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S. R. Dantuluri[a]; W. T. Davis[a]; R. M. Counce[b]; G. D. Reed[a]
[a] Civil Engineering Department, The University of Tennessee, Knoxville, TN [b] Chemical Engineering Department, The University of Tennessee, Knoxville, TN

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MATHEMATICAL MODEL OF SULFUR DIOXIDE ABSORPTION INTO A CALCIUM HYDROXIDE SLURRY IN A SPRAY DRYER

S. R. Dantuluri*
W. T. Davis*
R. M. Counce**
G. D. Reed*
Civil Engineering Department*
Chemical Engineering Department**
The University of Tennessee
Knoxville, TN 37996

ABSTRACT

This paper reports on the development of a comprehensive model to simulate the absorption of gaseous SO_2 into a calcium hydroxide slurry in a spray dryer flue gas desulfurization system. In this study, the model was modified to incorporate the input of surface area of the calcium hydroxide particles. Previous studies assumed spherical particles. A sensitivity analysis was then conducted to determine the sensitivity of the model to surface area at particle size of 2, 3, 4, and 6 micrometers.

INTRODUCTION

Since its first application to the control of flue gas emissions in 1978, the spray dryer has become an increasingly acceptable component of flue gas desulfurization systems on both utility and industrial coal-fired boilers. More recently, the spray dryer has been applied to the control of acid gases emitted from incineration systems. In all of these applications the spray dryer was followed by a fabric filter collector or an electrostatic precipitator to remove the final dried reaction products and flyash emitted from the combustion system. The acid gases, including sulfur dioxide, and hydrogen chloride, are removed by absorption into an atomized $Ca(OH)_2$ slurry in the spray dryer. After absorption into the atomized droplets, the gases react with dissolved $Ca(OH)_2$ in the slurry producing a precipitated reaction product, thus reducing the concentration of the gases and the dissolved $Ca(OH)_2$ in the slurry. This maintains the driving force for additional absorption of the gases into the droplet and simultaneous dissolution of the $Ca(OH)_2$ from the solid particles of $Ca(OH)_2$ which are suspended in the slurry. The removal occurs primarily in the constant rate drying period where a continuous liquid phase exists within the atomized slurry droplet. In dilute slurries, the removal of the gas continues until all of the $Ca(OH)_2$ is reacted. In slurries with higher $Ca(OH)_2$ concentrations, typical of flue gas desulfurization systems, the constant rate drying period proceeds until evaporation has reduced the liquid volume to the point where $Ca(OH)_2$ sorbent particles touch and the diffusion paths for reactants become restricted.

This paper reports on refinement of a comprehensive model for the constant rate period which involves the simultaneous evaporation of the droplet, absorption of SO_2 into the droplet, dissolution of the $Ca(OH)_2$ from the suspended particles in the droplet, and the reaction of SO_2 with the $Ca(OH)_2$. The original mathematical model developed by Damle (1) was referred to as SPRAYMOD. Partridge (2) later modified SPRAYMOD by incorporating an overall flux equation (Ramachandran and Sharma, 1969) (3) into the mathematical model which included the SO_2 absorption flux, and the $Ca(OH)_2$ dissolution flux. A comparison of the modified model referred to as the University of Tennessee Spray Dryer Model (1) (UTSDM1) to spray dryer data was made by Partridge et al (4) in which it was shown that the predicted SO_2 removal efficiencies were, on the average, slightly less than values observed in pilot plant studies. The underprediction was assumed to be partially attributed to the fact that the model was limited to the constant rate drying period.

Both the original model developed by Damle (1) and the modifications made by Partridge (2) assumed that the $Ca(OH)_2$ particles were perfect spheres of diameter, d_p, whose surface area was determined by the simple calculation, $a_p = \pi d_p^2$. This paper reports on the modifications of the above model to incorporate the input of the surface area of the $Ca(OH)_2$ particles into the above model based on experimental measurements which showed that the suface area a_p was significantly greater than that predicted by assuming perfect spheres. This latest version of the model is described herein. In addition, a sensitivity analysis is presented to show the potential importance of producing $Ca(OH)_2$ particles with high surface area.

THEORETICAL DESCRIPTION OF UTSDM1

The SO_2 absorption flux model utilized in UTSDM1 was reported earlier (4) and is summarized as follows. The absorption of SO_2 gas into a liquid slurry containing elementary $Ca(OH)_2$ particles involves a three-phase gas absorption system which has been described by using film models.(6) The elementary processes involved in the gas absorption system are diffusion of solute gas, dissolution of the elementary Ca(OH)2 particles and chemical reaction. (7)

The absorption of SO2 into aqueous calcium hydroxide slurries is accompanied by the liquid-phase reaction of the dissolved SO2 with dissolved Ca(OH)2:

$$SO_2(g) \rightarrow SO_2(\ell) \tag{1}$$

$$SO_2(\ell) + Ca(OH)_2(\ell) \rightarrow CaSO_3 \cdot \tfrac{1}{2} H_2O(\ell) + \tfrac{1}{2} H_2O(\ell). \tag{2}$$

This reaction is assumed to be instantaneous (Babu et al, 1984).(8) The disappearance of Ca(OH)2 in the liquid phase is related to the disappearance of SO2 from the gas phase,

$$d(LC_B)/dt = G\, d(P_A/P)/dt \tag{3}$$

where components A and B are SO2 and Ca(OH)2, respectively. The volumetric liquid rate is related to the product of the drop production rate and the volume per drop,

$$L = \phi V_D. \tag{4}$$

Substitution of equation 4 into equation 3 and rearrangement yields

$$\frac{d(V_D C_B)}{dt} = \left(\frac{G}{P\phi}\right)\frac{dP_A}{dt}. \tag{5}$$

Both the disappearance of Ca(OH)2 and SO2 may be related to the absorption flux R_A by

$$\frac{d(V_D C_B)}{dt} = \left(\frac{G}{P\phi}\right)\frac{dP_A}{dt} = R_A a_D, \tag{6}$$

where the area of the slurry droplet has been assumed to be that of a spherical droplet as follows:

$$a_D = \pi d_D^2. \tag{7}$$

Manipulating the gas-phase portion of equation 6 yields

$$\left(\frac{G}{P\phi}\right) dP_A = R_A a_D dt \tag{8}$$

which may be integrated over time as

$$\frac{G}{P\phi}\int_{P_{A_2}}^{P_{A_1}} \frac{dP_A}{R_A a_p} = \int_0^t dt \tag{9}$$

The model shown here is based on the film theory and is illustrated in Figure 1. The film thicknesses for the gas-phase, liquid-phase and the region adjacent to the solid $Ca(OH)_2$ particles are δ_g, δ_ℓ and δ_s, respectively.

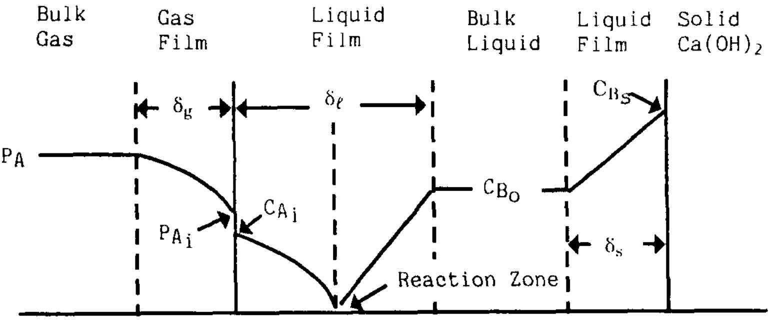

Figure 1. Constant Rate Period Film Model for UTSDM1.

The absorption flux of SO_2 may be represented by

$$R_A = k_{A_g}(P_A - P_{A_i}) \tag{10}$$

and

$$R_A = E k_{A_\ell} C_{A_i} \tag{11}$$

where the enhancement factor E is defined as

$$E = 1 + \frac{D_B C_{B_o}}{D_A C_{A_i}} \tag{12}$$

A Henry's constant may be used to relate the interfacial partial pressure and the concentration of SO_2. (9,10)

$$H_A = P_{A_i} / C_{A_i} \tag{13}$$

The solubility of $Ca(OH)_2$ is quite low and the capacity for physical SO_2 absorption is quite small so the absorption of SO_2 can be related to the dissolution of $Ca(OH)_2$,

$$R_A a_D = R_B a_p \tag{14}$$

Here, the total particulate area per droplet (a_p) is related to the number of particles per droplet (n_p) and the average $Ca(OH)_2$ particle diameter (d_p). For the modeling described here, the bulk-liquid concentration, C_{B_o}, of $Ca(OH)_2$ is assumed to be uniform and the dissolution flux of each particle is assumed to be equal. Assuming spherical $Ca(OH)_2$ particles,

$$a_p = n_p \pi d_p^2 . \tag{15}$$

The dissolution flux of $Ca(OH)_2$ may be related to its saturation concentration by

$$R_B = k_s (C_{B_s} - C_{B_o}) \tag{16}$$

Equations 10 through 16 may be combined into an overall flux equation (Ramachandran and Sharma, 1969) (3)

$$R_A = \frac{P_A / H_A + \beta C_{B_s}}{\dfrac{1}{k_{A_g} H_A} + \dfrac{1}{k_{A_\ell}} + \dfrac{\beta a_D}{k_s a_p}} \tag{17}$$

where

$$\beta = D_{B_\ell} / D_{A_\ell} .$$

The above equation 17 has certain constraints. It is only valid for the condition in which negligible dissolution of $Ca(OH)_2$ occurs in the liquid mass transfer film. The following criterion must be met:

$$\frac{k_s a_p D_A^2}{4 k_{A_\ell} D_B V_D} << 1 . \tag{18}$$

Based on equation 10, the maximum SO_2 absorption flux, R'_A is

$$R'_A = k_{A_g} P_A . \tag{19}$$

From equation 16, the maximum Ca(OH)$_2$ dissolution flux is

$$R'_B = k_s C_{B_s} . \tag{20}$$

If the absorption flux, R_A, as calculated from the overall equation 17, is greater than the maximum SO$_2$ absorption gas phase flux, R'_A, i.e.

$$R_A > R'_A \tag{21}$$

then R_A is limited to the dissolution flux:

$$R_A = R'_A . \tag{22}$$

Similarly, if the absorption flux calculated from equation 17 is greater than the dissolution flux, i.e.

$$R_A > R'_B a_p / a_D \tag{23}$$

then R_A is limited to the dissolution flux:

$$R_A = R'_B a_p / a_D . \tag{24}$$

The mass-transfer coefficients are the next focus of attention. The gas phase mass transfer coefficient is calculated as follows. At conditions in the spray dryer the gas-phase Sherwood number (d_D/δ_g) is approximately 2, (Ranz and Marshall, 1952) (12) so

$$\delta_g = d_D/2 \tag{25}$$

and therefore

$$k_{A_g} = \frac{D_{A_g}}{\delta_g RT} = \frac{2 D_{A_g}}{d_D RT} . \tag{26}$$

The liquid phase mass transfer coefficient is calculated using film theory as:

$$k_{A_\ell} = D_{A_\ell} / \delta_\ell \tag{27}$$

The thickness of the liquid film was determined as follows. The geometry of the slurry droplet system was used to set the upper bound for the thickness of the liquid film. The slurry droplet is visualized as consisting of sorbent particles spaced uniformly in the liquid phase. The liquid phase volume is equally distributed around the particle and the film thickness can not exceed one-half of the interparticle distance. The expression of film thickness (equal to one-half the interparticle distance) is as follows:

$$\delta_\ell \leq \tfrac{1}{2}\, IPD = 0.5\, d_p \left| \frac{1}{(1 - W^{\frac{1}{3}}} - 1 \right| \tag{28}$$

where W is the volume fraction occupied by the liquid. The film thickness is calculated using Equation 28 with the following additional boundary condition. As the slurry concentration decreases, the volume fraction occupied by the moisture increased and the film thickness increases. The upper boundary condition of the film thickness is approached as the slurry concentration decreases to that of a pure liquid stagnant drop. The boundary condition defined for this case has been reported by Al-Aswad (1985) (11) and is given by the following equation:

$$k_{A_\ell} = \frac{4\pi^2 D_{A_\ell}}{3d_p}. \tag{29}$$

Solving Equation 27 and 29 for the film thickness (δ_ℓ), the boundary condition for the case of a pure liquid stagnant drop is obtained:

$$\delta_s = 0.076 d_p. \tag{30}$$

The dissolution film thickness was also calculated for a Sherwood number of 2 (no internal motion around the calcium hydroxide particles) such that

$$\delta_s = \frac{d_p}{Sh} = \frac{d_p}{2}. \tag{31}$$

It was also subject to a similar constraint as the liquid-phase film thickness:

$$\delta_s \leq \tfrac{1}{2}\, IPD. \tag{32}$$

The dissolution mass-transfer coefficient is then calculated as

$$k_s = D_{B_\ell} / \delta_s. \tag{33}$$

The model presented in this paper is based on the assumption that the major portion of SO_2 absorption occurs in the constant rate period. The time for this period, t_{CR} may be estimated from an equation by Ranz and Marshall, (1952). (12) Now turning back to equation 9, numerical integration is required with the only unknown being the outlet SO_2 partial pressure P_{A_2}:

$$\frac{G}{P\phi}\int_{P_{A_2}}^{P_{A_1}} \frac{dP_A}{R_A a_D} = t_{CR}. \qquad (34)$$

DEVELOPMENT OF UTSDM2

As shown in the above equations, the diameter and surface area of the $Ca(OH)_2$ particles are both required inputs. The physical diameter is required in Equation 28 to determine the interparticle distance, whereas the surface area of the particles is needed in the overall flux Equation 17. In the original SPRAYMOD and the modified UTSDM1, the spherical diameter was used to calculate both. The modification to UTSDM1, referred to herein as UTSDM2 continues to use the measured diameter of the $Ca(OH)_2$ particles to determine the interparticle distance. However the surface area was added as an actual input to the model. In effect, this modification allows for the potential that the surface area and the particle diameter may not be related as was assumed in Equation 15. This is the case for many porous materials.

The above assumption, requiring the additional input of surface area, can be justified based on experimental observations. Dantuluri (5) has reported on the measurement of the surface area of 3.4 micrometer (Mass mean diameter) $Ca(OH)_2$ particles. The surface area was found to be 22.6 m^2/g whereas the surface area determined by equation 15, assuming spherical particles, was calculated to be only 0.79 m^2/g, a factor of 28 times less than the measured value.

SENSITIVITY ANALYSIS OF UTSDM2

In an effort to determine the relative importance of the above modification to the model, a sensitivity analysis was conducted to determine the effect of the surface area on the sulfur dioxide removal efficiency in the constant rate drying period. To provide a basis for comparison, a series of calculations was made to predict the sulfur dioxide removal efficiency as a function of the stoichiometric ratio of $Ca(OH)_2$ injected into the spray dryer. The stoichiometric ratio is defined as the moles of $Ca(OH)_2$ injected into the spray dryer in the atomized slurry divided by the moles theoretically required to remove all of the SO_2. A stoichiometric ratio of 1.0 would theoretically remove 100% of the SO_2. The input conditions utilized for the predictions were typical of those used for spray dryer applications on coal fired boilers. Table 1 summarizes the input values used in these comparisons. The reader is referred to previously published articles for a more detailed discussion of these input parameters. (1,2)

Table 1. Input parameters used in the model.

Parameter	Value
Inlet Gas Conditions	
Inlet Gas Temperature (TI)	300°F
% Water in Inlet Gas (WI)	6%
Inlet SO_2 Concentration (SI)	2000 ppm
Molecular Weight of Dry Inlet Gas (MG)	29.4
Operating Conditions	
Approach to Saturation (AT)	20°F
Stoichiometric Molar Ratio (SR)	1.0
Residence Time of Gas Phase (RT)	17s
Droplet Conditions	
Inlet Droplet Diameter (d_D)	80 μm
Inlet Droplet Temperature (TW)	95°F
$Ca(OH)_2$ Particle Diameter (d_p)	2, 3, 4, 6 μm
Molecular Weight of Sorbent (MS)	74.1
Density of Solid Sorbent (SG)	2.24 g/cm^3
Critical Moisture Content (XC)	29.2%

Figure 2 is a graph of the SO_2 removal efficiency versus stoichiometric ratio of $Ca(OH)_2$ as predicted by UTSDM2. In this graph, the surface area was assumed to be that of the spherical particles. At this condition UTSDM1 and UTSDM2 effectively yield the same results. For the four cases of $Ca(OH)_2$ particle diameter, d_p, of 6, 4, 3, and 2 micrometers, the spherical surface areas were determined to be 0.45, 0.67, 0.89, and 1.34 m^2/g, respectively. Focusing on a stoichiometric ratio of 1.0, the SO_2 removal efficiency ranged from only 35.3% for the 6 micrometer particles up to 67.0% for the 2 micrometer particles indicating that the predicted effect of particle size is significant. For all particle sizes, the SO_2 removal efficiency became less sensitive to stoichiometric ratio (SR) as the SR was increased, particularly above SR = 1.0.

In order to determine the effect of surface area within UTSDM2, additional calculations were made at a SR = 1.0 in which the particle size and surface area were input. Calculations were made

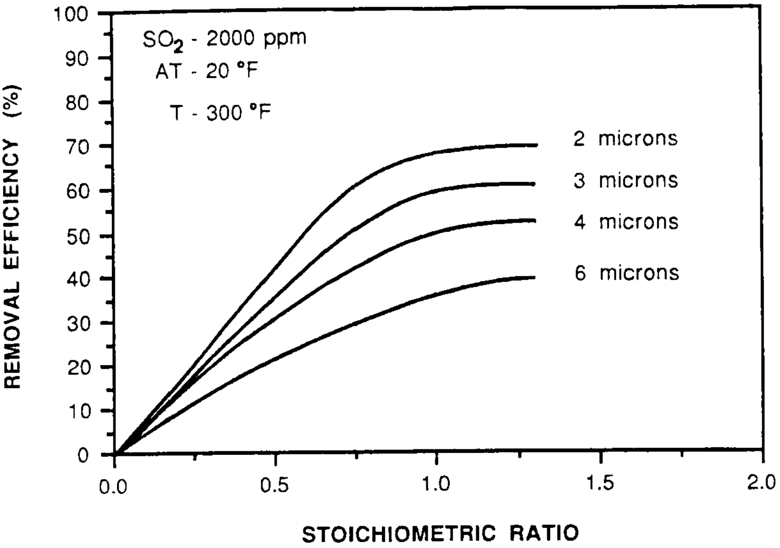

Figure 2. Removal Efficiency versus Stoichiometric ratio as a function of Particle Diameter.

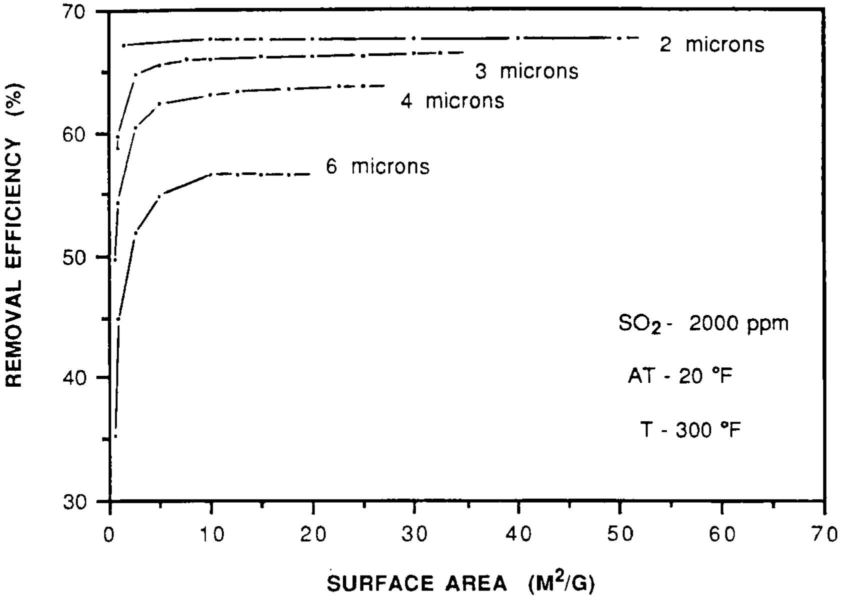

Figure 3. Removal Efficiency versus Surface Area for different particle sizes.

for particle sizes of 2, 3, 4, and 6 micrometers and for independent surface areas for each size ranging from a low value (equivalent to the spherical surface area) to a value of 40 m^2/g which was considered to be a reasonable upper limit for calculation purposes. The results are shown in Figure 3. For the case of 6 micrometers the SO_2 removal efficiency was predicted to increase rapidly as the surface area was increased up to a surface area of 10 m^2/g. Beyond 10 m^2/g, however, the efficiency tended to be limited to 56.6% efficiency. As the particle size was decreased, which improved the dissolution rate of the particles into the slurry, the predicted effect of enhanced surface area became less significant. For the 2 micrometer particles, the efficiency was predicted to be 67% for spherical particles and was increased to only 67.5% at surface area of 40 m^2/g.

SUMMARY

A comprehensive model, UTSDM2, has been developed to allow the input of both $Ca(OH)_2$ particle size and surface area for the prediction of SO_2 removal efficiencies in a spray dryer. The predictions made by this model, as shown in Figures 2 and 3 suggest that both the particle size and surface area of the particles may be important for particles greater than 3 micrometers. Field observations have shown that improper slaking of CaO has resulted in particles whose diameters were significantly greater than 3 micrometers and in reduced SO_2 removal efficiencies. These observations tend to support the general trends predicted by the model, although quantitative analyses have not yet been conducted. Further, the model results suggest that if particles of less than 3 micrometers diameter could be produced, that the surface area of the particles would not be as significant of a consideration as the actual particle size.

The revised model should be of value to those researchers currently investigating the effects of different slaking techniques and $CaO/Ca(OH)_2$ production techniques on the enhancement of the SO_2 removal efficiencies within spray dryer FGD systems. Additional experimental studies are being conducted to experimentally confirm the trends suggested by the model.

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NOMENCLATURE

A = SO_2
a_D = *surface area of droplet, m^2*
a_p = surface area of solid $Ca(OH)_2$ per droplet, m^2

B = $Ca(OH)_2$
C_j = liquid-phase concentration of component j, kgmol/m^3
C_{ji} liquid-phase concentration of component j at gas-liquid interface, kgmol/m^3
C_{jo} = liquid-phase concentration of component j in bulk liquid, kgmol/m^3
C_{js} = liquid-phase concentration of component j at liquid-solid interface, kgmol/m^3
d_D = diameter of droplet, m
d_p = diameter of $Ca(OH)_2$ particles, m
D_ℓ = liquid-phase diffusion coefficient for component j, m^2/s
D_{jg} = gas-phase diffusion coefficient for component j, m^2/s
E = enhancement factor-factor by which absorption flux is increased by reaction, dimensionless
g = gas
G = molar gas flow rate, kgmol/s
H_j = Henry's constant for component j, m^3atm/kgmol
i = interface
IPD = inter particle distance, m
k_{jg} = gas-phase mass-transfer coefficient, kgmol/m^2-s-atm
$k_{j\ell}$ = liquid-phase mass-transfer coefficient, m/s
k_s = liquid-phase dissolution mass-transfer coefficient, m/s
ℓ = liquid
L = volumetric liquid flowrate, m^3/s
n_p = number of $Ca(OH)_2$ particles per droplet
o = bulk phase
P = total pressure, atm
Pj = partial pressure of component j, atm
Pji = partial pressure of component j at gas-liquid interface, atm
Rj = absorption flux of component j, kgmol/m^2-s
R'j = maximum absorption flux of component j, kgmol/m^2-s
Sh = Sherwood number, dimensionless
t = time, s
VD = drop volume, m^3

Greek Letters

β = ratio of the liquid phase diffusively of Ca(OH)2 to that of SO_2, dimensionless
ϕ = droplet production rate, s^{-1}
ι = time, s
ιCR = time of constant-rate period, s
δ_g = gas-phase mass-transfer film thickness, m
δ_ℓ = liquid-phase mass-transfer film thickness at gas-liquid interface, m
δ_s = liquid-phase mass-transfer film thickness at liquid-solid interface, m