

Lawrence Berkeley National Laboratory

Recent Work

Title

NEAR-FIELD MASS TRANSFER IN GEOLOGIC DISPOSAL SYSTEMS: A REVIEW

Permalink

<https://escholarship.org/uc/item/06j960x4>

Authors

Pigford, T.H.
Chambre, P.L.

Publication Date

1987-11-01

c-2



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

EARTH SCIENCES DIVISION

BERKELEY LABORATORY

APR 19 1988

LIBRARY AND DOCUMENTS SECTION

Presented at the Materials Research Society
Symposium: Scientific Basis for Nuclear
Waste Disposal XI, Boston, MA,
November 30-December 3, 1987

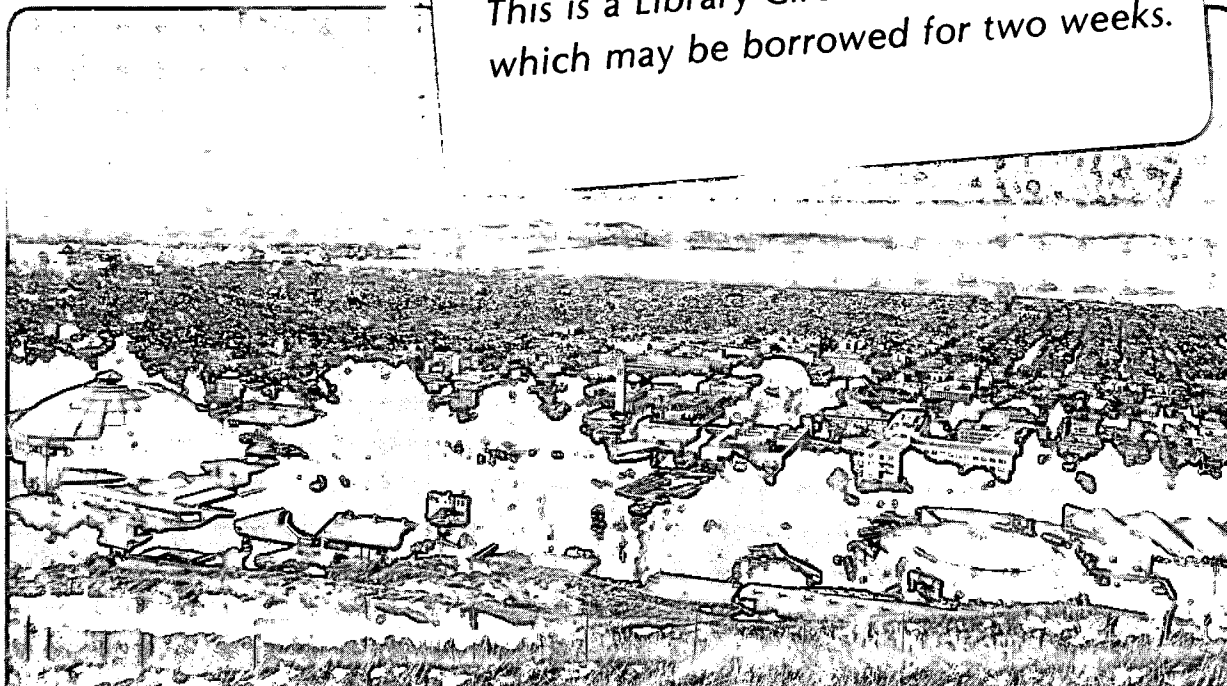
Near-Field Mass Transfer in Geologic Disposal Systems: A Review

T.H. Pigford and P.L. Chambre

November 1987

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.*



LBL-23689
c-2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

NEAR-FIELD MASS TRANSFER IN GEOLOGIC DISPOSAL SYSTEMS: A REVIEW

T. H. Pigford and P. L. Chambré

Department of Nuclear Engineering and Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720

ABSTRACT

A primary purpose of performance assessment of geologic repositories for radioactive waste is to predict the extent to which radioactive species are released from the waste solids and are transported through geologic media to the environment. Reliable quantitative predictions must be made of rates of release of radionuclides from the waste into the rock, transport through the geologic media, cumulative release to the accessible environment, and maximum concentrations in ground water and surface water. Here we review theoretical approaches to making the predictions of near-field release from buried waste solids, which provide the source terms for far-field release. The extent to which approaches and issues depend on the rock media and on regulatory criteria is discussed.

INTRODUCTION

Designers of geologic disposal systems for solid waste must predict the long-term time-dependent rate of dissolution of toxic contaminants in ground water, to provide the source term for predicting the later transport of these contaminants to the environment. If a container is provided to protect the waste from ground water for an extended period, it is necessary to predict the time when the container allows contaminants to be released to ground water, and it may be necessary to predict the rate of such releases through partly failed containers. Mass-transfer analysis is being used to predict rates of dissolution and release of radioactive constituents in future repositories for high-level radioactive waste, and it has been applied to predict the life of a copper container for high-level radioactive waste.

The U. S. Nuclear Regulatory Commission¹ has specified numerical limits for the rate of release of radioactive constituents into rock surrounding packages for high-level waste, including unprocessed spent fuel and reprocessing waste, and it has specified the required time for substantially complete containment of the radioactive constituents by the waste container. Other nations have not imposed such specific requirements on the waste package, but prediction of these same features will be needed for the overall prediction of repository performance.

Here we summarize the evolution and application of near-field mass-transfer analyses in high-level-waste programs.

HISTORICAL

Until the introduction of mass-transfer analysis for predicting long-term performance of waste packages in a repository, it had been generally assumed that the rate of release of contaminants from a waste solid would be controlled by the rate of chemical reaction of that waste solid with ground water. Samples of waste solids were exposed to simulated ground water in laboratory leach studies, where the rate of release into the water would be controlled by chemical reaction, by degradation of the solid, or by frequency of replacing the leachant. In 1978 Neretnieks² suggested that rate of dissolution in a geologic environment might be limited instead by solubilities and by rate of diffusive-convective transport of dissolved species from the waste surface.

Application of mass transfer analysis in the U.S. programs was stimulated by observations of the Na-

tional Research Council's Waste Isolation System Study,³ first made in 1981, that there was little validity in assumptions that the long-term dissolution rates in a geologic repository could be predicted from laboratory data on leach rates of waste samples. Laboratory leach data are empirically correlated, at a given temperature, with time of exposure and the concentration of dissolved species in the liquid. The latter depends on correlating parameters such as the ratio of sample surface to the volume of wellmixed liquid, liquid replacement frequency, etc. The actual processes of dissolution are reaction of the waste solid with ground water at the waste surface and diffusion and convection of the dissolved species from the surface into the ground water in the surrounding rock. In this open system of the repository there is no well-defined volume of well-mixed liquid as in the closed-system laboratory experiments. Here the concentration in the surface liquid depends on the mass-transfer properties of the surrounding medium.

Recognizing that the waste-solid matrix and most of its solid constituents are of low solubility, we first sought an upper limit on the net rate of dissolution by assuming that the solution at the waste surface is saturated with the individual waste constituents. The exact analytical solutions⁴ for the time-dependent mass transfer rate from a waste solid in contact with saturated porous rock showed that the limiting mass-transfer rates for the buried waste are so slow that the actual dissolution rate is expected to be limited by diffusive-convective transport in the pores in the rock and not by chemical reaction rate at the waste surface. By comparing these predicted diffusive-convective mass transfer rates with laboratory dissolution data obtained under conditions wherein solid-liquid reaction rate is controlling, it was concluded that the basic rate constants for the solid-liquid reaction were rapid enough, for the waste solids then studied, that the dissolved concentration in the surface liquid would be very close to the saturation concentration. This conclusion was valid for borosilicate glass waste, which had been extensively tested in laboratory experiments. It has since been demonstrated to be valid for the dissolution of uranium dioxide in spent fuel.

Mechanistic analysis of mass-transfer is based on well-established theory of diffusive-convective transport. Its application requires experimental measurement of well-defined parameters such as porosity, solubility, diffusion coefficient, and pore velocity. It relies on no arbitrary and adjustable parameters from empirical rate measurements; reliance on such parameters would undermine the reliability of the theory to predict dissolution rates in the long-term future. Mass-transfer theory can be used to predict the long-term steady-state dissolution rate in a repository, as well as the higher transient dissolution rates that can exist for hundreds and thousands of years after the waste-solid comes in contact with water. The first analysis in the U.S. program assumed a waste solid in direct contact with porous rock. The more realistic situations of backfill between the waste and rock, rock with discrete fractures as well as pores, and the effects of waste constituents of high solubility were among the many extensions of mass-transfer analysis left for future study.

The first results from this new mass-transfer theory were published in 1982,^{4,5} and the theory was highlighted by the Waste Isolation System Study³ as a recommended approach for predicting the long-term performance of waste solids in a repository.

Neretnieks² used simplified techniques of mass-transfer analysis to predict the steady-state rate of oxidation of the copper containers and to predict the rate of waste dissolution for the Swedish KBS studies. The validity of several approximations in his estimates can now be evaluated from the more accurate time-dependent analytical solutions developed by us.

Subsequently, near-field mass-transfer calculations have been used for the three U.S. waste-isolation projects,^{6,7,8,9} and some of the new Berkeley analytical tools^{5,13} have been incorporated in the Pacific Northwest Laboratory's computer code¹⁰ for waste-package performance assessment. Near-field mass-transfer analyses and calculations are now incorporated in the Canadian¹¹ and Swiss¹² repository programs.

MASS TRANSFER FROM A WASTE SOLID INTO POROUS ROCK

Illustrative results

Figure 1 illustrates some results obtained from mass-transfer theory. Here an equivalent spherical waste package containing spent fuel is surrounded by, and in direct contact with, saturated porous rock. Ground

water flow is slow enough that near-field transport is controlled by molecular diffusion, typical of expected conditions in the U.S. repository programs. The fractional release rate, defined here as the mass rate of dissolution of a radionuclide species divided by the initial inventory of that species in the waste solid, is plotted against the time since the beginning of dissolution. For long-lived species, such as U-234, Cs-135, and I-129, this is numerically equal to USNRC's fractional release rate based on the inventory of such species at 1000 years.

The lower curve is for the solubility-limited dissolution of species released congruently with uranium from UO_2 matrix, calculated from the exact analytical solutions⁵ for the time-dependent mass transfer, assuming saturation concentration of the dissolved uranium in ground water at the waste surface and for a uranium solubility of 0.001 g/m^3 for reducing conditions.³ Fractional release rates of such congruently dissolving species with half lives lower than that of uranium will depart from and fall below the uranium curve at times of the order of their half lives. These fractional release rates into the rock are well below the USNRC guideline of $10^{-5}/\text{yr}$. Under oxidizing conditions the uranium solubility can increase markedly, by five or six orders of magnitude, but not enough for the predicted rate of net dissolution to exceed the guideline limit.

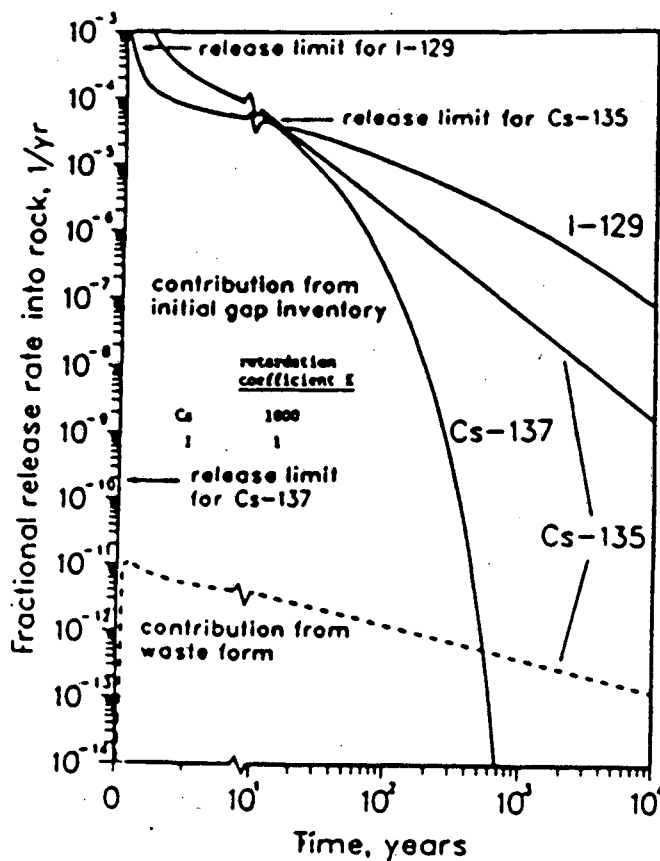


Figure 1. Fractional release rates into rock as a function of time (early container failure, 10 cm of void water, 1% of total cesium and iodine in gap. $D = 0.12 \text{ m}^2/\text{yr}$).

The upper curves of Figure 1 apply to the release of the more soluble species, e.g., cesium and iodine, that were released from the UO_2 matrix during reactor operation and are present in UO_2 grain boundaries and pores and in the fuel-cladding gaps. The curves are calculated from the analytical solutions¹³ for the transient diffusive mass transfer into surrounding porous rock, given a specified initial amount of soluble

species dissolved in ground water that has filled voids in the waste package. Assuming that 1 percent of the total inventory of these soluble species are in this readily soluble "gap activity", the predicted mass rates of release into the rock divided by the total initial inventory of each species are orders of magnitude greater than the fractional releases from matrix dissolution. Because the 1000-year inventories of cesium and iodine, expressed in curies, are each less than 0.1 percent of the total curie activity of the waste at 1000 years, numerical limits for fractional release rate of these species can be calculated¹⁴ from USNRC's numerical criteria for low-inventory constituents. These calculated limits, applicable when the fractional release rate is based on the inventory at the time of emplacement, are shown in Figure 1. The limits for Cs-135 and I-129 are exceeded for an individual waste package only during the first few days of dissolution and may be easily met for the average waste package if not all waste-package containers fail at the same time. The limit for Cs-137 is exceeded if an appreciable number of waste containers fail not long after emplacement, but it is easily met if all waste containers remain intact for 300 years or more.

The time-dependent mass release rates used to construct Figure 1 can also be used as time-dependent source terms for far-field transport analysis.

Subsequent sections of this report discuss possible limitations of the analyses used to produce Figure 1 and also discuss the effects of additions to the waste-package-rock system that may be more realistic in some situations, such as backfill, more rapid ground water flow, time-dependent temperatures, rock fractures, etc.

Mass Transfer for Solubility-Limited Species, Controlled by Diffusion in Pore Liquid

The illustrative results in Figure 1 are calculated from the equations for time-dependent mass transfer by molecular diffusion,^{5,13} applicable for the low ground-water flow rates typical for repositories in basalt, tuff, or salt. Exact analytical solutions for the time-dependent rate of mass transfer from waste forms of various shapes has been obtained.⁵ The steady-state form of that equation for a low-solubility long-lived species, assuming constant saturation concentration N^* in the liquid at the waste surface and assuming that the waste solid is surrounded by porous rock, is:

$$f_i = \frac{\beta \epsilon D N_i^*}{n_i} \quad (1)$$

where f_i is the fractional dissolution rate of species i , ϵ is the porosity of the rock, D is the diffusion coefficient in pore water, and n_i is the concentration of the species in the waste solid. β is a geometrical factor that can be calculated from the waste-form dimensions and is $3/R^2$ for a spherical waste of radius R .

It is also important to examine the higher release rates that occur before steady state is reached and that can occur with radioactive species, as predicted by the exact analytical solutions.⁵ If the waste solid can react with ground water rapidly enough to maintain near-saturation in liquid at the waste surface, the early rate of mass transfer will be high, and it will decrease as the concentration profile penetrates farther from the waste surface. Greater sorption retardation increases the time to steady state, and it increases the transient dissolution rate because sorption steepens the concentration gradient.

Solubility-Limited Mass Transfer With Diffusion and Advection

We have⁵ also developed the exact analytical solution for the time-dependent mass transfer when both diffusive and convective transport are important. The mathematical analysis makes use of the known distribution of ground water velocities around an infinite cylinder and through the pores of the surrounding rock. An asymptotic form of that analytical solution, applicable to steady-state mass transfer of a solubility-limited stable species with steady flow around a long waste cylinder surrounded by porous rock, is:

$$f_i = \frac{8\pi N_i^* (DU)^{1/2} (1 + R/L)}{(\pi R)^{3/2} n_i}, \quad Pe > 4 \quad (2)$$

The Peclet number Pe is given by UR/D , where U is the ground water pore velocity upstream of the waste solid, R is the radius of the waste solid, and L is the length of the waste cylinder.

Equations for the steady-state dissolution rate that are similar in form, but not identical, to Equation (2) have been obtained by others^{2,7,8,15} using boundary-layer approximations. However, only the exact mathematical solution provides a criterion of validity of the asymptotic steady-state equation, Equation (2). Ignoring the limit of validity and applying the steady-state asymptotic equation, or its equivalent^{7,8,15}, to predict mass transfer rate at the very low velocities expected in U.S. repositories is not valid and will give nonconservatively low estimates of the dissolution rate.

Correct and incorrect predictions of fractional dissolution rate over a wide range of Peclet numbers are illustrated in Figure 2, calculated for solubility-limited mass transfer of UO_2 , from a spherical-equivalent waste solid of radius 48.6 cm. The upper curve is estimated at 100 years, with a retardation coefficient of 100. The lower curve is for steady state. The dotted curve shows an incorrect extrapolation of the steady-state $Pe^{1/2}$ dependency from the high Pe region to the pore velocities of a few millimeters per year,⁷ expected in the tuff and basalt repositories; resulting in underestimates of the release rate by several orders of magnitude. The porosity used was 0.1, the diffusion coefficient 10^{-5} cm^2/sec ($315 \text{ cm}^2/\text{yr}$) and the UO_2 solubility in an oxidizing environment 5×10^{-5} g/cm^3 .

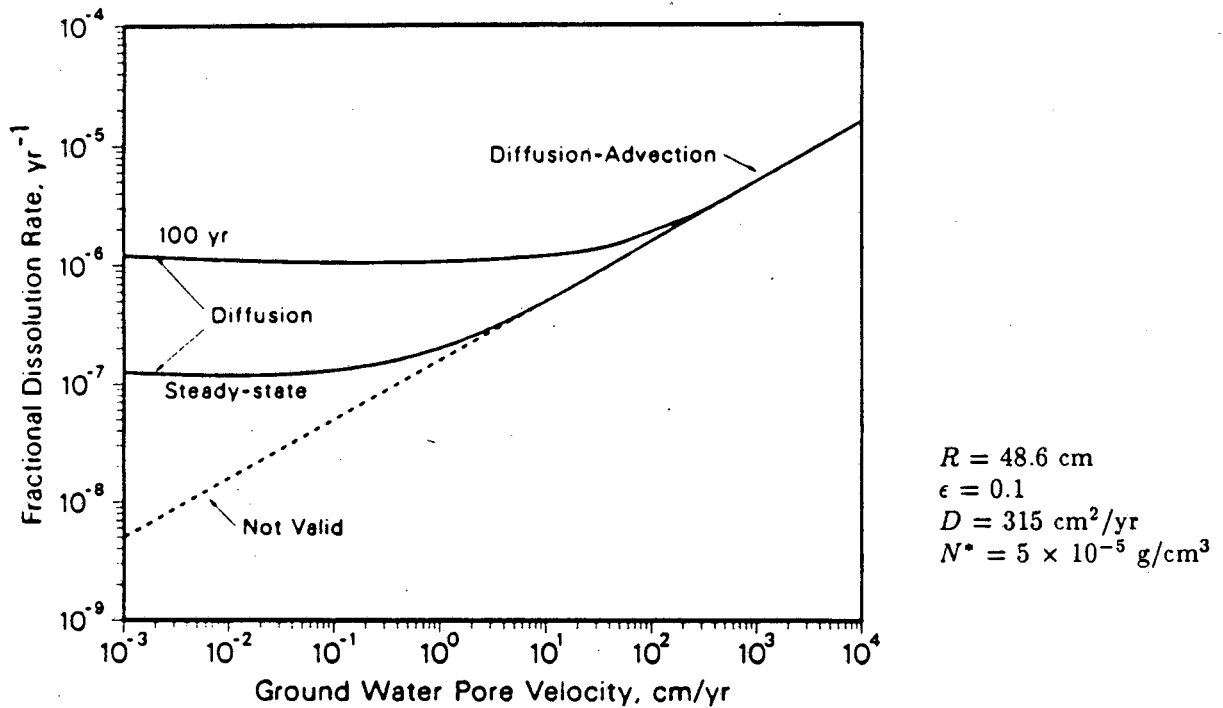


Figure 2. Extrapolations of fractional dissolution rates for UO_2 to low flows in an oxidizing environment.

For an assumed waste radius of 48.6 cm and an upper-limit value of the diffusion coefficient of 10^{-5} cm^2/sec ($315 \text{ cm}^2/\text{yr}$), which neglects tortuosity corrections, the ground water pore velocity must be about 3 m/yr or greater for the steady-state equation (2) to be applicable. Although such velocities may be expected in some repositories, the ground water velocities expected for prospective U.S. repositories in basalt, tuff, and salt are orders of magnitude lower. However, if tortuosity reduces the diffusion coefficient a hundred-fold, the steady-state equation (2) is applicable to pore velocities as low as 3 cm/yr, still larger than those predicted for the U.S. repositories. For the lower velocities the equations for diffusion-controlled release are applicable.

Equations for the time-dependent fractional release rate for a radioactive species with a constant-concentration boundary condition are also given.⁵ The early rate of mass transfer will be high, and it

will decrease as the concentration profile penetrates farther from the waste surface. With no decay, steady state is reached in as little as a year or not until a few hundred years, depending on the magnitude of the retardation coefficient K . Greater sorption retardation increases the time to steady state, and it increases the transient dissolution rate because sorption steepens the transient concentration gradient. Advective transport shortens the time to reach steady state.

Increasing the radioactive decay constant λ increases the rate of mass transfer by steepening the concentration gradient near the waste surface. Increasing the modified Damkohler modulus $K\lambda R/U$ from zero, for no decay, to 10 causes a more than fourfold increase in the steady-state dissolution rate, and it decreases the time to reach steady state. For a mixture of stable and unstable isotopes of a given element, the appropriate half life is the effective half life of the isotopic mixture at the time the decay correction is to be applied. Decay corrections are more important when mass transfer is controlled by diffusion, i.e., when the pore velocity is so low that convection does not affect dissolution.

Dependence on Waste-Form Material Properties: Solid-Liquid Reaction Rate

The analytical solutions discussed above for solubility-limited mass transfer have a clear meaning for a single-component waste solid that has a well-defined solubility appropriate to the chemical environment at the waste surface. Solubility is a conservative upper-limit boundary concentration, if effects of colloids can be neglected. The result is a bounding estimate of the release rate from the waste solid that does not depend on the particular chemical form of the waste solid unless that chemical form itself affects the solubility of the single-component species. Effects on other constituents within the waste solid will be discussed later.

In many studies it has been assumed that waste forms can be developed that will perform better in a repository because of low rates of chemical reaction of the waste solid with ground water. The proposition is reasonable but has been made without quantification of the effect of chemical reaction rate on the performance of a waste solid in a repository. In the mass-transfer analyses discussed above for solubility-limited species, it has been implicitly assumed that the solid-liquid reaction rate is rapid enough so that the dissolved material is at, or very near, the solubility limit at the waste surface. Actual chemical reaction rates do not enter that analysis, and the bounding results from that analysis are not influenced by factors which can affect solid-liquid reaction rate, such as interior cracks in the waste solid, devitrification if a glass, and other such mechanisms that could increase the surface area for solid-liquid reactions.

To illustrate an approach to determine the effect of solid-liquid reaction rate on the rate of mass transfer to ground water in a geological environment, an analytical solution for the rate of diffusive mass transfer of a dissolved waste into surrounding porous rock was developed,¹⁷ using chemical reaction rate as a boundary condition instead of assuming a solubility-limit boundary concentration. Leach-rate data¹⁸ for borosilicate glass waste suggest that the solid-liquid reaction rate can be approximated by a zero-order forward reaction and a back reaction that is first order with respect to the concentration of dissolved silica. The continuity boundary condition at the waste-liquid interface in a repository specifies that the current of dissolved species at the waste outer surface equal the net rate of dissolution by solid-liquid reaction:

$$-cD \frac{\partial N(R, t)}{\partial r} = j_o \left(1 - \frac{N(R, t)}{N^*} \right), \quad t > 0 \quad (3)$$

where $N(R, t)$ is the concentration of dissolved species in liquid at the spherical waste surface and j_o is the experimental forward reaction rate of the dissolved species per unit surface area. The forward reaction rate is measured when the surface is in contact with a liquid that contains none of the dissolved species being considered in Eq. (3).

Using the above boundary condition together with the diffusion equation and with other side conditions, the time-dependent concentration in the liquid in the porous rock and the time-dependent net dissolution rate $j(R, t)$ are obtained¹⁷. At steady state the concentration and mass-transfer rate at the surface are:

$$N(R, \infty) = N^* \frac{\alpha}{1 + \alpha} \quad (4)$$

$$j(R, \infty) = \frac{j_0}{1 + \alpha} \quad (5)$$

where

$$\alpha \equiv \frac{j_0 R}{\epsilon D N^*} \quad (6)$$

Eqs. (4) and (5) show that when α is large $N(R, \infty) \approx N^*$ and $j(R, \infty) \approx \epsilon D N^* / R$. Under these conditions the net dissolution rate is controlled by diffusion in the exterior field. When $\alpha \ll 1$ the surface concentration $N(R, \infty)$ is much less than the saturation concentration and the net mass-transfer rate is controlled by the solid-liquid reaction and is equal to j_0 . For intermediate values of α one must use Eqs. (4) and (5) for steady state and the analytical solution for transient values of $N(R, t)$ and $j(R, t)$. The analysis of the surface concentration and dissolution rate with species decay in the waste form and in the exterior field has also been treated.

To illustrate, we assume a waste glass cylinder of radius 0.15 m and length 2.4 m, resulting in an equivalent sphere of radius 0.44 m. From the laboratory leach data¹⁸ for PNL 76-68 borosilicate glass we derive the following effective values for silica at 90°C: $j_0 = 1.18 \text{ g SiO}_2/\text{m}^2\text{day}$, and $N^* = 200 \text{ g SiO}_2/\text{m}^3$. For an estimated diffusion coefficient of silicic acid in water at 90°C of $2 \times 10^{-2} \text{ m}^2/\text{d}$ and neglecting tortuosity corrections, and for a rock porosity of 0.01, we estimate $\alpha = 1240$. Assuming no sorption of silica on the rock ($K = 1$), the estimated time to steady state is 320 years. From Eq. (4) $N(R, \infty) = 0.999 N^*$ for silica. The steady-state mass transfer of silica will be controlled by exterior-field diffusion, and assuming saturation concentration N^* of silica at the waste surface is not only conservative but is also realistic.

Our more detailed illustration¹⁷ shows the surface mass flux of silica and the surface concentration as a function of time. If saturation at all times were assumed the early mass-transfer rate would be infinite, a result not physically reasonable. It is in these early times that the solid-liquid reaction rate is important for the dissolution of a low-solubility solid matrix. The actual surface concentration is initially zero, and it grows with time at a finite rate determined by the solid-liquid reaction rate. Within about seven minutes after bare glass waste has been placed in contact with low-porosity water-saturated rock the concentration of nonsorbing silica in the surface liquid will have reached 82 percent of saturation and the mass-transfer rate will be within 5 percent of that predicted for constant saturation at the surface, assuming no silica sorption in the rock. If silica sorbs with an assumed retardation coefficient of 100, this time is increased to 700 minutes.

The time to reach near-saturation concentration will be longer if there is stagnant liquid between the waste surface and the exterior porous medium. This time delay is easily added to the theory because the intervening liquid is likely to be well mixed.

Van Luik *et al.*¹⁹ list values of j_0 for unirradiated and irradiated UO_2 in deionized water and in brine at various temperatures. They adopt a conservatively low value of $j_0 = 0.005 \text{ g/m}^2 \text{ day}$. Assuming that uranium dissolution obeys a simple concentration dependence as described in Eq. (3), adopting uranium solubilities ranging from $2 \times 10^{-2} \text{ g/m}^3$ at pH 11 to $2 \times 10^{-8} \text{ g/m}^3$ at pH 6,¹⁹ and for other parameters the same as used in the above example for silica, we obtain an estimated flux ratio for the spent-fuel matrix of 5×10^4 to 5×10^5 , greater by one to seven orders of magnitude than that estimated for silica from borosilicate glass. If these data are correct, uranium dissolution in a geologic repository is likely to be controlled by exterior-field mass transfer and not by chemical reaction rate. More data are needed on solid-liquid reaction rate as a function of concentration of dissolved uranium and of temperature.

In a separate paper in these proceedings²⁰ we present a new analysis of the role of chemical reaction when steady-state mass transfer from the waste solid can be controlled by both advection and diffusion. For borosilicate glass waste in the temperature range of 57°C to 250°C, the steady-state dissolution rate is affected by chemical reaction rate only at Peclet numbers well above 100, far beyond any flow rate reasonably expected in a repository.

Release of Other Species From a Low-Solubility Waste Matrix

If there is no preferential leaching of other chemical elements contained in the low-solubility waste matrix, all constituents in the matrix will be released congruently as the matrix dissolves. For a congruently released species that dissolves when released from the waste solid, the instantaneous fractional dissolution rate of that species will be identical with the instantaneous fractional dissolution rate of the waste matrix and will be controlled by the matrix solubility. For rigor, the fractional dissolution rate must be interpreted here as the instantaneous mass rate of dissolution of a species divided by the inventory of that species at that same instant. Thus, if congruency of release and dissolution can be established, the equations for solubility-limited dissolution of a single-component waste solid can be applied to the waste matrix, thereby yielding the fractional dissolution rates of the constituents.

Leaching experiments on borosilicate glass containing waste actinides have shown that some of the contained actinides dissolve less rapidly than would be predicted by congruency with the silica matrix, and saturation concentrations of neptunium and plutonium in leach solutions are found to equal the solubilities of the stable compounds formed when these actinides react with the aqueous leachant.²¹ This suggests that actinides released when the silica dissolves form precipitates at the waste surface. For any such constituent whose dissolution rate is limited by its own solubility, the fractional dissolution rate can be predicted by applying the single-component mass-transfer equations developed by us, using the measured solubility of that species for its boundary concentration. The results will be valid if the instantaneous fractional dissolution rate of that species, based on its own solubility, is less than the instantaneous fractional dissolution rate of the waste matrix.

If the low-solubility constituent whose release is controlled by its own solubility is an isotope of an element with other isotopes present, the solubility concentration in the mass-transfer equation should be replaced by the elemental solubility multiplied by the isotopic fraction of the isotope of interest. This can be formulated exactly if the radionuclide of interest is a minor isotopic constituent of its elemental species in the waste solid. It is an approximation if the radionuclide of interest is present in an isotopic concentration similar in magnitude to that of another isotope of that element but of different half life.

In applying the mass-transfer theory to the dissolution of borosilicate glass waste in a typical repository environment, it is predicted^{3,22} that the actinides in the waste will dissolve at a rate limited by their own solubilities. However, for unprocessed spent fuel, the low solubility of uranium in reducing conditions and the high concentration of uranium in the waste result in a predicted fractional dissolution rate of the waste matrix in a repository environment that is much lower than for borosilicate glass. If the contained constituents are released congruently, they are predicted to dissolve at a rate limited only by uranium solubility. To make reliable predictions of the performance of spent fuel in a repository, it is important to establish experimentally the extent to which constituents in the uranium dioxide matrix dissolve congruently. The experiments should be performed with a leachant at near-saturation concentration with respect to the waste matrix, because this is the surface-liquid concentration predicted for the repository environment.

The instantaneous fractional release rate of a species limited by its own solubility is predicted to be proportional to the solubility of that species divided by its concentration in the waste solid. Species present only in small or trace concentrations are more likely to be limited in dissolution rate by the matrix solubility. Low-solubility radioactive species initially present in sufficient concentrations to be dissolution-rate-limited by their own solubility can eventually decay to a concentration low enough to be dissolution-rate-limited by the matrix solubility.

Diffusive Mass Transfer of Soluble Species

In a spent-fuel waste package the soluble cesium and iodine accumulated in fuel-cladding gaps, voids, and grain boundaries of spent fuel rods are expected to dissolve rapidly when groundwater penetrates the fuel cladding. Even though dissolution may be rapid, the rate of release of these soluble species from the waste package will be limited by the rate of mass transfer of the dissolved species into the surrounding porous media. We have developed the analytic solution for the fractional release rate of a readily soluble radioactive species, assuming instantaneous dissolution of the soluble species into a volume of ground water

that has penetrated in the waste package voids at $t = 0$, and assuming that the ground-water flow rate is small enough that mass-transfer into surrounding porous rock is controlled by molecular diffusion.

The results are illustrated in the upper curves in Figure 1, assuming that one percent of the total cesium and iodine is readily soluble "gap" activity and assuming void water equivalent to a 10-cm layer between the fuel rods and the surrounding rock. With these assumed parameters, the release rates of the soluble activity are more than 107-fold greater than the congruent release rates of these same species from the solubility-limited waste matrix. For early times the fractional release rates of cesium-135 and cesium-137 are almost equal, but the cesium-137 release rate decreases rapidly because of radioactive decay, whereas the release rate of 3×10^6 -year cesium-135 is characteristic of a long-lived or stable species. Because of the assumed negligible sorption of iodine in the surrounding rock, the early fractional release rate of 1.7×10^7 -year iodine-129 is lower than the rates of strongly sorbing cesium, but the less rapid early depletion of iodine in the void water results in a greater fractional release rate of iodine after about 20 years.

OTHER ASSUMPTIONS IN THE MASS-TRANSFER THEORY

Effect of a Liquid-Filled Annulus Between Waste and Rock

The mass-transfer analyses discussed above assume that the waste solid is in contact with porous rock containing ground water. The assumption of a constant solubility-limit boundary concentration for low-solubility species has been discussed above. The theory assumes conservatively that the corrosion-resistant container of the waste package has failed and that its corrosion products offer no resistance to mass transfer. If there is a liquid-filled annulus between the waste package and the rock, or between the waste solid and the rock, the mass-transfer equations are still applicable, provided there is no appreciable convective flow through the annulus. It is reasonable to assume that the liquid between the waste solid and rock is well mixed, so the dimensions of the borehole should be used for the geometrical parameters in the mass-transfer equations. The effects of convective transport in the annulus and convective flow through the waste solid have not been analyzed.

Effect of Flow Direction and Geometry

Extensions that include the effect of a porous backfill are described later. The analyses described above have assumed that ground water flows normal to the cylindrical axis of a waste package. Other flow directions are possible in a repository. We have considered flow parallel to the axis, as well as other waste-form geometries, and have shown that predicted dissolution rates are not significantly different.

Hydrodynamic Dispersion

It has been suggested by some¹⁶ that because of hydrodynamic dispersion the effective diffusion coefficient that appears in the analytical solutions should be a value greater than that for molecular diffusion. However, experimental data^{23,24} for effective diffusion coefficients in packed columns show that for the ground water velocities and dimensions typical for individual waste packages the value for molecular diffusion should be used. At locations far enough removed from the waste surface for hydrodynamic dispersion to become important, the concentration gradients are too small to affect the mass transfer from the waste surface. However, if the same governing equations were to be applied to mass transfer over greater distances, the effect of hydrodynamic dispersion should be considered. The effective diffusion coefficient will increase with distance, requiring equations for diffusive-advective transport with a space-dependent diffusion coefficient, such as that developed by us.²⁵

Effect of Radioactive Decay

The analysis discussed above were developed for radionuclides with no radioactive-decay precursors. Some of the radionuclides important in repository performance assessment are continuously generated by decay of precursors, e.g., Ra-226 from U-234 and Th-230, and Th-229/Ra-229 from Np-237 and U-233. It is

not necessarily conservative to apply the mass-transfer equations for a species with no precursor separately to each member of the decay chain, assuming that each species is at its solubility limit in ground water near the waste surface.²⁶ Decay of a precursor in the transport field can cause solubility-limited concentration of its daughter to occur in the field further from the waste surface, resulting in greater rates of mass-transfer into the rock. This is particularly important when mass-transfer theory is used to predict the rate of transport through backfill, or through other intervening diffusing media, into surrounding rock. The greater penetration of a long-lived precursor through the backfill is a means for a shorter-lived daughter to appear at appreciable distances from the waste surface. A near-field mass-transfer analysis applicable to the simultaneous diffusive transport of a radionuclide chain has been developed and is described later.

Local Sorption Equilibrium

Most of our analysis assumes local sorption equilibrium, with a constant retardation coefficient. Mass transport without local chemical equilibrium between liquid and solid phases has been analyzed in a previous report.²⁷ Mass transfer with local sorption equilibrium but with a concentration-dependent sorption distribution coefficient is discussed elsewhere in this report.

Surface Diffusion

Most of our analysis assumes no diffusion of sorbed species on or in the solid phase. However, some experiments with selected species and solids have demonstrated appreciable surface diffusion of adsorbed species. For accurate predictions of mass transfer an experimentally determined diffusion coefficient is desirable, rather than using the upper-limit value usually adopted in our numerical illustrations. In making such measurements, it is important to check also the possibility of surface diffusion. The mass-transfer equations can be reformulated if such measurements indicate that surface diffusion need be considered.

Interference from Other Waste Packages

Most of our analysis of mass transfer from individual waste packages conservatively neglects the overlapping concentration fields resulting from species dissolved from nearby waste packages. For high-level waste packages separated by several meters the concentration fields are not expected to overlap enough in the near field to significantly reduce the mass transfer from an individual package.

Although nearby waste packages do not appreciably affect the dissolution and release rates, the overlapping concentration fields do affect the calculation of far-field transport from arrays of waste packages. Our analyses of concentration fields from arrays of waste packages^{27,28,29} show a near region in which the concentrations vary greatly in the direction transverse to ground-water flow, an intermediate region in which the array can be treated as an infinite plane source of dissolving species of the same areal source strength, and a far-field region in which the array can be treated as a plane source of finite extent. The array equations have been developed for both porous and fractured media. These intermediate-field analyses will be useful to repository projects in making detailed predictions of releases to the environment.

Porous or Fractured Rock

In the mass-transfer analysis discussed above, and extensions of these solutions described in some of the following sections, we assume that the rock surrounding the waste solid can be reasonably characterized as a porous solid. The effect of rock fractures is discussed later.

Constant Temperature

The solutions described above assume that the waste solid and surrounding rock are at a constant and spatially uniform temperature. Extensions to account for time-dependent temperatures expected if the waste solid is exposed to ground water when the repository is heated by radioactive decay have been developed. Our mass-transfer equations that predict the rate of diffusive-controlled dissolution of a low-solubility waste solid surrounded by porous rock can be applied in integral form to predict the effect of

a time-dependent repository temperature on the dissolution rate. We assume, conservatively, that at any time t the waste and rock are at a spatially uniform temperature equal to the temperature at the surface of the borehole. Time-dependent rock temperatures at the borehole surface are specified from a calculation of transient heat conduction. From these data, from data on the change of solubility and diffusion coefficient with temperature³¹, we have demonstrated the application of temperature-dependent mass-transfer analysis of solubility-limited species from borosilicate glass waste in a basalt repository.^{30,31}

Calculation of the effect of repository heating on the rate of diffusive mass transfer of soluble species into the rock is simpler³² because the only parameter affected by temperature is the diffusion coefficient, if the retardation coefficient can be assumed constant. At very early times the higher diffusion coefficient causes greater mass transfer rate from the waste-package water into the surrounding rock, depleting the concentration in the waste-package water. This early depletion results in a later mass-transfer rate that is lower than would occur if the temperature were always at the ambient temperature. Thus, for most times of interest, the release rate predicted by using a diffusion coefficient evaluated at ambient temperature is conservatively higher than the release rates corrected for repository heating.

Constant and Uniform Chemical Environment

In predicting the dissolution rate of low-solubility species it is important to examine the possibility of solubility changing with time, due to changes in the local chemical environment. For example, dissolution of borosilicate glass waste causes local changes in pH, which affects solubility of several species. Also, the oxidizing environment due to air during construction and waste emplacement can revert to a more reducing environment after repository sealing and resaturation, resulting in large changes in solubility of uranium and other species. If the chemical environment stabilizes within a few hundred years, while the protective container is still effective, the solubility corresponding to the stabilized environment would be the appropriate value to use in predicting release rates.

A longer-term mechanism for changing the chemical environment is the radiolysis of ground water due to alpha particles from transuranics in the dissolving waste. If radiolytically-produced hydrogen can escape, radiolytic peroxide can result in a locally oxidizing environment and greater solubilities of uranium, particularly important in predicting the long-term release rate from spent fuel. Neretnieks³³ has analyzed the progress of such a redox front for a spent-fuel repository in granite, determined by the rate of peroxide generation, mass transfer of the peroxide from the waste surface, and reaction of peroxide with ferrous compounds in the water and rock. The result is a moving and expanding redox front, a transition from the oxidizing region of high uranium solubility near the waste surface to the low-solubility reducing region. To predict the net rate of release of uranium across this front, the equations for mass-transfer of low-solubility species can be applied, using the radius of the redox front as the geometrical parameter.

Alpha radiolysis can affect the release of other constituents from the uranium-dioxide matrix in spent fuel. If the species dissolve congruently with the uranium, they will dissolve at a rate controlled by the higher solubility of uranium at the waste surface. If these species do not precipitate at the redox front, alpha radiolysis will have resulted in a greatly increased release of contained radioactive species to the geosystem.

A partly failed iron container may prevent the radiolytically generated oxidant from moving into the rock, and corrosion products may decompose peroxide oxidants, but it is still possible that radiolysis can create a locally oxidizing environment near the spent fuel surface that accelerates release of constituents from the spent fuel matrix.³⁴

MASS TRANSFER WITH BACKFILL BETWEEN WASTE SOLID AND ROCK

Steady-State Mass Transfer Through Backfill

We have obtained the solution to the steady-state mass transfer rate from a waste solid, through surrounding backfill, and into porous rock²², and the results have been illustrated, as a function of the backfill-to-rock porosity ratio and the Peclet number. For equal porosities of backfill and rock, backfill reduces the

mass transfer rate into rock because of the assumed zero flow in the backfill. For backfill of much greater porosity than rock, as may be expected for backfill now contemplated in U.S. repositories, increasing the backfill thickness increases the rate of mass transfer into the rock, a consequence of the increasing area of the backfill-rock interface as the backfill thickness is increased. Unless the backfill can be made far less porous than the rock, introducing backfill cannot be expected to result in large reductions in the steady-state rate of release of stable and long-lived species into the rock, assuming that the chemical environment remains the same.

When radioactive decay is included in the analysis of steady-state mass transfer, the retardation coefficient also appears. The results demonstrate that a sorbing backfill does not necessarily reduce the steady-state release rate into surrounding rock.

Time-Dependent Mass Transfer of Solubility-Limited Radioactive Species Through Backfill

The equations for the time-dependent diffusive transport of radioactive species through backfill have been developed for solubility-limited species^{22,35,36} and for the rapidly dissolving "gap" activity in spent fuel.¹³ The equations are applicable for a radioactive species with no decay precursor and for diffusion-dominated mass transfer through the backfill and the surrounding porous rock.

During the early times of transient dissolution a higher backfill porosity greatly increases the dissolution rate, because the early resistance to mass transfer is entirely within the backfill. For typical backfill properties and for a retardation coefficient of 1000 the mass-transfer rate into the rock closely approaches that into the backfill after about 10^4 years, and steady state is reached after about 10^5 years.

Increasing sorption steepens the transient concentration gradient and increases the rate of diffusive mass transfer. Steady-state rates of mass transfer of stable species are not affected by sorption. For a given backfill retardation, increasing sorption by rock increases the maximum rate of mass transfer into the rock, showing that the rock properties and finite backfill must be included in the analysis, as has been done here. For typical parameters, the maximum rate of mass transfer into the rock depends mainly on the backfill retardation.

For neptunium-237, with a half life of 2.1×10^6 years, corrections for decay are minor. For carbon-14, with a half life of 5730 years, decay not only increases the rate of mass transfer into the backfill, because it steepens the concentration profile, but it also increases the transient and steady-state rates of mass transfer into the rock. For a radionuclide half life as short as 15.3 years, decay considerably increases the mass transfer rate into the backfill, but the half life is short enough that the species all decays while diffusing in the backfill. Thus, there is a range of half lives for which the rate of mass transfer into the rock is greater than the steady-state value for no decay. As illustrated here for carbon-14, some radionuclides important in repository performance analysis will fall within this range.

Previous backfill analyses^{37,38,39} have calculated the "breakthrough" time for a stable species at a specified distance in a backfill of infinite thickness and have used that time to estimate the amount of radioactive decay that will occur during diffusion through finite backfill in a repository. This has led to considerable overestimates of the possible retention of radionuclides in backfill. Mass-transfer analysis that take into account the diffusive properties of the rock should be used to predict release of radionuclides through a backfill of finite thickness.

Time-Dependent Mass Transfer of Soluble Radioactive Species Through Backfill

We have given analytical solutions for the time-dependent diffusion of readily soluble "gap" activity through backfill and into surrounding porous rock. Illustrative results⁴⁰ for a 30-cm layer of backfill of porosity 0.2 and 1 percent release of soluble species to the fuel-cladding gap show that nonsorbing iodine-129 arrives at the backfill-rock interface in less than a year, with a peak release rate about ten-fold less than the equivalent release-rate limit calculated from the USNRC criterion.^{1,14} The peak release rates of the sorbing cesium isotopes into rock, with an assumed retardation coefficient of 1000, occur at about 100 years. The normalized release rate of cesium-137 is less than that of cesium-135 because of decay in the backfill. The

peak release rate of cesium-135 is about 10-fold less than its release-rate limit. The release limit is exceeded for cesium-137 if an appreciable number of waste containers fail not long after emplacement. For these parameters, backfill several times thicker than in current repository designs would be needed for each waste package to comply with the release-rate criterion if no container is assumed, but the present designs should be adequate for cesium-137 if all waste containers last 300 years or more.

Effect of Non-Linear Sorption on Mass Transfer Through Backfill

In the previous analyses we have assumed linear sorption in the backfill, as expressed by a retardation constant independent of concentration. Some data show nonlinear sorption in bentonite, with a tendency towards saturation of the sorption sites. For such backfill materials, the mass-transfer characteristics can be far different than those analyzed above for linear sorption. Species can be released sooner and more rapidly into the rock if sorption saturation occurs in the backfill. Analytical solutions for a mass transfer with a simplified nonlinear sorption isotherm have been given.^{22,41}

Effect of Flow in Backfill

The above analyses have assumed no ground-flow in backfill. Flow in backfill is not expected to be important in U.S. repositories because of the very low flow in the surrounding rock. In the Swedish program, where greater ground-water flow is expected, the planned backfill is compacted bentonite, of low enough permeability to result in the negligible backfill water flow that is assumed in their mass-transfer analysis². From our analysis⁴² of water flow through a spherical shell of backfill surrounded by rock, the effect of backfill water flow can be predicted.

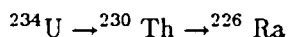
MASS TRANSFER IN FRACTURED ROCK

Neretnieks^{2,43,44} has developed an equation for steady-state mass transfer through backfill into ground water in discrete fractures, using boundary-layer approximations. The initial purpose was to predict the lifetime of a thick copper canister by predicting the rate of mass transfer of sulfide oxidant from groundwater to the canister surface. The boundary-layer approximation does not apply for very small fracture-flow Peclet-numbers, characteristic of U.S. repositories.

We have developed the solutions for time-dependent transport through backfill into a fracture with flow⁴⁵ and for transient diffusion from a waste solid with fractures in porous rock, with negligible water flow in the fractures.⁴⁶ These new analyses allow greater realism in predictions for U.S. repositories, and they also establish the region of validity of the earlier analyses of mass transfer into surrounding porous media.

MASS TRANSFER OF RADIOACTIVE DECAY CHAINS

To predict the time-dependent mass transfer of a radioactive species that is a daughter in a radioactive decay chain with long-lived precursors, it is necessary to include the simultaneous transport and decay of the precursors. We have published elsewhere⁴⁷ the fundamental equations for advective transport of decay chains in infinite media. Chambré has developed analytical solutions³⁶ to predict the release rates of decay chains with arbitrarily many members into porous rock from backfill of finite thickness. The predicted space-dependent concentrations at 1000 years after the beginning of dissolution, using Bateman-type boundary concentrations, are illustrated⁴⁸ for the decay chain



Appreciable concentrations of ²²⁶Ra near the backfill-rock interface are a consequence of the presence there of its precursors. The greatest release rate of ²²⁶Ra occurs at about 2×10^5 years.

RELEASE RATES FROM WASTE PACKAGES IN A SALT REPOSITORY

The Mass-Transfer Approach

In 1985 we proposed⁴⁹ a realistic and direct approach towards predicting radionuclide release rates in a salt repository based on mass-transfer analysis. Recognizing that within a few years after the emplacement of waste packages in a geologic repository salt creep is likely to close the air gap between a waste container and the borehole wall, we proposed that thereafter release rate of dissolved species from the waste solid is likely to be governed by mass transfer into brine in grain boundaries in the surrounding salt and in intersecting interbeds of other rock. Because of the low expected migration velocities of brine in the consolidated salt, mass transfer dominated molecular diffusion was a likely possibility. If so, many of the mass-transfer analyses described above could be adapted to predicting release rates in a salt repository.

Subsequent analyses of creep closure and consolidation by Brandshaug⁵⁰ confirms that consolidation is expected within a few years after emplacement.

Brine Migration Velocities

During the consolidation period most of the brine inclusions in salt crystals near the waste package are predicted to have moved to grain boundaries under the influence of temperature gradients. After salt consolidation brine in grain boundaries near the waste package can only migrate outward into the surrounding salt, under the influence of pressure gradients caused by transient heating of the salt. Hot salt near the waste package expands against the waste package and surrounding salt, resulting in high compressive stresses near the waste package. Grain-boundary brine expands more than does the salt and further increases the local pressures and pressure gradients that cause brine to flow outward into the cooler salt. Such outward flow of brine relieves the pressure gradient on the fluid, which finally relaxes to near-lithostatic pressure.

To determine the extent to which advection by brine in grain boundaries is an important transport mechanism for released radionuclides, we have estimated the time-dependent migration of brine after salt consolidation. Based on current interpretations of experimental data on the migration of grain-boundary brine in natural salt deposits, it is assumed that the migration velocity is proportional to the local gradient in fluid pressure. To find the time-dependent pressure profile, we have adopted the governing equations for the thermoelastic stresses and deformation of salt due to thermal expansion of the salt and of its contained grain-boundary brine developed by McTigue.⁵¹ Based on calculated time-dependent temperature profiles in the salt after waste emplacement and utilizing thermoelastic and permeability parameters deduced by McTigue for salt at the Waste Isolation Pilot Plant in New Mexico, our analytical solutions for the time-dependent profiles of pressure and brine velocity provide means to estimate the effect of brine migration on radionuclide release to salt.⁵² Consolidation is assumed to have occurred instantaneously. We assume, conservatively, that the waste container has completely failed during consolidation or shortly thereafter.

With these parameters, the brine migration velocity is nearly zero after ten years. Even the highest velocity is of the order of millimeters per year and occurs only with a meter or so of the waste package. The predicted velocities are so low that molecular diffusion may be the dominant transport process for radionuclides in salt. This is likely to be true if the diffusion coefficient is near 10^{-5} cm²/sec, a typical value for a liquid continuum, or even if it is reduced a hundred-fold by tortuosity.

More realistically, if the waste container is effective for several tens or hundreds of years, the temperature and pressure gradients will have relaxed and the migration velocities are expected to be so low that convective transport seems even less likely.

These conclusions are tentative, however, because of the considerable uncertainties in the appropriate properties of salt to be used in the calculation of pressure gradients and velocities.

Release Rates by Diffusion

As a result of the foregoing analysis of brine migration, we assume that after salt consolidation mass

transfer of dissolved species away from the waste solid is governed by molecular diffusion, so that the equations for the time-dependent diffusive transfer of dissolved species from a waste solid into porous rock can be applied. The waste container is conservatively to have failed during consolidation, or shortly thereafter, so that brine at the waste surface begins to dissolve the spent-fuel waste and its contained radioactive species. Assuming a waste solid 0.72 m in radius, a diffusion coefficient of 10^{-7} cm²/sec, salt porosity of 0.001, a uranium retardation coefficient of 20, and uranium solubility of 0.001 g/m³, we estimate the fractional release rate for uranium of the order of 10^{-12} /yr and less.⁹

Similarly, applying the equations for the time-dependent diffusive release of the readily-soluble gap inventory of cesium and iodine, assuming that one percent of the initial iodine and cesium is in the readily soluble form and assuming 0.45 m³ of void water in the failed waste package, we obtain fractional release curves for I-129, Cs-135, and Cs-137 similar to those shown in Figure 1, but of lower magnitude because of the expected lower diffusion coefficient.

To estimate the release rates from a waste package into more porous interbeds that may intersect the borehole in a salt repository, we can apply our new analytical solution for the time-dependent transport from a waste cylinder into a fracture with negligible water flow.

DIFFUSION-LIMITED RELEASE RATES FROM WASTE PACKAGES IN A TUFF REPOSITORY

The design for a waste repository in unsaturated tuff provides an air gap between each waste package and the surrounding rock. Infiltration water can drip on the waste package. During the thermal period the hot waste evaporates infiltration water at atmospheric pressure, resulting in no liquid pathways for transport of radionuclides from the waste package. The tuff project⁵³ estimates later liquid releases of dissolved radionuclides from a waste package by multiplying saturation concentrations of waste constituents by the volume flow rate of ground water contacting each waste package. The simple predictive theory seems reliable and requires only data on flow rate and saturation concentrations. It also requires validation that the porous rock does not contact the waste package or that the annular gap does not fill with sediments. Otherwise, diffusion pathways for dissolved species on the waste surface into ground water in the partly saturated pores of the surrounding rock can result in transient diffusive mass-transfer rates as much as three orders of magnitude greater than the bulk-flow solubility-limited release rate at the low flow rates predicted for the tuff repository, depending on the magnitude of the diffusion coefficient. Therefore, key issues of validating waste-package release rate predictions include the long-term integrity of the air gap and the diffusion coefficient for dissolved species in tuff.

The tuff project also presents⁵³ an alternative estimate of the release rate from a waste package in contact with moist tuff, based on a mass-transfer equation^{7,8} developed from a boundary-layer approximation. As has been pointed out earlier, it is invalid to apply such equations developed from boundary-layer approximations to predict mass transfer at the low water infiltration rates (ca. 0.003 to 1 mm/yr) estimated for the tuff project. Also, it is nonconservative to apply the equation for steady-state mass transfer, developed from boundary layer theory, because the transient release rates will be much higher than the steady-state rate for a very long period.

Our estimates for the possible release rates for a tuff repository, assuming conservatively that there are liquid diffusive pathways into the surrounding rock, are based on applying the equations for diffusive-controlled mass transfer discussed herein. The preliminary results for solubility-limited dissolution of spent fuel, based on solubility and porosity used by the tuff project and assuming a diffusion coefficient of 10^{-5} cm²/sec, predict diffusion-controlled release rates over 1000-fold greater than those estimated elsewhere,⁵³ but still within regulatory limits. Corrections for the time-dependent repository temperatures have not been included in these preliminary estimates.

RELEASE RATES FROM WASTE PACKAGES IN A BASALT REPOSITORY

Most of the mass-transfer analyses and topics discussed herein have been illustrated with data expected to be representative for a repository in basalt. Predictions from these analytical solutions can be used as an independent check of the numerical calculations made by the project. The more extensive mass-transfer analyses reported herein, such as the effect of repository heating and the transport of radionuclide decay chains, as well as the effect of discrete fractures in the rock, can be applied to the performance assessment of a basalt repository.

ACKNOWLEDGEMENT

Work supported in part by the U. S. Department of Energy via Contract DE-AC03-76SF00098.

REFERENCES

1. U.S. Nuclear Regulatory Commission, "Disposal of High-Level Radioactive Wastes in Geologic Repositories - Technical Criteria," 10 CFR 60, Fed. Reg., 48, 120, 18194, 1983.
2. I. Neretnieks, "Transport of Oxidants and Radionuclides Through a Clay Barrier," Report KBS TR-79, February 1978.
3. 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, D. E. White, *A Study of the Isolation System for Geologic Disposal of Radioactive Wastes*, National Academy Press, Washington, D.C., April 1983.
4. P. L. Chambré, T. H. Pigford, S. Zavoshy, "Solubility-Limited Dissolution Rate in Groundwater," *Trans. Amer. Nucl. Soc.*, 43, 153 (1982).
5. P. L. Chambré, T. H. Pigford, Y. Sato, A. Fujita, H. Lung, S. J. Zavoshy, R. Kobayashi, *Analytical Performance Models*, Lawrence Berkeley Laboratory Report LBL-14842, 1982.
6. M. S. Bensky and D. L. Oliver, "Transient Diffusional Release From Waste Packages in a Repository in Basalt", *Proceedings of the Materials Research Society, Scientific Basis for Nuclear Waste Management IX*, 1986.
7. J. F. Kerrisk, "Solubility Limits on Radionuclide Dissolution," *Proceedings of the Materials Research Society, Scientific Basis for Nuclear Waste Management VIII*, C. M. Jantzen, J. A. Stone, R. C. Ewing, eds., 44, 237-244, 1985.
8. J. F. Kerrisk, "Solubility Limits on Radionuclide Dissolution At a Yucca Mountain Repository," Report LA-9995-MS, May 1984.
9. P. L. Chambré, Y. Hwang, W. W.-L. Lee and T. H. Pigford, "Release Rates from Waste Packages in a Salt Repository," *Trans. Am. Nucl. Soc.*, 55, 131-132 (1987).
10. A. M. Liebetrau, M. J. Apted, D. W. Engel, M. K. Altenhofen, C. R. Reid, D. M. Strachan, R. L. Erikson, and K. I. Johnson, "The Analytical Repository Source-Term (AREST) Model: Description and Documentatuion," Pacific Northwest Laboratory Report PNL-6346, 1987.
11. N. C. Garisto and D. M. LeNeveu, "A Vault Model for the Assessment of Used Fuel Disposal in Canada," *Proceedings of the Materials Research Society, Scientific Basis for Nuclear Waste Management XI*, M. J. Apted and R. E. Westerman, eds., 1988.
12. R. J. Hopkirk, D. J. Gilby and W. H. Wagner, "Modelling of Solute Transport in the Near Field of a High Level Waste Repository," Report 85-26, Polydynamics Ltd, Zurich, 1986.
13. C. L. Kim, P. L. Chambré and T. H. Pigford, "Mass-Transfer-Limited Release of a Soluble Waste

- Species," Lawrence Berkeley Laboratory Report LBL-20899, June 1986.
14. T. H. Pigford, "Can Cs-137 be Dismissed Under the NRC Release-Rate Criterion for Geologic Repositories," Report UCB-NE-4088, July 1986.
 15. J. I. Scott and C. M. Koplik, "Analytic Models for Assessing the Performance of Engineered Barriers in a Basalt Repository," *Proceedings of the Materials Research Society, Scientific Basis for Nuclear Waste Management VII*, G. L. McVay, ed., 26, 1077-1084, 1984.
 16. B. Ross, "Models for Calculating Dissolution Rates of High-Level Waste," *Nuclear Safety*, 28, 362-373, September 1987.
 17. S. J. Zavoshy, P. L. Chambré, and T. H. Pigford, "Mass Transfer in a Geologic Environment," *Proceedings of the Materials Research Society, Scientific Basis for Nuclear Waste Management VIII*, C. M. Jantzen, J. A. Stone, R. C. Ewing, eds., 44, 311-322, 1985.
 18. L. R. Pederson, C. Q. Buckwalter and G. L. McVay, "The Effect of Surface Area to Solution Volume on Waste Glass Leaching," *Nucl. Tech.*, 62, 151 (1983).
 19. A. E. van Luik, M. J. Apted, W. J. Bailey, J. H. Haberman, J. S. Shade, R. E. Guenther, R. J. Serne, E. R. Gilbert, R. Peters, R. E. Williford, "Spent Nuclear Fuel as a Waste Form for Geologic Disposal: Assessment and Recommendations on Data and Modeling Needs," Report PNL-6329, 1987.
 20. P. L. Chambré, C. H. Kang, W. W.-L. Lee and T. H. Pigford, "The Role of Chemical Reaction in Waste-Form Performance," *Proceedings of the Materials Research Society, Scientific Basis for Nuclear Waste Management XI*, M. J. Apted and R. E. Westerman, eds., 1988.
 21. D. Rai and R. G. Strickert, "Maximum Concentrations of Actinides in Geologic Media," *Trans. Amer. Nucl. Soc.*, 33, 185 (1980).
 22. P. L. Chambré and T. H. Pigford, "Prediction of Waste Performance in a Geologic Repository," *Proceedings of the Materials Research Society, Scientific Basis for Nuclear Waste Management VIII*, G. L. McVay, ed., 26, 985-1008, 1984.
 23. T. K. Sherwood, R. L. Pigford, and C. R. Wilke, *Mass Transfer*, 129-137, McGraw-Hill, New York, 1975.
 24. H. O. Pfannkuch, "Contribution a l'etude des deplacement de fluides miscible dans un milieu poreux," *Rev. Inst. Fr. Petrol.*, 18(2), 215 (1982).
 25. C. H. Kang, P. L. Chambré, T. H. Pigford, "One-Dimensional Advective Transport with Variable Dispersion," *Trans. Am. Nucl. Soc.*, 50, 140-141 (1985).
 26. U.S. Department of Energy, "Environmental Assessment: Reference Repository Location, Hanford Site, Washington," Report DOE/RW-0070, 2, 1986.
 27. T. H. Pigford, P. L. Chambré, M. Albert, M. Foglia, M. Harada, F. Iwamoto, T. Kanki, D. Leung, S. Masuda, S. Muraoka, and D. Ting, *Migration of Radionuclides Through Sorbing Media: Analytical Solutions - II*, Lawrence Berkeley Laboratory Report LBL-11616, October 1980.
 28. C. L. Kim, P. L. Chambré, W. W.-L. Lee and T. H. Pigford, "Radionuclide Transport From an Array of Waste Packages in a Geologic Repository," *Trans. Am. Nucl. Soc.*, 54, 109 (1987).
 29. J. Ahn, P. L. Chambré, T. H. Pigford and W. W.-L. Lee, "Radionuclide Dispersion From Multiple Patch Sources Into a Rock Fracture," Report LBL-23425 (1987).
 30. P. L. Chambré, W. J. Williams, C. L. Kim and T. H. Pigford, "Time-Temperature Dissolution and Radionuclide Transport," *Trans. Am. Nuc. Soc.*, 46, 131 (1984).
 31. T. H. Pigford, P. L. Chambré, and S. Zavoshy, "Effect of Repository Heating on Dissolution of Glass Waste," *Trans. Am. Nucl. Soc.*, 44, 115 (1983).

32. C.-L. Kim, P. L. Chambré, W. W.-L. Lee, and T. H. Pigford, "Variable Temperature Effects on Release Rates of Readily Soluble Nuclides," Lawrence Berkeley Laboratory Report UCB-NE-4115, 1987.
33. I. Neretnieks, "Migration model for the near field, Final Report," KBS Report 82-24, (1982).
34. N. C. Garisto, K. B. Harvey, F. Garisto and L. M. Johnson, "Source Term Models for the Assessment of Nuclear Fuel Waste," *Proc. Waste Management '86*, 397-401, Tucson, Arizona, 1986.
35. P. L. Chambré, H. Lung, and T. H. Pigford, "Time-Dependent Mass Transfer Through Backfill," *Trans. Amer. Nucl. Soc.*, 46, 132 (1984).
36. 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*, Lawrence Berkeley Laboratory Report LBL-19430, 1985.
37. E. J. Nowak, "The Backfill Barrier as a Component in a Multiple Barrier Nuclear Waste Isolation System," Sandia National Laboratories Report SAND 79-1109, October 1978.
38. T. M. Ahn, K. S. Czyscinski, E. M. Franz, C. J. Klamut, B. S. Lee, N. S. McIntyre, K. J. Swyler, R. J. Wilke, "Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria for the NRC," Report NUREG/CR-23333, Vol. 4, 1982.
39. T. M. Ahn, R. Dayal, and R. J. Wilke, "Evaluation of Backfill as a Barrier to Radionuclide Migration in a High Level Waste Repository," Appendix A in: Dayal, *et al.*, "Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria for the NRC," Task 1, Waste Package Overview, Report NUREG/CR-23333, BNL-NUREG-51458, Vol. 1, 1982.
40. P. L. Chambré, C. H. Kang, W. W.-L. Lee and T. H. Pigford, "Mass Transfer of Soluble Species Into Backfill and Rock," *Trans. Amer. Nuc. Soc.*, 53, 136 (1986).
41. H. C. Lung, P. L. Chambré, T. H. Pigford, "Nuclide Migration in Backfill With a Nonlinear Sorption Isotherm," *Trans. Amer. Nucl. Soc.*, 45, 107 (1983).
42. P. L. Chambré, C. H. Kang and T. H. Pigford, "Flow of Ground Water Around Buried Waste," *Trans. Am. Nuc. Soc.* 52, 77 (1986).
43. I. Neretnieks, "Stationary Transport of Dissolved Species in the Backfill Surrounding a Waste Canister in Fissured Rock: Some Simple Analytical Solutions," *Nucl. Technol.*, 72, 194 (1986).
44. I. Neretnieks, "Source Term Modeling in the KBS-3 Study," Proceedings of the Workshop on the Source Term for Radionuclide Migration from High-Level Waste or Spent Fuel Under Realistic Repository Conditions, Albuquerque, November 1984, pp. 41-68, Report SAND85-0380.
45. C. H. Kang, P. L. Chambré, W. W.-L. Lee and T. H. Pigford, "Time-Dependent Nuclide Transport Through Backfill into a Fracture," *Trans. Am. Nucl. Soc.*, 55, 134-136 (1987).
46. J. Ahn, P. L. Chambré and T. H. Pigford, "Transient Diffusion From a Waste Solid Into Fractured Porous Rock," Lawrence Berkeley Laboratory Report LBL-24576, 1987.
47. M. Harada, P. L. Chambré, M. Foglia, K. Higashi, F. Iwamoto, D. Leung, T. H. Pigford, and D. Ting, *Migration of Radionuclides Through Sorbing Media: Analytical Solutions - I*, Lawrence Berkeley Laboratory Report LBL-10500, February 1980.
48. P. L. Chambré, H. C. Lung and T. H. Pigford, "Mass Transfer of a Radioactive Decay Chain Through Backfill," *Trans. Am. Nucl. Soc.*, 52, 78-80 (1986).
49. T. H. Pigford and P. L. Chambré, "Mass Transfer in a Salt Repository," Lawrence Berkeley Laboratory Report LBL-19918, May 1985.
50. T. Brandshaug, "Estimate of Consolidation of Crushed Salt Around a Spent Fuel Waste Package," RE/SPEC Report RSI-315, 1987.

51. D. T. McTigue, "Thermoelastic Response of Fluid-Saturated, Porous Rock," *J. Geophys. Res.*, *91*, B9, 9533 (1986).
52. Y. Hwang, P. L. Chambré, W. W.-L. Lee and T. H. Pigford, "Pressure-Induced Brine Migration in Consolidated Salt in a Repository," *Trans. Am. Nucl. Soc.*, *55*, 132 (1987).
53. U.S. Department of Energy, "Environmental Assessment: Yucca Mountain Site, Nevada Research and Development Area, Nevada," Report DOE/RW-0073, *2*, 1986.

*LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720*