MASS TRANSFER BETWEEN A MOVING GAS STREAM AND SINGLE PARTICLES OF SOME IMPORTANT SORBENTS FOR SULPHUR DIOXIDE

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For the particles of calcium oxide and active sodium carbonate an effect of mass transfer is explored on the overall rate of their reactions with sulphur dioxide. The results of a simple analysis show that the mass transfer resistance in the gas phase cannot be neglected. The extraordinary reactivity of active sodium carbonate can be fully utilized only in such contactors where very high rates of mass transfer are ensured.

Mass transfer between a moving gas stream and an external solid surface is an element of the overall reaction sequence which is relatively well understood. The rate of transport of a reacting component from the bulk of a gas stream to the solid surface has usually a considerable effect on the overall rate of reaction. The purpose of this brief study is to explore the role of the gas-phase mass transfer resistance in different hydrodynamic regimes and thus to verify the assumption of its negligibility which is often introduced without justification.

A simple analysis which follows is restricted to a single particle in the moving gas stream the composition of which does not change. A gas-solid reaction of the type (*1*) occurs in the system

$$\mathrm{A\,(g) + bB\,(s) = cC\,(g) + dD\,(s)}\,. \qquad (1)$$

The mass flux from the gas phase into the solid per unit solid surface can be written as a sum of the diffusion term and bulk flow term[1]

$$N_\mathrm{A} = h_\mathrm{D}(C_\mathrm{A} - C_\mathrm{AP})\,\varrho_\mathrm{GM} + x_\mathrm{A}(N_\mathrm{A} + N_\mathrm{C})\,, \qquad (2)$$

where N_C is the mass flux of the gaseous product C and x_A is the mole fraction of the reacting component A in the bulk of the gas phase. The components A and C are diffusing in the opposite directions and in the case of equimolar counterdiffusion, *i.e.* when $N_\mathrm{A} = -N_\mathrm{C}$, the bulk flow term in Eq. (*2*) vanishes. Thus, bulk flow effects do not play a role in many oxide reduction processes[2]. The term corresponding to bulk flow due to diffusion can be negligible in the systems in which the gas concentrations of reacting components are very low. Such cases are typical of the reactions employed for removal of harmful pollutants from waste gases or air. Since the processes of air pollution control are becoming more and more important at present, the analysis reported here is oriented towards such reaction systems.

The concentration of sulphur dioxide in flue gas depends on the content of sulphur in coal and on the regime of combustion. It is on the order of magnitude $10^{-1}\%$ by volume and therefore, it is possible to introduce the simplifying assumption that the bulk flow due to diffusion can be neglected in a reaction systems of this type. When the pseudosteady state and the uniform conditions within a particle are also assumed, the balance of the reacting component can be written as

$$h_D(C_A - C_{AP})\,\varrho_{GM}F_P = \varrho_{SM}\frac{\partial X}{\partial \tau}V_P\,, \tag{3}$$

where $\partial X/\partial \tau$ is the rate of reaction, F_P the surface area and V_P the volume of the reacting particle. In the case of a spherical particle the relative concentration of the reacting component at the solid surface is given by Eq. (*4*):

$$C_{AP}/C_A = 1 - \frac{D_P}{6}\frac{1}{h_D}\frac{\varrho_{SM}}{C_A\varrho_{GM}}\frac{\partial X}{\partial \tau}\,. \tag{4}$$

Practical experience shows that the mass transfer coefficient h_D appearing in Eq. (*4*) has to be obtained from empirical correlations rather than from the theoretical models of mass transfer.

Particle-fluid mass and heat transfer in packed and fluidized beds is an important element of the fundamental information needed for the design and modelling of various mass and heat transfer operations and chemical reactors. During the past three decades this subject has been widely investigated and the volume of the literature is large. The gas-phase mass transfer rates have been measured for the absorption of vapours from the gaseous streams and evaporation of liquids from the surface of porous particles and sublimation of suitable solids into gaseous streams. In majority of studies, the experimental results are correlated in terms of the dimensionless groups. The mass transfer coefficient is frequently expressed as a mass transfer Chilton–Colburn j_D factor[3], which is defined as

$$j_D = \mathrm{Nu}\,\mathrm{Re}^{-1}\,\mathrm{Sc}^{-1/3} \quad \text{or} \quad j_D = (h_D/U)\,\mathrm{Sc}^{2/3}\,. \tag{5}$$

Recently Dwiwedi and Upadhyay[4] collected available experimental mass transfer data of different researchers for various systems with a fixed or fluidized bed. Although some data had to be discarded because of their abnormal values, the bulk of the relevant data remained considerably scattered. On the basis of gas phase results Dwiwedi and Upadhyay developed by the regression analysis the correlating equation (*6*):

$$ej_D = 0.4548\ \mathrm{Re}^{-0.4069}\,. \tag{6}$$

This correlation fits the experimental data in the range of Reynolds number $1-10^4$ with an average deviation of ±20%. At very low and very high Reynolds numbers the accuracy of the proposed equation (*6*) is less. With respect to a large number of the experimental data points measured for various systems and employed in the regression analyses, Eq. (*6*) can be applied quite generally. That is why we have selected the correlation of Dwiwedi and Upadhyay among available equations in the literature[5-7].

Eqs (*4*)–(*6*) show that the relative concentration of a gaseous reacting component at the solid surface is effected by a considerable number of factors. Besides the particle size and porosity of the bed, the relative concentration depends on the hydrodynamics of the moving gas stream expressed by the Reynolds number, on the physical properties of the gas phase expressed by the Schmidt number and on the rate of reaction in the unit volume of the particle. Effects of the Reynolds number and of the rate of reaction on the relative concentration at the solid surface is illustrated in Fig. 1.

VERIFICATION BY EXPERIMENT

For the kinetic studies of the reaction of calcium oxide and sulphur dioxide, a differential reactor with a very thin, fixed layer of particles was employed[8,9]. In order to explore an effect of mass transfer, a series of experimental measurements was conducted at different superficial velocities of flue gas. The results revealed, that at superficial velocities about 2·5 m/s and higher (at standard pressure and 850°C), the conversions attained were not effected by the velocity of the gas phase. Thus, under such conditions we can consider the mass transfer resistance in the gas phase as negligible.

In our recent work[10] we developed for the reactive, micro-grained limestone CI a simple, empirical equation correlating the rate of its sulphation as a function of the conversion and concentration of sulphur dioxide in the gas phase:

$$\frac{\partial X}{\partial \tau} = \frac{0.2533C(1 - 1.250X)}{1 + 450.1CX(1 + 3.111X)} \tag{7}$$

$$X < 0.8$$

$$\bar{D}_p = 0.565\ \mathrm{mm}\,, \quad t = 850°\mathrm{C}\,.$$

On expressing the rate of reaction in Eq. (*4*) by Eq. (*7*) we get after some manipulations a quadratic equation for the concentration of sulphur dioxide at the surface of a particle of calcium oxide

$$AC_P^2 + BC_P + E = 0\,, \tag{8}$$

where

$$A \equiv \frac{6}{\bar{D}_P} h_D \frac{\varrho_{GM}}{\varrho_{SM}} X\,(450{\cdot}1 + 1400{\cdot}3X) \tag{9}$$

$$B \equiv -\left\{\frac{6}{\bar{D}_P} h_D \frac{\varrho_{GM}}{\varrho_{SM}} \left[CX\,(450{\cdot}1 + 1400{\cdot}3X) - 1\right] + 0{\cdot}3166X - 0{\cdot}2533\right\} \tag{10}$$

$$E \equiv -\frac{6}{\bar{D}_P} h_D \frac{\varrho_{GM}}{\varrho_{SM}} C\,. \tag{11}$$

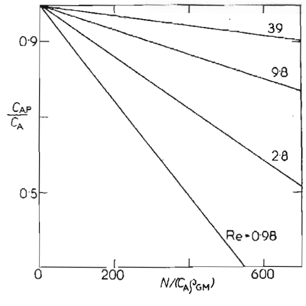

FIG. 1

Effect of the Rate of Reaction and Reynolds Group on the Concentration of a Reacting Gaseous Component at the Solid Surface

Sc = 2, $\bar{D}_P$ = 0·0565 cm, e = 1.

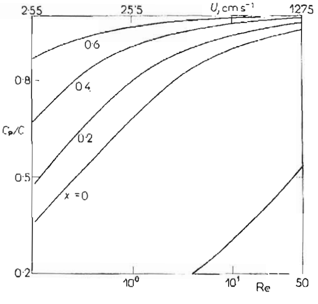

FIG. 2

Dependence of the Concentration of Sulphur Dioxide at the Surface of a Particle of Calcium Oxide on the Reynolds Group and Conversion

Limestone CI, $\bar{D}_P = 0{\cdot}0565$ cm, temperature 850°C, $e = 1$, $C = 3\,.\,10^{-3}$; active sodium carbonate, $\bar{D}_P = 0{\cdot}0565$ cm, temperature 150°C, $C = 3\,.\,10^{-3}$, $X = 0{\cdot}25$, $e = 1$ (curve Y).

Solutions of Eqs (*8*)–(11) with $-\sqrt{}$ were not physically meaningful and, therefore, they were not considered here. For selected values of the conversion of calcium oxide and bulk concentration of sulphur dioxide, the concentrations at the surface of reacting particles were computed from Eqs (*6*), (*8*)–(*11*). The computed results are presented in Fig. 2. The curves in this figure show that, except the limiting case of zero conversion of the particles, the concentration at the solid surface is only slightly different from that in the bulk of the gas stream for Re > 10. As the conversion increases, a fractional resistance in the gas phase decreases. In the system under consideration – the particles of calcium oxide and flue gas containing sulphur dioxide at 850°C – the superficial velocity of the gas corresponding to Re = 10 is 255 cm/s. This value is in good agreement with the superficial gas velocity 250 cm/s, determined by experiment, at which the gas flow rate in the reactor did not effect any more the rate of the sulphation reaction. A survey of the physical parameters of the system us shown in Table I.

In modelling the reactors with a fixed or fluidized bed of the particles, the mass transfer resistance of the gas film surrounding the particles is frequently neglected. When one realizes that the superficial gas velocity in such reactors is often on the order of magnitude of tens of cm/s, this simplifying assumption cannot be justified. In the presented case of our reaction system calcium oxide–sulphur dioxide, it is apparent that the mass transfer in the gas phase has also to be included in analysis of the process.

TABLE I
System Parameters

Variable	Dimension	Limestone CI	Active sodium carbonate
Temperature	°C	850	150
ϱ_{GM}	mol/cm^3	$1.085 \cdot 10^{-5}$	$2.880 \cdot 10^{-5}$
ϱ_G	g/cm^3	$3.09 \cdot 10^{-4}$	$8.350 \cdot 10^{-4}$
ϱ_{SM}	mol/cm^3	$1.565 \cdot 10^{-2}$	$1.286 \cdot 10^{-2}$
μ	g/(cms)	$4.45 \cdot 10^{-4}$	$2.30 \cdot 10^{-4}$
D	cm^2/s	0·75	0·14
U	cm/s	1.0–$5 \cdot 10^3$	1.0–$5 \cdot 10^3$
$\bar{D}_P$	cm	0·0565	0·0565
Re		0.039–$1.96 \cdot 10^2$	0.205–$1.026 \cdot 10^3$
Sc		1·92	1·97

SYSTEM ACTIVE SODIUM CARBONATE — SULPHUR DIOXIDE

Active sodium carbonate is another promising sorbent of sulphur dioxide and was selected for comparison and illustration with respect to its very high reactivity[11-13]. The rate of reaction depends on the partial pressure of sulphur dioxide and on the conversion of sodium carbonate to sulphite:

$$\frac{\partial X}{\partial \tau} = 9{\cdot}12 C_P X^{0.5} (1 - X)^{1.5} . \qquad (12)$$

The reaction proceeds most rapidly at conversion $X = 0{\cdot}25$. By a similar procedure as in the case of calcium oxide we get the equation for the concentration at the solid surface

$$C_P = \left[\frac{6}{\bar{D}_P} h_D \frac{\varrho_{GM}}{\varrho_{SM}} C\right] . \left[9{\cdot}12 X^{0.5}(1 - X)^{1.5} + \frac{6}{\bar{D}_P} h_D \frac{\varrho_{GM}}{\varrho_{SM}}\right]^{-1} . \qquad (13)$$

For selected values of the variables and physical parameters of the system summarized in Table I, the surface concentrations were computed and they are shown in Fig. 3. It can be seen from comparison of the curves in Fig. 3 and corresponding curves in Fig. 2 that the relative gas film resistance is substantially higher at active soda than in the case of calcium oxide. Only at conditions characterized by the values of Reynolds group, which are more than by an order of magnitude larger than those at calcium oxide, similar corresponding concentrations are attained. These results show an important fact, that the exceptional reactivity of active sodium carbonate can be fully utilized only in contactors where very high rates of mass transfer are ensured. In this respect the reactors bringing gas at high velocity into intimate contact

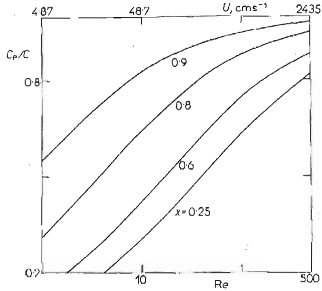

FIG. 3

Dependence of the Concentration of Sulphur Dioxide at the Surface of a Particle of Active Sodium Carbonate on the Reynolds Group and Conversion

$D_P = 0{\cdot}0565$ cm, temperature 150°C, $e = 1$.

with fine particles, such as the reactors with the fast fluidized bed or transport reactors, seem to be promising.

LIST OF SYMBOLS

C	volume fraction of sulphur dioxide in gas phase
C_i	volume fraction of component i in gas phase
C_P	volume fraction of sulphur dioxide at solid surface
C_{iP}	volume fraction of component i at solid surface
D	molecular diffusivity $(cm^2 s^{-1})$
$\bar{D}_P$	mean particle size (cm)
e	porosity
F_P	particle surface area (cm^2)
h_D	mass transfer coefficient $(cm s^{-1})$
j_D	Chilton and Colburn mass transfer factor
$N = \varrho_{SM}(\partial X/\partial \tau)$	rate of disappearance of sulphur dioxide $(mol cm^{-3} s^{-1})$
N_i	mass flux of component i $(mol cm^{-2} s^{-1})$
$Nu \equiv h_D\bar{D}_P/D$	Nusselt number
$Re \equiv \bar{D}_P U \varrho_G/\mu$	Reynolds number
$Sc \equiv \mu/(\varrho_G D)$	Schmidt number
U	superficial gas velocity $(cm s^{-1})$
V_P	particle volume (cm^3)
X	conversion
$\partial X/\partial \tau$	rate of reaction (s^{-1})
x_i	mole fraction of component i
μ	viscosity $(g(cm s)^{-1})$
ϱ_G	density of gas phase $(g cm^{-3})$
ϱ_{GM}	molar density of gas phase $(mol cm^{-3})$
ϱ_{SM}	molar density of solid phase $(mol cm^{-3})$
τ	time (s)

REFERENCES

1. Bird R. B., Stewart W. E., Lightfoot E. N.: *Transport Phenomena.* Wiley, New York 1960.
2. Szekely J., Evans J. W., Sohn H. Y.: *Gas–Solid Reactions.* Academic Press, New York 1976.
3. Chilton T. H., Colburn A. P.: Ind. Eng. Chem. *26*, 1183 (1934).
4. Dwivedi P. N., Upadhyay S. N.: Ind. Eng. Chem., Process Des. Develop. *16*, 157 (1977).
5. Rowe P. N., Claxton K. T.: Trans. Inst. Chem. Eng. *43*, T 231 (1965).
6. Evnochides S., Thodos G.: AIChE J. *7*, 78 (1961).
7. Hughmark G. A.: AIChE J. *13*, 1219 (1967).
8. Hartman M., Coughlin R. W.: AIChE J. *22*, 490 (1976).
9. Hartman M., Pata J., Coughlin R. W.: Ind. Eng. Chem., Process Des. Develop. *17*, 411 (1978).
10. Hartman M., Hejna J., Beran Z.: Chem. Eng. Sci. *34*, 475 (1979).
11. Mareček J., Mocek K., Erdös E.: This Journal *35*, 154 (1970).
12. Bareš J., Mareček J., Mocek K., Erdös E.: This Journal *35*, 1628 (1970).
13. Hartman M., Pata J.: Int. Chem. Eng. *18*, 712 (1978).

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