Effect of Fine Activated Carbon Particles on the Rate of CO_2 Absorption

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In catalytic slurry reactors, fine catalyst particles are suspended either by mechanical stirring or by passage of a gas (Deckwer and Alper, 1980). In the former, although the gas is normally sparged, in some applications a gentle stirring may be preferred (Alper et al., 1980). In this case, the surface renewal rates are low, resulting in low physical mass transfer coefficients. Under these circumstances, particles with high adsorbing capacity, such as activated carbon, may circulate between the diffusion layer adjacent to the interface where adsorption takes place, and the bulk where desorption occurs. Such a "shuttle" mechanism results in increased physical mass transfer rates; Alper et al. (1980) Alper and Deckwer (1983), Alper and Ozturk (1986), and Quicker et al. (1986a,b) have demonstrated this phenomenon clearly. The results of Kars et al. (1979), Bruining and Joosten (1984), and Mehta and Sharma (1985) can also be explained by a similar mechanistic feature (the latter two papers, however, consider absorption in the presence of an emulsified phase). In the case of sparged stirred tanks and/or bubble columns, mass transfer coefficients are considerably higher than those of stirred cells with plane interfaces, thus the thickness of the dissolved gas-rich layer adjacent to the interface is much smaller. On the other hand, it is probable that the particles may affect the mass transfer coefficient for physical absorption $k_L a$ by changing not only the liquid-side coefficient, k_L but also the gas-liquid interfacial area a. There is considerable work on the latter aspect, and the relevant literature has been cited by Quicker et al. (1984). These workers have also carried out experiments by absorbing oxygen from air into sulfite solutions containing Co^{++} in the absence and presence of fine solids, and determining the effective interfacial areas.

Quicker et al. (1984) found that fine particles such as activated carbon, alumina, and kieselguhr did not appreciably affect the interfacial area at low loadings (i.e., less than 10 g/L, which is realistic for catalytic slurry reactors). They therefore concluded that any increase in $k_L a$ by the addition of fine solid particles should be attributed to an increase in k_L, not to the gas-liquid interfacial area. However, it is desirable to determine the effect of fine particles (with high adsorption capacity) on both k_L and a simultaneously; this can be achieved from suitable Danckwerts plots.

In this work, carbon dioxide was absorbed from gas mixtures of CO_2/N_2 into 0.5 M Na_2CO_3/0.5 M $NaHCO_3$ solutions containing various amounts of arsenite, in the absence and presence of finely powdered activated carbon. Some additional experiments were also carried out using fine kieselguhr particles, which were not porous.

Experimental Method

All the measurements were carried out in a semibatch bubble column. The glass column had a 9.5 cm ID and was 140 cm long.

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It was partly thermostatted with a jacket through which constant-temperature water was circulated at 298 ± 0.1 K. Gas holdups were measured using a manometric method (Quicker, 1983). It was possible to change the gas distributor, and two types were used: a sieve-plate (19 holes, 0.108 cm dia.) or a single capillary (0.09 cm dia.). Gas flows were controlled by Brooks mass flow meters, and the entering gas mixture was humidified. The CO_2/N_2 mixtures were analyzed using an infrared gas analyzer (Unor 4N, Maihak).

The superficial gas velocities were varied between 0.6 and 4 cm/s. Experiments were carried out by absorbing CO_2 from the gas mixtures (CO_2/N_2) into 0.5 M Na_2CO_3/0.5 M $NaHCO_3$ buffer solutions in the absence and presence of activated carbon or kieselguhr particles. During the experiments, the pH was kept at 9.6 by automatic addition of 3 N or 6 N NaOH using an automatic titrator (Radiometer, Copenhagen), which enabled the control of the buffer ratio. Water was added batchwise in order to keep the concentrations of carbonate and bicarbonate ions the same. These experiments were carried out at a solids loading of 9 g/L and at various homogeneous catalyst ($NaAsO_2$) concentrations. Table 1 shows the properties of the solids. The adsorption capacities of activated carbon and kieselguhr (both obtained from Riedel de Haen) were recently reported by Quicker et al. (1986b); activated carbon has a high adsorption capacity for dissolved CO_2, which was also determined by Li and Deckwer (1982).

Additional experiments were carried out with gases containing high CO_2/N_2 ratios. The latter could only be realized in a column with a single capillary-type distributor.

Modeling of the Bubble Column

A simple model was used for data analysis. This consisted of assuming plug flow of gas and complete mixing in the liquid, which was realistic since the height/diameter ratio (140/9.5) was high. The changes in gas velocity due to absorption and expansion were corrected. For all the experiments, gas-side resistance could be considered negligible. The reaction between CO_2 and buffer solution could be considered irreversible and first order. The reaction rate constant k_1 was calculated from the measured $NaAsO_2$ concentration and from the estimated ionization to AsO_2^-. Details of these calculations can be found elsewhere (Quicker et al., 1986a). When the Danckwerts model is used, the gas absorption rate per unit gas-liquid interfacial area, R, is given as:

$$R = C^*(k_L^2 + Dk_1)^{0.5} \tag{1}$$

where C^* is the concentration of dissolved CO_2 at the interface. Expressing C^* in terms of mole fraction y and making a gas phase mass balance gives:

$$-d\left(u_G \frac{yP}{R_G T}\right) = a\frac{yP}{He}(k_L^2 + Dk_1)^{0.5} L\,dz \tag{2}$$

where

$$P = P_1[1 + \beta(1 - z)] \tag{3}$$

and

$$\beta = \rho_L g L(1 - \epsilon_G)P_1^{-1} \tag{4}$$

and

$$u_G = u_{Go}\frac{(1 + \beta)(1 - y_0)}{[1 + \beta(1 - z)](1 - y)}. \tag{5}$$

Integration of Eq. 2 with the boundary conditions of $z = 0: y = y_0$ and $z = 1: y = y_1$ gives:

$$\frac{Ra}{C^*} = G(y)\frac{u_{Go}}{R_G T}\frac{He}{L}\frac{1 + \beta}{1 + 0.5\beta} \tag{6}$$

where

$$G(y) = 1 - \frac{1 - y_0}{1 - y_1} + (1 - y_0)\ln\left(\frac{y_0}{1 - y_0}\frac{1 - y_1}{y_1}\right). \tag{7}$$

By measuring inlet and outlet gas compositions, gas holdups, pressures at the inlet, dispersion heights, and liquid (or slurry) density, Ra/C^* can be calculated from Eqs. 3–7. Thus the values of k_L and a can be obtained by plotting $(Ra/C^*)^2$ against k_1 according to:

$$\left(\frac{Ra}{C^*}\right)^2 = (k_L a)^2 + a^2 Dk_1. \tag{8}$$

There it is assumed that the activated carbon or kieselguhr does not affect the reaction rate between CO_2 and the buffer solution, as discussed by Quicker (1983) and Quicker et al. (1986a). Thus k_1 remains unaffected by solids addition but it can be varied by changing the arsenite concentration. The effects of arsenite addition on the diffusion coefficient D and the Henry's law constant He are also assumed to be negligible.

Table 1. Properties of Solids

	Activated Carbon	Kieselguhr
Density, kg/m^3	1,800	2,360
Surface area*, m^2/g	1,079	2
Diameter Range 10^{-6} m	Distribution** Number %	
0–4	47.5	32.2
4–6	26.0	26.4
6–10	15.4	24.7
10–20	9.1	15.6
>20	2.0	1.1

*N_2-BET method
**Omnicon Alpha image analyzer

Experimental Results

In the majority of the experiments the inlet mole fraction was kept constant at $y_0 = 0.048$. In a series of preliminary experiments at a superficial gas velocity of $u_{Go} = 1.2$ cm/s, it was found that the absorption rate increased by about 20% when activated carbon loading was 2 g/L. Further increase of activated carbon loading did not seem to have any further effect.

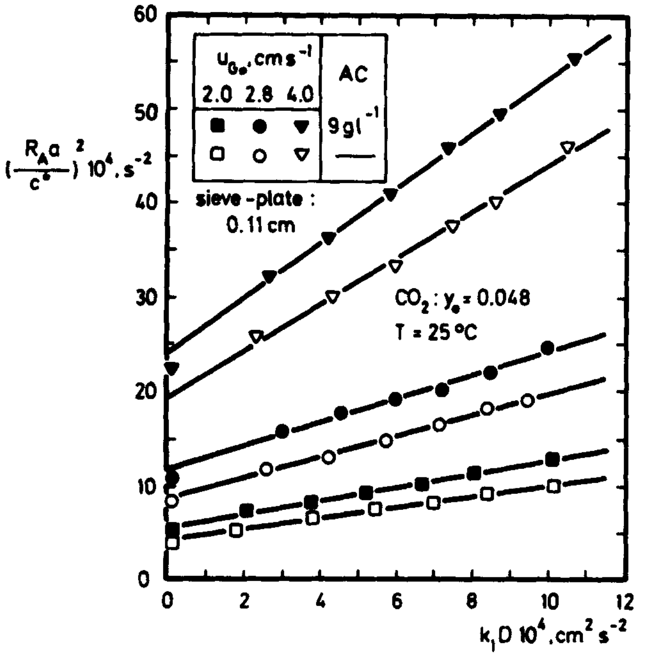

Figure 1. Danckwerts' plots at different gas flows.

Absorption of CO_2 into 0.5 M Na_2CO_3/0.5 M $NaHCO_3$ under variation of arsenite concentration

Therefore all the experiments reported here had a constant activated carbon concentration of 9 g/L.

The measured gas holdups depended on the superficial gas velocities (u_{Go} = 1.2–4 cm/s) and the data could be expressed by the following equation:

$$\epsilon_G = 0.037\, u_{Go}^{1.05}. \quad (9)$$

The value of exponent indicates that the flow was homogeneous (in this regime, the exponent varies between 0.7 and 1.2 [Deckwer, 1980]). The addition of arsenite to 0.5 M Na_2CO_3/0.5 M $NaHCO_3$ solutions did not change the holdup data. Similarly, the addition of 9 g/L activated carbon or kieselguhr did not also change the holdup, which immediately suggests that the gas-liquid interfacial area was not affected to any significant extent.

Figure 1 shows some of the typical Danckwerts plots that were obtained from Eqs. 3–8. The slopes and intercepts of these straight lines give the effective interfacial area, *a*, and $k_L a$, respectively. Thus the values of k_L and *a* were obtained simultaneously. Table 2 summarizes these results both for clear solution and for the slurry. It is seen that both the interfacial area *a* and the physical mass transfer coefficient k_L may be increased by the addition of 9 g/L activated carbon (up to 14% and 9%, respectively).

Table 2. Results of Experiments for Slurry and Clean Solutions Under the Same Conditions

	k_L, cm · s^{-1}		*a*, cm^{-1}		$k_L a$, s^{-1}	
u^*_{Go} cm · s^{-1}	Act. Carbon**	Clear Sol.	Act. Carbon	Clear Sol.	Act. Carbon	Clear Sol.
1.2	0.0228	0.0220	0.632	0.532	0.0144	0.0117
2.0	0.0267	0.0265	0.869	0.773	0.0232	0.0205
2.8	0.0305	0.0281	1.122	1.054	0.0342	0.0296
4.0	0.0285	0.0277	1.713	1.576	0.0488	0.0437

*Sieve plate (0.11 cm), CO_2: y_0 = 0.048
**Activated carbon, 9 g/L

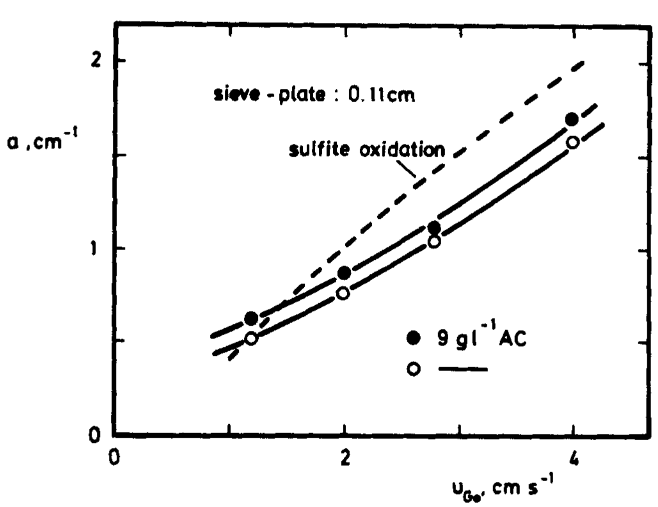

Figure 2. Comparison of experimental effective interfacial areas from different techniques.

Sulfite oxidation, Quicker et al. (1984)

Figure 2 shows the interfacial area as function of the superficial gas velocity. The results of Quicker et al. (1984) from the sulfite oxidation technique for the same bubble column are also given for comparison. The difference between these results is typical of gas-liquid dispersions where bubble size depends also on the actual chemical system.

Figure 3 shows both k_L and $k_L a$ values as a function of the gas velocity, u_{Go}. The $k_L a$ values varied linearly with u_{Go}, while k_L remained practically constant when u_{Go} exceeded 2 cm/s. These results are in agreement with those of Deckwer et al. (1974).

Experiments with High CO_2 Concentration in the Gas Phase

Previous experiments in stirred cells with plane interfaces, where considerable increase of k_L was observed, differed from

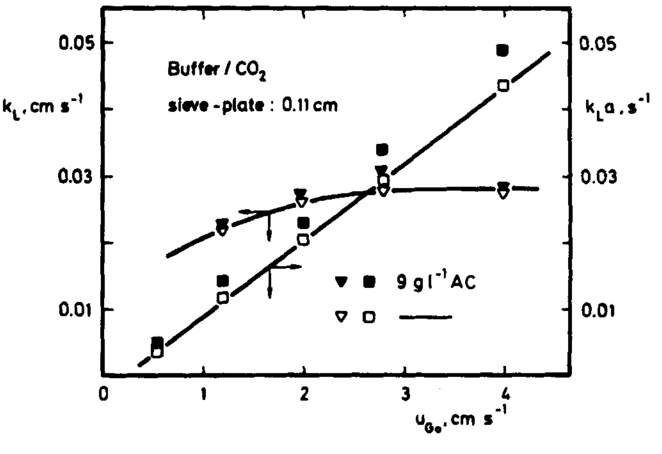

Figure 3. k_L and $k_L a$ as functions of superficial gas velocity.

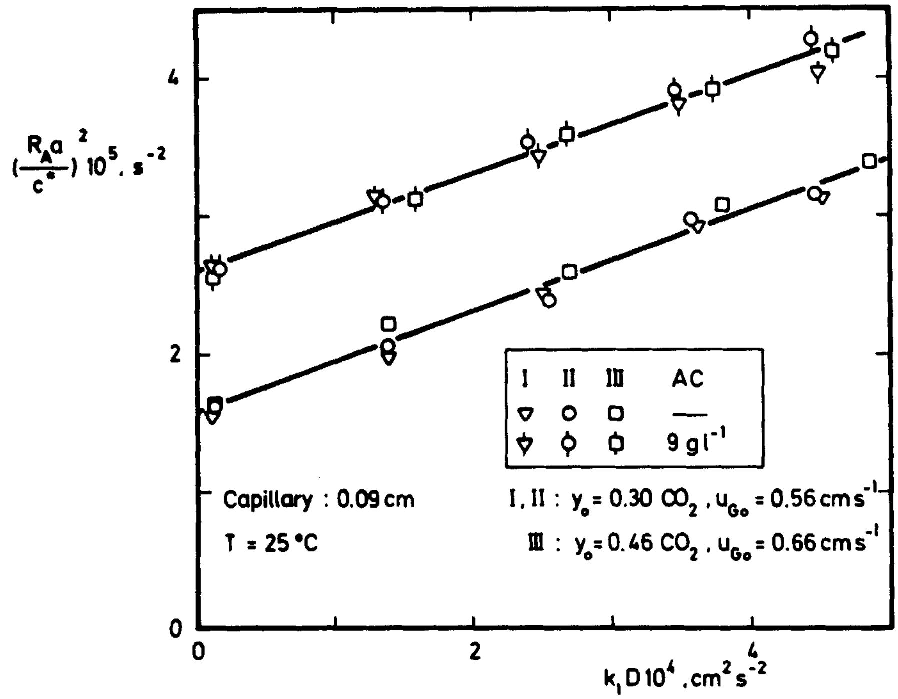

Figure 4. Danckwerts plot for absorption of CO_2 at high mole fractions.
0.5 M Na_2CO_3/0.5 M $NaHCO_3$ at various arsenite concentrations

the bubble column experiments in the value of C^*, that is, the concentration of dissolved carbon dioxide at the interface. Stirred cell experiments used pure CO_2 at atmospheric pressure and thus had much higher C^* values (about 2×10^{-5} mol/cm^3) than those of these bubble column experiments (in this case, C^* was less than about 8×10^{-7} mol/cm^2). Therefore it was decided to carry out some additional experiments with high CO_2 concentration in the gas phase. However, because of high conversion, such experiments were only possible with a capillary-type distribution. In these experiments, the inlet mole fraction of CO_2 was about 0.3 or 0.46 (as opposed to the previous value of 0.048). Thus the C^* value was increased by a factor of 7 and 11, respectively.

Figure 4 shows the corresponding Danckwerts plot and Table 3 shows the values of k_L and a. It is seen that while the interfacial area remains unaffected by the addition of activated carbon, the k_L values increased between 26 and 43%. This increase in k_L is significant, and to check whether it can be attributed to the high adsorption capacity of activated carbon for dissolved CO_2, some experiments were also carried out for slurries of kieselguhr, which has negligible capacity for CO_2 (Quicker, 1986b). Figure 5 shows the Danckwerts plots for the clear buffer solution and for the slurry containing 9 g/L kieselguhr. It is seen that both k_L and a remain practically unaffected upon addition of fine kieselguhr particles.

Table 3. Experimental Results at High CO_2 Mole Fraction in Gas Phase

	k_L, cm · s^{-1}		a, cm^{-1}		$k_La \times 10^3$, s^{-1}	
u^*_{Go} cm · s^{-1}	Act. Carbon**	Clear Sol.	Act. Carbon	Clear Sol.	Act. Carbon	Clear Sol.
0.56^a	0.0286	0.0200	0.179	0.193	5.12	3.86
0.55^b	0.0263	0.0209	0.194	0.189	5.10	3.95
0.66^b	0.0268	0.0206	0.189	0.196	5.07	4.04
	Kieselguhr**	Clear Sol.	Kieselguhr	Clear Sol.	Kieselguhr	Clear Sol.
0.60^c	0.0231	0.0210	0.204	0.211	4.71	4.43

*Capillary distributor, 0.09 cm
**Activated carbon, 9 g/L; Kieselguhr, 9 g/L
a. CO_2: y_0 = 0.297
b. CO_2: y_0 = 0.461
c. CO_2: y_0 = 0.303

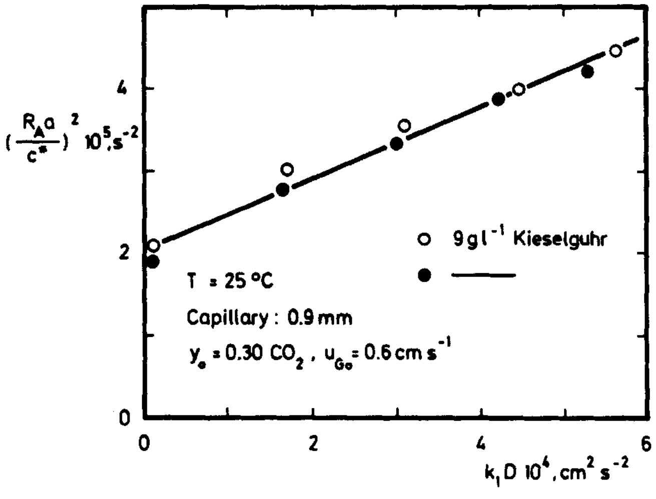

Figure 5. Danckwerts' plot for absorption of CO_2 into buffer for clear solution and for kieselguhr slurries.

Discussion and Conclusions

Results of gas absorption experiments in bubble columns containing fine particles (activated carbon or kieselguhr) at low loadings (which is typical of catalytic reactors) clearly show that the effective interfacial area is not influenced. This conclusion is also supported by literature data (Joosten et al., 1977, and especially that of Quicker et al., 1984). On the other hand, gas absorption rates were increased measurably by the addition of fine activated carbon, while they were affected negligibly when fine kieselguhr particles were added. The main difference between these two particles is in their adsorptive capacity. For instance, in a slurry of activated carbon, 1 g of solid could adsorb about 10 cm^3 CO_2 (at 273 K and 1 atm) when it is equilibrated with pure carbon dioxide at 1 atm (Li and Deckwer, 1982). This is several times higher than what dissolves in 1 g of water under the same conditions. On the other hand, 1 g of kieselguhr in a slurry adsorbs about the same amount that would be dissolved in 1 g of water (Quicker et al., 1986b). Consequently, the activated carbon particles may adsorb gas near the interface, followed by desorption in the bulk, leading to an increased mass transfer. A similar increase in mass transfer rate cannot, of course, be expected from the addition of inert particles, such as kieselguhr, and indeed experimental results seem to prove this mechanism.

When the concentration of dissolved gas was increased by increasing the partial pressure of carbon dioxide, there was considerable increase in k_L upon activated carbon addition (see Figure 4 and Table 3). Under the same conditions, kieselguhr particles had negligible effect (Figure 5). The reason for this increased effect on k_L at increased C^* values for activated carbon slurries is not clear. It is probable that the desorption in the bulk becomes contributing only if the driving force is sufficiently large. This, in turn, requires adsorption near the interface from a solution with high dissolved carbon dioxide concentrations.

The results obtained here clearly show that the gas-liquid interfacial area is not significantly influenced by the addition of fine particles at low loadings. On the other hand k_L may be influenced noticeably (in this case, about 30%) upon addition of fine activated carbon particles, which can be attributed to additional adsorptive transport as suggested by Alper et al. (1980, 1983, 1986). Since activated carbon is often used as either support or as catalyst itself, the proper analysis of such slurry reactors necessitates also consideration of an effect on k_L, even though this is much less significant than that observed for stirred cells with plane interfaces.

Notation

a = specific gas-liquid interfacial area, cm^{-1}
C^* = concentration of dissolved gas at interface in equilibrium with gas phase, mol/cm^3
D = molecular diffusion coefficient of dissolved carbon dioxide, cm^2/s
g = gravitational constant, cm/s^2
$G(y)$ = function, Eq. 7
He = Henry's law constant, $kPa \cdot cm^3/mol$
k_L = physical liquid-side mass transfer coefficient, cm/s
k_1 = pseudofirst-order reaction rate constant, s^{-1}
k_La = volumetric mass transfer coefficient for physical absorption, s^{-1}
L = dispersion height, cm
P = pressure, kPa
P_1 = pressure at top of bubble column, kPa
R = absorption rate per unit interface, $mol/cm^2 \cdot s$
R_G = gas constant, $kPa \cdot cm^3/mol \cdot K$
T = temperature, K
u_G = superficial gas velocity, cm/s
u_{G_0} = superficial gas velocity at inlet, cm/s
y = mole fraction of CO_2 in gas phase
y_0 = mole fraction at inlet
y_1 = mole fraction at outlet
z = dimensionless axial distance
β = defined by Eq. 4
ϵ_G = gas holdup
η = effectiveness factor
ρ_L = density of clear solution in slurry

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