Theoretical Basis for Variable Order Assumption in the Kinetics of Leaching of Discrete Grains

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In a previous article (Dixon and Hendrix, 1992), a model for leaching of solid reactants from porous ore particles was developed based on the unsteady-state diffusion and consumption of a rate-controlling reagent species within spherical ore pellets. These phenomena are described by the partial differential equation:

$$\frac{D_{Ae}}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial C_A}{\partial r}\right]-\frac{\rho k}{b}C_B^{\phi}C_A=\epsilon\frac{\partial C_A}{\partial t}$$

$$\left(\frac{\partial C_A}{\partial r}\right)_{r=0}=0$$

$$C_A(r,\ t=0)=0$$

$$C_A(r=R,\ t)=C_{As} \qquad (1)$$

which is coupled with an ordinary differential equation which describes the disappearance of solid reactant:

$$\frac{dC_B}{dt}=-kC_B^{\phi}C_A$$

$$C_B(t=0)=C_{B0} \qquad (2)$$

If the dissolving solid reactant M is taken to consist of discrete spherical micrograins, then the exponent ϕ assumes a value of 2/3 and Eq. 2 becomes the familiar "shrinking particle" model. However, since these grains are likely to occur over a range of sizes, the question arises of how this will affect the value of ϕ.

Bartlett avoided the question by assuming a log-normal weight distribution of spherical grains which would give a pseudo-first-order response and incorporating the result into his leaching model (Bartlett, 1973). Bartlett's method, while circumventing the problem, is rather limited in its range of application. Thus, it would seem desirable to estimate the effect of grain size distribution on the reaction order *a priori* to judge whether the issue warrants further consideration.

Beginning with a dimensionless version of Eq. 2:

$$\frac{d\sigma}{d\tau}=-\sigma^{\phi}\alpha$$

$$\sigma(\tau=0)=1 \qquad (3)$$

where σ represents the collective mass fraction of grains remaining at time t, α is the dimensionless reagent concentration, and

$$\tau=kC_{B0}^{\phi-1}C_{A0}t$$

the "shrinking-particle model" for each individual grain may be expressed as:

$$\frac{d\gamma}{d\tau'}=-\frac{\gamma^{2/3}\alpha}{\psi}$$

$$\gamma(\tau'=0)=1 \qquad (4)$$

where γ is the mass fraction remaining of the individual grain, ψ is the initial normalized radius of the grain relative to some reference grain radius, and

$$\tau'=\frac{3Mk'C_{A0}}{\bar{R}_g\rho_g}t$$

If a grain weight distribution function $f(\psi)$ is defined such that:

$$\int_{\psi_{\min}}^{\psi_{\max}}f(\psi)d\psi=1 \qquad (5)$$

then the collective mass fraction of solid reactant remaining may be expressed in terms of the individual grains with a volume average over each individual grain size fraction, thus

$$\sigma=\int_{\psi_{\min}}^{\psi_{\max}}f(\psi)\gamma(\psi,\ \tau')d\psi \qquad (6)$$

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Differentiating this equation with respect to time by Leibnitz' rule gives:

$$\frac{d\sigma}{d\tau}=\int_{\psi_{\min}}^{\psi_{\max}} f(\psi)\left[\frac{d\gamma}{d\tau}\right]d\psi \tag{7}$$

Defining $K=\tau'/\tau$, Eq. 4 becomes:

$$\frac{d\gamma}{d\tau}=-\frac{K\gamma^{2/3}\alpha}{\psi} \tag{8}$$

and combining Eqs. 3, 7 and 8 gives:

$$\frac{d\sigma}{d\tau}=-K\alpha\int_{\psi_{\min}}^{\psi_{\max}}\frac{f(\psi)}{\psi}\gamma^{2/3}(\psi,\tau')d\psi=-\sigma^{\phi}\alpha \tag{9}$$

At time $\tau=0$, applying the initial conditions to Eq. 9 one obtains:

$$\left(\frac{d\sigma}{d\tau}\right)_{\tau=0}=-K\alpha\int_{\psi_{\min}}^{\psi_{\max}}\frac{f(\psi)}{\psi}d\psi=-\alpha \tag{10}$$

from which the constant K is recognized as the inverse of the (-1)th ψ-moment distribution:

$$K=\frac{1}{\int_{\psi_{\min}}^{\psi_{\max}}\frac{f(\psi)}{\psi}d\psi} \tag{11}$$

Substituting Eq. 11 into Eq. 9 gives:

$$\frac{d\sigma}{d\tau}=-\frac{\alpha\int_{\psi_{\min}}^{\psi_{\max}}\frac{f(\psi)}{\psi}\gamma^{2/3}(\psi,\tau')d\psi}{\int_{\psi_{\min}}^{\psi_{\max}}\frac{f(\psi)}{\psi}d\psi}=-\sigma^{\phi}\alpha \tag{12}$$

Finally, from Eqs. 6 and 12 the effective reaction order as a function of reaction time is obtained:

$$\phi=\frac{\ln(\sigma^{\phi})}{\ln(\sigma)}=\frac{\ln\left[\int_{\psi_{\min}}^{\psi_{\max}}\frac{f(\psi)}{\psi}\gamma^{2/3}(\psi,\tau')d\psi\right]-\ln\left[\int_{\psi_{\min}}^{\psi_{\max}}\frac{f(\psi)}{\psi}d\psi\right]}{\ln\left[\int_{\psi_{\min}}^{\psi_{\max}}f(\psi)\gamma(\psi,\tau')d\psi\right]} \tag{13}$$

For purposes of discussion, it is assumed that the reagent concentration is constant at $\alpha=1$. This being the case, the exact solution of Eq. 4 is straightforward, giving

$$\gamma(\psi,\tau')=u(\psi,\tau')\left(1-\frac{\tau'}{3\psi}\right)^3 \tag{14}$$

where $u(\psi,\tau')$ is a unit step function such that

$$u(\psi,\tau')=\begin{Bmatrix}1, & \tau'\le 3\psi\\ 0, & \tau'>3\psi\end{Bmatrix}$$

Hence, Eq. 13 becomes:

$$\phi=\frac{\ln\left[\int_{\psi_{\min}}^{\psi_{\max}}\frac{f(\psi)}{\psi}u(\psi,\tau')\left(1-\frac{\tau'}{3\psi}\right)^2 d\psi\right]-\ln\left[\int_{\psi_{\min}}^{\psi_{\max}}\frac{f(\psi)}{\psi}d\psi\right]}{\ln\left[\int_{\psi_{\min}}^{\psi_{\max}}f(\psi)u(\psi,\tau')\left(1-\frac{\tau'}{3\psi}\right)^3 d\psi\right]} \tag{15}$$

While the choice of a distribution function in the absence of experimental data is an arbitrary one, the log-normal distribution (Aitcheson and Brown, 1957) allows easy comparison with the results of Bartlett. In dimensionless form, this function is:

$$f(\psi)=\frac{1}{\sqrt{2\pi}s\psi}\exp\left(-\frac{(\ln\psi)^2}{2s^2}\right) \tag{16}$$

where s = the standard deviation of the distribution. Integrating $f(\psi)$ between the limits $(0\le\psi\le\infty)$ results in a definite integral which satisfies the criterion of Eq. 5:

$$\begin{aligned}\int_{\psi_{\min}}^{\psi_{\max}}f(\psi)d\psi&=\int_0^{\infty}\frac{1}{\sqrt{2\pi}s\psi}\exp\left(-\frac{(\ln\psi)^2}{2s^2}\right)d\psi\\&=\frac{1}{\sqrt{2\pi}s}\int_{-\infty}^{+\infty}\exp\left(-\frac{(\ln\psi)^2}{2s^2}\right)d(\ln\psi)\\&=1\end{aligned} \tag{17}$$

In addition, the log-normal (-1)th ψ-moment distribution is readily solved:

$$\begin{aligned}\int_{\psi_{\min}}^{\psi_{\max}}\frac{f(\psi)}{\psi}d\psi&=\int_0^{\infty}\frac{1}{\sqrt{2\pi}s\psi^2}\exp\left(-\frac{(\ln\psi)^2}{2s^2}\right)d\psi\\&=\exp\left(\frac{s^2}{2}\right)\end{aligned} \tag{18}$$

Hence, the final expression for the reaction order as a function of reaction time is:

$$\phi=\frac{\ln\left[\int_0^{\infty}\frac{1}{\sqrt{2\pi}s\psi^2}\exp\left(-\frac{(\ln\psi)^2}{2s^2}\right)u(\psi,\tau')\left(1-\frac{\tau'}{3\psi}\right)^2 d\psi\right]-\frac{s^2}{2}}{\ln\left[\int_0^{\infty}\frac{1}{\sqrt{2\pi}s\psi}\exp\left(-\frac{(\ln\psi)^2}{2s^2}\right)u(\psi,\tau')\left(1-\frac{\tau'}{3\psi}\right)^3 d\psi\right]} \tag{19}$$

This equation involves only one parameter for its unique solution, the standard deviation, s, of the log-normal distribution. As a result, it is worth noting that the effective reaction order is independent of reagent concentration.

Solutions to Eq. 16 are plotted in Figure 1 for six values of the standard deviation. These values were chosen, after Bartlett, according to the relationship:

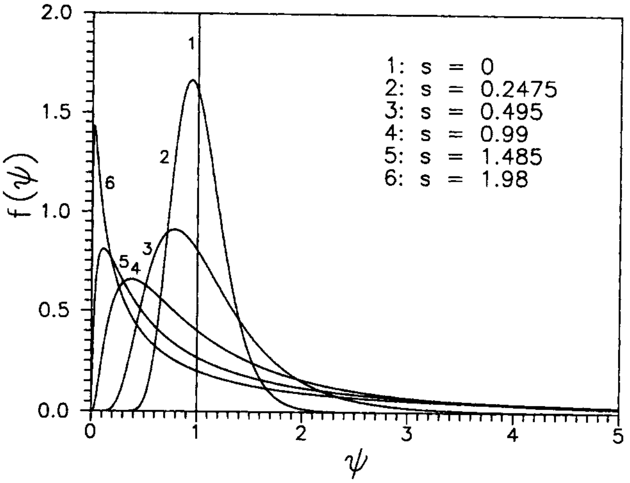

Figure 1. Log-normal distribution function.

Table 1. Properties of the Log-Normal Distributions Represented in Figure 1

Curve	s	$\psi_{0.99}/\psi_{0.01}$	$\psi_{0.01}$	$\psi_{0.99}$
1	0	10^0	1	1
2	0.2475	$10^{1/2}$	0.562	1.78
3	0.495	10^1	0.316	3.16
4	0.99	10^2	0.1	10
5	1.485	10^3	0.0316	31.6
6	1.98	10^4	0.01	100

$$\log\left(\frac{\psi_{0.99}}{\psi_{0.01}}\right)=\frac{2s}{0.99} \tag{20}$$

resulting in the distribution properties summarized in Table 1.

Semilog plots of σ vs. τ according to Eq. 6 for the six values of s are shown in Figure 2. These curves show qualitatively how wider distributions of grain size result in higher apparent orders of reaction. This observation is confirmed quantitatively in Figure 3, where plots of ϕ as calculated by Eq. 19 are plotted as functions of σ. It should be noted that these curves are completely independent of actual time of reaction. The dashed lines represent least-squares zero-order polynomial fits of the ϕ-σ curves to give "average" reaction orders which, as shown in Figure 4, bear a near-perfect quadratic relationship to the standard deviation.

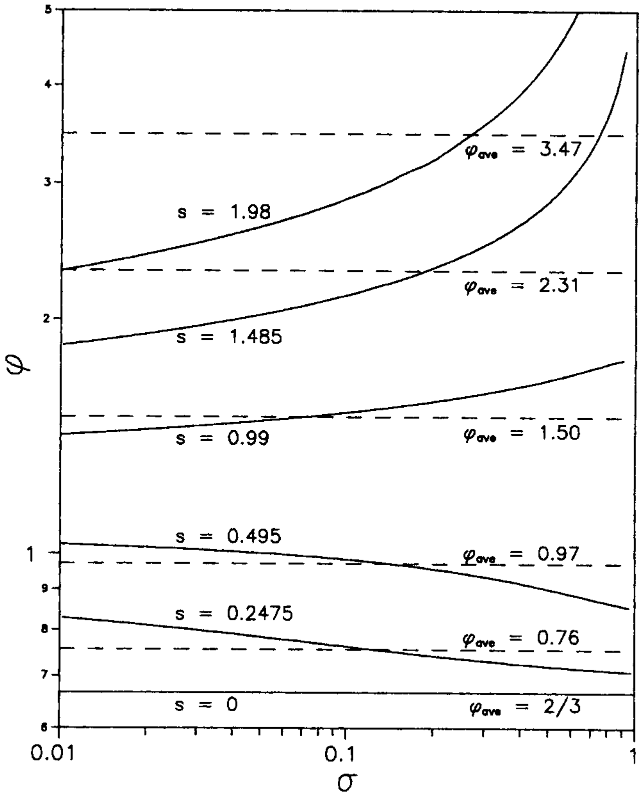

Figure 3. Apparent reaction order (ϕ) vs. collective mass fraction remaining (σ) for various grain weight distributions.

Returning to Figure 3, obviously, the range of ϕ over the course of leaching increases dramatically with increasing s.

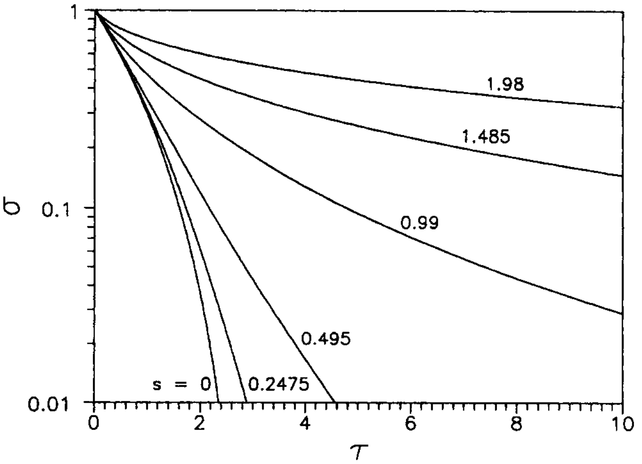

Figure 2. Collective mass fraction remaining (σ) vs. reaction time (τ) for various grain weight distributions.

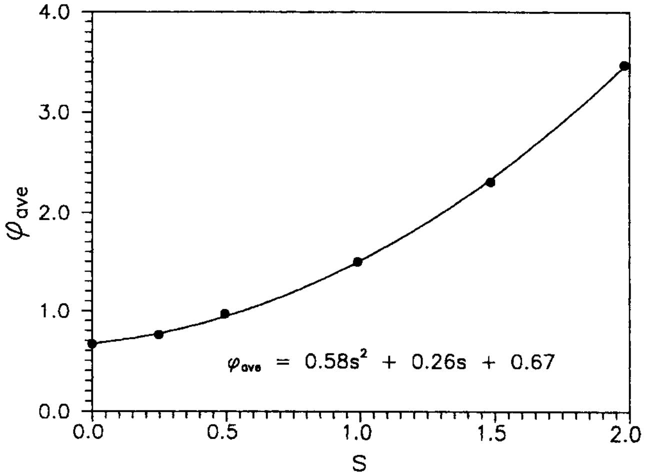

Figure 4. Average apparent reaction order (ϕ_{ave}) vs. the standard deviation of the log-normal grain weight distribution (s).

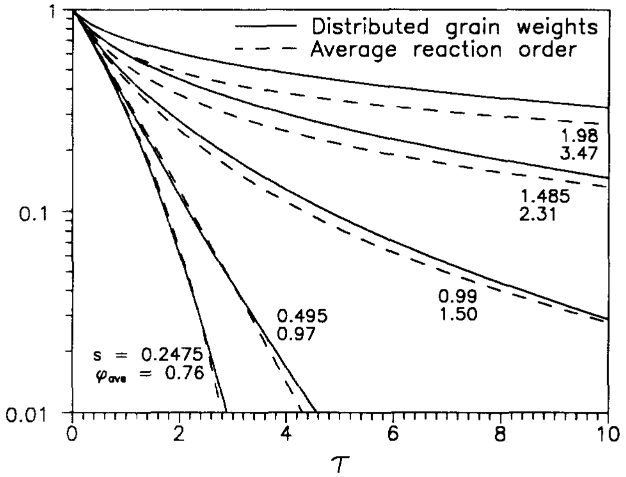

Figure 5. Collective mass fraction remaining (σ) vs. reaction time (τ) as calculated by Eq. 6 (——) and Eq. 3 using ϕ_{ave} (····).

However, as shown in Figure 5, when the values of ϕ_{ave} are used in the solution of Eq. 3, the results (dashed curves) fall surprisingly close to the actual σ-τ curves as calculated by Eq. 6 (solid curves), even at high s values. Thus, one may conclude that the assumption of a single average value for the overall order of reaction in the concentration of solid reactant in Eq. 3 is acceptable over a fairly wide range of grain size distributions. Furthermore, ϕ may possess a wide range of values greater than or equal to 2/3, but not less than 2/3, when the individual reacting grains are discrete and roughly spherical.

Notation

b = stoichiometric factor
C_A = reagent concentration
C_{As} = particle surface reagent concentration
C_B = solid reactant apparent concentration
C_{B0} = initial solid reactant apparent concentration
D_{Ae} = reagent effective diffusivity
$f(\psi)$ = grain weight distribution function
k = solid reactant collective rate constant
k' = solid reactant grainwise rate constant
M = solid reactant atomic weight
r = particle radius
R = external particle radius
$\overline{R}_g$ = reference grain radius
s = standard deviation of the log-normal distribution
t = time
$u(\psi, \tau)$ = unit step function defined in Eq. 14

Greek letters

α = dimensionless reagent concentration
γ = streamwise mass fraction of solid reactant remaining
ϵ = ore porosity
K = weight distribution modulus defined in Eq. 11
ρ = ore density
ρ_g = solid reactant density
σ = collective mass fraction of solid reactant remaining
τ = collective dimensionless reaction time
τ' = grainwise dimensionless reaction time
ϕ = apparent reaction order in the solid reaction apparent concentration
ψ = dimensionless grain radius
$\psi_{0.01}$ = dimensionless grain radius of the 1st percentile particles
$\psi_{0.99}$ = dimensionless grain radius of the 99th percentile particles

Literature Cited

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