DIFFUSIVE UPTAKE OF FLUIDS BY COAL PARTICLES -- EFFECTS OF PARTICLE SHAPE AND PARTICLE SIZE DISTRIBUTION

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INTRODUCTION

Diffusion into coals is of considerable technological importance since many coal modification processes, such as direct liquefaction, desulfurization, demineralization, and chemical modification, involve diffusion of liquids or gasses into the coal. Additionally, much of the fundamental chemical research on coals requires diffusion of liquids or dissolved reagents into the coal so that reactions can occur. Precise interpretation of these experiments often requires an understanding of the diffusional behavior. The rate that reactants diffuse into the particles is often a rate-limiting step. The variety of shapes and sizes of particles in the coal slurry greatly complicates the overall diffusion kinetics, and unless this heterogeneity is properly taken into account it can lead to erroneous analyses of the process. There is information in the literature on the diffusive uptake of fluids by differently shaped single particles for various concentration-dependent diffusion coefficients (1), and there is some literature on diffusion into coals (2,3). However, no information concerning the effect of the particle size distribution on the diffusive uptake of coals in a slurry is available. The objective of this paper is to determine the range of diffusive uptake behaviors which can result from the different particle shapes and the particle size distribution.

Coal samples are commonly prepared by breaking down the coal until it is below a selected mesh size. This procedure results in a wide distribution of particle sizes. Sometimes mesh cuts of the coal are taken in which only that coal which passes through a selected larger mesh size, but not through a selected smaller mesh size, is utilized. This reduces the breadth of the size distribution, but even in the limit of an infinitely narrow mesh cut there will still be considerable variations in the diffusive uptake of the various particles due to the wide range of shapes that result from the breakdown or fracture process, and also due to the cracks and heterogeneity of the coal's microstructure.

To assess the effects of the different particle shapes and of the particle size distribution, we adopted the following strategy. First, since typical distributions of particle shapes present in coal samples are unknown, to determine the range of diffusive uptake behavior caused by having different particle shapes in the slurry, we calculate diffusive uptakes for both slab-shaped particles (with infinite height-to-width ratios) and spherical particles. Most other particle shapes can be considered to be intermediate between these two shapes, so their uptakes can be expected to fall in between these two extreme cases. Thus, these pairs of uptake calculations bracket the range of diffusive uptakes for most particle shapes, and therefore bracket the uptakes for most distributions of particle shapes.

To determine the effects of the distribution of particle sizes, for each particle shape (slab or sphere) we calculate the diffusive uptakes of both a single particle and a slurry of differently sized particles with that shape. The particle size distribution used was obtained from an experimental study of ball milling of coal by P. Luckie, et al. at Pennsylvania State University (4), so the distribution is relevent to actual coal slurries. While these investigators found that there were some variations in the measured particle size distribution depending on the experimental conditions, a typical distribution is approximated by

(1) $$W(R) = 1 \text{ for } 0 \leq R \leq R_0$$
$$= 0 \text{ for } R > R_0 \quad ,$$

where W(R)dR is the weight fraction (or volume fraction) of particles whose size R is between R and R + dR. R_0, of course, gives the upper limit on the sizes of the particles. For spherical particles R is the particle radius. For slab-shaped particles, R is the half-thickness of the particle. The particle size distribution given by Eq. 1 is the distribution we use for all slurry calculations in this paper.

Besides the variations in particle shapes and sizes, there are a number of other factors which complicate diffusion in coal. These factors include the cracks and holes through the coal, the variety of macerals having different chemical and physical properties which make up the coal, the heterogeneity of the structure even within individual macerals, and the effects of intermaceral interfaces and mineral matter (5). These heterogeneities of the coal structures will not be explicitly treated in this paper, but they may cause substantial deviations from the usual diffusional behavior. The effects of particle shape and particle size distributions which are treated here should give a qualitative indication of the sorts of deviations which might result from these heterogeneities.

FORMULATION OF THE MODELS

In this section the diffusion models being considered are discussed briefly, and the mathematics describing the models is formulated. Two distinct modes of diffusion are treated, Fickian diffusion (6) and Case II diffusion (7). Fickian diffusion is the common form of diffusion in which the rate of flow of the penetrant is related to the concentration gradient by a proportionality factor, D(c), which is called the diffusion coefficient. For Fickian diffusion, the concentration c(t,x) of the penetrant within a particle obeys the following equation:

(2) $$\frac{\partial c}{\partial t} = \vec{\nabla} \cdot D(c) \vec{\nabla} c$$

For Fickian diffusion, D is either a constant or is an explicit function of the concentration c. Diffusion coefficients which are non-decreasing functions of concentration can be expected for the diffusion of most penetrants into coal, so only these are considered in this paper.

We impose the boundary and initial conditions

(3.1) $c = c^*$ at the particle's surface
(3.2) $c = 0$ at time t = 0 within the particle.

Here the (fixed) concentration c* is the concentration of penetrant within the coal particle which would be in equilibrium with the concentration of penetrant in the solution; i.e., c* is the saturation concentration of the penetrant within the coal. By using Eq. 3.1, we are assuming that the external surface of the particle is in equilibrium with the solution. By taking c* to be constant in time, we are assuming that the slurry is well-stirred and that the depletion of the penetrant in the solution is negligible. (Maintaining the proper boundary conditions in experiments we wish to interpret is crucial. For example, a frequent experimental procedure is to allow a penetrant to diffuse from a liquid resevoir through an inert gas to reach the particles. However, this procedure generally will not maintain the boundary condition (Eq. 3.1) sufficiently accurately, which may greatly perturb the results). The initial condition, Eq. 3.2 simply states that the particles contain no penetrant at the start of the experiment. Once the penetrant concentration c(t,x) within a particle has been determined from Eqs. 2, 3.1 and 3.2, the particle's uptake of penetrant at time t, m(t), is found by integrating over the particle's volume:

(4) $$m(t) = \iiint c(t,\vec{x})dV.$$

For the conditions of Eqs. 3, the uptake will be proportional to $\sqrt{t}$ for a semi-infinite medium so for any reasonably shaped particle it will be proportional to $\sqrt{t}$ at small enough times.

There is an important class of problems which do not involve pure diffusion, but which are also governed by Eqs. 2-4. If a substance undergoes both Fickian diffusion and chemical reaction within the particles, and if the reaction proceeds much more rapidly than the diffusion (so diffusion is the rate-limiting step), then the diffusive uptake of the substance by a particle is again given by Eqs. 2-4.

Among all non-decreasing diffusion coefficients D(c), there are two cases which represent extremes in the concentration dependence. One extreme case is simply a constant diffusion coefficient

$$D(c) = D_0 \quad \text{for all } c. \tag{5.1}$$

The other extreme case is found by considering a diffusion coefficient which is zero up to nearly the saturation concentration c*, but just short of this concentration the coefficient jumps to a large value and remains fixed until saturation. Mathematically, this diffusion coefficient is

$$\begin{aligned} D(c) &= 0 \quad \text{for } c \ll c^* - \varepsilon \\ &= \frac{A}{\varepsilon} \quad \text{for } c^* - \varepsilon < c \ll c^* \quad , \end{aligned} \tag{5.2}$$

where A is a constant, and $\varepsilon/c^* << 1$. This second extreme case is obtained by letting ε become arbitrarily small and thereby take the limit as $\varepsilon \to 0$.

We assert that the normalized uptake curve m(t) for any non-decreasing diffusion coefficient D(c) always lies in between the normalized uptake curves calculated for the two extreme cases given by Eq. 5.1 and Eq. 5.2 (in the limit of $\varepsilon \to 0$). (The normalization of the uptake curves is discussed in the next section.) Thus, the uptake curves calculated using the two extreme diffusion coefficients bracket the range of uptake curves for all non-decreasing diffusion coefficients D(c). We have tested this assertion with a very large number of different concentration dependent diffusion coefficients including, for example, diffusion coefficients which increase exponentially with concentration. In all cases the uptake curves remained between the two extremes. As we shall see, for slurry systems these two extreme cases yield normalized uptake curves which lie surprisingly close together. So the curves for all non-decreasing diffusion coefficients lie close together.

Case II diffusion is distinctly different from Fickian diffusion and cannot be described by similar equations. In Case II diffusion there is a sharp penetration front that propagates into the matrix material at a constant velocity, so the initial uptake of penetrant is linear in time. Ahead of the front the concentration is nearly zero, and behind the front the concentration is nearly constant. Then for Case II diffusion, the concentration c(t,x) of penetrant at position $\vec{x}$ in a particle is given by

$$\begin{aligned} c(t,x) &= c^* \text{ if } s \ll vt \\ &= 0 \text{ if } s > vt \ , \end{aligned} \tag{6}$$

where s is the distance from the point $\vec{x}$ to the particle's surface, and v is the velocity of the penetration front. Case II diffusion often occurs where the absorption of the penetrant results in a transition of the matrix material from a plastic to a rubbery or viscous state. Since some liquids are known to transform some coals from a plastic to a rubbery state (8,9), Case II diffusion or behavior intermediate between Case II and Fickian diffusion is a possibility for coals.

One of the most common and easiest methods of characterizing the diffusional behavior of a system is to expose the material to the fluid at t = 0, and to monitor the uptake as a function of time. This is the approach taken in this study. For this approach there are two aspects of these diffusional systems

that we are particularly interested in: (1) given the uptake behavior, what can be learned about the diffusion coefficient D(c); and (2) how well can the uptake be predicted without having detailed knowledge of the diffusion coefficient. To address these issues, the uptakes were calculated for the systems that were described above.

The uptakes were calculated from Eqs. 1-6 using numerical methods on a digital computer. The method used was the Crank-Nicolson scheme (10). The resuts were calculated to an accuracy of better than 0.1%, so any residual deviations from the exact results would not be observable in the figures.

METHOD OF PRESENTATION OF DATA

Results for each of the models with the conditions discussed in the Formulation Section are presented in this paper in graphical form. A few words are needed to describe the mode of presentation of the graphical data. The approach taken in this study is that the experimenter does not know anything a priori about the diffusive behavior of his system; rather he measures the penetrant uptake as a function of time and then attempts to determine such characteristics as the type of diffusion (e.g. Fickian, or Case II, or an intermediate behavior), and the concentration dependence of the diffusion coefficient. Our procedure, then, is to compute theoretical curves based on various models to which the experimenter can compare his data and attempt to determine the diffusive character of his system. The data computed for the different hypothetical models are conveniently displayed as normalized graphs or curves. The vertical axis measures the fraction of penetrant taken up by the medium, where 1.0 is the maximum value which occurs at saturation (i.e., equilibrium). The horizontal axis is the time axis. For Fickian diffusion having the boundary condition of constant concentration of penetrant at the fluid-solid interface, the uptake curve for any reasonably shaped particle will be proportional to $\sqrt{t}$ at small enough times. Since a linear curve (initially) is easy to evaluate visually, the time axis in the figures is scaled as $\sqrt{t}$. What remains is to scale the absolute magnitude of time along the time axis. We have found that a convenient criterion is to match the slopes of the various curves in a figure at zero time. Then the curves start off together and it is easy to observe how they deviate from the original slopes as time progresses. For the single particle data for Fickian diffusion, the scaling of the system is arbitrarily chosen to produce initial slopes of 45°. The uptake curves produced by plotting fractional uptake versus the square root of time, where the initial slopes are scaled to be 45°, will be referred to as "normalized uptake curves".

RESULTS

Fickian Diffusion

a. Fickian diffusion in a single slab-shaped particle

Figure 1 shows the normalized uptake curves for Fickian diffusion in a slab, for a constant diffusion coefficient and for the diffusion coefficient defined in Eqs. 5.2. (Recall that the normalized uptake curve for any non-decreasing diffusion coefficient lies in between these two curves). The lower curve is for the constant diffusion coefficient and the upper curve is for the coefficient which is zero except for concentrations very near saturation. The curves are straight and virtually indistinguishable up to an uptake of roughly 0.6. This behavior is not surprising since it is well known that for Fickian diffusion in a semi-infinite medium with the boundary condition described in Eq. 3.1, the curves would be straight for all time for any concentration dependence of the diffusion coefficient. A deviation from the straight line can only occur when there is an appreciable overlap of fluid diffusing in from one side of the slab with fluid which diffused in through the other side. That is, only when the fluid achieves an appreciable concentration at the center plane of the slab do differences occur between the finite thickness slab and a semi-infinite slab.

The diffusional behavior for the diffusion coefficient defined by Eqs. 5.2 is readily pictured physically. Since for this diffusion coefficient there can be no diffusion unless the fluid concentration is essentially at saturation, the fluid propagates into the medium as a sharp front with concentration zero ahead of the front, and it is essentially at its saturation value behind the front. The front propagates with a decreasing velocity which is proportional to $1/\sqrt{t}$. Only when the fronts propagating in from opposite sides of the slab meet, does the system recognize that the slab is not semi-infinite. Since Fickian uptake curves for non decreasing diffusion coefficients always remain concave towards the $\sqrt{t}$ axis (11), it is clear that the diffusion coefficient of Eqs. 5.2, which maintains the 45° straight line all the way to saturation gives an upper bound to the cummulative uptake at any time.

b. Fickian diffusion in a single spherical particle

In Figure 2, the same two diffusion coefficients used in Figure 1 are again utilized, but this time for a spherical particle. In addition, an intermediate concentration dependence is included -- the exponential concentration dependence $D(c) = e^{2c}$. The exponential diffusion coefficient gives the intermediate curve in Figure 2, which illustrates our general finding that the normalized uptake curve for any diffusion coefficient (that is non-decreasing with concentration) always lies in between the normalized uptake curves obtained from the extreme diffusion coefficients in Eq. 5.1 and Eqs. 5.2. For spherical particles the difference in the normalized uptake curves for the two diffusion coefficients which give the upper and lower bounds is much less evident than for the slab case. In fact, unless an experimental uptake curve had a very high accuracy, it would be difficult to determine whether the observed behaviour was produced by the most strongly concentration dependent diffusion coefficient possible (the upper curve) or by a constant diffusion coefficient (the lower curve), much less some intermediate concentration dependence.

It is seen in Figure 2, that the uptake curves depart from the initial straight line much earlier than for the slab. The deviation from the straight line by the upper curve, for which the penetrant propagates into the material as a sharp front, is caused by the smaller and smaller area of the surface defined by the front as it propagates towards the center of the sphere.

c. Fickian diffusion in a slurry of slab-shaped particles

Figure 3 shows the effect of the particle size distribution on the uptake behavior of slab-shaped particles. The curves in this slurry graph are scaled such that if all of the volume of the sample was used in making up particles of the same size as the largest particle in this distribution, then the curves would start out at 45° on this plot. Of course the presence of the smaller particles in the distribution results in a larger surface area than if the same volume resided in larger particles, so the initial slope for the slurry is considerably greater than 45°.

The top and bottom curves in Figure 3 are for the same diffusion coefficients as in Figure 1. It is immediately obvious by comparing Figures 1 and 3 that the particle size distribution dramatically changes the behavior of the normalized uptake curves. For example, for this slurry of slab-shaped particles there is significantly less difference between the uptake curves for the two extreme concentration dependencies shown than for the single particle case. In fact, the curves for the slurry of slab-like particles in Figure 3 are significantly closer together than the curves for the single spherical particle in Figure 2.

It is seen that the uptake curves in Figure 3 fall well below the initial slope at a much lower uptake value than even for the single spherical particle case. Qualitatively the reason for this early deviation is clear. The smaller particles in the distribution approach saturation quickly and then contribute little to the uptake. The close correspondence of the two curves at all times and the

dramatic differences between the curve shapes in Figures 1 and 3 suggest that the particle size distribution is the dominant factor in the uptake behavior.

d. Fickian diffusion in a slurry of spherical particles

Figure 4 presents slurry data for spherical particles calculated using the diffusion coefficients described previously. This figure should be compared with the single spherical particle curves of Figure 2. The uptake curves in Figure 4 lie very close together, even though the curves represent the two extreme cases of concentration dependence for (monotonically increasing) Fickian diffusion coefficients. It is clear from these results that for the sort of particle distribution used, it is extremely difficult, if not impossible, to get reliable concentration dependence information for the diffusion coefficient from the shape of the uptake curve.

Case II Diffusion and Comparison with Fickian Diffusion

As described previously, Case II diffusion exhibits behavior which is fundamentally different from Fickian diffusion, regardless of the concentration dependence of the Fickian diffusion coefficient. Case II diffusion is easy to visualize since it involves the propagation of a sharp front into the medium, with zero concentration ahead of the front and saturation behind the front. In this respect it is similar to the Fickian diffusion described by Eqs. 5.2, and discussed previously. However, physically and mathematically these two modes of diffusion are fundamentally different. For example, whereas (regardless of the concentration dependence) a Fickian front propagates into a semi-infinite medium at a velocity proportional to $1/\sqrt{t}$ (assuming the usual fixed concentration of penetrant at the surface), the Case II front propagates at a constant velocity.

a. Case II diffusion in a single slab-shaped particle

Figure 5 shows the penetrant uptake curve for Case II diffusion in a single slab-like particle. In this figure the Case II diffusion is compared to the two extremes of Fickian diffusion previously shown in Figure 1. The curve which starts off lowest in Figure 5 is from Case II diffusion, the other two curves are identical to the ones in Figure 1. The Case II uptake curve can not be conveniently normalized to a initial slope of 45° on this graph because of its initial linear-in-t time dependence. Therefore, the Case II curves were normalized in a different manner. In all of the remaining figures, the Case II curve is scaled along the square-root-of-t horizontal axis by requiring that the area under its curve be equal to the area under the curve for the constant Fickian diffusion coefficient. The dramatic difference in behavior between Case II diffusion and Fickian diffusion for any monotonically increasing concentration dependence is obvious from Figure 5. Presumably uptake curves for Fickian diffusion coefficients having any concentration dependence which is a non-decreasing function of concentration will fall between the two Fickian curves in Figure 5, whereas the Case II curve is far out of this range. While the Case II curve appears to be highly curved in this $\sqrt{t}$ plot, actually the Case II curve would be a straight line if the graph utilized a linear-in-t horizontal axis.

b. Case II diffusion in a slurry of slab-shaped particles

Figure 6 shows the uptake curve for Case II diffusion for a slurry of slab-like particles. The particle size distribution is given by Eqs. 1. The corresponding Fickian uptake curves for this particle shape and particle size distribution, which were shown in Figure 3, are displayed in Figure 6 for comparison. It is seen that there is slightly closer correspondence between the Fickian and Case II curves for the slurry than in Figure 5 for the individual particles, but the curves are still quite different. Comparing the Case II curve for the individual slab of Figure 5 with the Case II curve for the slurry of Figure

6, it is seen that in the region up to an uptake of about 0.8 the curve in Figure 6 has much less curvature than in Figure 5. In fact, over more than half of the entire uptake curve, from below 0.2 up to nearly 0.8, the Case II uptake curve in Figure 6 is very nearly straight. This is surprising since with our boundary conditions a straight line plot of uptake versus square root of time is commonly taken as the signature of Fickian diffusion. To add to the confusion, the Fickian curves in Figure 6 have much more curvature than the Case II curve. So, if the very early time curvature of the Case II curve were neglected (for example, there are frequently experimental difficulties or uncertainties at small times), it is possible that an experimenter would misinterpret the Case II curve as signifying Fickian diffusion, and would misinterpret the Fickian curves as signifing a non-Fickian type of diffusion. Recall also that the particle size distribution used for these calculations is not an arbitrary one, but is a fit to an experimentally derived curve from the ball milling of a coal. Therefore, it is crucial that an experimenter understand the effective particle size distribution of his sample before attempting to interpret diffusional data from uptake curves. A particle's effective size will be affected by the exact shape of the particle, and in fact, the effective particle size may be quite different from the particle's geometrical size. This distinction can be especially important for heterogeneous, crack-containing, and porous materials, such as coals, for which the geometrical surface and the region rapidly penetrated by fluids may differ substantially (5).

The change in shape of the Case II uptake curve for the slurry in Figure 6, as compared to the single particle uptake in Figure 5, is caused by the saturation of the smaller particles so that they no longer contribute to fluid uptake.

c. Case II diffusion in a single spherical particle

Figure 7 shows the Case II uptake curve for a single spherical particle. Also shown on the graph are the Fickian uptake curves for the corresponding system. The Case II uptake curve for the sphere differs from the linear-in-time behavior for the slab, because as the diffusion front propagates into the sphere towards the center, the position of the front describes a smaller and smaller sphere. It is noteworthy that for the single spherical particle, the Case II uptake curve has a long, relatively straight region from about 0.2 to 0.8 on the square-root-of-time plot. This is a longer (approximately) straight region than for the corresponding Fickian curves. Of course, the large curvature in the region below an uptake of 0.2 gives away the non-Fickian behavior of the Case II curve for this system.

d. Case II diffusion in a slurry of spherical particles

Figure 8 shows the uptake curve for Case II diffusion in a slurry of spherical particles whose size distribution is again given by Eqs. 1. The Fickian curves for the corresponding systems (i.e. Figure 4) are also shown. What is remarkable about this Case II curve is that it is nearly straight all the way from an uptake of about 0.05 to 0.7 uptake. If the particle size distribution was not taken into consideration one could very easily conclude (mistakenly) that this uptake curve is the result of Fickian diffusion.

It is clear from the above results that for slurry systems it is very difficult to determine the concentration dependence of the diffusion coefficient, or even the type of diffusion, from the usual continuous fluid uptake curve. If concentration dependent diffusional information is desired for a system, more effective, though less convenient, methods must be used, such as equilibrating the sample at various concentrations and making differential uptake measurements.

CONCLUSIONS

This study has shown that the fluid uptake behavior of particles in slurries can differ drastically from the uptake behavior of individual particles. Therefore, fluid uptake profiles for single particles must not be utilized to

interpret diffusional data on slurries without taking into consideration the particle size distribution. For a particle size distribution produced by the ball mill grinding of coal, it was found that the effect on the penetrant uptake was sufficiently severe that the initial uptake rate for Fickian diffusion was highly non-linear on a square-root-of-time plot. However, surprisingly, with this same particle size distribution, Case II diffusion gave a nearly linear graph on a square-root-of-time plot. So Case II diffusion might easily be mistaken for Fickian diffusion for this system. Thus faulty analysis of the diffusional system can readily occur.

This study also brought to light an unexpected similarity in the shape of fluid uptake curves for diffusion coefficients having drastically different concentration dependencies. For a coal slurry having a typical particle size distribution, the fluid uptake profiles for diffusion coefficients having extremes in concentration dependence are quite similar for slab-shaped particles, and for spherical particles the curve shapes are almost indistinguishable. These results show that the concentration dependence of diffusion coefficients can not be readily determined for slurry systems using continuous fluid uptake measurements. Other less convenient methods must be used, such as differential uptake measurements.

For coals and other micro-heterogeneous and micro-cracked materials, the problem of determining diffusional behavior is particularly complex because the external surface geometry may not satisfactorily indicate the rate of penetration of the fluid into the particles. In coal, for example, the uptake of fluid through holes, cracks, along maceral interfaces and along regions of mineral matter may contribute substantially to the diffusion process. In addition, the various macerals or microcomponents of the coal will have different diffusional characteristics. Even within the vitrinite classification different pieces of material may exhibit substantially different diffusion characteristics.

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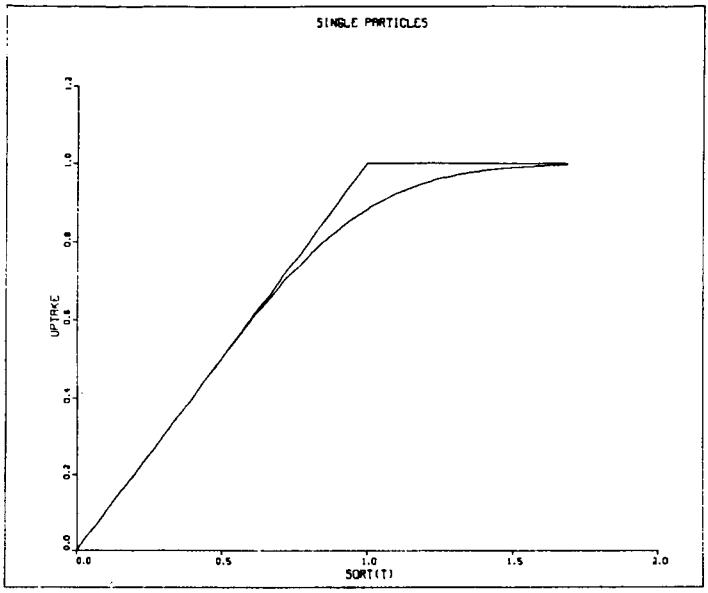

Figure 1. Solvent uptake for a single slab-shaped particle
a) Lower curve is for constant diffusion coefficient (concentration independent)
b) Upper curve is for extreme concentration dependent Fickian diffusion

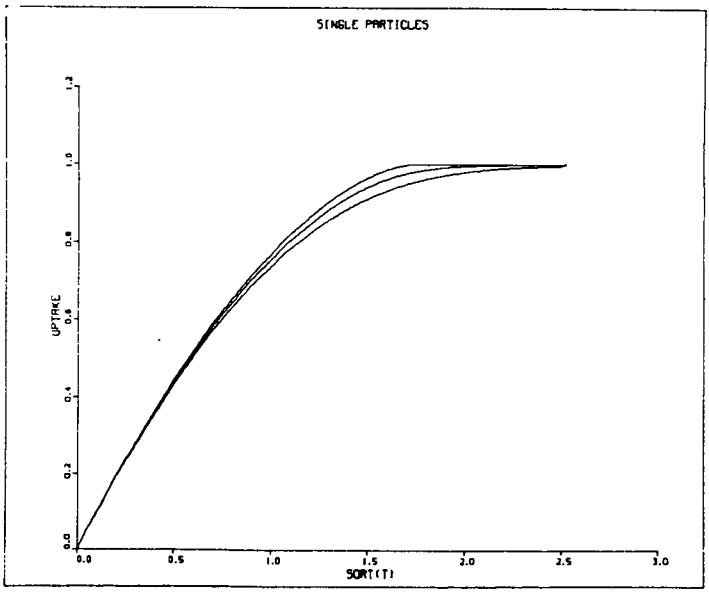

Figure 2. Solvent uptake for a single spherical particle
a) Lower curve is for constant diffusion coefficient (concentration independent)
b) Middle curve is for exponentially concentration dependent diffusion coefficient
c) Upper curve is for extreme concentration dependent Fickian diffusion

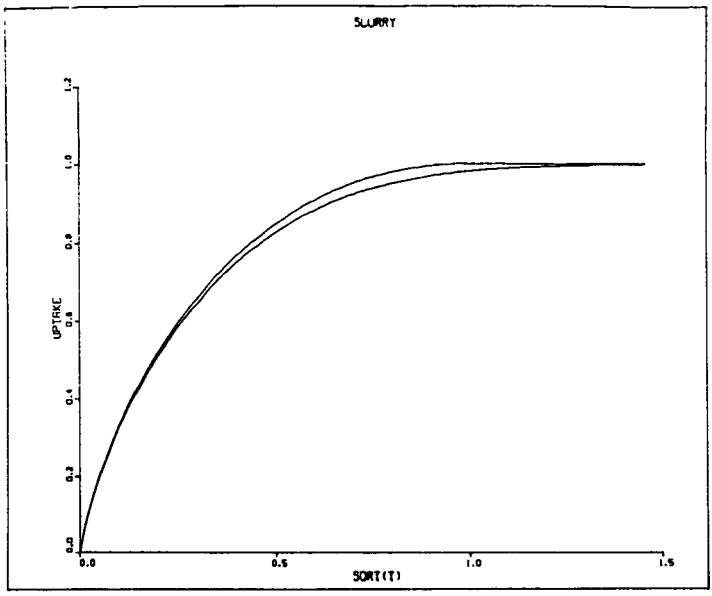

Figure 3. Solvent uptake for a slurry of slab-shaped particles

a) Lower curve is for constant diffusion coefficient (concentration independent)

b) Upper curve is for extreme concentration dependent Fickian diffusion

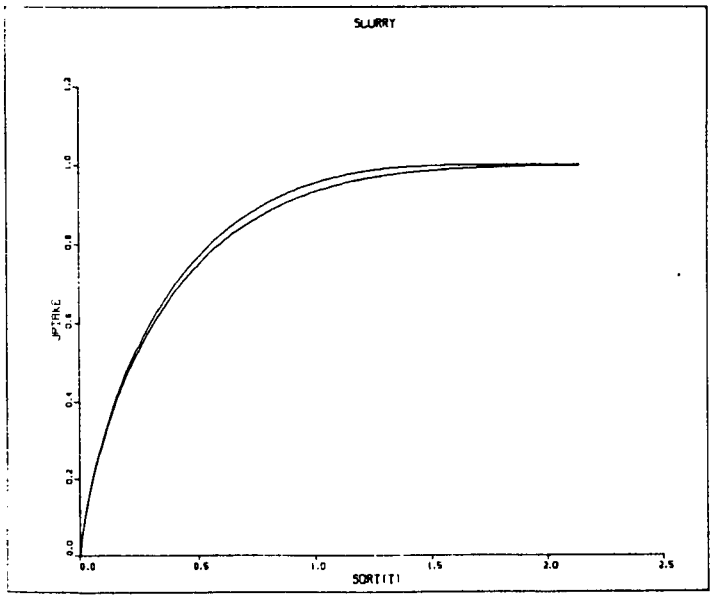

Figure 4. Solvent uptake for a slurry of spherical particles

a) Lower curve is for constant diffusion coefficient (concentration independent)

b) Upper curve is for extreme concentration dependent Fickian diffusion

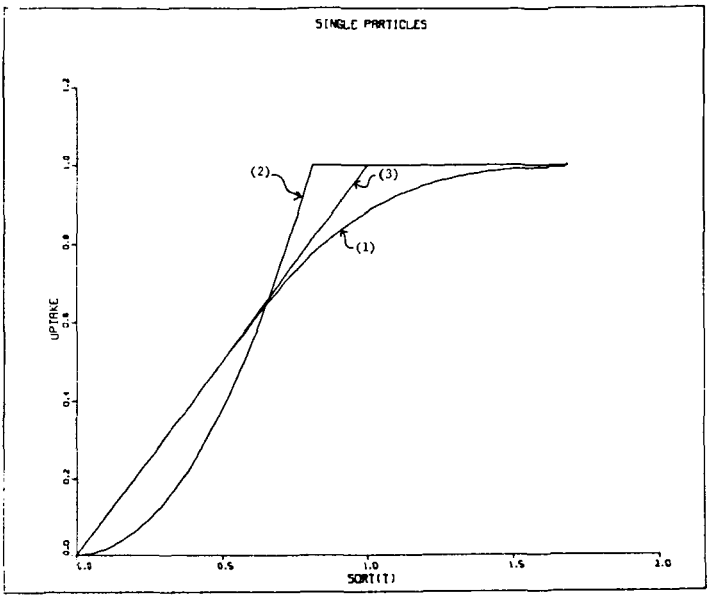

Figure 5. Solvent uptake for a single slab-shaped particle
a) Curve 1 is for constant diffusion coefficient (concentration independent)
b) Curve 2 is for extreme concentration dependent Fickian diffusion
c) Curve 3 is for Case II diffusion (constant velocity)

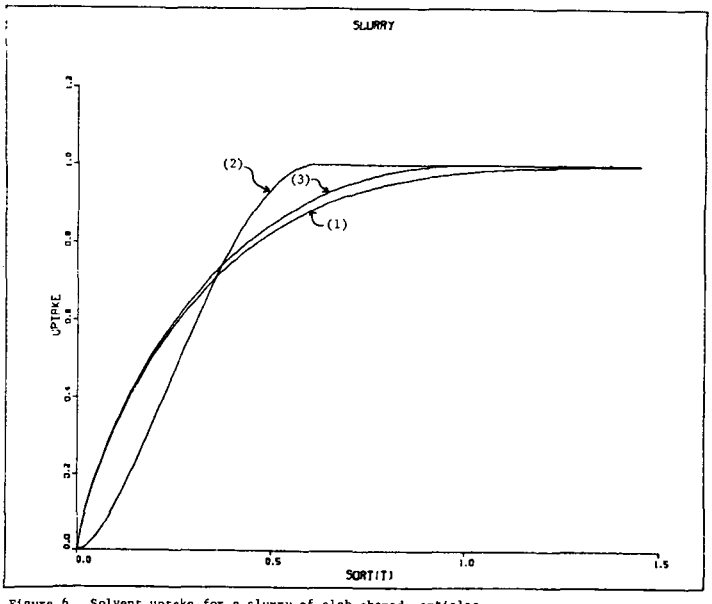

Figure 6. Solvent uptake for a slurry of slab-shaped particles
a) Curve 1 is for constant diffusion coefficient (concentration independent)
b) Curve 2 is for extreme concentration dependent Fickian diffusion
c) Curve 3 is for Case II diffusion (constant velocity)

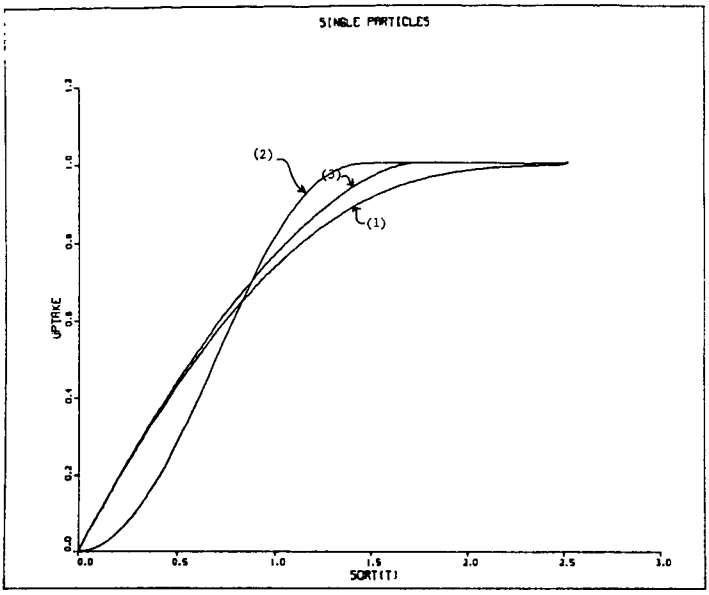

Figure 7. Solvent uptake for a single spherical particle
a) Curve 1 is for constant diffusion coefficient (concentration independent)
b) Curve 2 is for extreme concentration dependent Fickian diffusion
c) Curve 3 is for Case II diffusion (constant velocity)

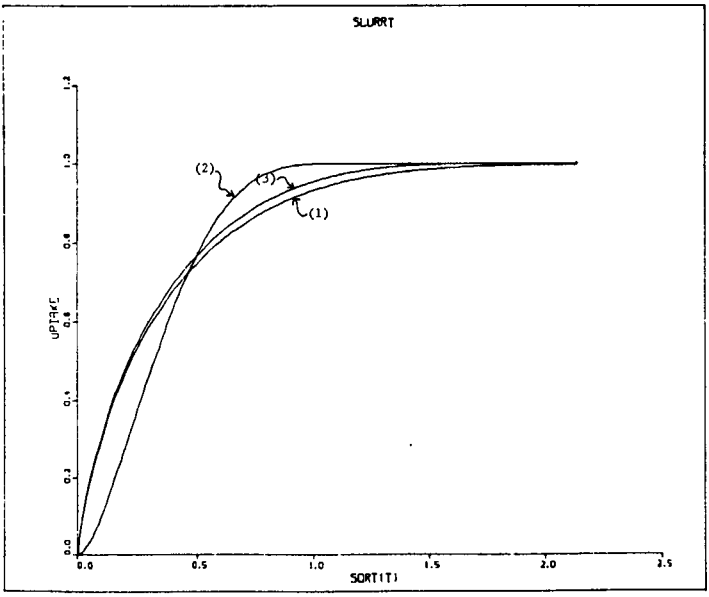

Figure 8. Solvent uptake for a slurry of spherical particles
a) Curve 1 is for constant diffusion coefficient (concentration independent)
b) Curve 2 is for extreme concentration dependent Fickian diffusion
c) Curve 3 is for Case II diffusion (constant velocity)