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### MASS TRANSFER IN GAS-LIQUID SLURRY REACTORS

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**Abstract**—A critical review is presented on the mass transfer characteristics of gas-liquid slurry reactors. The recent findings on the influence of the presence of solid particles on the following mass transfer parameters in slurry reactors are discussed: volumetric gas-liquid mass transfer coefficients ( $k_L a$ ,  $k_G a$ ), liquid-side mass transfer coefficients ( $k_L$  and  $k_S$ ) and specific gas-slurry contact area ( $a$ ). The second part of this paper reviews the recent progress in our knowledge and understanding of the enhancement of gas-slurry mass transfer due to the presence of solids. Five different cases are distinguished, i.e.

- enhanced mass transfer by physical adsorption on small particles,
- enhanced mass transfer by fast homogeneous reactions in the slurry, due to inert particles,
- enhanced mass transfer by homogeneous reaction in the liquid with dissolving particles,
- enhanced mass transfer due to reactive particles and
- enhanced mass transfer due to catalytic particles in heterogeneous reactive systems.

Prospective areas for additional research are identified.

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#### INTRODUCTION

Slurry reactors have widespread application in the chemical and biochemical industries. Doraiswamy and Sharma (1984) identified 50 different processes

and more applications can be expected. We restrict ourselves to slurry systems where the particles are kept in suspension by liquid eddies induced by gas flow and/or mechanical agitation. So, three-phase fluidized beds, defined as systems with particles of

such high density difference  $|\rho_s - \rho_L|$  and large particle size that a net upward (or downward) liquid flow is necessary to keep the particles in suspension, are excluded from this review. Review papers on Slurry reactors have been published by Chaudhari and Ramachandran (1980), Deckwer and Alper (1980), Alper and Deckwer (1983), Shah *et al.* (1981), Hofmann (1983), Shah *et al.* (1982), Pandit and Joshi (1984), Beenackers and van Swaaij (1986), Pandit and Joshi (1986), Kohler (1986) and Shah and Sharma (1987). A few textbooks on slurry reactors have also appeared, e.g. Doraiswamy and Sharma (1984) and Shah (1979). The present contribution concentrates on mass transfer characteristics of slurry reactors and on the enhancement of gas absorption into slurries by the presence of particles. In particular, we discuss the new developments since 1985 and refer to Beenackers and van Swaaij (1986) for the older literature.

Together with the system-specific reaction kinetics, the mass transfer parameters are particularly important in determining the average conversion rates in the slurry reactor. As an example, we consider the average conversion rate per cubic meter of the reactor of a gaseous reactant A being absorbed in the liquid of a well-stirred slurry semi-batch reactor and reacting according to irreversible first-order kinetics at the external surface of non-porous particles (Fig. 1) [see, e.g., Beenackers and van Swaaij (1986)].

$$J_A a = \bar{c}_{AG} \left/ \left\{ \frac{1}{k_G a} + \frac{1}{mk_L a E_A} + \frac{1}{mk_S a_S} + \frac{1}{mk_r'' a_p} \right\} \right. \quad (1)$$

In deriving eq. (1), it has been assumed that  $\bar{c}_{AG}$  is constant throughout the reactor,  $R_1, R_2, R_3$  and  $R_4$  are the so-called resistances that control the overall conversion rate, and the model used here shows all resistances in series.

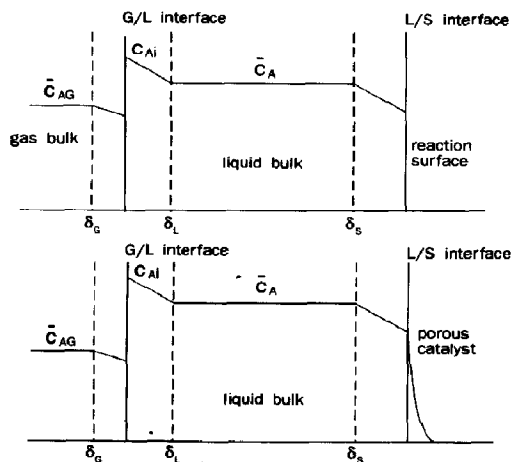


Fig. 1. Concentration profiles for mass transfer into a slurry with catalytic particles; no enhancement at gas-liquid interface: (above) mass transfer and reaction at L/S interface; (below) mass transfer and reaction in the porous particles.

$R_1 = 1/k_G a$	the resistance to mass transfer in the gas phase.
$R_2 = 1/mk_L a E_A$	the resistance to mass transfer in the liquid phase at the gas-liquid interface.
$R_3 = 1/mk_S a_p$	the resistance to mass transfer in the liquid phase at the liquid-solid interface.
$R_4 = 1/mk_r'' a_p$	the resistance to reaction at the external catalyst surface.

For a first-order reaction in porous particles,  $R_4$  should be replaced by  $R_4' = d_p / (6ma_p D_i \phi \tanh \phi)$  with the Thiele modulus,  $\phi$ , defined as

$$\phi = \frac{d_p}{6} \sqrt{\left( \frac{k_r'' a_S}{D_i} \right)} \quad (2)$$

Although inside the porous particle mass transport and reaction are in parallel, overall the process can still be described by resistances in series. From these resistances in series,  $R_2$  might be influenced by the presence of the particles in several ways:

- (1) The specific (gas liquid) interfacial area,  $a$ , can be changed by the presence of the particles.
- (2)  $k_L$  itself can be influenced by the presence of the particles even if these are inert.
- (3) In principle, in the case of dissolving particles, even the solubility of the gas phase component may change due to the presence of the dissolved particle materials and/or their products, but we neglect the effects of solubility.

It will be clear that to be conceptually sound, any enhancement effect should exclude factors 1-3. This requires careful definition of the flux enhancement due to the particles, for which we proposed (Beenackers and van Swaaij, 1986):

$$E_A = \frac{J_A \text{ with particles}}{J_A \text{ with the same but inert particles}} \quad (3)$$

in which  $J_A$  is evaluated at the same overall driving force. Inert means that neither the particles nor components produced from the particles participate in the reaction as a reactant or a catalyst. Further, inert particles do not adsorb the gas phase component transported towards the bulk of the slurry, nor any other reactant or reaction product. Our proposal to treat enhancement of mass transfer due to adsorption, reaction or catalytic effects on solid surfaces by the concept of an enhancement factor as defined by eq. (3) and to substitute this factor in eq. (1) in the way that is usual for any phenomenon of mass transfer with reaction in parallel has been criticized by Alper (1987), because these surface processes can also influence the bulk concentration by a mass transfer in series effect. However, in our approach the latter effects are included in  $R_4$ .  $E_A$  will be different from 1 only if  $R_4$  is small relative to  $R_2$ , resulting in a bulk concentration of  $\bar{c}_A = 0$  and in a real parallel mechanism of the

enhancement. In our view the advantage of the concept of the enhancement factor as defined by eq. (3) is the separation of the influence of hydrodynamic effects on gas-liquid mass transfer (incorporated in  $k_L$ ) and of the effects induced by the presence of a solid surface (incorporated in  $E_A$ ), indeed in a similar way as is common in mass transfer with homogeneous reactions. Of course, if the gas absorption is already enhanced by homogeneous liquid phase reactions the enhancement due to the presence of the particles still may occur, but this effect cannot always be separated meaningfully from the overall enhancement. The above analysis shows that an adequate description of mass transfer with chemical reaction in slurry reactors needs reliable data on:

- parameters which are specific for slurry reactors ( $k_G$ ,  $k_L$ ,  $a$ ,  $E_A$ ) and
- parameters which are not specific for the type of reactor applied (intrinsic reaction kinetics and particle properties such as  $a_p$ ,  $a_s$ ,  $d_p$  and to some extent also  $D_i$ ).

The scope of this review is limited to the parameters of type (a) only. It seems logical to start with a brief discussion on the value of the product of  $k_L$  and the specific contact area,  $a$ , ( $k_L a$ ) because this is often the overall rate controlling step.

#### THE VOLUMETRIC LIQUID-SIDE MASS TRANSFER COEFFICIENT AT THE GAS-LIQUID INTERFACE ( $k_L a$ )

Both with dynamic absorption techniques and with chemical techniques, direct information on the product  $k_L a$  can often be obtained in a relatively easy way. As a result much more information is available on the product  $k_L a$  than on  $k_L$  and  $a$  separately. For low solids concentrations one may assume that the solids do not affect the value of  $k_L a$  so that the existing relations for two-phase gas-liquid reactors can be applied. For recent reviews on these relations, see Lee and Foster (1990), for draft tube slurry reactors Goto *et al.* (1989), for bubble columns Deckwer and Schumpe (1993) and the book of Deckwer (1985), and for stirred-tank reactors Mann (1983) and Schlüter and Deckwer (1992).

Since the pioneering work of Joosten *et al.* (1977) [which is still the best up-to-date work; see Shah and Sharma (1987)], much research has been carried out on the influence of solids on  $k_L a$ . Despite this there is

still no universally applicable relation describing the influence of all types of particles in any weight fraction in any liquid.

If the density difference between the solids and liquids is small or if the liquid viscosity is high, the slurry behaves as a pseudo-homogeneous phase and relations for  $k_L a$  as function of the effective suspension viscosity can be applied successfully. Öztürk and Schumpe (1987) measured  $k_L a$  in a 9.5 cm inner diameter bubble column absorbing oxygen in organic slurries of ligroin ( $\rho_L = 729 \text{ kg/m}^3$ ;  $\mu_L = 0.54 \text{ mPa s}$ ) and tetralin ( $\rho_L = 968 \text{ kg/m}^3$ ;  $\mu_L = 2.08 \text{ mPa s}$ ) containing up to 40% of any of the solids described in Table 1. The result is shown in Fig. 2.

With the exception of alumina in ligroin, all results could be correlated according to

$$k_L a / (k_L a)_0 = (\mu_{\text{eff}} / \mu_0)^{-0.42} \quad (4)$$

with index 0 indication of no solids present; other conditions remain identical. So,  $\mu_0$  is the viscosity of pure liquid  $\mu_L$ . The correlation covers a superficial gas velocity up to 8 cm/s and an effective viscosity range of 0.54–100 mPa s with a mean error of 7.7%.

For non-Newtonian suspensions,  $\mu_{\text{eff}}$  is obtained from the Ostwald-de Waele equation

$$\mu_{\text{eff}} = k \dot{\gamma}_{\text{eff}}^{n-1} \quad (5)$$

with, for bubble columns (Schumpe and Deckwer, 1987),

$$\dot{\gamma}_{\text{eff}} = C u_G \quad (6)$$

and

$$C = 2800 \text{ m}^{-1}.$$

The consistency index  $n$  still has to be measured experimentally. The above result, obtained in organic media, agrees excellently with the results of Schumpe *et al.* (1987a), both for water and ionic aqueous solutions in the same bubble column applying kieselguhr (7  $\mu\text{m}$ ), alumina (8  $\mu\text{m}$ ) and activated carbon (5  $\mu\text{m}$ ). Provided  $\mu_{\text{eff}} > 2\mu_L$ , they found

$$k_L a / (k_L a)_0 = (\mu_{\text{eff}} / \mu_L)^{-0.39} \quad (7)$$

for  $u_G < 8 \text{ cm/s}$  and  $\mu_{\text{eff}}$  between 1 and 100 mPa s. It is remarkable that the relation was found to be valid for both electrolyte and non-electrolyte solutions. Fine high-density solids in low-viscous liquids such as alumina in ligroin or in low concentrations in aqueous solution give higher values of  $k_L a$  than predicted by eq. (4) or (7), possibly by increasing the mass

Table 1. Properties of solids applied by Öztürk and Schumpe (1987) in a bubble column

Material	$\rho_p$ ( $\text{kg m}^{-3}$ )	$d_p$ ( $\mu\text{m}$ )	Averaged by
		Number	Volume
Polyethylene (A)	940	24.6	46.2
Polyethylene (B)	965	106	369
Polyvinylchloride (PVC)	1380	82	100
Aluminium oxide	3180	10.5	21.6

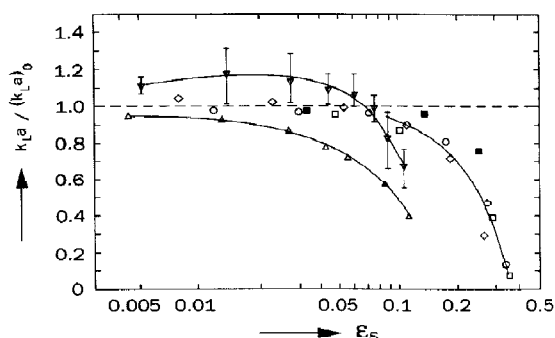


Fig. 2. Relative change in  $k_L a$  in bubble column with respect to the particle-free system as a function of the solid volume fraction (□) PE-A/lignoïn; (○) PE-B/lignoïn; (◇)  $\text{Al}_2\text{O}_3$ /lignoïn; (▽)  $\text{Al}_2\text{O}_3$ /tetralin; (■) PE/Exsol after Michael and Reichert (1983) (from Öztürk and Schumpe, 1987).

transfer coefficient  $k_L$ . This suggests eqs (4) and (7) to be conservative. However, non-wettable particles may reduce the value of  $k_L a$  substantially more than predicted by eqs (4) and (7). For non-wettable 164  $\mu\text{m}$  polypropylene particles in aqueous solutions of carboxymethylcellulose, the extra decrease could be described by assuming surface blocking of the gas-liquid interface by a Langmuir Hinshelwood type of adsorption of the non-wettable particles according to

$$\alpha = \frac{K' \varepsilon_s}{1 + K' \varepsilon_s} \quad (8)$$

where  $\alpha$  is the fraction of the interface covered by the particles and  $K' = 9$  for polypropylene (Schumpe *et al.*, 1987b). Insufficient information is available to predict  $K'$  as a function of, e.g., wettability, although it is known that  $K'$  increases with the gas-solid-liquid contact angle ( $\Theta$ ):  $K' = 9$  for  $\Theta = 120^\circ$  and  $K' = 6$  for  $\Theta = 96^\circ$  [Godbole *et al.*, 1990]. It is also remarkable that 5  $\mu\text{m}$  activated carbon particles in aqueous solutions have been found to obey relation (7) (Schumpe *et al.*, 1987a), because this material is also known to stick to the interface (see below under enhancement). Probably due to its large active area available for adsorption, surface coverage by activated carbon does not result in a partial blocking of the interfacial area for mass transfer as found with polypropylene particles.

A few years before the publication of relations (4) and (7), Nguyen-Tien *et al.* (1985) observed, for three-phase fluidized beds,

$$(k_L a)/(k_L a)_0 = \left(1 - \frac{\varepsilon_s}{0.58}\right). \quad (9)$$

Nigam and Schumpe (1987) found this relation equally applicable for slurry bubble columns (glass particles, 5  $\mu\text{m} < d_p < 200 \mu\text{m}$ , column diameter 9.5 cm) provided the measured solids fraction at the bottom is substituted into eq. (9). This fraction can be calculated with the model of Kato *et al.* (1972).

The experimental conditions applied in the research on slurry bubble columns resulting in eqs (4), (7) and

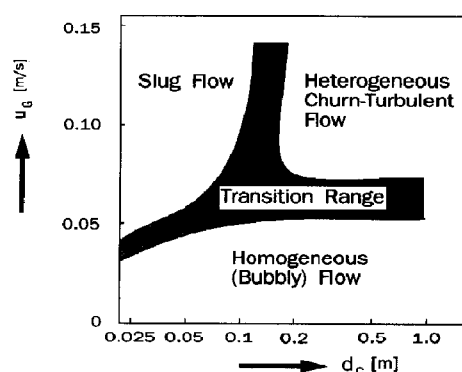


Fig. 3. Approximate dependency of flow regime on gas velocity and column diameter (water and dilute aqueous solutions) (from Shah *et al.*, 1982).

(9) have been restricted mainly to superficial gas velocities up to 8 cm/s and a column diameter of 9.5 cm, hence to the homogeneous bubbly flow regime (see Fig. 3). However, some data are available for a 30 cm column and these could also be described by relation (9) (Schumpe *et al.*, 1984).

Sada *et al.* (1986) also measured the influence of solids on  $k_L a$  in a small slurry bubble column ( $d_c = 7.8 \text{ cm}$ ). Both pure water and ionic aqueous solutions of various salts (up to 2.4 kmol/m<sup>3</sup>) as well as sugar solutions (up to 60 wt%) were applied. Gas velocities run as high as 20 cm/s, i.e. far into the slug flow regime.

Particles used were  $\text{Ca}(\text{OH})_2$  (7  $\mu\text{m}$ , 2480 kg/m<sup>3</sup>), glass (40 and 96  $\mu\text{m}$ , 2480 kg/m<sup>3</sup>) and nylon-6 (2 mm, 1140 kg/m<sup>3</sup>) up to 20 wt%.

All data could be correlated by

$$k_L a = C \varepsilon_G^{0.9} \quad (10a)$$

with

$$\varepsilon_G/(1 - \varepsilon_G)^4 = 0.046 u_G \quad (10b)$$

for pure water and no particles, and

$$\frac{\varepsilon_G}{(1 - \varepsilon_G)^3} = 0.019 u_G v_t^{1/16} \varepsilon_s^{(-0.125 v_t^{0.16})} \quad (10c)$$

for pure water with particles; here, according to Stokes law,  $v_t$  is the particle terminal velocity.

An unsatisfactory aspect of the approach is that  $C$  has to be measured experimentally and varies in an as yet unpredictable way with  $\varepsilon_s$ ,  $d_p$ , solids composition and type of electrolyte applied. Without electrolytes present, 5 wt% of 40  $\mu\text{m}$  glass particles need 50% lower  $C$  than 20 wt% of 96  $\mu\text{m}$  glass. The presence of electrolytes lowers the value of  $C$  and the presence of solids in an electrolyte solution results in a slight further lowering of  $C$ . For the industrially most important regimes of churn-turbulent flow and, to a lesser extent, the transition regime, the relations of Koida *et al.* (1984) probably have the widest range of applicability. These authors measured with sparger holes ranging from 0.5 to 2.5 mm, a static liquid

height of 1.5 m, and superficial gas velocities up to 0.2 m/s in bubble columns with diameters from 10 to 30 cm. Liquid viscosities ranged from water up to 18 mPa s,  $52 < \sigma_L < 72$  N/m,  $0.14 < D_L \times 10^9 < 2.4$  m<sup>2</sup>/s,  $\varepsilon_S$  up to 8%,  $50 < d_p < 200$   $\mu$ m,  $\rho_p = 2500$  kg/m<sup>3</sup> and for  $\rho_p = 8770$  kg/m<sup>3</sup> also with  $d_p = 80$   $\mu$ m.

They observed both  $\varepsilon_G$  and  $k_L a$  to be reduced by the presence of solids, although this reduction is less pronounced in the churn turbulent regime than in the transition regime. The relations of Koida *et al.* (1984) are

$$\frac{k_L a}{(k_L a)_0} = \left[ \frac{\varepsilon_{G,H}}{(\varepsilon_{G,H})_0} \right]^{1.18} \times \frac{1}{1 + 1.47 \times 10^4 \varepsilon_S^{0.612} N_{Fr,p}^{0.486} N_{Re}^{-0.345} N_S^{-0.477}} \quad (11a)$$

with, for the heterogeneous churn-turbulent flow regime,

$$\frac{(\varepsilon_{G,H})_0}{\{1 - (\varepsilon_{G,H})_0\}^4} \frac{(1 - \varepsilon_{G,H})^4}{\varepsilon_{G,H}} = \frac{0.277}{C} \left[ 1 + 4.35 \varepsilon_S^{0.745} \left( \frac{\Delta \rho}{\rho_L} \right)^{0.881} N_{Re}^{-0.168} \right] \quad (11b)$$

and for the transition regime

$$\frac{\varepsilon_{G,T}}{(\varepsilon_{G,T} - \varepsilon_{G,H})_0} = \frac{1}{1 + 49.1 \varepsilon_S^{0.619} \left( \frac{\Delta \rho}{\rho_L} \right)^{0.619} N_{Re}^{-0.496}} \quad (11c)$$

and  $(\varepsilon_{G,H})_0$  from

$$\frac{(\varepsilon_{G,H})_0}{\{1 - (\varepsilon_{G,H})_0\}^4} = 0.277 \left( \frac{u_G \mu_L}{\sigma_L} \right)^{0.918} \left( \frac{g \mu_L^4}{\rho_L \sigma_L^3} \right)^{-0.252} \quad (12)$$

Here,  $\Delta \rho = \rho_p - \rho_L$

$$N_{Re} = \frac{u_G \rho_L d_c}{\mu_L}$$

$$N_{Fr,p} = v_i / (d_c g)^{1/2}$$

$$N_S = d_c^2 g \rho_L / \sigma_L$$

(a dimensionless surface tension number).

The constant  $C$  is system-dependent:  $C = 0.277$  for water and aqueous solutions of glycerol and glycol;  $C = 0.364$  for aqueous solutions of organic electrolytes. It would be highly interesting if future research could result in a general relation of  $C$  for organic liquids.

Relations such as those of Sada *et al.* (1986) [eqs (10a)–(10c)], and the relations of Koida *et al.* (1984) [eqs (11) and (12)] are not applicable for systems where the density of the solids is close to the density of the liquid, because the concept of the terminal single-particle settling velocity then fails ( $v_i \rightarrow 0$ ).

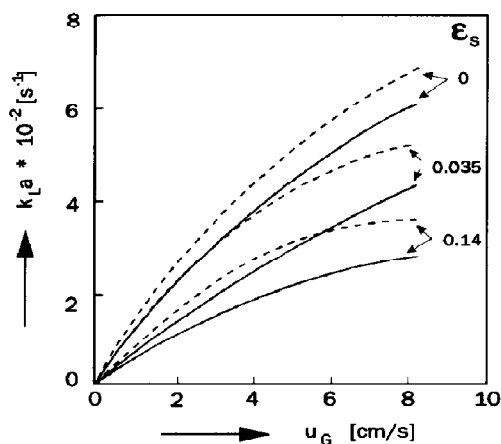


Fig. 4. Effect of large particles of nearly liquid density on  $k_L a$  as a function of superficial gas velocity in a 15 cm bubble column (air–water system): (—) Polyoxymethylene,  $\rho_p = 1255$  kg/m<sup>3</sup>,  $d_p = 2.8$  mm, perforated plate; (---) ion exchange resin,  $\rho_p = 1060$  kg/m<sup>3</sup>,  $d_p = 0.6$  mm, sintered plate (adapted from Sauer and Hempel, 1987).

Application of particles of the same density as the liquid is particularly relevant in biochemical engineering where polymer gels such as calcium alginate and carrageenan are often used to entrap living cells. The influence of alginate particles of  $k_L a$  in aqueous solutions has been reported by Sun *et al.* (1988), although only for a small bubble column diameter of 7 cm and superficial velocities below 7 cm/s.

A broader scope is seen in the research of Sauer and Hempel (1987), who studied a wide variety of low-density particles ( $1020 < \rho < 1381$  kg/m<sup>3</sup>) of relatively large diameter ( $0.4 < d_p < 2.9$  mm) in aqueous slurries up to 20 vol% solids (see Fig. 4). Also two solids consisting of small particles were included, of either low or high density (110  $\mu$ m PVC,  $\rho = 1376$  kg/m<sup>3</sup> and 200  $\mu$ m sand,  $\rho_p = 2780$  kg/m<sup>3</sup>).

Interestingly, they applied two different spargers (a sintered plate with 3  $\mu$ m pores and a perforated plate with 1 mm holes) in a relatively large bubble column of 15 cm diameter. They were able to correlate all results following the concept of an effective slurry viscosity by the empirical correlation:

$$k_L a \left( \frac{v_{sus}}{g u_G} \right)^{1/2} = C \left( \frac{u_G}{(v_{sus} g u_G)^{1/4}} \right)^{n_1} \times \left( \frac{v_{sus}}{\bar{v}_{eff, rad}} \right)^{n_2} \left( \frac{\bar{c}_S}{c_{S0}} \right)^{n_3} \quad (13)$$

where

$$v_{sus} = \mu_{sus} / \rho_{sus}$$

$$\mu_{sus} = \mu_L (1 + 2.5 \varepsilon_S + 10.05 \varepsilon_S^2 + 2.73 \times 10^{-3} \exp(16.6 \varepsilon_S)) \quad (14)$$

$$\rho_{sus} = \varepsilon_S \rho_p + (1 - \varepsilon_S) \rho_L$$

$$\bar{v}_{eff, rad} = 0.011 d_c \sqrt{g d_c} \left( \frac{u_G}{v_{sus} g} \right)^{1/8} \quad (15)$$

and  $\bar{c}_s/c_{s0}$  is the normalized solids distribution, i.e. the ratio of the mean solids concentration to that above the sparger, as follows from:

$$\bar{c}_s/c_{s0} = \{1 - \exp(-N_{Pe})\}/N_{Pe}$$

with  $N_{Pe}$  the Peclet number for the solids distribution to be obtained from the well-known relation of Kato *et al.* (1972).

Not surprisingly (Wilkinson, 1991), Sauer and Hempel (1987) could correlate their results in a satisfactory way only by applying different sets of numerical values for the constants  $C, n_1$ – $n_3$  for the two gas spargers (see Table 2).

From this we conclude that significant progress has been made during the last five years in establishing the influence of solids on  $k_L a$  in bubble columns. However, much is still unclear. Strikingly, information is virtually absent for the churn-turbulent flow regime which is probably the most relevant regime for industrial applications.

Although possibly dependent on the physicochemical properties of the system, Wilkinson (1991) recently demonstrated that both mass transfer and bubble hold-up are independent of column dimensions only if all the three following criteria are fulfilled:

- (1) The column diameter has to be larger than 0.15 m.
- (2) The column height to diameter ratio has to be in excess of 5.
- (3) The hole diameter of the sparger has to be larger than 1–2 mm.

Because of this, Wilkinson (1991) concluded that a scale-up procedure in which the gas hold-up, the

volumetric mass transfer coefficient and the interfacial area for a large-scale industrial bubble column are estimated on the basis of experimental data obtained in a pilot-plant bubble column with small dimensions ( $H/d_c < 5$ ,  $d_c < 0.15$  m) or with porous-plate-type spargers will, in general, lead to a considerable overestimation of these parameters, and therefore the use of a pilot-plant bubble column is recommended for which all the three above-mentioned criteria are fulfilled. Because slurry bubble columns are strongly related to these two-phase bubble columns, we assume that for slurry bubble columns it is also advisable to use a pilot plant with dimensions (and with the real slurry system) for which the above-mentioned criteria are all fulfilled.

Until now, only a few investigations on the influence of solids on  $k_L a$  in bubble columns meet these criteria (see Table 3). The study of Sauer and Hempel (1987) is a borderline case with  $d_c = 15$  cm and one sparger having 1 mm holes.

Further, no information is yet available for higher pressures and increased temperatures. In particular, the pressure influences bubble column hydrodynamics significantly via the gas density (Wilkinson, 1991).

Strictly speaking, bioreactors containing free bacteria in aqueous media are also slurries. With the cells being very small and having a density close to the aqueous medium, we may expect the concept of a pseudo-homogeneous liquid phase to be successful. Often this biophase is non-Newtonian. Recently, Kawase and Moo-Young (1991) derived a semi-theoretical relation for the volumetric gas to bioslurry mass transfer, both for the case when the slurry is a Bingham plastic and for a Casson fluid. The result for bubble columns is

$$k_L a = 7CF\sqrt{D_A} \frac{u_G \rho_L^{1/20} \sqrt{g}}{\mu_B^{1/4} \sigma^{0.6} d_c^{1/6}} \quad (16)$$

where

$$F = (1 - \beta)^{1/4} \quad \text{for Bingham fluids}$$

$$F = (1 - \sqrt{\beta})^{1/2} \quad \text{for a Casson fluid}$$

and with a Bingham plastic characterized by

$$\tau - \tau_y = \mu_B \dot{\gamma} \quad \text{for } \tau > \tau_y \quad (17)$$

Table 2. Constants in eq. (13) for two different spargers (Sauer and Hempel, 1987)

Constants	Sintered plate 3 $\mu$ m pores	Perforated plate 1 mm holes
$C$	$0.231 \times 10^{-4}$	$0.197 \times 10^{-4}$
$n_1$	0.305	0.385
$n_2$	–0.0746	–0.0712
$n_3$	–0.0127	–0.0114

Table 3. Experimental studies on mass transfer in slurry bubble columns meeting the criteria of Wilkinson for scale-independent results

Reference	$d_c$ (cm)	$H$ (cm)	$d_s$ (mm)	$d_p$ ( $\mu$ m)	Data
Adlington and Thomson (1965)	25	244		300–3000	$a$
Kato <i>et al.</i> (1973)	21	200	1, 2	63–177	$k_L a$
Joshi and Sharma (1976)	38	180	3.2	5	$a$
Schönau (1981)	20	250	3	75–595	$a$
Godbole <i>et al.</i> (1983)	30	244	1.7	2–300	$k_L a, a$
Godbole <i>et al.</i> (1990)	30	260	1.7	300	$k_L a$
Kawase and Moo-Young (1990)	23	122	1	Simulated by viscosity	$k_L$
Kawase and Moo-Young (1991)	23	122	1	Simulated by viscosity	$k_L a$
Koide <i>et al.</i> (1984)	30	150	0.5–2.5	50–200	$k_L a$
Jadhav and Pangarkar (1991)	40		2	500–1100	$k_s$

$$\dot{\gamma} = 0 \quad \text{for } \tau \leq \tau_y \quad (18)$$

and a Casson fluid by

$$\sqrt{\tau} - \sqrt{\tau_y} = \mu_C \sqrt{\dot{\gamma}}. \quad (19)$$

Further:

$$\beta = \tau_y / \tau.$$

The shear rate was obtained via eq. (6), although  $C$  was taken as  $5000 \text{ m}^{-1}$  instead of  $2800 \text{ m}^{-1}$ . Experimentally obtained values for  $k_L a$  in a fermentation broth of *C. cellulolyticum* and of *N. sitophila* could be reasonably predicted as  $f(u_G)$  assuming these fluids to be Bingham plastics.

A few studies have appeared on the influence of solids on  $k_L a$  and  $\epsilon_G$  in a draft tube slurry reactor (Fan *et al.*, 1987; Muroyama *et al.*, 1985, 1983). In these studies the inner tube diameters were rather small (5, 6.4 and 10 cm, respectively). Moreover, the particle diameters studied were rather large ( $> 250 \mu\text{m}$ ) so that these studies are probably at least partly in the three-phase fluidization regime.

Concerning the influence of solids on  $k_L a$  in stirred-tank reactors, a few very comprehensive studies have appeared recently.

Oguz *et al.* (1987) used several dynamic techniques to measure  $k_L a$  in various slurries in a baffled 14.5 cm diameter stirred-tank reactor. Water and three-organic liquids (*n*-butanol, 1-tetradecene and 1,2,4-trimethyl benzene) were used as liquid phases. The particles applied are summarized in Table 4.

The observed effects of the particles on  $k_L a$  are remarkably complex and appear at first sight to be confusingly different for different slurry systems (see Fig. 5). However, if the increase in apparent slurry viscosity due to the presence of the particles exceeds a factor of 1.3 relative to the solids-free liquid, then all data can be consistently correlated by a single function of power input, gas sparging rate, apparent slurry viscosity, surface tension and liquid diffusivity in a way rather similar to that proposed earlier by Yagi and Yoshida (1975) for no solids present. The results of Oguz *et al.* (1987) are as follows:

$$k_L a d_i^2 / D = 0.162 N_{Re}^{1.5} N_{Sc}^{0.5} N_{Fr}^{0.19} \times N_{GF}^{-0.6} N_A^{0.09} \sqrt{\sigma_{H_2O} / \sigma_L} \quad (20)$$

Table 4. The particles applied by Oguz *et al.* (1987) in measuring the influence of solids on the volumetric mass transfer coefficient in a stirred-tank reactor

Solid	Density ( $10^3 \text{ kg/m}^3$ )	Mean size ( $\mu\text{m}$ )
Sea sand	2.59	$< 80$
Kieselguhr	2.07	$< 50$
$\text{Al}_2\text{O}_3$	3.20	$< 32$
$\text{Fe}_2\text{O}_3$	4.38	$< 0.5$
$\text{TiO}_2$	3.61	$< 0.5$
$\text{ZnO}$	4.72	$< 1$
$\text{CaCO}_3$	2.29	$< 1$
$\text{BaSO}_4$	4.17	$< 1$

where  $d_i$  is the impeller diameter,  $D$  the liquid diffusivity,  $N_{Re}$  the impeller-based Reynolds number ( $\omega d_i^2 \rho_{\text{eff}} / \mu_{\text{eff}}$ ),  $N_{Sc}$  the slurry Schmidt number [ $\mu_{\text{eff}} / (\rho_{\text{eff}} D)$ ],  $N_{GF}$  the gas flow number [ $\sigma_L / (\mu_{\text{eff}} u_G)$ ] and  $N_A$  the aeration number ( $\omega d_i / u_G$ ).

As also found in bubble columns (see above), the concept of the effective viscosity fails for relatively high-density particles in low-viscosity liquids; see the study of Oguz *et al.* (1987) for a relative increase of  $\mu_{\text{eff}}$  below 1.3. Nevertheless, eq. (20) is a very remarkable result, although it must be kept in mind that the fluid consistency coefficient,  $k$ , and the flow behaviour index,  $n$ , from the Ostwald-De Waele equation [eq. (5)] have to be measured experimentally for each system because as yet there exists no method to predict them from theory. The shear rate  $\dot{\gamma}_{\text{eff}}$  has to be calculated from the relation of Metzner and Otto (1957).

The accuracy of eq. (20) is claimed to be within 15% provided

$$1.3 \leq \mu_{\text{eff}} \leq 41 \text{ mPa s}$$

$$0.84 \leq u_G \leq 4.2 \text{ mm/s}$$

$$0.75 \leq W/V_r \leq 6.3 \text{ kW/m}^3$$

$$24 \leq \sigma_L \leq 72 \text{ mN/m}$$

$$0.68 \leq 10^9 D \leq 2.4 \text{ m}^2/\text{s}.$$

Schmitz *et al.* (1987) also reported on the influence of solids on  $k_L a$  in stirred tanks. Although they applied only one type of solid (glass beads of 88 and  $320 \mu\text{m}$  average diameter) in aqueous solutions, their study is of particular interest because of the wide range in

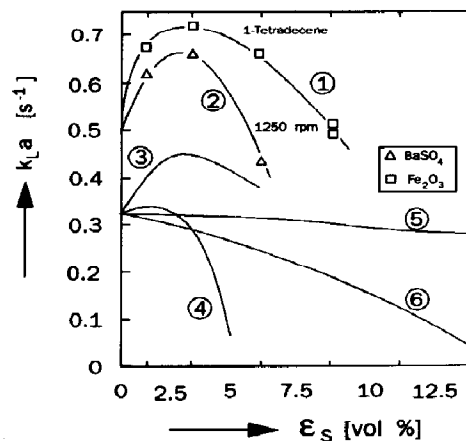


Fig. 5. Influence of solids on  $k_L a$  in a 0.15 diameter stirred-tank reactor: (1)  $\text{Fe}_2\text{O}_3$  ( $< 0.5 \mu\text{m}$ ) in 1-tetradecene; (2)  $\text{BaSO}_4$  ( $< 1 \mu\text{m}$ ) in 1-tetradecene; (3)  $\text{Fe}_2\text{O}_3$  in 1,2,4-trimethyl benzene; (4)  $\text{BaSO}_4$  in 1,2,4-trimethyl benzene; (5) sea sand ( $< 80 \mu\text{m}$ ) in water; (6) kieselguhr ( $< 50 \mu\text{m}$ ) in water. Stirrer speed: 21 rps except for experiments with trimethyl benzene (16 rps) (composed from several figures of Oguz *et al.*, 1987).

variation of liquid viscosity applied by adding carboxy methyl cellulose and by investigating the scale-up aspects by measuring both in a 20 and a 45 cm diameter stirred tank. As Schmitz *et al.* (1987) also point out their result

$$\frac{k_L a}{(k_L a)_0} = 1 - 3.54 (\varepsilon_s - 0.03) \quad (21)$$

obtained for  $0.03 \leq \varepsilon_s \leq 0.12$ ,  $d_p = 320 \mu\text{m}$ ,  $\rho_p = 2490 \text{ kg/m}^3$ ,  $300 < W/V_r \leq 10,000 \text{ W/m}^3$ ,  $0.34 \leq u_G < 4.2 \text{ cm/s}$  and  $5 < \mu_L < 75 \text{ mPa s}$ , is certainly not directly applicable to other systems. However, their finding that  $k_L a$  can be kept constant in scaling-up by maintaining the specific power consumption holds equally well for slurries as for two-phase stirred tanks and may turn out to be more generally applicable (see Fig. 6).

Kojima *et al.* (1987) reported results on the influence of particle size on  $k_L a$  in a 18 cm diameter stirred-tank reactor for particles  $\geq 150 \mu\text{m}$  only. All experiments were with tap water but the variation in solid properties was rather wide: glass (150–180  $\mu\text{m}$ ,  $\rho_p = 2390 \text{ kg/m}^3$ ); amberlite (840–1000  $\mu\text{m}$ ,  $\rho_p = 1270 \text{ kg/m}^3$ ); and polypropylene (2.7–4 mm,  $\rho_p = 867 \text{ kg/m}^3$ ). A similar relation to eq. (11) was observed, although with different constants:

$$(k_L a)/(k_L a)_0 = 1 - \varepsilon_s. \quad (22)$$

Both correlations are shown in Fig. 7. If anything, Fig. 7 clearly illustrates that relations with  $\varepsilon_s$  as the only parameter are too simple even if particle size and solids composition are comparable, as is the case in the two studies summarized in Fig. 7. A possible cause of the differences in behaviour shown in Fig. 7 is the different types of liquid used. Smits *et al.* (1987) used an ionic salt solution, i.e. a non-coalescing system, whereas Kojima *et al.* (1987) used tap water, which as such is poorly defined but which may have had coalescing properties.

Also of interest is the slightly older contribution of Albal *et al.* (1983). As far as we know, this is the only study in which the influence of pressure on  $k_L a$  in stirred-tank slurry systems has been investigated. No influence of pressure could be detected in the range from 2 to 9 MPa. Albal *et al.* (1983) also give a comprehensive review of the literature on  $k_L a$  in stirred tanks before 1983.

Iwanaka *et al.* (1985) measured the influence of solids on  $k_L a$  and  $k_L$  in a slurry reactor with vibrational agitation.

For recent system-specific studies on industrially important processes, see Table 5.

The paper of Stenberg and Schöön (1985) is also of interest for measurement techniques suitable for  $k_L a$  with catalytic reactions of kinetic orders different from 1, with side reactions present, with poisoning of the catalyst or when the reaction is chemically enhanced.

The contribution of Lindner *et al.* (1988) also is of interest because of the special effects of fine activated carbon particles on  $k_L a$ . Due to adsorption at the

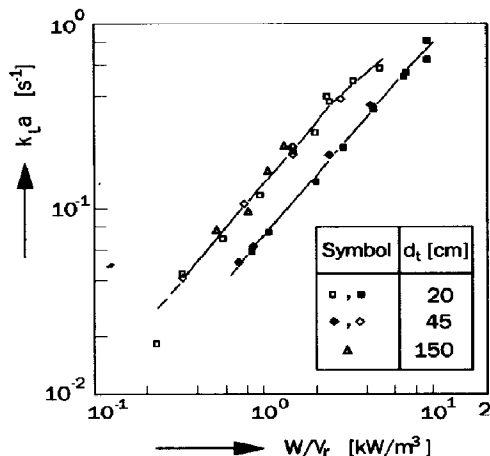


Fig. 6. Volumetric mass transfer coefficient as a function of total power consumption, for different reactor diameters. 320  $\mu\text{m}$  glass particles in water;  $u_G = 1.9 \text{ cm/s}$ ; closed symbols: 30 wt% solids; open symbols: no solids (adapted from Schmitz *et al.*, 1987).

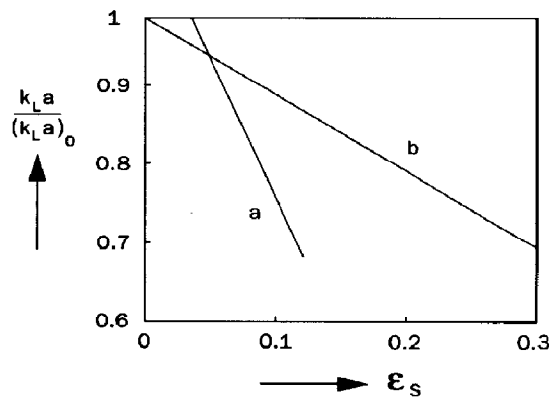


Fig. 7. Influence of solids fraction on  $k_L a$  in stirred tanks: (a) Smits *et al.* (1987), sodium sulphite aqueous solution; (b) Kojima *et al.* (1987), tap water.

gas-liquid interface, very small solids fractions can affect  $k_L a$  substantially (see Fig. 8). Lindner *et al.* (1988) expected an increase in  $a$  to be responsible for this. This is not impossible because they operated partly in the so-called region A (see below under interfacial area), where solids reportedly may have a positive effect on the value of  $a$ . However, an enhancement of  $k_L$  due to adsorption of surface-active carbon is also possible especially if significant numbers of particles have diameters in the order of a few microns (see below under the section on enhancement of gas-liquid mass transfer). Apparently, the liquid medium also plays an important role, because Schumpe *et al.* (1987a) did not find any increase in  $k_L a$  if water was used as the liquid phase (see dashed curve in Fig. 8). The presence of salts is believed to be necessary for the occurrence of a coalescence-hinder-



Table 5. System-specific studies on  $k_L a$ ,  $k_L$  and  $a$  in slurry reactors

System	Reactor	Data	Reference
Polymerisation of ethylene	BC	$k_L a f(T, \epsilon_S, u_G)$	Reichert <i>et al.</i> (1986)
Fisher-Tropsch synthesis	STR	$k_L a (p, \omega; \text{no solids})$	Albal <i>et al.</i> (1984)
Hydrogenation of ammonium nitrate (HPO process)	BC + STR	$k_L a (u_G, \epsilon_S, T)$	Lindner <i>et al.</i> (1988)
Hydrogenation of methyl oleate	STR	$k_L a (\omega, \epsilon_S)$	Stenberg and Schöön (1985)
Hydrogenation of 2 ethyltetrahydroantraquinone in the presence of palladium catalyst	STR	$a (\omega)$ $k_L (T)$ $k_S (\omega, T)$	Santacesaria <i>et al.</i> (1988b)
Alkylation of <i>p</i> cresol with isobutene	STR	$a (\omega)$ $k_S (\omega, d_p)$	Santacesaria <i>et al.</i> (1988a)
Hydrogenation of adiponitrile	STR	$k_L a (\omega, T)$ $k_S (\omega, T)$	Mathieu <i>et al.</i> (1992)
Hydrogenation of adiponitrile	STR	$k_L a (\omega, c_S, T, \text{activity catalyst})$	Dietrich <i>et al.</i> (1992)
Simultaneous absorption of propane and ethene	Stirred cells	selectivity as $f(k_L, c_S)$	Tinge <i>et al.</i> (1987, 1991)

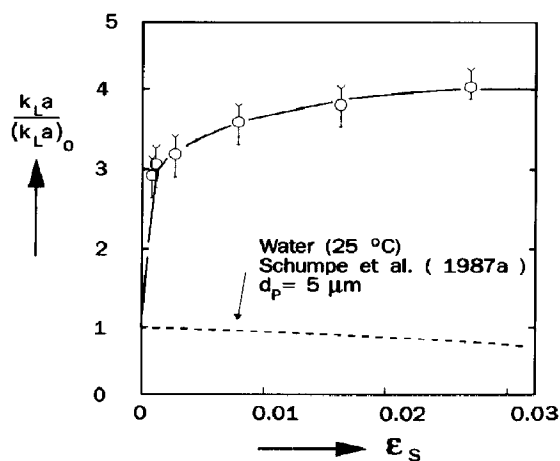


Fig. 8. Relative increase of the volumetric mass transfer coefficient in the bubble column by adding activated carbon,  $d_p \pm 40 \mu\text{m}$ , 2.2 M  $\text{H}_3\text{PO}_4 + 3 \text{ M KNO}_3$ , 50°C (from Lindner *et al.*, 1988).

ing effect by which the interfacial area can be increased (Lindner *et al.*, 1988; Schumpe *et al.*, 1987a). However, the exact mechanism is still unknown.

Of great interest is the hydrogenation study of Dietrich *et al.* (1992) in small stirred tanks of 0.5 and 1.3 dm<sup>3</sup>. In pure water, 2.3% wt active, pyrophoric Raney nickel decreases  $k_L a$  by about 80%, while inactive oxidic nickel increases  $k_L a$  by less than 20%, but in the hydrogenation mixture the effect of active pyrophoric nickel is just the opposite. Here an enhancement of  $k_L a$  up to 40% is observed at high stirrer speeds. These effects are not yet properly explained, although they are probably related to surface adsorption of the particles, and qualitatively fit with the models presented below under the section on enhancement of gas-liquid mass transfer.

#### THE VOLUMETRIC GAS-SIDE MASS TRANSFER COEFFICIENT ( $k_G a$ )

Despite the availability of the experimental techniques (Beenackers and van Swaaij, 1986), virtually no information is available on  $k_G a$  in slurry reactors (Hofmann 1983; Charpentier, 1981). One might argue that such information is not important, because for sparingly soluble gases  $k_G a$  is usually not rate controlling, while for very soluble gases conversion will often be complete whatever reactor design is selected due to the large numerical value of  $k_G a$ , making such processes extremely fast. However, the latter part of this reasoning is not always correct. If selectivity is affected by liquid concentrations of gaseous reactants, accurate information on  $k_G$  can be vital for designing a process unless the possibility of any gas phase rate-controlling effect can be excluded with certainty.

#### THE TRUE GAS-LIQUID SPECIFIC CONTACT AREA ( $a$ )

Especially for fast reactions, where enhancement at the gas-liquid interface occurs, knowledge of the true gas-liquid specific contact area,  $a$ , is desired rather than knowledge of the product  $k_L a$  only. For an overview of measurement techniques, see Beenackers and van Swaaij (1986). Recently, a new ultrasonic technique was introduced by Chang and Morala (1990). For a recent evaluation of the chemical method, see Oyevear and Westerterp (1989). Concerning the influence of the presence of solids on the value of the interfacial area, Pandit and Joshi (1986) proposed to distinguish four different regions, i.e. A-D. Of these, A and B are primarily of interest to slurry reactors and C and D to three-phase fluidization. We restrict our review to regions A and B only.

##### Region A

Region A is obtained for small particles, typically below 100  $\mu\text{m}$ , and a low solids hold-up below

0.6 vol%. In this region the small particles may cover the bubble surface, thus preventing coalescence of the bubbles and resulting in smaller bubbles and on increased specific surface via

$$a = \frac{6\varepsilon_G}{d_b} \quad (23)$$

The effect of an increase in  $a$  is enhanced further by the fact that smaller bubbles have lower rising velocities which lead to increasing gas hold-ups,  $\varepsilon_G$ , with decreasing  $d_b$ . An increase in solids content may increase the percentage of gas-liquid surface coverage, suggesting an increase of  $a$  with solids content. However, adding more fine particles (typically above 0.6 vol%) can result in a decrease, possibly because the extra particles cannot find any uncovered bubble surface left and have to remain in the bulk, so contributing to an increased effective viscosity of the slurry. The relative increase of  $a$  due to small amounts of small particles can be significant. Sharma and Mashelkar (1968) were pioneers in this field and observed an increase in interfacial area of more than a factor of 2 after adding 0.3% of fines.

Joshi and Sharma (1976) found  $a$  to increase linearly with the weight fraction of fine calcium carbonate particles in horizontal sparged contactors up to 70% for 0.6 wt% of solids. Sada *et al.* (1983) obtained an increase in interfacial area of up to 25% by using 7  $\mu\text{m}$   $\text{Ca}(\text{OH})_2$  particles. Remarkably, this relative increase could be maintained with solids contents as high as 25 wt%. Similar effects have been measured by Mehta and Sharma (1971) in a stirred-tank reactor although recent results from Nagaraj and Gray (1987) show only a negative influence of 25  $\mu\text{m}$  solids on the contact area, while Quicker *et al.* (1987) report no effect at all for 0.5% activated carbon and kieselguhr particles ( $d_p < 10 \mu\text{m}$ ).

Until now, the information have been so scattered that no correlation for the influence of solids could be presented. Nevertheless, this region is of great industrial importance because catalytic slurry reactors often operate with catalyst hold-ups below 0.6% and particle size below 100  $\mu\text{m}$ . If no experimental data are available, a conservative approach may be to assume no effect of solids on  $a$  in region A. However, it remains risky because of the negative influence observed by Nagaraj and Gray (1987).

### Region B

According to Pandit and Joshi (1986) this region covers the particle size range of 100–1000  $\mu\text{m}$  at any solids loading and the particle size range below 100  $\mu\text{m}$  for a solids loading above 0.6 vol%.

Schönau (1981) measured the influence of solids on both  $\varepsilon_G$  and bubble size distribution in a 20 cm bubble column meeting the criteria of Wilkinson (1991) (Table 3). Both ethanol and *n*-octanol were applied as the liquid, and superficial nitrogen velocities varied between 1 and 8 cm/s. Six different narrow size fractions of solids with average diameters ranging from 75 to 595  $\mu\text{m}$  were used. All hold-up results could be

correlated according to

$$\frac{\varepsilon_G/(1 - \varepsilon_G)}{[\varepsilon_{G,0}/(1 - \varepsilon_{G,0})]} = \left( \frac{\mu_0}{\mu_{\text{sls}}} \right)^{0.21} \left( \frac{\rho_{\text{sls}}}{\rho_0} \right)^{0.1} \quad (24)$$

with most deviations being within 10%. They further observed the Sauter bubble diameter  $d_{32}$  to be independent of solids hold-up so that the interfacial area directly follows from combining eqs (23) and (24). For gas hold-ups that are not too high, the result is

$$\frac{a}{a_0} = \left( \frac{\mu_0}{\mu_{\text{sls}}} \right)^{0.21} \left( \frac{\rho_{\text{sls}}}{\rho_0} \right)^{0.1} \quad (25)$$

This result agrees well with the work of Quicker *et al.* (1984), as revised by Schumpe *et al.* (1987a):

$$a = 651 u_G^{0.87} \mu_{\text{eff}}^{-0.24}$$

or

$$\frac{a}{a_0} = \left( \frac{\mu_0}{\mu_{\text{sls}}} \right)^{0.24} \quad (26)$$

for a 9.5 cm bubble column, with both activated carbon ( $\rho_p = 1800 \text{ kg/m}^3$ ,  $d_p = 5.4 \mu\text{m}$ ,  $0.5 \leq \varepsilon_s \leq 15\%$ ) and kieselguhr ( $\rho_p = 2360 \text{ kg/m}^3$ ,  $d_p = 6.6 \mu\text{m}$ ;  $0.2 \leq \varepsilon_s \leq 13\%$ ).

The effective slurry viscosity in these experiments varied between  $10^{-3}$  and 1 Pa s. The liquid used was either pure water or 0.8 M sodium sulphate. However, Quicker *et al.* (1984) also investigated alumina particles in the same column with the same liquids and found a much stronger decrease of  $a$  with increasing effective viscosity ( $\rho_s = 3180 \text{ kg/m}^3$ ,  $d_p = 8 \mu\text{m}$ ,  $0.3 < \varepsilon_s < 6.3\%$ ).

After revision of the data by Schumpe *et al.* (1987a) the interfacial areas with alumina are still small as compared to eq. (26), suggesting that effective viscosity alone is not sufficient to correlate all experimental findings.

The paper of Smith *et al.* (1984) is of interest with respect to the dependency of both  $\varepsilon_G$  and  $a$  on the radial position in the bubble column. For the water–nitrogen system and  $\varepsilon_s < 5\%$ ,  $20 \leq d_p \leq 100 \mu\text{m}$ ,  $2420 \leq \rho_p \leq 4000 \text{ kg/m}^3$  hardly any influence of the presence of solids on average  $a$  could be detected.

The most comprehensive set of data on the influence of solids on the interfacial area in stirred-tank reactors is probably from Schmitz *et al.* (1987). They applied glass beads of two sizes (88 and 320  $\mu\text{m}$ ) and changed the liquid viscosity by adding CMC to an aqueous sodium sulphite solution between 1.45 and 140 mPa s. For viscosities above 5 mPa s, all data could be correlated by

$$\varepsilon_s < 0.03, \quad a/a_0 = 1$$

and

$$0.03 < \varepsilon_s < 0.12, \quad \left( \frac{a}{a_0} \right) = 1 - 3.3(\varepsilon_s - 0.03) \quad (27)$$

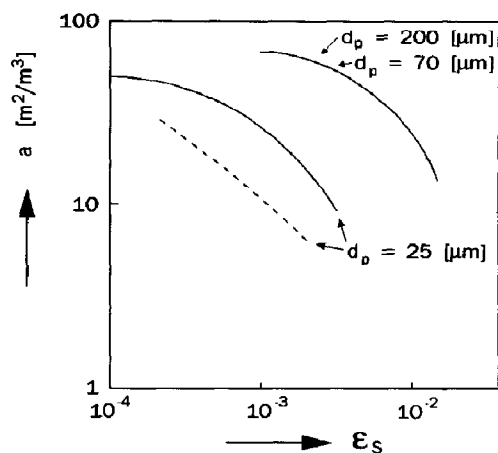


Fig. 9. Interfacial area in stirred-tank reactor with coalescing system (water) as function of volumetric solids hold-up: (—)  $W/V_r = 2.1$  W/kg; (---)  $W/V_r = 0.46$  W/kg (adapted from Nagaraj and Gray, 1987).

for

$$\begin{aligned} 300 &\leq W/V_r \leq 10^4 \text{ W/m}^3 \\ 0.34 &\leq u_G \leq 4.6 \text{ cm/s} \\ 5 &\leq \mu_L \leq 75 \text{ mPa s.} \end{aligned}$$

The relation is further restricted to geometrically similar tanks and for non-coalescing systems only. For viscosities below 5 mPa s, no uniform correlation for the influence of solids could be derived. Here the addition of solids could have both a reducing and an enhancing effect on  $a$  depending on stirrer speed and other factors not well understood.

Stirred-tank data for a coalescing system at low viscosity only (water) were published recently by Nagaraj and Gray (1987). These authors also used glass particles with diameters of 25, 70 and 200  $\mu\text{m}$ . No specific relation between  $a$  and  $\epsilon_s$  was proposed, but the authors showed that the particles can promote the coalescence frequency and thus reduce the specific contact area. Particularly with small particles ( $d_p = 25 \mu\text{m}$ ) and low power input, a significant reduction of  $a$  could be observed for solids contents as low as 0.1 vol% (see Fig. 9).

From the above we conclude that for stirred-tank reactors additional research is necessary in every region except for viscous non-coalescing systems with  $\mu \geq 5$  mPa s. Also, no information is available for relatively large particles with densities close to liquid density, as are often found in bioreactors.

#### THE LIQUID-SIDE MASS TRANSFER COEFFICIENT AT THE GAS-LIQUID INTERFACE ( $k_L$ )

Under special circumstances the gas-to-liquid mass transfer rate of a component A can be enhanced by the presence of particles due to adsorption on, catalysis by, and reaction with, the particles.

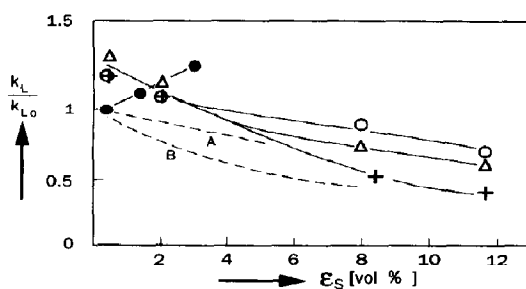


Fig. 10. The influence of small heavy particles on the mass transfer coefficient in small bubble columns relative to no solids present: (—) aqueous solutions of 0.8 M  $\text{Na}_2\text{SO}_4$ ; (●) Alumina,  $d_p = 8 \mu\text{m}$ ;  $\rho_p = 3180 \text{ kg/m}^3$ ,  $2 \leq u_G \leq 6 \text{ cm/s}$ ; open symbols: kieselguhr,  $d_p = 6.6 \mu\text{m}$ ,  $\rho_p = 2360 \text{ kg/m}^3$ ; (○)  $u_G = 6 \text{ cm/s}$ , (Δ)  $u_G = 4 \text{ cm/s}$ , (+)  $u_G = 2 \text{ cm/s}$ . Dashed curves: aqueous solution of 0.2 M NaOH: (A) calcium hydroxide,  $d_p = 7 \mu\text{m}$ ,  $\rho_p = 2240 \text{ kg/m}^3$ ; (B) magnesium hydroxide,  $d_p = 2 \mu\text{m}$ ,  $\rho_p = 2360 \text{ kg/m}^3$ .

As discussed above, these effects are not primarily dependent on local hydrodynamics and should preferably be dealt with via the enhancement concept as defined by eq. (3).

Here we discuss the influence of the presence of solids that are inert in any aspect with respect to the transferred component A. From the definition of  $k_L$ :

$$k_L = \frac{D_A}{\delta_L} \quad (\text{film theory}) \quad (28)$$

$$k_L = 2 \sqrt{\frac{D_A}{\pi t_c}} \quad (\text{penetration theory}) \quad (29)$$

it follows that inert solids may affect  $k_L$  in two ways.

Firstly, the presence of inert particles close to the interface may reduce the effective volume fraction of liquid available for diffusion. By this,  $k_L$  can be reduced via a lowering of the effective diffusivity  $D_A$ . This effect can be significant only for particle diameters of the order of the film thickness for mass transfer ( $\delta_L$ ) or smaller.

Secondly, the particles may influence the hydrodynamics close to the gas-liquid interface, thus affecting  $k_L$  via changing  $\delta_L$  and  $t_c$ .

Although no correlations are yet available on the influence of particles of high density relative to the liquid density on the mass transfer coefficient, there is some experimental evidence that such influence exists.

Figure 10 shows results obtained in small bubble columns with particle diameters in the order of  $D_A/k_L$ . The data with alumina and kieselguhr in an ionic solution of  $\text{Na}_2\text{SO}_4$  were taken from Schumpe *et al.* (1987a). The data for 0.2 M NaOH in water with fine particles of  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$  are from Sada *et al.* (1983). The picture does not yet look very consistent. Both alumina and Kieselguhr particles tend to enhance the mass transfer due to some hydrodynamic effect as long as the solids concentration is below 5 vol%. No theory is available to predict either the observed enhancement as such or the different relation of  $k_L/k_{L0}$  with  $\epsilon_s$  for alumina and kieselguhr.

Further, with equally dense calcium hydroxide particles of similar small size no enhancement was observed (see Fig. 10). Still smaller particles of  $2\ \mu\text{m}$  cause a more rapid decrease in  $k_L$  with increasing  $\varepsilon_S$ . Qualitative agreement does exist on the continuous decrease in  $k_L$  with increasing solids content above an effective viscosity increase by a factor of 2.

The results of both Schumpe *et al.* (1987a) and of Sada *et al.* (1983) might have been influenced by the fact that equipment dimensions did not meet the Wilkinson criteria (see above). Schumpe *et al.* (1987a) used a 9.5 cm bubble column with a single 0.9 mm orifice as a gas distributor and a height of 0.85 m. The column of Sada *et al.* (1983) was only 6.5 cm in diameter with a porous plate as the gas inlet. We feel that the experiments of Sada *et al.* (1983) in particular need to be checked under Wilkinson's conditions, preferably with inclusion of a validation of the experiments of Schumpe *et al.* (1987a) in the same column. Somewhat surprising is the result of Godbole *et al.* (1990), who found that poorly wettable particles as large as  $300\ \mu\text{m}$ , i.e. much larger than the boundary film thickness for mass transfer, can also reduce  $k_L$ . It must be noted, however, that in this case  $\rho_p \approx \rho_L$  and under such conditions it is possible that the particles dampen the turbulence near the interface. Schmitz *et al.* (1987) measured the influence of relatively heavy ( $\rho_p = 2490\ \text{kg/m}^3$ ) and large ( $d_p = 320\ \mu\text{m}$ ) particles on the mass transfer coefficient in stirred-tank reactors of various sizes ( $d_c = 0.2, 0.45$  and  $1.5\ \text{m}$ ). For liquid viscosities exceeding  $5\ \text{mPa s}$ , combinations of eqs (21) and (27) suggest

$$\frac{k_L}{k_{L0}} = \begin{cases} 1 & \text{for } \varepsilon_S < 0.03 \\ \frac{1 - 3.54(\varepsilon_S - 0.03)}{1 - 3.3(\varepsilon_S - 0.03)} & \text{for } 0.03 < \varepsilon_S < 0.12. \end{cases} \quad (30)$$

For the validity range of eq. (30), see under eq. (27). This equation is encouraging. At 12 vol% of solids, a decrease in  $k_L$  of only 3% is predicted.

Measurements with solids in stirred cells are always a bit tricky because flat surfaces can be maintained for low stirring speeds only. Under such circumstances the danger exists that relatively heavy particles are absent from the interface or present only at considerably below average concentrations. Hardly any influence of fine inert particles on  $k_L$  in stirred cells was observed for solids loadings below 10% (see Fig. 11). At higher loadings, a decrease of  $k_L$  with increasing solids content was also observed, due either to blockage of the interface or to the sharp increase of suspension viscosity (Quicker *et al.*, 1989).

For particles with densities close to the liquid density, such as are frequently found in bioreactors, the pseudo-homogeneous-liquid approach is often successful. For such systems Kawase and Moo-Young (1990) developed a theoretical relation for  $k_L$ , using a combination of Higbie's penetration theory [eq. (29)] and the Einstein-Li periodic viscous sublayer

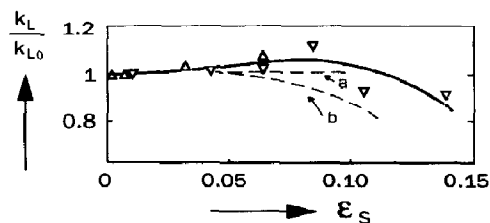


Fig. 11. Influence of inert solids on  $k_L$  in a stirred cell. (—) Aqueous  $0.5\ \text{M}\ \text{NaHCO}_3/0.5\ \text{M}\ \text{Na}_2\text{CO}_3$ . (▽)  $5\text{--}10\ \mu\text{m}$  kieselguhr, Quicker *et al.* (1989), (Δ)  $5\text{--}10\ \mu\text{m}$  alumina, Quicker *et al.* (1989). (---) Fine ( $10\ \mu\text{m}?$ )  $\text{Ca}(\text{OH})_2$  particles. (a) Sada *et al.* (1977), (b) Sada *et al.* (1984b).

model to predict the contact time  $t_c$  of eq. (29). The theory has been derived for a slurry behaving as a Bingham plastic which is known to be valid for various fermentation broths containing filamentous cells such as *Penicillium chrysogenum* and *Aspergillus niger*. Rheologically such a suspension is characterized by eqs (17) and (18). For  $\beta = \tau_y/\tau_w \leq 0.7$ , Kawase and Moo-Young derived for the contact time at solid surfaces

$$t_c = \frac{225}{4} \left( \frac{\mu_B}{\bar{e}\rho_L} \right)^{1/2} (1 - \beta)^{2.9}. \quad (31)$$

Assuming the contact time for mobile surfaces to be one quarter of the viscous sublayer bursting period for immobile surfaces they obtained, after combination with eq. (29),

$$k_L = \frac{8}{15\sqrt{\pi}} \left( \frac{\bar{e}\rho_L}{\mu_B} \right)^{1/4} (1 - \beta)^{1.45}. \quad (32)$$

Note that for bubble columns the specific energy dissipation  $\bar{e}$  follows from

$$\bar{e} = u_G g \quad (33)$$

whereas for Newtonian liquids  $\beta = 0$ . In the latter case eq. (32) reduces to

$$k_L = 0.3 N_{Sc}^{-1/2} \left( \frac{\bar{e}\mu_B}{\rho_L} \right)^{1/4}. \quad (34)$$

Relation (32) was tested in a sufficiently large bubble column (see Table 3) with various aqueous solutions of carboxypolymethylene, simulating slurries with  $\tau_y$  up to  $0.7\ \text{Pa}$  and Bingham viscosity as high as  $32\ \text{mPa s}$  (see Fig. 12). The standard deviation in Fig. 12 is 43% although it must be mentioned that Kawase and Moo-Young did not measure  $k_L$  directly, but measured  $k_{La}$  and calculated  $k_L$  from  $k_L = k_{La}/a$  with a relation for  $a$  obtained from the literature. As the authors pointed out themselves a decisive test for eq. (32) also requires experimental values of the contact area.

We conclude that particularly if the slurry can be considered as a pseudo-homogeneous phase, the effect of solids on  $k_L$  is relatively well understood, although the theory of Kawase and Moo-Young (1990) still has to be validated by accurate experiments on the value

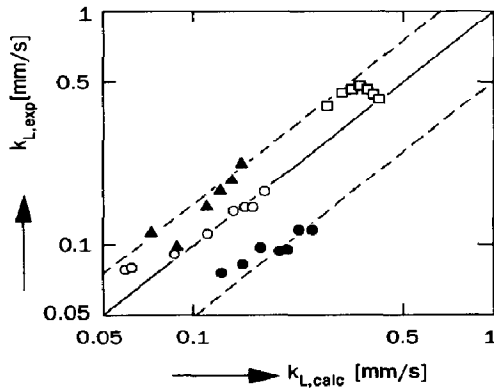


Fig. 12. Experimental testing of the relation of Kawase and Moo-Young (1990) [eq. (32)] with water ( $\square$ ) and various solutions of carboxypolymethylene

	$\tau_y$ (Pa)	$\mu_B$ (mPa s)
$\square$	0	0.92
$\bullet$	0.29	8.5
$\circ$	0.62	23
$\blacktriangle$	0.68	32

of the interfacial area. Much less clear is the situation with small fractions of heavy particles, which is typical in many catalytic slurry reactions. A moderate enhancement up to 30% seems possible depending on factors not yet well understood. A conservative approach would be to assume no effects at all, unless definite evidence to the contrary is available.

#### THE MASS TRANSFER COEFFICIENT AT THE LIQUID-SOLID INTERFACE ( $k_s$ )

For reviews on measurement techniques for  $k_s$ , see Ramachandran and Chaudhari (1983), Lazaridis (1990) and Deckwer (1985). For a new method proposed recently and applicable under reactive conditions without requiring *a priori* knowledge of the kinetics, see Gholap *et al.* (1987).

Relations for the mass transfer coefficient around the solid particles are usually presented in the form of

$$N_{Sh} = 2 + CN_{Re}^{n_1} N_{Sc}^{n_2} \quad (35)$$

with the Sherwood and Schmidt numbers defined as

$$N_{Sh} = \frac{k_s d_p}{D} \quad (36)$$

$$N_{Sc} = \mu_L / (\rho_L D). \quad (37)$$

In early attempts the Reynolds number was often based on the hindered particle settling velocity, i.e. the actual terminal particle slip velocity in the slurry,  $v_p$ :  $N_{Re} = (\rho_L v_p d_p) / \mu_L$ .

There are two difficulties in this approach. First, the slip velocity has to be related to the global system parameters, which is complicated, and second, the concept completely fails for density differences ap-

proaching zero, as is often the case in bioreactors. A recent illustration of the difficulties inherent in the slip velocity concept is the study on  $k_s$  in sparged slurry columns by Jadhav and Pangarkar (1988).

Although they put much effort into getting at the most realistic value of  $v_p$  by inclusion of the effects of  $\varepsilon_s$ ,  $\varepsilon_G$  and the liquid circulation velocity, they ultimately abandoned the concept (Jadhav and Pangarkar, 1991).

The second approach is based on the idea that  $k_s$  is dictated by the local turbulence around the particles. Based on Kolmogoroff's theory of local isotropic turbulence, this leads to a Reynolds number based on the velocity of the critical eddies responsible for most of the energy dissipation. For solid particles much larger than the Kolmogoroff scale of these eddies, this leads to

$$N_{Re} = C_1 \left( \frac{\bar{\varepsilon} d_p^4}{v_L^3} \right)^{1/3} \quad (38)$$

Here,  $\bar{\varepsilon}$  is the specific local energy dissipation rate per unit mass of liquid. If we may assume that all energy fed to the system is dissipated via these eddies, then

$$\bar{\varepsilon} = W / (\rho_L V_L) \quad \text{W/kg or m}^2/\text{s}^3. \quad (39)$$

For a bubble column

$$W = \Phi_{v,G} \Delta p = u_G g \rho_L V_L \quad (40)$$

so that

$$\bar{\varepsilon} = u_G g$$

and

$$N_{Re'} = \left( \frac{\bar{\varepsilon} d_p^4}{v_L^3} \right)^{1/3} = \left( \frac{u_G g d_p^4}{v_L^3} \right)^{1/3} \quad (41)$$

Note that this is a definition of  $N_{Re'}$ , because we arbitrarily took the constant  $C_1$  of eq. (38) equal to 1.

A number of investigations have followed this approach and the results are summarized in Table 6 and in Fig. 13. Recent progress in this area concentrates on the influence of liquid, gas and solid properties on  $k_s$  and on scale-up rules. Lazaridis (1990) measured the influence on  $k_s$  of  $d_p$ ,  $u_G$ ,  $\bar{\varepsilon}$ ,  $\mu_c$ ,  $\sigma_L$ ,  $\varepsilon_s$ , and bubble column height.

The equation of Lazarides (1990) can also be applied for non-Newtonian liquids. In that case  $\mu_L$  follows from eqs (5) and (6), but according to Lazaridis a value of  $C = 1000 \text{ m}^{-1}$  should be used in eq. (6) instead of 2800.

Particularly valuable is the work of Jadhav and Pangarkar (1991), who tested their relation in three columns of 10, 20 and 40 cm diameter. Therefore, their relation meets Wilkinson's criteria of a minimum scale to be applied for avoiding wall effects (Wilkinson, 1991). Although these authors also used the concept of the specific energy dissipation rate, their approach is slightly different. Defining the Reynolds number as

$$N_{Re''} = \frac{v_L' d_p}{v_L} \quad (42)$$

with  $v'_L$  the characteristic turbulence velocity [taken from Pandit and Joshi (1986)]:

$$v'_L = 0.43 \left\{ g d_c \left[ u_G - \varepsilon_G v_{b\infty} - \varepsilon_S v_t \left( \frac{(\rho_p - \rho_L)}{\rho_L} \right) \right] \right\}^{1/3} \quad (43)$$

Except for concentrated slurries, the last term of eq. (43) can often be neglected, so that

$$v'_L = 0.43 \{ g d_c [u_G - \varepsilon_G v_{b\infty}] \}^{1/3} \quad (44)$$

Actually  $v'_L$  is proportional to the liquid circulation velocity. The relation of Jadhav and Pangarkar is less easily applicable than the other relations given in Table 6. The reason is that knowledge of  $\varepsilon_G$  and  $v_{b\infty}$  is required. For the latter, Jadhav and Pangarkar (1988) suggested the relations of Grace *et al.* (1976) for "clean" systems and of Zuber and Findley (1965) for other systems.

The significance of the equation of Jadhav and Pangarkar stems not only from the large column diameters for which it has been tested but also from the relatively large superficial velocities, which are well into the industrially important churn turbulent regime. Risking the criticism of Jadhav and Pangarkar, we have used their relation (47) and substituted the maximum possible value of  $v'_L$ , i.e.

$$v'_L = 0.43 (g d_c u_G)^{1/3} \quad (49)$$

$$\text{Then } N_{Re''} = 0.43 \left( \frac{d_c}{d_p} \right)^{1/3} N_{Re'}.$$

With this relation the dashed curve in Fig. 13 was obtained for a 30 cm column and 100  $\mu\text{m}$  particles. Surprisingly the result fits nicely in between the other correlations available. Nevertheless, we advise the use of eq. (44) in practical applications.

The approach based on the energy dissipation rate as outlined above is not limited to a particular type of slurry reactor. Therefore, equations of type (35) and (41) have also been proposed for stirred-tank reactors. For  $\bar{\varepsilon}$  we must then use the total energy dissipation rate originating from both gas and power inputs via the stirrer. Hence,

$$\bar{\varepsilon} = \bar{\varepsilon}_G + \bar{\varepsilon}_\omega \quad (50)$$

$$\bar{\varepsilon} = u_G g + W_\omega / \rho_L V_L \quad (51)$$

where  $W_\omega$  is the power input via the stirrer. The available correlations are summarized in Table 7.

Note that the relation of Sano (1974) contains a correction factor for asphericity of the particles:

$$\psi = 6/(u_p d_p)$$

where  $\psi = 1$  for spheres.

Figure 14 shows that the various relations agree well with each other. We therefore conclude that, despite criticism of this rather rude approach (Chapman *et al.*, 1983), our knowledge of the value of  $k_S$  is relatively well established. Additional research should concentrate on larger tank reactors with volumes above 0.05  $\text{m}^3$  and for  $k_S$  in high intensity equipment such as ejectors.

Table 6. Particle-liquid mass transfer in three-phase sparged bubble columns<sup>†</sup>

Reference	System used	Range of $d_p$ ( $\mu\text{m}$ )	Range of $d_c$ (m)	Range of $u_G$ (m/s)	Range of $N_{Sc}$	Correlation proposed
Sano <i>et al.</i> (1974)	Dissolution of BA, $\beta$ -naphthol, K <sub>2</sub> MnO <sub>4</sub> in water, IER in aqueous HCl	60–2900	0.1–0.2	0.005–0.17	220–1410	$N_{Sh} = 2 + 0.400 N_{Re}^{0.25} N_{Sc}^{1/3}$ (45)
Sänger and Deckwer (1981)	IER in water, aqueous solution of glucoses, glycol	1100–8700	0.08	0.01–0.1	140–50,000	$N_{Sh} = 2 + 0.545 N_{Re}^{0.264} N_{Sc}^{1/3}$ (46)
Jadhav and Pangarkar (1988, 1991)	Dissolution of BA in water, aqueous solutions of glucose and CMC	500–1100	0.1–0.4	0.09–0.35	800–60,000	$N_{Sh} = 2 + 0.0915 N_{Re}^{0.265} N_{Sc}^{0.45}$ (47)
Lazaridis (1990)	IER and polystyrene in water, solutions of water and ethanol and butanol and thickeners (sugar, hydroxyethylcellulose, polyacrylamide)	280–3200	0.15	0.02–0.1	200–80,000	$N_{Sh} = 2 + 0.368 N_{Re}^{0.229} N_{Sc}^{1/3}$ (48)

<sup>†</sup>BA = benzoic acid, IER = ionic exchange resin.

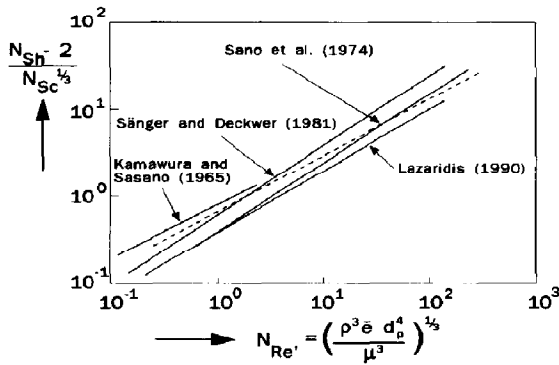


Fig. 13. Correlations for liquid-solid mass transfer coefficients in bubble columns. The dashed curve is from Jadhav and Pangarkar (1991) for  $d_p = 100 \mu\text{m}$ ,  $d_c = 0.3 \text{ m}$ ,  $Sc = 1000$  and  $v'_L$  from eq. (49).

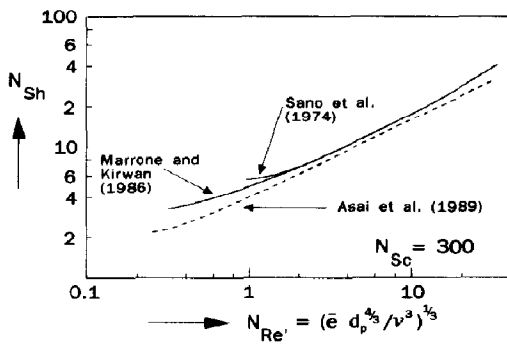


Fig. 14. Liquid-solid mass transfer coefficient,  $k_{LS}$ , in sparged stirred-tank reactors (adapted from Asai *et al.*, 1989).

#### ENHANCEMENT OF GAS-LIQUID MASS TRANSFER

Particles may enhance the gas absorption for several reasons. An overview of different mechanisms which may lead to enhancement is given in Table 8.

*Particles adsorb the transferred component only physically*

This type of enhancement can be illustrated by imagining a simple laboratory experiment in a stirred cell with a flat interface. A gas phase consisting of pure A is absorbed into, e.g., a water-activated-carbon slurry of very fine particles ( $d_p = 3 \mu\text{m}$ ) and the component A is adsorbed strongly on the surface of the activated carbon. Such experiments were first carried out by Kars *et al.* (1979) and Alper *et al.* (1980).

For comparison non-adsorbing particles of the same type are used. If the adsorption is at equilibrium and the solids concentration is not excessively high, the bulk liquid phase concentration may be written as

$$(1 + c_s K_{ad}) \frac{d\bar{c}_{AL}}{dt} = J_A a' \quad (55)$$

in which  $c_s$  is the solids concentration (kg solids/m<sup>3</sup>)

Table 7. Particle-liquid mass transfer in three-phase stirred-tank reactors

Reference	System used	Range of $d_p$ ( $\mu\text{m}$ )	$V_r$ ( $\text{dm}^3$ )	$\bar{\epsilon}_G/\bar{\epsilon}$	Range of $N_{Sc}$	Correlation proposed
Sano <i>et al.</i> (1974)	IER, benzoic acid, $\text{KMnO}_4$ and $\beta$ naphthene particles in aqueous solutions <sup>†</sup>	60–1500	0.7–50	0	220–1280	$N_{Sh} = [2 + 0.4 N_{Re}^{3/4} N_{Sc}^{1/3}] \psi$ (52)
Marrone and Kirwan (1986)	IER in aqueous solution of NaOH	17–90	10.9	0–1		$N_{Sh} = 2 + 0.36 N_{Re}^{3/4} N_{Sc}^{1/3}$ (53)
Asai <i>et al.</i> (1989)	IER in aqueous solution of NaOH and HCl	5–970	1.8	0–1	270–11,000	$N_{Sh} = [2^{2.5.8} + \{0.61 N_{Re}^{0.58} N_{Sc}^{1/3}\}^{5.8}]^n$ , $n = 1/5.8$ (54)

<sup>†</sup>IER = ionic exchange resin.

Table 8. Types of enhanced mass transfer at the gas-liquid interface due to the presence of small particles

- A. Particles in the mass transfer zone adsorb the transferred gas phase component only physically (also known as the shuttle mechanism or grazing particles).
- B. Particles in the mass transfer zone catalyse a chemical reaction involving the transferred gas phase component.
- C. Particles in the mass transfer zone react with the transferred gas phase component.
- D. Particles in the mass transfer zone dissolve and the dissolved reactant reacts with the transferred gas phase component.
- E. Combinations of A-D.

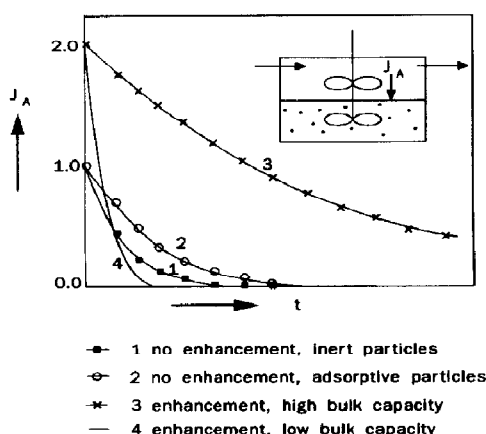


Fig. 15. Typical curves of the absorption rate as a function of time in gas absorption into a batch of slurry in a stirred cell: (—■—) 1 no enhancement, inert particles; (—○—) 2 no enhancement, adsorptive particles; (—×—) 3 enhancement, high bulk capacity; (—) 4 enhancement, low bulk capacity.

liquid) and  $K_{ad}$  the adsorption equilibrium constant ( $m_{liq}^3/kg$  solids). The flux  $J_A$  in the bulk of the slurry can be expressed as

$$J_A = (\bar{c}_{AG} - m\bar{c}_{AL}) / \left( \frac{1}{k_G a'} + \frac{1}{m k_L a' E_A} \right). \quad (56)$$

Here,  $E_A$  is the enhancement factor due to the adsorption of A on the particles in the mass transfer zone close to the gas-liquid interface and the subsequent desorption/redistribution of A in the bulk [the so-called grazing effect, first discovered by Kars *et al.* (1979)].

Figure 15 gives a few examples of the flux as a function of time, to be described by the mass balance. Depending on the different values of the parameters, saturation of the slurry may take an equal, longer or shorter period of time when adsorbing particles are used as compared to inactive particles.

Shorter times can be obtained if the grazing effect is already strong at relatively low particle concentrations. Then, the particles affect the mass transfer much more than the ultimate capacity of the fluid. As discussed below, this situation may arise if carbon particles are attracted to the gas-liquid interface and attain a much higher concentration there than in the bulk. It will be clear that in order to obtain enhance-

ment, the particles should indeed be grazing during their contact time in the mass transfer zone. A film model with stationary particles will not be able to describe this phenomenon. Therefore, a penetration type of model will be required for a proper description. Several factors related to the exact geometry aspects of the particles close to the gas-liquid interface are difficult to assess, and therefore we first discuss a simple quasi-homogeneous penetration model for gas absorption into slurries with particles showing adsorption.

First we consider the absorption of a gas phase component in a slurry (see Holstvoogd *et al.*, 1988) with a relatively simple homogeneous model based on the Higbie penetration theory, neglecting any gas phase resistance. A linear adsorption isotherm for adsorption of the dissolved gas A on the particles will be assumed and the concentration of adsorbed component can be expressed as

$$c_{AS} = n_A / (c_S K_{ad}) \quad (57)$$

where  $n_A$  is the number of moles A adsorbed on the particle phase/ $m^3$  liquid and  $c_{AS}$  the concentration of A in liquid in equilibrium with actual concentration at the solid surface.

As a further simplification the mass transfer and the adsorption on the particles will be considered to be processes in series

$$\begin{aligned} J_A a'_p &= k_S a'_p (c_A - c_{Ais}) = k_{ad} a'_p (c_{Ais} - c_{AS}) \\ &= k_p a'_p (c_A - c_{AS}) \end{aligned} \quad (58)$$

with

$$\frac{1}{k_p} = \frac{1}{k_S} + \frac{1}{k_{ad}} \quad (59)$$

and

$$a'_p = \frac{6c_S}{\rho_p d_p}$$

where  $c_{Ais}$  is the actual concentration of A in the liquid phase at the liquid-solids interface ( $\text{mol}/m^3$  liquid).

The differential equations for the penetration of gas A into a typical surface packet are

for dissolved A:

$$\frac{\delta c_A}{\delta t} = D_A \frac{\delta^2 c_A}{\delta x^2} - k_p a'_p (c_A - c_{AS}) \quad (60)$$



for adsorbed A:

$$\frac{\delta n_A}{\delta t} = k_p a'_p (c_A - c_{AS}) \quad (61)$$

where  $D_A$  is the liquid diffusion coefficient which could be affected by the presence of the particles. The boundary conditions are given here for the case of initial zero loading of the slurry packet (to start with a higher initial concentration, corresponding to a higher slurry bulk loading, is of course possible):

$$t = 0; x \geq 0 \text{ and } t \neq 0; x = \infty: c_A = c_{AS} = n_A = 0 \quad (62)$$

$$x = 0; t \geq 0: c_A = mc_{AG}.$$

The enhancement factor can be calculated from

$$E_A = \frac{\frac{1}{t_c} \int_0^\infty -D_A \frac{\delta c_A}{\delta x} \Big|_{x=0} dt}{\left[ 2 \sqrt{\frac{D_A}{\pi t_c}} (c_{A, x=0} - c_{A, x=\infty}) \right]} \quad (63)$$

Here,  $t_c$  is the Higbie contact time of the slurry element at the G-L surface. This system has been solved numerically by Holstvoogd *et al.* (1988) and we consider a few interesting asymptotic solutions.

— Instantaneous equilibrium between particles and their surrounding liquid. In this case, as was first published by Kars *et al.* (1979),

$$E_A = \sqrt{1 + c_S K_{ad}}. \quad (64)$$

— If the L-S mass transfer adsorption rate parameter  $k_p$  is finite and the particle adsorption capacity is so large that the degree of loading remains much smaller than 1 under all circumstances, then the rate parameters will completely determine the rate of adsorption. Then, the enhancement is described by the Hatta number only:

$$Ha_h = \frac{\sqrt{k_p a'_p D_A}}{k_L} \quad (65)$$

$$E_A = Ha_h / \tanh(Ha_h). \quad (66)$$

Generally, both the rate parameter and the particle capacity are important for the enhancement. A numerical example is given in Fig. 16. The parameter

$$\frac{\delta_{sL}}{\delta_L} = \frac{4(E_A - 1)}{\pi c_S K_{ad}} \quad (67)$$

is the relative saturation of the stagnant film for mass transfer,  $\delta_L$  being the stagnant film thickness and  $\delta_{sL}$  the equivalent saturated layer thickness. The latter thickness is calculated from  $J_{ad}$ , the flux to the particles,

$$\bar{J}_{ad} = \bar{J}_{wpp} - \bar{J}_{npp} = (E_A - 1) k_L m c_{AG} \quad (68)$$

where  $\bar{J}_{wpp}$  and  $\bar{J}_{npp}$  are the absorption rates with particles present and with no particles present, respectively.

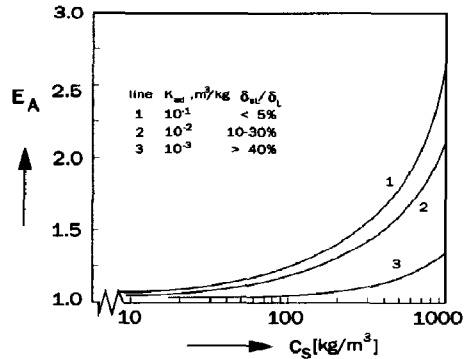


Fig. 16. Enhancement factor vs solids concentration for different adsorption equilibrium constants showing the influence of saturation in the film. Conditions:  $k_L = 3.6 \times 10^{-5}$  m/s,  $k_p = 10^{-6}$  m/s,  $d_p = 3 \mu\text{m}$  (Holstvoogd *et al.*, 1988).

$$\delta_{sL} = \frac{\bar{J}_{ad} t_c}{c_S K_{ad} m c_{AG}} \quad (69)$$

For  $\delta_{sL}/\delta_L < 5\%$ , almost the asymptote of no saturation is found, which generally can be stated as

No saturation for:

$$c_S K_{ad} > \frac{4[Ha_h / \tanh(Ha_h) - 1]}{0.05\pi}. \quad (70)$$

In the case when  $Ha_h > 2$ , then  $c_S K_{ad} \geq 27$ .

For  $\delta_{sL}/\delta_L > 0.4$ , we are practically in the regime where the capacity of the particles completely determines the enhancement. Combining this with eq. (64) gives the result that complete particle saturation occurs for  $c_S K_{ad} < 3.8$  provided the adsorption process is sufficiently fast, which is the case if

$$Ha_h / \tanh(Ha_h) \gg \sqrt{1 + c_S K_{ad}}.$$

Then we have

$$E_A = \sqrt{1 + c_S K_{ad}}. \quad (64)$$

A simple heterogeneous model based on film theory was recently developed by Vinke (1992) and is called the enhanced gas absorption model (EGAM). It includes the following assumptions.

- Under equilibrium conditions, the distribution of the gas between the particle and liquid is governed by a partition coefficient much larger than 1.
- The particles are spherical and of equal size.
- A fraction  $\alpha$  ( $0 \leq \alpha \leq 1$ ) of the surface of the gas bubbles is covered by particles.  $\alpha$  depends on:
  - the gas-liquid-solids contact angle,
  - the modified Eötvös number  $N_{Eo} = (\rho_p - \rho_L) g d_p^2 / (4\sigma_{LG})$ ,
  - $d_b/d_p$ ,
  - hydrodynamic conditions in the reactor and, as yet, has to be determined via fitting of the experimental results.

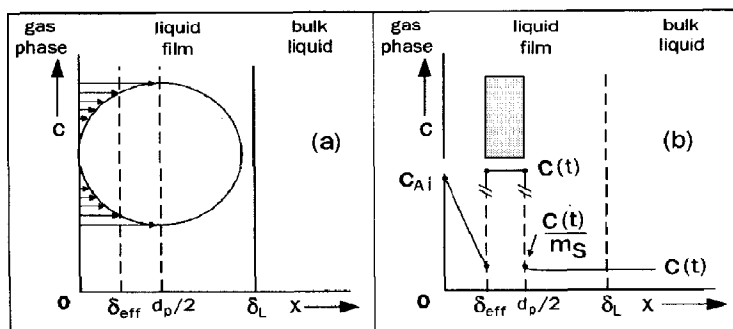


Fig. 17. (a) Gas-liquid interface with an adhering catalyst particle. The average distance between the gas-liquid interface and the spherical surface of the adhering catalyst particle is approximately  $d_p/4$ . (b) According to the enhanced gas absorption model, the adhering gas adsorbing particle is represented by a slab, which has the same gas adsorbing capacity as the particle in Fig. 17(a), and is positioned at a distance  $d_p/4$  from the gas-liquid interface. The effective resistance to mass transfer for the covered part of the gas-liquid interface is located in a film with thickness  $\delta_{eff} = d_p/4$  (from Vinke, 1992).

- The mass transfer of hydrogen through the gas-liquid interface is the sum of the gas absorption rate occurring through the uncovered part  $(1 - \alpha)$  of the gas-liquid interface and the gas absorption rate occurring through the covered part  $(\alpha)$  of the gas-liquid interface.
- The value of mass transfer coefficient  $k_L$  for the uncovered part of the gas-liquid interface is equal to the value measured in a particle-free gas-liquid dispersion under similar conditions.
- Based on experimental observations for the activated-carbon-water system, the particles adhere to the surface [as shown in Fig. 17(a)] so that they are almost completely immersed in the liquid (Vinke *et al.*, 1991a).
- The average distance between the gas-liquid interface and the spherical surface of an adhering catalyst particle is approximately  $d_p/4$  (see Fig. 17).
- The resistance to mass transfer for the covered part of the gas bubble is located in a stagnant liquid film with effective thickness  $\delta_{eff}$ , which is equal to  $d_p/4$  (see previous assumption).

Straightforwardly, this model results in an analytical expression for the enhancement factor  $E_A$ :

$$E_A = 1 + \alpha \left[ \frac{4D_A}{d_p k_L} \left( \frac{1 - \exp(-t_p/t_s)}{t_p/t_s} \right) - 1 \right]. \quad (71)$$

Here  $t_p/t_s$  is the ratio of the residence time of the particle at the surface and the particle saturation time  $t_s$  with

$$t_s = \pi m_s d_p^2 / (24 D_A). \quad (72)$$

Here,  $m_s$  is the dimensionless distribution coefficient between the solid and liquid ( $\text{m}^3 \text{ liquid} / \text{m}^3 \text{ solids}$ ). If we may estimate  $t_p$  from the penetration model for the liquid [eq. (29)], then

$$t_p = t_c = 4D_A / \pi k_L^2$$

and we substitute

$$k_L = \frac{D_A}{\delta_L} \quad (28)$$

where  $\delta_L$  is the boundary layer thickness for mass transfer, and ultimately get

$$\frac{t_p}{t_s} = \frac{96\delta_L^2}{\pi^2 m_s d_p^2} = \frac{9.7\delta_L^2}{m_s d_p^2}. \quad (73)$$

If we have particles, of, typically, half the film thickness then  $t_p/t_s \ll 1$  for  $m_s \gg 100$ .

For comparison, for ethene and propane in activated-carbon-water systems,  $m_s$  is 78 and 1440, respectively [see Tinge *et al.* (1991)]. Under such circumstances where  $t_p/t_s \ll 1$ , the particles remain far from saturation and eq. (71) reduces to

$$E_A = \frac{4\alpha D_A}{d_p k_L} = \frac{4\alpha \delta_L}{d_p}. \quad (74)$$

So, in contrast to homogeneous models, this heterogeneous model explains why the enhancement factor reaches a maximum as a function of  $\epsilon_s$  even if no particle saturation occurs. For complete surface coverage of the gas-liquid interface we have  $\alpha = 1$  and

$$E_{A, \max} = \frac{4\delta_L}{d_p} = \frac{4D_A}{k_L d_p}. \quad (75)$$

For  $k_L$  in aqueous systems typically  $10^{-4} \text{ m/s}$ ,  $D_A$  typically  $10^{-9} \text{ m}^2/\text{s}$  and  $d_p = 5 \mu\text{m}$  (which is half the film thickness) we have  $E_{A, \max} = 8$ , which is an important value for industrial applications.

**Experimental findings.** Enhancement of gas absorption in slurries due to adsorption on small particles has been observed by several authors (see Table 9). Generally, these observations have been done with activated carbon slurries in stirred cells with a flat interface, which means that the interfacial area is well known and the mass transfer without enhancement relatively low. A typical result is given in Fig. 18. As

Table 9. Minimum activated carbon concentration for maximum enhancement ( $c_{S,min}$ ) of gas absorption in various gas-activated-carbon (AcC) slurry systems

Gas-slurry system	$c_{S,min}$ (kg/m <sup>3</sup> )
1. O <sub>2</sub> in aqueous AcC-slurry (Alper <i>et al.</i> , 1980): $d_p \leq 5 \mu\text{m}$ , $T = 50^\circ\text{C}$	1.0
2. CO <sub>2</sub> in aqueous AcC-slurry (Alper <i>et al.</i> , 1980): $d_p \leq 5 \mu\text{m}$ , $T = 25^\circ\text{C}$	2.0–3.0
3. Propane in aqueous AcC-slurry (Kars <i>et al.</i> , 1979): $d_p = 34 \mu\text{m}$	No $c_{S,min}$ known, but, if $c_S = 4.9$ , $E_A = 1.2$
4. CO <sub>2</sub> in aqueous Na <sub>2</sub> CO <sub>3</sub> -buffer/AcC-slurry —(Alper <i>et al.</i> , 1980): $d_p \leq 5 \mu\text{m}$ —(Quicker <i>et al.</i> , 1984): $d_p \leq 5 \mu\text{m}$	2.0–3.0 0.2
5. O <sub>2</sub> in aqueous Na <sub>2</sub> SO <sub>3</sub> /AcC-slurry (Alper and Deckwer, 1983; Alper and Öztürk, 1986b): $d_p \leq 5 \mu\text{m}$	at $5^\circ\text{C}$ : 1.5 at $25^\circ\text{C}$ : 1.0
6. O <sub>2</sub> in aqueous Na <sub>2</sub> S/AcC-slurry —(Pal <i>et al.</i> , 1982): $d_p \leq 5 \mu\text{m}$ , $T = 80\text{--}150^\circ\text{C}$ —(Alper and Öztürk, 1986a): $d_p \leq 10 \mu\text{m}$ , $T = 15, 35^\circ\text{C}$ —(Chandrasekaran and Sharma, 1977): $d_p \leq 100 \mu\text{m}$ , $T = 70^\circ\text{C}$	0.6–16 0.1 1.0
7. O <sub>2</sub> in aqueous glucose/Pt on AcC-slurry —(Lee and Tsao, 1972): according to Alper no enhancement could be possible —(Alper <i>et al.</i> , 1980): $d_p \leq 5 \mu\text{m}$	0.4 10
8. CO <sub>2</sub> in aqueous Na <sub>2</sub> SO <sub>3</sub> -buffer/Pt or immobilized enzyme on AcC-slurry (Alper <i>et al.</i> , 1980; Alper and Deckwer, 1983; Alper and Öztürk, 1986b; Sada Kumazawa, 1982): $d_p < 20 \mu\text{m}$	2–3
9. CO <sub>2</sub> in alkanolamines in presence of AcC particles (Saha <i>et al.</i> , 1992): $d_p$ : 40% below $15 \mu\text{m}$	6

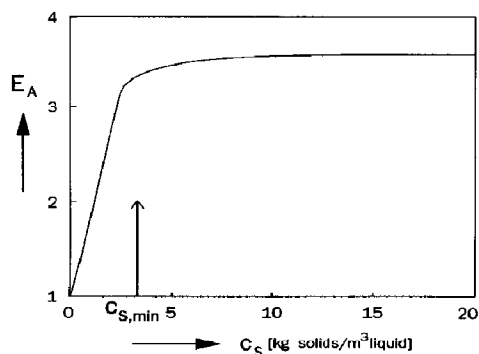


Fig. 18. Enhancement factor with physical absorption of CO<sub>2</sub> in aqueous solutions of activated carbon particles adsorbing CO<sub>2</sub>. Adapted from Alper *et al.* (1980). Flat interface stirred cell,  $\omega = 1.33 \text{ s}^{-1}$ ,  $d_p < 5 \mu\text{m}$ .  $c_{S,min}$  is the solids concentration where the enhancement levels off.

can be seen from this figure, active carbon particles do enhance the mass transfer but the enhancement reaches a stable value for relatively low solids loadings. This turned out to be generally valid also for systems where the carbon acts as a catalyst (Table 9) [see, e.g., Alper and Öztürk (1986b)]. The reason why the enhancement reaches a stable value was explained by Alper and Deckwer (1981) and Sada and Kumazawa (1982) from the assumption of the existence of a particle-free layer at the interface of a thickness of one particle diameter. As a consequence, the minimum effective film, acting as a resistance for mass

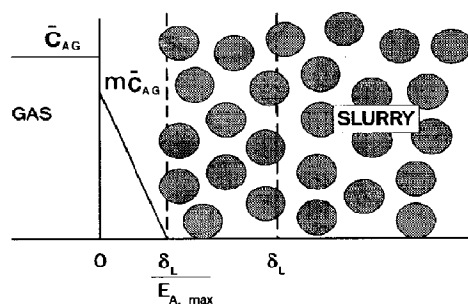


Fig. 19. The situation of maximum absorption enhancement by adsorbing carbon particles according to Alper and Öztürk (1986a).

transfer, has the dimension of the particle (see Fig. 19):

$$\delta_{eff} = \frac{\delta_L}{E_{A,max}} \approx d_p \quad (76)$$

or

$$E_{A,max} = \delta_L / d_p = \frac{D_A}{k_L d_p} \quad (77)$$

However, this model leaves several observations unexplained:

1. The maximum enhancement is reached at particle concentrations as low as  $0.2 \text{ kg/m}^3$  (Quicker *et al.*, 1989). At such low concentrations no uninterrupted particle layers are possible as long as

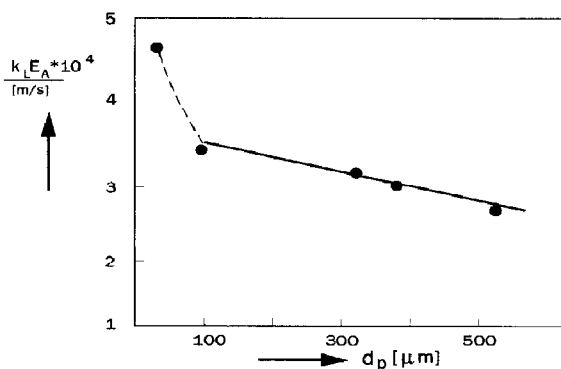


Fig. 20. Decrease of enhanced mass transfer of propane in activated-carbon-water slurries as a function of the average particle diameter; 1% activated carbon,  $\delta_L \approx 5 \mu\text{m}$  (from Kars *et al.*, 1979).

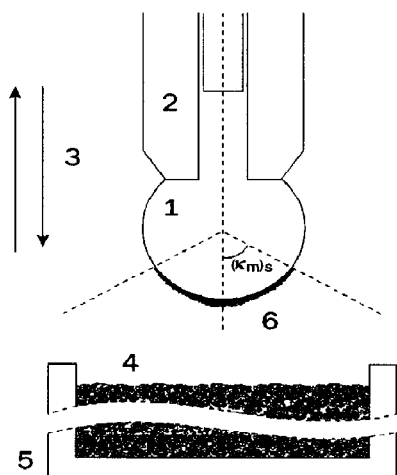


Fig. 21. View of the bubble pick-up (BPU) equipment of Wimmers and Fortuin (1988a). 1. gas bubble; 2. bubble holder (needle of a syringe); 3. stagnant liquid; 4. layer of sedimented particles; 5. cup; 6. layer of solid particles attached to the gas bubble under an angle of coverage ( $\kappa_m$ ).

we have an uniform particle distribution over the liquid.

2. Particles of somewhat larger diameter than the thickness of the mass transfer layer do enhance the gas absorption, although the enhancement decreases with increasing particle diameter (see Fig. 20) (Kars *et al.*, 1979).
3. Even with the assumption of instantaneous adsorption kinetics, the capacity of the carbon particles in the film and the overall kinetics of the mass transfer to the particles are not always sufficient to explain observed enhancement factors if a homogeneous distribution of the particles in the slurry is assumed.

The latter argument was tested quantitatively by Holstvoogd *et al.* (1988) analysing the experiments

of Alper *et al.* (1980) with the model given above. Although a few parameters had to be estimated, it became clear that the enhancement factors observed by Alper for a typical case of oxygen absorption in a carbon slurry could only be explained by a much higher concentration of particles in the mass transfer zone than in the bulk of the slurry. The same conclusions could be drawn for the experiments of Alper on  $\text{CO}_2$  absorption. This phenomenon is related to the wetting properties of the activated carbon. An elegant demonstration of this effect was given by Wimmers and Fortuin (1984, 1988a) in their bubble pick-up experiment, in which they showed that particles of activated carbon accumulate at the interface of a gas bubble (hydrogen) attached to a capillary tube (see Fig. 21). It therefore seems to be clear that the explanation of the enhancement factor shown in Fig. 18 is that activated carbon particles are attracted to the G-L interface reaching a high concentration there, and being refreshed just like the fluid element itself, thus reducing the effect of saturation. The limitation in the maximum enhancement shown in Fig. 18 is probably caused by a maximum solids concentration at the interface rather than by a solids-free zone.

All these phenomena can now be understood from the EGAM of Vinke (1992) as described above. Following Schumpe *et al.* (1987b) [see eq. (8)], Vinke (1992) also proposed a type of Langmuir adsorption isotherm to describe the G-L surface fraction  $\alpha$  covered by particles:

$$\frac{\alpha}{\alpha_{\max}} = \frac{K \bar{c}_s}{1 + K \bar{c}_s} \quad (78)$$

where  $K$  is a particle-to-bubble adhesion constant, to be found via fitting of the experimental results. Experimental results obtained in a stirred-tank reactor could be satisfactorily explained in this way (see Fig. 22). From the above it follows that it would be interesting to have experimental results from stirred cells but with aqueous solutions containing small hydrophilic particles with a large adsorption capacity instead of the hydrophobic carbon particles. Recently, such experiments have been carried out with highly porous kieselguhr (Quicker *et al.*, 1989).

As expected from what we now know, enhancement was observed if  $\text{CO}_2$  was absorbed in a slurry of such particles containing an aqueous buffer solution of carbonate and bicarbonate ions. Unfortunately, the explanation is not unambiguous. It may be that no enhancement was observed due to lack of solids accumulation at the interface, although the authors explain their observation as the possible blocking of the polar active sites by the strong polar carbonate and bicarbonate ions, which cannot be excluded either. Earlier, similar negative results were obtained with  $10 \mu\text{m}$  13X and 5A zeolites with the well-known oxygen-aqueous-sodium sulphite system (Alper and Öztürk, 1986b).

Here, strong adsorption of water on the active sites possibly prevented any adsorption of oxygen.

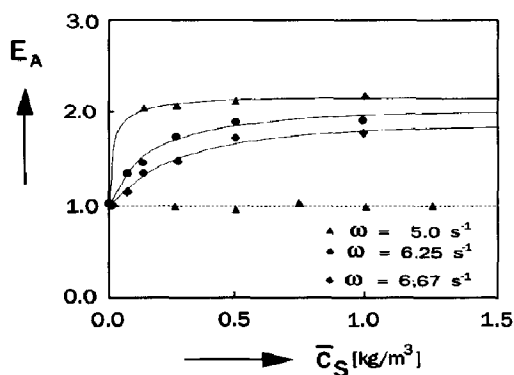


Fig. 22. Enhancement factor measured as a function of catalyst particle concentration in the suspension at different stirrer speeds. The solid lines are calculated with the model consisting of eq. (78) and the best-fit values of  $K$  and  $\alpha_{\max}$ . Dashed curve: system Rh/Al<sub>2</sub>O<sub>3</sub>-demi-water-hydrogen.  $\omega = 6.67 \text{ s}^{-1}$ , small amount of gas bubbles in the suspension. No particle-to-bubble adhesion occurs. Other curves: system Pd/C-demi-water-hydrogen. Applied stirrer speed ranged from  $\omega = 5.0 \text{ s}^{-1}$ , no gas bubbles (flat gas-liquid interface) to  $\omega = 6.67 \text{ s}^{-1}$ , small number of gas bubbles. Particle-to-bubble adhesion occurs (adapted from Vinke, 1992).

Such an explanation is not possible for the experiments of Wimmers and Fortuin (1988b), who compared catalytic active Pd on activated carbon with catalytic active Pd on hydrophilic alumina, which is also highly porous. With both catalysts having the same activity for converting absorbed hydrogen, significant enhancement was observed with active carbon as a carrier only. This provides experimental support for the accumulation of activated carbon at the interface as a cause of the enhancement. Extra support was obtained by Vinke (1992), who compared adsorption of hydrogen in demi-water with suspended rhodium-Al<sub>2</sub>O<sub>3</sub> and palladium-activated-carbon. Again, no enhancement was obtained for Al<sub>2</sub>O<sub>3</sub> particles (see Fig. 22), which is explained by the zero surface coverage  $\alpha$ .

Holstvoogd *et al.* (1988) and Holstvoogd (1988) studied the influence of the geometry and position of the first particle rows on the gas absorption with a numerical model taking into account the molecular diffusion to the particle surface. At high local particle concentrations and in the absence of particle saturation effects, they observed that enhancement is mainly determined by the first particle layer and its position with respect to the interface. In fact, this result supports the physical background of the surface coverage concept of Vinke (1992).

In most industrial reactors the G-L mass transfer constant  $k_L$  will be much higher than in stirred cells with a flat interface. With the mechanisms explained here it is not possible to predict exactly the resulting enhancement factor as unknown time constants for particle attraction to the interface are involved.

According to experiments reported by Alper (1987) and Quicker *et al.* (1987), the observed enhancement

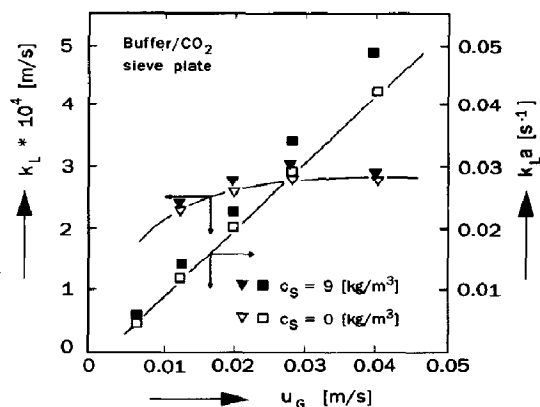


Fig. 23. Effective values of  $k_L$  and  $k_L a$  as a function of superficial velocity in the absence and presence of activated carbon particles in the bubble column showing hardly any influence of the particles; 73.5% of all particles  $< 6 \mu\text{m}$  (Alper, 1987 and Quicker *et al.*, 1987).

by the grazing effect in, e.g., a bubble column operating with activated carbon slurries is marginal or absent (see Fig. 23). On the other hand, Vinke (1992) calculated that enhancement factors up to a factor of 4 should be possible in large-scale bubble column reactors. This has to be confirmed by measurements.

These phenomena are very important, especially because they may proceed in parallel or as a first step in chemical reactions occurring on a catalyst on a carbon support. Activated carbon supports are used in many catalytic slurry systems and similar phenomena have been observed for other active solids (Alper and Deckwer, 1983; Alper and Öztürk, 1986).

Adding surface adhering particles as a non-catalytic shuttle to enhance mass transfer may also become attractive. An industrially important example is the absorption of carbon dioxide in aqueous amine solutions. Here addition of fine activated carbon particles could enhance the absorption rate by as much as a factor of 9 in a stirred cell (Saha *et al.*, 1992), although it will probably be lower in commercial absorbers.

Highly interesting for all the above reasons is a patent application of Vinke *et al.* (1991) to modify originally non-surface-adhering catalyst particles to surface-adhering particles. With these techniques they succeeded in creating surface-adhering properties in alumina particles and then observed enhancement with these particles.

Powerful tools for further investigation should include simultaneous absorption of various gases with different adsorption characteristics, allowing discrimination between the true effect of adsorption and other possible effects such as changes in  $k_L$  and  $a$  caused by the particles. This method has been used previously, although with different aims, by Robinson and Wilke (1974) and Beenackers and van Swaaij (1976).

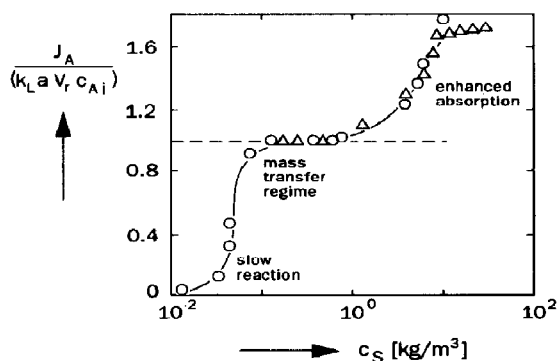


Fig. 24. Absorption of oxygen into glucose solutions containing fine particles of activated carbon (from Alper and Deckwer, 1988; Alper *et al.*, 1980).

*Particles catalyse a chemical reaction involving the absorbed gas phase component*

If the catalyst particles have a diameter much smaller than the thickness of the mass transfer film and if sufficient particles are available in the film, then enhancement of gas absorption due to chemical reaction may occur provided the specific chemical conversion rate is high enough. If the reaction within the film can be considered as quasi-homogeneous, then the system can be described by the well-known relations for gas absorption with homogeneous chemical reaction [see, e.g., van Krevelen and Hoftijzer (1948) or Westerterp *et al.* (1984)]. Then it is possible to use the simple film theory because no problem of depletion of particles will occur. However, one should always be aware of the possible complications of adsorption in parallel (on the catalyst carrier) or in series (on the active sites) with the chemical reaction. This again would involve effects of possible saturation, as mentioned above.

Another important complication may occur when particles are attracted to the gas-liquid interface, as has been observed for carbon-water slurries [see, e.g., Vinke (1992), Wimmers and Fortuin (1988b), Holstvoogd *et al.* (1988)] and for aqueous sulfur slurries [Wubs *et al.* (1990)]. Enhanced gas absorption will then occur at much lower bulk loadings of catalyst particles. Usually the assumption of zero or, in case of equilibrium reactions, equilibrium bulk concentrations of absorbed gases is realistic if enhancement is observed. This is due to the relatively high bulk volume as compared to the film volume in normal gas-liquid contactors (high "hinterland" ratio). A nice sketch of this situation has been given by Alper and Deckwer (1983) (see Fig. 24).

It has been argued that enhanced absorption in a slurry is a regime to be avoided because this would require excessive amounts of catalyst and/or would give rise to low selectivities in most reactions (although there are exceptions). In the situation of increased particle concentration at the gas-liquid interface, both statements are not necessarily true. Knowledge of the hinterland ratio and the bulk loading of

the catalyst are insufficient to describe the system if surface particle accumulation effects play a role.

For enhancement in a slurry reactor (first-order reaction, constant gas phase concentration, no liquid through-flow of bulk) Wimmers and Fortuin (1988b) derived

$$E_A^0 = \frac{(Ha_f)}{\sinh(Ha_f)} \times \left\{ \cosh(Ha_f) - \frac{1}{\cosh(Ha_f) + \left[ \frac{k'_r c_{Si} \sinh(Ha_f)}{k_L a' Ha_f} \right]} \right\} \quad (79)$$

in which

$$Ha_f = \frac{\sqrt{k'_r c_{Si} D_A}}{k_L} \quad (80)$$

where

$E_A^0$  is the actual absorption rate divided by  $k_L a V_r c_{A1}$ ; note that for fast reaction, where  $\bar{c}_A = 0$ ,  $E_A^0 = E_A$ .  $c_{Si}$  is the actual solids concentration in the gas-liquid film for mass transfer, described by Wimmers and Fortuin via a Freundlich isotherm still containing some empirical factors.

$k'_r$  is the pseudo-homogeneous first-order reaction rate constant,  $m^3/kg s$

In principle, the rate constant  $k'_r$  can contain a.o.t. mass transfer rates to the surface of the particles ( $k_S$ ) and diffusion limitation inside the particles. For example, for first-order reaction at the porous catalyst surface we may write

$$\frac{1}{k'_r c_{Si}} = \frac{1}{k_S a'_{pi}} + \frac{1}{a'_{pi} \sqrt{k''_r a'_s D_A} \tanh \phi} \quad (81)$$

with  $a'_{pi}$  the specific solids external surface area at the gas-liquid interface and  $\phi$  defined by eq. (2). In particular, if the true surface rate constant  $k''_r$  is relatively high compared to  $k_S$ , the reaction in the film can be limited by  $k_S$ .

If the concentration of solids at the gas interface is high, the enhanced mass transfer is very sensitive to the actual geometrical position of the particles, as pointed out by Holstvoogd *et al.* (1988).

More complex systems than the still rather simple first-order kinetics leading to eq. (79) have been analysed theoretically by Sada *et al.* (1984a). In applying the van Krevelen-Hoftijzer approximation, they also obtained approximate solutions for a bimolecular second-order catalytic reaction with a liquid component and for two absorbing components reacting with each other on the catalytic surface. For the latter system, experimental results were reported on the oxidation of  $SO_2$  on activated carbon in a stirred-cell reactor (see Sada *et al.*, 1983).

*Experimental results with catalyst particles.* Chemical-enhanced gas absorption with fine catalyst particles in slurries has been observed by several authors

and for several chemical systems (see Table 9). A special point of note is that because most experiments have been carried out in flat interface stirred cells, it is difficult to distinguish between the heterogeneous catalysis and the gas adsorption as the main cause of enhancement. A very interesting technique called the constant bubble size (CBS) method was used by Wimmers and Fortuin (1988a). Stagnant packets of particles are attached to a bubble whose volume is kept constant by adding a measured amount of gas to it through a needle. The enhancement caused by the particles is measured in a situation where they are motionless, and therefore shuttle effects are excluded. Wimmers and Fortuin used this technique for the hydrogenation of hydroxylamine phosphate in aqueous solution catalysed by small Pd/activated-carbon (AcC) particles. Experiments in a stirred-tank slurry reactor were also carried out (Wimmers and Fortuin (1988b) with varying concentrations of Pd/AcC and Pd/ $\text{Al}_2\text{O}_3$  particles. Typical results are given in Fig. 25. As can be seen, Pd/ $\text{Al}_2\text{O}_3$  particles gave no enhancement, but the Pd/AcC particles did even at relatively low bulk particle loadings. Wimmers and Fortuin also presented their results in terms of an increased particle concentration at the gas-liquid interface.

Holstvoogd *et al.* (1988) also mentioned enhancement factors in the same range for similar conditions. This shows that enhancement with catalyst particles can also be important under practical conditions. Enhancement factors of 3–4 can be very attractive, especially in high-pressure equipment with related high specific capital cost.

It must be mentioned here that the work of Wimmers and Fortuin has been criticized by Lindner *et al.* (1988), who studied the same reaction system. The increased absorption rate, which they too observed, was ascribed to an increased  $k_L a$  due to the addition of particles. They could substantiate their statement by showing that the bubble hold-up also increased. However, from Wimmers and Fortuin's result it can be found that, at a given catalyst bulk loading of  $c_s = 0.75 \text{ kg/m}^3$ , the enhancement factor does increase from 2 to 4 when the temperature increases from 20°C to 40°C (see Fig. 26). It therefore seems at least likely that chemical enhancement as well as  $k_L a$

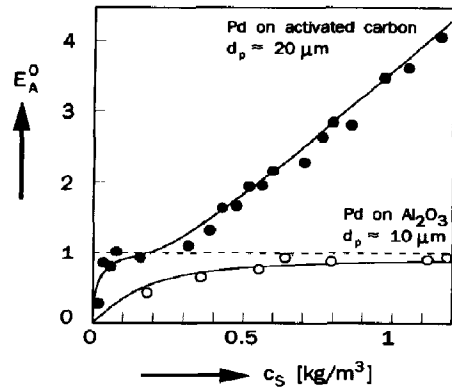


Fig. 25. Enhancement of absorption of hydrogen into aqueous hydroxylamine phosphate solutions by catalyst particles as a function of the catalyst loading of the bulk; stirred-tank reactor. Drawn lines are model calculations with best-fit parameters (from Wimmers and Fortuin 1988b).

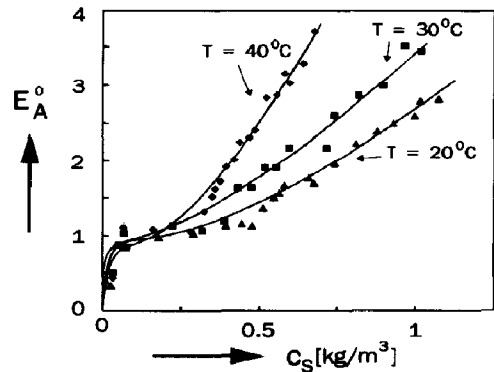


Fig. 26. Effect of temperature on enhancement factor for the same system as Fig. 25, catalyst Pd on activated carbon (Wimmers and Fortuin, 1988b).

do not enhance mass transfer. However, Vinke could modify the surface of the catalyst carrier in such a way that  $K$  and  $\alpha_{\max}$  could be changed [eq. (78)]. In this way, unambiguous proof could be obtained that enhancement both with gas bubbles and in stirred cells could be obtained via increasing surface adherence of the catalyst particles with increasing  $\alpha$  (see Fig. 27). Here

$$E'_A = \left\{ \frac{\text{gas absorption rate per unit mass of modified catalyst particles}}{\text{gas absorption rate per unit mass of unmodified catalyst particles}} \right\}_{\text{SHC}} \quad (82)$$

is the cause of the increased overall rate. This discussion shows the importance of evaluating all the variables of the problem at the same time. This can be done, for example, by simultaneous absorption with the reacting gas of a non-adsorbing and non-reactive gas, as discussed above.

Another equally effective approach was followed by Vinke (1992). Hydroxylamine was hydrogenated to ammonium with rhodium on alumina particles as a catalyst. As we have seen in Fig. 22, these particles

where SHC is the similar hydrodynamic conditions.

Wimmers *et al.* (1988) measured the influence of the particle diameter on the enhancement (see Fig. 28). The observed linear relationship between  $E'_A$  and  $1/d_p$  had already been theoretically predicted by Pal *et al.* (1982) for a high catalyst loading.

This can also be explained by eq. (79), which for  $Ha_f > 2$  reduces to

$$E'_A = \frac{Ha_f}{\tanh Ha_f} \simeq Ha_f = \frac{\sqrt{k'_r c_{Si} D_A}}{k_L} \quad (83)$$

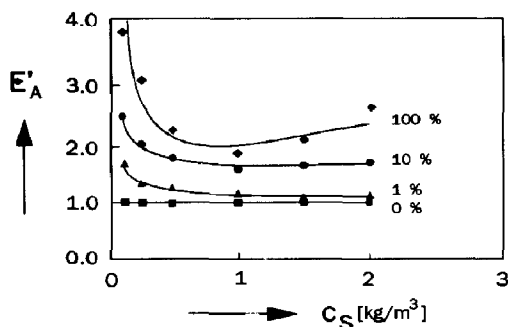


Fig. 27. Measured enhancement factor  $E'_A$  defined in eq. (82) as a function of the catalyst particle concentration and modification percentage. The solid lines were calculated with the enhanced gas absorption model of Vinke, using the following best-fit values: 0% unmodified catalyst; 1%  $\alpha_{\max} = 0.56$ ,  $K = 0.93 \text{ m}^3 \text{ kg}^{-1}$ ; 10%  $\alpha_{\max} = 0.81$ ,  $K = 0.61 \text{ m}^3 \text{ kg}^{-1}$ ; 100%  $\alpha_{\max} K = 0.18 \text{ m}^3 \text{ kg}^{-1}$  (Adapted from Vinke, 1992).

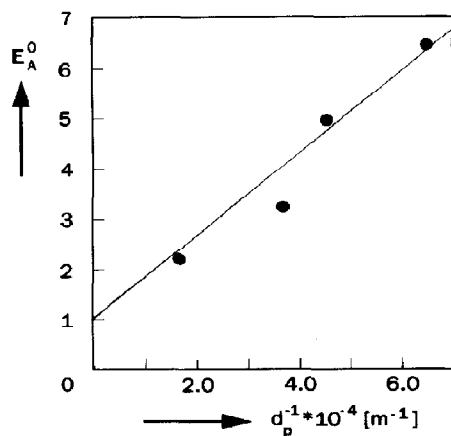


Fig. 28. Enhancement factor for hydrogen absorption in an aqueous hydroxylamine solution as a function of the reciprocal Sauter mean diameter of Pd/activated carbon catalyst particles.  $C_S = 1.5 \text{ kg/m}^3$ , flat interface stirred cell (from Wimmers *et al.*, 1988).

If the rate of reaction is controlled by mass transfer around the particles, then it follows from eq. (81) that

$$k'_r C_{Si} = k_S a'_{pi} = \frac{k_S 6\epsilon_{s,i}}{d_p} \quad (84)$$

Assuming  $Sh = 2$  around the particles

$$k_S = 2D_A/d_p$$

and we get

$$E_A^0 = \frac{D_A}{k_L} \sqrt{\frac{12\epsilon_{s,i}}{d_p}} \cdot \frac{1}{d_p} \quad (85)$$

Because all other data were known in their experiments, Wimmers *et al.* (1988) could establish that, at bulk particle loadings between 0.6 and  $1.5 \text{ kg/m}^3$ , the film concentration varied between 18 and  $120 \text{ kg/m}^3$

while the settled-bed density of the particles was  $235 \text{ kg/m}^3$ . It should be realized that these are average or effective film concentrations. The actual distribution in the film can be very far from an equal distribution. This can have an important impact on the calculated enhancement factor [see Holstvoogd *et al.* (1988) and Karve and Jevekar (1990)]. In many cases, with catalytic reactions, a levelling-off of the enhancement factor takes place at a certain catalyst loading. As mentioned above, this can be explained by the surface coverage model of Vinke (1992). Alper (1985) measured the absorption of oxygen into  $\text{Na}_2\text{S}$  using small carbon particles as a catalyst. Here also the enhancement factor reached a stable value beyond a certain activated carbon concentration. This was explained by the fact that oxygen has to diffuse through a small effective liquid layer before it can reach the first layer of particles. However, it followed clearly from their experiments that the enhancement was still influenced strongly by the concentration of  $\text{Na}_2\text{S}$ , which is the liquid phase reactant. This is not consistent with the effective particle free layer explanation. An alternative explanation for this levelling-off could be that the gas-liquid interface becomes effectively saturated with catalyst particles at a certain catalyst bulk loading (Vinke, 1992).

We may conclude that the enhancement of gas absorption in slurries by catalytic particles is an interesting phenomenon which can be of practical importance if particles accumulate at the gas-liquid interface. Simultaneous adsorption can be a complicating factor, although for a bubbling slurry column the latter phenomenon seems to be of less importance. The reason for the different impact may be as follows. If particles are attracted to the interface, their contact time at the bubble interface may be significantly longer than  $t_c$  of the fluid elements. The longer the residence time, the higher the saturation for adsorption, while the catalytic reaction enhancement will not be affected or will be less affected. However, much more experimental information will be required to solve this problem completely.

#### Reactive particles

Doraiswamy and Sharma (1984) have given an overview of such systems. Frequently no chemical enhancement occurs because, even if the reaction rates are intrinsically rapid, product layer diffusion will often limit the conversion rate. The latter will not be the case if the products rapidly dissolve in the liquid. If the particles are very small they may disappear during the contact time, and a penetration type of model should be used to calculate the absorption rates along the lines used by, for example, Holstvoogd *et al.* (1988).

Another case is the conversion of small hydridable metal particles in a slurry (Ptasinski *et al.*, 1983, 1986; Holstvoogd *et al.*, 1986). This problem is similar to the enhancement by adsorption, as here an equilibrium between hydrogen and the metal/hydride particles also plays a role, as well as saturation of the particles.



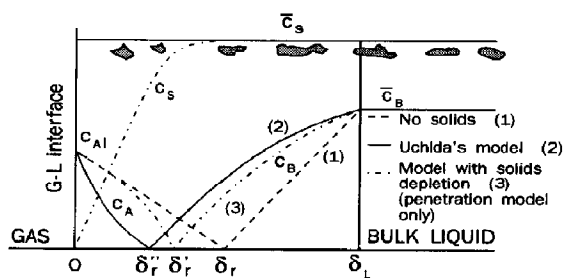


Fig. 29. Concentration profiles of dissolving gas A and sparingly soluble fine particles B (instantaneous reaction between A and B in the liquid phase, with and without depletion of solid particles at the gas-liquid interface).

However, the adsorption isotherms are strongly non-linear and form a kind of plateau. The hydride formation can be assumed to be very rapid and the external mass transfer of hydrogen to the particles is limiting the local rate. During the contact time hydride particles may become saturated, thus limiting the enhancement. It was shown by Holstvoogd *et al.* (1986), both from theory and by experiments, that the possible enhancement at 6% volume in silicon oil would remain limited (e.g. up to 1.4 in a flat interface stirred cell) unless accumulation of particles took place. This turned out not to be the case, as both the metal and the hydride are excellently wetted and no metal particles could be picked up by a gas bubble, which is in contrast to the water-activated-carbon system. Presently, no clear examples of important enhancement seem to be available in this category.

#### Dissolving particles

Reaction of a gas with a reactant originating from small dissolving particles is common. This system has been studied extensively and has been discussed elsewhere in more detail (Beenackers and van Swaaij, 1986). Many regimes are possible, even if we assume infinitely fast reactions [see, e.g., Uchida and Wen (1977)]. For special cases, film model solutions are available. These models can be sufficient if, during the contact time, the particles inside the surface elements will not dissolve completely. However, Fig. 29 shows a typical situation where this could happen due to an infinite rate of reaction between the gas phase reactant A and the reactant B originating from dissolving B particles in the bulk. If no particles were present inside the film, the resulting concentration profile would give a reaction plane inside the gas-liquid interface mass transfer film (shown as curve 1 in Fig. 29). If small particles are present in the film, particles tend to dissolve faster in the film than in the bulk due to a locally larger driving force. Close to the liquid-solid interface there will be microreaction planes in the form of a sphere around each particle. This will further enhance the dissolution rate of the particles. Therefore, the gas phase reactant A will also disappear earlier and the plane where all A has been reacted away moves towards the G-L interface. This

resulting extra enhancement of absorption of A has been described successfully by a model published by Uchida *et al.* (1975, 1981) (curve 2 in Fig. 29). However, close to the G-L interface, B particles could completely disappear. This cannot be described with a film model, but if properly described by a penetration model it would lower the extra enhancement of the absorption of A. This is shown qualitatively in Fig. 29 as curve 3.

It has been indicated previously (Beenackers and van Swaaij, 1986) that for practical systems the situation of disappearing particles may actually occur, and it would be worthwhile to establish a penetration model for that case.

#### Miscellaneous systems

Although strictly speaking outside the scope of this paper, we now mention a few cases of mass transfer intensification by other particles such as colloidal particles, (micro) emulsions, micelles, etc.

Bruining *et al.* (1986), Mehra and Sharma (1985, 1986), Littel (1991) and van der Meer *et al.* (1992) showed mass transfer enhancement by a second emulsified liquid phase.

Mehra (1990) recently studied the problem of absorption in slurries of finite capacity microphases. His set of analytical models is also suitable for non-linear equilibrium relations via segmental (piecewise) linearization.

Mehra (1988) and Mehra *et al.* (1988) published extended penetration models with reaction both inside and around ultrafine particles, microemulsions or micelles. With these models they were able to describe their experimental systems showing mass transfer intensification. Mehra and Sharma (1988) studied the absorption of  $H_2S$  in aqueous solutions of iodides containing dissolved iodine. Small particles of sulphur formed in this process tend to enhance the absorption above the value for the instantaneous gas-liquid reaction by simultaneous adsorption of  $H_2S$  on solid sulphur. As pointed out by Wubs *et al.* (1990), a substantially higher sulphur hold-up at the interface film compared to bulk conditions must be present. This is probably also true for the experiments of Mehra and Sharma.

Bhagwat (1990) and Bhagwat *et al.* (1987) give a theoretical treatment of the enhancement of liquid-solid mass transfer by penetration of very fine bubbles in the boundary layer for mass transfer around the particles. However, as far as we know, there is no experimental evidence as yet on how this phenomenon could be significant.

#### CONCLUSIONS

Significant progress has been made in establishing the influence of solids on the volumetric mass transfer coefficient,  $k_L a$ , in slurry reactors. If the liquid viscosity is high or if the density difference between particles and liquid is small, relations based on the effective suspension viscosity can be successfully applied. For dense particles in low-viscous liquid our knowledge is

still rudimentary. Our understanding of the influence of poorly wettable solids is also incomplete although preliminary models based on surface coverage by the particles have been published. Most available data have been obtained in reactors which are too small and often at gas loads which are too low to be of much value for scaling-up purposes. So, strikingly few data are available for the industrially most important regime of churn turbulent flow in bubble columns and virtually no information is available on the influence of pressure. For any system and all operating regimes, our relevant information on the behaviour of slurries in draft tube reactors is very limited. The positive news is that we now know what minimum dimensions the reactors should have to get relevant data for scale-up.

We have hardly any information on the *volumetric gas-side mass transfer coefficient*,  $k_G a$ , in slurry reactors.

With respect to the *true gas-liquid specific contact area*,  $a$ , we have no clear picture yet on the influence of solids below 100  $\mu\text{m}$  diameter at hold-ups below 0.6% (region A). Most data suggest substantial increases of  $a$  to be possible in this region where many heterogeneous catalytic slurry processes are operated. However, there are also reports on a lowering of  $a$  in this region due to the solids.

In region B, which covers the particle size range 100–1000  $\mu\text{m}$  at any solids loading and particles below 100  $\mu\text{m}$  for  $\epsilon_S > 0.6 \text{ vol}\%$ , useful relations have been developed for the conditions where the concept of the effective slurry viscosity is fruitful, say above 5 mPa s.

Additional work is necessary both for relatively dense particles in low-viscous liquids and for large particles of about the same density as the liquid, which is relevant for bioreactors. Particularly if the slurry can be considered as a pseudo-homogeneous phase, the effect of inert solids on the *true liquid mass transfer coefficient at the gas-liquid interface*,  $k_L$ , is relatively well understood, although the theory of Kamase and Moo-Young (1990) has yet to be validated by accurate measurements on the value of the interfacial area. Much less clear is the picture with small fractions of heavy particles, which is typical for heterogeneous catalytic slurry reactions. A moderate enhancement up to 30% seems possible depending on factors not yet well understood.

Our knowledge on the *true mass transfer coefficient at the liquid-solid interface*,  $k_S$ , is relatively well established. Additional research should be concentrated on larger tank reactors ( $> 0.05 \text{ m}^3$ ) and for  $k_S$  in high-intensity equipment such as ejectors.

The progress made during the last decade in our understanding of how small particles with a high physical adsorption capacity and catalytic particles may enhance the gas absorption rate into a slurry has been really impressive. Enhancement of physical absorption of gas in a slurry by particles of diameters of the order of, or smaller than,  $d_p = D/k_L$  via a shuttle mechanism is now reasonably well understood.

We also understand how hydrophobic particles in hydrophylic liquids tend to stick to the gas-liquid interface, and thus may realize a significant enhancement of the mass transfer up to a factor of 5, also at very low bulk concentrations of the catalyst. Here we need additional, carefully designed, experiments in industrial reactors of sufficient scale to confirm these predictions under practical circumstances. Meanwhile the first patents have been filed to improve the gas-liquid surface adhering properties of catalyst carriers. Powerful tools for further research should include simultaneous absorption of various gases with different absorption characteristics, thus allowing discrimination between the true effect of adsorption and other possible effects such as a change in  $k_L$  and  $a$  caused by the presence of the particles.

#### NOTATION

$a$	specific gas-liquid contact area, $\text{m}^2/\text{m}^3$ reactor
$a'$	specific gas-liquid contact area, $\text{m}^2/\text{m}^3$ liquid phase
$a_p$	specific external interface of solids, $\text{m}^2/\text{m}^3$ reactor
$a'_p$	specific external interface of solids, $\text{m}^2/\text{m}^3$ liquid phase
$a'_{pi}$	specific external interface of solids at gas-liquid interface, $\text{m}^2/\text{m}^3$ liquid
$a_S$	specific internal interface of solids per unit porous particle volume, $\text{m}^{-1}$
$c_A$	concentration of species A, $\text{kmol}/\text{m}^3$
$\bar{c}_A$	bulk concentration of species A, $\text{kmol}/\text{m}^3$
$c_{Ai}$	concentration of species A in liquid at gas-liquid interface, $\text{kmol}/\text{m}^3$ liquid
$c_{AiS}$	liquid concentration of A near solids interface, $\text{kmol}/\text{m}^3$ liquid
$c_{AS}$	concentration of A in liquid in equilibrium with actual concentration of A at the solid surface, $\text{kmol}/\text{m}^3$ liquid
$c_S$	concentration of solids in liquid, $\text{kg solids}/\text{m}^3$ liquid
$c_{Si}$	concentration of solids in liquid at gas-liquid interface, $\text{kg solids}/\text{m}^3$ liquid
$c_{S, \min}$	minimum concentration of solids for which maximum enhancement is obtained, $\text{kg solids}/\text{m}^3$ liquid
$C$	constant
CMC	carboxy-methyl cellulose
$d$	diameter, $\text{m}$
$d_b$	bubble diameter, $\text{m}$
$d_c$	column diameter, $\text{m}$
$d_i$	impeller diameter, $\text{m}$
$d_p$	particle diameter, $\text{m}$
$d_s$	sparger holes diameter, $\text{m}$
$D$	molecular diffusion coefficient, $\text{m}^2/\text{s}$
$D_i$	intraparticle diffusion coefficient, $\text{m}^2/\text{s}$
$D_S$	axial dispersion coefficient of particles, $\text{m}^2/\text{s}$

$\bar{e}$	average specific power input per kg liquid, W/kg			columns), dimensionless
$E_A$	enhancement factor of component A, defined by eq. (3), dimensionless	$N_{Re'}$		Reynolds number $[ = (\bar{e}d_p^4/v_L^3)^{1/2} ]$ [in bubble columns $= (u_G g d_p^4/v_L^3)^{1/2}$ ], dimensionless
$E_A^0$	$J_A/k_L c_{Ai}$ , dimensionless	$N_{Re''}$		Reynolds number $( = v_L' d_p/v_L )$ , dimensionless
$E_A^{\max}$	maximum enhancement factor, dimensionless	$N_S$		surface tension number $( = d_c^2 g \rho / \sigma )$ , dimensionless
$E_A'$	enhancement factor of component A, defined by eq. (82), dimensionless	$N_{Sc}$		Schmidt number $( = \mu / \rho D )$ , dimensionless
$g$	gravity constant, m/s <sup>2</sup>	$N_{Sh}$		Sherwood number $( = k_L d_p / D \text{ around bubbles} ) ( = k_s d_p / D \text{ around particles} )$ , dimensionless
$H$	height of column, m			
$Ha$	Hatta number, dimensionless	$p$		pressure in reactor, N/m <sup>2</sup>
$Ha_f$	modified Hatta number defined by eq. (80)	$R_1, R_2, R_3, R_4, R_4'$		resistances against mass transfer, s
$Ha_h$	modified Hatta number for heterogeneous applications, defined by eq. (65)	$t$		time, s
$J_A$	molar flux of A, kmol/(m <sup>2</sup> s)	$t_c$		contact time in penetration model, s
$J_{ad}$	adsorption flux to particles, kmol/(m <sup>2</sup> s)	$t_p$		residence time of particle at gas surface, s
$k$	fluid consistency index, Pa s <sup>n</sup>	$t_s$		saturation time of particle, eq. (72), s
$k_{ad}$	adsorption rate constant, m/s	$T$		temperature, K or °C
$k_G$	gas-side mass transfer coefficient, m/s	$u$		superficial velocity, m/s
$k_L$	liquid-side mass transfer coefficient, m/s	$v_{bx}$		bubble rise velocity, m/s
$k_p$	overall particle adsorption rate constant defined by eq. (59), m/s	$v_L'$		characteristic turbulence velocity defined by eq. (43), m/s
$k_r$	first-order reaction rate constant, 1/s	$v_t$		terminal settling velocity of single particle, m/s
$k_r'$	first-order reaction rate constant, m <sup>3</sup> /(kg solids s)	$v_p$		hindered particle settling velocity in slurry, m/s
$k_r''$	first-order surface reaction rate constant, m/s	$V_r, V_L$		volume of reactor and of liquid phase, m <sup>3</sup>
$k_S$	liquid-to-solid mass transfer coefficient, m/s	$W$		power input, W
$K$	Langmuir type of particle-to-bubble adhesion constant defined by eq. (78), m <sup>3</sup> liquid/kg solids	$x$		distance from gas-liquid interface, m
$K'$	Langmuir type of particle-to-bubble adhesion constant defined by eq. (8), dimensionless	<i>Greek letters</i>		
$K_{ad}$	adsorption equilibrium constant, m <sup>3</sup> liquid/kg solids	$\alpha$		fraction of surface covered by solids, dimensionless
$m$	gas solubility, $c_L/c_G$ at equilibrium	$\alpha_{\max}$		maximum fraction of surface covered by solids, dimensionless
$m_S$	dimensionless distribution coefficient between liquid and solids, m <sup>3</sup> liquid/m <sup>3</sup> solids	$\beta$		$\tau_y/\tau$ , dimensionless
$n$	exponent	$\dot{\gamma}$		shear rate, s <sup>-1</sup>
$n_A$	concentration of adsorbed A, mol/m <sup>3</sup> liquid	$\dot{\gamma}_{\text{eff}}$		apparent effective shear rate, s <sup>-1</sup>
$N_A$	aeration number in stirred tank $( = \omega d_i / u_G )$ , dimensionless	$\delta_{\text{eff}}$		effective film thickness for mass transfer in presence of solids; see, e.g., Fig. 17 and eq. (76), m
$N_{Fr}$	Froude number $( = \omega^2 d_i / g )$ , dimensionless	$\delta_L$		film thickness in terms of the film model $( = D / k_L )$ , m
$N_{Fr, p}$	particle Froude number $[ = v_t / (d_c g)^{1/2} ]$ , dimensionless	$\delta_G$		gas film thickness in terms of the film model, m
$N_{GF}$	gas flow number $[ = \sigma_L / (\mu u_G) ]$ , dimensionless	$\delta_S$		film thickness in terms of the film model for mass transfer to the particles, m
$N_{Pe}$	Peclet number for axial solids dispersion $( = v_p H / D_S )$ , dimensionless	$\delta_{sL}$		equivalent saturated film layer, m
$N_{Re}$	Reynolds number $( = \omega d_i^2 \rho / \mu \text{ in stirred tank} ) ( = u_G d_c \rho / \mu \text{ in bubble}$	$\Delta p$		pressure drop over reactor, Pa
		$\varepsilon_G$		gas hold-up, m <sup>3</sup> /m <sup>3</sup> reactor
		$\varepsilon_S$		solids hold-up, m <sup>3</sup> /m <sup>3</sup> liquid
		$\varepsilon_{Si}$		solids hold-up at gas-liquid interface, m <sup>3</sup> /m <sup>3</sup> liquid
		$\Theta$		gas-liquid-solid contact angle, ° or rad

$\mu$	dynamic viscosity, Pa s
$\mu_B$	Bingham viscosity, Pa s
$\mu_C$	Casson viscosity, Pa s
$\mu_{eff}$	apparent effective slurry viscosity, Pa s
$\nu$	kinematic viscosity, m <sup>2</sup> /s
$\rho$	density, kg/m <sup>3</sup>
$\rho_{eff}$	effective density of slurry, kg/m <sup>3</sup>
$\rho_p$	particle density, kg/m <sup>3</sup> solids
$\sigma$	surface tension, N/m
$\tau$	shear stress, Pa
$\tau_y$	yield stress, Pa
$\phi$	reaction or Thiele modulus, dimensionless
$\Phi_v$	volumetric flow rate, m <sup>3</sup> /s
$\psi$	Carmans surface factor, dimensionless
$\omega$	stirring speed, s <sup>-1</sup>

## Subscripts

A	component A
ad	adsorption
c	column
G	gas phase
H	in heterogeneous churn turbulent flow regime
L	liquid phase
max	maximum
min	minimum
0	no solids present, all other conditions identical
p	particle
s	saturated
S	solids
sus	suspension
$\omega$	due to stirring

## Superscript

— mean value, in the bulk

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