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Gas absorption into aqueous reactive slurries of calcium and magnesium hydroxide in a multiphase reactor

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Abstract

Investigation of absorption of SO_2 into aqueous slurries of fine and reactive hydroxide particle of calcium and magnesium was carried out in a stirred vessel at 298 K at realistically high mass transfer coefficients. Enhancement in the rate of gas absorption was measured at different solid loadings and speed of agitation. The absorption process is theoretically analyzed using two different models. For the SO_2–$Ca(OH)_2$ system, a single reaction plane model was used and for the SO_2–$Mg(OH)_2$ system, a two reaction plane model incorporating the solids dissolution promoted by the reactions with the absorbed SO_2 in the liquid film was employed. A correct procedure was adopted to estimate the contribution of the suspended particles in the enhancement of gas absorption. Theoretical enhancement factors thus obtained compared well with the experimental data. The extra enhancement observed for the SO_2–$Mg(OH)_2$ system could be explained from the reaction between SO_2 and the dissolved $[SO_3]^{2-}$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Reactive solids; Enhancement; Solid dissolution; Calcium hydroxide; Magnesium hydroxide; Sulfur dioxide

1. Introduction

The problem of gas absorption with reaction in a slurry containing fine particles has become important in the development of processes for the removal of acidic pollutants. $Mg(OH)_2$ as suspended solids may yield a high scrubbing capacity as a result of the presence of the more soluble reaction product magnesium sulfite, relative to the corresponding calcium salt [2]. The present work focuses on the enhancement of the absorption rate of a gas into a slurry of small reactive particles. The elementary processes involved in chemical absorption into the slurry are (i) diffusion of the solute gas in the film, (ii) chemical reaction, and (iii) dissolution of solid. Applying the so-called film theory for mass transfer, the chemical absorption and the solids dissolution are transfer processes either in series or in parallel, depending upon whether the suspended particles size is significantly smaller or larger than the thickness of the liquid film (film model, film thickness $= D/k_L$). The solids dissolution in the liquid film enhances the absorption rate and further the rate of solute dissolution is enhanced by the reaction between the dissolved gas and the dissolved solid in the liquid film when the particle size is significantly smaller than the film thickness. As a result, the rate of gas absorption is affected by the solid dissolution rate as well as the chemical reaction rate. The hydroxide particles being reactive, help to increase the rate of absorption of SO_2 in the slurry. Previous authors [1–5] have measured the enhancement factor at a speed range of 80–250 rpm which gives a very low mass

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Nomenclature

a	G/L interfacial area (m^2/(m^3 liquid))
$A_p = 6w/\rho d_p$	surface area of solid particle (m^2/(m^3 dispersion))
A^*	concentration of A at the gas–liquid interface (kmol/m^3)
C	concentration in the liquid phase (kmol/m^3)
d_p	particle diameter (m)
D	diffusivity in the liquid phase (m^2/s)
k_L	liquid side mass transfer coefficient (m/s)
k_s	solid side mass transfer coefficient (m/s)
m	$\sqrt{k_s A_p / D_B}$
N	solid dissolution parameter
p	partial pressure of the solute gas (Pa)
q_A	C_{Ai}/C_{Bs}
r_A	D_A/D_B
w	amount of solids (kmol/(m^3 slurry))
$x_1 = z_1/z_L$	dimensionless position of the first reaction plane
Y	dimensionless concentration in liquid phase relative to that at gas–liquid interface or at solid surface
z_1	position of the first reaction plane as shown in Fig. 5b (m)

Greek symbols

δ	film thickness (m)
λ	reaction plane for SO_2–$Ca(OH)_2$ system (m)
ν	overall reaction stoichiometry
ρ	density of solid particle (kg/m^3)

Subscripts

A	component A [SO_2]
B	component B [$OH]^-$
E	component E [$SO_3]^{2-}$
F	component F [$HSO_3]^-$
i	value at gas–liquid interface
s	at the surface of the solid particle
0	value in the absence of suspended particles ($N = 0$)

Superscripts

0	value at time $t = 0$
∞	value at time $t = \infty$

transfer coefficient (2–4×10^{-5} m/s) which is much lower than applied in industrial practice. The purpose of the present work is to present the absorption data for the removal of SO_2 by micro-sized reactive particles of calcium and magnesium hydroxide at stirring speeds of 3–15 rps ($Re > 10^5$) and to check whether the experimentally observed enhancement factors can be described by a suitable model.

2. Experimental

The experiments were carried out in a thermostatted reactor (0.105 m diameter, 1.8 l capacity) made of glass and stainless steel as shown in Fig. 1. A six-bladed turbine stirrer was located centrally in the liquid at a height above the reactor bottom equal to half the reactor diameter. Four symmetrically mounted glass baffles increased the effectiveness of stirring and prevented the formation of a vortex. The pressure and temperature transducers together with valves 1 and 2 were connected to an Olivetti M240 computer, thus enabling automatic data collection and programmed

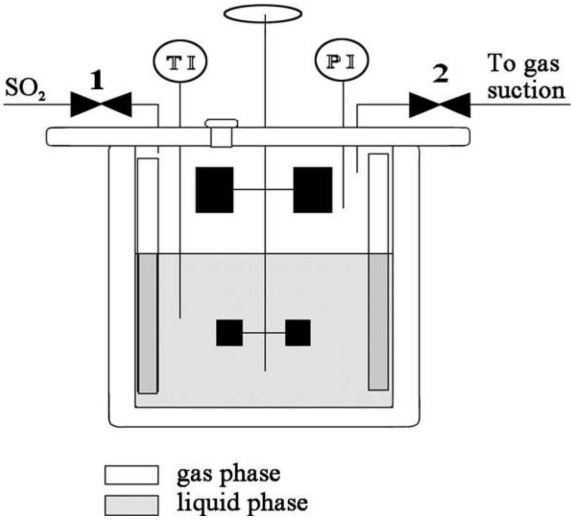

Fig. 1. Stirred cell.

reactor operation. After filling the reactor with the desired slurry, the liquid was degassed by closing valve 1 and opening valve 2. Once the slurry was equilibrated under the vapor pressure of water, N_2O was fed to the reactor up to a fixed pressure (0.08 MPa). Then, the stirrer was started and the decrease of pressure due to the physical absorption of N_2O was recorded over time. These data were used to estimate the solubility of the gas and the liquid side mass transfer coefficient.

After the physical absorption experiments, the chemical absorption of pure SO_2 into aqueous slurries of $Ca(OH)_2$ and $Mg(OH)_2$ was carried out. All the experiments carried out were batchwise, both with respect to gas phase and the slurry solution. The volume of the slurry loaded in the reactor was always kept at $1 \times 10^{-3}\,m^3$ and the slurry concentration was varied from 0 to 20 wt.%. The reactive particles of $Ca(OH)_2$ and $Mg(OH)_2$ of size 4.35 and 21.2 μm were used for the experimentation.

The rate of SO_2 absorption in the slurry follows from

$$J_A a = \frac{V_G}{V_L RT}\left(\frac{-\mathrm{d}P_A}{\mathrm{d}t}\right) = k_L E C_{Ai} \tag{1}$$

The experimental enhancement factor was calculated by taking the ratio of the initial rates in the presence of solids and in the absence of suspended solid particles, i.e. the saturated solution of the hydroxide involved.

3. Theory of gas absorption

$[OH]^-$ ions are fed by the dissolution of the solid particles in the liquid film. In the case of the SO_2–$Ca(OH)_2$ system, the reaction between SO_2 and $[OH]^-$ is instantaneous and the product of the reaction $CaSO_3$ is insoluble in the medium [5]. The reaction scheme for this process of gas absorption can be represented as

$$SO_{2(g)} \rightarrow SO_{2(aq)} \tag{i}$$

$$Ca(OH)_{2(s)} \rightarrow [Ca]^{2+} + 2[OH]^- \tag{ii}$$

$$SO_{2(aq)} + 2[OH]^- \rightarrow [SO_3]^{2-} + H_2O \tag{iii}$$

As the rate of solid dissolution is enhanced by the instantaneous reaction of SO_2 and $Ca(OH)_2$, the model proposed by Uchida et al. [1] can be used to describe the absorption process. The rate of gas absorption is given by the expression:

$$J_A = mD_A A^* \coth m\lambda + \frac{mD_B C_{Bs}}{z}\left(\coth m\lambda - \frac{1}{\sinh m\lambda}\right) \tag{2}$$

The parameter λ can be calculated by the equation:

$$\frac{D_B C_{Bs}}{2}\left(\coth m\lambda + \coth m(\delta - \lambda) - \frac{1}{\sinh m\lambda}\right) - \frac{D_A A^*}{\sinh m\lambda} = 0 \tag{3}$$

When the solution contains no suspended solids, the expression becomes

$$J_0 = k_L A^*\left(1 + \frac{D_B B_s}{D_A A^*}\right) \tag{4}$$

In the SO_2–$Mg(OH)_2$ slurry process, however, the product of the reaction $MgSO_3$ has a much higher solubility in water than that of $Mg(OH)_2$. $MgSO_3$ formed exists in a dissolved state. The dissolved SO_2 thus also reacts with $[SO_3]^{2-}$ and forms $[HSO_3]^-$ which in turn further enhances the rate of absorption. Thus, dissolved SO_2 is consumed by

$$SO_2 + 2[OH]^- = [SO_3]^{2-} + H_2O \tag{I}$$

$$SO_2 + [SO_3]^{2-} + H_2O = 2[HSO_3]^- \tag{II}$$

$$[HSO_3]^- + [OH]^- = [SO_3]^{2-} + H_2O \tag{III}$$

In the process of SO_2 absorption in $Mg(OH)_2$ slurry with no suspended particles, $[HSO_3]^-$ cannot coexist with $[OH]^-$, so that reaction (I) never takes place directly (Fig. 2a). The above consideration shows that reactions (II) and (III) take place at two differently located planes in the two reaction plane model. However, in the slurry process, both dissolved SO_2 and the $[HSO_3]^-$ to be produced by reaction (II) can react with $[OH]^-$ which is fed by the dissolution of the solid particles in the liquid film. So, dissolved SO_2 can be consumed by reactions (I) and (II) simultaneously. For a saturated solution of magnesium hydroxide, a plausible sketch of the concentration profile is given in Fig. 2a. When the particles are suspended in the liquid film, the concentration profiles shift as shown

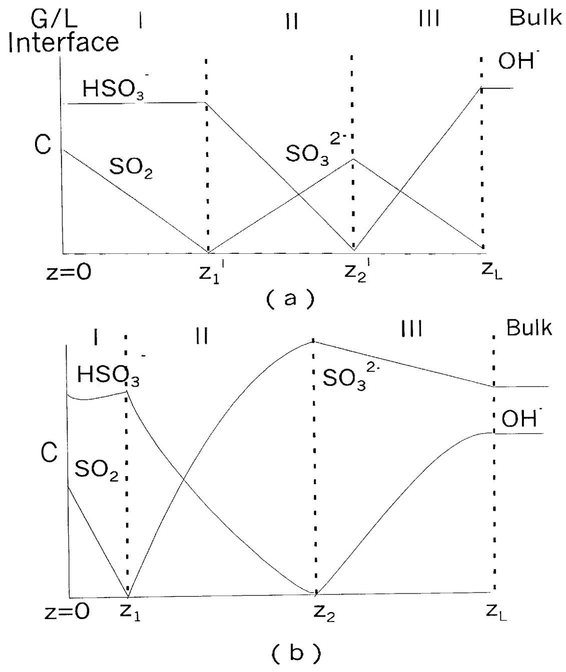

Fig. 2. Concentration profile for SO_2/$Mg(OH)_2$ slurry: (a) no suspended solids; (b) in the presence of suspended solids.

in Fig. 2b. The mass balances for the relevant species in the regions I, II and III are as follows:

Region I:

$$D_A \frac{d^2 C_A}{dz^2} - \frac{k_s}{2}\left(1 + \frac{2 D_A C_A}{C_{Bs} D_B}\right) A_p C_{Bs} = 0 \tag{5}$$

$$D_F \frac{d^2 C_F}{dz^2} - k_s \left(1 + \frac{D_F C_F}{C_{Bs} D_B}\right) A_p C_{Bs} = 0 \tag{6}$$

Region II:

$$D_F \frac{d^2 C_F}{dz^2} - k_s \left(1 + \frac{D_F C_F}{C_{Bs} D_B}\right) A_p C_{Bs} = 0 \tag{7}$$

$$D_E \frac{d^2 C_E}{dz^2} + k_s \left(1 + \frac{D_F C_F}{C_{Bs} D_B}\right) A_p C_{Bs} = 0 \tag{8}$$

Region III:

$$D_B \frac{d^2 C_B}{dz^2} + k_s A_p (C_{Bs} - C_B) = 0 \tag{9}$$

$$D_E \frac{d^2 C_E}{dz^2} = 0 \tag{10}$$

The boundary conditions imposed are

$$\text{At}\, z = 0, \quad C_A = C_{Ai}, \quad \frac{dC_F}{dz} = 0 \tag{11}$$

$$\text{At}\, z = z_1, \quad C_A = C_E = 0, \quad C_F = C_F^* \tag{12}$$

$$-D_A \left(\frac{dC_A}{dz}\right) = D_E \left(\frac{dC_E}{dz}\right) \tag{13}$$

$$\text{At}\, z = z_2, \quad C_B = C_F = 0, \quad C_E = C_E^* \tag{14}$$

$$D_B \left(\frac{dC_B}{dz}\right) = -D_F \left(\frac{dC_F}{dz}\right) \tag{15}$$

$$\text{At}\, z = z_L, \quad C_B = C_{Bs}, \quad C_E = C_{E0} \tag{16}$$

The expression for the enhancement factor as suggested by Sada et al. [5] is

$$E = \left[1 + \frac{1}{2 r_A q_A}\right] \frac{\sqrt{N}}{\tan \sqrt{N}\, x_1} - \left[\frac{1}{2 r_A q_A}\right] \frac{\sqrt{N}}{\sinh \sqrt{N}\, x_1} \tag{17}$$

E_0 represents the enhancement factor for a clear solution saturated with the hydroxides and is defined by

$$E_0 = 1 + \frac{1}{2 r_A q_A} \tag{18}$$

4. Results and discussion

To show the contribution of the presence of solids to the absorption rate, the ratio of enhancement factor into slurry to that into saturated solution (E/E_0) is plotted against weight percent of solids in Figs. 3 and 4. The ratio E/E_0 represents the degree of enhancement owing to the presence of solid particles in the slurry. For the case of SO_2 absorption in $Ca(OH)_2$ slurry, the concentration of $[SO_3]^{2-}$ (in the bulk) to be produced by the reaction of SO_2 and $Ca(OH)_2$ is extremely low, because the solubility of $CaSO_3$ in water is about 25 times lower than that of $Ca(OH)_2$. Consequently, the reaction between dissolved SO_2 and $[SO_3]^{2-}$ can be neglected. The solid curves plotted in Fig. 3 (Lines 1–4) are obtained from the theoretical values of the enhancement factor. These theoretical values are calculated using the model proposed by Uchida et al. [1]

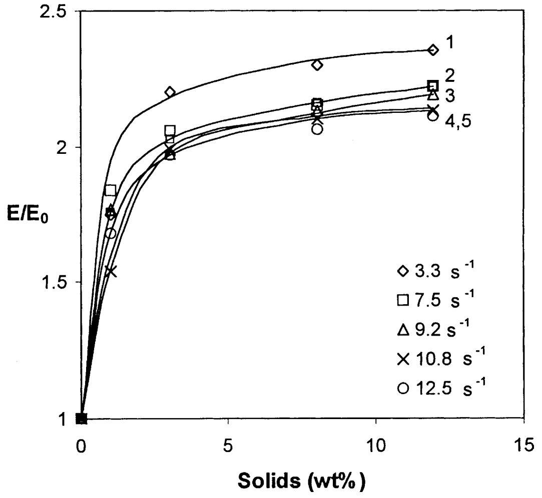

Fig. 3. Enhancement factor ratio as a function of solid concentration for SO_2 absorption in $Ca(OH)_2$ slurry (Lines 1–4: from theoretical values of enhancement factor predicted according to Uchida et al. [1]).

by using Eqs. (2)–(4). In order to compare the experimental results with the theoretical predictions for the SO_2–$Mg(OH)_2$ system, it is necessary to know the values of the dimensionless parameters r, q and N. For the evaluation of r, the diffusivity of SO_2 in the slurry was assumed to be the same as that in pure water. Thus, the value of r is 1.22 for this system. The value of q was calculated from the ratio of concentration of SO_2 at the gas–liquid interface and the solubility of the hydroxide in water. x_1 and x_2 were calculated computationally by using the equations suggested by Sada et al. [5]. The position of the primary reaction plane was smaller than the average diameter of the suspended particles, typically z_1/d_p was in the range of 0.4–0.45. Fig. 4 gives the variation of E/E_0 with the solid loading for the absorption of SO_2 in $Mg(OH)_2$ slurry. For the estimation of the parameter N, Sada et al. [5] compared their experimental results with the theoretical prediction according to Model II [4]. However, as Model II did not take into account the extra reaction between SO_2 and $[SO_3]^{2-}$ (reaction (II)), the values of experimental enhancement factors predicted by Sada et al. [5] did not match with the theoretical values predicted by Model II. The enhancement observed in this system is considered to be attributed due to both the presence of solid particles (reactant of reactions (I) and (III)) in the liquid film and the extra reaction of SO_2 and $[SO_3]^{2-}$ (reaction (II)). The concentration of $[SO_3]^{2-}$ is allowed to be a function of time. $[SO_3]^{2-}$ is produced in the film by the reaction of SO_2 and the hydroxide ions (reaction (I)) and also by the reaction of $[HSO_3]^-$ and the hydroxide ions (reaction (II)). The consumption of $[SO_3]^{2-}$, however, is only by its reaction with SO_2. Hence the rate of

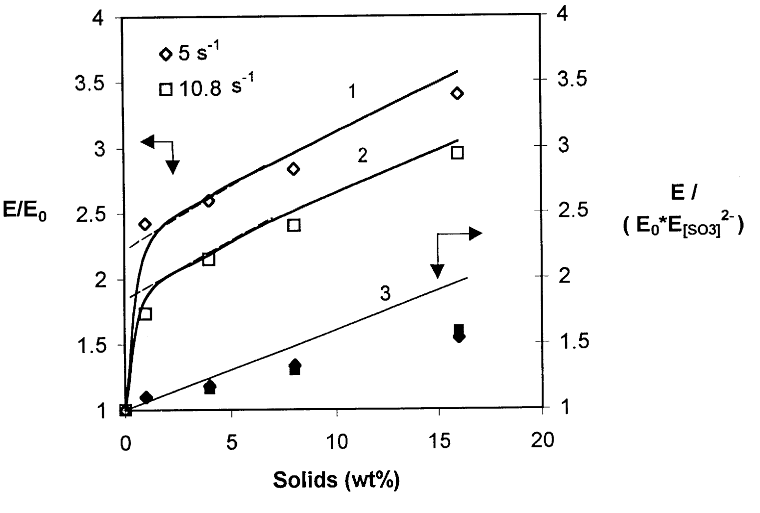

Fig. 4. Enhancement factor ratio as a function of solid concentration for SO_2 absorption in $Mg(OH)_2$ slurry ((◆) and (■): experimental values of $[E/E_0(E/E_0)_{w=0}]$ at 650 and 300 rpm, respectively, Lines 1 and 2: theoretical values [5] with correct N/w values, Line 3: theoretical values predicted by Model II).

generation of $[SO_3]^{2-}$ is greater than its consumption in the film, due to which the concentration of $[SO_3]^{2-}$ starts building up in the film. The concentration of $[SO_3]^{2-}$ in the film is larger than its concentration in the bulk liquid due to which $[SO_3]^{2-}$ diffuses in the liquid bulk.

The enhancement caused by the reaction between SO_2 and $[SO_3]^{2-}$ formed was assessed by extrapolating the observed enhancement in the presence of solids to that for a saturated solution of magnesium hydroxide, i.e. $(E/E_0)_{w=0}$. This value was found experimentally to be 1.8 at $10.8\,s^{-1}$ and 2.4 at $5\,s^{-1}$ (Fig. 4). To estimate the contribution of solids in the observed enhancement factor, the degree of enhancement which was also caused due to the reaction (II) was avoided by Sada et al. [5] by converting the ratio E/E_0 to the quantity $[E/E_0 - ((E/E_0)_{w=0} - 1)]$, where the quantity $[(E/E_0)_{w=0} - 1]$ corresponded for the extra enhancement due to reaction (II). Model II predicts the data of effect of addition of solids on enhancement factor at different values of N/w. Sada et al. [5] thus estimated the value of N/w to be 12.3 by comparing their experimental findings with the theoretical values predicted by Model II. However, their procedure of calculating the contribution of solids to the enhancement factor does not seem to be correct as the enhancement effects are multiplicative and hence they cannot be subtracted. Hence, in our calculations, the ratio of E/E_0 was converted to the quantity $[E/E_0(E/E_0)_{w=0}]$, to estimate the effect of solid on the enhancement factor where the quantity $(E/E_0)_{w=0}$ counts for the additional increase in the enhancement due to reaction (II) which is represented by $E_{[SO_3]^{2-}}$. The values of $[E/E_0(E/E_0)_{w=0}]$ are represented as the dark points in Fig. 4. These dark points show the contribution to the enhancement in the rate of absorption due to the presence of the suspended solids only. For comparison, the values predicted by Model II for $N/w = 12.3$ is shown in the form of a solid line in Fig. 4. The difference in the values between our experimental findings and the Line 3, specially at higher solid loadings, is due to the more accurate procedure for the estimation of contribution of solids in the enhancement used in our calculations. For the slurry process, the Sherwood number can be defined as $Sh = k_s d_p / D_B$ which gives the value of solid dissolution parameter $N = Sh(6w/\rho)(z_L/d_p)^2$. This indicates that the quantity N/w is dependent on Sh and d_p. For calculation of N/w, $Sh = 2$ was assumed in our calculations which resulted into the value of $N/w = 11.31$ for $5\,s^{-1}$. This value of N/w was used to calculate the theoretical enhancement factors due to the presence of solids using Eq. (17), which are indicated by the two solid curves (1 and 2) represented in Fig. 5. Fig. 5 shows the variation of the enhancement factor with time as observed for reactive SO_2 absorption in a $Mg(OH)_2$ slurry. It can be seen that the enhancement is constant at the start for some time and then decreases and ultimately becomes zero. Initially, at higher partial pressures of SO_2, the consumption of $[SO_3]^{2-}$ by reaction (II) is balanced by its regeneration by reaction (III). Hence, the enhancement remains constant. Then, as the absorption of SO_2 proceeds, the pressure in the reactor and also the amount of the gas absorbed reduces and hence results in a reduction of the enhancement. The solid lines are the theoretical values. Fig. 6 shows the variation of enhancement factor with time for $SO_2/Ca(OH)_2$ process. The enhancement factor is found to decrease as a function of time which could be due to the decrease in the film thickness with time due to which the number of reactive particles present in the film get reduced and hence the decrease in the enhancement. The theoretical values compared well with the experimental.

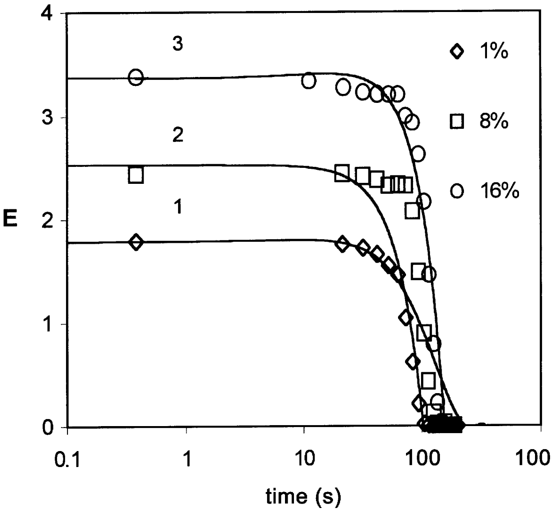

Fig. 5. Variation of enhancement of SO_2 absorption with time (system: $SO_2/Mg(OH)_2$ slurry, Lines 1–3: theoretical values predicted according to Sada et al. [5]).

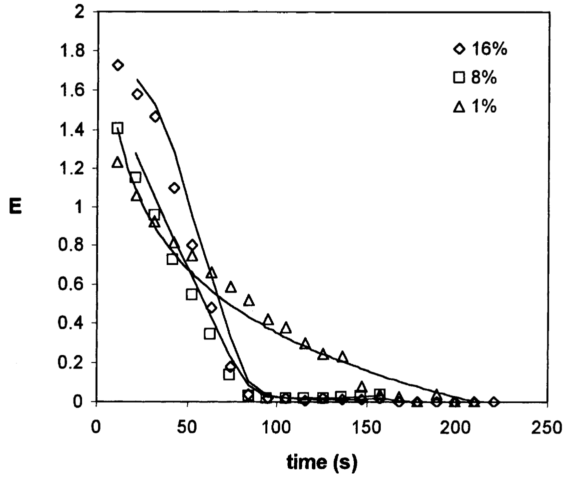

Fig. 6. Variation of enhancement of SO_2 absorption with time (system: $SO_2/Ca(OH)_2$ slurry, solid lines: theoretical values according to Uchida et al. [1]).

5. Conclusions

The absorption of sulfur dioxide into aqueous slurries containing fine suspended reactive particles of calcium and magnesium hydroxide was performed in a stirred cell at relatively high mass transfer coefficients. The enhancement of the mass transfer due to the presence of fine particles increased with the solid concentration. Experimental data on the absorption rates were compared with the theoretical predictions using two different models, i.e. a model proposed by Uchida et al. [1] for the $Ca(OH)_2$ slurry and the two reaction plane model proposed by Sada et al. [5] for the $Mg(OH)_2$ slurry. For the later system, the results could be accurately described by a new approach defining an overall enhancement factor E which is defined as $E = E_0 E_s E_{[SO_3]^{2-}}$ with E_s and $E_{[SO_3]^{2-}}$ being the factorial enhancement factors due to the effects of suspended solids and the reaction of SO_2 and $[SO_3]^{2-}$, respectively. The enhancement factor thus calculated proved to predict the values observed experimentally very well.

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