

# Dissolution of Powdered Minerals: The Effect of Polydispersity

S. E. LeBlanc  
H. S. Fogler

Department of Chemical Engineering  
University of Michigan  
Ann Arbor, MI 48109

Few studies have examined the effect of polydispersity on dissolution processes. A thorough review of the pertinent literature has already been presented (LeBlanc and Fogler, 1987). Mixed regime refers to kinetics in which the mass transfer and intrinsic surface reaction rates are of the same order of magnitude. Polydisperse mineral systems which have some particles dissolving simultaneously in both rate limiting regimes can be analyzed with this method (i.e., for broad initial distributions, the large particle dissolution may be mass transfer limited, while the smaller particles are surface reaction rate limited).

## Model Development

For purposes of illustration, first order surface reaction kinetics which yield an analytically solvable population balance, will be considered. More complex kinetics, such as second or  $n$ th order or Langmuir kinetics, can also be handled using the mixed regime technique, however, the resulting population balances must be solved numerically. The surface reaction dissolution rate for first order kinetics may be set equal to the surface mass transfer rate, to obtain a general expression for the particle dissolution kinetics.

### Single particle shrinkage rate

For small spherical particles which "move with the flow," the Reynolds No. is small, the Sherwood No. is 2, and the expression for the particle shrinkage rate becomes:

$$R = -\frac{dD}{dt} = \frac{2C_A K_r}{\rho_s} \left[ 1 + \frac{D}{D_o} \right]^{-1} = \alpha \left[ 1 + \frac{D}{D_o} \right]^{-1} \quad (1)$$

where  $D_o$  is the diameter at which the surface reaction and mass transfer resistances are equal. Once calculated,  $D_o$  may then be compared to the initial particle size distribution, and the rate

controlling regime(s) governing the dissolution behavior of the distribution can be determined. From our definition, we can form the following dimensionless quantity:

$$\frac{K_r}{K_m} = \frac{D}{D_o} \quad (2)$$

The magnitude of this dimensionless term indicates the rate controlling regime. For example, if the particle diameter is much less than  $D_o$  (i.e.,  $D \ll D_o$  and  $K_r \ll K_m$ ), then the surface reaction rate is controlling.

We shall soon see that if one tries to make predictions using only single particle information, the results may be directly opposite to those observed experimentally for polydisperse systems.

### Population balance for polydisperse systems

The population balance for dissolution processes was previously shown to be (LeBlanc and Fogler, 1987):

$$\frac{\partial F}{\partial t} + \frac{\partial}{\partial D} (RF) = 0 \quad (3)$$

In terms of dimensionless parameters, this becomes:

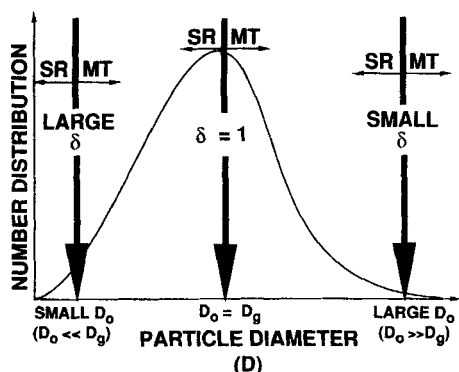
$$\frac{\partial \phi}{\partial \theta} - \zeta^{-1} \frac{\partial \phi}{\partial \zeta} = -\phi \zeta^{-2} \quad (4)$$

The method of characteristics can now be applied to this dimensionless population balance to determine its solution, which is:

$$\phi = \zeta H[\zeta^2 + 2\theta] \quad (5)$$

where  $H$  is an arbitrary function whose form is to be determined from the initial particle size distribution. The distributions most

S. E. LeBlanc is currently at the University of Toledo.



**Figure 1. Dissolution regime for a particle size distribution.**

frequently used to model particulate systems are the lognormal and Rosin-Rammler distributions (Allen, 1981). The treatment below, illustrates the method with a lognormal distribution; for an analogous solution using Rosin-Rammler distributions, the reader is referred to the literature (LeBlanc, 1985).

### Lognormal solution

The size distribution of many real particle samples can be closely approximated using lognormal distributions. The equation for a dimensionless initial lognormal particle size distribution (using the above notation) takes the following form:

$$\phi(\xi, 0) = \frac{D_0 F(D, 0)}{N(0)} = \frac{1}{\ln \sigma_g \sqrt{2\pi} [\xi - 1]} \exp \left[ - \frac{\left[ \ln \left( \frac{(\xi - 1)}{\delta} \right) \right]^2}{2 [\ln \sigma_g]^2} \right] \quad (6)$$

The magnitude of  $\delta$  is indicative of the rate controlling regime. If  $\delta \ll 1$ , then the particle size distribution consists of

particles whose diameters are considerably smaller than  $D_0$  and hence the dissolution will be surface reaction rate limited. Figure 1 illustrates this concept. Similarly, if  $\delta \gg 1$ , the particle size distribution lies primarily above  $D_0$ , and the dissolution is mass transfer limited.

Experimental data for the dissolution of several manganese oxides in a number of acids are shown in Table 1.  $D_0$  was calculated using experimentally determined diffusivities and surface reaction rate constants obtained from slurry reactor dissolution experiments (LeBlanc 1985). For the surface reaction rate limited cases ( $E_{act} > 42$  kJ/gmol), the values of  $\delta$  are much less than 1.0, and similarly, for the mass transfer limited cases ( $E_{act} < 21$  kJ/gmol),  $\delta$  is greater than 1.0, as we would expect. We will soon see that these values of  $\delta$  are sufficient to allow these systems to be modeled using the limiting regime analyses presented earlier (LeBlanc and Fogler, 1987).

The dimensionless population balance, Eq. 4, may be solved using the method of characteristics for a sample having an initial lognormal distribution (LeBlanc, 1985). The solution is shown in Eq. 7.

$$\phi(\xi, \theta) = \frac{\xi}{\ln \sigma_g \sqrt{2\pi} [\xi^2 + 2\theta]} \left[ \frac{1}{[\xi^2 + 2\theta]} \right]^{1/2} \left[ \frac{1}{[\xi^2 + 2\theta]^{1/2} - 1} \right] \cdot \exp \left[ - \frac{\left[ \ln \left( \frac{[\xi^2 + 2\theta]^{1/2} - 1}{\delta} \right) \right]^2}{2 [\ln \sigma_g]^2} \right] \quad (7)$$

### Important distribution parameters

As the particle size distribution shifts during the dissolution process, its properties change. Several important parameters of the shifting distributions, such as conversion and surface area per unit mass, may be determined from the dimensionless population balance solutions. For example, the conversion as a function of dimensionless time may be expressed as:

$$x(\theta) = 1 - \frac{\int_1^\infty (\xi - 1)^3 \phi(\xi, \theta) d\xi}{\int_1^\infty (\xi - 1)^3 \phi(\xi, 0) d\xi} \quad (8)$$

**Table 1. Experimentally Determined Reduced Diameters for Manganese Oxides\***

| Mineral                 | $\sigma_g$ | $D_{gn}$<br>( $\mu\text{m}$ ) | Acid | $D_0$<br>(25°C)<br>( $\mu\text{m}$ ) | $\delta$             | $E_{act}$<br>[kJ/gmol] | Rate<br>Controlling<br>Regime |
|-------------------------|------------|-------------------------------|------|--------------------------------------|----------------------|------------------------|-------------------------------|
| $\text{MnO}_2$          | 1.26       | 102                           | HCl  | $5.5 \times 10^6$                    | $1.9 \times 10^{-5}$ | 45.6                   | SR                            |
|                         |            |                               | HBr  | $1.2 \times 10^5$                    | $6.2 \times 10^{-4}$ | 42.7                   | SR                            |
|                         |            |                               | HI   | 10.5                                 | 9.7                  | 18.4                   | MT                            |
| $\text{Mn}_2\text{O}_3$ | 2.58       | 0.68                          | HCl  | $1.5 \times 10^5$                    | $4.5 \times 10^{-6}$ | 96.7                   | SR                            |
|                         |            |                               | HBr  | $5.8 \times 10^4$                    | $1.2 \times 10^{-5}$ | 59.0                   | SR                            |
|                         |            |                               | HI   | 618                                  | $1.1 \times 10^{-3}$ | 47.7                   | SR                            |
| $\text{Mn}_3\text{O}_4$ | 2.34       | 0.52                          | HCl  | $1.2 \times 10^5$                    | $4.4 \times 10^{-6}$ | 84.1                   | SR                            |
|                         |            |                               | HBr  | 5830                                 | $8.8 \times 10^{-5}$ | 65.3                   | SR                            |
|                         |            |                               | HI   | 124                                  | $4.2 \times 10^{-3}$ | 56.5                   | SR                            |
| $\text{MnO}$            | 1.34       | 77.3                          | HCl  | 10.5                                 | 7.4                  | 20.1                   | MT                            |
|                         |            |                               | HBr  | 10.5                                 | 7.4                  | 20.1                   | MT                            |
|                         |            |                               | HI   | 10.5                                 | 7.4                  | 20.1                   | MT                            |

\*SR = Surface reaction rate limited; MT = Mass transfer limited

Similarly, the dimensionless surface area per unit mass of the dissolving particle sample is:

$$\frac{S(\theta)}{S(0)} = 1 - \left[ \frac{1}{1 - x(\theta)} \right] \frac{\int_1^\infty (\zeta - 1)^2 \phi(\zeta, \theta) d\zeta}{\int_1^\infty (\zeta - 1)^2 \phi(\zeta, 0) d\zeta} \quad (9)$$

These dimensionless distribution parameters can provide significant insight into the dissolution behavior of polydisperse solid particles.

## Discussion of Results

The mixed regime population balance model enables us to examine the effect of combined surface reaction rate and mass transfer limitations on the dissolution process. The rate controlling regime is very sensitive to the distribution of particle sizes present.

The effect of the geometric mean particle diameter,  $D_g$ , on the rate controlling regime, is illustrated in Figure 1. Let us assume that we have a given solid sample (i.e., a fixed particle size distribution) that we wish to dissolve. If we vary the solvent being used for the dissolution, the value of  $D_o$  will change as well. One can observe that for large values of  $D_o$  (or for small  $\delta$ ), the majority of the particles in the distribution are smaller than  $D_o$ , and the sample is primarily in the surface reaction controlled regime. Conversely, for small values of  $D_o$ , (large  $\delta$ ) most of the particles fall in the mass transfer limited regime.

These relationships are quantitatively illustrated in Figure 2 for a lognormal distribution having a  $\sigma_g = 2.50$ . For this case, a system with  $\delta = .01$  dissolves totally in the surface reaction rate limited regime until very high conversions ( $>90\%$ ) are attained. For a value of  $\delta = 5$ , the sample dissolves, virtually completely, in the mass transfer limited regime. However, as the particles shrink to very small diameters, they must eventually pass from the mass transfer limited into the surface reaction limited regime, but, as shown by Figure 2, there is no significant fraction of the particles in the surface reaction controlled regime at any time.

For monodispersed particles we would predict that the dissolution proceeds more rapidly in the mass transfer limited case than in the surface reaction rate limited case, providing the initial rates are equal. (The reason being that, as the particles shrink, the dissolution rate per unit area increases for the mass transfer limited case, due to the diameter dependence of the

mass transfer coefficient, while the rate per unit area remains constant for the surface reaction limited case.)

This type of dissolution behavior (mass transfer limited rate  $>$  than surface reaction limited rate) is *not* necessarily the case however, when a distribution of particle sizes exists. In fact, the *opposite* is frequently true. The phenomenon exhibited by particle size distributions is also due to the dependence of the mass transfer coefficient on the particle diameter. For very large particles in the distribution, the mass transfer coefficient is small and their overall dissolution rate is slower. Since a significant fraction of the total mass of the distribution is contained in these larger particles, the overall approach to total conversion is thus slowed. The broader the initial distribution, the more pronounced this effect becomes. For example, from a limiting regimes analysis (LeBlanc, 1985), the dimensionless times required for 50% dissolution of a particle sample may be calculated as a function of the distribution breadth. For this comparison the particle dissolution rates for the two limiting regime processes are taken to be equal at the geometric mean diameter (that is,  $K_r = K_m @ D = D_g$ ). As shown in Figure 3, the times required for 50% conversion, cross at  $\sigma_g = 1.1$  for the two regimes. As the distribution broadens, the 50% conversion times deviate significantly for the two cases. For example, at  $\sigma_g = 3.0$ , the dimensionless time for the mass transfer limited case is 400, while for the surface reaction rate limited case, it is only 13.5. This surprising result is again due to the dependence of the mass transfer coefficient on the particle size and is just the opposite of what one would predict, using a single particle analysis.

Other interesting observations we can make, using this model to analyze the dissolution of polydisperse solids, are:

- The model, as expected, yields the limiting regime solutions for large and small values of  $\delta$ .
- The changes that occur in the surface area per unit mass of the sample during the course of the dissolution can be predicted. For samples with a broad distribution (high  $\sigma_g$ ) the surface area per unit mass decreases with increasing conversion, while for those with a narrow distribution of particle sizes, it increases. This result explains why the surface area per unit mass decreases for some samples during dissolution and increases for others.
- We can predict the effect of polydispersity on the conversion vs. time behavior, for a distribution reacting with mixed regime kinetics. As the breadth of the sample becomes larger

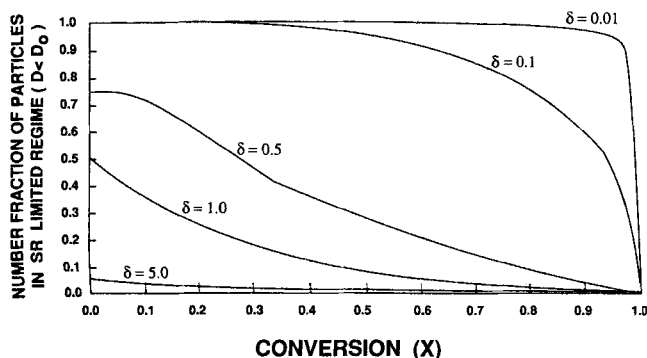


Figure 2. Number of particles dissolving in surface reaction rate limited regime vs. conversion.

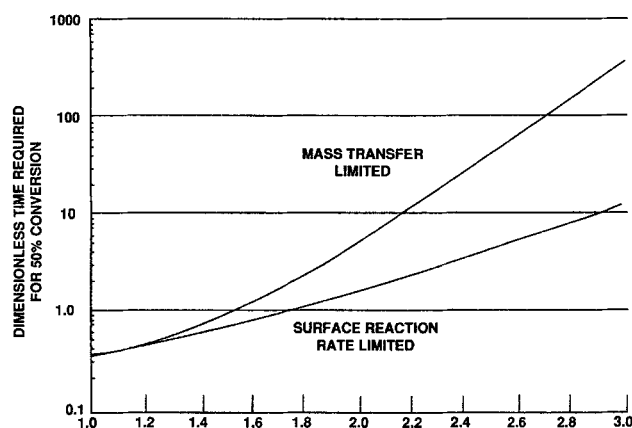


Figure 3. Time required for a 50% conversion limiting regimes vs. polydispersity.

(increasing polydispersity), a longer time is required to attain a given conversion. We have already shown this to be the case for the limiting regime cases (LeBlanc, 1987); therefore, *regardless* of the reaction regime, increasing the polydispersity of samples with the same mean diameter, increases the time required to attain a specified conversion.

## Notation

$C_A$  = bulk phase solvent concentration  
 $D$  = particle diameter  
 $D_g$  = geometric mean diameter  
 $D_o$  = diameter at which surface reaction rate = mass transfer rate  
 $F(D, t)$  = particle number distribution at any time,  $t$   
 $H$  = arbitrary function arising from method of characteristics solution  
 $K_m$  = mass transfer coefficient  
 $K_r$  = surface reaction rate constant  
 $N(0)$  = initial total number of particles present  
 $R$  = particle shrinkage rate  
 $S$  = surface area/mass  
 $t$  = time  
 $x$  = conversion

## Greek letters

$\alpha = (2C_A K_r)/\rho_s$  = constant for large excess of solvent  
 $\rho_s$  = solid molar density  
 $\theta = \alpha t/D_o$  = time  
 $\phi$  = number particle size distribution

$\sigma_g$  = geometric standard deviation  
 $\xi = [1 + (D/D_o)]$  = diameter  
 $\delta = D_g/D_o$  = reduced diameter

## Literature Cited

- Allen, T., *Particle Size Measurement*, 3rd ed., Chapman and Hall, London (1981).  
 Bird, R. B., W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York (1960).  
 Cooper, S., "The Use of Particle Size Distributions in the Modeling of Combustion Systems," *Comb. and Flame*, **56**, 279 (1984).  
 Dickinson, D. R., and W. R. Marshall, "The Rates of Evaporation of Sprays," *AIChE J.*, **14**, 541 (1968).  
 Fogler, H. S., *Elements of Chemical Reactor Design*, Prentice-Hall, NJ (1986).  
 Irani, R. R., and C. F. Callis, *Particle Size: Measurement, Interpretation, and Application*, Wiley, New York (1963).  
 LeBlanc, S. E., PhD Dissertation, "Enhanced Mineral Dissolution," University of Michigan (1985).  
 LeBlanc, S. E., and H. S. Fogler, "Population Balance Modeling of the Dissolution of Polydisperse Solids: Rate Limiting Regimes," *AIChE J.*, **33**, 54 (Jan., 1987).  
 Levenspiel, O., *Chemical Reaction Engineering*, 2 ed., Wiley, New York (1972).  
 Randolph, A. D., and M. A. Larson, *Theory of Particulate Processes*, Academic Press, New York (1971).  
 Shapiro, A. H., and A. J. Erickson, "On the Changing Size Spectrum of Particle Clouds Undergoing Evaporation, Combustion, or Acceleration," *ASME Trans.*, 775 (May, 1957).

*Manuscript received Jan. 2, 1988, and revision received Jan. 17, 1989.*