Effect of Organic Acid Additives on SO_2 Absorption into $CaO/CaCO_3$ Slurries

The absorption rate of sulfur dioxide from a gas mixture of SO_2 and N_2 into aqueous acetic acid and adipic acid solutions at *p*H 4 to 6 has been measured at 25°C in a continuous stirred vessel with an unbroken gas-liquid interface. The experimental data have been modeled by approximate surface renewal theory with multiple equilibrium reactions. The model has been used to evaluate the relative effectiveness of eleven organic acid additives at typical limestone scrubber conditions. Adipic, sulfopropionic, sulfosuccinic, and hydroxypropionic acids appear to be the most promising alternatives.

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SCOPE

SO_2 absorption from waste gases by lime/limestone slurries is frequently limited by liquid-phase mass transfer resistance. Experimental results have shown that buffer additives such as organic acids can effectively enhance the mass transfer rate (Hatfield and Potts, 1971; Hatfield et al., 1972; Holliden et al., 1974; Wasag et al., 1975; Head et al., 1979). Several investigators (Rochelle and King, 1977; Cavanaugh, 1978) have extensively evaluated the available carboxylic acids on the basis of cost, buffer capacity, solubility and other factors. The combined use of buffer additives and forced oxidation have been tested as a means of dewatering waste solids more easily, thereby minimizing loss of the soluble additive (Rochelle and King, 1978; Head et al., 1979). In this paper, a mass transfer model is developed for SO_2 absorption with and without buffer additives and forced oxidation.

Film theory mass transfer with equilibrium reactions was first discussed by Olander (1960). Danckwerts (1968) proposed a simple physical mass transfer concept for equal diffusivity systems. Chang and Rochelle (1980) studied the equilibrium reaction effect on mass transfer rate by surface renewal theory with unequal diffusivities. This mass transfer model is suitable for SO_2 absorption processes because the dissolved SO_2 is hydrolyzed instantaneously and reversibly. Chang employed the model to interpret experimental data of SO_2 absorption into pure water (Chang and Rochelle, 1981) and several other aqueous solutions (Chang, 1979).

The major objective of this work is to use surface renewal theory with equilibrium reactions to model the SO_2 absorption by aqueous solutions buffered with organic acids. Experimental data are presented with adipic acid and acetic acid solutions for 25°C, 0.5 M NaCl, and *p*H 4 to 6. The mass transfer model will be further employed to evaluate appropriate buffer additives under SO_2 scrubbing conditions at 55°C with 0.1 M $CaCl_2$. The amount of adipic acid needed for a typical SO_2 scrubber will be estimated.

CONCLUSIONS AND SIGNIFICANCE

SO_2 absorption into buffered solutions of acetic or adipic acid can be modeled by approximate surface renewal theory with multiple equilibrium reactions. The model predicts that as little as 10 to 20 mM adipic acid should be sufficient to provide most of the benefit from mass transfer enhancement by buffer additives in lime/limestone slurry scrubbing for stack gas desulfurization. Adipic, sulfopropionic, sulfosuccinic, and β-hydroxypropionic acids are the most promising buffer additives. The model also predicts that forced oxidation in the scrubber loop will improve SO_2 absorption by enhancing SO_2 hydrolysis in the boundary layer.

CHEMICAL ABSORPTION MECHANISM

When sulfur dioxide is absorbed into an aqueous solution of a difunctional buffer such as adipic acid in the *p*H range from 4 to 7, the following four reactions should be considered:

$$SO_2 + H_2O \rightleftarrows H^+ + HSO_3^- \tag{1}$$

$$HSO_3^- \rightleftarrows H^+ + SO_3^= \tag{2}$$

$$H_2Ad \rightleftarrows H^+ + HAd^- \tag{3}$$

$$HAd^- \rightleftarrows H^+ + Ad^= \tag{4}$$

where H_2Ad represents adipic acid and HAd^-, $Ad^=$ its ions. The first reaction corresponds to the hydrolysis of absorbed SO_2. Its forward reaction rate constant has been measured as $3.4 \times 10^6\ s^{-1}$ at 20°C (Eigen et al., 1961). Reactions 2, 3 and 4 are proton transfer reactions and have much higher reaction rates than that of reaction 1. Therefore, all four reactions can be regarded as instantaneous.

The values of the equilibrium constants, K_1, K_2, K_3 and K_4 of reactions 1, 2, 3 and 4, respectively, are:

$$K_1 = \frac{a_{H^+}\, a_{HSO_3^-}}{a_{SO_2}} = 1.3 \times 10^{-2} \text{ (Johnstone and Leppla, 1934)}$$

$$K_2 = \frac{a_{H^+}\, a_{SO_3^=}}{a_{HSO_3^-}} = 6.2 \times 10^{-8} \text{ (Tartar and Garretson, 1941)}$$

$$K_3 = \frac{a_{H^+}\, a_{HAd^-}}{a_{H_2Ad}} = 3.82 \times 10^{-5} \text{ (Gane and Ingold, 1931)}$$

$$K_4 = \frac{a_{H^+}\, a_{Ad^=}}{a_{HAd^-}} = 3.87 \times 10^{-6} \text{ (Gane and Ingold, 1931)}$$

at 25°C and infinite dilution. Under typical conditions of $CaO/CaCO_3$ slurry scrubbing, reaction 1 must be treated as a reversible reaction. Therefore, SO_2 absorption is a process of simultaneous mass transfer with multiple equilibrium reactions.

According to surface renewal theory, the total component material balance gives for SO_2 species:

$$D_{SO_2} \frac{\partial^2 [SO_2]}{\partial x^2} + D_{HSO_3^-} \frac{\partial^2 [HSO_3^-]}{\partial x^2} + D_{SO_3^=} \frac{\partial^2 [SO_3^=]}{\partial x^2} = \frac{\partial [SO_2]}{\partial t} + \frac{\partial [HSO_3^-]}{\partial t} + \frac{\partial [SO_3^=]}{\partial t} \tag{5}$$

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0001-1541-82-4643-0261-$2.00

For H_2Ad species:

$$D_{H_2Ad}\frac{\partial^2[H_2Ad]}{\partial x^2}+D_{HAd^-}\frac{\partial^2[HAd^-]}{\partial x^2}+D_{Ad^=}\frac{\partial^2[Ad^=]}{\partial x^2}=\frac{\partial[H_2Ad]}{\partial t}+\frac{\partial[HAd^-]}{\partial t}+\frac{\partial[Ad^=]}{\partial t} \quad (6)$$

For local charge:

$$D_{H^+}\frac{\partial^2[H^+]}{\partial x^2}-D_{HSO_3^-}\frac{\partial^2[HSO_3^-]}{\partial x^2}-2D_{SO_3^= m}\frac{\partial^2[SO_3^=]}{\partial x^2}-D_{HA^-}\frac{\partial^2[HA^-]}{\partial x^2}-2D_{Ad^=}\frac{\partial^2[Ad^=]}{\partial x^2}=\frac{\partial[H^+]}{\partial t}-\frac{\partial[HSO_3^-]}{\partial t}-2\frac{\partial[SO_3^=]}{\partial t}-\frac{\partial[HA^-]}{\partial t}-2\frac{\partial[A^=]}{\partial t} \quad (7)$$

Furthermore, the chemical equilibrium relations of reactions 1, 2, 3 and 4 are effective at every point in the liquid phase. Three non-linear second order partial differential equations with three unknowns can be obtained by substituting the equilibrium relations into Eqs. 5, 6 and 7. There is no analytical solution for this set of equations; however, an approximate analytical solution can be obtained by replacing the diffusivity ratios in the solution of film theory by their square roots (Chang, 1979; Chang and Rochelle, 1980). The general solutions of the film theory material balance equations are:

$$D_{SO_2}[SO_2]+D_{HSO_3}[HSO_3^-]+D_{SO_3^=}[SO_3^=]=b_1x+b_2 \quad (8)$$

$$D_{H^+}[H^+]-D_{HSO_3^-}[HSO_3^-]-2D_{SO_3^=}[SO_3^=]-D_{HA^-}[HA^-]-2D_{Ad^=}[Ad^=]=b_3x+b_4 \quad (9)$$

$$D_{H_2Ad}[H_2Ad]+D_{HAd^-}[HAd^-]+D_{Ad^=}[Ad^=]=b_5x+b_6 \quad (10)$$

All the concentrations are subject to the equilibrium relations of reactions 1, 2, 3 and 4. The boundary conditions are:

$$\text{at } x=0,\ [SO_2]=[SO_2]_i$$

$$D_{H^+}\frac{d[H^+]}{dx}-D_{HSO_3^-}\frac{d[HSO_3^-]}{dx}-2D_{SO_3^=}\frac{d[SO_3^=]}{dx}-D_{HA^-}\frac{d[HA^-]}{dx}-2D_{Ad^=}\frac{d[Ad^-]}{dx}=0$$

$$D_{H_2Ad}\frac{d[H_2Ad]}{dx}+D_{HAd}\frac{d[HAd^-]}{dx}+D_{Ad^=}\frac{d[Ad^=]}{dx}=0$$

$$\text{at } x=\delta,\ [SO_2]=[SO_2]_o,\ [H^+]=[H^+]_o,\ [H_2Ad]=[H_2Ad]_o$$

where $[SO_2]_i$ represents the physical solubility of SO_2. The other two differential equations reflect the inability of adipate species and charge to penetrate through the gas-liquid interface.

The absorption rate of SO_2, N, is given by:

$$N=k_\ell^oA\ \phi\ ([SO_2]_i-[SO_2]_o)$$

The enhancement factor, ϕ, based on approximate surface renewal theory, is given by:

$$\phi=1+[\sqrt{D_{HSO3^-}}([HSO_3^-]_i-[HSO_3^-]_o)+\sqrt{D_{SO_3^=}}([SO_3^=]_i-[SO_3^=]_o)]/[\sqrt{D_{SO_2}}([SO_2]_i-[SO_2]_o)] \quad (11)$$

The values of all the concentrations at the gas-liquid interface can be estimated by numerical solution of a fifth order algebraic equation derived from Eqs. 8, 9 and 10 and their boundary conditions with all the diffusivity ratios replaced by their square roots.

This mass transfer model can also be employed with other buffers by the substitution of appropriate equilibrium constants and diffusivities. With monofunctional buffers such as acetic acid, the mass transfer enhancement factor can be obtained by using the single buffer K_a value for K_3 and a dummy value for K_4 outside the range of 10^{-4} to 10^{-7}, such as 10^{-13}. The value of K_3 used for acetic acid in the model calculation is 1.75×10^{-5} at 25°C (MacInnes and Sedlovsky, 1932).

EXPERIMENTAL APPARATUS AND PROCEDURES

Experiments on the absorption of sulfur dioxide by aqueous acetic acid and adipic acid solutions were carried out in an agitated vessel with an unbroken gas-liquid interface, as used by Chang and Rochelle (1981) in previous work. The absorber had continuous flow with respect to both gas and liquid phases, enabling steady-state operation. The physical gas and liquid phase mass transfer coefficients were measured by Chang and Rochelle (1981) as a function of stirrer rate. The stirrer speed was kept at 300 rpm for all experiments reported here, giving k_ℓ^oA and k_gA values of 2.5×10^{-4} L/s and 1.4×10^{-7} gmol/s-Pa, respectively.

Sulfur dioxide was diluted by nitrogen and fed into the stirred vessel at a constant flow rate. An appropriate amount of sodium chloride was added to the aqueous solutions to disperse the effect of electrical potential gradient on the diffusivities of ionic species. All the runs were performed at ambient pressure and 25 ± 1°C.

The sulfur dioxide partial pressure of the outlet gas stream was measured by a pulsed fluorescent SO_2 analyzer. (Thermoelectron model 40). The hydrogen ion activity of the outlet liquid stream was measured by a *p*H meter. Solution samples were collected after the system reached steady state. The absorbed sulfur dioxide was oxidized into sulfate species by addition of 30% hydrogen peroxide solution to the liquid sample. An ion chromatograph was used to analyze the total sulfate concentration. The sulfur dioxide absorption rate, N, was calculated from the liquid phase material balance. The enhancement factor, ϕ, was calculated as follows from N, k_gA, k_ℓ^oA and H:

$$[SO_2]_i=(P_{SO_2}-N/k_gA)/\mathrm{H}$$

$$\phi=\frac{N}{k_\ell^oA([SO_2]_i-[SO_2]_o)}$$

PHYSICAL PROPERTIES

The concentration of molecular sulfur dioxide at the gas-liquid interface was obtained from the following equation given by Rabe and Harris (1963):

$$[SO_2]_i=P_{SO_{2,i}}/\mathrm{H}$$

$$ln\ \mathrm{H}=-2851.1/T+20.90 \quad (12)$$

Since all the equilibrium constants are in thermodynamic units, appropriate activity coefficients must be incorporated with the concentration of each component to estimate the effective equilibrium constant in concentration units. For example,

$$K_{c,1}=K_1\frac{\gamma_{SO_2}}{\gamma_{H^+}\gamma_{HSO_3^-}} \quad (13)$$

Individual ion activity coefficients at 25°C were calculated by a modified Debye-Hückel limiting law (Lowell et al., 1970):

$$\log\gamma_j=0.315\eta_j^2\left[\frac{-I^{1/2}}{1+0.312\,C_{3j}\,I^{1/2}}+C_{4j}\,I\right] \quad (14)$$

where η_j is the charge on the jth ion, I represents the ionic strength, and C_{3j} and C_{4j} are the characteristic parameters for each ion species. The values of those two parameters for H^+, HSO_3^- and $SO_3^=$ were listed in a previous paper (Chang and Rochelle, 1981). 3.0 and 0.3 were the values used for C_{3j} and C_{4j}, respectively, for all other charged species. The activity coefficients of hydrated sulfur dioxide, acetic acid and adipic acid in solutions were estimated by (Harned and Owen, 1958):

$$\log\gamma=0.076\,I \quad (15)$$

The liquid phase diffusivity, D_{SO_2}, of sulfur dioxide in water was taken as 2.00×10^{-5} cm²/s at 30°C (Peaceman, 1951). The value of D_{SO_2} at 25°C was predicted by correcting for the temperature and viscosity of water according to Stokes-Einstein relation. All experimental runs were made with 0.5 M NaCl solutions to disperse the effect of electrical potential gradient on the diffusion of ionic

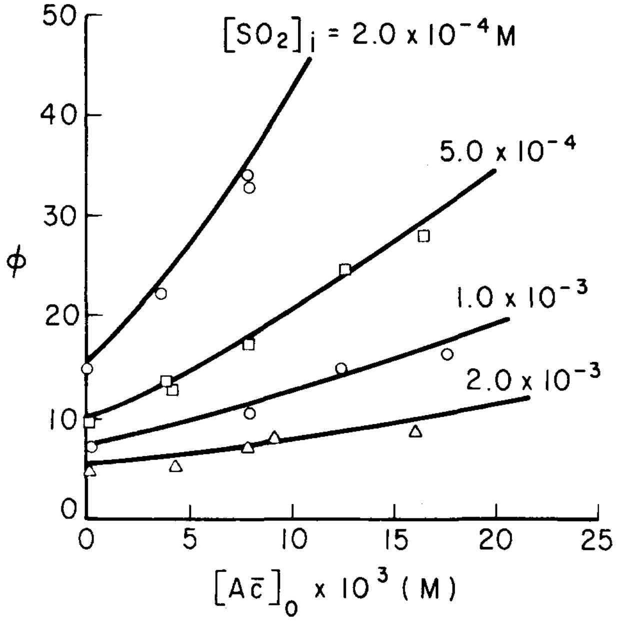

Figure 1. Mass transfer enhancement by acetic acid, 25°C, 0.5 M NaCl, *p*H 4 to 6.

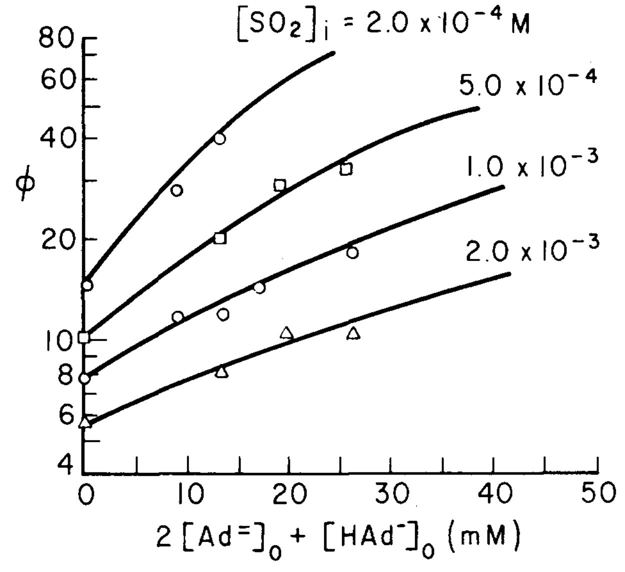

Figure 2. Mass transfer enhancement by adipic acid, 25°C, 0.5 M NaCl, *p*H 4 to 6.

species (Chang and Rochelle, 1981). Therefore, the effective diffusivities of all the ionic species were assumed to be equal to their true diffusivities, as calculated from equivalent ionic conductivities by

$$D = \frac{RT\lambda_o}{n_j(\mathrm{Fa})^2} \tag{16}$$

where Fa is the Faraday number and λ_o the equivalent ionic conductivity. The values of λ_o for H^+, HSO_3^-, $SO_3^=$ and acetate at 25°C and infinite dilution are 350, 50, 72 and 40.9 cm^2/mole-ohm, respectively (Landolt-Bornstein, 1960).

The value of acetic acid diffusivity in water at 25°C was taken as 1.19×10^{-5} cm^2/s (Lewis, 1955). The diffusivities of adipic acid and adipate ion in water at 25°C were reported to be 0.736×10^{-5} and 0.705×10^{-5} cm^2/s, respectively (Albery et al., 1967; Jeffery and Vogel, 1935). Since those two values are very close to each other, the diffusivity of HAd^- was taken to be their arithmetic mean.

EXPERIMENTAL RESULTS

Figures 1 and 2 give experimental results for SO_2 absorption into acetic and adipic acid solutions at 25°C and *p*H 4 to 6 with less than 1 mM total dissolved SO_2. The experimental data agree well with approximate surface renewal theory, shown by the curves on the figures. Under these conditions, the enhancement factor is independent of pH and dissolved SO_2 and depends only on the concentration of the basic buffer species and the SO_2 concentration at the gas/liquid interface. Even with no buffer present, significant enhancement results from SO_2 hydrolysis (reaction 1), which is more significant at lower $[SO_2]_i$. Enhancement by a given buffer concentration is also more significant at lower $[SO_2]_i$.

MODEL FOR SLURRY SCRUBBING CONDITIONS

Typical conditions in a $CaO/CaCO_3$ slurry scrubber are listed in Table 1. In order to evaluate the effectiveness of organic acids as buffer additives, physical properties for the present mass transfer model were modified to include the effects of 0.1 M $CaCl_2$ (rather than 0.5 M NaCl) and higher temperature (55°C).

The presence of dissolved Ca results in formation of the calcium sulfite ion pair:

$$Ca^{++} + SO_3^= \rightleftarrows CaSO_3^\circ \tag{18}$$

$$K_{CaSO_3^\circ} = \frac{a_{CaSO_3^\circ}}{a_{Ca^{++}}\, a_{SO_3^=}}$$

$CaSO_3^\circ$ can react with dissolved SO_2 and acts like sulfite ion. Therefore, if $CaSO_3^\circ$ is assumed to have the same diffusivity as $SO_3^=$, a modified equilibrium constant of reaction 2 can be used to account for $CaSO_3^\circ$ in the presence of excess Ca^{++}.

$$K'_2 = \frac{a_{H^+}\, a'_{SO_3^=}}{a_{HSO_3^-}} \tag{19}$$

where $a'_{SO_3^=} = a_{SO_3^=}(1 + a_{Ca^{++}}K_{CaSO_3^\circ})$
The value of $K'_{c,2}$ at 55°C in 0.1 M $CaCl_2$ was estimated to be 2.02×10^{-6} M (Lowell et al., 1970).

Higher temperature is accounted for by changes and appropriate assumptions for equilibrium constants, activity coefficients, and diffusivities. The diffusivity ratios and effective equilibrium constants were assumed to be independent of temperature. Minor modifications were made in the computation of activity coefficients for $K_{c,1}$ and $K_{c,2}$ by the method of Lowell et al. (1970).

OPTIMUM pK_c OF BUFFER ADDITIVES

To be effective for mass transfer enhancement, additives should buffer between the *p*H of the gas/liquid interface and the pH of the bulk liquid. Figure 3 shows the optimum pK_c values for a hypothetical monofunctional buffer as predicted by the modified mass transfer model (55°C, 0.1 M $CaCl_2$) for several sets of $[SO_2]_i$, $[HSO_3^-]_o$, $[H^+]_o$ and $[A^-]_o$. For each data set, the buffer pK_a was varied to maximize ϕ. The optimum pK_c values are very nearly equal to the average of the pH values at the gas/liquid interface and in the bulk liquid.

The pH at the gas/liquid interface is primarily a function of SO_2 gas concentration but also varies with total dissolved sulfite and

TABLE 1. TYPICAL CONDITIONS IN $CaO/CaCO_3$ SLURRY SCRUBBER

Temperature	55°C
P_{SO_2}, in	50 to 500 Pa
P_{SO_2}, out	2 to 20 Pa
*p*H	4.5 to 5.5
Total Dissolved Sulfite	0 to 20 mM
Total Dissolved Calcium	0.05 to 0.2 M

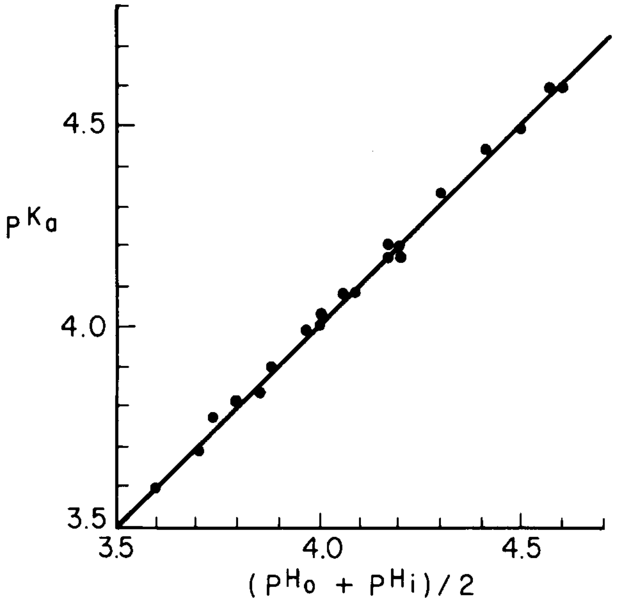

Figure 3. Optimum pK_c values for monofunctional buffers.

buffer concentration. In a typical absorber calculated values of pH at interface decrease from 4.0 in the top of the absorber to 3.0 in the bottom. At more extreme conditions, interface pH can be as low as 2.0 or as high as 4.5. Bulk solution pH is typically 4.5 to 5.5. Therefore, the optimum pK_c value of a monofunctional buffer should lie between 3.5 and 4.5. Polyfunctional buffers should also have pK_c values near 3.5 to 4.5 for maximum effectiveness. In concentrated solutions such as 0.1 M $CaCl_2$, pK_c values will be 0.3 to 0.6 units less than the true pK_a values.

EVALUATION OF BUFFER ADDITIVES

Eleven buffer additives with appropriate pK_c values have been assessed by the modified mass transfer model. The diffusivities and pK_c values are listed in Table 2. For some buffers, the diffusivities were estimated by the following equation for carboxylic acids (Albery et al., 1967):

$$\log D = -(4.04 + 0.49 \log V') \tag{20}$$

where V' is the molecular volume of the organic acid estimated by the method of Le Bas (1915). The carboxylic ions were assumed to have the same diffusivities as their molecules. In several cases, pK_c values were measured by Cavanaugh (1978) by acid-base titration in 0.1 M $CaCl_2$ at 25°C.

The relative effectiveness and costs of eleven organic acids are given in Table 3. Adipic acid was taken as the basis of comparison. The modified mass transfer model was used to determine the buffer concentration required to give an enhancement factor of 20. Sulfopropionic, β-hydroxypropionic, sulfosuccinic, and adipic acids were found to have suitable properties as buffer additives for the throwaway flue gas desulfurization process. Formic and acetic acids are apparently the two least expensive buffer additives, but their expected volatility (Rochelle and King, 1977) may result in economically or environmentally significant losses in the scrubber. Benzoic, glycolic, phthalic, succinic, and lactic acids are economically unattractive because of their high cost per lb mole or because of their relatively poor effectiveness. Other factors such as availability and chemical stability should also be considered.

EFFECT OF ADIPIC ACID ON SCRUBBER PERFORMANCE

Figure 4 shows mass transfer enhancement by adipic acid in a $CaCO_3$ slurry scrubber. The gas and liquid phase mass transfer resistance ratio was set at a typical value of 0.2 (Bengtsson, 1974):

TABLE 2. PHYSICAL PROPERTIES OF ORGANIC ACID ADDITIVES AT 25°C

Acid	Diffusivity × 10^5 (cm^2/s) Acid[a]	Anion[b]	pK_c[c]	
Formic	1.46	1.433	3.45[d]	
Acetic	1.19[f]	1.09	4.45[d]	
Benzoic	1.21	0.862	3.9	
Glycolic	0.98	—	3.424	
Lactic	0.987	—	3.36	
Sulfopropionic	0.82	—	4.06	
Hydroxypropionic	0.987	—	4.26	
Phthalic	0.717	0.692	2.82	4.4
Succinic	0.86	0.812	3.98[d]	4.6[d]
Sulfosuccinic	0.731	—	3.1	4.4
Adipic	0.736	0.705[e]	3.98	4.86

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[a] Measured by Albery et al., (1967) or estimated by his method.

[b] Estimated from ionic conductivities in Landolt-Bornstein (1960).

[c] Effective equilibrium constants in 0.1 M $CaCl_2$, $K_c = a_{H^+}[A^-]/[HA]$, measured by Cavanaugh (1978).

[d] Estimated from activity coefficients and accepted pK_a values at infinite dilution.

[e] Jeffery and Vogel, 1935.

[f] Lewis, 1955.

$$\frac{1/k_g}{1/Hk_\ell^o} = 0.2 \tag{21}$$

The ordinate, K_g/k_g, represents the ratio of gas phase mass transfer resistance to overall mass transfer resistance. As K_g/k_g increases, overall scrubber performance will improve. If dissolved SO_2 in bulk liquid is assumed to be negligible, then:

$$\frac{K_g}{k_g} = \frac{P_{SO_2} - P_{SO_{2i}}}{P_{SO_2}} \tag{22}$$

The low value of P_{SO_2} represents scrubber conditions near the gas outlet or for flue gas of low-sulfur coal. The high value of P_{SO_2} represents typical conditions at the gas inlet. It is seen that the SO_2 absorption is more gas-phase controlled with low P_{SO_2}. Therefore, adipic acid is relatively more effective with high P_{SO_2}.

Forced oxidation in the scrubber loop usually results in low total sulfite. Figure 4 shows that at pH 5 the overall mass transfer coefficient of slurry without sulfite is greater than that with 10 mM sulfite. In other words, the SO_2 absorption efficiency is improved by forced oxidation as observed by Borgwardt (1978). At pH 5, most of the total dissolved sulfite is present as bisulfite which depress the SO_2 hydrolysis. In the absence of bisulfite, increased SO_2 hydrolysis enhances mass transfer.

As adipic acid is added to the system, liquid phase mass transfer rate is enhanced by the buffering couples of H_2Ad/HAd^- and

TABLE 3. ORGANIC ACID ADDITIVE COSTS
Basis: ϕ = 20, 55°C, pH 5.0, 0.1 M $CaCl_2$, 10 mM Total Sulfite, 1000 ppm SO_2

Organic Acid	Concentration (mM)	Price[a] ($/kg-mole)	Relative Cost
Formic	17.7	28	0.38
Acetic	14.3	25	0.28
Adipic	9.4	140	1.0
Sulfosuccinic	7.8	97[d]	0.57
Sulfopropionic	16.1	63[b]	0.77
Hydroxypropionic	14.6	63[b]	0.70
Phthalic	13.2	128[c]	1.29
Succinic	7.3	233[c]	1.30
Benzoic	15.8	81	0.97
Glycolic	22.4	67	1.14
Lactic	24.7	163	3.05

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[a] Chemical Marketing Reporter, July 2, 1979.

[b] Acrylic acid.

[c] Acid anhydride.

[d] Maleic anhydride.

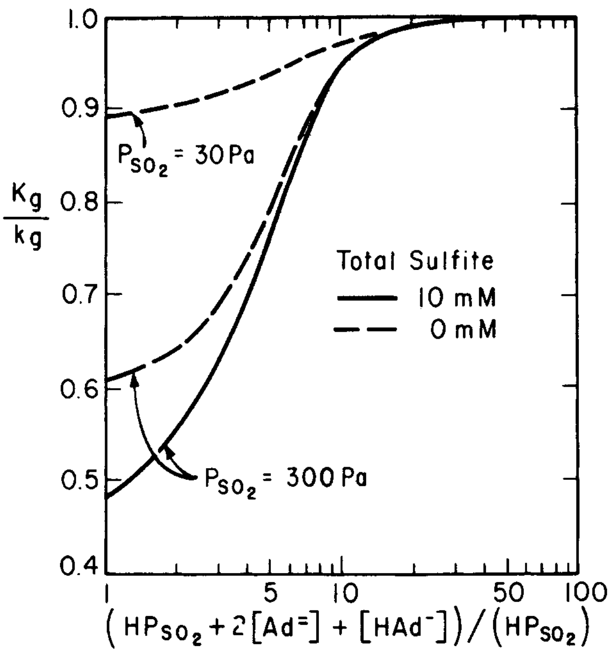

Figure 4. Overall mass transfer enhancement by adipic acid, 55°C, 0.1 M $CaCl_2$, *p*H 5.

$HAd^-/Ad^=$. Less overall mass transfer enhancement is obtained with low P_{SO_2} because it is more gas-phase controlled. All three curves approach the asymptotic value of 1.0 at a high concentration of adipic acid, where SO_2 removal is totally controlled by gas phase resistance. Further addition of adipic acid or other buffer will not improve SO_2 removal. At 55°C, *p*H 4.9, 10 mM total sulfite, 10 mM adipic acid, and 3,000 ppm of SO_2 (300 Pa), the abscissa of Figure 4 is about 11, giving K_g/k_g equal to 0.95. Therefore, in a typical $CaCO_3$ slurry scrubber, 10 to 20 mM should be adequate to provide most of the benefit from adipic acid addition. This is very close to the experimental results obtained by Head et al. (1979).

NOTATION

a = component activity, M
A = mass transfer area, cm^2
b = integration constant in Eqs. 8, 9 and 10
D = diffusivity of component, cm^2/s
Fa = Faraday = 96488 coulumbs/g-equiv
H = Henry's constant, Pa/M
I = ionic strength, M
K = thermodynamic equilibrium constant
K_c = effective equilibrium constant in concentration units
k_g = gas-phase mass transfer coefficient, $gmol/cm^2$-Pa-s
K_g = overall gas-phase mass transfer coefficient, $gmol/cm^2$-Pa-s
k_ℓ^o = liquid-phase mass transfer coefficient, L/cm^2-s
M = molarity, gmol/L
mM = molarity $\times 10^3$
n = valence
N = absorption rate, gmol/s
P_{SO_2} = SO_2 partial pressure, Pa
t = time, s
T = temperature, °K
V' = molecular volume, $cm^3/gmol$
x = distance, cm
ϕ = mass transfer enhancement factor
γ = activity coefficient
λ_o = equivalent ion conductance, cm^2/gmol-ohm
δ = film thickness, cm

SUBSCRIPTS

1, 2, 3, 4 = reaction 1, 2, 3, 4
i = at gas-liquid interface
j = component j
o = at bulk liquid
[ ] = concentration, gmol/L

LITERATURE CITED

Albery, W. J., A. R. Greenwood, and R. F. Ribble, "Diffusion Coefficients of Carboxylic Acids," *Trans. Far. Soc.*, **63**, 360 (1967).

Bengtsson, B., "The Absorption and Oxidation of SO_2 in $CaCO_3$ and $Ca(OH)_2$ Suspensions," Ph.D. Dissertation, Technical University of Munich (1974).

Borgwardt, R. H., "Effect of Forced Oxidation on Limestone/SO_x Scrubber Performance," Proceedings: Symposium on Flue Gas Desulfurization, Hollywood, FL, EPA-600-7-78-058a, p. 205 (1978).

Cavanaugh, C. M., "Buffer Additives for Flue Gas Desulfurization Processes," M.S. Thesis, University of Texas at Austin (1978).

Chang, C. S., "Mass Transfer with Equilibrium Chemical Reaction, Sulfur Dioxide Absorption in Aqueous Solutions," Ph.D. Dissertation, University of Texas at Austin (1979).

Chang, C. S., and G. T. Rochelle, "SO_2 Absorption into Aqueous Solutions," *AIChE J.*, **27**, 292 (1981).

Chang, C. S., and G. T. Rochelle, "Surface Renewal Theory for Simultaneous Mass Transfer and Equilibrium Chemical Reaction," presented at AIChE 88th National Meeting, Philadelphia (June 8–12, 1980).

Danckwerts P. V., "Gas Absorption with Instantaneous Reaction," *Chem. Eng. Sci.*, **23**, 1045 (1968).

Eigen, M. K. Kustin and G. Maas, "Die Geschwindigkeit der Hydration von SO_2 in Wassriger Losung," *Z. Phys. Chem., Frankfurt*, **30**, 130 (1961).

Gane, R., and C. K. Ingold, "Electrometric Titration Curves of Dibasic Acids, Part IV," *JACS*, **53**, 2153 (1931).

Harned, H. S. and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold, NY (1958).

Hatfield, J. D., and J. M. Potts, "Removal of Sulfur Dioxide from Stack Gases by Scrubbing with Limestone Slurry: Use of Organic Acids," *Proceedings of Second International Lime/Limestone Wet-Scrubbing Symposium*, **I**, p. 263, APTD-1161, (1971).

Hatfield, J. D., Y. K. Kim and R. C. Mullins, "Study of the Effect of Organic Acids on the West Limestone Scrubbing Process," U.S. Environmental Protection Agency, APTD-1137, PB210-793 (1972).

Head, H. N., S. C. Wang, D. T. Rabb, R. H. Borgwardt, J. E. Williams and M. A. Maxwell, "Recent Results from EPA's Lime/Limestone Scrubbing Programs," *Proceedings: Symposium on Flue Gas Desulfurization—Las Vegas, Nevada, March 1979*, **I**, p. 342, EPA-600/7-79-167a (July, 1979).

Hollinden, G. A., N. D. Moore, and J. J. Schultz, "Removal of Sulfur Dioxide from Stack Gases by Scrubbing with Limestone Slurry: Effect of an Organic Additive at TVA Pilot Plant," Presented at Fourth Annual Environmental Engineering and Science Conference, Louisville, KY (1974).

Johnstone, H. F., and P. W. Leppla, "The Solubility of Surface Dioxide at Low Pressures. The Ionization Constant and Heat of Ionization of Sulfurous Acid," *JACS*, **56**, 2233 (1934).

Jeffery, G. H., and A. F. Vogel, "Dissociation Constants of Organic Acids, XI. Thermodynamic Primary Dissociation Constants of Some Normal Dibasic Acids," *J. Chem. Soc.*, 21 (1935).

Landolt-Bornstein Physikalisch-Chemische Tabbellen, Bd 11-7, p. 255, Spring, Verlag, Berlin, Germany (1960).

Le Bas, G., "The Molecular Volume of Liquid Chemical Compounds," Longman Green, London (1915).

Lewis, J. B., "Some Determination of Liquid-Phase Diffusion Coefficients by Means of the Improved Diaphragm Cell," *J. Appl. Chem.*, **5**, 228 (1955).

Lowell, P. S., D. M. Ottmers, K. Schwitzgebel, T. I. Strange and D. W. Deberry, "A Theoretical Description of the Limestone Injection—Wet Scrubbing Process," **I**, U.S. Environmental Protection Agency, APTD 1287, PB 193-029 (1970).

MacInnes, D. A., and T. Shedlovsky, "The Determination of the Ionization Constant of Acetic Acid, at 25°C, from Conductance Measurements," *JACS*, **54**, 1429 (1932).

Olander, D. R., "Simultaneous Mass Transfer and Equilibrium Chemical Reaction," *AIChE J.*, **6**, 2, 233 (1960).

Peaceman, D. W., "Liquid-Side Resistance in Gas Absorption with and without Chemical Reaction," Sc. D. Thesis, Mass. Inst. Tech., Cambridge, MA (1951).

Rabe, A. E., and J. F. Harris, "Vapor Liquid Equilibrium Data for the Binary System, Sulfur Dioxide and Water," *J. Chem. Engr. Data*, **8**, 333 (1963).

Rochelle, G. T., and C. J. King, "The Effects of Additives on Mass Transfer in $CaCO_3$ or CaO Slurry Scrubbing of SO_2 from Waste Gases", *Ind. Eng. Chem. Fund.*, **16**, 67 (1977).

Rochelle, G. T., and C. J. King, "Alternatives for Stack Gas Desulfurization by Throwaway Scrubbing," *Chem. Eng. Prog.*, p. 65 (February, 1978).

Tartar, H. V., and H. H. Garretson, "The Thermodynamic Ionization Constants of Sulfurous Acid at 25°C," *JACS*, **63**, 808 (1941).

Wasag, T., J. Galka, and M. Fraczak, "Effects or Organic Acids on the Kinetics of SO_2 Absorption," *Air Conservation*, **9**, 16 (1975).

Manuscript received November 26, 1979; revision received March 19, and accepted May 15, 1981

Analysis of Annular Bed Reactor for Methanation of Carbon Monoxide

A new reactor configuration, the annular bed reactor, is mathematically modeled to assess its capabilities as a CO methanation reactor. The results show that the reactor offers excellent temperature control characteristics and negligible pressure drop, and that it is a promising configuration for this as well as other reaction systems.

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SCOPE

It was the purpose of the present work to introduce a new reactor configuration, the annular bed reactor (ABR), and to assess its capabilities for use as a methanation reactor. This reactor is made up of an annular catalyst bed of very small particles next to the heat transfer surface with the inner core of the annulus packed with large, inert spheres. The main fluid flow is in the axial direction through the core where the inert packing promotes radial transport to the catalyst bed. The annular bed reactor is susceptible to deactivation as the tube wall reactor. However, the effect of deactivation on the overall reactor performance is less pronounced (in the same time span) in the ABR due to the large amount of catalyst.

CONCLUSIONS AND SIGNIFICANCE

Using a feed mixture of 25% carbon monoxide in hydrogen at 290-310°C and 2.17 MPa, the reactor model predicted near-isothermal, near-isobaric behavior in that maximal axial and radial temperature gradients were 10 and 4°C, respectively, while the pressure gradients never exceeded 1% of the inlet pressure. Large inert particles in the core increased exit conversion due to enhancement of radial transport processes. The reactor behavior was sensitive to the catalytic bed thickness. For a given reactor length, the exit conversion increased with increased bed thickness, but for a given mass of catalyst it was found that a longer thin bed outperformed a shorter thick bed due to the increased residence time. Increasing residence times, i.e., decreasing Reynolds numbers, were found to increase exit conversions and axial temperature gradients.

From the simulations presented in this work it can be seen that the annular bed reactor is a very promising configuration for the carbon monoxide methanation reaction.

INTRODUCTION

Due to the escalating demand for natural gas and the growing shortage of supply, there is considerable interest in the production of substitute natural gas (SNG) from coal. None of the state-of-the-art coal gasification processes can produce pipeline quality gas unless the gasifier effluent is subjected to methanation. The overall reactions of the methanation step are:

$$CO + 3H_2 = CH_4 + H_2O,\ \Delta H_r = -49.3 \text{ kcal/mol}, \quad (1)$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O,\ \Delta H_r = -39.5 \text{ kcal/mol}. \quad (2)$$

Owing to the highly exothermic nature of the reactions, temperature control of methanation reactors becomes difficult. Various reactor configurations such as the parallel plate and the coated tube wall (Haynes et al., 1977; Penline et al., 1979) have been proposed as methanation reactors because of their novel methods of heat removal. Penline et al. (1979) were able to successfully methanate high concentrations of CO (25% or less) in a coated tube wall reactor (TWR) but observed severe deactivation with feed sulfur concentrations around 66 ppb.

Another reactor system, the parallel passage reactor (DeBruijn et al., 1978), appears to be a likely candidate for accomplishing

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