Absorption/Desorption Model of Diffusion for Heterogeneous Rate Processes

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In a previous article (Chaiken, 1992), an absorption/desorption (A/D) model of diffusion was introduced to describe leaching processes involving solid particles with heterogeneously distributed porosities. A generalized rate expression for diffusion was derived based upon the concept that there existed a distribution of shortest distances λ along which diffusing species travel at a velocity v_λ, between points of interest within the particles. These shortest distance diffusion paths might be between the particle surface and the interior of the particle or between macroporous and microporous regions of the particles. With this approach and assuming a lognormal distribution of shortest distances $f(\lambda)$ a rate expression was developed for diffusion limited reactions

$$R(t) = f(\lambda) v_\lambda = \frac{h e^{-\left[h \ln\left(\frac{t+t_a}{t_o}\right)\right]^2}}{(t+t_a)\sqrt{\pi}} \tag{1}$$

Here, $t = \lambda / v_\lambda$ is an elapsed time variable which replaces both λ and v_λ as parameters; h is the spread factor of the lognormal distribution (related to variance); $R(t)$ is the rate of reaction with time corrected for preaging; t_o is the time it takes for diffusing species to travel the mean shortest distance λ_o; and t_a is a preaging time constant introduced *ad hoc* to account for reaction that might have occurred prior to the start of an experiment (such as during storage of samples or setup of an experiment). Equation 1 is essentially the same (within a constant normalization factor) as that derived originally, and was used to curve-fit experimental data from several diverse multiphase reaction processes involving leaching and gas desorption. In principle, the t_o parameter relates directly to the system transport properties (such as diffusion coefficient and concentration gradient); therefore, its curve-fitted value should not only correlate with those transport properties, but should also offer physical insight into the reaction mechanism. It is the purpose of this note to demonstrate this for two multiphase reaction systems—a metal ore leaching process, and a gas/solid redox reaction.

Since the original development of the A/D model, an addendum to Eq. 1 has been made to account for monotonic changes in t_o as they might occur during diffusion (Chaiken, 1995). Such changes could arise if, during solids leaching, precipitating salts alter the porosity of the particle (changing v_λ or λ_o), or if during particle absorption of gases, the gas concentration (driving force for diffusion) varies (changing v_λ). These effects can be simulated by arranging t_o to have a suitable time dependency. A two-parameter function is chosen *ad hoc* to impart this time dependency

$$t_o(t) = t'_o(1 + ae^{-b/t}) \tag{2}$$

Equation 2 has the following attributes: it is continuous and single-valued over all time; it has a finite value at time zero; and it approaches a limiting value with increasing time. With appropriate values for the arbitrary constants a and b the exponential term can emulate almost any monotonic change of t_o with time.

Application to Leaching of Pyrite From Chalcopyrite Ore

In Figure 1, Eqs. 1 and 2 are applied to a three-phase leaching system, viz., copper from chalcopyrite ore. The rate

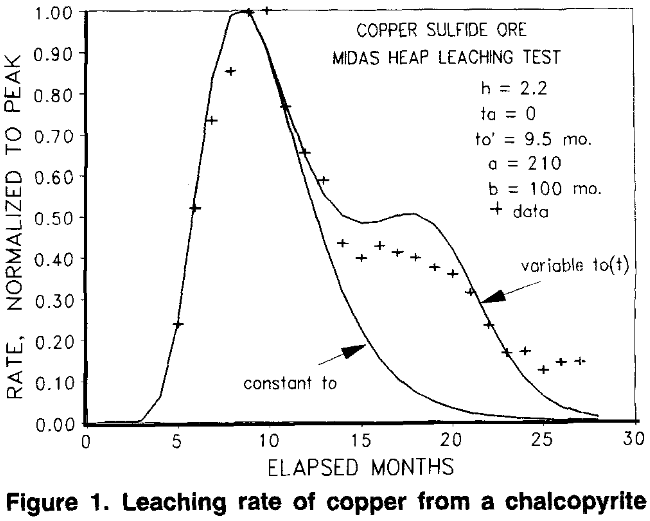

Figure 1. Leaching rate of copper from a chalcopyrite ore.

data refer to a multitonnage heap leaching trial called the MIDAS test (Cathles, 1979). Both the measured and calculated (curve-fit) rates are normalized to their peak (1.8% per month in the MIDAS test) to allow direct comparison between the two. Cathles attributed the multiple peaks in the measured rate data to increasing temperatures—the major first peak occurring at 9 months was due to self-heating by the sulfide oxidation reaction, and the minor second peak occurring at 18 months was due to seasonal temperature effects (i.e., higher summer temperatures). Cathles suggested a rate process that is chemical-controlled during the acceleration phases of the rate curve and diffusion-controlled during the deceleration phases. The A/D model, which yields a reasonably good fit to all the data, suggests that the rate of leaching is entirely diffusion controlled, with the second peak the result of decreasing permeability caused by precipitation of complex metal salts within (intra) the ore particles. Complex iron salts such as jarosite $KFe_3(OH)_6(SO4)_2$ and rhomboclase $Fe(HSO_4)(SO_4)\cdot 4H_2O$ have been identified as solid products in the leaching of copper from sulfide ore tailings (Blowes et al., 1991).

It is interesting to note that Cathles, using a shrinking core model with detailed chemistry (Cathles and Apps, 1975), was also able to obtain a good fit to the data of Figure 1. This indicates once more that goodness-of-fit to experimental rates does not necessarily make for a "correct" reaction mechanism. However, from a practical point of view, knowing the actual mechanism(s) controlling a leaching reaction could make a difference in designing and operating a reactor for optimum metal recovery.

Application to Nickel Oxide Reduction

An absorption process that reflects on how t_o varies with concentration of diffusing species is the two-phase gas/solid reaction involving the reduction of porous pellets of nickel oxide by carbon monoxide

$$\mathrm{NiO(solid)} + \mathrm{CO(gas)} = \mathrm{CO_2(gas)} + \mathrm{Ni(solid)} \qquad (3)$$

From the experimental and theoretical work of Krasuk and Smith (1972), and Ramachandran and Smith (1977), the reaction given by Eq. 3 is believed to be controlled by intraparticle diffusion; hence, Eqs. 1 and 2 should be applicable. The experimental data points shown in Figure 2 represent the fractional extent of reaction vs. time for four different mole fractions of carbon monoxide, $X_{CO} = 0.113$ to 0.333, surrounding the particle, and which remained essentially constant during the course of reaction. The continuous curves in Figure 2 are computed from Eq. 1 (i.e., with time independent t_o) integrated over time, and normalized to account for an extent of fractional NiO prereaction (0.002 to 0.052) due to preaging. Four different values of the t_o parameter were found to correspond with the four different values of X_{CO}, with the other parameter values ($h = 0.85$ and $t_a = 700$ s being kept the same. From the description of the experiment, there is no clear-cut reason for a nonzero t_a, although lengthy preparations were carried out prior to the start of the experimental time zero—including high-temperature sintering of pellets. During these preparations, a small amount of prereaction may have occurred.

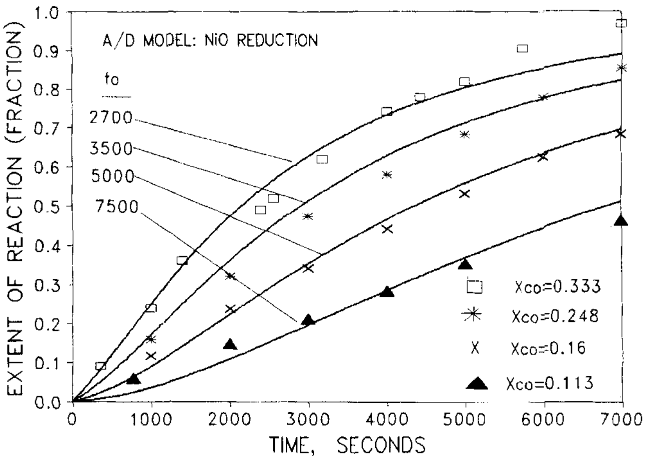

Figure 2. Reduction of NiO pellets by carbon dioxide at various mole fractions of CO.

The excellent curve-fits to the data (Figure 2) supports the validity of the A/D model as well as the choice of a lognormal distribution function for $f(\lambda)$. Alternatively, these curve-fits might be interpreted simply as an example of the versatility of lognormal functions to accommodate curve-fitting. However in this case, the effect of varying X_{CO} (i.e., the driving force for diffusion of CO) should reflect directly on the applicable value of v_λ and hence t_o for each of the X_{CO} values. The parameter λ_o, being a material property of the NiO particles, would be expected to be independent of X_{CO}. In Fickian flow, the diffusive flux is linearly proportional to the concentration gradient, or in this case, to the value of X_{CO}. Likewise, v_λ should also be directly proportional to X_{CO}. With λ_o expected to have the same value for each of the four cases depicted in Figure 2, the product of t_o and X_{CO} should be same for each case, i.e.,

$$t_o X_{CO} = \text{constant} \qquad (3)$$

or

$$\frac{t_o}{t_o^*} = \frac{X_{CO}^*}{X_{CO}} \qquad (4)$$

Evaluating the constant at $t_o^* = 3{,}500$, $X_{CO}^* = 0.248$, allows a test of the interpretation of t_o and Eq. 3. Figure 3 depicts a plot of the ratio ($0.248/X_{CO}$) vs. the ratio ($t_o/3{,}500$) using the curve-fit parameters of Figure 2. Ideally this plot should fall on a straight line of slope = 1. It is readily seen that the ideal line is closely followed by the plotted points, thereby, supporting the above interpretation of t_o as a combined material property and mass-transport coefficient. It also suggests experimental approaches for evaluating the curve-fit parameters.

Conclusion

From a curve-fitting perspective, the A/D model with a lognormal distribution of shortest path distances, and a time-dependent t_o parameter, serves well to correlate experimental data on two-phase and three-phase reaction processes

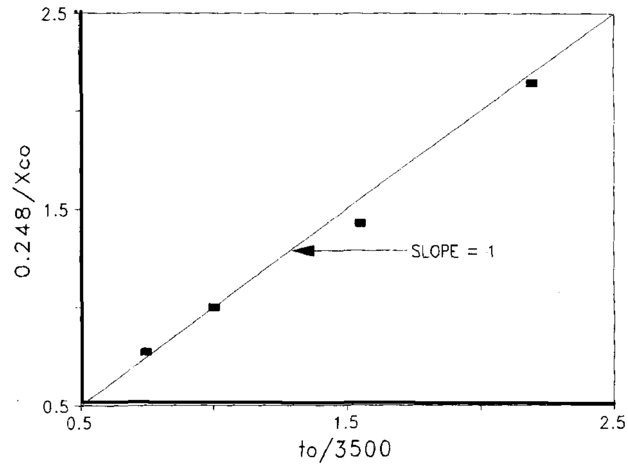

Figure 3. Test of Eq. 9: variation of A/D model time parameter with CO mole fraction from data on NiO reduction.

that are believed to be diffusion-limited. However, as implied above in connection with the chalcopyrite ore leaching experiment, good correlation does not prove a model to be unique or even correct, and this is certainly true in the case of the A/D model, which is heuristic in its approach to treating heterogeneity of material properties. On the other hand, the A/D model is based on physical concepts and employs curve-fit parameters whose values reflect specific material properties, such as diffusivity, permeability, reactant concentration, and so on, which determine the rate of the diffusion process. It still remains to define these parameters in a way that will be predictive before the fact, in addition to being explanative after the fact.

The apparent good correlation between CO concentration and t_o in the case of the NiO experiment suggests an approach that could be pursued where applicable. For example, if the redox reaction were carried out at constant X_{CO}, but with pellets having varying degrees of heterogeneous porosity, the different values observed for the curve-fit t_o parameter would relate solely to the value of λ_o which along with the h parameter defines the appropriate statistical distribution of λ (the degree of heterogeneity) as it reflects on the diffusion process. It is anticipated that future correlations of experimental data by the A/D model will continue to lend support to the model, as well as demonstrate how the pertinent model parameters can be determined and predicted.

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Literature Cited

Blowes, D. W., E. J. Reardon, J. L. Jambor, and J. A. Cherry, "The Formation and Potential Importance of Cemented Layers in Inactive Sulfide Mine Tailings," *Geochim. Cosmochim. Acta*, **55**, 965 (1991).

Cathles, L. M., "Predictive Capabilities of a Finite Difference Model of Copper Leaching in Low Grade Industrial Sulfide Waste Dumps," *Math. Geology*, **11**, 175 (1979).

Cathles, L. M., and J. A. Apps, "A Model of the Dump Leaching Process that Incorporates Oxygen Balance, Heat Balance, and Air Convection," *Metall. Trans.*, **6B**, 617 (1975).

Chaiken, R. F., "An Absorption/Desorption Model of Solids Leaching," *Geochim. Cosmochim. Acta*, **56**, 2589 (1992).

Chaiken, R. F., "Diffusion of Cu^{2+} in Calcium Alginate Gel Beads: Further Analyses," *Biotechnol. Bioeng.*, **45**, 454 (1995).

Krasuk, J. H., and J. M. Smith, "Kinetics of Reduction of Nickel Oxide with CO," *AIChE J.*, **18**, 506 (1972).

Ramachandran, P. A., and J. M. Smith, "A Single-Pore Model for Gas-Solid Noncatalytic Reactions," *AIChE J.*, **23**, 353 (1977).

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