

Modeling of SO₂ scrubbing in spray towers

Amitava Bandyopadhyay^{a,b,*}, Manindra N. Biswas^a

^a Department of Chemical Engineering, Indian Institute of Technology, Kharagpur 721 302, India

^b West Bengal Pollution Control Board, Alipore Regional Office, Industry House, 2nd Floor, 10, Camac Street, Kolkata, 700 017, India

Received 18 August 2006; received in revised form 6 April 2007; accepted 19 April 2007

Available online 13 June 2007

Abstract

The present article aims at developing simple realistic models in order to describe the gaseous removal process of SO₂ by absorption with and without chemical reaction in spray towers. Effects of droplet size, droplet velocity, superficial gas velocity, liquid flow rate and tower height on the performance of such a system are theoretically predicted. Model calculations bring out some very interesting facets of gas scrubbing as functions of droplet diameter and velocity. Four distinct regimes, viz. droplet lean, dense droplet, rigid droplet and droplet inertia controlling regimes, are found important in spray scrubbing process. Model calculation also elucidates the existence of rigid droplet (sphere) for a distinct droplet size at a specific droplet velocity. Theoretical considerations reveal that best performance can be achieved in the droplet inertia-controlling regime. Effect of turbulence on scrubbing is also considered for modeling. The model development and experimental data are limited to use of water-soluble alkaline scrubbing. However, the predicted values agree reasonably well with the available experimental data at lower gas and liquid flow rates for relatively smaller droplets. Models can also be applied to any gas–liquid spray absorption process subject to the assumptions and conditions necessary to describe the specific physico-chemical hydrodynamics of the system. However, incorporation of various droplet interactions can further refine the models for better prediction of removal efficiency.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Spray tower; SO₂ absorption model; SO₂ scrubbing; Air pollution control; Rigid droplet

1. Introduction

The removal of SO₂ from flue gases has received considerable attention over the years because of its various deleterious effects to all forms of lives. Among the various physico-chemical wet and dry methods, wet method is considered to be the simplest and the most economical method for gas scrubbing with very high

removal efficiency. Thus compliance with SO₂ standards will in many cases result in the installation of wet scrubbers. Tomany (1975) concluded that despite some of its inherent shortcomings wet scrubber could effectively combat the gaseous pollution. Wet scrubbers with column internals are replaced with spray towers (Kohl and Reisenfeld, 1985) due to its ability to treat large volume of gas as also it offers (b) least pressure drop (compared to any other gas–liquid contacting devices) and hence is cost effective (b) a very high turn down ratio, (c) higher service factor, (d) smaller onsite plot space, (e) no scaling problem as a flue gas desulfurization scrubber, and (f) simpler operation than any other air emission control device.

* Corresponding author. West Bengal Pollution Control Board, Alipore Regional Office, Industry House, 2nd Floor, 10, Camac Street, Kolkata, 700 017, India. Tel./fax: +91 33 22823358.

E-mail addresses: amitava.bandy@gmail.com (A. Bandyopadhyay), mani@che.iitkgp.ernet.in (M.N. Biswas).

Literature indicates that commercial spray towers in various forms have been investigated for the absorption of SO₂ in water and alkaline solutions over the decades but the realistic treatment for characterizing the spray tower does not seem to be available. Available literatures were reviewed some of which are briefly discussed here. Hixson and Scott (1935) reported on the gas-side mass transfer coefficient as a function of gas flow rate, liquid flow rate and tower height for SO₂–H₂O spray absorption system using droplet diameter in the range of 1500 to 2000 μm, but drop size was not considered for characterizing the absorption process studied. Although Johnstone and Williams (1939) reported on the rates of absorption of SO₂ by falling alkaline (NaOH) droplets of diameter ranging between 2670 and 5970 μm, the outlet concentration of SO₂ and the liquid flow rate were not specified. Mehta and Sharma (1970a,b) reported on the effects of gas flow rate, liquid flow rate, and tower height on the gas side mass transfer coefficient as well as on the interfacial area of contact in a spray tower using SO₂–dilute NaOH absorption system. But the inlet and outlet concentrations of SO₂ were not reported. Furthermore, none of these studies reported on the spray tower removal efficiency as a function of the pertinent variables under consideration. On the other hand, although Epstein et al. (1975) reported on SO₂ removal in spray tower, they did remain silent about the droplet size. Operation of Combustion Equipment Associates Prototype Double Alkali Process was reported (Kohl and Reisenfeld, 1985) for SO₂ scrubbing comprising a venturi scrubber followed by an absorber designed to operate as either a tray or a spray tower. In this process, the gas was contacted with a clear solution containing NaOH or Na₂CO₃ or Na₂SO₃ as the first alkali followed by a lime solution as the second outside the scrubber circuit to eliminate problems associated with scaling within the operating scrubber. This investigation reported on the removal efficiency, inlet and outlet SO₂ concentrations and flow rate. But droplet size and droplet velocity in the spray section were not reported.

It is conceivable from the foregoing discussion that the droplet size smaller than about 250 μm (e.g., 50 μm–150 μm range) was not considered in these early studies, possibly due to the (i) shortcomings often associated with the commercial atomizers to generate such smaller droplets and (ii) chances of their significant entrainment. To overcome the difficulty of generation of small droplets with uniform spray pattern the design features of the commercial atomizers need be modified. On the other hand, the entrainment could be restricted by increasing the droplet relative velocity (e.g., ≈20–30 m/s) in the gas

stream and in the process such droplets could shear off the gas boundary layer significantly and reduce its thickness as much as possible to achieve high mass transfer rates for the gas side controlling systems. Operation of a spray section using such small droplets for achieving high removal efficiency of SO₂ formed one of the objectives of our study reported earlier (Bandyopadhyay and Biswas, 2006) using water and dilute NaOH solution. An energy efficient and cost effective two-phase critical flow atomizer developed by Biswas (1982) was used for generating small droplets at very high velocity without sacrificing spray uniformity and entrainment. The reported removal efficiency was correlated with droplet Sauter Mean Diameter (SMD), droplet mean velocity, other flow variables and physico-chemical properties of the system studied. Besides reporting typical drop size distribution, droplet SMDs reported were 41.6 μm, 72.2 μm, 102.3 μm, 119.8 μm and 139.8 μm having respective droplet mean velocities of 26.38 m/s, 25.18 m/s, 25.90 m/s, 27.36 m/s and 22.06 m/s measured at a distance of 1 m from the atomizer discharge end. The semi-empirical correlation developed for alkaline (NaOH) scrubbing indicated that the removal efficiency would increase with the decrease in droplet SMD and also with the increase in the reagent (NaOH) concentration. Thus, reducing the droplet size with decreased NaOH concentration could increase the removal efficiency and in that, the consumption of the reagent would be reduced. Very high removal efficiency (≈100%) was achieved in the system in alkaline scrubbing using dilute NaOH solutions in the concentration range varied between 0.2 and 5 mol/m³.

Critical appraisal of the existing literature on the overview of the reagents that are being commercially used for SO₂ scrubbing indicates that the selection of a suitable absorbent or scrubbing liquid poses a very complex problem for removing SO₂ from waste gas stream and is of significant importance for process design as well. Many of the problems, experienced at various facilities, are the result of the misapplication of a scrubbing process. For instance, a limestone slurry scrubber that works well on steady and weak SO₂ emitting stream generated in a coal-fired boiler will not be suitable for stronger and fluctuating SO₂ emitting stream produced by the metallurgical processes. Common commercial scrubbing processes utilized lime/limestone slurry, spray dry scrubbing with lime, once through sodium alkali, once through seawater and dual alkali. A brief overview of the scrubbing liquids that are being utilized commercially is presented below:

Lime and limestone slurry scrubbing is suitable for relatively low concentrations of SO₂ and moderate

collection efficiencies. They are characterized by very high liquid circulation rates, most often in-situ forced oxidation of sulfite to sulfate, can often be designed for zero effluent discharge and can produce a marketable quality of gypsum. *Spray dry scrubbing (using lime)* is applicable to hot gases with a significant amount of evaporative capacity. SO₂ absorption occurs as water evaporates leaving behind a dry mixture of sulfate and sulfite solids. Because final collection occurs in a Bag House Filter or in an Electrostatic Precipitator, there is no segregation of process and CaSO₃/CaSO₄ solids. Once through sodium process uses soda ash or caustic and produce a solution of soluble sodium salts. They are quite simple and effective. *Seawater scrubbers* are actually a form of this, making use of natural alkalinity in seawater (sodium bicarbonate). While there are several types of *dual alkali* processes in operation, they all use a soluble scrubbing agent (usually sodium or aluminum based) that is regenerated by reacting with another alkali (usually lime). These processes offer the advantages of solution scrubbing, a solid by-product and ability to handle a very high concentration of SO₂ at the inlet.

The details of applicability of various reactive processes of SO₂ scrubbing are furnished in Table 1 in terms of reagents to be used, range of inlet SO₂ concentration and percentage of removal efficiency of SO₂. It can be seen from the table that 99%+ removal efficiency can only be achieved by sodium based scrubbing processes. Perhaps due to this reason, it has been pointed out by Brady (1987) that the neutralization capacity of NaOH for SO₂ is extremely high. The exit concentration of SO₂ below 5 ppm_v (Threshold Limit Value of SO₂) can best be achieved with sodium alkalis only. Furthermore, when concentration of SO₂ absorbed became sufficiently large to make the economics of a simple throwaway process uneconomical, the waste solutions can be regenerated in the dual alkali process by reacting it with lime e.g., Ca(OH)₂ outside the scrubber circuit. This approach permits the gas to be contacted with a clear solution of highly soluble salts, thereby minimizing scaling, plugging and erosion problems in

the absorbent circuit. The use of a clear reactive solution, instead of a slurry as in case of lime or limestone scrubbing, also offers potential for almost complete SO₂ absorption rate because the SO₂ removal reaction is not limited by the rate of dissolution of solid particles. In addition, the dual alkali process has the ability to handle a very high initial concentration of SO₂ amongst all other processes reported so far (Table 1).

In the light of the above findings, dilute NaOH solution has been selected as a suitable reagent for the present study (which constitutes a part of the dual alkali process) in order to attain very high removal efficiencies. On the other hand, water has been chosen in our prelude study to analyze the system behavior in water scrubbing since this will help in understanding the extent of enhancement of removal efficiency of SO₂ while studying NaOH scrubbing. Water scrubbing thus forms a primary part of the overall NaOH scrubbing.

In the present article an attempt has been made to develop simple realistic models for predicting the performance of a spray tower ascribing similar spray hydrodynamics reported earlier (Bandyopadhyay and Biswas, 2006) with a view to attain definite insight into the process of absorption of SO₂ in water and in alkaline droplets and to validate the models with the data reported earlier. The prime objective of the present study is to develop models that can easily calculate the removal efficiency of SO₂ both in water and in alkali (dilute NaOH) scrubbing using the pertinent variables of an operating spray tower specially for droplet diameters ranging between 40 and 150 μm moving at very high velocity (≈20–30 m/s).

2. Modeling of the spray tower

In a spray column the soluble components from the gas phase are transferred to the liquid phase by continuous counter-current contact of the two phases as the swarm of drops flowing downward and the gas flowing upward. The actual flow situation is very complex and normally defies mathematical interpretation. Attempts are being

Table 1
Details of applicability of SO₂ scrubbing processes in alkaline reagents (Kohl and Reisenfeld, 1985; Hay et al., 2004)

Process	Reagents	Inlet concentration of SO ₂ (ppm _v)	By products	Efficiency (%)
Lime slurry	CaO	<100–6500	Calcium based solids	90–95
Limestone slurry	CaCO ₃	1000–4500	Calcium based solids	~95
Spray drying — lime	CaO, Ca(OH) ₂	<100–3000	Calcium based solids	90–95
Dual alkali: lime sodium	NaOH or Na ₂ CO ₃ ; and CaO or Ca(OH) ₂	1200–150,000	Calcium based solids	99+
Dual alkali: Dowa	CaCO ₃ and Al ₂ (SO ₄) ₃	1000–25,000	Calcium based solids	85–98
Once through seawater	NaHCO ₃ (CaO)	Up ~2000	Calcium based solids	~98
Once through sodium	NaOH or Na ₂ CO ₃	<100–10,000	Na ₂ SO ₃ ; Na ₂ SO ₄	99+

made for developing models on the performance of SO₂ scrubbing (in water and alkali) in a spray tower followed by analysis of predicted values.

2.1. Theoretical model for water scrubbing under laminar flow

In the proposed model following assumptions are being made (Bandyopadhyay, 1996):

1. The shapes of all the droplets are spherical.
2. No reaction takes place in the gas phase.
3. The effect of pH on the droplet surface is neglected.
4. Steady state operation of the spray column.
5. Insignificant heat effects due to the physical mass transfer (true as the heat capacity of water is large compared to the gas).
6. The gas phase concentration is uniformly distributed at the inlet and outlet of the column and the same concentration gradient exists inside the downward flowing drops that take into account the functionality of concentration with height.
7. The mass transfer decreases during down flow of the drops and is a function of time it is exposed to the gas phase. The efficiency of the drop would also vary with time.
8. Small diameter to length ratio of the spray column.
9. Insignificant wall effect.
10. The flow of gas and droplets is regarded as plug flow with negligible gas phase back mixing.
11. Droplet breakup, droplet coalescence and multi-droplet interactions in a cloud are neglected.
12. The limiting case of $Re=0$ is unattended since such a situation is rarely been realized in an operating spray tower with very high droplet velocity.
13. Kinetics of SO₂ absorption in water: Absorption of SO₂ in water is considered as a physical mechanism (Lynn et al., 1955) with the following reactions occur in the liquid phase,



In this article the mathematical derivation for absorption follows from the treatment reported in detail by Beg et al. (1991) for stripping considering the mass transfer from the gas phase in the droplet surface and into the interior of it by diffusion instead of mass transfer from the droplet to the air by diffusion as in

stripping. Accordingly the concentrations are adjusted in the derivation. A material balance in a section of the tower shows that under the above assumptions, the overall removal efficiency is the same as the efficiency of a single droplet and the overall mass transfer of SO₂ into the drop can be given by the following expression [see Appendix for detailed derivation]

$$m = 2.36D_{dj}DRe^{1/2}Sc^{1/3}C_{\infty} \left(1 - \frac{DRe^{1/2}Sc^{1/3} + (C'/C_{\infty})D'\phi(Fo')}{DRe^{1/2}Sc^{1/3} + \frac{RT\rho_a}{HM_w}D'\phi(Fo')} \right) \quad (1)$$

where, $\phi(Fo') = 5.32 \sum_{n=1}^{\infty} \exp\left(-\frac{4\pi^2 n^2 Dt}{D_{dj}^2}\right)$ [see Appendix] Eq. (xxia).

The removal efficiency of gas (SO₂) for the j th droplet size range without any chemical reaction, can be defined as

$$\eta_{bj} = \frac{\text{amount of gas (SO}_2\text{) entering into the drop}}{\text{amount of gas (SO}_2\text{) flowing through a circle whose diameter is that of the drop}} \quad (2)$$

In a spray tower, the gas (SO₂) removal efficiency is the result of the collective absorbing capacities of all the droplets present in the tower. Therefore, the amount of SO₂ entering into the droplet can be evaluated by integrating the rate of mass transfer of SO₂ into the drops over the whole time period during which the droplets remain in relative motion with respect to the gas. Hence, Eq. (2) can be written as

$$\eta_{Nj} = \frac{\int_0^t m dt}{[(Q_G C_{\infty})/n_j]} \left[\text{where, } n_j = \frac{Q_L}{(\pi/6)D_{dj}^3} \right] \quad (3)$$

Distinct droplet diameter from the array of droplets may be used in Eq. (3) by measuring the droplet size distribution, in conjunction with the number of droplets available from the distribution analysis. Else, the average droplet diameter may be used in conjunction with the number of droplets derived from considering the homogeneous droplet flow model as used by Beg et al. (1991). While using the homogeneous droplet flow model instead of considering the specific drop size distribution, a single droplet diameter (average) is chosen and the overall result entails an error as was considered by Beg et al. (1991). The error has been eliminated in the present model by considering the distinct droplet diameter as D_{dj} and is used in Eq. (3) that covers all the droplet diameters existing in the array of droplets introduced into the spray tower.

In order to determine the spray tower removal efficiency it is necessary to normalize Eq. (3) with

respect to time. Such normalization can be done by assuming a dimensionless time τ as

$$\tau = t/(L/v_g) \tag{4}$$

$$\text{and } dt = (L/v_g)d\tau \tag{4a}$$

for which the boundary conditions are at $t=0, \tau=0$ and at $t=L/v_g, \tau=1$.

The spray tower removal efficiency with this concept of normalization for j th droplet size range can be derived using Eqs. (1), (3), (4) and (4a)

$$\eta_{Nj} = \frac{2.36D_{dj}DRe^{1/2}Sc^{1/3}C_{\infty}L}{v_g[(Q_G C_{\infty})/n_j]} \int_0^1 \left(1 - \frac{DRe^{1/2}Sc^{1/3} + \frac{C'}{C_{\infty}}D'\phi(Fo'')}{DRe^{1/2}Sc^{1/3} + \frac{RT\rho_a}{HM_w}D'\phi(Fo'')} \right) d\tau$$

substituting $n_j = \frac{Q_L}{(\pi/6)D_{dj}^3}, v_g = \frac{Q_G}{(\pi/4)D_T^2}$ and on simplification we get

$$\eta_{Nj} = 3.54 \left(\frac{LD_T^2}{D_{dj}^2} \right) \left(\frac{Q_L}{Q_G^2} \right) (DRe^{1/2}Sc^{1/3}) \int_0^1 \left(1 - \frac{DRe^{1/2}Sc^{1/3} + \frac{C'}{C_{\infty}}D'\phi(Fo'')}{DRe^{1/2}Sc^{1/3} + \frac{RT\rho_a}{HM_w}D'\phi(Fo'')} \right) d\tau \tag{5}$$

where $\phi(Fo'')$ is similar to that of Eq. (xxia) [see Appendix] in terms of τ .

Eq. (5) actually describes the removal efficiency when the scrubbing liquid is recycled through the spray tower. Similarly, the removal efficiency for once through scrubbing of the liquid can be obtained by putting $C'=0$ into Eq. (5)

$$\eta_{Nj} = 3.54 \left(\frac{LD_T^2}{D_{dj}^2} \right) \left(\frac{Q_L}{Q_G^2} \right) (DRe^{1/2}Sc^{1/3}) \int_0^1 \left(1 - \frac{DRe^{1/2}Sc^{1/3}}{DRe^{1/2}Sc^{1/3} + \frac{RT\rho_a}{HM_w}D'\phi(Fo'')} \right) d\tau \tag{6}$$

Eq. (6) may be directly used for average droplet diameter (e.g., droplet SMD i.e., the volume to surface mean droplet diameter which is generally used for the purpose of gas–liquid absorption studies) for calculating the overall spray tower removal efficiency of SO_2 . While the overall spray tower removal efficiency of SO_2 for all droplet size ranges available from droplet size

distribution may be calculated from the following expression

$$\eta_{NO} = \sum_{j=1} \eta_{Nj}n_j \tag{7}$$

2.2. Theoretical model for water scrubbing under turbulent condition

The analysis of removal efficiency under turbulent flow field is the main objective of this section (Bürkholz, 1989). The gas molecules are molecularly more random than the liquid molecules and their movement is generally been characterized by statistical process under turbulence due to mixing. On the other hand, droplets in any spraying device are characterized as distinct particles with specific diameter and when the gas is constantly mixing under turbulence then droplets will no longer have distinct trajectories. Thus the gas scrubbing becomes a statistical process in such a situation. The probability of removal of SO_2 under this condition is random and the efficiency may be derived as follows:

$$\begin{aligned} &[\text{change of gas phase concentration due to scrubbing}] \\ &= [\text{gas concentration}] \\ &\quad \cdot [\text{fraction of mass transferred into droplet phase in time } dt] \\ &\text{and fraction of mass transferred into droplet phase} \\ &= \frac{\text{mass transferred to all the droplets}}{\text{amount of mass available for transfer to all the droplets}} \\ &= \frac{m \cdot n_j}{(Q_G C_{\infty})} = \frac{m}{(Q_G C_{\infty}/n_j)} \end{aligned}$$

$$\text{Or, } dc = -c \cdot \left(\frac{m}{Q_G C_{\infty}/n_j} \right) \cdot dt \tag{8}$$

Eq. (8) upon integration and combining with Eq. (5) yields

$$\int_{C_{in}}^{C_{out}} \frac{dc}{c} = - \int_0^t \left(\frac{m}{Q_G C_{\infty}/n_j} \right) \cdot dt = -\eta_{Nj}$$

$$\text{or, } \ln \frac{C_{out}}{C_{in}} = -\eta_{Nj}; \text{ or, } \frac{C_{out}}{C_{in}} = \exp(-\eta_{Nj});$$

$$\text{or, } 1 - \frac{C_{out}}{C_{in}} = 1 - \exp(-\eta_{Nj});$$

$$\text{or, } \eta_{T,Nj} = 1 - \exp(-\eta_{Nj}) \tag{9}$$

$$\text{and similarly : } \eta_{T,NO} = 1 - \exp(-\eta_{NO}) \tag{9a}$$

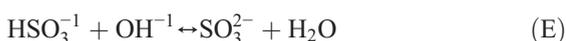
Eqs. (9) and (9a) are analogous to the famous Deutsch Equation for interpreting the exponential particle collection efficiencies under random turbulent motion and is purely described by a statistical probability. It may so happen while using the equation under laminar flow model that the removal efficiency exceeds the value of 1.0 (i.e., 100%) that is meaningless because such a value of percentage removal of more than 100% is not meaningful. But the exponential nature of the equation under turbulent flow in such a situation can yield meaningful values within 100%. This is discussed in details latter.

Eqs. (6), (7), (9) and (9a) can be applicable to any gas–liquid spray scrubbing process without chemical reaction based on the assumptions and boundary conditions specified by the physico-chemical hydrodynamics of the system. It is evident from Eq. (6) that the removal efficiencies for water scrubbing of SO₂ and the like gases are independent on the concentration of gas in either of the phases probably so because chemical reactions are neglected. The efficiency of removal mainly depends on the spray hydrodynamics, physico-chemical properties of the system, operating variables (i.e., gas and liquid flow rates), dimensions (i.e., height and cross-sectional area) of the spray tower. The impacts of the assumptions are discussed later.

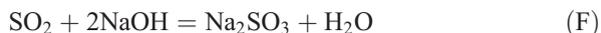
2.3. Theoretical model for reactive scrubbing

In order to incorporate the effect of the reagent (e.g., NaOH) on the scrubbing of SO₂ by a falling droplet, it is necessary to make the following additional assumptions as made in case of water scrubbing:

1. At the surface nearer to the gas, there will be a zone throughout which the reagent will be expended.
2. The presence of a uniform reaction front valid at any time.
3. The pollutant gas (SO₂) diffuses across the reagent free zone from the surface of the drop to the reaction front and the reagent on the other hand, diffuses from the interior of the drop toward the reaction front.
4. The concentrations of both the pollutant and the reagent are zero at the reaction front.
5. Kinetics of alkaline absorption of SO₂: The following two reactions should be considered for the absorption of SO₂ by aqueous NaOH solution, in addition to the reactions (A), (B) and (C) mentioned earlier,



Both reactions (D) and (E) may be regarded as instantaneous reactions (Hikita et al., 1977) and affect the alkaline scrubbing of SO₂. The overall reaction is



The ratio of the rates of mass transfer of the pollutant gas with and without chemical reaction occurring inside the drop is proportional to the respective removal efficiencies of the pollutant gas in the spray tower. The final form can be expressed by (Bandyopadhyay and Biswas, 2006)

$$\frac{m_{Cj}}{m_{Nj}} = \frac{\eta_{Cj}}{\eta_{Nj}} = \left(1 + i \frac{M'D' HM_w C''}{M'' D' RT \rho_d C_\infty} \right) \quad (10)$$

Therefore, the overall spray tower removal efficiency of SO₂ for the entire array of the dropelts and without scrubbing liquid being recycled can be given as

$$\eta_{\text{CO}} = \sum_{j=1} \eta_{Cj} n_j \quad (11)$$

Under turbulent condition the removal efficiency can be expressed similar to Eq. (9) as

$$\eta_{\text{T,Cj}} = 1 - \exp(-\eta_{Nj}) \quad (12)$$

$$\text{and similarly : } \eta_{\text{T,CO}} = 1 - \exp(-\eta_{\text{CO}}) \quad (12a)$$

Eqs. (11), (12) and (12a) can be similarly applicable to any gas–liquid spray scrubbing process with chemical reaction based on the assumptions and boundary conditions specified by the physico-chemical hydrodynamics of the system. It is evident from Eq. (11) that the removal efficiency of alkaline scrubbing of SO₂ and the like gases are strongly dependent on the initial gas phase concentration and the initial reagent concentration in the liquid phase. It can be further noted that the removal efficiency would decrease with an increase in the initial gas phase concentration while it would increase with an increase in the initial reagent concentration. The removal of SO₂ arrived at in alkaline scrubbing using Eq. (11) or (12) has been considered 1.0 (i.e., 100% removal efficiency) while it exceeds 1.0, since such a situation (i.e., percentage removal more than 100%) is not practically possible.

3. Prediction of removal efficiency of SO₂

A model study has been attempted on the scrubbing of SO₂ in H₂O and NaOH using Eqs. (6) and (11) respectively on a hypothetical spray tower operating

counter-currently for predicting its behavior as a function of pertinent parameters of the system. Eq. (9) has been used while predicting the performance of the spray tower under turbulent condition in water scrubbing. Distinct droplet diameter has been used as the study droplet diameter for the purpose of model calculation. The length and diameter of the tower assumed are 2.0 m and 0.2 m respectively having length to diameter ratio of 10 and is comparable to the reported data ranging between 6 and 30 (Schmidt and Stichlmair, 1991).

Eq. (6) was numerically solved subject to the boundary conditions. It may be noted that this numerical integration cannot be extended to zero time and hence evaluation of time intervals will always entail a small error depending upon the initial time interval selected for the computational work. This error, however, could be kept small by choosing a sufficiently small length of interval of τ near $\tau=0$. The initial value of τ assumed was in the order of 10^{-8} for achieving the numerical solution realistically.

To analyze the performance of the tower, values of v_{∞} are needed. The value of the droplet terminal settling velocity, for free fall under the influence of gravity, is to be used for v_{∞} (Crawford, 1980). In our study, the droplet radius of concern is in the range of 40 to 150 μm , moving at a very high mean velocity ($\approx 20\text{--}30$ m/s) as discussed earlier within a finite length of the tower (2 m). Under these circumstances, the terminal settling velocities are negligible compared to the mean droplet velocities. Therefore, the mean droplet velocities are used in our computational work without entailing any error.

The rise in temperature on the droplet surface due to absorption of SO_2 (for 100–1400 ppm) is found to be of the order of $10^{-7}\text{--}10^{-9}$ $^{\circ}\text{C}$, using the equation proposed by Danckwerts (1970) and the heat of absorption of SO_2 in a saturated solution is considered to be 6.7 kcal/mol (Roth, 1935). Such heat effects, however, appeared to be significant in atmospheric absorption process where relatively larger drops (≈ 1000 μm) were moving at terminal settling velocities (Reda and Carmichael, 1982). Further, insignificant evaporation loss of small drops moving at very high velocity ($\approx 20\text{--}30$ m/s) in a tower (of $L=2$ m) may be attributed to negligible exposure time (≈ 0.1 s–0.067 s). Therefore, the heat effects due to mass transfer is considered insignificant and is neglected in the present work.

The droplet surface can represent a resistance to SO_2 especially if the droplet pH is low (≈ 3). Ostensibly, the atmospheric droplets with such lower pH values limit the absorption capacity for SO_2 . The present work, on the contrary, attempts to develop theoretical models using water and dilute alkali for scrubbing of SO_2 in a spray tower wherein the pH of the scrubbing liquid

would be much higher (for instance, 7 to 11) and this phenomenon is entirely different from the reported atmospheric absorption processes so far (Brimblecombe and Spedding, 1972; Liss, 1971). This justifies in ignoring the effect of pH in the present work. Furthermore, the concentration of SO_2 would increase at the droplet surface due to absorption of SO_2 with time and consequently the diffusion fluxes would reduce. This phenomenon has however, been considered in our modeling (see Appendix Eqs. (xv) and (xvi)).

Wall effect and gas phase back mixing are known to have influence over the operation of a spray tower. Wall effect is assumed insignificant in our modeling because the separation of wall flow from the spray region flow does not have any practical significance (Mehta and Sharma, 1970a,b; Schmidt and Stichlmair, 1991). Actual wall flow cannot be properly differentiated from the spray region, because of the splashing of liquid from the wall. On the other hand, gas phase back mixing is reported to be negligibly small under plug flow condition in pilot scale units and it increases with the diameter of the column as in industrial units (Mehta and Sharma, 1970a,b). The gas phase back mixing is, therefore, neglected in our study.

The internal circulation has been analyzed for SO_2 absorption by a single water droplet falling at terminal settling velocity (Chen, 2001a) and it has been elucidated that the impact of internal circulation is comparable to mass diffusion for finer droplets. On the other hand, it has been shown that larger drops ($D_d \geq 500$ μm) are deformed into oblate spheroids, which with increasing size develop a flattened base and subsequently a concave depression (Le Clair, 1972). Therefore, the area over which the tangential stress, exerted by the flowing gaseous stream, acts on the drop becomes rapidly smaller with increasing drop deformation. Thus increased drop deformation results in decreased internal circulation. It has further been illustrated by Chen (2001b) that the internal circulation can be observed significantly for droplets having diameter larger than about 500 μm while investigating the SO_2 absorption in falling rain drops at terminal settling velocity. Furthermore, drops of diameter greater than about 500 μm have a tendency to oscillate and subsequently it has clearly been demonstrated by Pruppacher and Beard (1970) that such oscillation tend to disrupt organized internal circulation. Internal circulation on the other hand, does not play significant role in affecting the drop size. Therefore, drop deformation and internal circulation play roles simultaneously in gas-droplet absorption process especially for larger drops ($D_d \geq 500$ μm) and would not affect the

mass transfer greatly as their effects are compensating in nature to each other. As discussed earlier, our prime interests in this study are to predict the percentage removal of SO_2 through simple model and validation of the predicted values with the available reported data for much smaller droplets (ranging between 40 and 150 μm) moving at very high velocities (≈ 20 – 30 m/s). Under these circumstances, the droplet deformation and droplet internal circulation do not seem to have significant influence on the mass transfer and thus ignoring their effects has been justified.

In Eq. (1), Fo' , the Frossling number, is the mass transfer Fourier number (Crawford, 1980) for the region inside the drop. It represents the internal mass transfer within the drop (i.e., it takes care of the liquid side resistance to mass transfer) while the mass transfer on the surface of the drop from the bulk of the gas phase is represented by the term “ $DRe^{1/2}Sc^{1/3}$ ” (which takes care of the gas side resistance to mass transfer). Therefore, the integrand in Eq. (6) combines both the effects in tandem. Furthermore, in the present work, the droplet size distribution is considered and mass transfer is determined by integrating with respect to the dimensionless time from 0 (zero) to τ . Eq. (6), hence gives the combined effects of droplet hydrodynamics during its stay in the scrubber excepting droplet interactions, for instance, droplet breakup, droplet coalescence and multi-droplet interactions in a cloud (Silverman and Sirignano, 1994).

The values of the physical parameters used in the models are as follows: Diffusivities of SO_2 in air, water and NaOH are calculated to be 1.32×10^{-5} m^2/s , 2.13×10^{-9} m^2/s and 2.58×10^{-9} m^2/s respectively (Chapman and Cowling, 1970; Wilke and Chang, 1955; Vinograd and Mc Bain, 1941). While calculating the diffusivity in NaOH, it is assumed that the ratio of diffusivities required in Eqs. (11) and (12) is independent of temperature and viscosity. The other values used in the model calculation are $H=4.85 \times 10^6$ N/m^2 , $\nu=1.56 \times 10^{-5}$ m^2/s , $R=8314$ $\text{J}/\text{kmol K}$, $\rho_d=1000$ kg/m^3 and $T=305$ K .

3.1. Effect of droplet diameter and droplet velocity

Fig. 1 shows the effect of performance of the system in water scrubbing with drop size at different droplet velocities. The figure exhibits four distinct regimes as discussed below:

3.1.1. Regime — I: $1000 \mu\text{m} \geq D_d \geq 300 \mu\text{m}$

In this regime, the percentage removal is slowly increasing with decreasing droplet diameter for a fixed hydraulic loading (i.e., $Q_L=1.11 \times 10^{-5}$ m^3/s — the study liquid flow rate). The percentage removal is

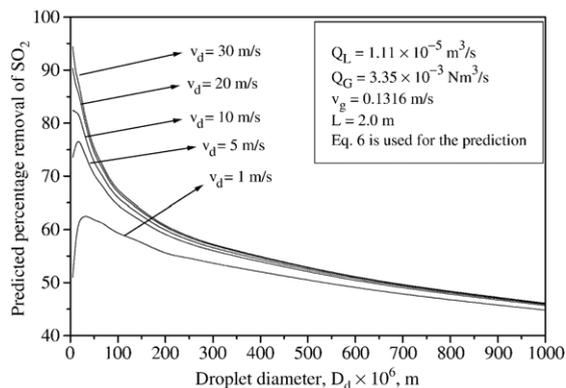


Fig. 1. Effect of droplet diameter on the predicted percentage removal of SO_2 for different droplet velocities.

increased from about 45–46% to about 54–57% in decreasing the droplet diameter from 1000 μm to 300 μm . Increase in droplet velocity has a subtle effect on the percentage removal in this regime. It may be attributed to the fact that the surface area increases at slower rate with the reduction in droplet size that may not be sufficient enough to yield high mass transfer. The increase in mass transfer in reducing the droplet diameter is attributed due to the gradual reduction in the liquid side resistance. This regime is termed here as *droplet lean regime* and is an ineffective gas absorption regime.

3.1.2. Regime — II: $300 \mu\text{m} \geq D_d \geq 30 \mu\text{m}$

In this regime, the increase in percentage removal with the decrease in droplet diameter and with the increase in droplet velocities becomes very rapid. The percentage removal is increased from about 54–57% to about 62–82% in decreasing the droplet diameter from 300 μm to 30 μm . It may be attributed to the fact that very fast increase in surface area with the reduction in droplet size might have reduced the liquid side resistance [effect of Fo'] and also a large number of high velocity droplets might have reduced the gas side resistance [effect of “ $DRe^{1/2}Sc^{1/3}$ ”], thereby drastically reducing the overall resistance in the gas–liquid interface. It could be also due to the dramatic reduction of the characteristic time for diffusion of SO_2 in the liquid phase [$D_{ij}^2/\pi \cdot D'$] (Seinfeld, 1986) with the reduction in droplet diameter that resulted in very fast increase in percentage removal. This regime is termed here as the *dense droplet regime*.

3.1.3. Regime — III: $D_d \leq 30 \mu\text{m}$, $v_d \leq 10$ m/s

In this regime, increase in surface area with a further decrease in droplet diameter is not sufficient to compensate the decrease in mass transfer resistance owing to increasing

rigidity of the droplets resulting in the percentage removal of SO₂ decreases. The mass transfer cannot be increased further on decrease in droplet size for $v_d \leq 10$ m/s. This means that maximum reduction in liquid side resistance has been achieved under this condition. The reduction in gas side resistance is also becoming limited at $v_d = 10$ m/s which, however, can be further reduced in increasing v_d beyond 10 m/s as discussed latter. The overall resistances to mass transfer shifts solely to the continuous gas phase for very small droplets ($D_d \leq 30$ μm), which behave as solid or rigid sphere. It can be further seen from the figure that the onset of droplet rigidity at $v_d = 1.0$ m/s, 5.0 m/s and 10 m/s appear at droplet diameters of 25 μm , 14 μm and 7 μm respectively. Clearly, this demonstrates that besides the droplet diameter, the droplet velocity is a strong function of the droplet rigidity. This regime is termed as the *rigid droplet (sphere) regime*. Studies on the rigid droplet (sphere) have been a subject of significant importance since long back to a legion of researchers (Le Clair et al., 1972; Clift et al., 1978; Dutta et al., 1988). But all of them characterized the rigid droplet (sphere) either in terms of droplet Reynolds number or in terms of dimensionless radius ratio. We have, however, obtained here specific droplet size within the hydro dynamical regime studied for the existence of rigid droplet (sphere) that does not seem to exist in the literature.

3.1.4. Regime — IV: $D_d \leq 30$ μm , $v_d > 10$ m/s

In this regime, the percentage removal of SO₂ is increased to a maximum ($\approx 95\%$ for $v_d = 30$ m/s; as can be seen from the figure) on increasing the droplet velocities. Eq. (6) is dominated by Fo' for droplets to behave as rigid droplet up to a v_d of 10 m/s (ca.); while $[DRe^{1/2}Sc^{1/3}]$ dominates Eq. (6) for overcoming the droplet rigidity at velocities somewhat greater than 10 m/s thereby increasing the mass transfer. This dramatic behavior of the rigid droplets might be due to the reduction in available residual gas-phase resistance as discussed in Regime III earlier, possibly by the shearing off of the gas boundary layer by the high velocity rigid droplets. This regime is termed as the *droplet inertia-controlling regime*.

3.2. Effect of superficial gas velocity and liquid flow rate

The effect of superficial gas velocity on the percentage removal in water scrubbing for different liquid flow rates at a constant droplet velocity is shown in Fig. 2. It may be seen from the figure that at lower liquid flow rates, the percentage removal increases very sharply than at higher liquid flow rates with the decrease

in superficial gas velocity. It is also seen from the figure that the performance of the system remains almost insignificant at lower liquid flow rates and at superficial gas velocities greater than 5 m/s. But, the performance is becoming functional of superficial gas velocity even beyond 5 m/s at higher liquid flow rates and the change in percentage removal of SO₂ is very slow. It may be attributed to the fact that the liquid side resistance is reduced drastically at high superficial gas velocity stemming from the intrinsic behavior of gas-droplet absorption process described by Eq. (6) discussed earlier. The increase in removal efficiency with the increase in liquid flow rate (at a constant droplet diameter) might be due to the increase in droplet loading into the scrubber per Eq. (6). On the other hand, decrease in removal efficiency with the increase in v_g up to about 5 m/s could be attributed to the lowering of the gas phase residence time and to its inverse variation with the square of the gas flow rate per Eq. (6). The effect of v_g and Q_L on the percentage removal of SO₂ also indicates that the percentage removal would increase with the Q_L/Q_G ratio. The theoretical analysis on the effects of v_g and Q_L/Q_G ratio on the percentage removal of SO₂ elucidated in this study support the experimental observations made by Schmidt and Stichlmair (1991).

The dotted line in Fig. 2 shows the percentage removal calculated using Eq. (9) under turbulent condition. It can be seen that at low liquid flow rates, the values calculated by Eqs. (6) and (9) correspond very closely. However, at high liquid flow rate, for example, at 5.13×10^{-4} m³/s, expectedly a noticeable reduction in the percentage removal under turbulent condition is observed up to a superficial gas velocity of approximately 5 m/s. Owing to random turbulent motion of the gas molecules and the liquid droplets

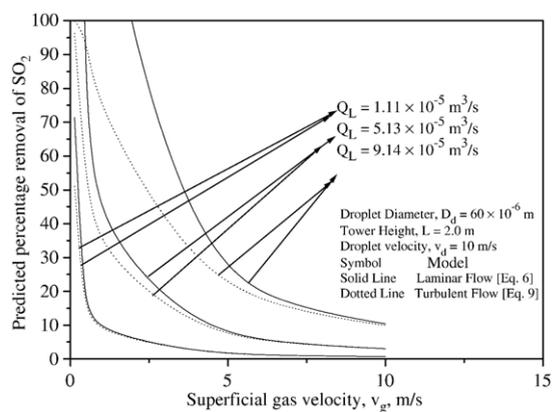


Fig. 2. Effect of superficial gas velocity on the predicted percentage removal of SO₂ for different liquid flow rates.

the probability of removal of SO_2 yields somewhat lower values than that obtainable under laminar flow as discussed while Eq. (9) is derived. It can further be noted from the figure that the removal of SO_2 [laminar model: Eq. (6)] reaches beyond 100% for $Q_L = 5.13 \times 10^{-5} \text{ m}^3/\text{s}$ at v_g of about 0.63 m/s and for $Q_L = 9.14 \times 10^{-5} \text{ m}^3/\text{s}$ at v_g of about 2.5 m/s. While turbulent model under these flow regimes achieves removal of SO_2 to a maximum of 100% due to the exponential nature of Eq. (9). Therefore, the application of these equations [Eqs. (6) and (9)] to a specific gas–liquid system can ascertain the flow behavior that can be further established by experimentation.

3.3. Effect of tower height

The effect of tower height on the percentage removal of SO_2 in water scrubbing for different liquid flow rates ($1.11 \times 10^{-5} \text{ m}^3/\text{s}$ and $1.39 \times 10^{-5} \text{ m}^3/\text{s}$) is shown in Fig. 3. It is seen from the figure that the percentage removal improves with the increase in tower height, which can be attributed to the increased gas–liquid contact time. As expected, it can also be seen from the figure that the increase in the liquid flow rate increased the percentage removal of SO_2 as discussed earlier. The change in percentage removal of SO_2 is significant up to a tower height of about 3 m under the range of variables studied.

3.4. Effect of concentration ratio

In alkaline scrubbing of SO_2 using NaOH solution, the effect of concentration ratio (CR) on the percentage removal of SO_2 for different initial droplet velocities is shown in Fig. 4. Expectedly, it can be seen from the figure that the curves move upward on increasing the

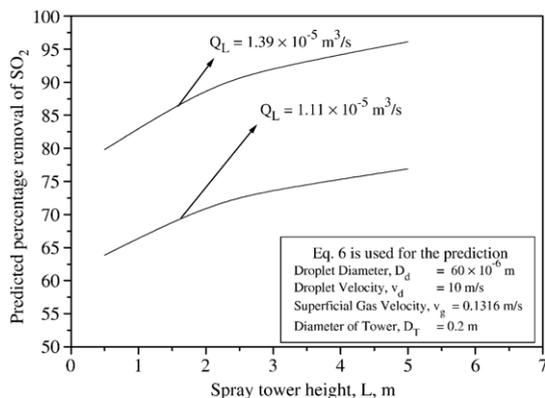


Fig. 3. Effect of spray tower height on the predicted percentage removal of SO_2 for different superficial gas velocities and for constant liquid flow rate.

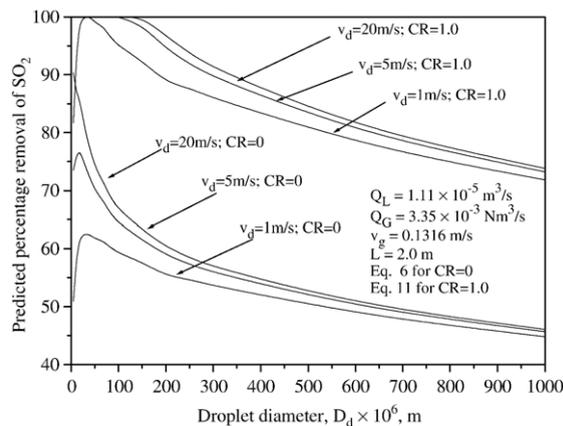


Fig. 4. Effect of droplet diameter and concentration ratio on the predicted percentage removal of SO_2 .

CR from zero (reagent free situation in water scrubbing) to 1.0, i.e., the percentage removal of SO_2 would yield higher values in alkaline scrubbing than in water scrubbing owing to the reduction in liquid side resistance in alkali scrubbing. For example, removal efficiency of about 55% can be achieved for $D_d = 200 \mu\text{m}$, $v_d = 1 \text{ m/s}$ in water scrubbing (CR=0) while the removal efficiency becomes almost 90% in alkaline scrubbing (CR=1.0) under similar operating conditions in the model scrubber. It can also be seen from the figure that the percentage removal of SO_2 of about 86.25% can be obtained in alkaline scrubbing with CR=1.0 for $D_d = 400 \mu\text{m}$, $v_d = 20 \text{ m/s}$ while the same removal efficiency can be achieved in water scrubbing by using $D_d = 30 \mu\text{m}$ and same droplet velocity ($v_d = 20 \text{ m/s}$). Clearly, this indicates that the reduction in droplet diameter can reduce the reagent consumption. Furthermore, the figure also reveals that 95% removal of SO_2 can be achieved for $D_d = 100 \mu\text{m}$, $v_d = 1 \text{ m/s}$ in alkaline scrubbing (CR=1.0) while the removal efficiency would increased to nearly 100% by increasing the v_d up to 5 m/s under other conditions remained unaltered. Clearly, it demonstrates that the increase in droplet velocity can also reduce reagent consumption significantly. The improvement of removal efficiency in alkaline scrubbing demonstrates that the desired performance can be adjusted by manipulating the different operating variables.

4. Experimental verification of the theoretical models

The validation of the models has been performed with the experimental data available in the literature (Bandyopadhyay and Biswas, 2006). The pertinent

variables of experimentation in water scrubbing were $Q_G = 3.35 \times 10^{-3}$ to $5.54 \times 10^{-3} \text{ Nm}^3/\text{s}$; $Q_L = 5.56 \times 10^{-6}$ to $3.11 \times 10^{-5} \text{ m}^3/\text{s}$; $C_\infty = 500$ to 1300 ppm_v ; $L = 2.0 \text{ m}$; $D_T = 0.1905 \text{ m}$ and $T = 305 \pm 1 \text{ K}$. The droplet velocities and droplet diameter were discussed earlier. Reported distinct droplet size distribution and other data enabled using Eq. (7) for the purpose of predicting the removal efficiency in water scrubbing under laminar condition. Predicted values in water scrubbing are compared with the experimental values reported and are presented in Fig. 5. It can be seen from the figure that the laminar model fits the experimental data excellently well up to $Q_L = 1.11 \times 10^{-5} \text{ m}^3/\text{s}$. While turbulent model is in excellent agreement at $Q_L = 1.83 \times 10^{-5} \text{ m}^3/\text{s}$. It is therefore, conceivable that the model predicts the experimental values exactly under the assumptions made during modeling. It also indicates that the effect of internal circulation does not seem to have noticeable influence in such a situation. Furthermore, within this range of liquid flow rate, the effect of droplet break up, droplet coalescence and multi-droplet interactions in a cloud might be mutually nullifying with each other so that droplet interactions did not have noticeable impact on the overall scrubbing, resulting in predicted values agreeing excellently well with the reported experimental data. However, for $Q_L \geq 1.83 \times 10^{-5} \text{ m}^3/\text{s}$, the experimental values were over predicted by the model (turbulent) ($\approx 10\%$). It is evident from the figure that the larger the droplet SMD is the larger was the deviation. It could be possibly due to the fact that droplet interactions that were ignored in our modeling were important for larger droplets in hindering mass transfer.

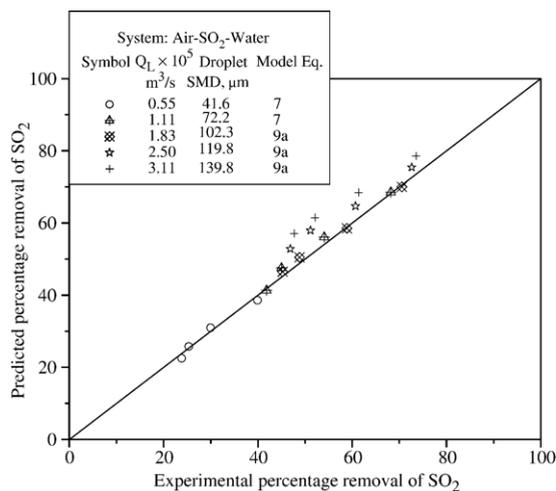


Fig. 5. Comparison of predicted and experimental values of removal of SO_2 in water scrubbing.

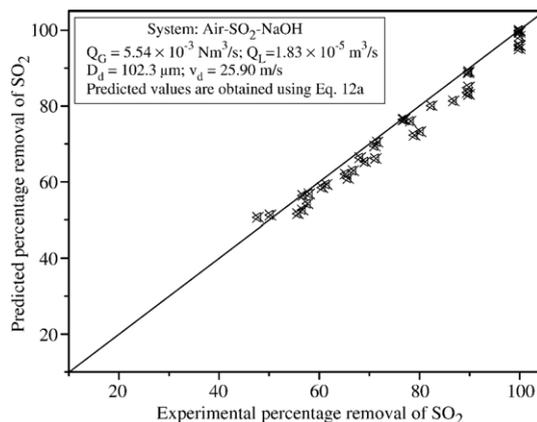


Fig. 6. Comparison of predicted and experimental values of removal of SO_2 in alkali (dilute NaOH) scrubbing.

It may be explained as follows. The effect of the droplet breakup and droplet coalescence are opposite in nature; i.e., droplet breakup enhances the overall mass transfer due to increased surface area while droplet coalescence reduces it owing to reduction in the surface area for mass transfer. The multi-droplet interactions in a cloud would enhance the gas-droplet absorption than that for an isolated droplet in the size range of 40 to 100 μm (Silverman and Sirignano, 1994). Furthermore, it has also been pointed out that this interaction with finer drops ($\approx 40 \mu\text{m}$) has a strong influence than with larger drops ($\approx 100 \mu\text{m}$). From the foregoing critical analysis of our model derived results coupled with these available information in the literature on the effect of droplet interaction on gas-droplet mass transfer it can, therefore, be qualitatively concluded that droplet coalescence over dominates amongst other factors not considered for the development of the model. It can also be seen from the figure that the deviation was increased with the increase in gas flow rate. Besides droplet interactions as discussed earlier, it might be due to the fact that the droplet surface reached the equilibrium concentration of SO_2 rapidly at higher gas flow rate and could not get enough time to diffuse into the bulk of the droplet phase that hindered further absorption of SO_2 into the droplet. Experimental findings thus revealed that there was no noticeable internal circulation otherwise the situation could have been different from what was observed. In contrast, at lower gas flow rate, the absorbed SO_2 might get sufficient time to diffuse into the bulk of the droplet phase and distribute uniformly within the droplet and as a result the mass transfer was greater than what it could be at higher gas flow rate. Thus the experimental findings indicate that internal circulation did not have considerable role within

the range of spray hydrodynamics analyzed under the present context, which supports the observation made by Chen (2001a).

The various experimental parameters reported (Bandyopadhyay and Biswas, 2006) in alkali scrubbing were $Q_L = 1.83 \times 10^{-5} \text{ m}^3/\text{s}$ [satisfying the turbulent condition in the present work]; distinct droplet size distribution with droplet SMD = 102.9 μm , velocity of which was mentioned earlier; $Q_G = 5.54 \times 10^{-3} \text{ Nm}^3/\text{s}$; $C'' = 2 \times 10^{-4}$ to $50 \times 10^{-4} \text{ kmol}/\text{m}^3$; $C_\infty = 1$ to 1318 ppm_v and $T = 305.6 \pm 1 \text{ K}$. Experimental values reported were compared with the predicted values and were presented in Fig. 6. It can be seen from the figure that the predicted values agreed excellently well with the experimental values [$\approx 5\%$ deviation].

5. Conclusions

Simple realistic models were developed in order to describe the gaseous removal process of SO_2 by scrubbing with and without chemical reaction in spray towers. Effects of droplet size, droplet velocity, superficial gas velocity, liquid flow rate and tower height on the performance of such a system were theoretically predicted for distinct drop size. Some striking features were observed while predicting the performance as functions of droplet diameter and velocity in a hypothetical spray tower using the models developed. Four distinct regimes, viz. droplet lean, dense droplet, rigid droplet and droplet inertia controlling regimes, were found important in spray scrubbing processes. Model calculation also elucidated the existence of rigid droplet (sphere) for a distinct droplet size at a specific droplet velocity that does not seem to be available in the literature. Theoretical studies indicated that the rigidity of the droplet was a strong function of the droplet diameter and the droplet velocity. Theoretical considerations further revealed that the spray tower could perform best in the droplet inertia-controlling regime. The effect of turbulence owing to mixing stemming from the random movement of the gas molecules and the droplets was discussed as a part of modeling and it was expressed through an exponential equation analogous to the famous Deutsch Equation. It was pointed out that the turbulent flow model would yield meaningful values of removal efficiencies maximum up to 100% whence laminar flow model yielded values more than 100% removal efficiencies. The flow behavior could be ascertained by applying the equations under conditions of laminar and turbulent flow fields to a specific gas–liquid system, which could be established by experimentation subsequently. The model developed

for water scrubbing indicated that the removal of SO_2 was found independent on the concentration of gas in either of the phases for once-through use of the scrubbing liquid; whereas, it was found to vary with the concentration of gas in both the phases when the scrubbing liquid would be recycled. Apart from the concentration of gas, the removal efficiency was found to be a strong function of spray hydrodynamics, flow rates and dimensions of the spray tower. On the other hand, the model for alkali scrubbing indicated that the removal of SO_2 was dependent on both gas phase concentration and reagent concentration apart from the physico-chemical and hydrodynamic parameters of the system. It was further noted that the removal efficiency would decrease with the increase in the initial gas phase concentration while it would increase with an increase in the initial reagent concentration. When the model-calculated value of the removal efficiency in alkaline scrubbing would exceed 1.0 (i.e., 100% removal efficiency), it was suggested to consider the value as 1.0 since such a situation (i.e., removal efficiency more than 100%) was not meaningful.

Distinct droplet diameters from the array of droplets were used from the droplet size distribution in conjunction with the actual number of droplets present in that array for validating the models with available experimental data. Predicted data agreed reasonably well with the experimental data at lower liquid flow rates with relatively smaller droplet while it over predicted even with the turbulent model at higher liquid flow rates with relatively larger droplet. The deviation between the predicted and the experimental values was reported to be predominantly due to droplet coalescence amongst other factors not considered during modeling. Similar was the trend of deviation at higher gas flow rates for larger droplet SMD and such deviation was reported to be due to the effect of absorbed SO_2 on the droplet surface, besides the droplet interactions mentioned earlier. Comparison of model predicted values with the available experimental data revealed that the internal circulation did not have significant influence on the percentage removal for small droplets having diameter ranging between 40 to 140 μm . On the other hand, the predicted values in alkali scrubbing were in excellent agreement with the experimental values reported in the literature. Finally, the models developed could also be applied to any gas–liquid spray absorption process subject to the assumptions and conditions necessary to describe the specific physico-chemical hydrodynamics of the system. However, it was suggested that further refinement could be made for taking the droplet interactions into account in order to accurately predict the removal efficiency.

A. Derivation of theoretical model for water scrubbing under laminar flow

Let us assume a drop moving through a mixture of air and SO₂. The velocity of the air relative to the drop is v_∞ at a substantial distance from the drop; the concentration of SO₂ is C_∞ at that point. A concentration boundary layer will be formed next to the surface of the drop, across which the concentration will change from essentially C_∞ to C_v at the surface of the drop and C_t is the concentration of SO₂ within the drop at any time and at any radial direction. The mass transfer rate is at maximum when the droplet is initially formed, i.e., they are in the vicinity of the nozzle. It decreases during down flow and, therefore, is a function of time it is exposed to the gas phase, which suggests that the efficiency of the drop would also vary with time. Analysis of the boundary layer, considering a cubic polynomial for the concentration profile, leads to the following expression for the concentration field

$$(C_t - C_v) = (C_\infty - C_v) \left[\frac{3}{2} \frac{y}{\delta_c} - \frac{1}{2} \left(\frac{y}{\delta_c} \right)^3 \right] \quad (\text{i})$$

The boundary layer thickness for axisymmetric bodies can be given as (Kays, 1966),

$$\delta = \frac{5.02v^{1/2}}{R_1 U_\infty^3} \left[\int_0^x U_\infty^5 R_1^2 dx \right]^{1/2} \quad (\text{ii})$$

with the following conditions assuming potential flow,

$$U_\infty = \frac{3}{2} v_\infty \sin\theta; \quad R_1 = \frac{D_{dj}}{2} \sin\theta; \quad x = \frac{D_{dj}}{2} \theta \quad (\text{iii})$$

The instantaneous mass flux can be expressed as

$$\frac{m}{A} = \frac{3D}{2\beta\delta} (C_\infty - C_v) [\text{where } \delta_c = \beta\delta] \quad (\text{iv})$$

The mass transfer across an area element of spherical droplet is given by :

$$dm = \frac{3\pi D D_{dj}^2}{4\beta\delta} \sin\theta \, d\theta (C_\infty - C_v) \quad (\text{v})$$

where, D_{dj} is the characteristic diameter of the j th droplet size range.

Eq. (v) on integration over the entire hemisphere of the droplet ($\theta: 0 \rightarrow \pi/2$) and on rearrangement under the above hydrodynamic condition, we obtain

$$m = 1.783 \frac{D_{dj}^2 D}{\beta} (C_\infty - C_v) \left(\frac{v_\infty}{v D_{dj}} \right)^{1/2} \quad (\text{vi})$$

A mass balance about the control volume located within the concentration boundary layer around the drop, gives the mass transfer rate m as:

$$m = C_\infty \int_0^{\delta_c} 2\pi \frac{D_{dj}}{2} u dy - \int_0^{\delta_c} C' 2\pi \frac{D_{dj}}{2} u dy \quad (\text{vii})$$

Integration of the above equation and substitution of m from Eq. (vi) yields,

$$\beta = 1.088 (Sc)^{-1/3} \quad (\text{viii})$$

Substituting the value of β from Eq. (viii) into (vi) gives,

$$m = 1.64 D_{dj}^2 D (C_\infty - C_v) Sc^{1/3} \left(\frac{v_\infty}{v D_{dj}} \right)^{1/2} \quad (\text{ix})$$

The mass transfer coefficient, k , is given as:

$$k = \frac{m}{\pi D_{dj}^2 (C_\infty - C_v)} \quad (\text{x})$$

Combining Eqs. (ix) and (x) gives

$$Sh = 0.522 Sc^{1/3} (v_\infty D_{dj}/v)^{1/2} = 0.522 Sc^{1/3} Re^{1/2} \quad (\text{xi})$$

The constant in Eq. (xi) takes into account only the mass transfer from the front half of the drop. An empirical correlation for the overall mass transfer to a sphere is considered (Geankoplis, 1972) here for taking the mass transfer into the rear half of the drop with wake effects into account in the present model as given below

$$Sh = 2 + 0.522 Sc^{1/3} Re^{0.53} \quad (\text{xii})$$

A comparison between Eqs. (xi) and (xii), considering the difference in exponents on the Reynolds number, suggests that a coefficient of 0.75 would be more appropriate for Eq. (xi) to represent the overall mass transfer from the entire surface of the drop. Therefore, Eq. (xi) may be rewritten as

$$Sh = 0.75 Sc^{1/3} Re^{1/2} \quad (\text{xiii})$$

Using the modified coefficient of Eq. (xiii), Eq. (ix) becomes,

$$m = 2.36 D_{dj}^2 D (C_\infty - C_v) Sc^{1/3} \left(\frac{v_\infty}{v D_{dj}} \right)^{1/2} = 2.36 D_{dj}^2 D (C_\infty - C_v) Sc^{1/3} Re^{1/2} \quad (\text{xiv})$$

In Eq. (xiv), C_v is time dependent and it should be expressed as a function of time for finding the

efficiency. When the drop is first introduced into the gas flow, its content of SO₂ is uniformly distributed. As the scrubbing process proceeds, SO₂ is absorbed into the drop, and its concentration becomes higher at the surface than that at points inside the drop. This effect hinders the absorption rate of SO₂.

The absorption rate of SO₂ can also be obtained from the concentration distribution within the drop as a function of radial position and the time, under the boundary conditions prevailing at the surface of the drop. Hence the mass flux is given by

$$\frac{m}{A} = D' \frac{\delta C_t'}{\delta r} \Big|_{(r=\frac{D_{dj}}{2})} \quad (xv)$$

Accordingly the boundary condition can be expressed as:

$$\frac{\delta C_t'}{\delta r} \left(\frac{D_{dj}}{2}, t \right) = 0.75 \frac{D}{D'} Sc^{1/3} \left(\frac{v_\infty}{v D_{dj}} \right)^{1/2} \quad (xvi)$$

$$\left[C_\infty - \frac{HM_w}{RT \rho_d} C_t' \left(\frac{D_{dj}}{2}, t \right) \right]$$

A simpler and sufficiently accurate solution can be obtained if the concentrations at the interface of the drop are assumed to reach equilibrium immediately. The solution is then slightly adjusted to allow for the mass transfer rate into the drop as given by Eq. (xiv). The general solution under unsteady state condition is then given by

$$C_t'(r, t) = C_s' + \frac{D_{dj}}{\pi} (C_s' - C_t') \frac{1}{r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{2\pi nr}{D_{dj}} \exp \left(- \frac{4\pi^2 n^2 D t}{D_{dj}^2} \right) \quad (xvii)$$

In the above equation the factor (1/r) in the 2nd term of the right hand side has been correctly derived as this factor is shown as (1/2) in the model presented by Beg et al. (1991) [see their Eq. (27)].

Henry's law can correlate the two concentrations as,

$$C_v = \frac{HM_w}{RT \rho_d} C_s' \quad (xviii)$$

Eq. (xvii) on differentiation yields.

$$\frac{\delta C_t'}{\delta r} \Big|_{(r=\frac{D_{dj}}{2})} = \frac{4}{D_{dj}} (C_s' - C_t') \sum_{n=1}^{\infty} \exp \left(- \frac{4\pi^2 n^2 D t}{D_{dj}^2} \right) \quad (xix)$$

Substitution of Eq. (xv) into Eq. (xviii) yields,

$$m = 12.566 D_{dj} D' (C_s' - C_t') \sum_{n=1}^{\infty} \exp \left(- \frac{4\pi^2 n^2 D t}{D_{dj}^2} \right) \quad (xx)$$

Solving Eqs. (xiv) and (xx) simultaneously we obtain

$$2.36 D_{dj} D (C_\infty - C_v) Sc^{1/3} Re^{1/2} = 12.566 D_{dj} D' (C_s' - C_t') \sum_{n=1}^{\infty} \exp \left(- \frac{4\pi^2 n^2 D t}{D_{dj}^2} \right)$$

or

$$D Sc^{1/3} Re^{1/2} (C_v - C_\infty) = 5.32 D' \left(C' - \frac{RT \rho_d}{HM_w} C_v \right) \sum_{n=1}^{\infty} \exp \left(- \frac{4\pi^2 n^2 D t}{D_{dj}^2} \right)$$

putting C_v from Eq. (xviii) we get

$$C_v \left(D Sc^{1/3} Re^{1/2} + \frac{RT \rho_d}{HM_w} D' 5.32 \sum_{n=1}^{\infty} \exp \left(- \frac{4\pi^2 n^2 D t}{D_{dj}^2} \right) \right) = C_\infty \left(D Sc^{1/3} Re^{1/2} + \frac{C'}{C_\infty} D' 5.32 \sum_{n=1}^{\infty} \exp \left(- \frac{4\pi^2 n^2 D t}{D_{dj}^2} \right) \right)$$

$$\text{or, } \frac{C_v}{C_\infty} = \frac{D Re^{1/2} Sc^{1/3} + \frac{C'}{C_\infty} D' \phi(Fo')}{D Re^{1/2} Sc^{1/3} + \frac{RT \rho_d}{HM_w} D' \phi(Fo')} \quad (xxi)$$

$$\text{where, } \phi(Fo') = 5.32 \sum_{n=1}^{\infty} \exp \left(- \frac{4\pi^2 n^2 D t}{D_{dj}^2} \right) \quad (xxia)$$

Substitution of the (C_v/C_∞) from Eq. (xxi) into Eq. (i), leads to Eq. (1) for the rate of mass transfer of SO₂ into the drop under the assumptions considered. Eq. (1) derived in the present mathematical model should not have any concentration term outside the integral of the right hand side, which however, is not the case of Eq. (33) as derived by Beg et al. (1991). This has been correctly derived in our modeling.

References

- Bandyopadhyay A. Some studies on the abatement of particulate laden sulphur dioxide pollution. 1996. PhD Thesis. Indian Institute of Technology, Kharagpur, India.
- Bandyopadhyay A, Biswas MN. Prediction of the removal efficiency of a novel two-stage hybrid scrubber for flue gas desulfurization. Chem Eng Technol 2006;29:130–45.
- Beg SA, Rehman SO, Hassan MH. Theoretical analysis of gas stripping performance of spray towers. Chem Eng Technol 1991;14:347–52.

- Biswas MN. Atomization in two-phase critical flow. Proc. of the 2nd Int. Conf. on Liquid Atomization and Spray Systems-II, Madison, 5-1, Wisconsin, USA; 1982. p. 145–51.
- Brady JD. Flue gas scrubbing process for sulfur dioxide and particulate emission preceding CO₂ absorption. Environ Prog 1987;6:9–12.
- Brimblecombe P, Spedding DJ. Rate of solution of gaseous sulphur dioxide at atmospheric concentrations. Nature 1972;236:225.
- Bürkholz A. Droplet separation. VCH Verlagsgesellschaft, Weinheim (Federal Republic of Germany) and VCH Publishers, New York, USA, 1989.
- Chapman S, Cowling TG. The mathematical theory of non-uniform gases. 3rd ed. UK: Cambridge University Press; 1970. Chapters 10 and 11.
- Chen WH. Unsteady absorption of sulfur dioxide by an atmospheric water droplet with internal circulation. Atmos Environ 2001a;35:2375–93.
- Chen WH. Dynamics of sulfur dioxide absorption in a raindrop falling at terminal velocity. Atmos Environ 2001b;35:4777–90.
- Clift R, Grace JR, Weber ME. Bubbles, drops and particles. New York: Academic Press; 1978. p. 98–125.
- Crawford M. Air pollution control theory. New Delhi, India: Tata McGraw Hill Book Company Ltd.; 1980. p. 463–78. Chapter - 11.
- Danckwerts PV. Gas-liquid reactions. NY, USA: McGraw Hill Book Company; 1970. p. 54–5.
- Dutta BK, Middya U, Ray P. Mass transfer with instantaneous chemical reaction in a rigid drop. AIChE J 1988;34:694–7.
- Epstein M, Sybert L, Wang SC, Levio CC, Princiotta FT. Limestone test results at the EPA alkali wet scrubbing test facility at the TVA Shawnee Power Plant. AIChE Symp Ser 1975;71:256–71.
- Geankoplis CJ. Mass transfer phenomena. New York, USA: Holt, Rinehart and Winston, Inc.; 1972. p. 291.
- Hay S, Porretta F, Wiggins B. Design and start-up of acid plant tail gas scrubber. New South Wales, Australia. 2004. Available at www.hatch.ca/non_ferrous/articles/design_startup.pdf; accessed on 16.02.2007.
- Hikita H, Asai S, Tsuji T. Absorption of sulfur dioxide into aqueous sodium hydroxide and sodium sulfite solutions. AIChE J 1977;23:538–44.
- Hixson AW, Scott CE. Absorption of gases in spray towers. Ind Eng Chem 1935;27:307–14.
- Johnstone HF, Williams GC. Absorption of gases by liquid droplets: design of simple spray scrubbers. Ind Eng Chem 1939;31:993–1001.
- Kays WM. Convective heat and mass transfer. New York, USA: McGraw Hill Book Company; 1966. p. 92.
- Kohl AL, Reisenfeld FC. Gas purification. Houston, Texas, USA: Gulf Publishing Company; 1985. p. 299–419. Chapter-7.
- Le Clair BP, Hamielec AE, Pruppacher HR, Hall WD. A theoretical and experimental study of the internal circulation in water drops falling at terminal velocity in air. J Atmos Sci 1972;29:728–40.
- Liss PS. Exchange of SO₂ between the atmosphere and natural waters. Nature 1971;233:327–9.
- Lynn S, Straatemeier JR, Kramers H. Absorption studies in the light of penetration theory — I. Long wetted-wall columns. Chem Eng Sci 1955;4:49–57.
- Mehta KC, Sharma MM. Mass transfer in spray columns. Br Chem Eng 1970a;15:1440–4.
- ibid. Mass transfer in spray columns. Br Chem Eng 1970b;15:1556–8.
- Pruppacher HR, Beard KV. A wind tunnel investigation of the internal circulation and shape of water drops falling at terminal settling velocity in air. Q J R Meteorol Soc 1970;96:247–56.
- Reda M, Carmichael GR. Non-isothermal effects of SO₂ absorption by water droplets — I. Model development. Atmos Environ 1982;16:145–50.
- Roth A. Z Phys Chem 1935; A173, 313; in Lynn, S, Straatemeier, JR, Kramers, H, Absorption studies in the light of penetration theory — I. Long wetted-wall columns. Chem Engng Sci 1955; 4, 49–57.
- Schmidt B, Stichlmair J. Two-phase flow and mass transfer in scrubbers. Chem Eng Technol 1991;14:162–6.
- Seinfeld JH. Atmospheric chemistry and physics. New York: John Wiley and Sons; 1986. p. 263.
- Silverman I, Sirignano WA. Multi-droplet interaction effects in dense sprays. Int J Multiph Flow 1994;20:96–116.
- Tomany JP. Air pollution: the emissions, the regulations and the standards. New York, USA: American Elsevier Publishing Co., Inc.; 1975.
- Vinograd JR, Mc Bain JW. Diffusion of electrolytes and of the ions in their mixtures. J Am Chem Soc 1941;63:2008–15.
- Wilke CB, Chang P. Correlation of diffusion coefficients in dilute solutions. AIChE J 1955;1:264–70.