Schluderberg, D. C., R. L. Whitelaw, and R. W. Carlson, "Gaseous Suspensions—A New Reactor Coolant," *Nucleonics*, 19, 67 (1961).

Sparrow, E. M., T. M. Hallman, and R. S. Siegel, "Turbulent Heat Transfer in the Thermal Entrance Region of a Pipe with Uniform Heat Flux," Appl. Sci. Res., Section A, 7, 37 (1957).

Tien, C. L., "Heat Transfer by a Turbulently Flowing Fluid-Solids Mixture in a Pipe," J. of Heat Transfer, Trans. ASME, Series C, 83, 183 (1961).

Tien, C. L., and V. Quan, "Local Heat Transfer Characteristics of Air-Glass and Air-Lead Mixtures in Turbulent Pipe Flow," ASME Paper No. 62-HT-15 (1962). Wahi, M. K., "Heat Transfer to Flowing Gas-Solid Mixtures," J. of Heat Transfer, Trans. ASME, Series C, 99, 145 (1977).

Wilkinson, G. T., and J. R. Norman, "Heat Transfer to a Suspension of Solids in a Gas," *Trans. Instn. Chem. Engrs.*, **45**, 314 (1967).

Wood, R. E., and W. H. Wiser, "Coal Liquefaction in Coiled Tube Reactors," Ind. Eng. Chem. Process Des. Dev., 15, 144 (1976).

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Interfacial Area, Bubble Coalescence and Mass Transfer in Bubble Column Reactors

Relationships are developed for determining interfacial areas as a function of bubble coalescence and for predicting liquid-film-controlled mass transfer in deep seal bubble column reactors. Interfacial area is inversely dependent on mean bubble size; the mass transfer constant is directly dependent on bubble size. A correction for enhancement due to liquid-phase reaction must be applied, and enhancement is shown to decrease with increasing bubble size.

Experimental measurements on the catalyzed rate of oxygen absorption from air in aqueous sodium sulfite solutions were made in a 0.299 m diameter × 9.14 m high glass column. Water and aqueous solutions of a surfactant and corn syrup were used to simulate ranges of surface tensions, densities, and viscosities. Perforated plates with 0.00635-m holes and 2.85% open area were inserted at 1.524-m spacing on half of the experimental runs to show the effects of gas redispersion. Two-phase flow velocities were adjusted to cover ranges of interest in full-scale, commercial bubble column reactor design.

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SCOPE

Reactions in which gas-liquid contacting is required for interphase mass transfer of a reactant are often carried out in deep seal bubble columns. Although reaction occurs in the liquid phase, the interphase mass transfer step is often a rate-limiting consideration in these systems.

The size requirement for reactors of this type is continually increasing, and reliable scale-up of performance from small-scale test data is a problem of ever-increasing importance.

Characterization of liquid-film-controlled mass transfer involves determination of two parameters: interfacial area a and the mass transfer constant k_L . Interfacial area decreases in deep seal contacting with increasing distance from the initial point of dispersion as bubble coalescence occurs. The overall mass transfer coefficient, which is the product $k_L a$, can decrease by an order of magnitude or more through a 10-m contacting zone as the result of bubble coalescence.

The mass transfer constant can be considerably enhanced over the value for purely physical absorption, where there is liquid-phase reaction. This effect increases with increasing reaction rate and is most pronounced when all the reaction occurs in the liquid film at the phase interface. Two studies on the prediction of interfacial area and mass transfer in gas-liquid contacting have been reported in the recent literature (Bhavaraju, Russell and Blanch, 1978; Mersmann, 1979). Both are based on small-scale test work and are useful for relatively low two-phase holdup times. They do not, however, cover changes that occur with bubble coalescence as holdup times are extended in deep seal contracting.

Calderbank et al. (1962) studied bubble coalescence in a cross-flow contactor. A rectangular column 0.1016×0.1016 m square in cross section and 3 m high was used. Gas was sparged in at the bottom; and liquid fed uniformly through one side over the full column height and withdrawn through the opposite downstream side. With this system balanced for uniform flows, aeration and interfacial areas were measured by light transmittance and gamma ray radiation techniques. Bubble coalescence was found to follow a first-order rate dependence on bubble concentration.

This study was undertaken to develop design procedures for predicting mass transfer performance in bubble-column reactors with two-phase cocurrent upflow, which is the configuration most common in industrial practice.

CONCLUSIONS AND SIGNIFICANCE

A procedure has been developed for predicting liquid-filmcontrolled mass transfer in deep seal reactors where transfer of a reactant occurs between gas and liquid phase in cocurrent upflow. Interfacial areas were found to be dependent on bubble coalescence which in turn follows a first-order dependence on bubble concentration. The first-order constant or frequency for bubble coalescence was correlated with two-phase velocity. The correlation has been developed for ranges of liquid-phase surface tensions, densities, and viscosities commonly found in

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practice and for both open columns and columns with perforated plates for gas redispersion.

Both interfacial areas and the enhanced mass transfer coefficients were obtained directly from mass transfer and aeration measurements in the cobalt-catalyzed oxidation of aqueous sodium sulfite solutions. Data on the rate constant and oxygen diffusivity for this model reaction system were taken from the literature (Linek, 1971; Reith, 1968). A rate dependence on sulfite concentration was observed and a correction factor to the rate expression obtained by trial and error best fit to overall performance. The "chemical method" used in this analysis was confirmed by checking interfacial areas calculated from the

correlation that was developed against the independent measurements made by Towell et al. (1965).

A few experimental measurements were made of mass transfer and aeration in copper-catalyzed oxidation of aqueous sodium sulfite solutions to show the comparison with a slower liquid-phase reaction effect. Enhanced mass transfer coefficients and chemical rate constants for the copper-catalyzed system were obtained using these data and interfacial areas calculated via the correlation discussed previously.

The enhanced mass transfer coefficients were found to be dependent on mean bubble size, and correlations were developed for both oxidation systems.

THEORETICAL BACKGROUND

Flow Regime

The two-phase flows in this study were chosen to cover conditions common in deep seal reactors, where gas-liquid contacting and mass transfer can influence overall rates.

Two vertical, two-phase flow pattern studies are reported in the recent literature. Cichy, Ultman and Russell (1969) modified the air-water chart developed by Govier et al. (1957) to include the effects of variations in physical properties. Oshinowo and Charles (1971) provide an independent analysis.

Both developments are based on data obtained in 0.0254 m i.d. vertical pipes, and the gas and liquid rates were substantially higher than those of this study. By Govier's classification, the flows of this study fall in the bubble, bordering on slug flow regimes. By Oshinowo's nomenclature, the flows are in the quiet and dispersed slug flow regimes. Quiet slug flow is defined as gas movement in large, well-defined bullet-shaped bubbles. Dispersed slug flow is described as similar but with froth formation at the trailing edges of the bubbles.

Aeration

A review of correlations reported in the literature for gas holdup in vertical two-phase flow along with recommendations on the preferred calculation procedure is available elsewhere (Miller, 1980).

Interfacial Area

Interfacial area determined in the various experimental runs of this study was determined by the "chemical method." This procedure is reviewed in standard texts (Pigford et al., 1975; Danckwerts, 1970). Briefly, this involves measurement of a liquid-film-controlled gas absorption accompanied by rapid depletion of the solute through reaction in the liquid film. The following simple mathematical representation is applicable presuming the film thickness to be very large relative to the depth of penetration of solute:

$$D\frac{d^2c}{dx^2} - k_n c^n = 0 (1)$$

The solution of this expression (with the boundary condition c=0 at $x=\infty$) for the concentration gradient evaluated at the interface, yields

$$\frac{dc}{dx}\Big|_{x=0} = \sqrt{\frac{2k_n c^{n+1}}{(n+1)D}} = \frac{N}{a(1-\phi)DV_1}$$
 (2)

from which,

$$a = \frac{N}{(1 - \phi)V_1 \sqrt{\frac{2k_n c^{n+1} D}{n+1}}}$$
(3)

If the reaction kinetics and solute diffusivity are known, interfacial area can be calculated from mass transfer measurements via Eq. 3

The absorption of oxygen in aqueous sodium sulfite solution catalyzed with cobaltous sulfate has been used as the model system for this determination. There is a long history associated with the use of catalyzed sodium sulfite oxidation for this purpose. Linek (1981) provides an excellent review and comprehensive bibliography. Cupric sulfate used as a catalyst in early studies (Cooper et al., 1944; Yoshida et al., 1960; Westerterp et al., 1963) was found to be much less effective and reliable for this purpose than cobaltous sulfate (de Waal and Okeson, 1966; Linek, 1966).

The sulfite oxidation has been determined to be tirst-order dependent on cobalt concentration and second-order dependent on oxygen below a partial pressure of 10⁵ Pa (Linek, 1970). At higher oxygen partial pressures, there is a shift to first-order oxygen dependency. Temperature and pH are also important control variables. The relationship developed by Linek (1971) for the low-pressure rate constant with a sulfite concentration of 0.795 kg-mol·m⁻³ follows:

$$\begin{aligned} k_2 &= 0.1440 \times 10^{11} c_{\text{Co}^{++}} \left\{ \frac{p_{\text{H}} - 7.9 + 0.04t}{0.6 + 0.04 t} \right\}^2 \\ &= \exp\left\{ -8,450 \left(\frac{1}{T} - \frac{1}{293} \right) \right\} \end{aligned} \tag{4}$$

Most of the work in this field has been done with 0.795 kg·mol- $\rm m^{-3}$ sodium sulfite. Wesselingh and Van't Hoog (1970) noted an increase in k_2 with decreasing sulfite concentration, however, and attributed this to an inhibiting effect of sulfite on oxygen solubility. Linek (1971) later showed this explanation to be insufficient and suggested that the effect could be partially the result of rate inhibiting impurities present in the sulfite. More recently, this latter explanation has come into question, and Linek (1981) concludes that the sulfite effect "has not yet been properly investigated and described."

In this study, the negative dependence on sulfite concentration was also observed and a multiplying factor extracted for Eq. 4 which provides the best overall fit to the data. As an independent check on the validity of this expression, the final correlation developed for interfacial area was tested against the results reported by Towell et al. (1965). Towell's interfacial area determinations were made by photographing air-water dispersions in cocurrent upflow through a vertical glass column and then scaling dimensions of the individual bubbles on the photographs.

Bubble Size

Mean bubble size is related to aeration and interfacial area as follows:

$$D_{BM} = 6\phi/a \tag{5}$$

Lehrer (1971) discusses the prediction of bubble size produced at the orifices of a sparger. He notes, however, that the relatively

large sizes predicted are really conceptual since breakup is almost immediate. In this study, results were found to correlate best with a minimum, initial bubble size. This minimum size is produced in the close vicinity of the sparger by the shearing action of the liquid feed. Coalescence then proceeds as the bubbles move upward. This conclusion is supported by the observation of Towell et al. (1965) that different sparger designs in their equipment had no effect on bubble size. Liebson et al. (1956) show the minimum bubble size for air-water to be 0.00450 m.

Mass Transfer

Ideally, mass transfer between phases in gas-liquid contacting is characterized by the Boussinesq (1905) equation,

$$N_{Sh} = \sqrt{\frac{4}{\pi}} N_{Pe}^{1/2} \tag{6}$$

The Peclet number $(N_{Pe} = D_{BM}u_t/D)$ contains the terminal bubble velocity of rise, which can be calculated from Mendelson's (1967) wave equation,

$$u_t = \left\{ \frac{2\sigma}{\rho_1 D_{BM}} + \frac{g D_{BM}}{2} \right\}^{0.5} \tag{7}$$

In practice, however, the mass transfer coefficient in the Sherwood number $(N_{Sh} = k_L D_{BM}/D)$ is dependent on mean bubble size. As bubble size increases, k_L increases because of increased interfacial fluctuations and distortions. Smaller bubbles tend to approach rigid spherical configurations for which k_L is smaller. The experimental k_L 's determined in this work have been referred to the correspoding values calculated from Eq. 6. These reduced k_L^* values, which can be used as correction factors in Eq. 6, have been correlated with D_{BM} as will subsequently be discussed.

EXPERIMENT

Apparatus

The equipment used in this study was the same as in the gas holdup and pressure drop work reported earlier (Miller, 1980). A schematic is shown in Figure 1. Air and liquid feeds were passed through a 0.229-m diameter \times 9.14-m-high glass column in cocurrent upflow. Vertical two-phase flow behavior is influenced by pipe size for diameters up to 0.1524 m as shown by Fair (1962) and Akita (1973). The 0.229-m diameter was chosen large enough to avoid any influence of wall effects on performance. Air was introduced through a 0.1270-m diameter 0.01270-m Schedule 40-pipe ring sparger with 96 0.003175-m diameter holes on the underside of the pipe. Liquid feeds were pumped in through a nozzle centered in the bottom head

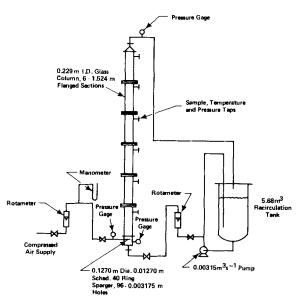


Figure 1. Equipment schematic.

of the column. The gas-liquid effluent from the top of the column was put to a 5.68 m³ hold tank, where gas disengaged and was vented. Liquid was then recirculated to the bottom of the column with a 0.00315 m³-s¬¹ pump. Both gas and liquid feed rates were measured with rotameters. Pressure was measured with Bourdon gages at top and bottom of the column, and temperatures were measured with in-line thermometers.

The column was built in six 1.524-m-high flanged sections. Nozzles at the top of each section and at the pump were used for liquid sampling.

During the last half of the experimental program, perforated plates were installed between the column sections. Each plate had thirty-seven 0.00635-m holes on 0.0349-m triangular spacing.

Procedure

The tank was charged with the liquid to be tested containing 0.8~kg-mol·m $^{-3}$ of Na_2SO_3 along with an oxidation catalyst.

A sample was taken of the tank mix and the pH determined. Air and liquid feeds were turned on to the column and rates adjusted to the desired settings. After equilibration, liquid samples were taken at each of the five positions in elevation on the column and at the feed point. Temperature and pressure readings were taken and the feeds then shut off. Aeration in the column was determined by measuring the static height of clear liquid after gas disengagement.

The samples were analyzed for sodium sulfite contents by the idiometric titration. The cumulative oxygen interphase mass transfer rate to each sample point was then calculated from the corresponding measured depletion of sulfite ion concentration.

Pressure at each sample point on the column was calculated by the method outlined earlier (Miller, 1980). The corresponding oxygen partial pressure in the gas phase was calculated by overall material balance, allowance being made for the saturation water content.

The mean driving force for oxygen mass transfer to each position in elevation on the column was calculated by graphically integrating the area under the plot of oxygen partial pressure vs. column height for each experimental run.

The Henry's Law coefficient for oxygen in the liquid being tested was calculated from,

$$H_{\rm O_2} = \exp(12.907 - 2832/T - 9.665c_{\rm SO_3} = +3.181c_{\rm SO_3} = /T)$$
 (8)

which was fit to the experimental data reported by Linek (1971). Based on data available in the International Critical Tables (1928), H_{0_2} was increased by 20% for those liquids tested with viscosities in excess of 0.01 Pa·s.

Overall liquid film controlled mass transfer coefficients were calculated assuming zero oxygen concentration in the bulk liquid:

$$k_{L}a = H_{O_{2}}N_{O_{2}}RT/(1-\phi)V_{1}P_{O_{2M}}$$
 (9)

Air and four different liquids were tested in the open column. The liquids included water, water with 0.005% Triton X-100, water with 40% corn syrup, and water with 60% corn syrup. The column with perforated plates was also tested with air and four different liquids. In this case, the first three liquids were repeated; the fourth was water with both 0.005% Triton X-100 and 40% corn syrup. The Triton X-100 surfactant was used to simulate lower surface tensions; corn syrup for higher density and viscosity. The ranges of these variables covered were: 0.030 to 0.064 N-m $^{-1}$; 1,000 to 1,280 kg·m $^{-3}$; and 0.0005 to 0.054 Pa·s.

The air-water runs were made at four gas rates at each of three liquid rates. Superficial liquid velocities averaged 0.00508, 0.01372, and 0.0503 m·s⁻¹; superficial gas velocities averaged 0.00559, 0.0300, 0.0625, and 0.1803 m·s⁻¹. All other runs were made at an average superficial liquid velocity of 0.01372 m·s⁻¹, each with four gas rates which averaged 0.00610, 0.0310, 0.0630, and 0.1814 m·s⁻¹.

The oxidation catalyst used for the major portion of this test work was 0.000550 N cobaltous sulfate. The runs with water and water with 0.005% Triton X-100 were repeated with 0.001 N cupric sulfate as the catalyst to get comparative rate information.

Analysis of Results

Interfacial Area

Interfacial areas were calculated for the various runs from the mass transfer rate and aeration measurements using Eqs. 3 and 4. The molecular diffusivity for oxygen in sulfite solutions in Eq. 3 was calculated from (Reith, 1968),

$$D_{\rm O_2} = 0.795 \times 10^{-7} T/\mu \tag{10}$$

TABLE 1. INITIAL BUBBLE SIZE

Air-Liquid System	D_{BO} , m
Water	0.00450
Water with 0.005% Triton X-100	0.00400
Water with 40% Corn Syrup	0.00475
Water with 60% Corn Syrup	0.00500

The absorption of oxygen from air in aqueous sulfite solutions being a liquid film controlled rate process, the mean oxygen concentration at the liquid interface for use in Eq. 3 was obtained from:

$$c_{\mathbf{O}_{2M}}^{\star} = P_{\mathbf{O}_{2M}} / H_{O_2} RT \tag{11}$$

Mean bubble size for each run was next calculated from aeration and interfacial area using Eq. 5.

Mean bubble sizes were observed to increase up through the aerated column as the result of bubble coalescence. Presuming coalescence to occur as a first-order rate dependence on mean bubble concentration,

$$N_{BM} = N_{BO} \exp(-f\theta) \tag{12}$$

Two-phase holdup time is calculated from,

$$\theta = 4V_{TP}/\pi d^2 u_{TP} \tag{13}$$

and two-phase velocity from,

$$u_{TP} = 4(W_g/\rho_g + W_1/\rho_1)/\pi d^2$$
 (14)

Bubble concentrations for either mean or initial conditions are obtained from,

$$N_B = 6\phi/\pi D_B^3 \tag{15}$$

Bubble coalescence frequencies back-calculated from Eq. 12

TABLE 2. COALESCENCE FREQUENCY CONSTANTS

Column	Air-Liquid System	C_1 , s·m ⁻¹	C_2 , $s^2 \cdot m^{-2}$
Open	Water	0.850	1.890
_	Water with 0.005% Triton X-100	0.500	1.255
	Water with 40% Corn Syrup	1.000	2.55
	Water with 60% Corn Syrup	1.055	2.70
	Water with 0.005% Triton X-100 and 40% Corn Syrup	0.535	1.245
Plates	Water	0.700	1.500
	Water with 0.005% Triton X-100	0.1765	0.255
	Water with 40% Corn Syrup	0.760	1.615
	Water with 0.005% Triton X-100 and 40% Corn Syrup	0.250	0.505

for all the experimental data were plotted versus two-phase velocity. N_{BM} was obtained using the measured values of D_{BM} in Eq. 15; N_{BO} , using the minimum air-water bubble size D_{BO} from Liebson et al. (1956). Slightly different D_{BO} values were found to provide the best fit for the other air-liquid systems studied. Minimum initial bubble sizes for the various systems are shown in Table 1

The correlation of coalescence frequencies with two-phase velocities was also substantially improved by correcting k_2 for sulfite concentration. The final form of Linek's (1971) equation for k_2 with the correction factor providing the best fit to all the data is,

$$k_2 = [0.263 - 0.1500c_{\text{SO}_{3M}} =]$$

$$\times 10^{11} c_{\text{Co}^{++}} \left[\frac{pH - 7.9 + 0.04t}{0.6 + 0.04t} \right]^{2}$$

$$\exp \left[-8450 \left(\frac{1}{T} - \frac{1}{293} \right) \right]$$
 (16)

Mean values of sulfite ion concentration in this study ranged from 0.1 to 0.7 kg·mol·m⁻³.

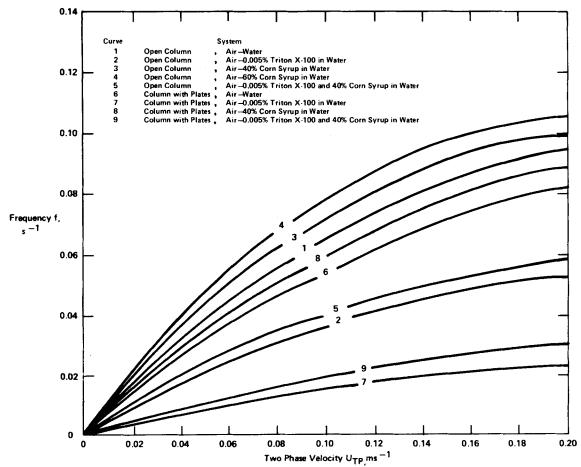


Figure 2. Coalescence frequency vs. two-phase velocity.

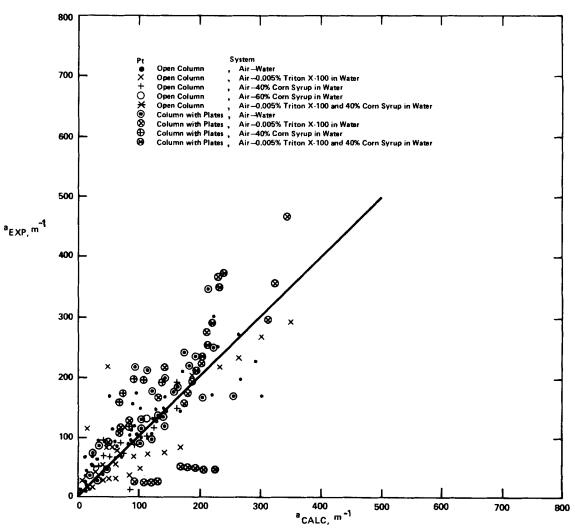


Figure 3. Experimental vs. calculated Interfacial areas for the data of this study.

The coalescence frequency vs. two-phase velocity curves are shown in Figure 2. As expected, the values differ for the open column and the column with perforated plates, as well as for each of the gas-liquid systems studied.

The coalescence frequencies have the following dependence on two-phase velocity,

$$f = C_1 u_{TP} + C_2 u_{TP}^2 (17)$$

and the constants for each system are given in Table 2.

The open column frequencies for water with 0.005% Triton X-100 and 40% corn syrup were obtained from the data taken in the bottom column section under the first plate on the runs made with perforated plate inserts.

The plot of experimental versus calculated interfacial areas in Figure 3 shows the effectiveness of the correlation. The experimental values for the various runs of this study were obtained from the mass transfer rate and aeration data using Eqs. 3, 10, and 16; the calculated values were obtained by applying Eqs. 11 through 15, 17, and 5.

As an independent check, the experimental interfacial area data of Towell et al. (1965) were compared with the corresponding values calculated using Eqs. 12 through 15, 17, and 5. Towell used an air-water system in a 0.406 m diameter \times 2.74 m high Plexiglass column. Mass transfer rate measurements were made by stripping $\rm CO_2$ from the liquid phase. Interfacial area measurements were made by photographic measurements as has been discussed. Three sparger types were used:

 Forty 0.001588-m holes on the sides of four radial branches from a center-feed pipe.

- 2. A single 0.00356- or 0.01016-m orifice centered in the column.
- 3. Twenty 0.00635-m holes in a cone-shaped cap on a 0.0762-m diameter pipe.

Superficial linear liquid velocities in the Towell work were 0.00254, 0.00711, and 0.01219 m·s⁻¹; and superficial gas velocities averaged 0.01778, 0.0721, 0.1448, and 0.290 m·s⁻¹. No significant differences in performance were detected resulting from the three different sparger types.

The plot of Towell's experimental interfacial areas versus the corresponding values calculated using the correlation developed in this study is shown in Figure 4.

Mass Transfer

For the cobalt catalyzed runs, values of the mass transfer coefficient were calculated from,

$$k_L = \sqrt{\frac{2k_2 c_{O_{2M}} D_{O_2}}{3}}$$
 (18)

These values referred to the corresponding constants calculated from the Boussinesq Eq. 6 are plotted vs. D_{BM} on Figure 5, which illustrates the characteristic increase in k_L^* with increasing bubble size,

$$k_{LCo}^* = 57.6 D_{BM}^{0.370} \tag{19}$$

Also shown is the curve of k_L^{o*} vs. D_{BM} derived in an earlier study (Miller, 1974, 1979) for stripping CO₂ from aqueous solution, a purely physical desorption process,

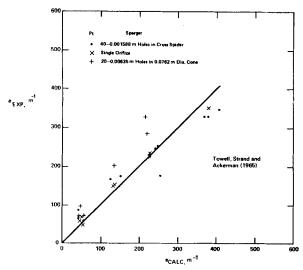


Figure 4. Experimental vs. calculated interfacial areas for Towell et al. (1965).

$$k_L^{o*} = 691 D_{BM}^{1.391} \tag{20}$$

The calculated Towell (1965) k_L^{o*} data for CO₂ stripping show a broad scatter (0.32 to 1.79) within a relatively narrow D_{BM} range (0.00415 to 0.0127 m), but generally confirm the placement of the k_L^{o*} curve.

The ratio of Eq. 19 to Eq. 20 is the Hatta number, which is a measure of the mass transfer enhancement resulting from chemical reaction,

$$N_{Ha_{Co}} = k_{L_{Co}}/k_L^o = 0.0834 \ D_{BM}^{-1.021} \tag{21}$$

Note that chemical enhancement decreases with increasing bubble size, and apparently disappears at a bubble size of about 0.10 m for the cobalt catalyzed oxidation.

A few runs were made with water and water with 0.005% Triton X-100 using 0.001 N cupric sulfate at the catalyst. The copper

catalyzed oxidation of aqueous sulfite is thought to be first-order dependent on oxygen and cupric ion concentrations (Westerterp et al., 1963; de Waal and Okeson, 1966). The mass transfer coefficient was calculated by dividing the measured $k_L a$ values from Eq. 9 by the corresponding interfacial areas calculated from Eqs. 12 through 15, 17, and 5.

The reduced k_{LCu}^* values are shown plotted vs. D_{BM} on Figure 6.

$$k_{LCu}^* = 15.46 D_{BM}^{0.303} \tag{22}$$

and,

$$N_{Ha_{Cu}} = k_{L_{Cu}}/k_L^o = 0.0224 \ D_{BM}^{-1.099}$$
 (23)

Chemical enhancement with copper is only about 0.4 that with cobalt and the enhancement effect apparently disappears at a bubble size about 0.033 m.

The first-order rate constants for copper catalyzed sulfite oxidation were back-calculated from Eq. 3 using measured mass transfer rates and aerations along with the calculated interfacial area values. The following first-order rate expression were derived,

$$k_1 = 0.460 \times 10^{15} c_{\text{Cu}}^{++} \exp(-6190/T)$$
 (24)

The activation energy is taken from Westerterp (1963); the pre-exponential constant was fit by trial and error to provide the best overall fit to the data.

The greater scatter in the copper catalyzed data partially reflects the fact that no correlation with sulfite ion concentration was attempted. These values ranged from 0.1 to 0.5 kg·mol·m⁻³ on the copper catalyzed runs.

RECOMMENDATIONS

The following procedure is recommended for predicting liquid film controlled mass transfer performance in bubble column reactors:

- 1. Calculate two-phase velocity from Eq. 14.
- 2. Calculate two-phase holdup time from Eq. 13.

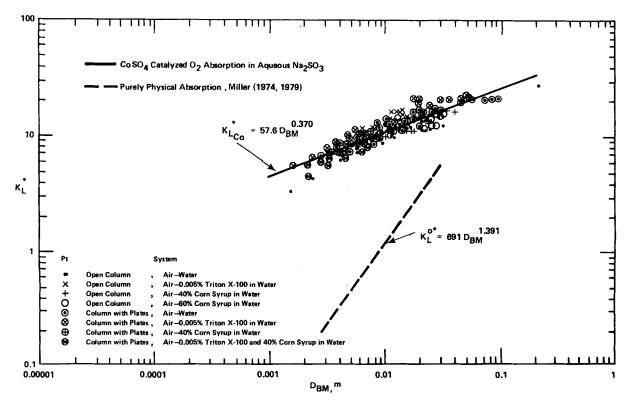


Figure 5. KL vs. DBM for COSO4 catalyzed O2 absorption in NA2SO3.

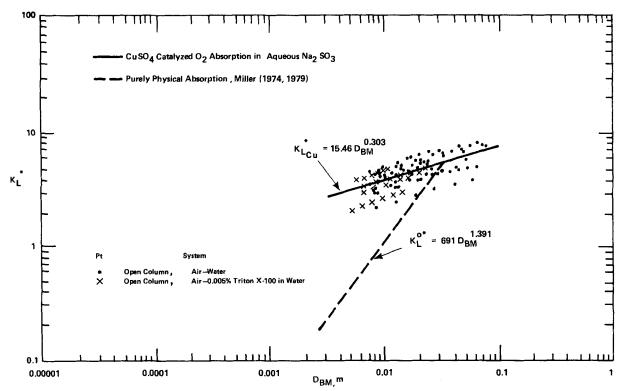


Figure 6. K_L^* vs. D_{B_M} for CUSO₄ catalyzed O_2 absorption in NA₂SO₃.

- 3. Obtain coalescence frequency using Eq. 17 with the appropriate constants.
- 4. Obtain gas holdup as outlined in the prior literature (Miller, 1980).
- 5. Calculate the initial bubble concentration using the appropriate minimum bubble size in Eq. 15.
 - 6. Calculate the mean bubble concentration from Eq. 12.
- 7. Get the mean bubble size using mean bubble concentration in Eq. 15.
 - 8. Obtain interfacial area from Eq. 5.
- 9. Calculate the Boussinesq mass transfer constant using Eq.
- 10. Apply the $k_L^{e^*}$ correction from Eq. 20 as a multiplying factor to the Boussinesq constant to get the corrected value for purely physical absorption.
- 11. Apply the appropriate Hatta correction as a multiplying factor to the constant for physical absorption (Eqs. 21 and 23) to get the constant with chemical enhancement.

The product of the mass transfer constant k_L (from step 10 for physical absorption or from step 11 for chemically enhanced mass transfer) by interfacial area a (from step 8) yields the overall mass transfer coefficient $k_L a$ for characterizing mass transfer performance.

Interfacial area is inversely dependent on mean bubble size (Eq. 5); and the mass transfer constant is directly dependent on D_{BM} (Eq. 20). Although these dependencies are opposed, the former effect predominates; and, as has been noted, the overall combined product $k_L a$ decreases as coalescence produces increased bubble size.

NOTATION

a	= interfacial area per unit aerated volume, m ⁻¹
C	= constant
c	= solute concentration, kg·mol·m ⁻³
D	= diffusivity m ² ·s ⁻¹
D_B	= bubble diameter, m
d	= diameter, m

$$f = \text{bubble coalescence frequency, } s^{-1} \\ g = \text{acceleration of gravity, } m^2 \cdot s^{-1} \\ H = \text{the equilibrium distribution kg·mol·m}^{-3} \text{ in gas per kg·mol·m}^{-3} \text{ in liquid} \\ k = \text{reaction rate constant, } (m^3 \cdot \text{kg·mol}^{-1})^{n-1} s^{-1} \\ k_L = \text{mass transfer rate constant, } m \cdot s^{-1} \\ N = \text{mass transfer rate, kg·mol·s}^{-1} \\ N_B = \text{bubble concentration, } m^{-3} \\ & \frac{\sqrt{\frac{2k_nc^{n-1}D}{n+1}}}{k_L^0}, \text{ Hatta number} \\ N_{Ha} = \frac{D_{BM}u_t}{D}, \text{ Peclet number} \\ N_{Sh} = \frac{k_LD_{BM}}{D}, \text{ Sherwood number} \\ n = \text{reaction order} \\ p = \text{partial pressure, Pa} \\ pH = \text{logarithm base 10 of the reciprocal of } c_{H+} \\ R = \text{gas constant, Pa·m}^3 \cdot \text{kg·mol·}^{-1} \cdot \text{K}^{-1} \\ T = \text{temperature, K} \\ t = \text{temperature, C} \\ u = \text{velocity, m·s}^{-1} \\ W = \text{flow rate, kg·s}^{-1} \\ \end{cases}$$

Subscripts

Co++ Cu++	= cobaltous ion
Cu++	= cupric ion
g	= gas
H ⁺	= hydrogen ion
l	= liquid
M	= mean
0	= initial
O_2	= oxygen
$SO_3^=$	= sulfite ion
TP	= two phase
1	= first order
2	= second order

Greek Letters

 θ = two-phase holdup time, s = viscosity, Pa·s μ = density, $kg \cdot m^{-3}$ ρ = surface tension, N·m⁻¹ = fraction gas holdup

Superscripts

- = Reduced or equilibrium quantity
- = purely physical absorption 0

LITERATURE CITED

- Akita, K., and F. Yoshida, "Gas Holdup and Volumetric Mass Transfer Coefficient in Bubble Columns," Ind. Eng. Chem. Process Design Develop., 12, No. 1, 76 (1973).
- Bhavaraju, S. M., T. W. F. Russell, and H. W. Blanch, "The Design of Gas Sparged Devices for Viscous Liquid Systems," AIChE J., 24, No. 3, 454 (1978).
- Boussinesq, J., "Calculation of the Cooling Effects of Fluid Streams," J. Math Phys. Appl., 6, 285 (1905).
- Calderbank, P. H., M. B. Moo-Young, and R. Bibby, "Coalescence in Bubble Reactors and Absorbers," Symp. on Drops and Bubbles, Cambridge University, England, 91 (1962).
- Cichy, P. T., J. S. Ultman, and T. W. F. Russell, "Two-Phase Reactor Design Tubular Reactors," Ind. Eng. Chem., 61, No. 8, 6 (1969).
- Cooper, C. M., G. A. Fernstrom, and S. A. Miller, "Performance of Agitated
- Gas-Liquid Contactors," *Ind. Eng. Chem.*, 36, 504 (1944).

 Danckwerts, P. V., "Gas-Liquid Reactions," McGraw-Hill, Inc. New York
- de Waal, K. J. A., and J. C. Okeson, "The Oxidation of Aqueous Sodium Sulfite Solutions," Chem. Eng. Sci., 21, 559 (1966).
- Fair, J. R., A. J. Lambright, and J. W. Anderson, "Heat Transfer and Gas Holdup in a Sparged Contactor," Ind. Eng. Chem. Process Design Develop., 1, No. 1, 33 (1962).
- Govier, G. W., B. A. Radford, and J. S. C. Dunn, "The Upwards Vertical
- Flow of Air-Water Mixtures," Can. J. Chem. Eng., 58 (1957).
 "International Critical Tables," 5, 15, McGraw-Hill, Inc., New York
- Lehrer, J. H., "Gas Holdup and Interfacial Area in Sparged Vessels," Ind. Eng. Chem. Process Design Develop., 10, No. 1, 37 (1971).

- Leibson, I., E. G. Holcomb, A. G. Cacoso, and J. J. Jacmic, "Rate of Flow and Mechanics of Bubble Formation from Single Submerged Orifices," AIChE J., 2, No. 3, 296 (1956).
- Linek, V., "Determination of the Phase Interface in a Gas Sparged Reactor Equipped with Mechanical Agitation," Chem. Eng. Sci., 21, 777
- Linek, V., and J. Mayrhoferova, "The Kinetics of Oxidation of Aqueous Sodium Sulfite Solution," Chem. Eng. Sci., 25, 787 (1970).
- Linek, V. and J. Tvrdik, "A Generalization of Kinetic Data on Sulfite Oxidation Systems," Biotech. and Bioeng., 13, 353 (1971)
- Linek, V., "The Oxidation of Aqueous Sulfite Solutions," Chem. Eng. Sci., 26, 491 (1971).
- Linek, V., "Chemical Engineering Use of Catalyzed Sulfite Oxidation Kinetics for the Determination of Mass Transfer Characteristics of
- Gas-Liquid Contactors," Chem. Eng. Sci., 36, No. 11, 1747 (1981).

 Mendelson, H. D., "The Prediction of Bubble Terminal Velocities from Wave Theory," AIChE J., 13, 250 (1967).

 Mersmann, A. "Design and Scale-Up of Bubble and Droplet Columns,"
- Chem. Ing. Tech., 49, No. 9, 679 (1977).
 Miller, D. N., "Scale-Up of Agitated Vessels Gas-Liquid Mass Transfer,"
- 20, No. 3, 445 (1974).
- Miller, D. N., "Gas Holdup and Pressure Drop in Bubble Column Reactors," Ind. Eng. Chem. Process Design Develop., 19, No. 3, 371 (1980).
- Miller, D. N., Letter to the Editor, AIChE J., 25, No. 1, 207 (1979).
 Oshinowo, T., and M. E. Charles, "Vertical Two-Phase Flow Part I Flow Pattern Correlations," Can. J. Chem. Eng., 52, 25 (1971).
- Reith, T., "Physical Aspects of Bubble Dispersions in Liquids," Ph.D. Dissertation, Delft University, Delft, The Netherlands (1968).
- Sherwood, T. K., R. L. Pigford, and C. R. Wilke, "Mass Transfer," McGraw-Hill, Inc., New York (1975).
- Towell, G. D., C. P. Strand, and G. H. Ackerman, "Mixing and Mass Transfer in Large Diameter Bubble Columns," AIChE Symp. Ser., No. 10 (1965).
- Wesselingh, J. A., and A. C. Van't Hoog, "Oxidation of Aqueous Sulfite Solutions: A Model Reaction for Measurements in Gas-Liquid Dispersions," Trans. Instr. Chem. Engrs., 48, T69 (1970).
- Westerterp, K. R., L. L. van Dierendonck, and J. A. de Kraa, "Interfacial Areas in Agitated Gas-Liquid Contactors," Chem. Eng. Sci., 18, 157
- Yoshida, F., A. Ikeda, S. Imakawa, and Y. Miura, "The Sulfite Oxidation Method . . . Oxygen Absorption Rates in Stirred Gas-Liquid Contactors, Ind. Eng. Chem., 52, No. 5, 435 (1960).

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