A Solid Reactant Particle in a Gaseous Pollutant System of Variable Strength

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Introduction

Dry methods on removal of SO_2 in stack gas system have aroused gradually investigators' attention in the air pollution control field. These methods have the advantage of minor loss in drafting power as compared with the result of wet scrubbing method. Two different processes have been studied by the U. S. Bureau of Mines[1] and the Canadian Fuel Research Center[2]. The former process is an absorption of SO_2 by passing flue gases through a fluid bed reactor of solid particles, whereas the latter is a method by making use of solid additives in fuel oils. A common significance of these two methods is that the strength of SO_2 surrounding the solid reactant varies from time to time. Early studies[3],[4],[5],[6] pertaining to solid-gas reactions are considered mainly on a system of constant gaseous concentration. It is a purpose of this paper to study parametric effects of a solid-gas system on the rate of reduction of gaseous pollutant level.

Analysis

A general case of a solid additive in a receding pollutant level will be considered in the present study. However, the mathematical model can be equally applicable to the case of a fluid bed reactor of solid particles provided that the relationship between gaseous pollutant concentration and a time factor can be formulated mathematically. It is reasonable to assume that relaxation in momentum transfer between solid and gaseous phases is neglible if flue gas velocity is much slower than the local sound velocity and that the major dimension of a solid particle is at the order of a few microns. Within the field of physical interest, a non-catalytic and irreversible chemical reaction is considered

$$\underset{\text{(Gas Reactant)}}{\nu_1 A_1} + \underset{\text{(Solid Reactant)}}{\nu_2 A_2} \longrightarrow \underset{\text{(Solid Product)}}{\nu_3 A_3} \qquad (1)$$

where A_1, A_2, are the solid and gaseous reactant respectively, A_3 the solid product, ν_1, ν_2 and ν_3 stoichiometric coefficients. For the sake of simplicity, a model as shown in Fig. 1 is presented in such a way that a spherical solid reactant having its initial radius R is surrounded by a gaseous sphere having radius R_g and a common center at 0. After a period of time t a shell of solid product with a thickness of $R-r_c$ occurs around the reactant core of radius r_c. The rate of consuming A_1 due to chemical reaction is assumed to be much more faster than the rate of gas diffusion through the product layer of species A_3. By this assumption, the shrinkage of the reactant A_2 is, in turn, dominated mainly by the gas diffusion rate. Furthermore, since solid-gas chemical reaction is considered to be very fast, gaseous concentration of species A_1 vanishes on the interphase boundary with radius r_c. The system is also assumed to be thoroughly isothermal and of a constant coefficient of

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diffusivity in solid-gas phase. Upon these conditions governing equations can be formulated as follows:
The diffusion equation.

$$\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r} = \frac{1}{D}\frac{\partial C}{\partial t} \tag{2}$$

with the initial condition

$$C = C_o, \quad t \leq 0, \quad R \leq r \leq R_g \tag{3}$$

and boundary conditions

$$C = C_s, \quad t > 0, \quad r = R \tag{4}$$

$$C = 0, \quad t > 0, \quad r = r_c \tag{5}$$

where C is gaseous concentration of reactant A_1, and D diffusivity of A_1 in solid phase A_3.
The rate of boundary movement for species A_2 is,

$$\frac{dr_c}{dt} = -\eta_1 \frac{\partial C}{\partial r} \tag{6}$$

where

$$\eta_1 = \eta_3 D$$

and

$$\eta_3 = \frac{\nu_2 M_2}{\nu_1 \rho_2}$$

M_2 and ρ_2 are molecular weight and density of A_2.
Gaseous concentration in the region $R_g < r < R$

$$C_s = C_o + \frac{1}{V_g}\int_R^{r_c} \frac{\nu_1}{\nu_2} \frac{4\pi \rho_2 r_c^2}{M_2}\left(\frac{dr_c}{dt}\right) dt$$
$$= C_o + \eta_2 (r_c^3 - R^3)/3 \tag{7}$$

where

$$\eta_2 = \frac{4\pi \nu_1 \rho_2}{\nu_2 V_g M_2}$$

V_g is volume of the gaseous sphere.

Eq. (2) along with its non-linear boundary conditions presents formidable mathematical difficulties for obtaining a true solution. However, some alternative methods, for example, used for solving boundary layer problems by Karman[7] may be available for the closed solution of Eq. (2). The mathematical technique is generally referred as Karman's integral method, which will be employed for attempting a solution of our diffusion problem. Physical significance of the integral method applied to our problem implies an overall mass-transfer-balance throughout the shell layer of product A_3. By making use of a closed form of C in a second-degree polynomial, $C = \alpha_1 (r - r_c) + \alpha_2 (r - r_c)^2$ the partial differential equation (2) can reach a final form

$$\frac{dr_c}{dt} = -\frac{R^2[\alpha_1 + 2\alpha_2 (R - r_c)]}{[r_c^2/\eta_1 + \psi(r_c)/D]} \tag{8}$$

where α_1 and α_2 are the coefficients of the second-degree polynomial, ψ a parameter of r_c. Since α_1, α_2 and ψ are the dependents of r_c, Eq. (8) can be solved readily by numerical method. The results of moving boundary r_c and the skin concentration C_s will be presented and discussed in the section to be followed.

Results and Discussions

The analytical results presented in this paper deal mainly with the parametric effects (D, η_3, C_s and R_g) on the reduction of gaseous pollutant concentration and on the location of moving boundary. In view of understanding a wide range of possible variations, physical conditions employed in the present study are as follows:

Flue gas pressure	1033 gm/cm2
Flue gas temperature	500- 1000 k

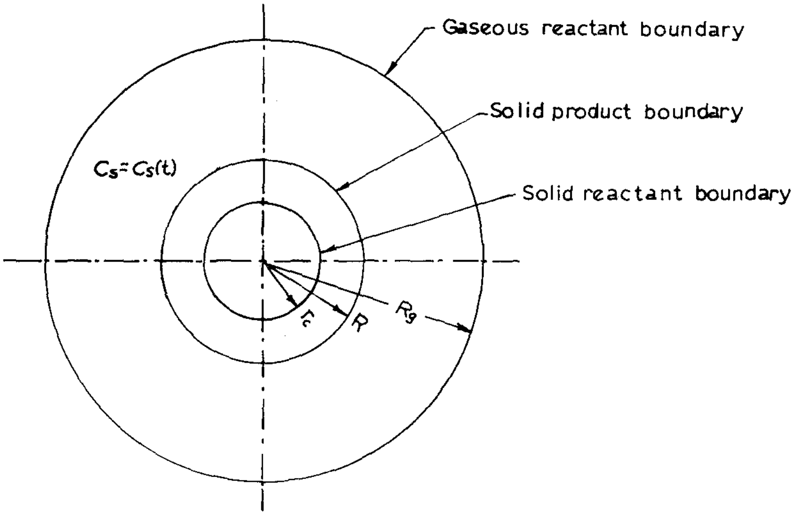

Fig.1 Configuration of a solid gas reaction in a receding gas concentration atmosphere.

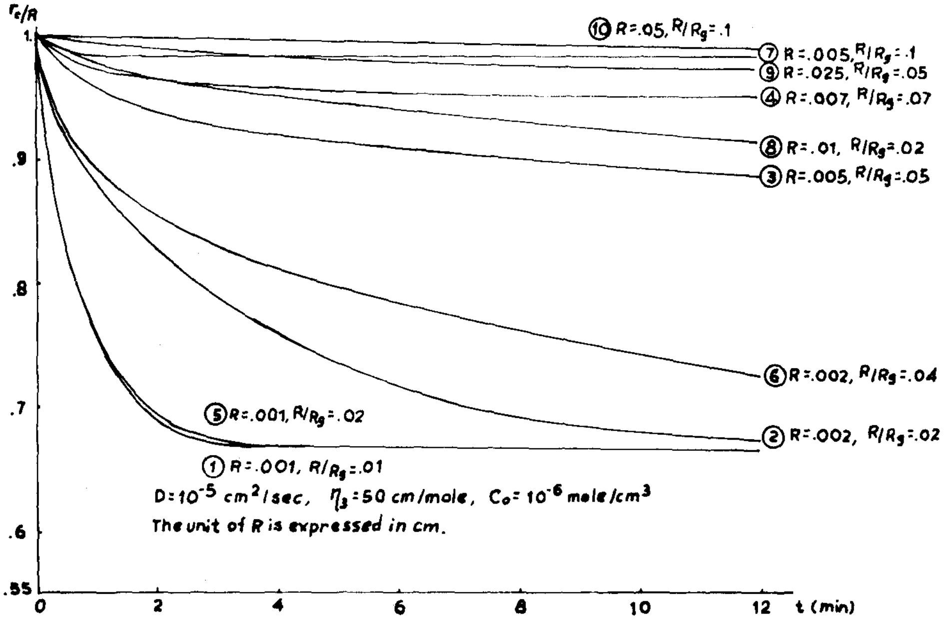

Fig. 2 The development of moving boundary

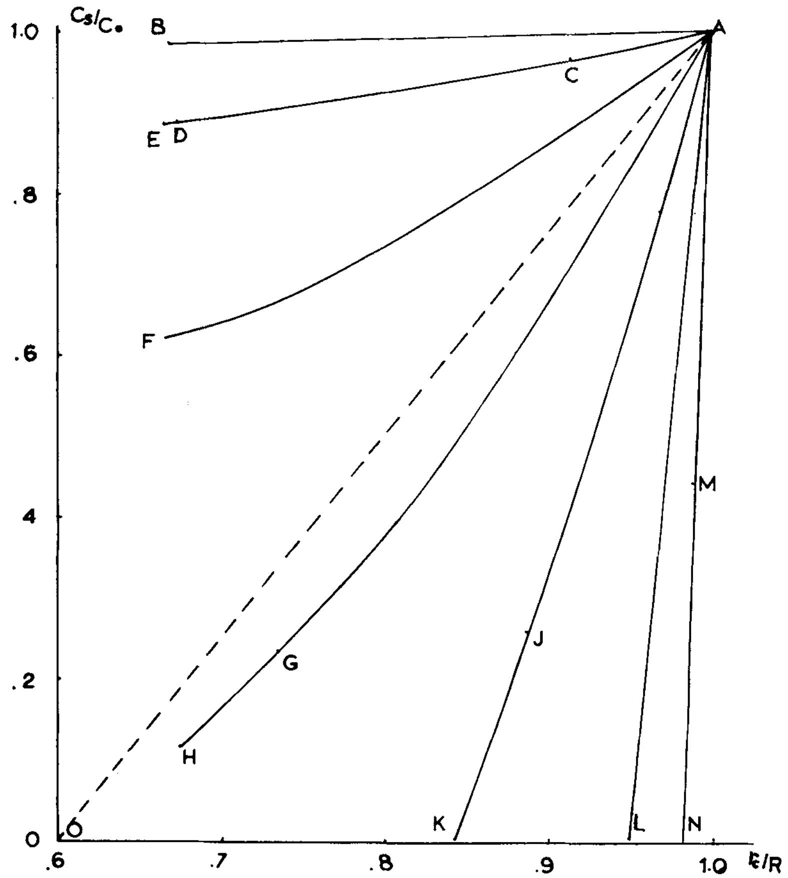

Fig. 3 Relationship between the reduction of surrounding gas concentration and the depth of moving boundary.

Curve	AB	AC	AD	AE	AF	AG	AH	AI	AJ	AK	AL	AM	AN
R(μ)	1	10	2	1	1	2	1	25	5	1	7	50	5
R/Rg	.01	.02	.02	.02	.03	.04	.04	.05	.05	.05	.07	.1	.1

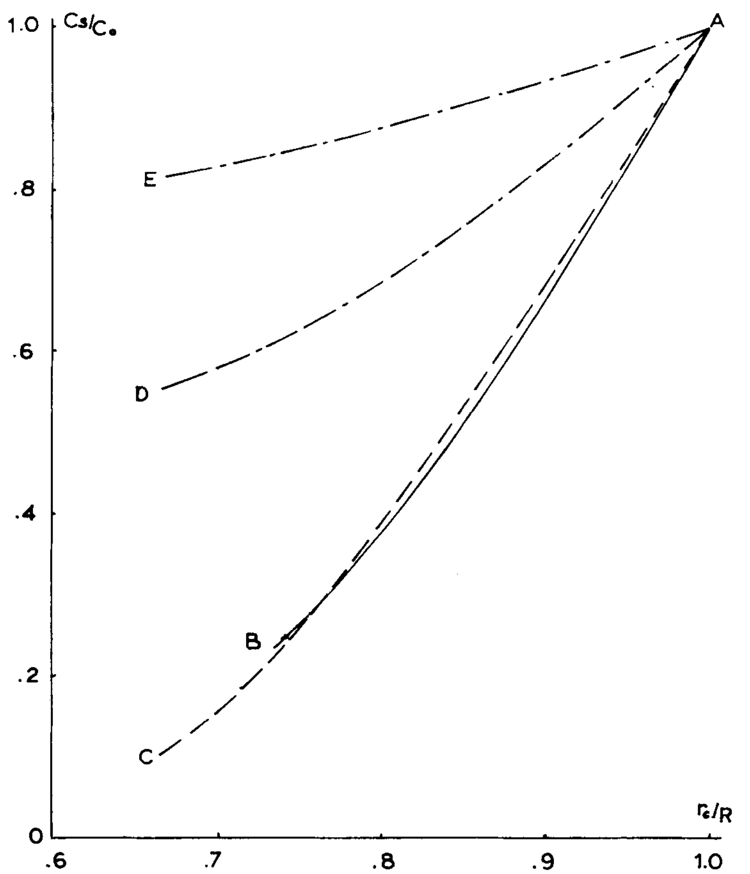

Fig. 4 Parametric effects of D, η_3, and C_o on the reduction of surrounding gas concentrations.

	R, μ	R/Rg	D, cm^2/sec	η_3, c.c./mole	C_o, mole/c.c.
AB	2	0.02	10^{-5}	50	10^{-6}
AC	2	0.02	10^{-4}	50	10^{-6}
AD	2	002	10^{-5}	100	10^{-6}
AE	2	002	10^{-5}	50	5×10^{-6}

Pollutant initial concentration	10^{-6} - $5x10^{-6}$	mole/c.c.
Diffusivity D	10^{-5} - 10^{-4}	cm^2/sec
Parameter η_3	50 - 100	cm^3/mole
Radius ratio R/R_g	0.01 - 0.1	

Fig. 2 shows the moving boundary r_c/R vs. time t at different particle radius R and different gas atmosphere radius R_g. Curves (1) through (4) have the same R_g amounted 0.1cm., while curves (5) through (10) are subjected to a condition of R_g amounted .5cm. Curves(1) and (5) have the same R but different R_g. Curves (1), (2) and (5) show the gas penetration to the solid at first few minutes are considerably fast, then it almost ceases to move inward during subsequent time development. The phenomena can be reasoned by three factors. Firstly, the particle concentrations of these three curves are considerably low amounted in the range of $10^{-6}$to $8x10^{-6}$ cm^3/cm^3 and, hence, the consumption of the solid additives does not yield any significant effect on the concentration of the surrounding gas. Thus the whole system is very likely under a constant gas concentration atmosphere. This speeds up the gas penetration at the initial stage of absorption. Secondly, the chance for a gas to get into solid depends mainly on the surface/volume ratio of the solid particle. This situation gives smaller particles a better performance on the rate of penetration. Comparison on the charateristics of curves (1) and (5) with those of (2) reveals very clearly the significance of surface/area ratio. Thirdly, the diffusion equation (2) shows that when r_c reaches the deep core of the solid, the second term on the right hand side of the equation becomes the dominant part to describe the diffusion phenomena. Since neither $\partial^2c/\partial r^2$ nor $\partial c/\partial t$ becomes infinity as r_c approaches zero, it is quite logical that as r_c moves into the deep core of the sphere, $\partial c/\partial r$ tends gradually to zero. This leads the characteristic curve of a moving boundary i.e. r_c/R vs. t, to have an asymptote in the vicinity of the core center. A general trend demonstrates in Fig. 2 that increasing the R/R_g ratio increases the value of r_c/R at the end of 12 minutes interval. This further shows the importance of surface/volume ratio to the rate of penetration. Besides, the higher R/R_g ratio results in reducing the mass fraction of gaseous reactant in the whole gas-solid system. This situation enhances the higher R/R_g ratio curves to become more flat in the early stage of penetration because the reactive gas concentration in the surrounding atmosphere drops markedly. On curves (8) and (9) the final results of r_c/R after 12 minutes of diffusion and reaction are higher than those appearing on the curves of the same value of R/R_g. This again can be attributed to the influence of surface/volume ratio of a particle.

Fig. 3 indicates the relationship between the surrounding gas concentration and the depth of the moving boundary. The significance of this presentation is that the trend of each curve is governed by the particle relative radius R/R_g. Taking an example of curve AIJK, we see that the curve AK (R = .001cm, R/R_g = .05) coinsides with the two others AJ (R = .005cm, R/R_g = .05) and AI (R = .025cm, R/R_g = .05). The only discrepancy among these three curves is the final results after 12 minutes of penetration. Thus, it can be seen from the curve AIJK that the smaller the diameter of a particle, the deeper the penetration occurs in the solid body within the same duration of time interval (i.e. 12 minutes). Moreover, increasing R/R_g ratio increases the slop of a curve. Consequently,optimum curves should be in the vicinity of the line AO, because around the point O the absorbent is fully utilized and at the same time the surrounding gas concentration reduces to a considerably low level. Curves occurring in the upper left corner of the line AO reveals no significant reduction of surrounding gas concentration, because of low particle concentration. On the contrary, curves occurring in the lower right corner of the line demonstrates poor utilization of solid absorbents. Furthermore, it can be seen that the characteristics of curves which occur in the vicinity of the optimum line AO are markedly sensitive to the parameter R/R_g. Thus, this indication is essentially important to choosing a proper additive diameter in order to achieve economical use of the solid absorbent. Fig. 3 reveals that the global trend is favorable to the use of fine particles. However, another problem may rise from dust collection in flue gas system due to fine powders. Thus there must be certain criterion to restrain the use of very fine particles, and details of this aspect are beyond the scope of this paper.

Fig. 4 shows parametric effects on the degree of gas penetration into the solid particle and the reduction of surrounding gas concentration. The diffusivity D used for the calculation of curve AC is greater than that used for curve AB by a factor 10. By comparing these two curves, we can easily see that the parameter D does not alter the global characteristics of a curve markedly, and that it only results in further reducing the surrounding gas concentration by 15% and increasing the depth of penetration by 7%. Upon this indication, it is quite clear that the parameter of diffusivity D merely increases the rate of penetration. Hence the result agrees very well with the physical meaning of diffusivity D. Curve AD indicates that its value of η_3 is greater than the corresponding parameter applied on the curve AB by a factor of 2. The final value of C_s/C_0 for the curve AB is lower than that for the curve AD by 33%. The increment of penetration on AD is amounted 8% as compared with the final depth of penetration on AB. This situation can be attributed to two reasons. Firstly, a higher value of η_3 requires a larger amount of solid absorbent to react with each mole of the reactive gas. Secondly, a higher final surrounding gas concentration is also in favor of gas diffusion into the solid. However, for the present calculated result of the curve AD, the moving boundary r_c at the end of 12-minute penetration is quite close to its asymptotic value. Thus, the increment of penetration presented on the curve AD is relatively small. Curve AE demonstrates the effect of increasing the initial surrounding gas concentration C_0 on the absorption of gas and the depth of penetration. The C_0 value of curve AE is higher than that applied on the AB by a factor of 5. Since at the end of absorption the moving boundary of curve AB reaches the neighbourhood of its asymptotic value, increasing the initial gas concentration does not increase significantly the penetration of curve AE as expected. Because of higher initial concentration C_0 and the limitation of moving boundary, the surrounding gas concentration for the curve AE becomes remarkedly higher than that for the curve AB. Numerically, the increment of concentration on curve AE is almost up to 75%. For the present example of a closed optimum curve AB, its final gas concentration is sensitive to the parameters η_3 and C_0 but less sensitive to the diffusivity D.

Upon discussion of the above results, we can draw some conclusions as follows:

(1) The time rate of the moving boundary is very sensitive to the surface/volume ratio of the solid particle.

(2) An asymptotic value of r_c appears near the center of the solid sphere.

(3) The characteristics of curves of C_s/C_0 vs. r_c/R depend strongly upon the parameter R/R_g. Curves with the same R/R_g but different R occur on the same line.

(4) Near the optimum region, the reduction of surrounding gas concentration is very sensitive to the relative radius (R/R_g) of the particle.
(5) Near the optimum region, the effects of initial gas concentration C_o and the material property η_3 on the reduction of sourrounding gas concentration becomes remarkedly important.

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