DIRECT CALCULATION OF SULFUR DIOXIDE ABSORPTION BY WATER DROPS

A. Saboni[*], S. Alexandrova[1], A. Assenov[1]

(Groupe Ecoulements Transferts de Matière et de Chaleur, LTP, Université de Caen, Dépt GTE,
120 rue de l'Exode, 50 000 Saint Lô, FRANCE
[1]Department of Chemical Engineering, University of Chemical Technology and Metallurgy,
8 K. Ohridski Blvd, 1756 Sofia, BULGARIA)

Absorption of pollutant gases into water drops is one of the major removal mechanism in clouds, rain and scrubbers. The aim of this article is to present a new model for prediction of the mass transfer in gas-liquid dispersed systems encountered in scrubber or atmospheric systems. In the liquid phase, a model based on local scales, interfacial liquid friction velocity and drop size diameter is used. In the continuous gas phase the well known Beard and Pruppacher model is applied. Data obtained by the modelling of the SO_2 absorption in a single drop are compared to published experimental results and a fairly good agreement was found. Finally, we present a particular and important application of the above model as an illustration of its use. As an example, sulfur dioxide washout by rain, falling through a polluted plume, is considered.

Key words: absorption, sulfur dioxide, modelling, drops

Introduction

Removal of sulfur oxides plays an important role in the air pollution control. In the atmosphere, chemical reactions occur between sulfur oxides, aerosol particles, and trace gases, such as nitrogen oxides. Some products of the reactions, absorbed by the cloud and rain drops, render the acidic precipitation.

A knowledge of the mass transfer mechanism in the case of gas absorption (from / into) drops is necessary to understand the scavenging of trace gases in clouds, rain and wet scrubbers. Mass transfer between gas phase and water drops depends on the physical and chemical properties of the diffusing gas, the drop size and the hydrodynamics around and inside the moving drops.

The transport of trace gases from the air into the falling drop is controlled by molecular diffusion, as well as by the convective mass transfer outside and inside the falling drops. The internal circulation, generated by the aerodynamic drag on the drop surface, facilitates the redistribution of the absorbed gas [3, 19, 7]. For instance, the short residence time of some gases in the atmosphere is due to the fact that these gases are preferentially absorbed by cloud and rain droplets and removed in this way from the air. As a consequence the acidic precipitations are strongly affecting the aquatic

deterioration and material degradation, resulting in agricultural productivity, forest growth and known or anticipated effect on human health .

A number of mathematical models have been proposed and many experimental investigations have been carried out in the area of air-pollution control in order to provide better understanding of the scavenging of trace gases in clouds, rain drops, and industrial wet scrubbers. For drops, falling in a well soluble gas medium (in this case the transfer resistance is located in the gas phase), the survey of the published works [4, 1, 11, 19] show that a number of good numerical models exist, as well as experimental correlations for prediction of the mass transfer coefficients in the gas film. For liquid phase controlled resistance, [16] proposed a model based on local scales, interfacial liquid friction velocity and drop diameter. The model were validated experimentally by Amokrane et al. [2] compared literature models with the experimental data of Garner and Lane [9], Kaji et al. [11] Walcek et al. [19] and Lindhjem [1]. They found considerable discrepancies between the experimental data and the published models. On the contrary, they observed that the Saboni model [16] fits the experimental data very well. The experimental study and model validation in the case of sulfur dioxide absorption by water drops falling through

high gas concentration (few %) has been described in details by Amokrane et al. [2]. The purpose of this article is to test a new model to predict the SO_2 absorption and desorption by falling drops in air containing traces of sulfur dioxide.

If absorption is to be modeled as local process, based on the overall simulation of the two phase flows, two approaches are possible ; a) To compute the hydrodynamics and the mass transfer at each point in the system as a function of the local conditions. b) Using the experimental results together, with a complete numerical simulation, to develop and refine approximate models for the mass transfer between the two phases.

At the present time option (a) is completely excluded by limitations in computational power. The calculations will be prohibitively expensive and impractical for routine application to the description of scrubber and atmospheric systems. An example of option (b), similar to that used by Walcek et al. [17, 18, 19], is presented in this article. The authors proposed a simplified theoretical approach which was validated by experimental data. They applied it to describe the scavenging of trace gases by drops. Their simplified theory has an important advantage over the rigorous model (Navier-Stokes and diffusion-convection equations), as it is computationally much faster, since the two dimensional problem is transformed into a 1-dimensional one. However calculations remain too slow for routine application (in cloud models and mesoscale pollution transport models, as mentioned by Mitra et al., [14]). In this study, an application, which simplify considerably the computations, is presented.

Model formulation

Starting from the expression for mass flux across the interface, we can write :

$$V_l \frac{dC_l}{dt} = S_l k_l \left(C_{li} - C_l \right) \qquad (1)$$

where S_l and V_l are the surface area and the droplets volume respectively, where k_l is the local liquid mass transfer coefficient, C_{li} is the equilibrium concentration at the interface and C_l is the average concentration in the drop. According to Saboni [16] and Amokrane et al. [2], the liquid mass transfer coefficient is given as :

$$k_l = 0.8 \sqrt{\frac{D_l u^*}{d}} \qquad (2)$$

with

$$u^* = U \sqrt{\frac{\rho_g}{\rho_l} \frac{C_D}{2}} \qquad (3)$$

where D_l is the liquid phase molecular diffusivity, u^* is the interfacial liquid friction velocity, ρ_g is the gas density and ρ_l is the liquid density.

The total drag coefficient, C_D can be deduced from the equation proposed by Berry and Pranger [6]:

$$\ln(\text{Re}) = -3.126 + 1.013 * \ln\left(C_D \text{Re}^2\right) - \\ + 0.01912 * \left[\ln\left(C_D \text{Re}^2\right)\right]^2 \qquad (4)$$

In this relation the Reynolds number range between 1 and 3550 and the term $C_D \text{Re}^2$ between 2.4 and 10^7

Mass transfer across the interface reduces the concentration of the diffusing specie in one of the phases and increases it in the other. The change in each of the two phases is given by:

$$V_g \frac{dC_g}{dt} = -V_l \frac{dC_l}{dt} = -S_l k_l \left(C_{li} - C_l \right) \qquad (5)$$

Where V_g and V_l are the volume of the gas and the liquid phase, respectively and t is the time. C_g and C_l are the concentration of the diffusing specie in the continuous and the dispersed phase, respectively.

Local equilibrium is supposed at the interface between liquid and gas phase concentration. For this reason and supposing that the pH value does not exceed 5.5 we can write :

$$C_{li} = K_H C_{gi} + \sqrt{K_H K_l C_{gi}} \qquad (6)$$

where K_H and K_l are the equilibrium constants and C_{gi} is the gas concentration at the interface.

In addition to equilibrium, mass flux continuity across the interface give the gas concentration at the interface:

$$C_{gi} = C_{g\infty} - \frac{k_l}{k_g} \left(C_{li} - C_l \right) = C_{g\infty} - \frac{k_l \delta_g}{D_g} \left(C_{li} - C_l \right) \qquad (7)$$

with

$$\delta_g = \frac{2a}{\text{Sh}} \qquad (8)$$

where $C_{g\infty}$ is the bulk gas concentration, where k_g is the local gas mass transfer coefficient.

The gas concentration boundary layer, δ_g, is calculated from the expression for the Sherwood number in the gas phase (Beard and Pruppacher [5]; Pruppacher and Rasmussen [15]):

$$\text{Sh} = 1.61 + 0.718 \text{Re}^{0.5} \text{Sc}^{0.33} \qquad (9)$$

where Sc is the Schmidt number.

Only results for the total sulfur concentration will be presented. $C = [H_2SO_3] + [HSO_3^-] + [SO_3^=]$, the concentrations of the individual species being obtained from the total concentrations by simple relations (Appendix).
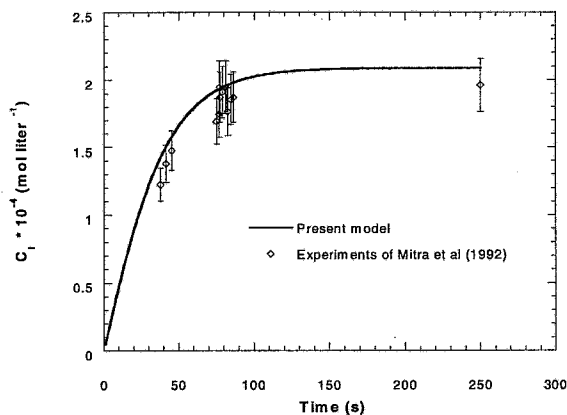
Fig.1 Concentration within a drop as a function of time of exposure to SO_2 (for a 2.88 mm drop radius, drop temperature =10 °C, $[SO_2]$ = 1035 ppbv)
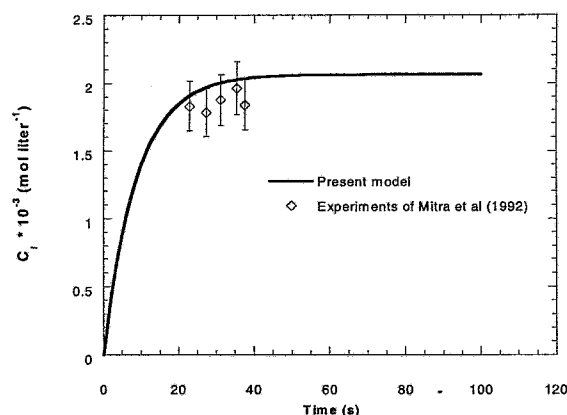

Fig.3 The variation of the rate $C_t/C_{initial}$ of S(IV) desorption with time exposure SO_2 (for a 2.88 mm drop radius, drop temperature = 15 °C, $C_{initial}$ = 3.39 10^{-3} mole $liter^{-1}$)

of the average total sulfur dioxide concentration vs. the time exposure in the case of 1035 ppbv SO_2 concentration in the gas phase. In Fig.2 results are reported for the absorption in the case of 97 ppm SO_2 concentration in the gas phase. From Fig.1 and Fig.2, we observe that the values predicted by the present model are in good agreement with the experimental results. In the second category of experiments (Mitra et al., [14]), a drop initially containing S(IV) was exposed to sulfur-free air to determine the rate of sulfur dioxide desorption.

Fig.3 shows the evolution of the average total sulfur dioxide concentration vs. the time exposure for a 3.39 10^{-3} mol $liter^{-1}$ drop initial concentration. The results obtained from the model agree well with those from experiments.

Fig.2 Concentration within a drop as a function of time of exposure to SO_2 (for a 2.88 mm drop radius, drop temperature =12.5 °C, $[SO_2]$ = 97 ppm)

Results and discussion

Comparison with Laboratory Studies

For a constant gas concentration , which is the typical case for laboratory studies, the Eqs.(1), (2), (6) and (7) are sufficient to describe sulfur dioxide absorption by individual freely falling large water drops.

In order to evaluate the model adequacy, we test the model for the case of low and intermediate gas concentration (the mass transfer resistance is located both in the gas and the aqueous phase). The comparison is made between the model and the experimental results for sulfur dioxide absorption from individual large water drops. The model is compared to the Mitra et al. [13] and Mitra et al. [14] experimental results concerning two broad categories of sulfur dioxide absorption. The experiments were carried out in a vertical wind tunnel which allows to freely suspend a single drop in the vertical air stream of the tunnel. In the first category a 2.88 mm radius drop were exposed to sulfur dioxide - air mixture. Fig.1 shows the evolution
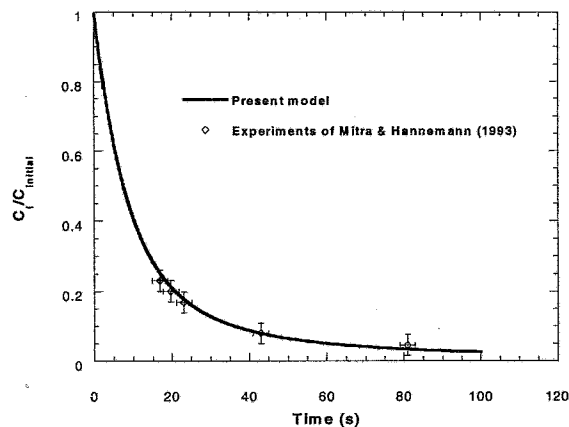
Example of Model application

A brief illustration of the proposed model, applied to the sulfur dioxide washout by rain falling through a polluted plume, is shown below. This case is of growing interest, because the precipitation scavenging constitutes an important sink for gases in the atmosphere and can influence their local, regional and global distributions. A similar attempt was first made by Barrie [4] extended by Walcek et al. [17, 18, 19] and Hannemann et al. [10]. The Walcek et al. [17, 18, 19] procedure, adapted to the present model, may be summarized by the following:

Let us consider a vertical column containing of air and sulfur dioxide. We suppose gaussian concentration distribution in the plume with a peak centered 200 m above the ground. Assuming the absence of SO_2 initially, the drops are supposed to fall sequentially in the air column that is devised into 300 layers, each of one meter in height. The drops enters a given layer of air with concentration C_{top} and exit at its bottom with concentration C_{bot}. C_{bot} is calculated from Eqs.(1), (2), (6) and (7), and represents the C_{top} value for the next layer.
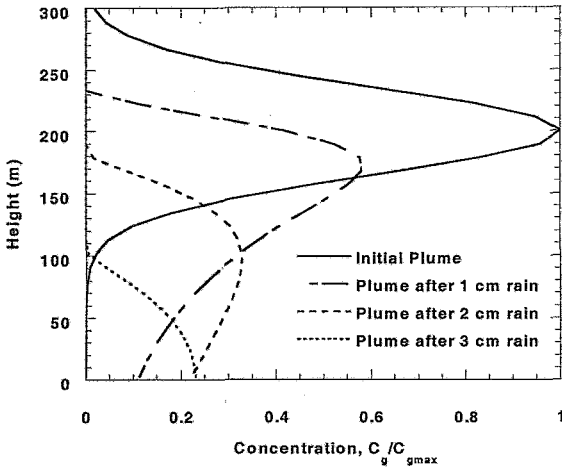
Fig.4 Variation of SO$_2$ concentration with height in pollution layer after specified amounts of raindrops have fallen through. Initial concentration is 500 ppb (v). Rainfall rate, $R = 1$ mm/h

Fig.5 Variation of SO$_2$ concentration with height in pollution layer after specified amounts of raindrops have fallen through. Initial concentration is 500 ppb (v). Rainfall rate, $R = 15$ mm/h

The gas phase concentration is calculated from Eq.(5) which is rewritten in discrete form as:

$$\frac{C_g^{n+1} - C_g^n}{\Delta t} = -\frac{V_d}{V_g}\frac{\left(C_{bot} - C_{top}\right)}{\Delta t} \quad (10)$$

where C_g^n and C_g^{n+1} are the concentration in the layer before and after the drops have passed trough . V_g is the air volume and V_d is the volume of raindrops falling through the layer.

The same equation was applied to each layer as the drop progress through the entire column. From Eq.(10) the gas concentration in each layer is determined according to,

$$C_g^{n+1} = C_g^n - \left(C_{bot} - C_{top}\right)\frac{\Delta Q}{\Delta z} \quad (11)$$

where ΔQ is the rainfall increment and Δz is the layer height (respectively 0.1 mm and 1 m, in this study). The gas profile will be modified after each ΔQ, (corresponding to a given set of drops falling through the column). Another set of drops is allowed to fall through this new profile and the procedure is repeated until the trace gas reaches a certain gas concentration.

For further simplification, we consider the mean raindrop radius, r_m representative for this distribution:

$$r_m = 0.55 R^{0.232} \quad (12)$$

where r_m is given in mm and the rainfall rate, R, in mm/h.

Plume washout results

Plume washout was calculated for precipitation intensity, R, of 1 mm/h and 15 mm/h. Fig.4 shows the time evolution of the specified gaussian distribution of sulfur dioxide concentration as a population of drops falls trough the plume pollution with an initial peak profile concentration of 500 ppb (v). In the case of
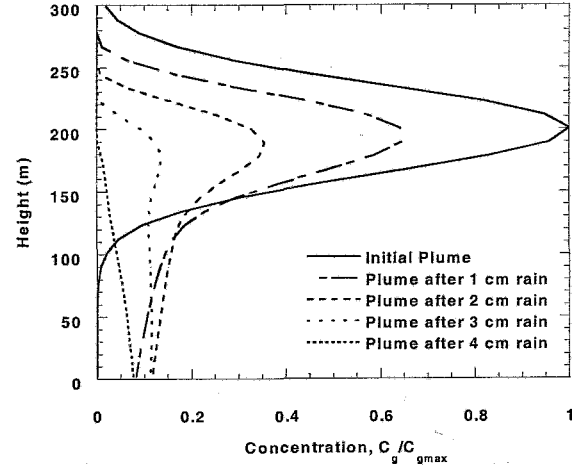
1 mm/h rainfall rate , corresponding to small drop size ($<d_m> = 1.1$ mm), the drops absorb and desorb the sulfur dioxide rapidly. We see that the gas concentration have a maximum and that the corresponding height$_{max}$ depends on rainfall quantity passed through the plume. The maximum gas concentration is displaced to shorter height with increasing rainfall quantity.

For rainfall rate of 15 mm/h (Fig.5), corresponding to larger raindrop ($<d_m> = 2.06$ mm), the average concentration is reduced, while the height of the plume remains roughly constant. To. explain the difference between these two cases, combination of the following two effects has to be considered : residence time (drop terminal velocity) and the absorption ability (drop diameter and gas concentration). From Fig.4 and 5, we can note also that the scavenging is mainly controlled both by the total amount and intensity of the rainfall, which is in agreement with some in situ observations (see for example Durana et al. [8]).

Conclusion

In the first part of this paper, a simple analytical model was used to determine the sulfur dioxide absorption/desorption by freely falling drops. Data obtained by the model of the SO$_2$ absorption/desorption by single drop are compared with published experimental data and a fairly good harmony was found.

In the second part, a particular important application of the above model is presented as an illustration of its predictive ability. As an example, sulfur dioxide washout by rain, falling through a pollution plume, is considered. The model predicts the redistribution of the plume through which the raindrops had fallen as function of the rainfall rate.

Although the observed agreement between model and experimental results, from which some useful predictions on the atmospheric scavenging can be drawn, further investigations are needed for the initial rate under realistic conditions. Effects as multi-

component gas phase, oxidation, break-up and/or coalescence, evaporation, air motions, have to be considered.

SYMBOLS

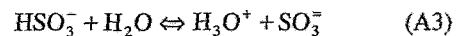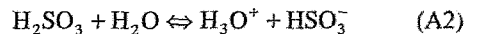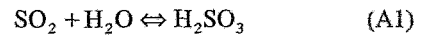|	
a	radius of drop
C	dimensionless concentration
C_g	bulk gas concentration
C_{gi}	interface gas concentration
C_D	drag coefficient
C_l	concentration of drop
C_{li}	equilibrium concentration of drop
d	drop diameter
$D_{g,l}$	molecular diffusivity gas/liquid phase
k_l	liquid mass transfer coefficient
k_g	gas mass transfer coefficient
R	Rainfall rate
Re	Reynolds number
r	radial coordinate
r_m	mean drop radius
S	surface area
Sc	Schmidt number
Sh	Sherwood number
t	dimensional time
U	Terminal velocity
u^*	Interfacial liquid friction velocity
V	drop volume
$\rho_{g,l}$	fluid density (gas/liquid)

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APPENDIX

Equilibrium relations for sulfur dioxide in water

When sulfur dioxide is absorbed into water, the resulting equilibrium relations (Walcek et al. [17, 18, 19], Amokrane et al.,[2]) are written as:

$$SO_2 + H_2O \Leftrightarrow H_2SO_3 \qquad (A1)$$

$$H_2SO_3 + H_2O \Leftrightarrow H_3O^+ + HSO_3^- \qquad (A2)$$

$$HSO_3^- + H_2O \Leftrightarrow H_3O^+ + SO_3^= \qquad (A3)$$

The values of the equilibrium constants K_H, K_1 and K_2, of the reactions A1, A2 and A3 are respectively (Maahs [12], Mitra et al. [13]):

$$K_H = \frac{[H_2SO_3]}{[SO_2]} = 10^{\left(\frac{1376.1}{T} - 6.521\right)} RT \text{ (moles/moles)} \quad (A4)$$

$$K_1 = \frac{[HSO_3^-][H_3O^+]}{[H_2SO_3]} = 10^{\left(\frac{853}{T} - 4.74\right)} \text{ (moles/liter)} \quad (A5)$$

$$K_2 = \frac{[SO_3^=][H_3O^+]}{[HSO_3^-]} = 10^{\left(\frac{621.91}{T} - 9.278\right)} \text{ (moles/liter)} \quad (A6)$$

Where T is the absolute temperature expressed in Kelvin.
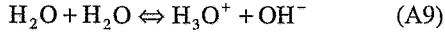
The total sulfur concentration $[S]$ is written as

$$[S] = [H_2SO_3] + [HSO_3^-] + [SO_3^=] \qquad (A7)$$

After several manipulations from *Eqs.(A4)-(A6)*, together with the following conditions.

- Condition of electroneutrality:

$$[H_3O^+] = [OH^-] + [HSO_3^-] + 2[SO_3^=] \quad \text{(A8)}$$

- Condition of water ionization:

$$H_2O + H_2O \Leftrightarrow H_3O^+ + OH^- \quad \text{(A9)}$$

- The equilibrium constant of the ionization of water is defined by:

$$K_w = [H_3O^+][OH^-] \left(\text{that is } K_w = 10^{-14} \text{ at } 25\,^\circ C\right) \quad \text{(A10)}$$

- The total sulfur concentration as function of pH of the solution is given by:

$$[S] = \left([H_3O^+] - \frac{K_w}{[H_3O^+]}\right) \frac{[H_3O^+]^2 + K_1[H_3O^+] + K_1K_2}{K_1[H_3O^+] + 2K_1K_2} \quad \text{(A11)}$$

For pH < 5.5, reaction A3 may be neglected. Thus the total S concentration is then given by:

$$[S] = [H_2SO_3] + [HSO_3^-] = \frac{[H_3O^+]^2 + K_1[H_3O^+]}{K_1} \quad \text{(A12)}$$

Which may be written in this form:

$$[S] = [H_2SO_3] + [HSO_3^-] = K_H[SO_2]_g + \sqrt{K_1K_H[SO_2]_g} \quad \text{(A13)}$$