

Research Article

Mathematical Modeling of Wet Magnesia Flue Gas Desulphurization Process

M. K. Mondal

Department of Chemical Engineering and Technology, Institute of Technology, Banaras Hindu University, Varanasi 221005, Uttar Pradesh, India

Correspondence should be addressed to M. K. Mondal, mkmondal@bhu.ac.in

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Desulphurization of flue gases from various chemical industries in a techno-econo-enviro manner is a demanding technology. The concentrations of sulphur dioxide in and around these plants overshoot the danger point. In recent years, the process analysis of chemical absorption in a slurry has become important in rational design and development of wet scrubbing processes for the removal of SO₂ from flue gases. The elementary steps encountered in wet scrubbing by slurries are diffusion and reaction of gaseous species and solid dissolution in liquid film. In the present work, the process of the absorption of sulphur dioxide into wet magnesia slurry was theoretically analyzed according to the two-reaction plane model incorporating the solid dissolution promoted by the reactions with absorbed sulphur dioxide in the liquid film. A model based on Fick's second law has been developed to calculate enhancement factor for absorption of Sulphur dioxide into Mg(OH)₂ slurry. The concentration of accumulated species in the bulk of the liquid phase (sulphite ions for this case) which substantially control the absorption rates was included in the model for the prediction of theoretical enhancement factor. The values of theoretical enhancement factors obtained from model were compared with experimental enhancement factors available in literature. The model values of enhancement factors agreed well with the values of experimental enhancement factor available in literature.

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1. INTRODUCTION

It has long been known that besides being a hazard to human health, emission of sulphur dioxide contributes to the acidification of soil and waterways. Sulphur dioxide has also been reported to support the reactions which create ozone depletion in the stratosphere. Many countries have therefore adapted strict regulations regarding SO₂ emissions from coal and oil fired boilers which are one of the primary sources of SO₂ emissions. Many different methods are available in the market for reducing the emissions of SO₂ from coal and oil fired boilers [1]. The dominating flue gas desulphurization (FGD) technology is based on wet scrubbing specially slurry scrubbing [2].

Slurry reactions have a widespread application in chemical and biochemical industries [3]. The gas absorption with chemical reaction in a slurry containing fine particles has become important in the development of processes for the removal of acidic pollutants. At present, most wet scrubbing

processes for the removal of SO₂ are by lime and limestone slurry. The major disadvantage of lime/limestone slurry processes is the problem of disposal of calcium sulphate sludge. Wet magnesia FGD system can eliminate scrubber sludge disposal problem and also provide saleable byproduct. In India, most of the sulphur is imported, and hence this process will be very useful to meet the sulphur need in the country.

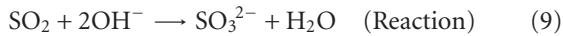
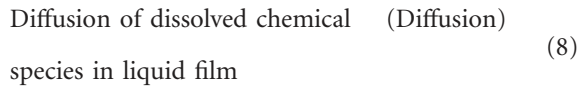
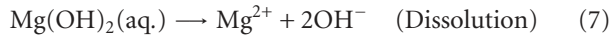
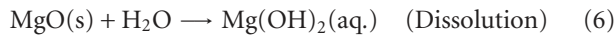
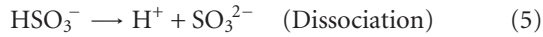
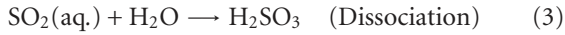
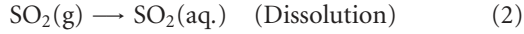
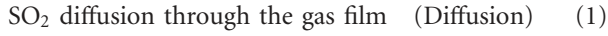
Several models available for absorption of SO₂ are based on lime/limestone slurry [4, 5]. Some models are also available in literature regarding the absorption of SO₂ in sea water [6, 7]. A little work has been done on the modeling of wet magnesia FGD slurry. This paper focuses the model for wet magnesia FGD slurry process in terms of the two-reaction-plane model incorporating the solid dissolution promoted by the reactions with SO₂ in the liquid film. The objective of this work has been to develop a model of the absorption of SO₂ into wet magnesia slurry using an unsteady state mass transfer theory (i.e., Fick's second law)

and to use the model to quantify the enhancement of the absorption rate of SO_2 into a slurry containing small reactive $\text{Mg}(\text{OH})_2$ particles.

2. MODEL DESCRIPTION

2.1. Model of absorption through reaction planes

Regarding the SO_2 absorption mechanism into wet magnesia slurry, the following processes can be considered [8]:



Initially, SO_2 gas diffuses from bulk of the gas phase to the gas-liquid film, dissolves into the bulk liquid and dissociates. Simultaneously, solid MgO also dissolves and dissociates. After that, the sulphite and hydroxyl ions react with each other in the liquid film according to (9)–(11). The principal chemical species of the reaction are subjected to acid dissociation; it is necessary to consider the pH of the absorbent liquid, which largely influences the degree of dissociation.

2.2. Basic equations

In the process of SO_2 absorption in magnesia slurry with no suspended particles, HSO_3^- cannot coexist with OH^- , so that reaction (9) never takes place directly. The above condition shows that reactions (10) and (11) take place at two different located planes in the two-reaction-plane model. However, in the slurry process, to be considered here, both dissolve SO_2 and the HSO_3^- , to be produced by reaction (10), can react with OH^- which is fed by the dissolution of the solid particles in the liquid film. So in this case, dissolved SO_2 can be consumed by reactions (9) and (10) simultaneously. The concentration of SO_3^{2-} in the bulk liquid increases as the absorption proceeds. For a saturated solution of magnesia, a plausible sketch of the concentration profile is given in Figure 1(a). When the particles are suspended in the liquid film, the concentration profiles shift as shown in Figure 1(b) [9].

The model considers the presence of 4 basic species: SO_2 , OH^- , SO_3^{2-} , and HSO_3^- . The basic equations were derived to form the mass balance of perspective chemical species as shown below. The first terms of (12)–(15) deal with the diffusion of the species according to Fick's second law, while the second term shows the consumption due to their reaction with $\text{Mg}(\text{OH})_2$ within the liquid film. The subscripts A, B, E, F in the equations, respectively, indicate the chemical species SO_2 , OH^- , SO_3^{2-} and HSO_3^- .

Liquid film—Region I: it holds that

$$D_A \cdot \frac{d^2}{dz^2} C_A - \frac{K_s \cdot [1 + 2 \cdot ((C_A \cdot D_A)/C_{B_s} \cdot D_B)] \cdot A_p \cdot C_{B_s}}{2} = 0, \quad (12)$$

$$D_F \cdot \frac{d^2}{dz^2} C_F - K_s \cdot \left(1 + \frac{C_F \cdot D_F}{C_{B_s} \cdot D_B}\right) \cdot A_p \cdot C_{B_s} = 0. \quad (13)$$

Liquid film—Region II: it holds that

$$D_E \frac{d^2}{dz^2} C_E - K_s \cdot \left(1 + \frac{C_F \cdot D_F}{C_{B_s} \cdot D_B}\right) \cdot A_p \cdot C_{B_s} = 0, \quad (14)$$

$$D_F \cdot \frac{d^2}{dz^2} C_F - K_s \cdot \left(1 + \frac{C_F \cdot D_F}{C_{B_s} \cdot D_B}\right) \cdot A_p \cdot C_{B_s} = 0.$$

Liquid film—Region III: it holds that

$$D_B \cdot \frac{d^2}{dz^2} C_B + K_s \cdot A_p \cdot (C_{B_s} - C_B) = 0, \quad (15)$$

$$D_E \cdot \frac{d^2}{dz^2} C_E = 0. \quad (16)$$

The boundary conditions imposed are as follows:

$$\text{at } z = 0, \quad C_A = C_{A_i} \frac{d}{dz} C_F = 0,$$

$$\text{at } z = z_1, \quad C_A = C_E = 0, \quad C_F = C_F^*,$$

$$-D_F \cdot \frac{d}{dz} C_F = D_E \cdot \frac{d}{dz} C_E$$

$$-D_F \cdot \frac{d}{dz} C_F|_{z=z_1^-} + D_F \cdot \frac{d}{dz} C_F|_{z=z_1^+} = 2 \cdot D_E \cdot \frac{d}{dz} C_E|_{z=z_1^+}$$

$$\text{at } z = z_2, \quad C_B = C_F = 0, \quad C_E = C_E^*,$$

$$D_B \cdot \frac{d}{dz} C_B = -D_F \cdot \frac{d}{dz} C_F$$

$$= D_E \cdot \frac{d}{dz} C_E|_{z=z_2^-} - D_E \cdot \frac{d}{dz} C_E|_{z=z_2^+},$$

$$\text{at } z = z_L, \quad C_B = C_{B_s}, \quad C_E = C_{E0} = 0.$$

(17)

Here, C_E^* and C_F^* represent the concentrations of E at z_2 and F at z_1 , respectively.

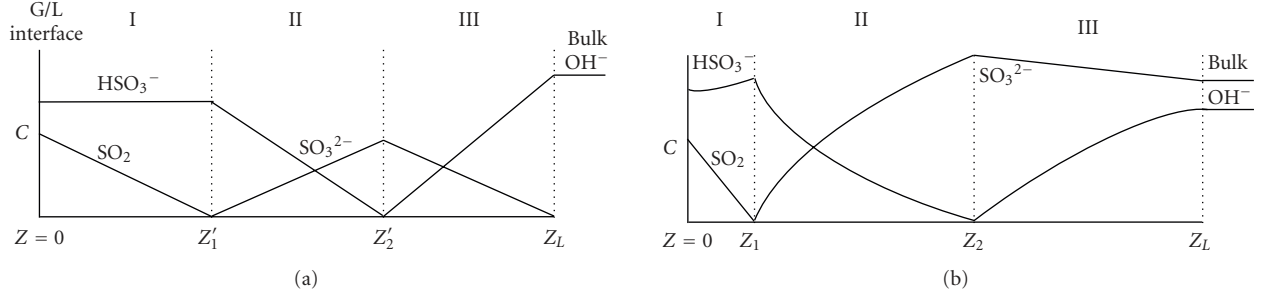


FIGURE 1: Concentration profile for $\text{SO}_2/\text{Mg}(\text{OH})_2$ slurry: (a) no suspended solids, (b) in the presence of suspended solids.

The mass balance equations in the dimensionless form reduce to the following.

Region I:

$$\frac{d^2}{dx^2} Y_A - N \cdot Y_A = \frac{N}{2 \cdot r_A \cdot q_A}, \quad (18)$$

$$\frac{d^2}{dx^2} Y_F - N \cdot Y_F = \frac{N}{r_F}, \quad (19)$$

Region II:

$$\frac{d^2}{dx^2} Y_E - \frac{N \cdot r_F}{r_E} \cdot Y_E = \frac{-N}{r_E}, \quad (20)$$

$$\frac{d^2}{dx^2} Y_F - N \cdot Y_F = \frac{N}{r_F}, \quad (21)$$

Region III:

$$\begin{aligned} \frac{d^2}{dx^2} Y_B - N \cdot Y_B &= -N, \\ \frac{d^2}{dx^2} Y_E &= 0 \end{aligned} \quad (22)$$

subject to

$$x = 0; \quad Y_A = 1, \quad \frac{dY_F}{dx} = 0,$$

$$x = x_1; \quad Y_A = Y_E = 0, \quad Y_F = Y_F^*,$$

$$-r_A \cdot q_A \cdot \frac{d}{dx} Y_A = r_E \cdot \frac{d}{dx} Y_E,$$

$$\begin{aligned} -r_F \cdot \frac{d}{dx} Y_F|_{(x=x_1^-)} + r_F \cdot \frac{d}{dx} Y_F|_{(x=x_1^+)} \\ = 2 \cdot r_E \cdot \frac{d}{dx} Y_E|_{(x=x_1^+)}, \end{aligned} \quad (23)$$

$$x = x_2; \quad Y_B = Y_F = 0, \quad Y_E = Y_E^*,$$

$$\begin{aligned} \frac{d}{dx} Y_B &= -r_F \cdot \frac{d}{dx} Y_F \\ &= r_E \cdot \frac{d}{dx} Y_E|_{(x=x_2^-)} - r_E \cdot \frac{d}{dx} Y_E|_{(x=x_2^+)}, \end{aligned}$$

$$x = 1; \quad Y_B = 1, \quad Y_E = 0.$$

When the concentration of gaseous species is extremely low and the enhancement factor for the solid dissolution can be regarded as unity, (18)–(21) are simplified as follows:

Region I:

$$\frac{d^2}{dx^2} Y_A = \frac{N}{2 \cdot r_A \cdot q_A}, \quad (24)$$

$$\frac{d^2}{dx^2} Y_F = \frac{N}{r_F}. \quad (25)$$

Region II:

$$\frac{d^2}{dx^2} Y_E = \frac{N}{r_E}, \quad (26)$$

$$\frac{d^2}{dx^2} Y_F = \frac{N}{r_F}, \quad (27)$$

Equations (24)–(27), (22) give the enhancement factor as

$$E = \frac{N \cdot x_1}{4 \cdot r_A \cdot q_A} + \frac{1}{x_1}. \quad (28)$$

E_0 represents the enhancement factor for a clear solution saturated with $\text{Mg}(\text{OH})_2$ and is defined by

$$E_0 = 1 + \frac{1}{2 \cdot r_A \cdot q_A}. \quad (29)$$

The dimensionless positions of two reaction planes, x_1 and x_2 , can be determined by the following equations [10]:

$$\begin{aligned} \left(\frac{x_2}{2} - \frac{x_1}{4} \right) \cdot N \frac{r_A q_A}{x_1} + \frac{1 - x_2}{1 - x_1} \\ \cdot \left[\frac{\sqrt{N}}{\tanh[\sqrt{N} \cdot (1 - x_2)]} + \frac{N \cdot (x_2 - x_1)}{2} \right] = 0, \\ \left(\frac{3}{2} \cdot x_1 - x_2 \right) \cdot N + \frac{2x_2 - x_1 - 1}{1 - x_2} \\ \cdot \left[\frac{r_A \cdot q_A}{x_1} - \left(\frac{x_2}{2} - \frac{x_1}{4} \right) \cdot N \right] = 0. \end{aligned} \quad (30)$$

3. RESULT AND DISCUSSION

3.1. Model parameter estimation

In order to have the numerical results of the above model regarding enhancement factor, it is necessary to know the

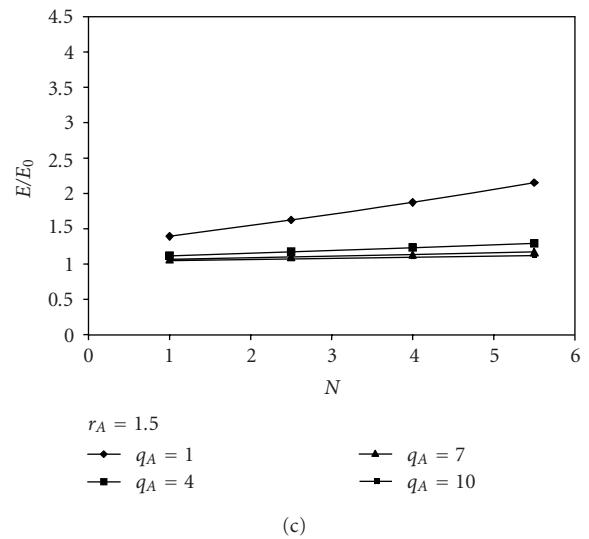
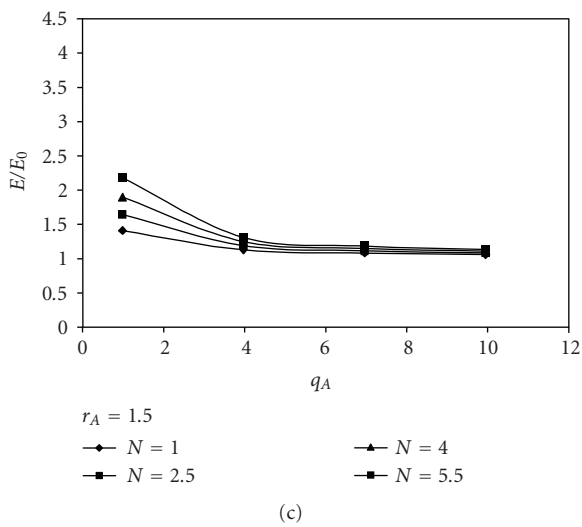
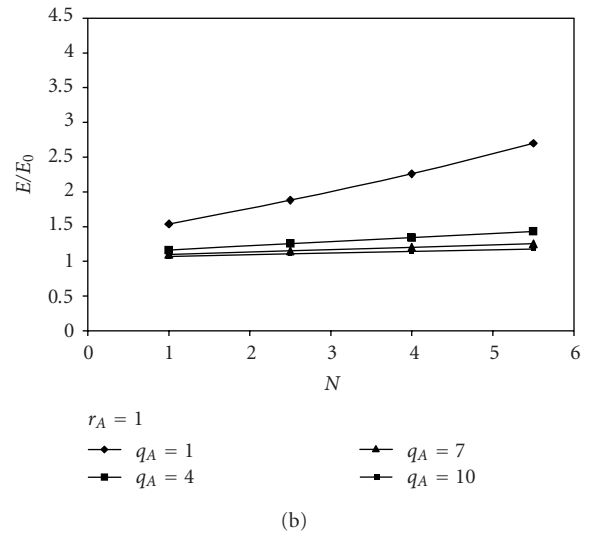
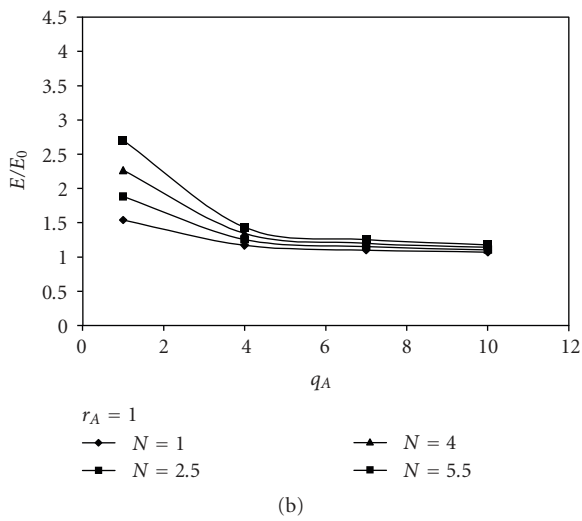
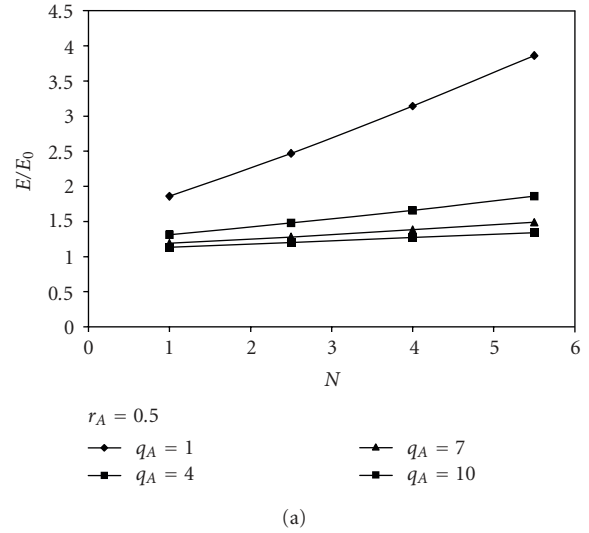
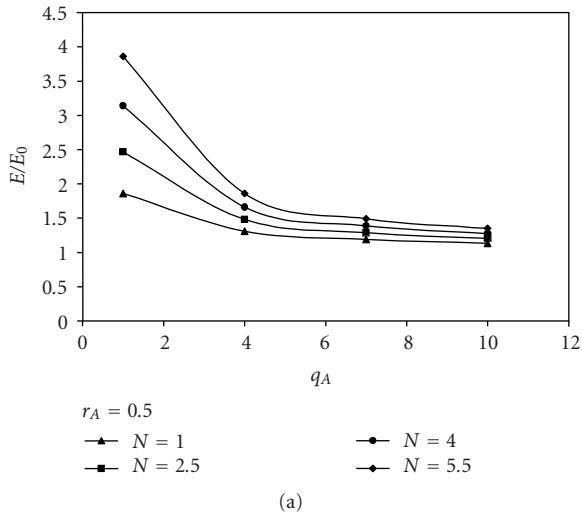


FIGURE 2: Enhancement factors as a function of q_A for the SO_2 - $\text{Mg}(\text{OH})_2$ slurry system. Enhancement factors as a function of q_A for the SO_2 - $\text{Mg}(\text{OH})_2$ slurry system. Enhancement factors as a function of q_A for the SO_2 - $\text{Mg}(\text{OH})_2$ slurry system.

FIGURE 3: Enhancement factors as a function of N for the SO_2 - $\text{Mg}(\text{OH})_2$ slurry system. Enhancement factors as a function of N for the SO_2 - $\text{Mg}(\text{OH})_2$ slurry system. Enhancement factors as a function of N for the SO_2 - $\text{Mg}(\text{OH})_2$ slurry system.

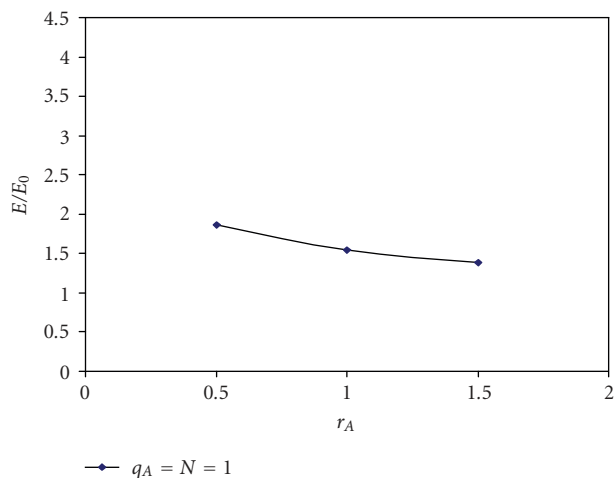


FIGURE 4: Enhancement factor as a function of r_A for SO_2 – $\text{Mg}(\text{OH})_2$ slurry system.

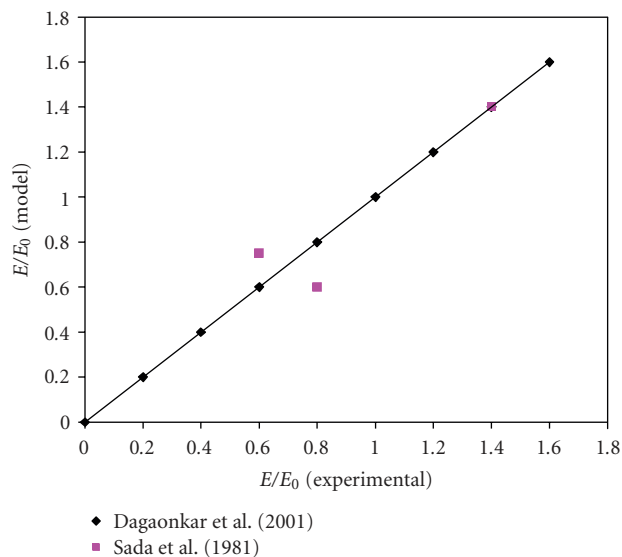


FIGURE 5: Comparison between experimental values available in literature and model values of the enhancement factor for the SO_2 – $\text{Mg}(\text{OH})_2$ slurry system.

values of the dimensionless parameters r_A , q_A , and N . The values of r_A , q_A , and N have been considered as same as the experimental data by various workers available in the literature. To show the contribution of the presence of the solids to the absorption rate, the ratio of enhancement factor into the slurry to that into saturated solution (E/E_0) is plotted against q_A in Figures 2(a)–2(c). The ratio E/E_0 represents the degree of enhancement owing to the presence of solid particles in the slurry. The parameter regarding the solid dissolution, N , is fixed (1.0–5.5), and the parameter r_A regarding the ratio of diffusivity of SO_2 to that of liquid is also fixed (0.5–1.5). From the figures, it is observed that E/E_0 initially decreases with the increase in q_A , and then it is almost independent of q_A . It indicates that when C_{A_i} is

kept constant, the enhancement in gas absorption rate due to the presence of the suspended reactant particles is almost independent of the gas-phase concentration. The influences in gas-phase concentration and N improve the absorption characteristics.

To show the effect of solid dissolution (N) on absorption rate, the ratio of enhancement factor (E/E_0) is plotted against N (see Figures 3(a)–3(c)) for constant value of r_A . It is seen from the figures that the difference of the enhancement factors is very small with the variation of q_A from 4 to 10, and E/E_0 is almost independent on N .

For the contribution of r_A on absorption rate, a plot is drawn between E/E_0 versus r_A by considering both q_A and N to be the same as shown in Figure 4. In this case, the diffusivity of SO_2 in the slurry was assumed to be the same as that of the pure water, and the concentration of SO_2 at the gas-liquid interface was assumed to be equal to the solubility of the hydroxide in the water. Under these circumstances, Figure 4 shows that E/E_0 decreases as r_A increases.

3.2. Model verification

Figure 5 shows the comparison between the experimental values available in literature [3, 11] and the values (obtained from model) of enhancement factor owing to the presence of solid particles for magnesium hydroxide in the slurry. It is evident that the experimental values available in literature and the model values are in good agreement.

4. CONCLUSION

In spite of noticeable progress in conventional flue gas desulphurization (FGD) process development, claims for more efficient, more economic, and nonpollutant technological innovations become more and more important. The new technology essentially is the wet magnesia FGD process which is technically and economically competitive with once-through FGD process. In this article, a model based on Fick's Second law has been developed for dynamic absorption rate of sulphur dioxide into $\text{Mg}(\text{OH})_2$ slurry with the help of two reaction planes.

Numerical solutions for the absorption of SO_2 in aqueous slurries of $\text{Mg}(\text{OH})_2$ are presented in Figures 2–5. The dissolution of fine solid $\text{Mg}(\text{OH})_2$ particles has significant effect on enhancement factor which contributes to the absorption rate of SO_2 from bulk of the gas phase to the liquid. It is efficient to understand that the reaction of SO_2 with accumulated species SO_3^{2-} promotes the absorption rate. The theoretical enhancement factors obtained from present model were compared well with experimental data available in literature. The model presented can be applied to any highly complicated reactive absorption processes. It should be stressed that analytical approximations are often oversimplified and cannot be expected to predict the absorption rates for a wide range of conditions.

LIST OF SYMBOLS

A_p : Surface area of solid particles = $6 \cdot w/\rho \cdot d_p \text{ m}^2/\text{m}^3$ dispersion
 C : Concentration in liquid phase (kmol/m^3)
 D : Diffusivity in liquid phase, m^2/s
 d_p : Average diameter of the solid particles, m
 E : Enhancement factor
 k_s : Mass transfer coefficient for solid dissolution, m/s
 N : Solid dissolution parameter = $k_s \cdot A_p \cdot (Z_L)^2/D_B$.
 q_A : C_{Ai}/C_{Bs}
 r_1 : (D_I/D_B) ($I = A, B, E$ and F)
 x : Dimensionless distance from gas-liquid interface = Z/Z_L
 x_1 : Z_1/Z_L
 x_2 : Z_2/Z_L
 Y : Concentration in the liquid phase relative to that at the gas-liquid interface or at the solid surface
 z_1, z_1 : Position of one reaction plane as shown in Figure 1(m)
 z_2, z_2 : Position of another reaction plane as shown in Figure 1, m
 z_L : Thickness of the liquid film (gas absorption), m

GREEK SYMBOLS

ρ : Analysis of variance

SUBSCRIPTS

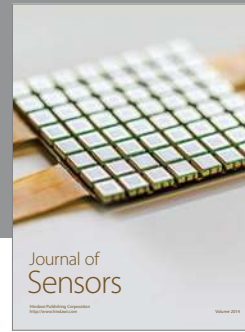
A: SO_2
 B: OH^-
 E: SO_3^{2-}
 F: HSO_3^-
 I: At the gas-liquid interface
 S: At the surface of solid particle
 0: In the bulk of the liquid

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