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WASTE DISSOLUTION WITH CHEMICAL REACTION, DIFFUSION AND ADVECTION

P.L. Chambré, C.H. Kang, W.W.-L. Lee, and T.H. Pigford

June 1987

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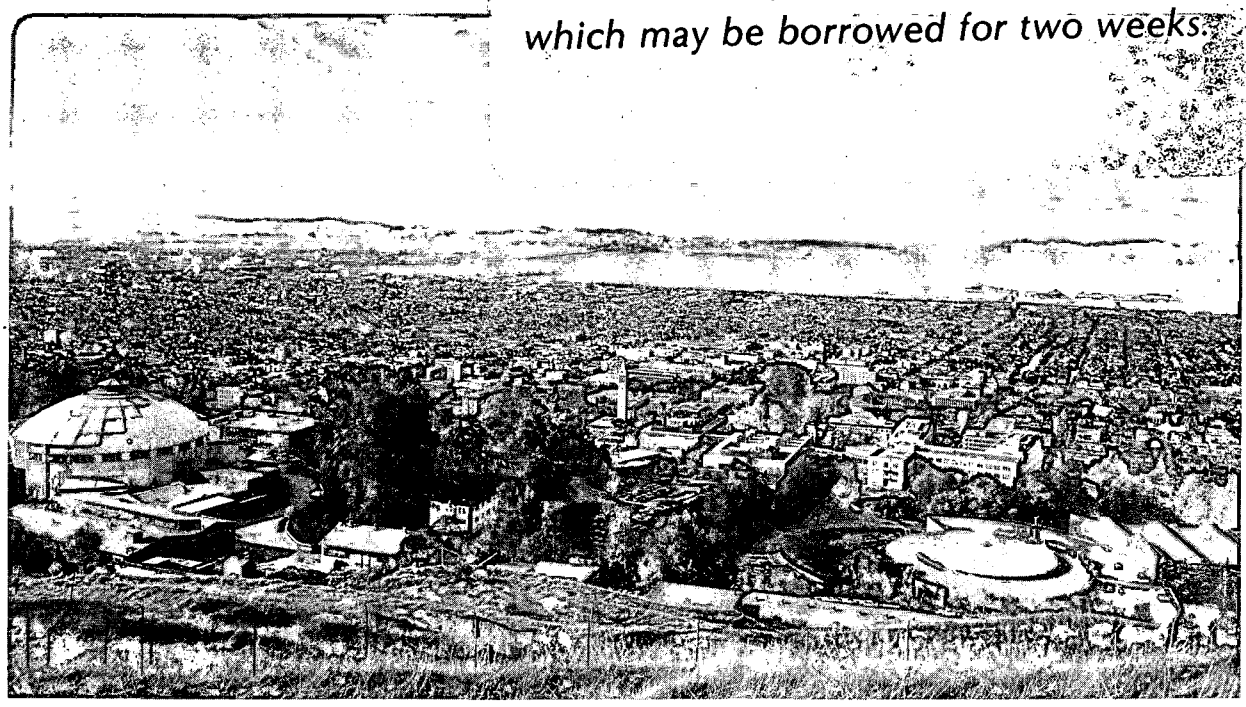

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Waste Dissolution with Chemical Reaction, Diffusion and Advection*

P. L. Chambré, C. H. Kang, W. W.-L. Lee and T. H. Pigford
Department of Nuclear Engineering & Lawrence Berkeley Laboratory
University of California, Berkeley, CA 94720

Our analytic equations[1,2] predict the rate at which low-solubility species in a waste solid dissolves in ground water, conservatively assuming that each dissolved species is at its saturation concentration in the liquid at the surface of the waste solid. We then considered[3] the effect of a chemical-reaction-rate boundary condition, using empirical rate data determined from laboratory leach tests, and provided a means of calculating the time-dependent concentration of dissolved species near the waste surface and the time-dependent diffusive mass transfer into the surrounding rock. Surface-liquid concentrations of low-solubility species from borosilicate glass waste and spent fuel soon reach values close to saturation. The present paper extends the mass-transfer analysis to include the effect of advective transport in predicting the steady-state dissolution rate, with a chemical-reaction-rate boundary condition at the surface of a waste form of arbitary shape. This new theory provides an analytic means of predicting the ground-water velocities at which dissolution rate in a geologic environment will be governed entirely by the chemical reaction rate.

As an illustration, we consider the steady-state potential flow of ground water in porous rock surrounding a spherical waste solid. Adopting a reaction-rate equation representing zero-order forward reaction and a first-order back reaction,[3] Chambré has developed the steady-state concentration isopleths shown in Figure 1 as a function of the Peclet number $Pe \equiv Ur_o/D$ and the reaction rate modulus $\alpha \equiv j_o r_o/\epsilon D C_s$, where U is the upstream pore velocity of the ground water, r_o is the radius of the spherical-equivalent waste solid, D is the coefficient for molecular diffusion in the pore water, j_o is the forward reaction rate per unit area of waste solid, ϵ is the rock porosity, and C_s is the saturation concentration of the dissolving species.

The rate of dissolution is obtained from the Sherwood number $Sh \equiv kr_o/\epsilon D$ where k is the coefficient for mass transfer from the waste solid to pore water in the rock, defined as the mass flux at the waste surface divided by the saturation concentration C_s. Figure 2 shows the Sherwood number as a function of the Peclet number, for various values of the reaction rate modulus α, obtained by an integral-method approximation and verified by asymptotic solutions in the large and small Pe ranges. For small values of Pe and large α, Sh is essentially independent of Pe because molecular diffusion controls. For $Pe > 10$, and for values of α of

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about 100 and greater, typical of borosilicate glass[3] and spent fuel at 90°C and greater, Sh increases as the square root of the Peclet number, showing that diffusive-advective mass transfer controls. At much larger Pe, well beyond the range of this figure, the curve levels out when the exterior-field mass transfer is so rapid that chemical reaction rate controls the net rate of dissolution.

For α=1, as can obtain for small separated grains of dissolving solid or for dissolution at much lower temperature, chemical reaction rate reduces the Sherwood number over the entire range and causes the net dissolution rate to be less affected by advective transport.

This new theory provides an analytic means for predicting steady-state dissolution as affected by chemical reaction rate, diffusion and advection.

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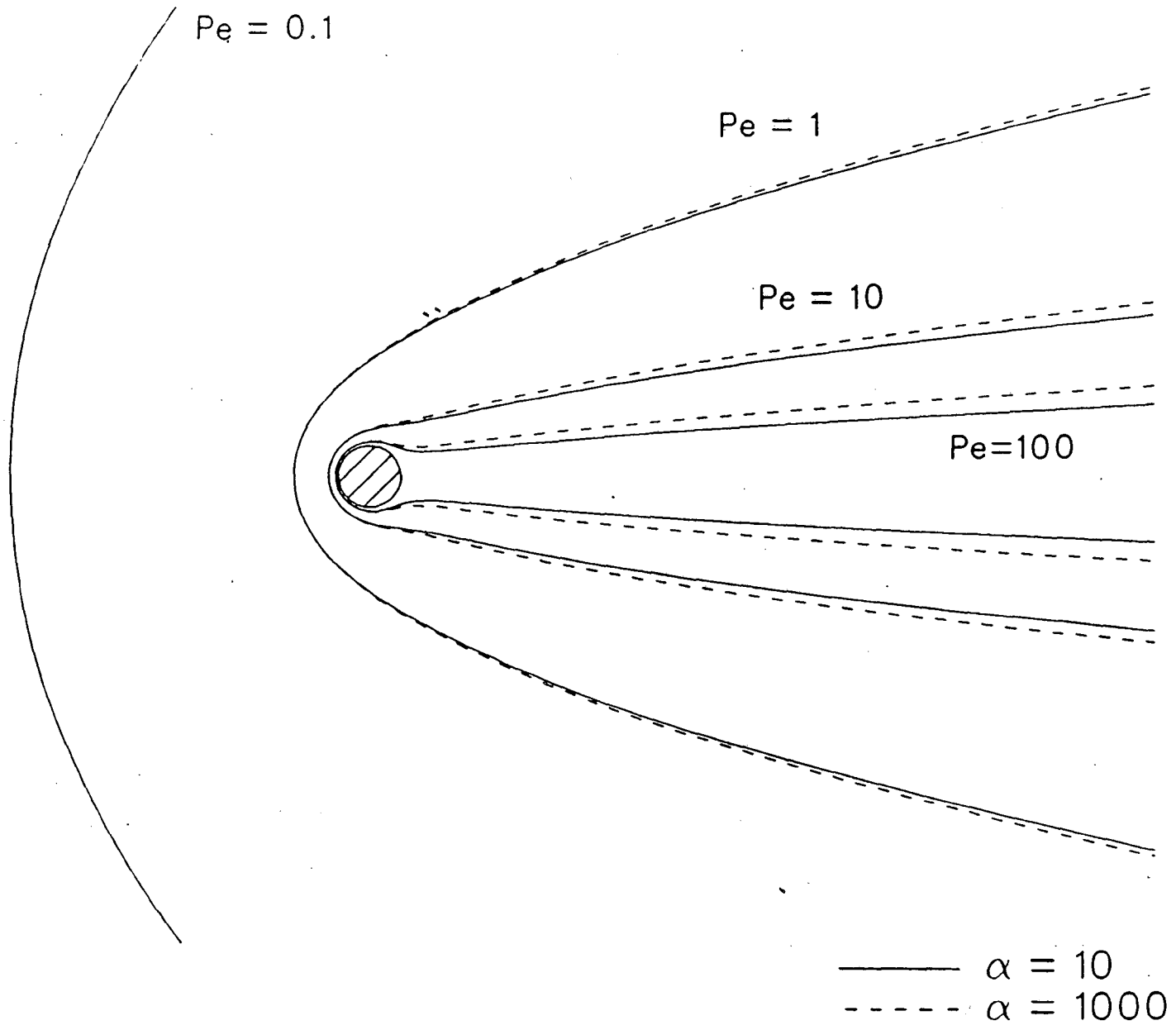

Figure 1 The concentration boundary layer for various values of the Peclet number and reaction rate modulus

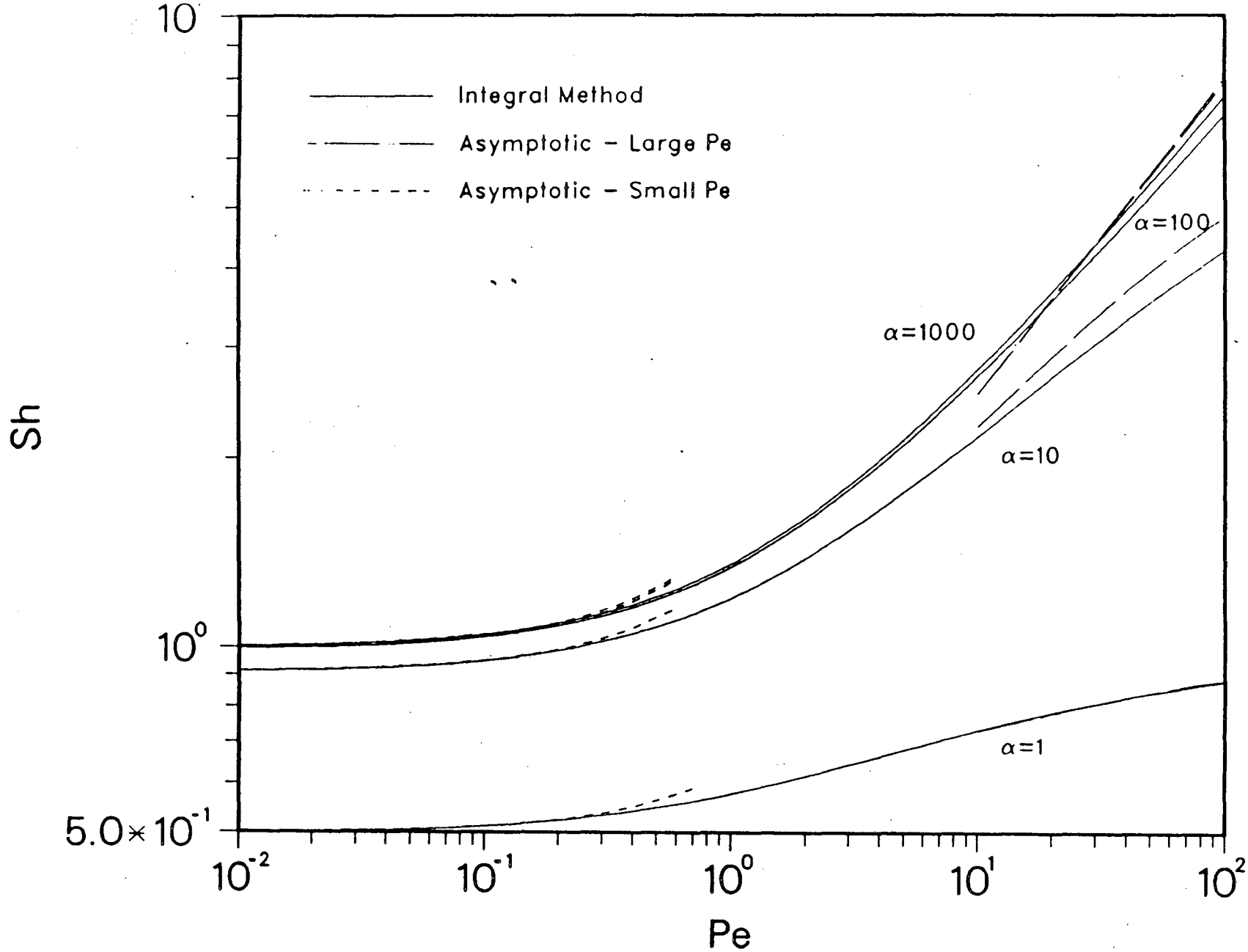

Figure 2 The Sherwood number as a function of the Peclet number, with the reaction rate modulus as a parameter

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