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THE ROLE OF CHEMICAL REACTION IN WASTE-FORM PERFORMANCE

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ABSTRACT

The dissolution rate of waste solids in a geologic repository is a complex function of waste form geometry, chemical reaction rate, exterior flow field, and chemical environment. We present here an analysis to determine the steady-state mass transfer rate, over the entire range of flow conditions relevant to geologic disposal of nuclear waste. The equations for steady-state mass transfer with a chemical-reaction-rate boundary condition are solved by three different mathematical techniques which supplement each other. This theory is illustrated with laboratory leach data for borosilicate-glass and a spherical spent-fuel waste form under typical repository conditions. For borosilicate glass waste in the temperature range of 57°C to 250°C, dissolution rate in a repository is determined for a wide range of chemical reaction rates and for Peclet numbers from zero to well over 100, far beyond any Peclet values expected in a repository. Spent-fuel dissolution in a repository is also investigated, based on the limited leach data now available.

INTRODUCTION

The prediction of dissolution rates is the starting point of safety assessments for nuclear waste disposal. The steady-state rate of dissolution is a function of the waste solid geometry, solid-liquid reaction rate, exterior flow field surrounding the waste-solid, diffusion coefficient in the ground water, and solubility of the dissolved constituent. Numerous leaching experiments have been conducted under laboratory conditions such that the chemical reaction rate is the rate-controlling mechanism. In previous analyses [1,2,3] we showed that diffusive-advective mass transfer in rock or other porous medium surrounding the waste solid is expected to control the dissolution rate of low-solubility species in waste-solid sizes expected in a repository with low water flow. Hughes, Marples and Stoneham [4] have suggested qualitatively various flow regimes that could control mass loss rate in a repository, and they point out that at sufficiently high flow rates exterior-field mass transfer may no longer be the controlling mechanism. Here we introduce a new analytic theory that allows quantitative prediction of waste dissolution rates over a wide range of ground water flow rates.

Our earlier analytic equations [2,5] 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 the effect of a chemical-reaction-rate boundary condition [3], using empirical rate data determined from laboratory glass 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 are predicted to 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 arbitrary shape. The solution has been obtained by three different approaches, an integral method, asymptotic expressions, and an interpolation formula. The interpolation formula is an especially convenient tool for calculating dissolution rates.

THEORETICAL RESULTS

In this paper we consider as an example of the theory a spherical waste solid surrounded by water-saturated porous rock with a steady-state potential flow of ground water. A chemical-reaction-rate boundary condition representing zero-order forward reaction of waste solid with water and a first-order backward reaction [3] is assumed at the sphere surface

$$-\epsilon D \frac{\partial C(r_o, t)}{\partial r} = j_o \left(1 - \frac{C(r_o, t)}{C_s} \right), \quad t > 0 \quad (1)$$

where C is the concentration of the dissolved species in ground water, r_o is the radius of the waste sphere, ϵ is the porosity of the rock, D is the species diffusion coefficient in the liquid, j_o is the reaction rate per unit area of waste solid at vanishing $C(r_o, t)$, and C_s is the saturation concentration of dissolving species.

The results relate the modified Sherwood number, Sh , and the Peclet number, Pe , with the square of the modified Thiele modulus, α , which is defined as the ratio of the reaction rate per unit area at r_o to the steady-state diffusive mass-transfer rate per unit area at r_o .

$$Sh = \frac{k r_o}{\epsilon D} \quad (2)$$

$$Pe = \frac{U r_o}{D} \quad (3)$$

$$\alpha = \frac{j_o r_o}{\epsilon D C_s} \quad (4)$$

Here U is the upstream pore velocity of ground water and k is the average mass-transfer coefficient for the spherical waste surface, such that the product kC_s gives the steady-state mass-transfer rate per unit area of sphere surface. The mathematical problem has been solved by three separate methods. The methods and forms of the solutions are too lengthy to be presented here. The solution results and numerical examples are summarized below.

Integral Method

The integral method yields an approximate solution valid over the entire range of Peclet numbers, $0 \leq Pe < \infty$. It agrees well with the asymptotic solutions for small and large Peclet numbers.

Asymptotic Expressions

Chambré also developed asymptotic expressions for small Pe and for large Pe numbers. These asymptotic expressions have relatively simple forms, but they are not valid over the entire range of Peclet numbers. These asymptotic expressions are useful for checking the limiting results of the integral method.

Interpolation Formula

The interpolation formula is relatively simple and valid for the entire range of Peclet numbers.

$$Sh \approx \alpha \frac{1 + 0.5\sqrt{0.5\pi Pe} + 0.5Pe}{1 + 0.5\sqrt{0.5\pi Pe} + 0.5Pe + \alpha(1 + 0.5\sqrt{0.5\pi Pe})}, \quad 0 \leq Pe < \infty \quad (5)$$

This formula has been tested by comparing it with the integral method and with the asymptotic expressions. The numerical difference of this formula, compared with the integral method, is less than 3 percent throughout the range of Peclet numbers, $0 \leq Pe \leq 100$ and $1 \leq \alpha \leq 1000$. For very small Peclet, when advection is unimportant, the modified Sherwood number becomes

$$Sh \rightarrow \frac{\alpha}{1 + \alpha}, \quad Pe \rightarrow 0 \quad (6)$$

When the Peclet numbers are very large,

$$Sh \rightarrow \alpha, \quad Pe \rightarrow \infty \quad (7)$$

NUMERICAL ILLUSTRATIONS

Figure 1 shows the relative effects of Peclet numbers and α on concentration boundary layers of any solubility-limited constituent that obeys Eq. (1). The concentration boundary layers shown in Figure 1 are isopleths estimated by the integral-method approximations for concentrations approaching zero. Material which is dissolving from the waste sphere at vanishing ground-water flow rate will form a spherical concentration boundary layer around the waste solid. As the ground-water flow increases, increasing the Peclet number, the flow sweeps past the waste solid, compressing the concentration boundary layer and forming it into paraboloid-shaped wake. The concentration boundary layers shown in Figure 1 are actually the edges of detectable concentration.

For a small Peclet number, e.g., $Pe = 0.1$, the boundary layers for $\alpha = 10$ and $\alpha = 1000$ are almost identical, because at low flow velocities molecular diffusion is more important than advection in species transport. At higher Peclet numbers, the downstream boundary layers differ somewhat for $\alpha = 10$ and $\alpha = 1000$, but the upstream boundary layers thickness remains almost the same.

Figure 2 shows the modified Sherwood number as a function of the Peclet number, for various values of the square of the modified Thiele modulus α , obtained by the integral method and verified by the asymptotic expressions in the large Pe and small Pe ranges. In the range of $0.01 \leq Pe \leq 1$ it can be seen that the modified Sherwood number is almost constant for fixed values of α , see Eq. (6). In this same range of Peclet number, a hundred-fold increase in α , say from 10 to 1,000, results in only a 10 per cent increase in modified Sherwood number. At $Pe = 100$, increasing α from 10 to 1,000 almost doubles the mass-transfer rate. For $40 < Pe < 10^8$, well outside the range of Peclet numbers and flow speeds anticipated in geologic repositories, and for values of α of about 100 and greater, the modified Sherwood number is approximately proportional to the square root of the Peclet number, showing that diffusive-advective mass-transfer controls [2]. At even larger Pe , see Eq. (7), well beyond the range of this figure, the curves level out when the exterior-field mass-transfer is so intense that chemical reaction rate controls the dissolution rate. For $\alpha=1$, as can obtain for small separated grains of a dissolving solid or for dissolution at very low temperature, chemical reaction rate reduces the influence on the modified Sherwood number over the entire range of Pe and causes the dissolution rate to be less affected by advective transport.

The comparison of the asymptotic expressions with the integral method agree well for $Pe < 0.5$, and $Pe > 10$ if $\alpha = 1$. For larger α values the asymptotic expression for large Pe agrees with the integral method, for $Pe > 10^3$.

Figure 3 compares the integral method with the interpolation formula. The maximum numerical difference in using the interpolation formula is less than 3 per cent throughout the range of Peclet number, $0 \leq Pe \leq 100$. For the range $100 \leq Pe \leq 10^8$, the difference between the interpolation formula, Eq. (5), and the integral method is within 7 per cent.

APPLICATION TO BOROSILICATE GLASS WASTE

To apply this theory to simulate repository conditions, we made calculations for a potential repository in basalt. Calculated temperatures at the emplacement hole wall [6] for various times after emplacement are listed in Table I. For illustration, we assume that at each instant the waste and rock are all at the listed temperature and that the steady-state mass-transfer theory applies. We assume a glass waste form with an equivalent spherical radius of 0.44 m. From the laboratory data for PNL 76-68 borosilicate glass [8,9], we derive the temperature-dependent reaction rate values j_o , which are also listed in Table I. Adopting earlier estimates [5,7] of the effects of temperature on silica solubility and on the diffusion coefficient, we calculate the values of the square of the modified Thiele modulus shown in Table I. α does not always increase as temperature increases, because α is also a function of other parameters such as C_s , D , and j_o , as shown in Eq. (4).

Figure 4 shows the steady-state mass-transfer rate from the surface of a glass waste in a basalt repository as a function of ground water pore velocity with temperature as a parameter, computed from Eq. (5). The reaction rate j_o at 250°C is about 260 times greater than that at the pre-emplacement repository temperature of 57°C, as shown in Table I. However, Figure 4 shows the silica mass-transfer

rate at $U = 0.01$ m/yr at the maximum temperature is only about 40 times greater than that at the pre-emplacement repository temperature. For $U = 100$ m/yr at the maximum temperature, the mass-transfer rate is only 17 times greater than the mass-transfer rate at the pre-emplacement temperature.

Table I. Calculated Square of the Modified Thiele Modulus for a Basalt Repository

Temperature °C	Time After Emplacement (a)	C_s g/cm ³	D cm ² /sec	j_o g/cm ² -sec	α
250	5	5.8×10^{-4}	1.6×10^{-4}	7.9×10^{-8}	3.7×10^3
130	100	2.3×10^{-4}	6.5×10^{-5}	1.5×10^{-8}	4.4×10^3
90	500	1.5×10^{-4}	3.9×10^{-5}	3.4×10^{-9}	2.5×10^3
57	>5000	9.8×10^{-5}	2.2×10^{-5}	3.0×10^{-10}	6.0×10^2

APPLICATION TO SPENT FUEL

Using a value of $j_o = 5.79 \times 10^{-11}$ g/cm²-sec and an uranium saturation concentration of 2.38×10^{-11} g/cm³ [10], and assuming the uranium-water reaction rate in Eq. (1), we calculate for the uranium in spent fuel a value of α of the order of 10^8 . The implication is that dissolution of uranium from spent fuel is mostly controlled by exterior-field diffusion and advection. Although much greater solubilities of uranium can occur in oxidizing ground water, perhaps several orders of magnitude greater than the solubilities used in this estimate, the α for spent fuel is likely to remain much greater than unity.

CONCLUSIONS

This analysis provides a means for predicting steady-state dissolution as affected by chemical reaction rate, diffusion and advection. For the ground-water velocities, waste dimensions, and temperatures expected in geologic repositories, the dissolution of borosilicate glass is predicted to be controlled by the mutual interplay of these three mechanisms. The ground water velocities required for chemical-reaction rate of borosilicate glass to control dissolution rate are far beyond any reasonably expected in a repository. Chemical reaction rate and rate of diffusion from a borosilicate glass waste form can control the dissolution rate at temperatures much lower than are expected in a nuclear waste repository, i.e. when $\alpha \leq 1$. Preliminary data indicates that similar conclusions may be applicable for spent fuel, but more data are needed on solid-liquid reaction rate as a function of concentration of dissolved uranium and of temperature.

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REFERENCES

1. T. H. Pigford, J. O. Blomeke, T. L. Brekke, G. A. Cowan, W. E. Falconer, N. J. Grant, J. R. Johnson, J. M. Matusek, R. R. Parizek, R. L. Pigford, and D. E. White, *A Study of the Isolation System for Geologic Disposal of Radioactive Wastes*, Washington: National Academy Press, 1983.
2. P. L. Chambré, T. H. Pigford, Y. Sato, A. Fujita, H. Lung, S. Zavoshy, and R. Kobayashi, *Analytical Performance Models*, Report LBL-14842, 1982.
3. S. J. Zavoshy, P. L. Chambré and T. H. Pigford, "Mass Transfer in a Geologic Environment," in C.

- M. Jantzen, J. A. Stone and R. C. Ewing (eds.), *Scientific Basis for Nuclear Waste Management VIII*, Pittsburgh, Materials Research Society, pp. 311-322, 1985.
4. A. E. Hughes, J. A. C. Marples and A. M. Stoneham, "The Significance of Leach Rates in Determining the Release of Radioactivity from Vitrified Nuclear Waste," *Nuclear Technology*, 61, 496, 1983.
 5. P. L. Chambré, T. H. Pigford, W. W.-L. Lee, J. Ahn, S. Kajiwara, C. L. Kim, H. Kimura, H. Lung, W. J. Williams and S. J. Zavoshy, *Mass Transfer and Transport in a Geologic Environment*, Report LBL-19430, 1985.
 6. M. K. Altenhofen, "Waste Package Heat-Transfer Analysis: Model Development and Temperature Estimates for Waste Packages in a Repository Located in Basalt," Report RHO-BWI-ST-18, 1981.
 7. T. H. Pigford, P. L. Chambré and S. J. Zavoshy, "Effect of Repository Heating on Dissolution of Glass Waste," *Trans. Am. Nuc. Soc.*, 44, 115, 1983.
 8. L. R. Pederson, C. Q. Buckwalter and G. L. McVay, "The Effect of Surface Area to Solution Volume on Waste Glass Leaching," *Nuclear Technology*, 62, 151, 1983.
 9. J. H. Westsik, Jr., C. O. Harvey and W. L. Kuhn, *High-Temperature Leaching of Actinide-Bearing, Simulated High-Level Waste Glass*, Report PNL-3172, 1983.
 10. M. J. Apted, A. M. Liebetrau and D. W. Engel, *The Analytical Repository Source-Term (AREST) Model; Analysis of Spent Fuel as a Nuclear Waste Form*, Report PNL-6347, 1987.

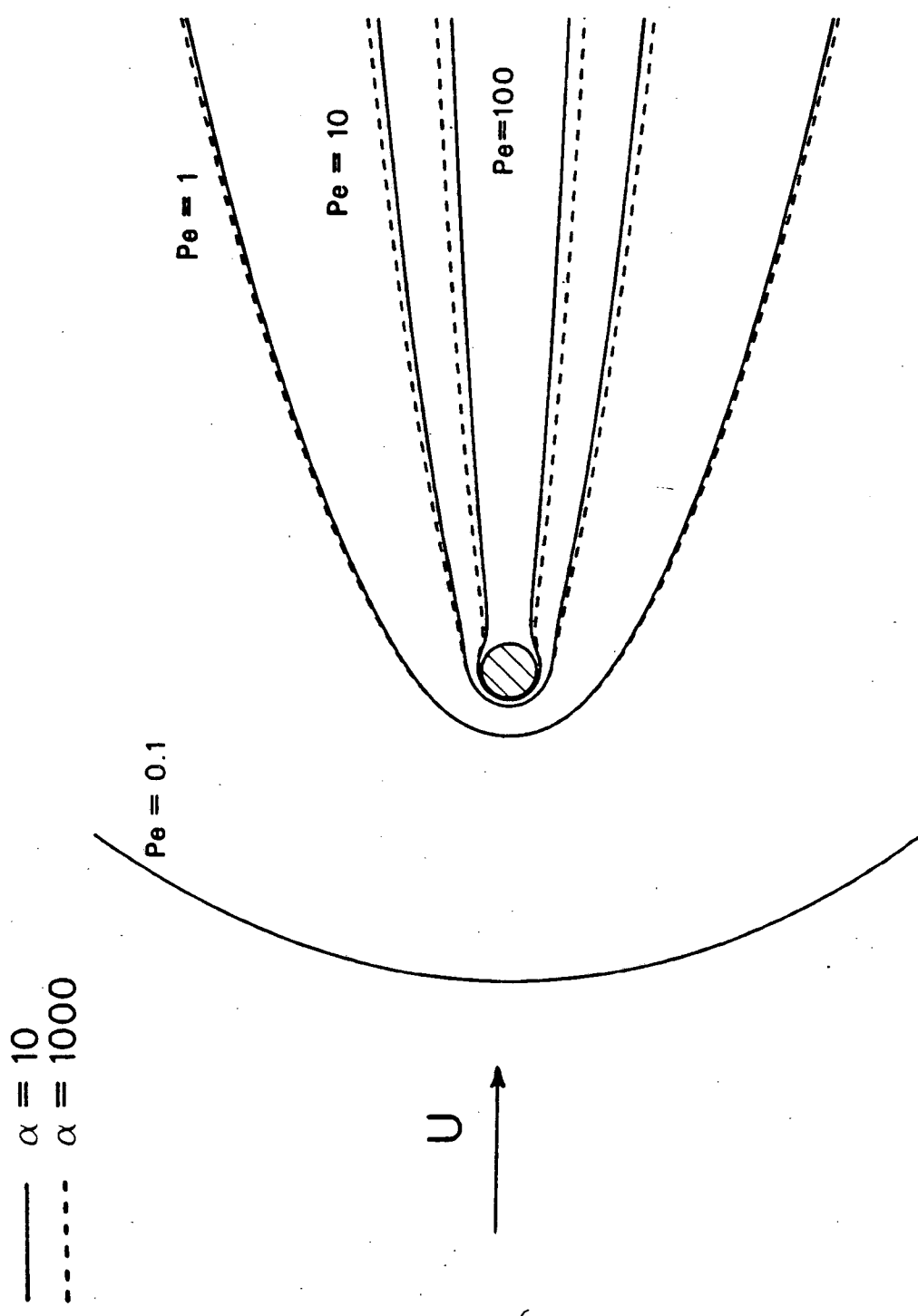


Figure 1. The concentration boundary layer about a sphere for various values of the Peclet number and the square of the modified Thiele modulus.

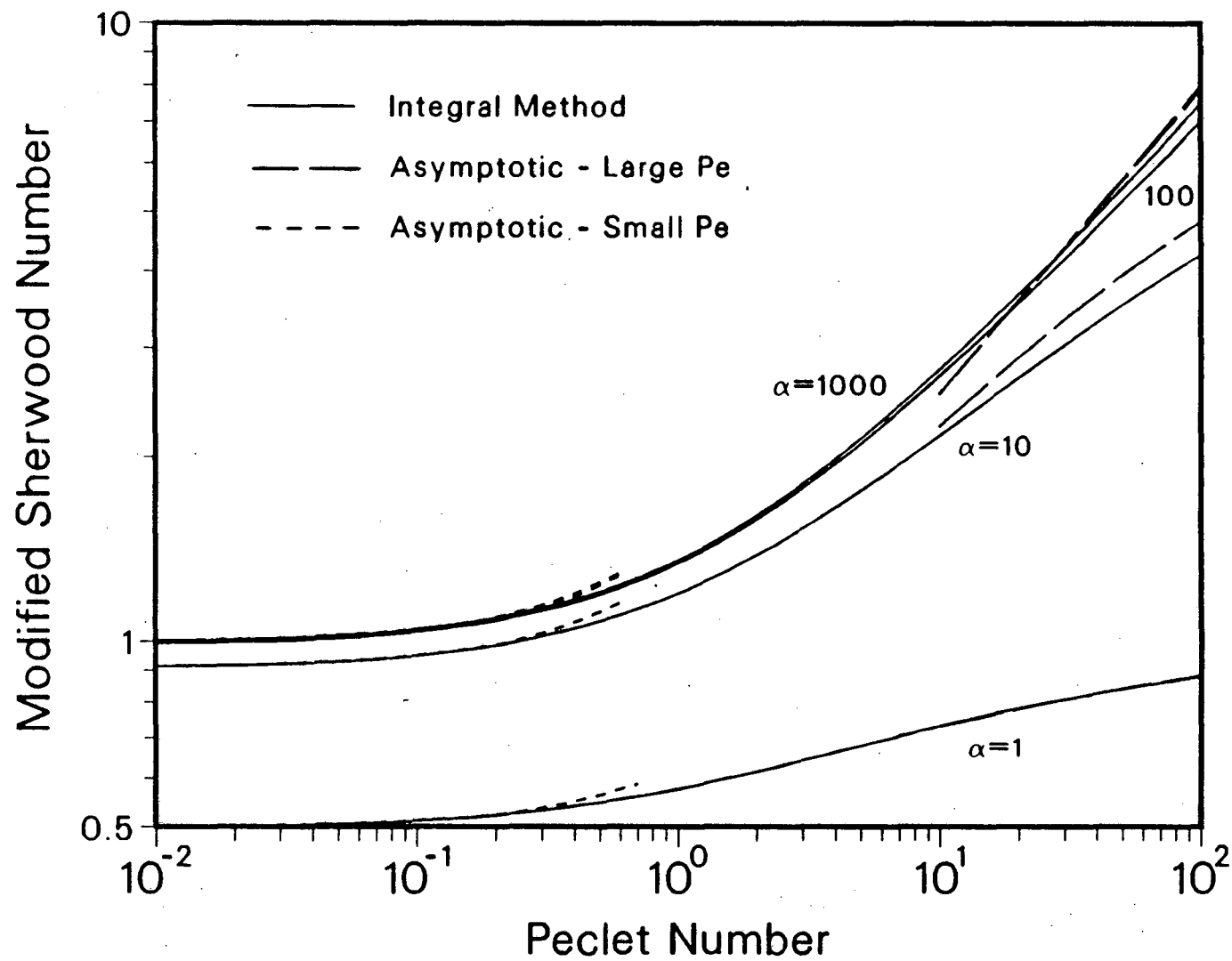


Figure 2. The modified Sherwood number as a function of the Peclet number, with the square of the modified Thiele modulus as a parameter.

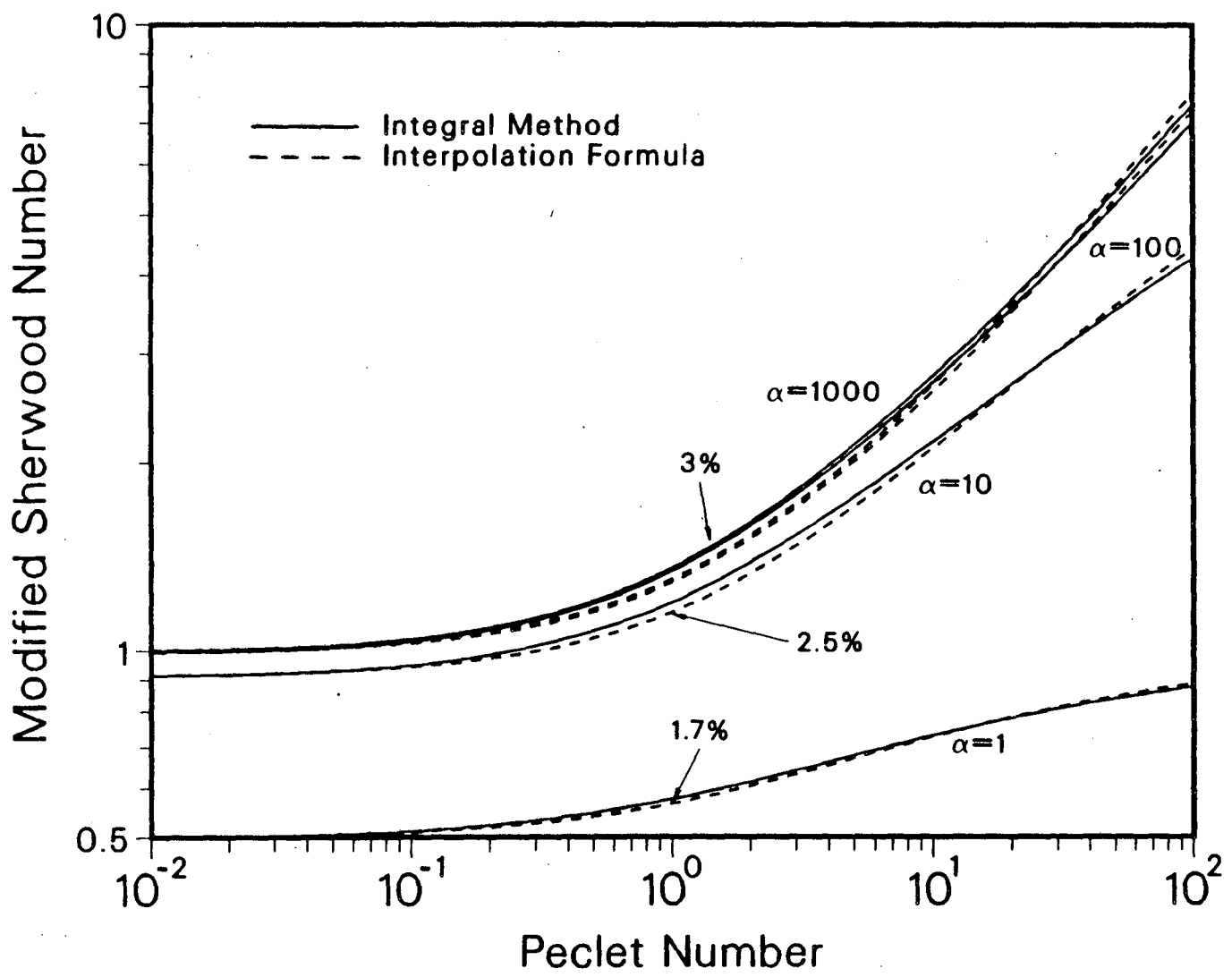


Figure 3. Comparison of the integral method and the interpolation formula.

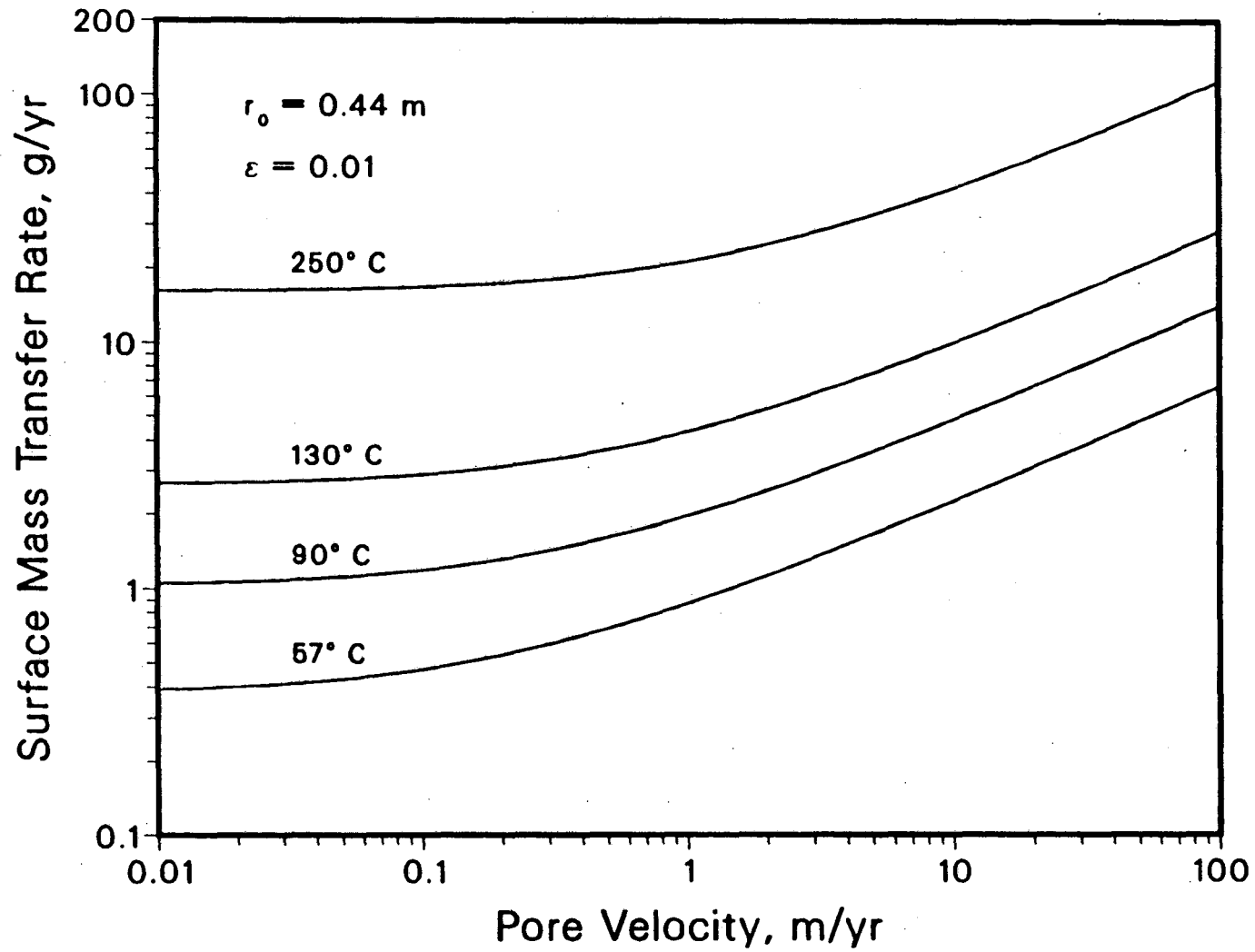


Figure 4. Surface mass transfer rate of a spherical borosilicate glass waste form in a basalt repository.

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