

化學 및 冶金工程에서 流固體間에 일어나는 非觸媒的  
反應의 速度論\* : IV. 多粉體系의 設計와 分析

孫 洪 鏞

Department of Mining, Metallurgical and Fuels Engineering  
University of Utah, Salt Lake City, Utah 84112, U. S. A.

Kinetics of Non-Catalytic Fluid-Solid Reactions in Chemical  
and Extractive Metallurgical Processes: Part IV Design  
and Analysis of Multiparticle Systems\*

H. Y. Sohn

Department of Mining, Metallurgical and Fuels Engineering  
University of Utah, Salt Lake City, Utah 84112, U. S. A.

요 약

工業的으로 重要한 fixed bed, moving bed, fluidized bed 그리고 continuously stirred tank reactor等의 多粉體系의 設計와 分析을 여기에 檢討한다. 第一, 二, 三部에서 檢討한 單一固體의 反應을 多粉體系에 應用하는 節次를 例示하였다. 또한 最近에 開發된 多粉體系의 反應을 敘述하는데 있어 強力한 數學的 方法인 "population balance model"을 함께 紹介한다. 이 方法이 앞으로 化學과 冶金工程에서 일어나는 여러가지 多粉體系의 分析에 많은 應用이 되리라 믿는다.

Abstract

The design and analysis of a multiparticle fluid-solid reaction system is discussed. The types of contacting devices discussed are fixed beds, moving beds, fluidized beds, and continuously stirred tank reactors. The analysis, however, can be extended to other multiparticle systems. It is shown how the analysis of the reaction of individual solid particles discussed in the previous parts of this

\* Part I: Hwahak Konghak (J. Korean Inst. Chem. Engrs.), 14(1976), 3.  
Part II: 14(1976), 65.  
Part III: 14(1976), 135.

review forms the basis for analyzing a multiparticle system combined with the reactor configuration, fluid flow, and the rate of supply of the fluid reactant.

Also in this article, a powerful mathematical technique called the "population balance model" for describing a reaction of a multisized particle system is introduced. It is believed that this recently developed technique will find many applications in the design and analysis of various chemical and extractive metallurgical processes involving particulate assemblages.

In the preceding parts of this review, fluid-solid reactions occurring in single particles have been discussed. The eventual objective for studying simple particle systems is, of course, to apply the results of such a study to analyzing, predicting and designing multiparticle systems. Most practical fluid-solid systems of industrial importance consist of particulate assemblages. Examples of multiparticle fluid-solid contacting equipment include packed beds, moving beds, fluidized beds, and rotary kilns. The extension of single-particle studies to multiparticle systems will depend on the nature of the particulate assemblages, the mode of fluid-solid contacting, and the spatial variation of the fluid properties within the system. These problems are quite analogous to those involved in extending the catalytic reaction in a single pellet to an industrial catalytic reactor.

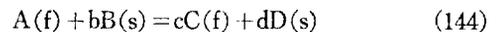
In this review, it will be assumed that the reader is familiar with various properties of multiparticle systems such as residence time distribution, pressure drop and velocity distribution, axial and radial dispersion, and heat and mass transfer characteristics.

Needless to say, one cannot generalize the techniques of describing multiparticle systems. Different groups must be considered separately. A number of commonly encountered multiparticle contactors will be discussed in this review, which will form a basis of treating other specific systems. In the following, reactions of uniformly sized particles in fixed, moving, and fluidized beds will be described. Finally, the appli-

cation of the recently developed population balance model to the reaction of multisized particle systems will be presented.

#### 4.1 Fixed-bed systems

Let us consider the reaction of solid particles with a reactant fluid in a fixed bed. The reaction is given by



For mathematical simplicity, we will consider an isothermal system. Nonisothermal systems can be analyzed similarly by adding equations of energy. We shall further assume an irreversible reaction. For such a system, the governing equation for the fluid reactant can be written as

$$D_a \frac{\partial^2 C_A}{\partial Z^2} - U \frac{\partial C_A}{\partial Z} - (-R_A) = 0 \quad (145)$$

where  $D_a$  is the axial dispersion coefficient,  $U$  is the superficial velocity and  $(-R_A)$  is the rate of consumption of gas A per unit volume of the bed. In Eq. (145) we neglected the accumulation of A in the void space of the bed  $\left(-\frac{\partial C_A}{\partial t}\right)$  term.

The rate of consumption of solid B per unit volume of the bed at any  $Z$  can be written as follows:

$$\begin{aligned} -R_B &= -bR_A = \left(\frac{\text{number of particles}}{\text{per unit volume of bed}}\right) \times \\ &\left(\frac{\text{rate of consumption of}}{\text{solid B per particle}}\right) = \left(\frac{1-\varepsilon_B}{V_p}\right) \alpha_B \rho_B V_p \frac{\partial X}{\partial t} \\ &= (1-\varepsilon_B) \alpha_B \rho_B \frac{\partial X}{\partial t} \end{aligned} \quad (146)$$

where  $\alpha_B$  is the fraction of particle volume, re-

ardless of whether the solid is porous or non-porous, occupied by solid B (=1 for dense, pure solid B) and  $\rho_B$  is the true molar density of solid B (=number of moles of B per unit volume of pure B).

The term  $\partial X/\partial t$  depends upon the specific reaction and the nature of reactant and product solids as discussed in Parts I<sup>(64)</sup> and II<sup>(65)</sup> of this review. For the purpose of illustration and because of their frequent appearance in important fluid-solid reaction processes, we shall consider the following two cases:

1. Shrinking unreacted-core system (discussed in Part I) in which initially nonporous solids of uniform sizes react with fluid forming a porous product layer.
2. Porous solids of uniform sizes reacting to form porous products, as discussed in Part II.

For an initially nonporous solid, by rearranging Eq. (21) in part I<sup>(64)</sup>, we have

$$\frac{\partial X}{\partial t} = \frac{bkC_A}{\alpha_B \rho_B} \left( \frac{A_p}{F_p V_p} \right) \left\{ g'_{F_p}(X) + \sigma_s^2 \left[ p'_{F_p}(X) + \frac{2}{Sh^*} \right] \right\}^{-1} \quad (147)$$

For an initially porous solid, from Eq. (105) in part II<sup>(65)</sup> we obtain

$$\frac{\partial X}{\partial t} = \frac{bkC_A}{\rho_s} \left( \frac{A_g}{F_g V_g} \right) \left\{ g'_{F_g}(X) + \sigma^2 \left[ p'_{F_g}(X) + \frac{2}{Sh^*} \right] \right\}^{-1} \quad (148)$$

The solution procedure is as follows: At  $t=0$ , the conversion is zero throughout the bed, and we can determine  $\partial X/\partial t$  as a function of  $C_A$  from Eq. (147) or (148) as the case may be. We can use these equations for changing  $C_A$  because diffusion is a first-order process and we assumed a first-order chemical reaction. Then we incorporate this relationship between  $\partial X/\partial t$  and  $C_A$  into Eq. (145) through the use of Eq. (146). Now Eq. (145) can be solved to give  $C_A$  as a function of the bed length  $Z$  using ap-

propriate boundary conditions. When the dispersion term is included, the boundary conditions become rather involved; when plug flow is assumed ( $D_a=0$ ), the boundary condition becomes straightforward. With this concentration profile, we can evaluate  $\partial X/\partial t$  at any  $Z$ . We then integrate Eq. (147) between  $t=0$  and  $\Delta t$ , which yields  $X$  vs.  $Z$  at  $\Delta t$ . This  $X$ -vs.  $-Z$  relationship is used to solve Eq. (145) for  $C_A$  vs.  $Z$  at  $\Delta t$ . This procedure is repeated until the desired value of  $t$ . It should be noted that, when  $X$  reaches unity at certain  $Z$ , no further reaction occurs at that position and hence  $\partial X/\partial t$  and  $R_A$  must be set equal to zero. Numerical results for the case of porous solids have been reported in the literature<sup>(66)</sup>.

The operating conditions in terms of bed length, flow rate, etc., would depend on whether gaseous or solid product is the desired product.

## 4.2 Moving-bed systems

In moving-bed reactors both the solid and the gas move cocurrently or countercurrently. We will illustrate the analysis for a steady-state system with the fluid and solid moving in plug flow.

The governing equation for the fluid reactant is

$$U \frac{dC_A}{dZ} + (-R_A) = 0 \quad (149)$$

where

$$-R_A = -\frac{1}{b} R_B = -\frac{(1-\epsilon_B) \alpha_B \rho_B}{b} \frac{dX}{dt} \quad (150)$$

and  $dX/dt$  is given by either Eq. (147) or (148).

The governing equation for the solid reactant is

$$G_B \frac{dX}{dt} - (-R_B) = 0 \quad (151)$$

where  $G_B$  is the molar flow rate of B per unit cross-sectional area of the bed. For cocurrent

flow  $G_B$  has the positive sign and for counter-current flow it has the negative sign.

The boundary condition for Eq. (149) is

$$\text{at } Z=0, C_A=C_{A0} \quad (152)$$

and that for Eq. (151) is

$$\text{Cocurrent flow: at } Z=0, X=0 \quad (153a)$$

$$\text{Countercurrent flow: at } Z=L, X=0 \quad (153b)$$

Dividing Eq. (151) by  $b$  and adding the resultant equation to Eq. (149), we obtain

$$\frac{d \left( UC_A + \frac{G_B X}{b} \right)}{dZ} = 0 \quad (154)$$

Integrating this equation with boundary conditions (152) and (153), we obtain

$$\frac{C_A}{C_{A0}} = - \frac{G_B}{bUC_{A0}} [X - X(0)] \quad (155)$$

Using Eq. (155) in Eq. (147) or (148), as the case may be, and substituting the resultant equation in Eq. (151), we obtain a first-order ordinary differential equation for  $X$  as a function of  $Z$ , which can be easily integrated analytically. The concentration profile can then be obtained from Eq. (155).

The spherical shrinking unreacted-core system was considered by Ishida and Wen<sup>67)</sup> and the system of porous pellets was studied by Evans and Song<sup>66)</sup>. Moving-bed systems in which axial dispersion is important can be studied following a similar procedure. Nonisothermal conditions can be easily incorporated, although the mathematical procedure will become more involved.

In the above, for both fixed-bed and moving-bed systems, the sizes of particles were assumed uniform. A remark may be made at this point concerning a system with a certain particle size distribution. When the distribution is either Gaussian (normal) or log-normal in terms of weight fractions, McIlvried and Massoth<sup>68)</sup> have shown that the overall rate of conversion is not much affected by the spread (within a reasonable limit of naturally and industrially encountered

values) as long as the weight-mean size is used. This may not be the case when the distribution is of the Gaudin-Schuhmann form<sup>69)</sup>. The extension of the above analyses to a system with a size distribution is rather straightforward. Examples of this type have been discussed by Evans and Song<sup>70)</sup> who made use of Eq. (103) of Part II obtained by Sohn and Szekely<sup>71)</sup>. A somewhat different example using the so-called population balance model will be discussed later in this article.

### 4.3 Fluidized-bed systems

The behavior of solid particles and fluid in a fluidized bed is quite complex<sup>72)</sup>. It is possible to incorporate more complex models of fluid flow and mixing in describing fluid-solid reactions in a fluidized bed<sup>72,73)</sup>. We will, however, present here an approach<sup>66,74)</sup> based on the assumption that within the bed the solid particles are well-mixed and the fluid is passing in plug flows. [The solid is well-stirred by the fluid contained in large bubbles which makes an insignificant contribution to reaction.]

Again, it is assumed that the solid particles have uniform size and the bed is isothermal. Since the solid particles are assumed to be perfectly mixed, we may assume that during the residence time, the solid encounters the spatial mean gas concentration,  $\bar{C}_A$ , to be determined later. [This is possible for a first-order reaction.]

Thus, Eqs. (21) and (105) are applicable provided that  $t^*$  is defined using  $\bar{C}_{A0}$ . We then obtain, from either of these equations,  $X$  as an explicit function of  $t^*$ : (We need to do this numerically.)

$$X = X(t^*, Sh^*, \sigma_S^2 \text{ or } \hat{\sigma}^2) \quad (156)$$

The age distribution of the solids in the bed

is

$$E(\bar{t}^*) = \frac{1}{\bar{t}^*} e^{-t^*/\bar{t}^*} \quad (157)$$

where  $\bar{t}^*$  is the dimensionless form of the residence time  $\bar{t}$  of the solids in bed:

$$\bar{t}^* = \frac{bk\bar{C}_A}{\alpha_B \rho_B} \left( \frac{A_p}{F_o V_p} \right) \bar{t} \text{ for nonporous solids} \quad (158a)$$

$$= \frac{bk\bar{C}_A}{\rho_B} \left( \frac{A_p}{F_g V_g} \right) \bar{t} \text{ for porous solids} \quad (158b)$$

The average conversion of the solids leaving the system is given by

$$X(\bar{t}^*, Sh^*, \sigma_s^2 \text{ or } \hat{\sigma}^2) = \int_0^{\infty} \frac{E(t^*) X(t^*, Sh^*, \sigma_s^2 \text{ or } \hat{\sigma}^2) dt^*}{\bar{t}^*} \quad (159)$$

Since we assume that the gas in the emulsion phase passes through the bed in plug flow, the appropriate mean gas concentration is the log-mean value between the inlet and outlet concentrations:

$$C_A = \frac{C_{A \text{ in}} - C_{A \text{ out}}}{\ln(C_{A \text{ in}}/C_{A \text{ out}})} \quad (160)$$

The outlet concentration  $C_{A \text{ out}}$  can be calculated from an overall mass balance as follows:

$$G_B \bar{X} = b G_A (1 - C_{A \text{ out}}/C_{A \text{ in}}) \quad (161)$$

where  $G_A$  is the molar flow rate of gas A per unit cross-sectional area through emulsion phase. The calculation of the overall conversion thus involves a trial-and-error procedure.

#### 4.4 Application of population balance model to multiparticle systems

In the previous sections, systems of monosized particles were discussed. In this section we will discuss some examples of the treatment of multisized particle systems. In particular, we will introduce a powerful technique for handling reactions of particles which have distributions of properties such as size, composition, porosity, etc. This is based on a general accounting procedure which can be used to predict changes in property distributions for multiparticle

processes involving chemical and physical interactions.

In 1964, Hulburt and Katz<sup>75)</sup> and Randolph<sup>76, 77)</sup> proposed a population balance equation for the continuity of particle numbers. This balance equation can be applied to an infinitesimal control volume as in the case of momentum, heat and mass transfer (microscopic form). In this review, however, we will illustrate the use of the population balance model by considering systems in which the population balance equation may be written over a reactor volume such as batch or continuously stirred tank reactor (macroscopic form). The application of the population balance model to systems described in Sections 4.1~4.3 would involve the microscopic form of the model. In general, the solution of problems involving the microscopic form is quite complex.

##### 4.4.1 Mathematical Expressions of Property Distributions

Before describing the application, it would be of interest to take a brief look at the mathematics of distributions. The property distributions are expressed in terms of density functions  $f(D)$  and distribution functions  $F(D)$ . Let us consider the particle size distribution. The fraction of the particles in a population which have a size between  $D$  and  $D+dD$  is given by  $f(D)dD$ . The fraction of the particles smaller than some size  $D_1$ , can be obtained by summing the fractions of particles from the minimum size in the population,  $D_{\min}$ , to  $D_1$ . For an infinitesimal  $dD$ , the summation becomes an integral:

$$F(D_1) = \int_{D_{\min}}^{D_1} f(D) dD \quad (162)$$

Of course,  $F(D_{\max}) = 1$ , and the fraction of particles in any size interval  $D_1$  and  $D_2$  can be calculated from

$$\int_{D_1}^{D_2} f(D) dD = F(D_2) - F(D_1) \tag{163}$$

The functions  $f(D)$  and  $F(D)$  may be given in terms of fractions of the total number or mass (or volume) of particles. In the population balance model we are concerned with keeping an account of the number of particles. However, the distribution is frequently determined by sieving the particles and weighing each size fraction, which gives rise to mass (or volume) distribution. Thus, it is required to convert one type of size distribution to another. The relationship between a number distribution, denoted by  $f_0(D)$ , and a mass distribution, denoted by  $f_3(D)$ , is obtained by considering the following equality:

$$\left( \begin{array}{l} \text{Mass of one particle} \\ \text{of size between} \\ D \text{ and } D+dD \end{array} \right) \times \left( \begin{array}{l} \text{Number of parti-} \\ \text{cles in that size} \\ \text{interval} \end{array} \right) = \left( \begin{array}{l} \text{Mass of particles} \\ \text{in that size inter-} \\ \text{val} \end{array} \right)$$

$$\rho C_3 D^3 N f_0(D) dD = W f_3(D) dD \tag{164}$$

where  $N$  is the total number of particles in the system,  $W$  is the total mass of particles in the system,  $\rho$  is the solid density, and  $C_3$  is the volume shape factor (volume of one particle =  $C_3 D^3$ ). If  $\rho$  and  $C_3$  are independent of  $D$ , we obtain from Eq. (164)

$$f_0(D) = \frac{D^{-3} f_3(D)}{\int_{D_{\min}}^{D_{\max}} D^{-3} f_3(D) dD} \tag{165}$$

and

$$f_3(D) = \frac{D^3 f_0(D)}{\int_{D_{\min}}^{D_{\max}} D^3 f_0(D) dD} \tag{166}$$

Equations (165) and (166) permit the transformation of one type of size distribution to the other.

We can extend the description of property distributions to the system in which there are more than one properties of interest. We may be interested in the distribution of size,  $D$ , and the content of the reactant solid,  $\rho_B$ , in a particle assembly. The number fraction of particles

with size between  $D$  and  $D+dD$  and molar concentration of the reactant solid between  $\rho_B$  and  $\rho_B+d\rho_B$  is given by  $f_0(D, \rho_B)$ .

The distribution function is

$$F_0(D_1, \rho_{B1}) = \int_{\rho_{B\min}}^{\rho_{B1}} \int_{D_{\min}}^{D_1} f_0(D, \rho_B) dD d\rho_B \tag{167}$$

In this case,  $F_0(D_{\max}, \rho_{B\max}) = 1$ . The size distribution irrespective of reactant-solid content can be obtained by

$$f_0(D) = \int_{\rho_{B\min}}^{\rho_{B\max}} f_0(D, \rho_B) d\rho_B \tag{168}$$

and the distribution of reactant-solid content irrespective of size can be obtained by

$$f_0(\rho_B) = \int_{D_{\min}}^{D_{\max}} f_0(D, \rho_B) dD \tag{169}$$

In principle, this procedure can be extended to any number of properties of interest, but in practice, the complexity of distribution precludes the simultaneous consideration of more than two properties.

#### 4.4.2 Macroscopic Population Balance Model

The starting point for a population balance is the following balance equation for the number of particles with certain properties.

$$\left( \begin{array}{l} \text{Rate of number} \\ \text{of particles in} \end{array} \right) - \left( \begin{array}{l} \text{Rate of number} \\ \text{of particles out} \end{array} \right) + \left( \begin{array}{l} \text{Net rate of number} \\ \text{generation of particles} \end{array} \right) = \left( \begin{array}{l} \text{Rate of number accu-} \\ \text{mulation of particles} \end{array} \right)$$

$$\tag{170}$$

Let us consider a reactor which at time  $t$  contains  $N(t)$  particles per unit volume. The number of particles per unit volume of reactor with the first property between  $\zeta_1$  and  $\zeta_1+d\zeta_1$ , the second property between  $\zeta_2$  and  $\zeta_2+d\zeta_2$ , etc., can be written as

$$\psi dR = N(t) f_0(\zeta_1, \zeta_2, \dots, \zeta_M, t) \zeta_1, d\zeta_2, \dots, d\zeta_M \tag{171}$$

The rate at which particles in the specified property intervals are entering the reactor is:

$$\left( \begin{array}{l} \text{rate of} \\ \text{input} \end{array} \right) = N_{\text{in}} Q_{\text{in}} f_{0,\text{in}}(\zeta_1, \zeta_2, \dots, \zeta_M, t) d\zeta_1, d\zeta_2, \dots,$$

$$\dots, d\zeta_M = Q_{in}\phi_{in}dR \quad (172)$$

Similarly, the rate at which such particles are leaving the reactor is:

$$\begin{aligned} (\text{rate of output}) &= N_{out}Q_{out}f_{o,out}(\zeta_1, \zeta_2, \dots, \zeta_M, t)d\zeta_1, d\zeta_2, \\ &\dots, d\zeta_M = Q_{out}\phi_{out}dR \quad (173) \end{aligned}$$

The net rate of generation of particles in the specified property interval is:

$$\begin{aligned} (\text{Net rate of generation}) &= V \left[ (\delta_B - \delta_D) - \sum_{j=1}^M \frac{\partial}{\partial \zeta_j} (V_j \cdot \phi) \right. \\ &\left. dR \right] \quad (174) \end{aligned}$$

where  $V$  is the active volume of the reactor, and  $\delta_B$  and  $\delta_D$  are the rate per unit volume at which particles are "born" and "die," respectively, in the specified property interval. ( $\delta_B$  and  $\delta_D$  are the result of discrete changes such as breakage or coalescence.) The term involving the summation represents the net rate of disappearance of particles in the specified interval due to continuous changes in the properties  $\zeta_1$  to  $\zeta_M$ .  $v_j$  is the time rate of change of property  $j$ , i. e.

$$v_j = \frac{d\zeta_j}{dt} \quad (175)$$

The rate of number accumulation of particles with properties in these intervals in the reactor is the rate of change of particle number:

$$(\text{Rate of accumulation}) = \frac{\partial(V\phi)}{\partial t} dR \quad (176)$$

Substituting Eqs. (171)~(176) in Eq. (170), we obtain the macroscopic population balance equation:

$$\begin{aligned} \frac{\partial}{\partial t}(V\phi) &= Q_{in}\phi_{in} - Q_{out}\phi_{out} + V \left[ (\delta_B - \delta_D) - \right. \\ &\left. \sum_{j=1}^M \frac{\partial}{\partial \zeta_j} (v_j\phi) \right] \quad (177) \end{aligned}$$

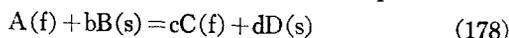
In order to solve this equation, one must have independent knowledge about the terms  $\delta_B$ ,  $\delta_D$  and  $v_j$ 's. The terms  $\delta_B$  and  $\delta_D$  usually involve physical change whereas the terms  $v_j$ 's are due to chemical reaction. Therefore, the analyses

for the reaction of a single particle discussed in the previous parts of this review will supply information on these latter terms.

In the following, we shall present some examples on how the macroscopic population balance equation can be used for analyzing the behavior of particulate reaction systems. These examples are drawn from Ref. [78].

#### 4.4.3 Application to Bath Processes

Let us consider a well-mixed batch reactor in which the following reaction takes place:



We assume that the sizes of particles remain the same during the reaction. The only property of interest in this system is the mass of B remaining in a particle. There is no breakage or coalescence of particles, i. e.,  $\delta_B = \delta_D = 0$ . For a batch process  $Q_{in} = Q_{out} = 0$ . Thus, Eq. (177) becomes

$$\frac{\partial}{\partial t} \left[ V \cdot \phi(m_B, t) \right] = -V \frac{\partial}{\partial m_B} \left[ v_B \cdot \phi(m_B, t) \right] \quad (179)$$

The solution, for an initial distribution  $\phi(m_B, 0)$ , of which is\*

$$\phi(m_B, t) = \phi(m_B - \int_0^t v_B \cdot dt, 0) \quad (180)$$

The overall conversion of B can be obtained as follows:

$$\begin{aligned} \bar{X} &= \left\{ V \int_{m_{B,\min}}^{m_{B,\max}} m_B \cdot \phi(m_B, 0) dm_B - V \int_{m_{B,\min}}^{m_{B,\max}} m_B \cdot \phi(m_B, t) dm_B \right\} / V \int_{m_{B,\min}}^{m_{B,\max}} m_B \cdot \phi(m_B, 0) dm_B \quad (181) \end{aligned}$$

We let  $m_B = [1 - X(D_0, C_A, t)]\rho_B C_3 D_0^3$  where  $X(D_0, t)$  is the fraction reacted for a particle of size  $D_0$ , introduce Eq. (180) into Eq. (181), and transform from a number distribution to a mass distribution. Equation (181) then becomes

$$\bar{X} = \int_{D_{\min}}^{D_{\max}} X(D_0, C_A, t) f_3(D_0, 0) dD_0 \quad (182)$$

The concentration of fluid reactant A at time  $t$

\* See, for example Ref. [79].

can be obtained from a mass balance on A:

$$C_A V = C_{A0} V - \frac{1}{b} \bar{X} M_{B0} \quad (183)$$

where  $M_{B0}$  is the total number of moles of B initially present in the system. Rearranging Eq. (183), we obtain

$$\frac{C_A}{C_{A0}} = 1 - \frac{M_{B0}}{bVC_{A0}} \bar{X} \quad (184)$$

It can be seen from this equation that  $C_A \approx C_{A0}$  when  $\frac{M_{B0}}{bVC_{A0}}$  is small, i. e., the fluid reactant A exists in large excess in the system, and  $X(D_0, C_{A0}, t)$  in Eq. (182) can be written explicitly. When  $\frac{M_{B0}}{bVC_{A0}}$  is large,  $X(D_0, C_A, t)$  must in general be evaluated by numerically integrating the given expression for  $\frac{dX}{dt}$  for a small time increment, computing  $\bar{X}$  from Eq. (182), calculating  $C_A$  from Eq. (184), and repeating the procedure.

#### 4.4.4 Application to Continuous Processes

In this section we shall discuss the application of the population balance model to a continuous process operated at steady state. Specifically, let us consider the reaction of solid particles suspended in liquid in a continuously stirred tank reactor. The particles are nonporous initially and react according to the shrinking unreacted-core scheme discussed in Part I<sup>64</sup>. Again, the reaction can be represented by Eq. (178). We also assume that the overall size of a particle remains unchanged during the reaction. The only property of interest in this system is the position of reaction interface  $D_c$  or the fractional conversion  $X$ . One could formulate the problem with either of the two, but it is conceptually easier to use  $D_c (=2r_c)$  as the property of interest. Equation (177) can now be written as

$$Q\phi_{in} - Q\phi_{out} - V \frac{\partial}{\partial D_c} [v_B \cdot \phi] = 0 \quad (185)$$

Since we assume perfect mixing,

$$\phi_{out} = \phi \quad (186)$$

and

$$C_{Aout} = C_A \quad (187)$$

The term  $v_B$  depends on the controlling step(s) and solid geometry. For a spherical solid, we have from Eq. (20) or (147)

$$v_B = \frac{dD_c}{dt} = -\frac{2bkC_A}{\alpha_B \rho_B} \left\{ 1 + \frac{kD}{2D_c} \left[ \left( \frac{D_c}{D} \right) - \left( \frac{D_c}{D} \right)^2 \right] + \frac{k}{k_m} \left( \frac{D_c}{D} \right)^2 \right\}^{-1} \quad (188)$$

where  $D$  is the overall size of a particle.

Rearranging Eq. (185), we get

$$\frac{d\phi(D_c/D)}{dD_c} + \left[ \frac{dv_B(D_c/D)/dD_c}{v_B(D_c/D)} + \frac{1}{\tau \cdot v_B(D_c/D)} \right] \phi(D_c/D) = \frac{\phi_{in}(D_c/D)}{\tau \cdot v_B(D_c/D)} \quad (189)$$

where

$$\tau = V/Q$$

Equation (189) is a first-order linear differential equation which can be solved using the following integrating factor:

$$\begin{aligned} I.F. &= \exp \left\{ \int_{D_c^c}^{D_c^D} \left[ \frac{dv_B(D_c/D)/dD_c}{v_B(D_c/D)} + \frac{1}{\tau v_B(D_c/D)} \right] dD_c \right\} \\ &= \frac{(1+k/k_m)}{1 + \frac{k}{2D_c} \left( D_c - \frac{D_c^2}{D} \right) + \frac{k}{k_m} \left( \frac{D_c}{D} \right)^2} \exp \left\{ \frac{\alpha_B \rho_B}{2bk\tau C_A} \left[ (D - D_c) + \frac{k}{12D_c} \left( D^2 + \frac{2D_c^3}{D} - 3D_c^2 \right) + \frac{k}{3k_m} \left( D - \frac{D_c^3}{D^2} \right) \right] \right\} \quad (191) \end{aligned}$$

The solution is given by

$$\int_{D_c^c=D_c^c}^{D_c^D=D_c^D} d \left[ I.F. \times \phi(D_c/D) \right] = \int_{D_c^c=D_c^c}^{D_c^D=D_c^D} \frac{I.F. \times \phi_{in}(D_c/D)}{\tau \cdot v_B(D_c/D)} dD_c \quad (192)$$

which can be evaluated to give

$$\begin{aligned} I.F. \times \phi(D_c/D) - I.F. |_{D_c=D} \times \phi(D_c/D) &= - \\ & \frac{\alpha_B \rho_B (1+k/k_m)}{2bkC_{Ain} \tau} \int_{D_c^c=D_c^c}^{D_c^D=D_c^D} \frac{C_{Ain}}{C_A} \phi_{in}(D_c/D) \times \exp \left\{ \frac{\alpha_B \rho_B}{2bk\tau C_A} \left[ (D - D_c) + \frac{k}{12D_c} \left( D^2 + \frac{2D_c^3}{D} - 3D_c^2 \right) + \frac{k}{3k_m} \left( D - \frac{D_c^3}{D^2} \right) \right] \right\} dD_c \end{aligned}$$

$$3D_c^3) + \frac{k}{3k_m} \left( D - \frac{D_c^3}{D^2} \right) \Big] \cdot dD_c \quad (193)$$

For a single reactor with a fresh feed,

$$\phi_{in}(D_c/D) = \delta(D_c - D) \phi_{in}(D) \quad (194)$$

where  $\delta(D_c - D)$  is the "Dirac delta function."

We also recognize that the initial condition is

$$\phi(D/D) = 0. \quad (195)$$

Substitution of Eqs. (194) and (195) in Eq. (193) yields:

$$\phi(D_c/D) = -\frac{\alpha_B \rho_B (1 + k/k_m)}{abkC_A \tau \times I. F.} \phi_{in}(D) \quad (196)$$

Integrating over all sizes  $D$ , we get  $\phi(D_c) =$

$$\int_{D_c}^{D_{\max}} \phi(D_c/D) dD \quad (197)$$

The lower limit of integration would normally be  $D_{\min}$ . In this case, however, we must recognize that  $D$  cannot be smaller than  $D_c$ . In general  $C_A$  will differ from  $C_{Ain}$ , and must be determined from the following mass balance on A:

$$C_{Ain} Q - C_A Q = \frac{1}{b} Q \left[ \int_{D_{\min}}^{D_{\max}} \alpha_B \rho_B C_3 D^3 \phi_{in}(D) dD - \int_0^{D_{\max}} \alpha_B \rho_B C_3 D_c^3 \phi(D_c) \cdot dD_c \right] \quad (198)$$

Equations (196) to (198) must be solved simultaneously. The overall conversion can then be obtained from

$$\bar{X} = \left\{ \int_{D_{\min}}^{D_{\max}} \alpha_B \rho_B C_3 D^3 \phi_{in}(D) \cdot dD - \int_0^{D_{\max}} \alpha_B \rho_B C_3 D_c^3 \phi(D_c) \cdot dD_c \right\} / \int_{D_{\min}}^{D_{\max}} \alpha_B \rho_B C_3 D^3 \phi_{in}(D) \cdot dD \quad (199)$$

In general, the computation must be carried out numerically, although certain special cases permit simple solutions.

Although we have not specified the size distribution  $\phi_{in}(D)$ , there are well-known distribution functions describing naturally occurring particulate systems or those arising as a result of comminution. Some examples are the log-normal, the Gaussian, and the Gaudin-Schuhmann distributions. As one can see, the population balance model enables one to treat the

reaction of particles with a size distribution in a systematic and unified manner.

This approach becomes even more powerful in analyzing a system in which both discrete and continuous changes occur, such as simultaneous grinding and leaching of minerals.

#### 4.5 Summary

In this article the procedures for analyzing and designing the reactions of multiparticle systems in various fluid-solid contacting devices have been described. It was shown that these procedures require the knowledge of rate processes occurring within the individual solid particles which were discussed in Parts I to III<sup>64, 66, 80</sup> of this review. The kinetics of individual particles is combined with the particular configuration of each reactor in terms of fluid flow, residence time distribution, mass balance, etc., to construct the overall picture of the system.

Examples were presented for the analyses of fixed-bed, moving-bed, fluid-bed, and continuously stirred tank reactors. A recently developed, powerful method, called the population balance model, for treating the reaction involving a multisized particle system has been introduced. It is hoped that this versatile method will find many applications for analyzing and designing chemical and extractive metallurgical processes involving particulate assemblages.

#### Nomenclature

- $A_g, A_p$  External surface area of individual grain and the pellet, respectively
- $b$  Number of moles of solid B reacted by one mole of fluid reactant A
- $C_3$  Volume shape factor [see Eq. (164)]
- $C$  Molar concentration of fluid species

- $D$  Diameter of a particle
- $D_a$  Axial dispersion coefficient
- $D_e$  Effective diffusivity in porous solid
- $f_0(D), f_3(D)$  Density function for number and mass distributions, respectively
- $F$  Shape factor (=1, 2, and 3 for flat plates, long cylinders and spheres, respectively)
- $F(D)$  Distribution function [see Eq. (162) or (167)]
- $g(X)$  Conversion function [ $=1 - (1-X)^{1/F}$ ]
- $G$  Molar flow rate per unit cross-sectional area
- $k$  Reaction-rate constant
- $k_m$  External mass-transfer coefficient
- $L$  Length of a fixed or a moving bed
- $m_B$  Mass of solid reactant B remaining in a particle at any time
- $M_{B0}$  Total number of moles of solid reactant B initially present in the system
- $N$  Total number of particles in the system
- $p(X)$  Conversion function defined by Eq. (26)
- $Q$  Volume flow rate
- $R_A, R_B$  Rate of generation per unit volume of the fluid reactant A and the solid reactant B, respectively
- $Sh^*$  The modified Sherwood number [ $= (k_m / D_e)(F_p V_p / A_p)$ ]
- $t$  Time
- $t^*$  Dimensionless time defined by Eq. (22) or (89) for a nonporous or porous particle, respectively
- $\bar{t}^*$  Dimensionless residence time defined by Eq. (158a) or (158b)
- $U$  Superficial velocity of fluid
- $v_j$  Time rate of change of property  $j$  defined by Eq. (175)
- $V$  Volume
- $X$  Fractional conversion of the solid
- $Z$  Distance from the fluid inlet into the bed

### Greek Symbols

- $\alpha_B$  Fraction of volume occupied by reactant solid B
- $\delta_B, \delta_D$  Rate per volume at which particles are "born" and "die," respectively, as the result of discrete changes
- $\zeta_i$   $i$ th property of interest
- $\varepsilon_B$  Voidage of bed (not including the porosity of solid)
- $\rho$  Mass density
- $\rho_B$  True molar density of solid reactant B
- $\hat{\sigma}$  Generalized gas-solid reaction modulus for a porous solid defined by Eq. (102)
- $\sigma_s$  Shrinking-core reaction modulus defined by Eq. (23)
- $\tau$  Nominal holding time defined by Eq. (190)
- $\phi$  Function defined by Eq. (171)

### Subscripts

- $A$  Fluid A
- $B$  Solid B
- $c$  Value at reaction interface
- $g$  Grain
- $p$  Particle or pellet

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- References 1~31 are given in Part I, 32~57 in Part II, and 58~63 in Part III of this review.
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