Theories of Precipitation Induced by Dissolution

When a porous solid is placed in acid, the solid dissolves at its surface. However, the same solid can precipitate or dissolve in pores inside the solid. The internal precipitation is a consequence of a nonlinear solubility product amplified by fast chemical kinetics. The internal dissolution can be enhanced by unequal diffusion coefficients. Both precipitation and dissolution can occur simultaneously but in different regions, mimicking the patterns of mineral found in teeth.

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Introduction

This theoretical paper is concerned with the dissolution of porous solids. In three earlier papers, we showed that dissolution at the surface of such solids can lead to both precipitation and dissolution in different regions within the solid (Cussler and Featherstone, 1981; Cussler, 1982; Cussler et al., 1983). We developed a theory of these effects, and verified some qualitative aspects of this theory.

The success of our earlier papers is diluted by two restrictive assumptions that are by no means exact. The first of these is that nonlinear, reversible chemical reactions in the solid are much faster than the diffusion. This assumption implies that all chemical reactions are essentially at equilibrium. To be sure, similar assumptions do work well in other areas, like the modeling of facilitated diffusion across membranes (Cussler, 1984). However, the assumption leads to indeterminant terms in the continuity equation, terms that include the product of a rate constant which is becoming very large and a concentration difference which is approaching zero (Noble and Way, 1987). This first assumption is at best disquieting.

The second assumption is as restrictive but more blatant and hence less upsetting: all diffusion coefficients within the solid are assumed to be equal. This assumption is a major approximation, because the porous solids are dissolving in acid, and the diffusion of H^+ is five or more times faster than the diffusion of Ca^{++}, Na^+, Cl^-, and $SO_4^=$ (Cussler, 1984). Upon reflection, we realize that this assumption may not be as bad as it seems, for the diffusion of H^+ may be retarded by electrostatic coupling between different ions. As a result, the average diffusion of HCl is closer to that of Cl^- than of H^+. Still the assumption that all diffusion coefficients are exactly equal risks oversimplifying this problem.

In this paper we examine in detail the effects of these two assumptions by numerically solving the problem without them. We show when our earlier analyses are most accurate, and we explain some experimental observations that previously were mysteries. In this effort, we build upon ideas developed for alloys that were later applied to fog formation and to spontaneous emulsification (Wagner, 1950; Kirkaldy and Brown, 1963; Toor, 1971; Rushak and Miller, 1972; Miller, 1988). These ideas merit a brief review. They involve calculating a diffusion path without chemical reaction, that is, without any dissolution or precipitation. When the diffusion coefficients are equal, the diffusion path in concentration space is a straight line. By concentration space, we mean in our case a plot of the concentration of dissolved solid vs. the concentration of acid. In many cases such a path will remain below saturation, so that only dissolution can occur. In other cases the diffusion path will move through both regions of undersaturation and supersaturation, so that both dissolution and precipitation are possible. Explicit expressions for these diffusion paths are given elsewhere (Kopinsky, 1985). The degree to which these processes actually occur depends on the kinetics; the degree to which straight diffusion paths are realistic depends on the near-equality of the diffusion coefficients. Evaluating these degrees is the purpose of this paper.

Theory

To put these ideas on a more quantitative basis, we consider a porous solid S dissolving in acid to produce a dissolved species $M^{\nu+}$. Such a dissolution follows the reaction

$$\nu H^+ + S \rightleftharpoons M^{\nu+} \tag{1}$$

For example, if the solid is $Ca(OH)_2$, ν is 2 and the dissolved species is Ca^{++}. Water produced by the reaction does not appear

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in the equation because it is always present in excess. The continuity equations for these species are

$$\frac{\partial[\mathrm{H}]}{\partial t} = D_{\mathrm{H}} \frac{\partial^2[\mathrm{H}]}{\partial z^2} - \nu r \qquad (2)$$

$$\frac{\partial[M]}{\partial t} = D_M \frac{\partial^2[M]}{\partial z^2} + r \qquad (3)$$

$$\frac{\partial[S]}{\partial t} = -r \qquad (4)$$

where r is the rate of reaction. If r is positive, solid is dissolving; if it is negative, solid is precipitating.

These equations imply three assumptions. First, diffusion of the solid is sensibly neglected. Second, the solid is treated as a continuum, neglecting any local architecture. This implies that the concentration gradients in the process persist over many individual particles or pores, which is true for the chemical systems of greatest interest to us (Toor, 1971; Kopinsky, 1985). Third, we have assumed that each diffusion coefficient is concentration-independent, free from multicomponent effects. Diffusion coefficients are often nearly constant, but do drop abruptly in supersaturated solutions (Chang and Myerson, 1985). Moreover, while these solutions are dilute, where multicomponent effects are minor they are ionic, so multicomponent effects become significant sooner (Cussler, 1976). Still, these three assumptions all seem reasonable.

To solve Eqs. 2–4, we will assume that the dissolution rate apes the stoichiometry of the overall reaction

$$r = k_1[\mathrm{H}]^{\nu} - k_{-1}[M] \qquad (5)$$

The solid concentration does not appear because it has a constant activity equal to one. However, the forward reaction cannot occur if there is no solid. Within the solid, the equilibrium between acid and dissolved solid is

$$[M] = K[\mathrm{H}]^{\nu} \qquad (6)$$

Thus we rewrite the rate equation as

$$r = (k_1[\mathrm{H}]^{\nu} - k_{-1}[M])\,\mathrm{H}\,([S])\,H\,(K[\mathrm{H}]^{\nu} - [M]) + (k_1[\mathrm{H}]^{\nu} - k_{-1}[M])\,H\,([M] - K[\mathrm{H}]^{\nu}) \qquad (7)$$

in which H is the Heavyside function

$$H(y) = 1 \qquad y \geq 0$$
$$H(y) = 0 \qquad y < 0 \qquad (8)$$

In addition, we choose the boundary conditions of solid in a semiinfinite domain, in which both dissolved species have their concentrations fixed at the stationary boundary located at $z = 0$:

$$t = 0 \quad \text{all } z \quad [\mathrm{H}] = [\mathrm{H}]_\infty$$
$$[M] = [M]_\infty$$
$$[S] = [S]_\infty \qquad (9)$$

$$t > 0 \quad z = 0 \quad [\mathrm{H}] = [\mathrm{H}]_0$$
$$[M] = [M]_0 \qquad (10)$$

$$t > 0 \quad z = \infty \quad [\mathrm{H}] = [\mathrm{H}]_\infty$$
$$[M] = [M]_\infty \qquad (11)$$

where each of the subscripted concentrations is a constant. The behavior of our system is similar to that of the well-known Stefan problem (Rubinstein, 1971), which, for example, describes the freezing of the ground. In the freezing of ground, however, it is a good assumption to assume that the temperature at the front is a constant (i.e., the freezing temperature). In our case the amount of solid at the boundary changes with time, an additional complication.

To solve this system of equations, we use an implicit finite difference method, which has the advantage of being unconditionally stable. The method used to position our grid points is the same as that described by Eigenberger and Butt (1976). The prime feature of their method is the automatic positioning of grid points at required positions, thus considerably reducing the total number of grid points and hence the amount of computer time. Their method is particularly effective here since the final algebraic equations are in tridiagonal form. This allows the solution to the equations to be obtained very rapidly. Since the boundary is moving, we vary the time step so that the boundary is always at a grid point, following the method of Douglas and Gallie (1955). The value of the time step is determined iteratively so that the front moves to the next grid point. The numerical method was checked out by comparison with limiting cases (Kopinsky, 1985).

One important limit of these results merits special mention: the limit of fast reaction. In this limit, the concentrations of H^+ and $M^{\nu+}$ everywhere within the solid are almost in equilibrium, that is, their concentrations are approximately related by Eq. 6. However, such equilibrium concentrations do *not* mean that the reaction rate within the solid is negligible. To see why, we rewrite Eq. 5 as

$$r = k_1([\mathrm{H}] - [M]/K) \qquad (12)$$

When the reaction is fast, the quantity in parentheses is close to zero. Still, k_1 is very large, close to infinity. Thus for fast reactions, the value of r is indeterminant and must be found by other routes. In calculating this limit, we have depended especially heavily on the mathematically analogous problem of fog formation (Toor, 1971).

This important limit is the reason we have not written the equations above in dimensionless form. One obvious way to do this is to define (Bluman and Cole, 1974):

$$\eta = z\,\sqrt{k_1[\mathrm{H}_0]^{\nu-1}/D_M} \qquad (13)$$

$$\tau = k_1[\mathrm{H}_0]^{\nu-1}t \qquad (14)$$

$$\rho = -r/(k_1[\mathrm{H}_0]^{\nu}) \qquad (15)$$

$$\zeta = z/\sqrt{D_M t} \qquad (16)$$

However, if k_1 becomes large, then η and τ approach infinity and ρ is indeterminant. Only ζ remains well defined. Different definitions are difficult for the semiinfinite geometry, for there are no other characteristic lengths or times. We have confronted this by introducing a characteristic scaling time $1/k_1^*$, defining a perturbational parameter $\epsilon(= k_1^*/k_1)$, and making our calculations in the limit as ϵ goes to zero. Details are given elsewhere (Kopinsky, 1985). The resulting mathematical gymnastics are complicated but not difficult; they seem to us to obscure more than clarify the physical significance of the results. Consequently, we will give our results in terms of η whenever possible.

Results

In this section, we report calculated solid concentration profiles and precipitation rates within the porous solids. In doing so, we use the values of parameters summarized in Table 1. These parameters are divided into two sets. In the first set, the solid boundary moves and kinetics may not be fast. This first set, for which solid concentration profiles are calculated, is the more realistic situation but the more difficult to calculate. In the second set of parameters, the solid is present in excess, so the solid boundary moves only a small amount. The chemical kinetics are usually fast so the concentrations of acid and salt within the solid are often close to equilibrium. These conditions provide a limit where individual factors are easily isolated. Other parameters, common to both data sets, are also given in Table 1.

Concentration profiles of the solid calculated from data set 1 are shown in Figure 1. Solid is initially located at position $\eta = 0$. At finite time, the solid has eroded to a position where $\eta > 0$. At such a finite time, the solid concentration rises abruptly at this position, passes through a maximum, and then asymptotically approaches its initial value. Solid concentration profiles at increasing times show more erosion, and a maximum wave of solid precessing inward.

Thus the concentration of solid just below the moving solid interface is higher than the solid initially present. Dissolution at the solid's surface has caused precipitation directly below the surface. Such an unexpected result is counterintuitive. It occurs because solute dissolving at the surface diffuses both into the adjacent solution and into the solid's pores. That diffusing into solution is lost from the process. That diffusing into the pores is essentially racing against the acid. When the reaction equilibrium is greater than first order, as is the case here, the solute effectively wins the race (Cussler, 1982). The reprecipitated material is part of that dissolved at the surface.

Solid concentration profiles like those in Figure 1 can be almost superimposed by plotting them vs. $\zeta(= \eta/\sqrt{\tau})$, as shown in Figure 2. In addition to the same three curves replotted from Figure 1, Figure 2 contains a fourth curve calculated for fast reaction kinetics (Kopinsky, 1985). The three original curves approach the fourth as the dimensionless time $\tau(= k_1[H_0]t)$ becomes large. All four curves show the same general characteristics. They show a solid boundary located near a finite value of ζ. At smaller ζ, there is no solid. At larger ζ, there is a maximum solid concentration above that originally present. At very large ζ, there is no effect of acid attack at the boundary.

Table 1. Parameters Used in Calculations

Data Set 1
Solid conc. $S_\infty = 0.005$ mol/L
Acid conc. $H_0 = 0.02$ mol/L
Salt conc. $M_0 = 0.02$ mol L
Kinetics are finite

Data Set 2
Solid present in excess
Acid conc. in equilibrium with salt
Kinetics are usually fast

Normally True for Both Data Sets
Equilibrium const. $K = 100$ L/mol
Stoichiometric coeff. $\nu = 2$
Diffusion coeff. ratio $D_M/D_H = 1$

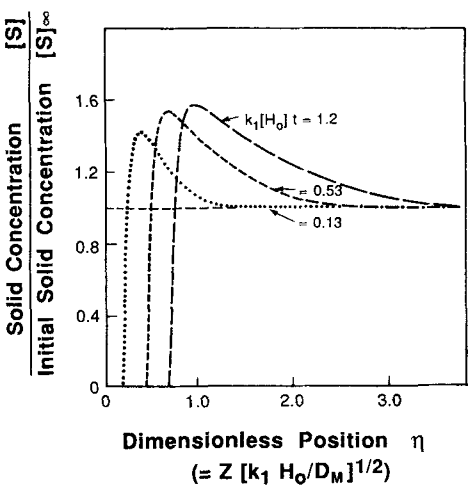

Figure 1. Solid concentration vs. position and time.

Solid, initially present as a step function, erodes at small z but increases at intermediate values of z

This dissolution engendered precipitation is a function of four chief variables: the equilibrium constant K, the chemical kinetics, the stoichiometric coefficient ν, and the diffusion coefficients. Each of these four factors is considered in the following paragraphs.

The maximum amount of solid precipitated rises with the equilibrium constant K, as shown in Figure 3 for the values in data set 1. This is expected, for larger values of K imply stronger interactions between acid and solid. Note that for equal diffusion coefficients and $\nu = 2$, which is the case here, dissolution never occurs within the solid. Dissolution does occur at the surface of the solid; but within the pores, precipitation is the norm.

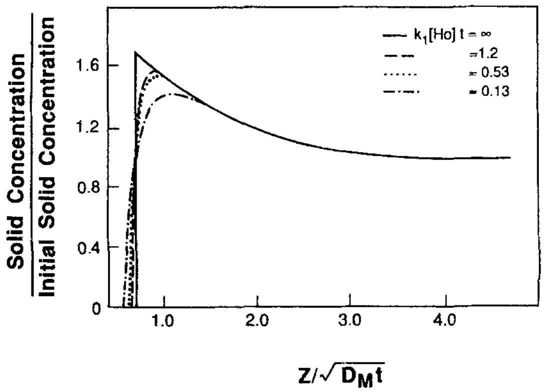

Figure 2. Solid concentration vs. $z/\sqrt{D_M t}$.

Concentration profiles of Figure 1 are almost superimposed by this replotting

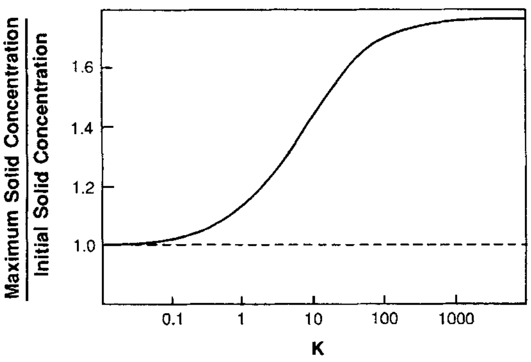

Figure 3. Maximum solid concentration vs. equilibrium constant *K*.
More solid precipitates in pores when *K* is large

The effect on this precipitation of different kinetic rate constants is illustrated in Figure 4. This figure differs from the first three in two major ways. First, it reports the precipitation rate, not the solid concentration. Second, it uses the values in data set 2 but with finite kinetics. In particular, it assumes that excess solid is present, so that the solid boundary moves very little.

The results in Figure 4 show that the precipitation rate increases as the chemical kinetics get faster. Obviously, the forward reaction rate increases as shown by the values of $k_1[H_0]_t$, attached to each line. Less obviously, the reverse reaction rate constant k_{-1} increases simultaneously, because the equilibrium constant $K(=k_1/k_{-1})$ is being held constant. Moreover, the limit of infinitely fast reaction is calculated not from finite difference methods, but from the earlier, approximate, analytical theory (Cussler, 1982; Kopinsky, 1985). The consistency among all of these results demonstrates the reliability of the calculations.

The effect on the precipitation rate of different stoichiometric coefficients is illustrated in Figure 5. These calculations use the parameters in data set 2, with both excess solid and fast chemical kinetics. As a result, the heavy solid line in Figure 5 (=2) is identical with the heavy solid line (=∞) in Figure 4. The result in Figure 5 shows that reprecipitation within the solid will not occur if $\nu \leq 1$. In other words, the dissolution-engendered reprecipitation described in this paper requires that the concentration of dissolved solid at equilibrium must vary with more than the first power of the concentration of acid. This conclusion is consistent with the earlier approximate theories and with most earlier experimental data (Cussler, 1982; Cussler et al., 1983). It does depend on a major approximation: that all diffusion coefficients are equal.

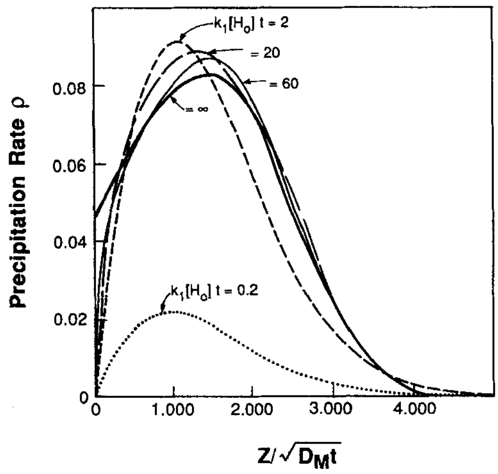

Figure 4. Precipitation vs. position and time.
As rate constant k_1 gets larger, precipitation rate approaches the limit of fast kinetics (heavy line, $k_1[H_0]t = \infty$)

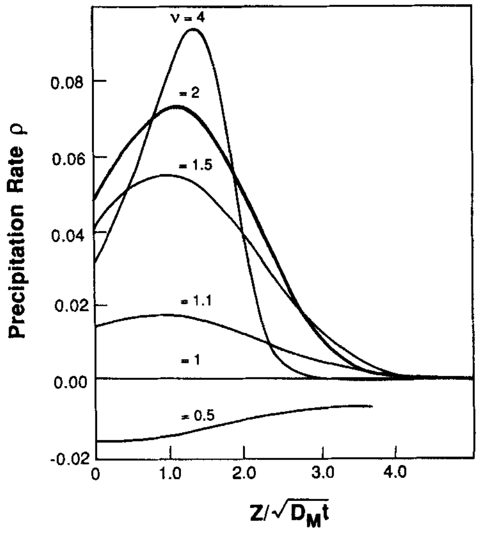

Figure 5. Precipitation vs. stoichiometry.
Results for the limit of fast kinetics; heavy line ($\nu = 2$) is the same as in Figure 4

The effect of differences in diffusion coefficient is illustrated in Figure 6. As in the previous two figures, these results are based on excess solid; as in Figure 5, kinetics are assumed to be fast. Other parameters are those in data set 2, including $\nu = 2$. As a result, the heavy solid line (=1) in Figure 6 is again the heavy solid line in Figures 4 and 5. It shows precipitation within the solid caused by dissolution at the solid's surface.

However, the striking results in Figure 6 occur for $\Delta \leq 0.2$, when the diffusion coefficient of acid is five or more times larger

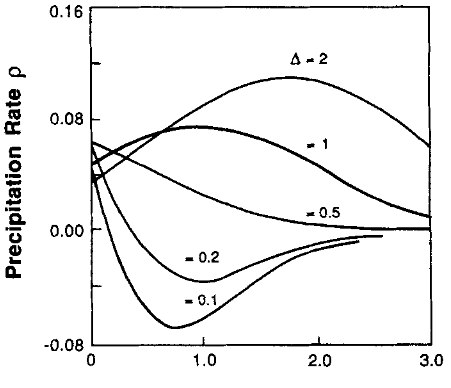

Figure 6. Precipitation for unequal diffusion coefficients.
When ratio of diffusion coefficients $\Delta \leq 0.2$, dissolution and precipitation occur near surface, but dissolution also occurs well below surface; heavy line ($\Delta = 1$) is the same as in Figures 4 and 5

than the diffusion coefficient of dissolved solid, a rough approximation of the expected behavior. In this case, dissolution still occurs at the solid's surface, and precipitation still occurs just within the solid. However, at greater depths the precipitation rate becomes negative and solid again dissolves. Thus we get a pattern of dissolution–precipitation–dissolution. Again, such a pattern requires both a nonlinear chemical reaction and diffusion coefficients that are unequal. The implications of these results are considered next.

Discussion

The results in the previous section can be summarized qualitatively by the three-dimensional plot in Figure 7. This figure shows the solid concentration in a porous solid as a function of position and time, for finite kinetics, for a limited amount of solid, and for unequal diffusion coefficients. It includes features of the six previous figures and of a large number of other calculations given elsewhere (Kopinsky, 1985). It tries to encapsulate our knowledge of the dissolution of porous solids.

Figure 7 shows a solid concentration that is initially constant. It shows a solid that does not change at positions far within the solid. It shows reprecipitation with a resulting solid maximum near the solid's eroding surface, a maximum due to a stoichiometric coefficient ν that is significantly greater than 1. The figure shows that deeper than this maximum, there is a minimum in solid concentration, a consequence of unequal diffusion coefficients.

All this detail results from the coupling between diffusion and nonlinear chemical reaction. As a result, this research represents yet another study of mass transfer with chemical reaction, a subject that has enriched the literature of chemical engineering (Astarita, 1967; Astarita et al., 1983; Fogler and Rege, 1986). In the vast majority of past cases, the chemical reactions are first order. When nonfirst-order reactions are considered, solute transport is commonly by flow, not by diffusion. Our work supplies the missing limit of nonlinear reactions where solute transport is only by diffusion.

Applications of this work may also occur in the dissolution of minerals and the decay of masonry. We have already considered the decay of hydroxyapatite, a nonstoichiometric calcium phosphate that is the principle mineral in human teeth (Kim and Cussler, 1987; Featherstone and Cussler, 1987). When acid produced by oral microorganisms attacks this phosphate, dissolution occurs at the tooth surface and partial demineralization occurs well within the tooth (Featherstone, 1984). Remineralization occurs near the surface and within the tooth, producing a region of high mineral concentration known clinically as a "white spot." Dentists look for these spots as precursors of dental caries. The research in this paper does predict these regions of dissolution and remineralization, and hence provides one explanation for the clinical observations.

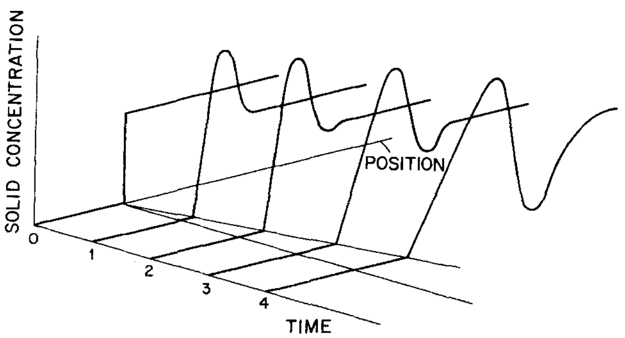

Figure 7. Solid concentration vs. position and time.
Results of dissolution at solid surface and of both precipitation and dissolution with solid

Similar dissolution and precipitation will occur in other porous minerals challenged by altered pH. These effects will be most interesting for mixed porous minerals with large stoichiometric coefficients ν and with little if any flow. In many ways, such a situation is a complement to those similar mineralogical problems without diffusion but with flow, problems that often lead to chromatographiclike separations (Walsh et al., 1984). Our results may also find application in the decay of masonry (Rossi-Manaresi, 1976). Acid gases or acidic aerosols attack the calcium carbonate in masonry to produce more soluble bicarbonates and sulfates. In a few cases, subsurface reprecipitation and demineralization are observed. Other possible applications include solution mining (Schlitt and Hiskey, 1981) and drying of wood and other porous materials (Ashworth, 1982). In the latter case, water is analogous to the dissolved solute and temperature corresponds to the acid.

We want to sound some notes of caution. First, in the introduction we promised to remove the two assumptions of rapid chemical kinetics and unequal diffusion coefficient that restricted earlier theories. We have done so. However, we have ignored a third, implicit assumption, that the changing void fraction of the porous solid has little effect on the results. This assumption is implicit, because it is included in the definition of the chemical reactions. These reactions are taken as homogeneous, but in fact are heterogeneous. In other words, a rate constant like k_{-1} really should be $(k'_{-1}\, \mathbf{a})$, where k'_{-1} is the rate constant of a heterogeneous reaction, and $\mathbf{a}$ is the surface area per volume, a function of the void fraction. As this void fraction changes during dissolution and precipitation, $\mathbf{a}$ and hence k_{-1} must change. The effective diffusion coefficients will also change. We have ignored all this, and assumed average values in our analysis.

The effect of this implicit assumption is hard to judge. When the void fraction is large, the effect on diffusion will be minor, but that on chemical rate constants may be large. When the void fraction is small, as is true in teeth, the changes in diffusion will be larger than those in the rate constants. We decided not to include these effects in the current theory because we had no experimental information against which to test our results. We look forward to obtaining this information in the future.

As a second note of caution, we assert that our results are significantly different from those described as Liesegang rings (Liesegang, 1924; Hedges, 1932; Henisch, 1970). The currently accepted theories of Liesegang phenomena are based on coupled diffusion and chemical reaction, just as the calculations in this paper are (Prager, 1956; Keller and Rubinow, 1981; Muller et al., 1982; Vengl and Ross, 1982). However, the key aspect of the Liesegang theories is the presumption of an autocatalytic reaction, possibly associated with some form of Ostwald ripening. Such an autocatalytic reaction leads to predictions of many periodic bands like those actually observed. In contrast, our calculations assume nonlinear but not autocatalytic reactions, and produce only a single band. Thus we believe that the effects described in this paper differ from those commonly grouped as Liesegang phenomena.

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Notation

$[c]$ = concentration of species c
D = diffusion coefficient, assumed equal for all species
D_c = diffusion coefficient of species c
H = Heavyside function, Eq. 8
k_1, k_{-1} = forward and reverse reaction rate constants
k_1^* = reciprocal of scaling time
K = equilibrium constant, Eq. 6
r = rate of solid dissolution, Eq. 5
t = time
z = position

Greek letters

Δ = diffusion coefficient ratio D_M/D_H
ϵ = pertubation, k_1^*/k_1
ζ = dimensionless coordinate, Eq. 16
η = dimensionless position, Eq. 13
ν = stoichiometric coefficient
ρ = dimensionless precipitation rate, Eq. 15
τ = dimensionless time, Eq. 14

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