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February 1988



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**THE EFFECT OF A STATIONARY PRECIPITATION FRONT ON
NUCLIDE DISSOLUTION AND TRANSPORT: ANALYTIC SOLUTIONS**

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THE EFFECT OF A STATIONARY PRECIPITATION FRONT ON NUCLIDE DISSOLUTION AND TRANSPORT: ANALYTIC SOLUTIONS

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1. Introduction

Waste material in a geologic repository will dissolve and migrate away. For many waste components, this process will be limited by the solubility of the waste matrix and species involved. In this paper we deal with a single contaminant species and analyze the effect of a precipitation front caused by a discontinuity in the solubility of the contaminant at some distance from the waste package. The precipitation front may be due to local geochemical changes such as changes in temperature, pH or redox potential, caused by nearby geologic features or the waste itself.

In contrast with other work on precipitation fronts,^{1,2,3,4} we provide analytic solutions to the problem of precipitation at a stationary front. Numerical illustrations of these solutions are also presented.

2. Analysis

A spherical waste solid of radius r_0 is embedded in an infinite water-saturated porous medium. There is no contaminant in the porous medium when dissolution begins at time $t = 0$ and direct contact is assumed between the waste and the porous medium (no container or other barriers). The solubility discontinuity, or so called precipitation front, is assumed to be a concentric spherical shell of radius r_p surrounding the waste package (Figure 1). The dissolution rate at the waste surface is governed by a solid-liquid reaction-rate law with the maximum rate occurring when there is no contaminant in the pore water and the minimum rate, zero, approached only as the contaminant concentration in the pore water approaches the solubility at the waste surface. In the limit that the reaction rate goes to infinity, this law reduces to a constant concentration boundary condition.

Transport in the porous medium is by fluid-phase diffusion only, with no advection. Retardation of the contaminant in the porous medium is treated by equilibrium sorption.

The precipitation front is assumed to be at a known, fixed location. Inside the spherical front and near the waste package, the solubility of the contaminant, C_0 , is high. Outside the front and further away from the waste, the reduced solubility, C_r , is lower. This creates the possibility that some of the contaminant being released from the waste will precipitate at the front and become immobilized. At early times, when the concentration is below the solubility limits at the front location, the front is transparent to the transport process.

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The domain from the waste surface to infinity is then treated as a single homogeneous region and we have

$$\frac{\partial C_1}{\partial t} = \frac{D}{K} \nabla^2 C_1, \quad r_0 < r < \infty, \quad 0 < t < t_p \quad (1)$$

where $C_1(r, t)$ is the fluid-phase contaminant concentration for $0 < t < t_p$, D is the contaminant diffusion coefficient in the pore fluid, and t_p is the time at which the solubility limit is reached and precipitation begins. The initial concentration and the concentration at infinity are both assumed to be zero

$$C_1(r, 0) = 0, \quad r_0 < r < \infty \quad (2)$$

$$C_1(\infty, t) = 0, \quad 0 < t < t_p \quad (3)$$

The reaction-rate controlled dissolution rate at the waste surface as a function of concentration is

$$-\epsilon D \frac{\partial C_1}{\partial r} \Big|_{r=r_0} = j_0 \left(1 - \frac{C_1}{C_0} \right) \Big|_{r=r_0}, \quad 0 < t < t_p \quad (4)$$

where ϵ is the porosity and j_0 is the forward dissolution reaction rate (assumed constant). To determine the precipitation time, t_p , we first solve eq. (1)-(4). The contaminant concentration predicted by eq. (1)-(4) increases steadily with time and monotonically decreases with distance from the waste. The concentration may not reach the solubility limit anywhere, but if it does it will occur first at the front location, r_p , and we can then determine t_p implicitly from the equation

$$C_1(r_p, t_p) = C_r \quad (5)$$

At time $t = t_p$, when precipitation begins, the governing equation (1) is no longer valid at the front so we divide the domain into two regions, one inside the front and the other outside the front. For the inner region

$$\frac{\partial C_2}{\partial t} = \frac{D}{K} \nabla^2 C_2, \quad r_0 < r < r_p, \quad t_p < t < \infty \quad (6)$$

where $C_2(r, t)$ is the contaminant concentration for $r_0 < r < r_p$ and $t_p < t < \infty$. The initial condition for this problem is given by C_1 evaluated at $t = t_p$

$$C_2(r, t_p) = C_1(r, t_p), \quad r_0 < r < r_p \quad (7)$$

The boundary condition at the waste surface is the reaction-rate law as before with C_2 replacing C_1

$$-\epsilon D \frac{\partial C_2}{\partial r} \Big|_{r=r_0} = j_0 \left(1 - \frac{C_2}{C_0} \right) \Big|_{r=r_0}, \quad t_p < t < \infty \quad (8)$$

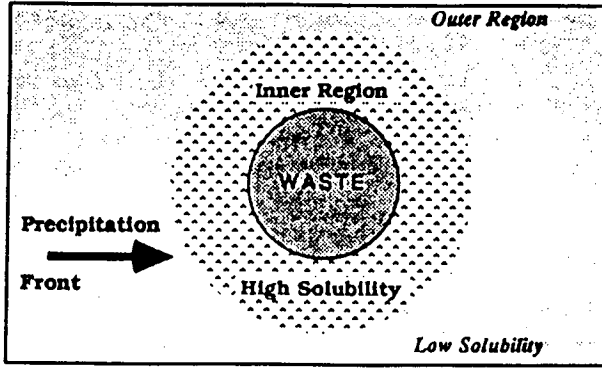


Figure 1. The Stationary Precipitation Front

At the new boundary, $r = r_p$, we set the concentration to the reduced solubility limit C_r

$$C_2(r_p, t) = C_r, \quad t_p < t < \infty \quad (9)$$

This is a result of the physical requirement that the concentration be continuous across the front and that we are (somewhat artificially) limiting the concentration to the C_r limit in the region $r_p < r < \infty$. In reality, the front would extend over some non-zero transition thickness without well-defined boundaries.⁵ We assume instead an abrupt discontinuity and also neglect the effect which the accumulating precipitate might have on the transport process such as by filling the pores or by moving as a colloid.

The region outside the precipitation front is treated similarly with the governing equation given by

$$\frac{\partial C_3}{\partial t} = \frac{D}{K} \nabla^2 C_3, \quad r_p < r < \infty, \quad t_p < t < \infty \quad (10)$$

and the side conditions

$$C_3(r, t_p) = C_1(r, t_p), \quad r_p < r < \infty \quad (11)$$

$$C_3(r_p, t) = C_r, \quad t_p < t < \infty \quad (12)$$

$$C_3(\infty, t) = 0, \quad t_p < t < \infty \quad (13)$$

The solution to eq. (1)-(4) is

$$C_1(\rho, \tau) = \frac{C_o}{\sigma \rho} \operatorname{erfc} \left(\frac{\rho - 1}{2\sqrt{\tau}} \right)$$

$$-\frac{C_o}{\sigma \rho} \exp(\sigma \alpha (\rho - 1) + \sigma^2 \alpha^2 \tau) \operatorname{erfc} \left(\frac{\rho - 1}{2\sqrt{\tau}} + \sigma \alpha \sqrt{\tau} \right), \quad \begin{matrix} 1 < \rho < \infty \\ 0 < \tau < \tau_p \end{matrix} \quad (14)$$

with these dimensionless parameters $\sigma = 1 + 1/\alpha$, $\alpha = j_o r_o / \epsilon D C_o$, $\rho = r/r_o$, $\tau = tD/Kr_o^2$. Using this result, eq. (5) is solved implicitly to obtain a numerical value for $\tau_p = t_p D/Kr_o^2$. Assuming a known value for τ_p , which is dependent on α and C_o/C_r , eq. (6)-(9) are solved by the Fourier Method with the result in infinite series form

$$C_2(\rho, \tau) = C_o \left[a + \frac{b}{\rho} + \frac{1}{\rho} \sum_{n=1}^{\infty} A_n \Phi_n(\rho) e^{-\lambda_n(\tau - \tau_p)} \right], \quad \begin{matrix} 1 < \rho < \rho_p \\ \tau_p < \tau < \infty \end{matrix} \quad (15)$$

where

$$a = \frac{\sigma \rho_p C_r / C_o - 1}{\sigma \rho_p - 1}$$

$$b = \frac{\rho_p (1 - C_r / C_o)}{\sigma \rho_p - 1}$$

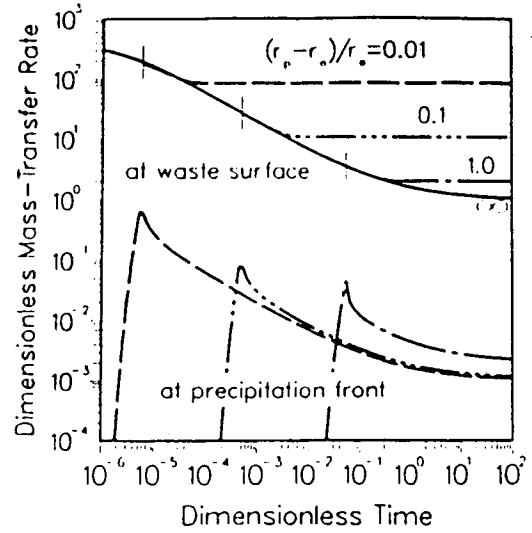


Figure 2. Mass-Transfer Rate at the Waste Surface & Precipitation Front, $\alpha = 500$, $C_o/C_r = 10^{-3}$

the series coefficients A_n are given by

$$A_n = \frac{1}{\|\Phi_n\|^2} \int_1^{\rho_p} \Phi_n(\rho) [\rho C_1(\rho, \tau_p) / C_o - (a\rho + b)] d\rho$$

where

$$\|\Phi_n\|^2 = \int_1^{\rho_p} \Phi_n^2(\rho) d\rho$$

the eigenfunctions Φ_n are defined

$$\Phi_n(\rho) = \sin \left[\sqrt{\lambda_n} (\rho_p - \rho) \right], \quad 1 < \rho < \rho_p$$

and the eigenvalues λ_n are determined implicitly from

$$\tan \left[\sqrt{\lambda_n} (\rho_p - 1) \right] = \frac{-\sqrt{\lambda_n}}{1 + \alpha}$$

Equations (10)-(13) are solved by Green's Function Method to yield the solution

$$C_3(\rho, \tau) = \frac{\rho_p C_r}{\rho} + \frac{1}{\rho} \int_{\rho_p}^{\infty} [\eta C_1(\eta, \tau_p) - \rho_p C_r] \times \left(\frac{\exp \left[\frac{-(\rho - \eta)^2}{4(\tau - \tau_p)} \right] - \exp \left[\frac{-(\rho + \eta - 2\rho_p)^2}{4(\tau - \tau_p)} \right]}{\sqrt{4\pi(\tau - \tau_p)}} \right) d\eta, \quad \begin{matrix} \rho_p < \rho < \infty \\ \tau_p < \tau < \infty \end{matrix} \quad (16)$$

The mass-transfer rate \dot{M} , representing the flow rate of contaminant species through a concentric sphere of radius r at time t , is proportional to the concentration gradient, in this case

$$\dot{M}(r, t) = -4\pi r^2 \epsilon D \frac{\partial C}{\partial r} \quad (17)$$

where $C_1(r, t)$, $C_2(r, t)$, or $C_3(r, t)$ is inserted for $C(r, t)$ depending on the place and time of interest.

3. Numerical Illustration

Figure 2 summarizes the principal results of the numerical illustration. The normalized mass-transfer rates at two locations are plotted against dimensionless time, with the location of the precipitation front as a parameter. The mass-transfer rate M [M/T] is normalized by the constant $4\pi r_0 DC_0$ [M/T]. The dimensionless time τ is obtained by dividing actual time by Kr_0^2/D [T]. As indicated on the caption for Figure 2, the solubility C_r in the outer region is set at 10^{-3} of the solubility of the inner, higher-solubility region. The calculations have been done for $\alpha=500$, to ensure that dissolution is controlled primarily by diffusion.

The upper set of curves in Figure 2 shows the mass-transfer rates at the surface of the waste sphere, r_0 , for four locations of the precipitation front r_p . The start of precipitation is indicated by the vertical bars. If the precipitation front is close to the waste surface, precipitation starts soon and steady state is reached in early times. The mass-transfer rate at steady-state is about 100 times higher for the precipitation front at $(r_p - r_0)/r_0=0.01$ than for the precipitation front at infinity. The precipitation front is essentially an additional sink for dissolving contaminants, and putting it closer to the waste surface magnifies its effect.

The lower set of curves shows the mass-transfer rates at the location of the precipitation front. The contaminant takes some time to arrive at this location. At a certain time the precipitation concentration is reached and precipitation begins. Once precipitation starts, the mass-transfer rate out of the precipitation front decreases dramatically. The location of the precipitation front affects the time when precipitation begins. It also affects the steady-state mass-transfer rate out of the precipitation front, but only slightly.

4. Conclusion

At early times, the release rate is controlled by the solid-liquid reaction rate represented by the dimensionless quantity α . At later times extending to steady state, the release rate depends on the location of the precipitation front and on the solubility ratio C_0/C_r .

The result of pegging the front concentration at C_r is to steepen the concentration gradient on the waste package side of the front and to flatten the gradient in the region outside the front. The rate of contaminant transport from the waste to the front location is thereby maintained at a higher than normal rate while the rate of transport away from the front is held to lower levels. The difference in the transport rates at the front determines the rate of precipitation. Nearly all of the species released at C_r from the waste form is immobilized, as was also observed in a parallel study.⁵ Whether this scenario is more or less desirable than other predictions without precipitation depends on the goals — whether we care about the waste dissolution rate, or far-field transport rates — and whether the assumed uniform solubility is nearer to C_0 or C_r .

If a near-field region of high solubility is viewed as a perturbation to the normal low solubility case, then we may conclude that the effect of the perturbation is to increase the release rate at the waste surface as well as at the precipitation front. The release rate at the waste surface may be greatly affected if the front is very close to the waste surface and the ratio C_0/C_r is very large. The release rate from the front location will increase with increasing size of the high solubility region due to the larger radius at which the concentration C_r is maintained.

The effect at the waste surface has the greatest potential for dramatic influence.^{1,2,3,4} If we apply our model to a controlling matrix species, the dissolution of which releases other waste components, we see that if these components are not solubility limited, their release toward the far-field could be greatly accelerated by a

local high-solubility region for the controlling matrix species.

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