Physical Absorption of a Gas in Laboratory Models of a Packed Column

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The hydrodynamics of liquid flowing down in a packed column absorber is very complicated. Therefore, theoretical models of gas absorption in a packed column have to replace the exact physical situation by a much simpler one, and a number of simplified models, such as film and various surface renewal models with different surface age distributions, have already been proposed (Higbie, 1935; Danckwerts, 1951, 1963; Davidson, 1959; Porter, 1966). Alternatively, Danckwerts (1955) and Andrew (1961) discuss a surface rejuvenation model whereby liquid underlying the gas-liquid surface below a certain depth may be thoroughly mixed at discontinuities between packings, leaving a layer on the surface which is effectively stagnant.

Since the hydrodynamics of a packed column is extremely complex and also only the value of k_La (not k_L) can be measured by the physical absorption of a pure gas into an inert solution, it is rather difficult, if indeed possible, to infer from packed column experiments. Attempts to measure or estimate the interfacial area a (for instance by chemical methods) will introduce further error. Therefore, a number of different models of a packed column with known interfacial areas has been proposed. For instance, in a string of disks column, alternate disks are placed at right angles, and the liquid flows over disks in a similar fashion to that of packed columns. The liquid usually wets the whole of the disks so that a is known exactly. The string of spheres column operates similarly; here, spheres are used in place of disks. Owing to similar flows in a packed column and in these models, it seems reasonable to assume that the flow behavior and mixing between packings happen in a similar fashion. This suggests that the examination of careful gas absorption experiments in these models may show whether the surface renewal or surface rejuvenation is more likely to occur. Indeed, the aim of this communication is to report the results of some carefully carried out string of disk experiments which suggest that the surface rejuvenation, rather than complete surface renewal, may occur in such equipments.

EXPERIMENTAL APPARATUS

The disks were made of pyrophylitte and were 1.5 cm in diameter and 0.5 cm thick. Generally, the flow pattern is very sensitive to small changes in the construction of the column, and a variation of ± 20% is usual in liquid film coefficients given by individual standard columns for the same absorption process under similar conditions (Alper, 1971). Since absorption experiments with different number of disks exposed to the gas are required here, the removal or putting back of some of the disks may result in lack of reproducibility. Therefore, a disk column, which was shown schematically in Figure 1, was constructed where the number of disks exposed to the gas could be changed easily while the disks remained fixed to each other. The perspex piece A of Figure 1 could be taken out, the string of disks could be lowered (or moved up) accordingly, and the piece A could be put back. Then the glass inlet tube could be adjusted accordingly so that the distance between the nozzle and the first disk was always the same. As the liquid level was kept just above the bottom of the perspex piece A, only a small area of horizontal liquid surface was exposed to the gas.

GAS-LIQUID INTERFACIAL AREA A

The effective interfacial area per disk (A) was measured by a standard chemical method, that is, absorption of oxygen into a sulfite solution containing Co^{++} [pertinent details of the experiments and the analysis can be found elsewhere (Alper, 1971)]. The results showed that the measured area is slightly larger than the geometrical area, but the maximum difference between the two is less than 4%, increasing with increased flow rate. It is thought that this can undoubtedly be attributed to the thickness of the liquid film.

LIQUID SIDE MASS TRANSFER COEFFICIENT k_L

The liquid side mass transfer coefficient k_L is usually determined by absorbing a pure gas into an inert solution and measuring the total absorption rate. Then, the following equation is usually used to calculate k_L:

$$k_La'(C^* - C)dH = QdC \tag{1}$$

$$k_L = \frac{Q}{Ha'} \ln\left(\frac{C^* - C_o}{C^* - C_N}\right) \tag{2}$$

It seems, however, more realistic to write down the equivalent of Equation (1) in terms of a difference equation. Thus

$$k_{L,N}A(C^* - C_{N-1}) = Q(C_N - C_{N-1}) \tag{3}$$

If we take A as constant and assume $k_{L,N} = k_{L,N-1} \ldots = k_{L,1} = k_L$, Equation (3) can be solved to give

$$\ln\left(\frac{C^* - C_o}{C^* - C_N}\right) = -N \ln\left(1 - \frac{k_LA}{Q}\right) \tag{4}$$

Equation (4) can now be compared with Equation (2), and it is seen that only if $k_LA/Q << 1$ are these two identical. Hence, Equation (4), rather than Equation (2), will be used here. Thus, if we carry out experiments with a different number of disks exposed to the gas and plot $\ln(C^* - C_o/C^* - C_N)$ against N, we should obtain straight lines with slopes of $-\ln[1 - (k_LA)/(Q)]$ if only k_L remains constant, since A and Q do not depend on N.

EXPERIMENTAL RESULTS

Pure carbon dioxide was absorbed into tap water containing initially no carbon dioxide (that is, $C_o = 0$), and total absorption rates were measured at different liquid flow rates. From experimental results, C_N was calculated, and taking C^* as 0.826 cm^3 of CO_2/cm^3 of water at 25°C and 1 atm (Seidell and Linke, 1952), $(C^* - C_N)$ was plotted against N on semilogarithmic graphic paper (Figure 2). According to Equation (4), these plots should be straight lines if k_L is independent of the number of disks exposed to the gas. However, Figure 2 suggests that k_L decreases when the number of disks increases at first, then remains constant.

DISCUSSION

It has been speculated that the k_La measured at the top part of a packed column may be different from that

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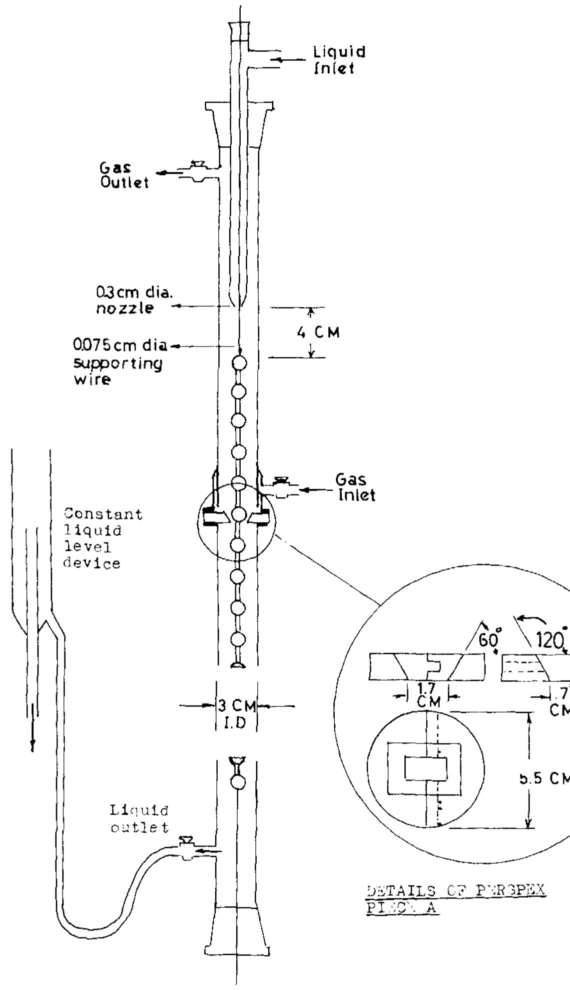

Fig. 1. String of disks column.

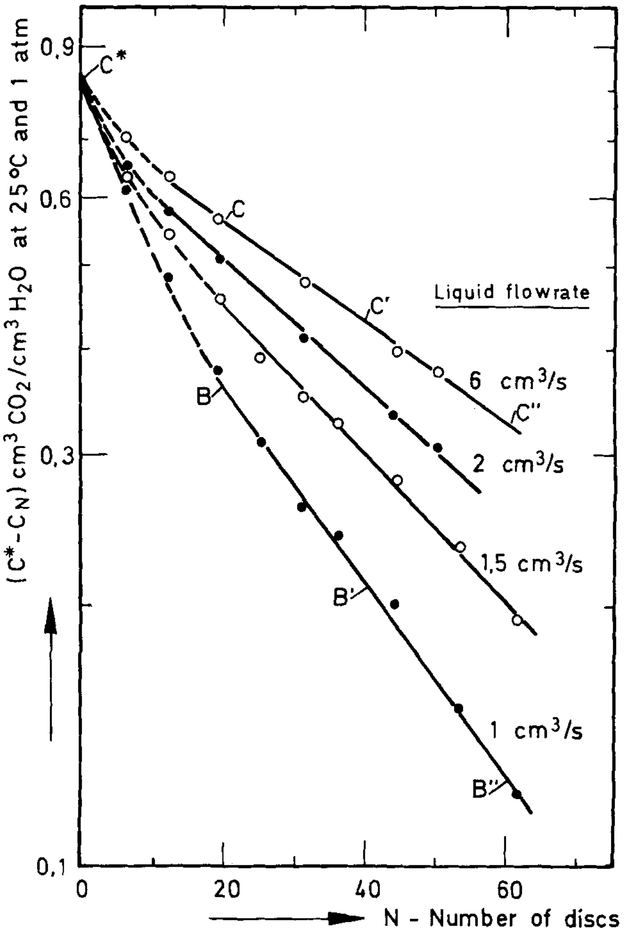

Fig. 2. Plots of $(C^* - C_N)$ against N at different liquid flow rates.

of the rest of the column. This is usually attributed to the fact that the liquid distribution and flow pattern in this part of a packed column may be quite different. This behavior is not, however, expected to manifest itself in a string of disks (or spheres) column. On the other hand, when Equation (2) is used to calculate k_L (this is the method of calculation used by every investigator in the past), (k_LA/Q) is the slope of the line which passes through C^*B for twenty disks at a liquid flow rate of 1 cm³/s. When the number of disks are forty and sixty, the slopes of lines which pass through C^*B' and C^*B'' will provide the values of (k_LA/Q) at the same liquid flow rates, respectively. Clearly, the value of k_L from Equation (2) will depend on the number of disks in the column. For instance, the value of k_LA is 4.17×10^{-2} cm³/s or 3.2×10^{-2} cm³/s when the liquid flow rate is 1 cm³/s and the number of disks are twenty or forty, respectively. Therefore, the difference between these two k_L values is more than 20%. When the liquid flow rate is 6 cm³/s, this difference is about 17%. An examination of other workers results shows the same behavior (Roberts and Taylor, 1956; Stephens and Morris, 1951; Yoshida and Koyanagi, 1958; Cullen, 1957). For instance, Roberts and Taylor (1956) carried out experiments with columns containing fifty and sixty disks, and the values of k_L for fifty disks were higher than those for sixty (see their Figure 9). Yoshida and Koyanagi (1958) used a string of spheres column, and their results show clearly that k_L for a column with large number of spheres is lower than that of a column with a small number of spheres; the differences between the two k_L values is higher at low liquid flow rates (see, for instance, Figure 2 of Yoshida and Koyanagi). These results are in complete agreement with ours.

In all these investigations, the flow of liquid was predominantly laminar over the disks (or spheres), and mixing to some extent occurred at junctions. A probable explanation why k_L decreases over the first few disks (or spheres) and then remains constant can be given if one supposes that surface rejuvenation occurs at junctions. If this is the case, absorption over the first few disks (or spheres) will be identical to absorption into a quiescent liquid until the gas penetrates into the mixing region below the stagnant layer. Consequently, the average value of k_L measured from physical absorption experiments should continue to decrease until the gas penetrates into the mixing region. Afterwards, it should remain constant. It seems also reasonable to think that if surface rejuvenation occurs, then the thickness of the stagnant layer should decrease with increasing liquid flow rate, and the following analysis shows this behavior. Using Mika's (1959) analysis, we can show that for a laminar flow of liquid, the thickness of the stagnant layer is given by

$$x = K\,N/Q^{2/3} \tag{5}$$

TABLE 1. VARIATION OF THE THICKNESS OF THE STAGNANT LAYER WITH THE LIQUID FLOW RATE

Q (cm³/s)	N	x (cm)
6.0	10	3.03 K
2.0	12	7.56 K
1.5	16	12.21 K
1.0	18	18.00 K

Here, K is a constant which depends only on the disk dimensions, the diffusivity of dissolved gas, and the liquid viscosity and density. N is the number of disks over which an appreciable amount of gas has not yet penetrated into the rejuvenation depth. Values of N can be estimated from Figure 2, and Table 1 shows the calculated results.

It is seen from Table 1 that the depth of the stagnant layer decreases with an increasing liquid flow rate, thus supporting also that the surface rejuvenation, rather than surface renewal, is more likely to occur in these absorbers.

NOTATION

a' = interfacial area per unit height
A = interfacial area per disk (or sphere)
C_N = concentration of dissolved gas in the liquid which is leaving N^{th} disk
C^* = concentration of dissolved gas at gas-liquid interface
H = height
k_L = physical liquid side mass transfer coefficient
$k_{L,N}$ = physical liquid side mass transfer coefficient for N^{th} disk
Q = liquid flow rate
x = thickness of stagnant layer at the surface

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Direct Evidence for the Existence of Gaseous Intermediates in the Calcium Sulfide-Calcium Sulfate Reaction

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The apparent solid-solid reaction

$$CaS + 3CaSO_4 \rightarrow 4CaO + 4SO_2$$

has been utilized in the sulfuric acid-cement process (Hull et al., 1953). It has also been recognized as the common basic reaction in the advanced processes for reductive regeneration of lime based sorbents in the technology of fluidized-bed combustion of coal (Ruth, 1976). The reaction proceeds at significant rates at temperatures higher than 950°C (Hubble et al., 1975; Turkdogan and Vinters, 1976).

The reaction is obviously not an elementary one. It is not resolved with regard to the mechanism whether the reaction is a solid state reaction, that is, through a solid-solid diffusion mechanism similar to the formation of cement, or it indeed involves gaseous intermediates. Although the latter mechanism seems plausible, it has not been demonstrated. Since the reaction is of vital importance in developing advanced regenerative processes for fluidized-bed combustion of coal, we set forth to study the mechanism and kinetics of this reaction. In this communication we present, as a first step to the understanding of the reaction, a direct evidence for the existence of gaseous intermediates.

EXPERIMENTAL

As illustrated on Figure 1, rates were measured of the thermal decomposition of calcium sulfate with and without physically separated calcium sulfide. The samples were pelletized disks made of reagent grade powder. The disks were 1.3 cm in diameter and were physically separated for a distance of 2 mm by three quartz beads. The stacked disks were mounted on the sample holder of an automatic recording microbalance (Mettler TA-1). Rate measurements were accomplished by continuously recording the weight loss. The thermogravimetric reactor and the procedures of the rate measurement have been described fully elsewhere (Yang and Steinberg, 1976). An inert gas flow (nitrogen) was maintained at a linear velocity of approximately 1 cm/s in the reactor. The gas was purified from traces of oxygen and water vapor to levels of well below 1 ppm.

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