. Also, the Pasquill curves are based on relatively long-time average plume profiles that include some plume meander, not on instantaneous profiles that would govern the rate of chemical reactions between plume constituents. The diminished rate of dispersion reflected in the TVA measurements may in part be due to the shorter averaging times in those studies (12).

On the other hand, the TVA measurements for slightly stable and stable conditions would appear not to reflect near-stack, buoyancy-induced dispersion, which would sharply diminish the rate of second- and third-order reactions. If, however, the rate of dispersion subsequently decreases to the lower values shown, second-order reactions, and under stable conditions, third-order reactions, would ultimately proceed to completion.

The phenomenon of dilution quenching of chemical reactions has been recognized for some time in the somewhat different circumstance of an expanding instantaneous puff that might be suitable for modeling reactions in an urban pall (10). The phenomenon was exhibited for a stack plume in a model calculation by Freiberg (4) for a mechanism that is third order in plume constituents, with dispersion index  $n = 1$ , and was indicated as well in the initial Brookhaven paper on the Northport plume oxidation study (1). However, in neither of the latter papers is there a description, as displayed here in Equation 20, of the generality of dispersion-induced quenching.



**Figure 2.** Data of Northport Run 2, ref. 1, plotted according to Equation 18 for pseudo-second-order mechanism for indicated values of plume dispersion index  $n$

$f$  is fraction of  $\text{SO}_2$  remaining unoxidized at time of measurement. Dimensionless variable  $R$ , defined in text, increases with increasing time. Symbol + indicates infinite time extrapolated, or quenched, value of  $f^{-1}$

The Northport study, in fact, provides a useful case for illustrating the sensitivity of the interpretation of the extent of further oxidation of  $\text{SO}_2$  within the plume, to rather slight changes in the index  $n$  that characterizes the dispersion of the plume. Figure 2 presents the data of Northport Run 2 graphed according to Equation 19 for reaction order  $p = 2$  and for several values of the dispersion index  $n$ . Unfortunately, the dispersion was not well characterized. For Run 2 the lapse rate at plume altitude ( $\sim 0.9^\circ\text{C}/100\text{ m}$ ) indicated a neutral to slightly stable atmospheric stability (9); a value for  $n$  of 1–2 was suggested from the decrease in  $\text{SO}_2$  concentration with distance. Because of this uncertainty we treat  $n$  as an adjustable parameter, constant throughout the run. In Figure 2  $f^{-1}$  is plotted vs. the dimensionless quantity

$$R\left(\frac{t}{t_0}\right) = \begin{cases} \frac{1}{nr-1} \left[ 1 - \left(\frac{t}{t_0}\right)^{nr-1} \right], & nr \neq 1 \\ \ln\left(\frac{t}{t_0}\right), & nr = 1 \end{cases} \quad (22)$$

that appears to the right-hand side of Equation 19.  $R$  is an increasing function of time with the properties that  $R(1) = 0$ ;  $R(\infty) = 1/(nr-1)$  for  $nr > 1$  and  $\infty$  for  $nr \leq 1$ . As in the original paper, values of  $t$ , which range from 1.3 to 27 min, were determined from the mean wind speed (Equation 2);  $t_0$  is taken as the value of  $t$  at the distance of the initial measurement.

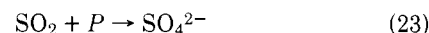
From Figure 2, an acceptable straight-line fit to Equation 19 is obtained for values of  $n$  ranging roughly from 0.8 to 1.4; i.e., any value of  $n$  within this range would be consistent with the present model. Values of  $n$  within this range are consistent as well with the range suggested in Figure 1 for the indicated atmospheric stability. The plot of the oxidation data according to Equation 19 also permits an estimate to be made of the ultimate extent of reaction, by extrapolation of  $R$  to its infinite time value. The extent of this extrapolation depends strongly on  $n$ . For  $n \leq 1$ ,  $R$  is unbounded,  $f^{-1}$  increases without bound at long time, and  $f$  approaches zero. However, for  $n > 1$ ,  $R$  and  $f^{-1}$  cannot increase beyond the limits shown in Figure 2; thus,  $f$  is interpreted as approaching a limit that, depending on the value of  $n$ , may be quite significant compared to unity. For example, for  $n = 1.4$  the model predicts the ultimate quenched value of  $f$  to be  $f_\infty = 0.82$ , i.e., only 18% of the sulfur species emitted into the plume would ultimately be oxidized to sulfate by the second-order, in-plume mechanism under consideration. This compares to the measured value of 13% sulfate at 27 min. This strong quenching contrasts with the absence of quenching indicated for  $n \leq 1$ , and exemplifies the importance of the value of  $n$  to the interpretation of plume reaction measurements.

In Figure 3 the data from the same run are plotted according to Equation 19 for a pseudo-third-order mechanism ( $p = 3$ ),

again for several values of  $n$ . A mechanism that is third-order in plume constituents has been advanced, for example, by Freiberg (4, 15), representing the contributions of two  $\text{SO}_2$  molecules and of iron catalyst to the oxidation rate. An acceptable straight-line fit of  $f^{-2}$  vs.  $R$ , as required by Equation 19, is obtained for values of  $n$  ranging roughly from 0.4 to 0.7, and again the critical value of  $n$  that would lead to quenching,  $n = 0.5$ , falls within this range. As with the second-order mechanism the predicted values of  $f_\infty$  range from zero to 0.82 as  $n$  is varied throughout the acceptable range. However, it would appear that the pseudo-third-order mechanism may be excluded, since values of  $n$  that give a linear fit to Equation 19 seem too low to be consistent either with the measured decrease in  $\text{SO}_2$  concentration with distance ( $l$ ) or with the range expected from Figure 1 for the indicated stability. In other words, the rate of oxidation did not decrease fast enough to be consistent both with a third-order reaction and with the rate of plume dispersion.

#### Effect of Reagent Depletion on Rate and Extent of Reaction

In the preceding discussion consideration has been restricted to a stoichiometric condition in which the several reagents are consumed proportionately. In this section we consider the adequacy of this approach by treating a second process that may preclude the complete oxidation of  $\text{SO}_2$  within stack plumes, viz., the depletion of oxidative or catalytic activity of a second reagent as the oxidation of  $\text{SO}_2$  proceeds. Such a process might be expected to occur, for example, as the acidity of the aqueous film surrounding catalytic particulates is increased as  $\text{SO}_2$  is oxidized to sulfuric acid or as an initially emitted oxidizing species or free-radical precursor (e.g., HONO) is depleted. Since depletion of oxidative capacity by this mechanism would be dependent upon the extent of  $\text{SO}_2$  oxidation that has occurred, it seems reasonable to model this process as if the particulate (or other oxidant)  $P$  were a reagent that is exhausted during the course of the oxidation,



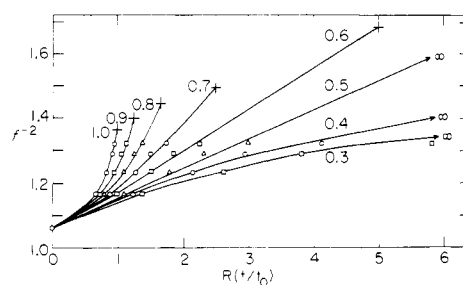
This mechanism may be represented by the rate expression

$$\frac{\partial(\text{SO}_2)}{\partial t} = -k_2(\text{SO}_2)_2(P) \quad (24)$$

where  $(P)$  denotes the concentration of particulate (or other oxidant) that is both being diluted as the plume expands and being depleted as the oxidation proceeds. Equation 24 may readily be expressed in terms of  $f$ , the fraction of  $\text{SO}_2$  remaining unoxidized, by the same procedure as carried out above. By analogy to Equation 5, we introduce the notation

$$[P] = [S](f - e) \quad (25)$$

where  $e$  represents the extent, normalized to  $[S]$ , by which the amount of  $\text{SO}_2$  initially present exceeds that of the particulate,



**Figure 3.** Data of Northport Run 2 plotted according to pseudo-third-order mechanism for indicated values of plume dispersion index  $n$

according to the "Reaction" 23. For  $0 < e < 1$ , the particulate would ultimately become the "limiting reagent", and  $e$  represents the normalized fraction of  $[S]$  that would remain unoxidized as the reaction proceeds to completion. For  $e < 0$ , the particulate is present in excess over the amount needed to react completely with the  $\text{SO}_2$  present in the plume; here  $-e$  represents the amount of particulate, again normalized to  $[S]$ , that would remain as the reaction goes to completion.

With the introduction of this notation the differential equation for the time dependence of  $f$  becomes (cf. Equation 12 for  $p = 2$ ):

$$\frac{df}{dt} = -k_2(S)_0 f(f - e) \quad (26)$$

As in Equation 12 the effective rate coefficient depends directly upon plume expansion; the effective plume area  $A_*$  is now given by  $[f(\text{SO}_2)dA] \times [f(P)dA]/[f(\text{SO}_2)(P)dA]$  rather than by Equation 10. This dependence on expansion continues to obtain even for large negative  $e$ ,  $-e \gg 1$ . In this limit  $[P]/[S]$  is effectively constant, as the oxidation reaction proceeds, i.e., the oxidant or catalytic particulate is only conservatively diluted with the plume. Nevertheless, the participation in the oxidation mechanism of a second species, which is continuously being diluted, remains manifested in the effective rate coefficient. Thus, even under this extreme condition the plume dilution still permits an observable distinction between a first-order reaction and the first-order limit of a second-order reaction.

With the assumption of the power-law dispersion expression (Equation 18), Equation 26 may be analytically integrated. We express this result as

$$L(t) - L(t_0) = k_2(S)_0 t_0 R \left( \frac{t}{t_0} \right) \quad (27)$$

where we have introduced

$$L(t) \equiv -\frac{1}{e} \ln \left( 1 - \frac{e}{f(t)} \right) \quad (28)$$

and where  $R$  was defined in Equation 22. Equation 27 represents an extension of Equation 19 to the general second-order mechanism (Equation 24). The RHS of Equation 27 is identical with that of Equation 19 so that the concept of quenching pertains to the general reaction as well. For  $e > 0$  ( $\text{SO}_2$  in excess over particulate), whether the long-time value of  $f$  approaches  $e$  or some greater quenched value depends on the long-time behavior of  $R$ , as discussed above. For  $e < 0$  (particulate in excess over the amount needed to oxidize the  $\text{SO}_2$  completely),  $f_\infty$  will approach zero or a finite value, again depending upon the long-time behavior of  $R$ . In fact, the quenching phenomenon is quite general and depends only on the overall reaction order in plume constituents, since changes in mechanism, for a given reaction order, will affect only the left-hand side of Equation 13, whereas the quenching arises entirely from the integration of the right-hand side.

Two limiting cases are of interest for the left-hand side (LHS) of Equation 27. For  $e \rightarrow 0$ , i.e., the pseudo-second-order limit,  $L \rightarrow f^{-1}$ , in agreement with the LHS of Equation 19. For large negative  $e$ , the conservative reagent limit, the LHS of Equation 27 approaches  $e^{-1} \ln(f_i/f_0)$ .

To examine whether a given set of experimental data is consistent with the mechanism of oxidant or catalyst depletion, the quantity  $L$  may be plotted against  $R$  for assumed values of the plume expansion index  $n$  and the excess reagent parameter  $e$ ; a linear relation is expected for appropriate values of  $n$  and  $e$ . In the treatment that follows, we consider the linearity of the fit of such a plot for the Northport data for  $e$  considered as a variable parameter, holding the value of  $n = 1$ . This value of  $n$  is selected here since a substantially lower value appears to be excluded on the grounds noted above, and

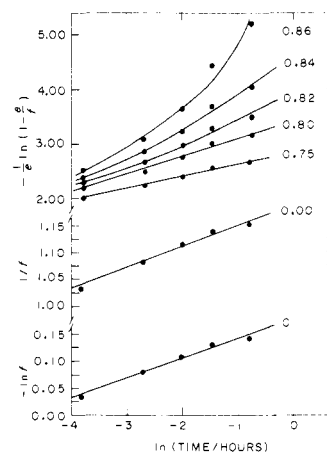


Figure 4. Data from Northport Run 2 plotted according to general second-order mechanism under plume dilution ( $n = 1$ ) for indicated values of excess reagent parameter  $e$

C denotes conservative particulate or large negative limit. Adherence to model is indicated by fit of data to straight line

since a higher value would enhance the role of plume dilution over that of reagent depletion in controlling the rate and extent of oxidation in the plume.

Figure 4 shows the quantity  $L$  computed from the data of Northport Run 2 ( $I$ ) plotted for values of the excess reagent parameter  $e$  ranging from 0.86 to the "large negative", conservative reagent, limit. (Since the extent of reaction was followed in this study to 13% of the  $\text{SO}_2$  oxidized, values of  $e$  greater than 0.87 are summarily excluded.) For values of  $e$  greater than 0.82, a significant departure from linearity is observed, but for all values of  $e$  less than 0.82 including negative values (i.e., particulate in excess of  $\text{SO}_2$ ), an acceptable straight-line plot is obtained. Thus, the fit to the function  $f^{-1}$  corresponding to the pseudo-second-order mechanism treated above, is not a unique description of the  $\text{SO}_2$  oxidation rate, but is one of a family of equally adequate descriptions corresponding to the general second-order mechanism for various values of the parameter  $e$ .

The more general analysis given here sustains the interpretation given above that oxidation was occurring by a second-order mechanism. The insensitivity of the linearity of these graphs to the value of  $e$ , due largely to the limited extent of oxidation represented in the data, supports the use of the pseudo-second-order mechanism ( $e = 0$ ) in the consideration of the effects of dispersion on the rate and extent of reaction. This insensitivity also precludes the precise determination of  $e$ . At one extreme ( $e = 0.82$ ) the data are consistent with an amount of oxidative or catalytic activity sufficient to oxidize as little as 18% of the  $\text{SO}_2$  initially present; the observed 13% oxidation would, at this extreme, correspond to depletion of roughly three-fourths of the catalyst. At the other extreme the data are consistent with an interpretation that requires no depletion of catalytic activity whatsoever, with the decrease in the observed oxidation rate due entirely to plume dilution. This more detailed analysis thus, while confirming the role of dilution in diminishing the oxidation rate, does not support the heuristic suggestion of Newman et al. (1) that the oxidation was limited by catalyst depletion and that conversions much greater than 20% are not to be expected. Rather, this analysis demonstrates that the data under examination cannot provide information relative to the question of exhaustion of particulate activity as the oxidation reaction proceeds.

#### Discussion and Conclusions

Perhaps the strongest conclusion to be derived from this analysis is that for higher than first-order reactions in dis-

persing plumes, the value of dispersion index  $n$  plays a controlling role in determining the rate and ultimate extent of reaction. This dependence follows naturally from two assumptions of the model by which the reaction was described, specifically: The dispersion of plume constituents occurs according to the  $n$ th power of the time following emission, Equation 18; and the oxidation of  $\text{SO}_2$  takes place entirely by a mechanism that is  $p$ th order in plume constituents, Equation 7. While we consider these features of the model to be approximately correct in regions relatively close to the stack where in-plume reactions would be most important, ultimately we would expect each of these assumptions not to hold. We consider here the implications of these assumptions upon the interpretation of plume experiments and upon the design of future studies.

Because of the demonstrated strong dependence of the rate and extent of plume reactions upon the index of dispersion  $n$ , it would appear mandatory in future studies that this parameter be determined independently of the oxidation measurements, and with a degree of precision consistent with the important role of this parameter. Alternatively, in view of the strong influence of the rate of dispersion upon the rate of chemical reactions in expanding plumes and upon mechanistic interpretations derived from these measurements, it would appear highly worthwhile to carry out experiments in which the  $\text{SO}_2$  profile is actually determined at various distances, by real-time, fast-response instruments. This would permit a direct determination of  $A_*$  (Equation 10) and  $S_*$  (Equation 11) and in turn would permit the  $\text{SO}_2$  oxidation data to be interpreted via Equation 13 without the imposition of a model for the plume dispersion. Additionally, such measurements would permit interpretation of quenching of faster reactions for which the similarity assumption would be inapplicable because of flattening of the concentration profile due to reaction. This flattening would enhance the rate of increase of  $A_*$  with time and thus contribute further to quenching of reaction.

With respect to the assumption that  $\text{SO}_2$  is oxidized only by reactions between plume constituents, we would note that in addition to this process, oxidation may be expected to occur as  $\text{SO}_2$  in the plume is admixed with constituents present in the ambient atmosphere. This may occur either by a heterogeneous mechanism involving aerosol particles or by a homogeneous mechanism involving active intermediates. Either process would be first order in *plume constituents*, and hence would be expected to dominate the  $\text{SO}_2$  oxidation at long times. Thus, the continuously diminishing oxidation rate implied in Equation 12 or 19 will ultimately level off at a nonzero value characteristic of the local burden of catalytic or active species; therefore, the final measured value of the oxidation rate in a plume may be taken as an upper limit to this ambient oxidation rate. From the Sudbury plume data (2, 3), we may take this upper limit as  $\sim 0.5\% \text{ h}^{-1}$ ; the low rates of  $\text{SO}_2$  oxidation measured in coal-fired plumes (5, 6) suggest a similar upper limit to this rate. Oxidation of  $\text{SO}_2$  at the low, ambient rate will then continue, along with deposition processes, until the  $\text{SO}_2$  is entirely consumed.

Note that the picture of  $\text{SO}_2$  oxidation described here differs substantially from that depicted, for example, by Wilson et al. (16). According to that picture,  $\text{SO}_2$  is oxidized principally by species present at low concentrations in the ambient atmosphere, and this oxidation is suppressed in concentrated plumes by the large excess of plume constituents. An example of such a mechanism would be oxidation of  $\text{SO}_2$  by free radicals whose concentration is coupled to the ambient ozone concentration, which is strongly diminished by nitric oxide present in the plume. Similarly, if ammonia were required to neutralize sulfuric acid formed during the  $\text{SO}_2$  oxidation be-

fore oxidation could proceed further, the depletion of this species in the concentrated plume might suppress the reaction until the plume became sufficiently diluted with ambient air. If  $\text{SO}_2$  oxidation were occurring by such a process, one might expect an *increase* in the oxidation rate until the ambient level was attained. This increase might be gradual and continuous or, alternatively, might be characterized by a more or less abrupt onset at some distance downwind from the stack at which a critical plume constituent, e.g.,  $\text{NO}$ , has become "titrated" by admixture with the ambient air. In fact, a limited amount of evidence for a process of the latter sort has been presented (16). While ultimately the choice between the two pictures must await further experimentation, we feel at the present time that there is substantial evidence demonstrating the absence of any increase in the  $\text{SO}_2$  oxidation rate out to distances upward of 60 km, and plume ages in excess of 3 h, for oil-fired (1, 17), coal-fired (5, 6), and smelter plumes (3), and consequently that the ambient oxidation rate must be of the order of  $0.5\% \text{ h}^{-1}$  or less.

With regard to the examination of a possible oxidant on catalyst depletion mechanism for limiting  $\text{SO}_2$  oxidation in oil-fired and smelter plumes, we conclude that the observed decrease in the  $\text{SO}_2$  oxidation rate as a function of time subsequent to emission from the stack does *not require* the assumption of such a mechanism, despite plausible arguments that have been presented previously (1), based upon the relative mass emissions of particulates and  $\text{SO}_2$ , that such a mechanism might be expected. Rather, the decrease in oxidation rate may be due entirely to plume dispersion, and the data are entirely consistent with the  $\text{SO}_2$  surrogate, pseudo-second-order mechanism.

The oxidation measured in the Northport plume contrasts with the results of the studies of  $\text{SO}_2$  oxidation in certain other oil-fired plumes (17) and in coal-fired plumes (5, 6), where the oxidation is not interpretable in terms either of a second- or a first-order mechanism. In those studies the extent of oxidation seldom exceeded 5% and was generally only 1–3%. Furthermore, any oxidation subsequent to emission was quite minimal and appeared to be arrested within the first 5 km. We thus continue to feel that the ascription of the arrest of oxidation in coal-fired and certain oil-fired plumes to catalyst poisoning remains plausible, although an alternative interpretation might be that the observed sulfate is largely produced prior to stack emission and that the emitted particulates are essentially catalytically inactive.

#### Note Added in Proof

Since completion of this work, we have learned of a study by J. Freiberg, to be published in the proceedings of the International Symposium on Sulfur in the Atmosphere, that reaches similar conclusions concerning the quenching of  $\text{SO}_2$  oxidation in plumes.

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We thank Paul Michael for his valuable suggestions and continued interest in this work, Ronald Meyers for incisive discussion, and Robert Brown for his careful reading of the manuscript. We thank a referee for pointing out the applicability of Briggs' treatment to the discussion of quenching.

#### Nomenclature

- ( ) = concentration of the indicated species as a function of  $x$ ,  $y$ , and  $z$  in the plume
- [ ] = amount of the indicated species per unit extent of the plume in the  $x$ -direction; a function of  $x$  only
- ( $S$ ) = total sulfur concentration = ( $\text{SO}_2$ ) + ( $\text{SO}_4^{2-}$ )
- ( $S$ )<sub>\*</sub> = effective sulfur concentration, Equation 10; a function of  $x$  only

$(S)_0$  = effective sulfur concentration at initial time  $t_0$   
 $(SO_2)_*$  = effective  $SO_2$  concentration, Equation 13  
 $(P)$  = concentration of catalytic particulates  
 $(C)$  = plume centerline concentration of conservative tracer  
 $dA = dydz$  = differential area element of plume cross section  
 $A_*$  = effective cross-sectional area of plume, Equation 10; a function of  $x$   
 $\chi$  = normalized  $(SO_2)$  distribution function, Equation 14; a function of  $y$  and  $z$  only  
 $\eta(x), \zeta(x)$  = scaling parameters of  $\chi$  in  $y$  and  $z$  dimensions  
 $\Gamma$  = shape factor, Equation 15, a constant for a given reaction order and plume distribution function  
 $x, y, z$  = distance variable in the directions of plume travel, cross-wind, and vertical, respectively  
 $u$  = mean wind speed in the  $x$  direction  
 $t$  = plume age, Equation 2  
 $f$  = fraction of sulfur present as  $SO_2$ , a function of  $x$  or  $t$   
 $f_0$  = fraction of sulfur present as  $SO_2$  at initial time  $t_0$   
 $f_\infty$  = fraction of sulfur ultimately remaining as  $SO_2$   
 $e$  = excess reagent parameter, Equation 24  
 $p$  = order of reaction in plume constituents  
 $r = p - 1$   
 $n$  = index of plume dispersion, Equation 18  
 $k_p$  = reaction rate coefficient for  $p$ th order reaction  
 $R$  = dimensionless, increasing function of time, Equation 21  
 $L$  = measure of extent of reaction, for general second-order mechanism, Equation 28

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## Measurement of Cu and Zn in San Diego Bay by Automated Anodic Stripping Voltammetry

Alberto Zirino\*, Stephen H. Lieberman<sup>1</sup>, and Cesar Clavell

Chemistry and Environmental Sciences Group, Naval Ocean Systems Center, San Diego, Calif. 92152

■ Cu and Zn values were measured in San Diego Bay by anodic stripping voltammetry with a specially built, automated instrument. During 1975-1977, trace metal surveys were conducted in the bay from a small vessel. Samples were collected and analyzed aboard the craft while under way. Cu and Zn concentrations were less than 0.1 and 0.6  $\mu\text{g/L}$ , respectively, at the mouth of the bay and increased toward the center of the bay to approximately 2.5 and 2.9  $\mu\text{g/L}$ , respectively. Also, synoptic measurements made at a stationary pier location showed that Cu and Zn concentrations coincided precisely but inversely with tidal cycles. Cu and Zn measurements made by automated anodic stripping voltammetry were compared to measurements made by extraction on Chelex 100 followed by analysis by flame atomization atomic absorption spectrophotometry. The two methods produced values that were indistinguishable within experimental error.

Cu and Zn are of interest in the study of marine environments because these elements are necessary to living organisms at trace concentrations, while at higher levels they rapidly become toxic. The concentrations and distributions of Cu and Zn in the waters of metropolitan bays and harbors are of

particular concern because of potential industrial and urban discharges and because circulation in these basins is restricted. Antifouling paints and cathodic protection devices used on ships are also potential sources for these metals. We have measured Cu and Zn in surface waters in and around San Diego Bay, Calif., with an automated anodic stripping voltammetry (AASV) device which enabled us to make a determination for either Cu or Zn every 10-20 min. We made hundreds of determinations at a stationary pier location and conducted a general study of the surface distributions of the metals in the bay from aboard a small vessel. We also wished to compare Cu and Zn concentrations obtained by AASV with those obtained by a spectrophotometric procedure. Therefore, in parallel with our voltammetric determinations we collected discrete samples of bay water and measured their Cu and Zn content by extraction on Chelex 100 followed by analysis by flame atomization atomic absorption spectrophotometry.

This report discusses new improvements to the voltammetric system, presents the results of the voltammetric surveys and those of the intercomparison of methods, and attempts to relate these measurements to the circulation pattern of the bay and to speciation models proposed by other investigators.

### Experimental

**Voltammetry. Cell Modifications.** All measurements were made with a tubular mercury graphite electrode (TMGE),

<sup>1</sup> Present address, Department of Oceanography, University of Washington, Seattle, Wash. 98105.