

# Effect of Solids on Oxygen Transfer in Agitated Three-Phase Systems

A dynamic response method was used to measure the volumetric mass transfer coefficient for oxygen in a mechanically agitated vessel containing an aqueous suspension of 66  $\mu\text{m}$  glass beads. At constant stirring speed and superficial gas velocity the volumetric gas transfer coefficient  $k_L a$  was found to decrease with solids loading. A generalized equation correlated the results in terms of the volume concentration of the solids, the total power input per slurry volume, and the superficial gas velocity.

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## Introduction

Processes that require the presence of gas, liquid, and solid phases are conducted in a variety of industries. Hydrogenation reactions in a slurry of catalyst particles in oil and aerobic fermentations in aqueous suspensions are common examples. The transfer of gas into the liquid is often the rate-limiting step. Consequently,  $k_L a$ , has been a subject of numerous studies. For oxygen transfer in gas-liquid systems, Van't Riet (1979) has reviewed measurement methods, and Shugerl (1981) has reviewed various  $k_L a$  correlations in stirred tanks. One correlation commonly employed for design purposes is of the form (Cooper et al., 1944):

$$k_L a = b(P/V)^x V_g^y \quad (1)$$

Addition of solids to a liquid clearly affects the gas transfer, yet only limited information is available, especially for high particle concentrations. Particle suspension behavior in three-phase stirred vessels was treated by Wiedman et al. (1985) and more recently by Nienow et al. (1986). Suspended solids most frequently studied were either microorganisms or inorganic and polymeric particles, which might be inert, reactive, or catalytic. Oxygen transfer into fermentation media has recently been reviewed (Kargi and Moo-Young, 1985; Charles, 1985). Suspensions in these cases may contain individual microbial, plant, or animal cells; cells immobilized on larger support particles; or rheologically complex filamentous organisms. Although our research interests are in oxygen transfer in bioreactors, the complexity of cellular systems suggested that systematic studies of the influence of solids begin with inert well-defined particles.

Studies involving defined particles are scattered and few in

number. Chandrasekaran and Sharma (1977) found that the  $k_L a$  of oxygen increased by as much as 60% in the presence of only 0.2 wt.% activated carbon. Similarly, Alper et al. (1980) reported that  $k_L a$  in slurries of 0.1–3.3 wt.% activated carbon were about 150% greater than those obtained in the presence of powdered quartz, sand, or oxirane-acrylic beads. Lee et al. (1982) used the absorption of carbon dioxide into a carbonate-bicarbonate solution to measure  $k_L a$  in the presence of 0–30% v/v glass beads or Orlon particles. The  $k_L a$  values, measured at a constant stirring speed, decreased nearly linearly with increasing solids. Greaves and Loh (1985) measured  $k_L a$  values for oxygen transfer to aqueous slurries containing large glass spheres (up to 20% v/v;  $d_p = 655$ – $1,300 \mu\text{m}$ ) and organic ion exchange resins (up to 30% v/v;  $d_p = 780 \mu\text{m}$ ). In both systems  $k_L a$  was found to decrease significantly after a certain level of solids and then level out. Gas holdup was decreased by the presence of glass beads but only slightly lowered by the ion exchange particles. Frijlink and Smith (1986) recently examined the effect of suspended solids on coalescence behavior in three-phase aqueous systems as reflected in gas-liquid mass transfer and gas holdup.

A few studies have been conducted on solids suspended in organic liquids. Joosten et al. (1977) measured  $k_L a$  for helium transfer to suspensions of glass beads, sugar, or polypropylene particles (0–40% v/v) in kerosene at a constant power input per slurry volume. The values measured increased somewhat when a small volume fraction of solids was added, but with further solids loading they remained constant until about 20% v/v. Beyond 20%  $k_L a$  declined with a severity that depended upon the density and size of the particles. Recently, Bartos and Satterfield (1986) investigated the effect of finely divided solids suspended in an organic liquid on the  $k_L a$  of helium. Both  $k_L a$  and  $a$  were reported to decrease linearly, at constant stirring speed, with

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increased solids loading (0–45% v/v), irrespective of particle density.

From the information currently available it is not yet possible to generalize the effects of particle size and density. Further, previous studies examined the effect of suspended solids on the volumetric mass transfer coefficient for fixed stirring speeds, gas velocities, or power input per unit volume. In this initial phase of our study we examined the effect of both gas velocity and power input for a given particle. Aqueous slurries of 66  $\mu\text{m}$  glass spheres containing NaCl at an ionic strength typical of a fermentation fluid were used. Although this particle diameter is larger than that of cells, it can reasonably correspond to the sizes of biomass support particles. Certainly the most significant application of oxygen transfer to aqueous slurries would involve bioreactors containing free or immobilized cells. Our continuing work will involve particles of density and size corresponding to cells as well as studies on cellular systems themselves.

## Experimental Method

### Apparatus

The determination of  $k_L a$  was accomplished with the apparatus shown in Figure 1. Glass beads were suspended in a fully baffled, cylindrical glass vessel equipped with a six-blade flat disk turbine. The dimensions of the vessel are:

$$D_T = 28.8 \text{ cm}$$

$$H_T/D_T = 1.0 \quad W_I/D_I = 0.20 \quad H_B/H_I = 0.47$$

$$D_I/D_T = 0.34 \quad L_I/D_I = 0.25 \quad H_I/D_T = 0.30$$

where  $D_T$  and  $D_I$  are respectively the tank and impeller diame-

ters,  $H_B$  and  $H_I$  are the baffle (or sparger) and impeller clearances,  $H_T$  is the height of ungassed slurry, and  $L_I$  and  $W_I$  are the blade length and width of the impeller.

Four baffles were mounted on the perforated cover of the vessel and were separated from the vessel wall by a clearance of 2 mm. The vessel, fitted with an acrylic dished bottom to aid in solids suspension, was maintained at  $25.0 \pm 1.5^\circ\text{C}$  by means of electric heating tape wound around the external wall of the vessel. Agitation was provided by a Chemineer agitator (model ELB), which consisted of a  $\frac{1}{4}$  hp motor and a planetary transmission system with a variable speed of 0 to 1,100 rpm. The motor and transmission were mounted on a drive base that rested on a thrust bearing. An arm on the drive base was connected to a horizontally mounted force gauge. The impeller rotational speed was measured with a stroboscope.

Air or nitrogen, filtered and metered by calibrated rotameters, was introduced into the vessel through a ring sparger having a diameter  $\frac{1}{10}$  that of the impeller and located approximately halfway between the impeller and the bottom. The sparger ring contained 11 equally spaced 1.02 mm dia. holes in the underside. A mercury manometer measured inlet pressure, and thus clogging of the sparger by the glass beads could be detected. To eliminate surges when switching gas streams, a Whitey four-way air-actuated valve was used.

A polarographic dissolved-oxygen probe (YSI model 5739), attached to a metal rod, was introduced to the vessel through a transparent plastic cylinder located in the space between the liquid level and cover lid of the vessel. The probe was covered with a 0.051 mm thick Teflon membrane, which has sufficient mechanical strength in the agitated slurry as well as a short response time. The gas stream not being directed to the sparger was fed into this cylinder through two openings. The probe was

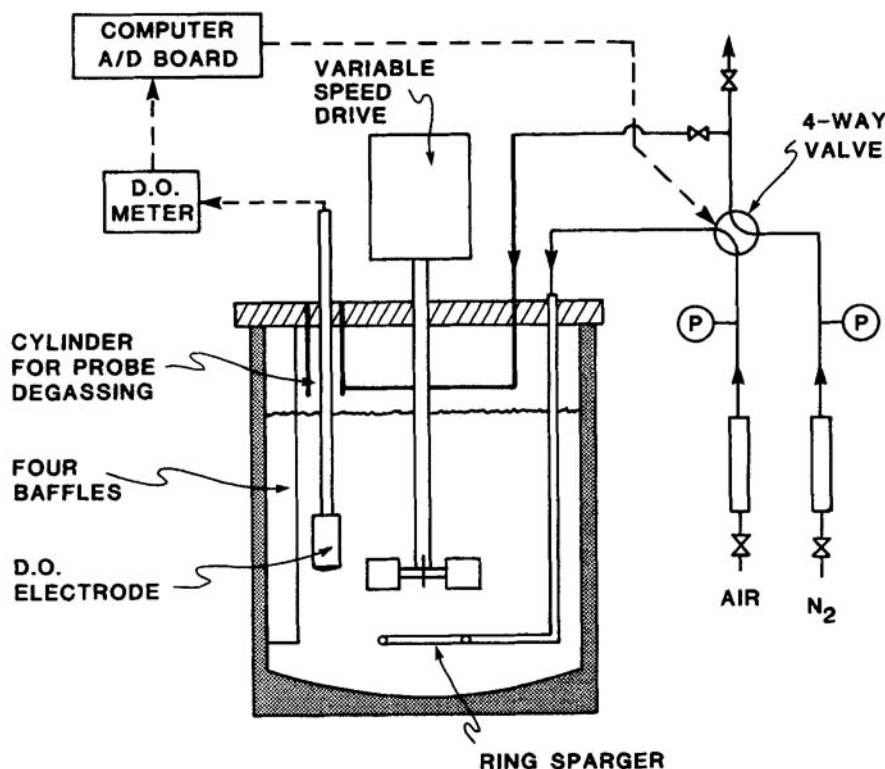


Figure 1. Apparatus for  $k_L a$  and mixing power determination.

connected to an oxygen analyzer (YSI model 54 ARC) and the signal was amplified by an Omega OMNI-AMP thermocouple amplifier and sampled every 0.54 s by a grounded Cyborg ISAAC data acquisition and control system operated by an Apple II microcomputer.

The soda-lime glass beads used had a particle density of 2.46 g/cm<sup>3</sup>, a mean diameter of 66 μm, a size range of 44–88 μm (90%), a spherical shape (90%), and a hardness value of 6 moh. After each set of runs at a particular solids concentration, a sample of the suspension was checked with a phase contrast microscope and neither attrition nor aggregation was observed. Before use, the beads were washed four times in distilled water or solutions of NaCl. Distilled water was frequently added to compensate for evaporation.

Conductivity measurements, occasionally done on the suspension liquid, indicated that the levels of residual ionic impurities from the beads and uncompensated evaporation were negligible.

### Measurement of power input and $k_L a$

Power input and  $k_L a$  were measured for each of the solids concentrations, 0, 10, 20, 30, and 40% v/v; superficial gas velocities, 0.36, 0.65, and 1.13 cm/s; and stirring speeds, 600, 650, 700, 750, and 800 rpm. The gas velocities were equivalent to gas flow rates of 0.85, 1.51, and 2.63 vvm (see Notation), respectively. In all experiments the sum of the volumes of the condensed phases—liquid and solids—was kept constant at 16.8 L.

Determination of  $k_L a$  at each experimental condition by the dynamic method required measurement of the probe response to:

1. A step change in the composition of dissolved gas in the probe environment, and
2. A step change in the composition of the inlet gas to the vessel (Dang et al., 1977)

The response to the step change in the probe environment permitted a determination of the significance of the probe response time with respect to the response to a step in the gas composition. The probe response measurement was accomplished by rapidly dropping a deoxygenated probe (upon computer signal) from the cylinder above the liquid into the oxygenated slurry. The probe was stopped mechanically at its final position in the tank at the level of the impeller discharge. A 1 s lag was used to compensate for the time it took for the probe to reach its final position after the signal had been initiated.

Prior to the recording of probe response to a step change in the inlet gas, the slurry and the immersed probe were first deoxygenated with nitrogen. At a computer controlled command, the four-way valve switched between the two gas streams and, simultaneously, recording of the probe signal began. The flow rates of the two gases were kept identical in order to avoid a disruption of the hydrodynamics of the three-phase system while making the switch. Since the valve was located very close to the vessel, the maximum time required for the gas to reach the sparger was only 0.2 seconds. The probe signals were subsequently normalized, numerically integrated, and processed to estimate the parameters required for the determination of  $k_L a$  using moment analysis.

The impeller power was determined from the measured torque and the stirring speed. The gas power was computed as the expansion work across the unaerated slurry. The gas holdup was determined visually. The turbine speeds at which the solids

were fully suspended in the absence and in the presence of gas were visually determined.

### Mathematical Model

The determination of the volumetric mass transfer coefficient depends on appropriate models for the gas and liquid phases. For this purpose, pseudosteady-state methods or dynamic response techniques have been used. Van't Riet (1979) reviewed the experimental methods for  $k_L a$  measurement and recommended dynamic response techniques on the condition that probe response time and gas phase residence time were taken into account. Ruchti et al. (1981) compared various types of dynamic response models and found that the model of Dang et al. (1977) provided a satisfactory combination of accuracy and simplicity. The latter was therefore adopted in this study with the following assumptions:

1. The liquid and gas phases are well mixed
2. The probe electrode responds as a first-order system with a time constant  $\tau_E$
3. The liquid film adjacent to the membrane responds as a first-order system with a time constant  $\tau_F$
4. The hydrodynamics are unchanged by the step input in composition
5. The counterdiffusion of nitrogen is negligible, as verified by Linek et al. (1982)

Accordingly, the oxygen mass balances are:

Gas phase:

$$\frac{dC_G}{dt} = (C_O - C_G)/\tau_G - k_L a(C_L^* - C_L)V_L/V_G \quad (2)$$

Liquid phase:

$$\frac{dC_G}{dt} = k_L a(C_L^* - C_L) \quad (3)$$

where  $C_L^* = RTC_G/H$

Liquid diffusion film:

$$\frac{dC_F}{dt} = (C_L - C_F)/\tau_F \quad (4)$$

$$\frac{dC_E}{dt} = (C_F - C_E)/\tau_E \quad (5)$$

The initial conditions are:

$$t = 0; \quad C_L = C_F = C_E = 0; \quad C_G = C_G^0$$

This system of four linear and coupled differential equations was treated according to the method of Dang et al. based on moment analysis. The method results in an expression for the zeroth moment,  $\alpha_0$ .

$$\alpha_0 = \frac{1}{k_L a} + \frac{RT}{H} \frac{V_L}{V_G} \tau_G + \tau_G + \tau_E + \tau_F \quad (6)$$

$\alpha_0$  is equal to the area between the response curve of the normalized probe signal  $\bar{C}_E = C_E/C_{E,\infty}$  vs.  $t$  and the  $\bar{C}_E = 1.0$  line, i.e.,

$$\alpha_0 = \int_0^\infty (1 - \bar{C}_E) dt \quad (7)$$

A similar treatment for the response of only the probe (membrane plus diffusion film) to a change in its environment leads to:

$$\alpha_{0E} = \tau_E + \tau_F = \int_0^\infty (1 - \bar{C}_E) dt \quad (8)$$

Thus, by subtracting the area of the probe response curve from that of the response to a step change in inlet gas,  $k_L a$  can be readily computed, if  $\tau_G$  is independently measured.

$$\Delta\alpha = \frac{1}{k_L a} + \frac{RT}{H} \frac{V_L}{V_G} \tau_G + \tau_G \quad (9)$$

Figure 2 shows typical computer-sampled data of the oxygen probe response under three different conditions. The time constant for the probe,  $\tau_E + \tau_F$ , was 5 s as determined from curve *a*, which shows the response of a deoxygenated probe suddenly immersed in an agitated (700 rpm), air-sparged ( $V_s = 0.65$  cm/s) solution of 0.1 M NaCl saturated with oxygen. Further, the probe time constant measured in solutions and suspensions under various agitation and aeration conditions was substantially the same. This indicated that the membrane resistance dominated. Nevertheless, the probe response was measured under each condition. It should be noted that only the sum of  $\tau_E$  and  $\tau_F$  is needed to determine  $k_L a$ . Curve *b* is the response to a step change in the inlet gas composition fed to a clear solution. The areas above curves *a* and *b* are given by Eqs. 8 and 7, respectively, and their difference, expressed by Eq. 9, is represented by the hatched region in the figure. Curve *c* is the response to a step change in inlet gas fed to a 40% v/v slurry. The difference in areas for curves *b* and *c* represents the effect of solids under identical stirring and aeration conditions.

The determination of  $k_L a$  also requires a knowledge of the gas residence time,  $\tau_G$ , which was calculated from the measured gas flow rate and holdup. The holdup was determined by visual observations in the presence and absence of gas flow. Measured holdups ranged from 0.03 to 0.07 volume gas per volume of aerated slurry (Mills, 1986). Holdup increased with increasing gas velocity or agitation. As the solids content increased, the holdup declined at an increasing rate with a total reduction of about 50% at 40% v/v solids. Although the visual estimation of holdup was imprecise ( $\pm 20\%$ ),  $\tau_G$  typically accounted for less than 20%

of  $1/k_L a$ . Therefore, this measurement uncertainty introduced less than a 4% uncertainty for  $k_L a$ .

As an example of the ability of the model to represent the system response, the lines drawn through the data points in Figure 2 are computed from the model equations using the calculated values of  $k_L a$ ,  $\tau_E$ ,  $\tau_F$ , and  $\tau_G$ . The fit is quite satisfactory over time, thus lending validity to the model assumptions.

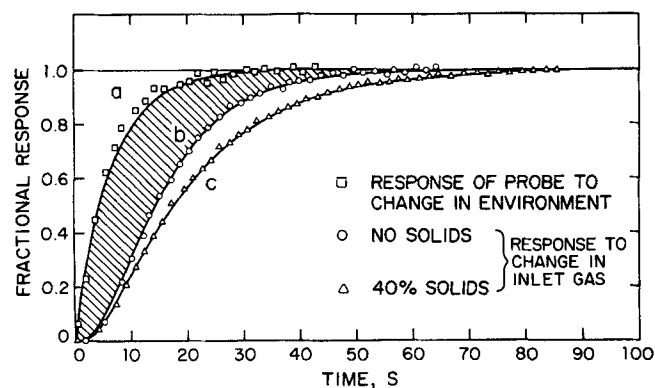
## Results and Discussion

Prior to measurement of the gas-liquid transfer rates, care was taken to ascertain that both the gas and the solids were well distributed in the slurries under the mixing conditions studied. A minimum stirring speed of 600 rpm was chosen because it provided a tip speed in excess of the critical tip speed necessary to insure a well-mixed gas phase (Hanhart et al., 1963). This minimum speed was found to be much higher than the speed required to prevent any particles from resting on the bottom of the vessel for longer than 1 s under ungassed or gassed conditions (Zwietering, 1958; Chapman et al., 1983a). The minimum impeller speeds required to achieve suspension in ungassed and gassed ( $V_s = 1.13$  cm/s) were found to be 200 and 360 rpm, respectively. In both cases the suspension speeds were found to be essentially independent of solids concentration. Zwietering and Chapman et al. (1983a) found slight solids dependencies, which would have been difficult to detect with the side viewing of solids suspension employed here. Since it has previously been established that the minimum stirring speed for complete gas dispersion in slurries is less than that for complete solids suspension (Chapman et al.) our experiments conducted at agitation speeds of 600–800 rpm should correspond to complete gas dispersion and mixing as well as complete solids dispersion. Furthermore, to minimize contributions from surface aeration, the lowest superficial velocity was chosen according to the flow number criterion,  $Q/ND_i^3 > 0.015$  (Chapman et al., 1980).

### Volumetric mass transfer coefficients in slurries of glass beads

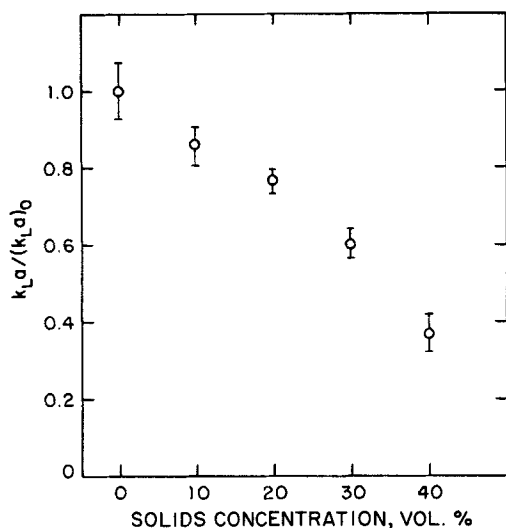
The suspension liquid was chosen to be an aqueous solution of NaCl in deionized water to override the influence of any electrolytic contaminant associated with the glass beads. However, the presence of ions in water is known to reduce bubble size by reducing the coalescence rate (van't Riet, 1979) resulting in larger  $k_L a$  values. Our measurements of  $k_L a$  in clear solutions at 650 rpm and  $V_s = 0.65$  cm/s were 0.075, 0.120, 0.175, and 0.175 s<sup>-1</sup> at NaCl concentrations of 0, 0.1, 0.25, and 0.5 M, respectively. The intermediate concentration of 0.1 M was chosen to avoid the lesser precision of the method when measuring higher oxygen transfer coefficients; in addition, this concentration is representative of the ionic strength of fermentation liquids.

A typical example of the overall effect of the various concentrations of glass beads on the observed mass transfer coefficient at 800 rpm and gas velocity of 1.13 cm/s is shown in Figure 3. The presence of the particles reduced  $k_L a$  significantly with respect to that of the clear solution (63% for 40% v/v solids). A similar total decrease was reported by Lee et al. (1982) who observed, unlike in our study, a steeper decline in  $k_L a$  values at low solids content. Frijlink and Smith (1986) reported a relative decrease of  $k_L a$  of approximately 20% in the presence of 20% v/v glass beads of either 45 or 120  $\mu$ m dia. A similar result can



**Figure 2. Normalized response of a dissolved oxygen probe immersed in three environments.**

—○— model prediction of response for determined values of  $k_L a$ ,  $\tau_E$ ,  $\tau_F$ ,  $\tau_G$ ; hatched area given by Eq. 9



**Figure 3. Overall effect of solids on  $k_L a$  of slurries with respect to clear liquid ( $k_L a$ )<sub>0</sub> at  $N = 800$  rpm,  $V_s = 1.13$  cm/s.**  
Bars = 95% confidence limits

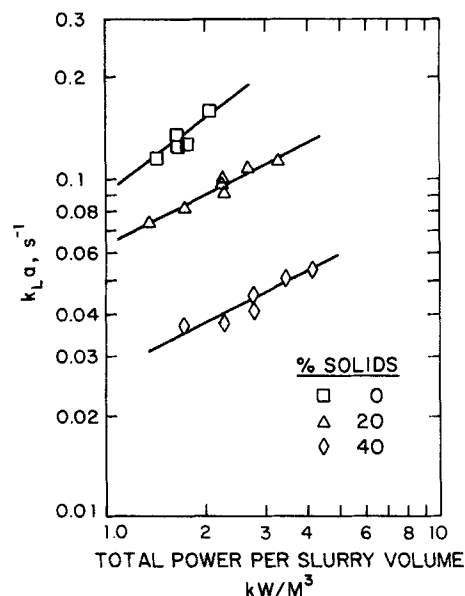
be seen in Figure 3 for the 66  $\mu$ m dia. glass beads employed in our study. The linear drop of  $k_L a$  at constant agitation rate, measured by Bartos and Satterfield (1986) in suspensions of solids in an organic liquid has already been mentioned. However, in contrast with the monotonic decrease of  $k_L a$  with solids loadings observed by the above investigators as well as by us, Joosten et al. (1977) and Chapman et al. (1983b) reported definite ranges of solids concentrations—below 20 and 3%  $V$ , respectively—in which  $k_L a$ , measured at constant power input, was nearly constant or showed a slight increase.

#### Correlation for each solids concentration

The measured  $k_L a$  values were correlated for each solids concentration in the form of the multiplicative model involving power input per unit volume and superficial gas velocity, Eq. 1. Most previous studies used the mechanical impeller power input  $P_I$ , while only a few (Joosten et al., 1977) used the total power input  $P_T$ , which includes the gas expansion power. In our experiments,  $P_T$  was used although the contribution from the gas power did not exceed 15%. The reference volume for  $P_T$  was selected to be the volume of liquid plus solids. The interfacial area per unit volume was also referenced to the liquid plus solids volume.

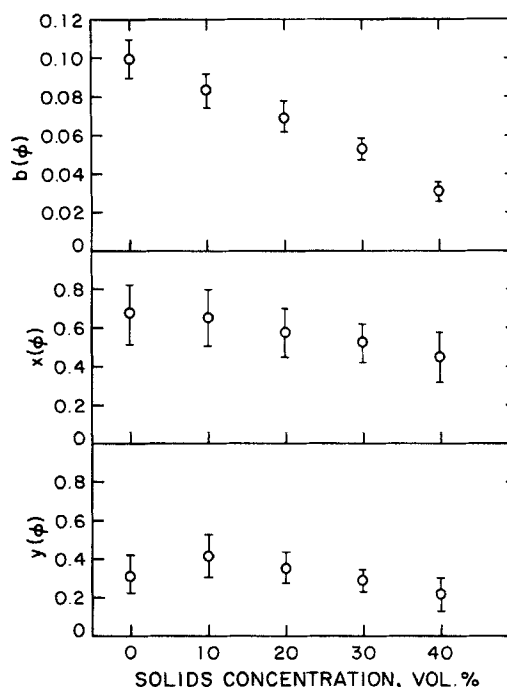
The measured  $k_L a$  values were found to correlate linearly with the total power per unit volume in a log-log plot, at a given superficial velocity and solids concentration. Figure 4 is an example of such a plot for a clear liquid and two slurries aerated at  $V_s = 0.65$  cm/s.

Multivariable linear regression analysis was performed for all data at each level of solids concentration using Eq. 1. The leading coefficient,  $b$ , and the exponents  $x$  and  $y$  are depicted with their 95% confidence intervals in Figure 5 for each solids concentration. The multiple correlation coefficients (Draper and Smith, 1981) were 0.910, 0.924, 0.942, 0.954, and 0.901 for, respectively, 0, 10, 20, 30, and 40% solids. The leading coefficient and the exponents are all dependent on solids concentrations. The coefficient  $b$  decreased almost linearly as particle



**Figure 4. Effect of total power input on volumetric mass transfer coefficient in liquid and in slurries air-sparged at  $V_s = 0.65$  cm/s.**

concentration increased, while  $x$  and  $y$  vary within relatively narrow limits around the corresponding values for the liquid alone. A slight change in  $x$  and  $y$ , as exponents, may in theory exert a noticeable impact on the magnitude of  $k_L a$ . However, the statistical significance of this impact is diminished because of the substantial overlap of the confidence intervals of all exponents. This and the narrow variation of  $x$  and  $y$  have prompted



**Figure 5. Variation of parameters of Eq. 1 with solids loading.**  
Bars = 95% confidence limits

us to adopt a unifying approach: all experimental data were re-analyzed while imposing the exponent values of the clear liquid phase for  $P_T/V$  and  $V_S$ .

### Unified $k_L a$ correlation

Imposing the exponents of the clear liquid implies that the effect of the solids on  $k_L a$  would be attributed primarily to the coefficient  $b$ . (The solids content also increases  $P_T$  at a given  $V_S$  and  $N$ ). Another regression analysis was performed on all data, and this resulted in the relationship between a new coefficient  $B$  and the volume percentage  $\phi$  of solids. Figure 6 shows the excellent fit of  $B(\phi)$  to a linear relationship, as evidenced by the high correlation coefficient of 0.996. The unified  $k_L a$  correlation for the glass beads suspension can now be represented by:

$$k_L a = (0.10 - 0.0018\phi) \left( \frac{P_T}{V} \right)^{0.67} V_S^{0.31} \quad (10)$$

The effectiveness of this correlation is demonstrated in Figure 7, in which  $k_L a$  values computed from Eq. 10 are compared with the corresponding measured values. The measured values are most scattered at 0% solids because the larger values for  $k_L a$  (smaller values of  $1/k_L a$ ) that occur there have the largest relative error when calculated by the method of moments. The correlation coefficient is 0.92 and the maximum deviation is  $\pm 20\%$  for this correlation, as compared to 0.98 and  $\pm 16\%$  for the correlation with exponents depending upon  $\phi$ . Thus, the assumption that the exponents  $x$  and  $y$  are independent of solids concentration is pragmatically justified.

An important implication of the  $k_L a$  correlation, Eq. 10, concerns the change in operating conditions necessary to maintain a certain  $k_L a$  value. Figure 8 indicates the computed total power consumption necessary to maintain a  $k_L a$  value of  $0.1 \text{ s}^{-1}$  in agitated slurries for several superficial gas velocities. Up to solids concentration of 30%  $V$ , only a modest increase in power is required. However, as the solids loading approaches 40%, a drastic increase is needed. Furthermore, in a biological system

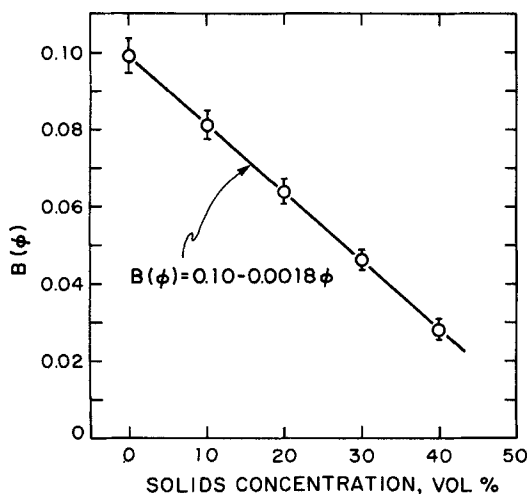


Figure 6. Variation of modified coefficient  $B$  in Eq. 1 with solids loading.

Bars = 95% confidence limits

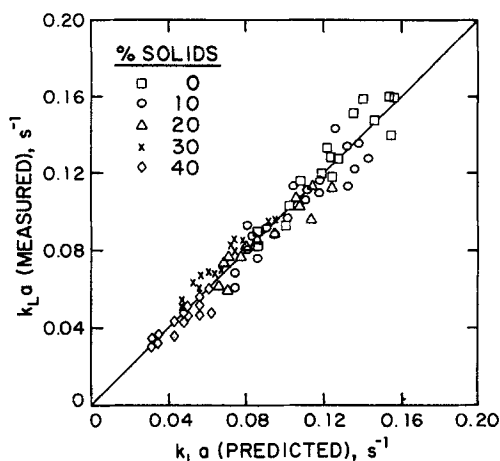


Figure 7. Comparison of measured values of  $k_L a$  with values predicted by Eq. 10.

an increase in solids (cells) implies an increased oxygen demand, so that  $k_L a$  or the driving force for oxygen transfer must be increased. Unreasonably large power inputs would be required.

### Overall effect of solids on $k_L a$

The presence of particles may influence gas transfer rate by affecting either  $k_L$  or  $a$ . Frijlink and Smith (1986) observed that the relative  $k_L a$  decrease in suspensions of glass beads in either water or a salt solution followed the same pattern, thus indicating that the  $k_L a$  reduction is more a function of the added solids than of the inherent properties of the liquid. Inert solids may alter  $k_L$  by modifying interfacial turbulence (Kada and Hanratty, 1960), or by creating a diffusion blocking effect (Lee et al., 1982). Since increased interfacial turbulence appears to occur only for small solids loadings (0.1–2.5% v/v), it may account for the small increases in  $k_L a$  observed by Joosten et al. (1977) but

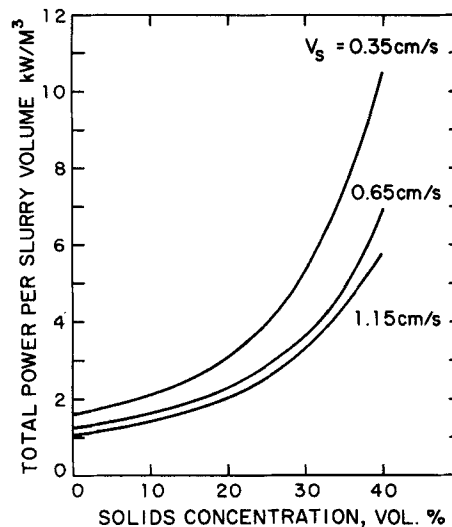


Figure 8. Total power input required to obtain a  $k_L a$  value of  $0.1 \text{ s}^{-1}$  in slurries sparged at various superficial velocities, as predicted by Eq. 10.

does not appear relevant to our studies at high solids concentrations. The reduction of  $k_L$  due to the blocking effect proposed by Lee et al., (1982, 1974) could be applicable to our results but requires an independent measure of  $k_L$  or  $a$  to be tested.

The specific interfacial area,  $a$ , is most likely affected by the presence of inert solids through an increase in the apparent viscosity and altered bubble coalescence rates (Lee et al., 1974). Bartos and Satterfield (1986) stated that a change in mass transfer parameters resulting from an increase in viscosity depends upon whether the viscosity increase is caused by the addition of solids or by the addition of a high-viscosity fluid. Indeed, while Sharma and Mashelkar (1968) demonstrated an increase in interfacial area with increased viscosity for a glycerol-water mixture in a bubble column, Gollakota and Guin (1984) reported a decrease in  $a$  with increased solids loadings.

The origin of the decrease of the volumetric mass transfer coefficients with increased glass bead concentrations in the present study is also believed to be due primarily to the decrease in interfacial area. The decrease of  $a$  probably reflects the decrease in gas holdup with increased solids concentrations. For each stirring speed, a systematic decrease of gas holdup was observed for all suspensions at each level of gas flow rate. The general pattern consisted of a moderate decrease in the range of 0–30% solids followed by a steeper decline to 40% (Mills, 1986). Interestingly, Lee et al. (1982) reported a reverse pattern: a steep decrease for 0–20%, followed by a moderate decline to 50%. However, their experiments were conducted in a regime where surface aeration could be important. On the other hand, Bartos and Satterfield observed little change in gas holdup in the range of 0–45% solids.

The rheological behavior of suspensions may change in the presence of high solids loadings. Rutgers (1962) reviewed experimental results and viscosity correlations and reported that many investigators observed a Newtonian behavior of slurries up to a volume concentration of 25% and several others found such a behavior up to 50%. A dispersion in a nonviscous Newtonian medium of smooth and nonaggregating rigid spheres that are wetted and electrically neutral may exhibit Newtonian behavior even at a high solids concentration. The suspensions used in the present study comply with these characteristics. Therefore, correlation of the behavior of the concentrated slurries of 30 and 40% in a manner similar to the more dilute ones was possible.

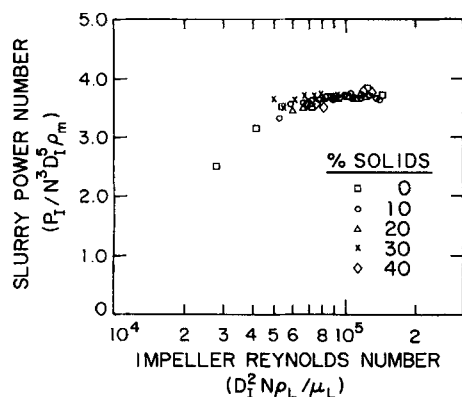


Figure 9. Correlation of slurry power number with impeller Reynolds number.

### Estimation of $k_L a$ in solids suspensions

The use of Eq. 10 for estimating a  $k_L a$  value in a solids suspension requires a knowledge of the gassed power input as a function of the operating conditions and vessel geometry. The impeller power number of the various unaerated slurries used in this work is correlated in Figure 9 with the impeller Reynolds number. The latter was calculated using the liquid density, while the power number employed the mean bulk density  $\rho_m$  as suggested by Greaves and Loh (1984).

$$\rho_m = 0.01 \phi \rho_s + (1 - 0.01 \phi) \rho_L \quad (11)$$

The clear solution viscosity was incorporated into the Reynolds number because no viscosity measurements were made and because viscosity correlations for high solids concentrations may not be reliable (Rutgers, 1962). In fact, the use of suspension physical properties in the impeller Reynolds number is not essential since the power number is independent of Reynolds number in the turbulent regime (Greaves and Loh). This is illustrated in Figure 9, in which the power number for all slurries had a value of approximately 3.7 whenever  $N$  exceeded 250 rpm.

The ratio of gassed to ungassed impeller power observed in this work correlated with flow number for each gas velocity, Figure 10. The values for slurries clustered about the values for clear liquid in agreement with the results of Greaves and Loh. The values reported in Figure 10 are only for stirring speeds in which the solids are fully suspended (600–800 rpm).

Figures 9 and 10, along with Eq. 10 may be used for estimating  $k_L a$  for a slurry of known solids concentration to be stirred at a given rate and aerated at a given superficial velocity.

### Conclusions

Equation 10 effectively correlates ( $\pm 20\%$ ) the volumetric oxygen transfer coefficient with power input and superficial velocity for solids concentrations up to 40% by volume. The presence of high volumetric concentrations of solids causes a significant reduction in the mass transfer coefficient. As particle size, density, and shape have not been investigated, the correlations for  $k_L a$  and power in slurries presented here are restricted to slurries of 66  $\mu\text{m}$  dia. glass spheres in 0.1 M NaCl solutions.

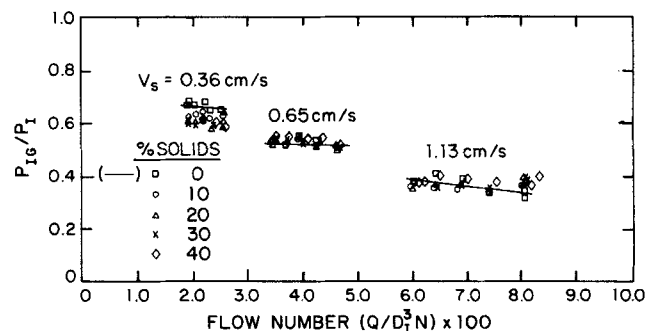


Figure 10. Correlation of ratio of aerated to unaerated impeller power with flow number for liquids and slurries.

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## Notation

$a$  = interfacial area per volume of slurry,  $\text{m}^2/\text{m}^3$  solid plus liquid  
 $b$  = leading coefficient function, Eq. 1  
 $B$  = leading coefficient, Eq. 1, with exponents fixed at clear liquid values  
 $C_L^*$  = equilibrium oxygen concentration in liquid,  $\text{kmol}/\text{m}^3$   
 $\bar{C}_E$  = normalized oxygen concentration in probe electrode,  $\text{kmol}/\text{m}^3$   
 $C_E, C_F, C_G, C_L, C_G^0$  = oxygen concentration in electrode, liquid diffusion film, gas phase, liquid phase, and inlet gas phase,  $\text{kmol}/\text{m}^3$   
 $C_{E,\infty}$  = final oxygen concentration measured by electrode,  $\text{kmol}/\text{m}^3$   
 $D_I, D_T$  = impeller and tank diameter, m  
 $H_B$  = clearance of baffles or sparger from vessel bottom, m  
 $H_I$  = clearance of impeller, m  
 $H_T$  = height of ungassed slurry, m  
 $H$  = Henry's law constant for oxygen,  $\text{kmol}/\text{MPa} \cdot \text{m}^3$   
 $k_L$  = mass transfer coefficient,  $\text{m}/\text{s}$   
 $k_{La}, (k_{La})_0$  = volumetric mass transfer coefficient in a slurry, in a liquid,  $\text{s}^{-1}$   
 $L_I$  = impeller blade length, m  
 $N$  = stirring speed, rpm  
 $P, P_I, P_{IG}, P_T$  = power, ungassed power, gas impeller power, total power,  $\text{kW}/\text{m}^3$   
 $Q$  = volumetric gas flow rate,  $\text{m}^3/\text{min}$   
 $R$  = gas constant,  $\text{MPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K}$   
 $t$  = time, s  
 $T$  = temperature, K  
 $V$  = volume of condensed phases, liquid and solid,  $\text{m}^3$   
 $V_L, V_G$  = volume of liquid phase, gas phase,  $\text{m}^3$   
 $V_S$  = superficial gas velocity,  $\text{cm}/\text{s}$   
 $\text{vvm}$  = volume of gas per slurry volume per minute,  $\text{m}^3/\text{m}^3 \cdot \text{min}$   
 $W_B$  = baffle width, m  
 $W_I$  = impeller blade width, m  
 $x$  = exponent, Eq. 1  
 $y$  = exponent, Eq. 1

## Greek letters

$\alpha_0, \alpha_{0E}$  = zeroth moment of probe response to a step change in inlet gas, probe environment, s  
 $\phi$  = volume concentration of solids, % v/v  
 $\tau_E, \tau_F$  = time constant of probe electrode, liquid diffusion film, s  
 $\tau_G$  = mean residence time of gas phase, s  
 $\rho_L, \rho_m, \rho_S$  = density of liquid, bulk mean density of slurry, density of solid,  $\text{kg}/\text{m}^3$

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