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ABSTRACT

Establishing reliable estimates of long-term performance of a waste repository requires emphasis upon valid theories to predict performance. Predicting rates that radionuclides are released from waste packages cannot rest upon empirical extrapolations of laboratory leach data. Reliable predictions can be based on simple bounding theoretical models, such as solubility-limited bulk-flow, if the assumed parameters are reliably known or defensibly conservative. Wherever possible, performance analysis should proceed beyond simple bounding calculations to obtain more realistic—and usually more favorable—estimates of expected performance. Desire for greater realism must be balanced against increasing uncertainties in prediction and loss of reliability. Theoretical predictions of release rate based on mass-transfer analysis are bounding and the theory can be verified. Postulated repository analogues to simulate laboratory leach experiments introduce arbitrary and fictitious repository parameters and are shown not to agree with well-established theory.

I. INTRODUCTION

The Performance Assessment National Review Group[1] recommended that the U. S. geologic repository projects give greater emphasis to realistic and reliable predictions of long-term performance of repositories. Predictive reliability, the assurance that the actual performance will be as good or better than that stated by the performance prediction, is essential for any engineering project and particularly for a geologic repository, because real-time testing to confirm the repository design and to confirm the predictions of long-term performance is impossible. In any system design the use of well established and easily verified calculational techniques to establish the bounding values of predicted performance must be balanced with the desire to refine the performance prediction for greater realism. To predict what happens in tens of thousands of years in a repository we must emphasize sound theories of prediction, more so than in conventional engineering design wherein performance can be predicted, validated, and remedied by real-time testing. Here we review the state of technology for predicting the long-term rate of dissolution of radionuclides from waste packages in a repository.

II. MECHANISTIC ANALYSIS OF RADIONUCLIDE RELEASE RATES

A. Release Estimates For Saturated Bulk Flow

Bounding analyses can be used to establish predictive reliabiity and to estimate limiting features of system behavior. In some instances, physically unrealistic assumptions or input values are used to obtain a conservative "bounding result".

1. **Bounding estimates when all ground water is assumed saturated.** To calculate radionuclide release rates from emplaced waste packages some repository projects have assumed unrealistically that all ground water flowing through the repository becomes saturated by the radioelements in the waste or by the waste matrix. If the values chosen for the saturation concentrations and water flow rates are defensible, then the calculated releases are defensible as a conservative upper bound and are expected to be reliable. If the predicted releases are suitably below the limits established for acceptable performance, then the bounding calculation may be sufficient to demonstrate that the waste packages and repository will meet the regulatory criteria.

Wherever possible, performance analysis should proceed beyond simple bounding calculations to obtain more realistic—and usually more favorable—estimates of expected performance[1]. For example, because the emplaced waste packages are discrete and separated from each other, it is impossible for all water potentially flowing through a repository to become saturated with any waste constituent, assuming that it is not already saturated with that constituent before encountering the waste and assuming no large changes in saturation concentration in the repository environment. The only place that concentrations near saturation are expected is in the liquid immediately adjacent to the waste surface. All other water will be below the saturation concentration, and the average concentration in ground water leaving the repository will be below saturation. Thus, a more realistic calculation, if suitably reliable, is likely to be preferable to the extreme conservatism of saturated bulk flow.

2. **Nonbounding estimates for partial bulk flow.** The tuff project[2] estimates waste-package release rate by multiplying the saturation concentration of the waste matrix by the volume flow rate of ground water that is calculated to flow through rock equal in cross section to the cross sectional area of the waste canister. Radionuclides in the waste matrix are assumed to dissolve congruently with the matrix. The result is not necessarily bounding or conservative, for it predicts zero release at zero flow, but it will be shown later (Equation (2)) that if there are direct pathways for molecular diffusion of dissolved species from the waste surface into surrounding stagnant groundwater a finite and continuing release of dissolved species will occur. The ground water infiltration velocities predicted for tuff are so low, about 0.003 to 1 mm/year, that diffusional release will be more important than convective transport if the waste solid is conservatively assumed to be surrounded by groundwater and moist tuff. Also, assuming that radionuclides are released congruently with matrix dissolution is not conservative for borosilicate glass waste[1,4]. To develop a more

reliable prediction that can be defended as conservative and bounding, a more mechanistic analysis of mass transfer of radionuclides to ground water could be adopted.

B. Mass-Transfer Analysis of Release Rate

Mass-transfer analysis is a general approach, highly refined in the field of chemical engineering[3], to predict rates of transport of species within a phase and between phases, as affected by diffusion, convection, chemical reaction, adsorption, etc. It quantifies the actual mechanisms affecting the transport rate. An application by Chambre' et al.[4-9] to a waste package surrounded by wet porous rock conservatively assumes that all the waste solid is suddenly exposed to ground water when the corrosion-resistant barrier fails, and it conservatively assumes saturation concentration of dissolved radioelements in the liquid at the waste surface. Exact theoretical analysis of the diffusive-convective transport of the dissolved species from the waste surface into the surrounding porous rock results in an upper limit to the time-dependent dissolution rate that can occur.

Though more realistic than saturation bulk flow, Chambre''s mass-transfer analysis for a bare waste solid is still conservatively unrealistic in neglecting the finite resistance to mass transfer presented by the partly failed waste canister and fuel cladding. It is further conservative in application by assuming saturation concentrations at the waste surface. More detailed mechanistic analysis[10] shows that saturation concentration is a close approximation to reality for borosilicate glass and for the spent-fuel matrix for all but the very early time of exposure in a repository. The theory contains no arbitrary adjustable parameters. For steady-state release rate it requires experimental data on saturation concentrations, diffusion coefficients, porosity, ground water approach velocity, as well as specifications of waste size and geometry. For transient releases, data on sorption retardation coefficients are also required. Because of the saturation boundary condition, information on degree of waste cracking and solid-liquid reaction rate does not enter the prediction. Even if solid-liquid reaction rate is included as a boundary condition, increased reaction surface from waste-cracking does not appreciably affect the dissolution rate after the first few days of exposure to groundwater.

The important feature of this mass-transfer analysis is not that it predicts favorably low dissolution rates for most radionuclides, but that it is a mechanistic theory based on well-understood governing equations and conservatively bounding boundary conditions. The theory itself can be examined in detail. It can be subjected to verification in experimental real time tests, as has been done at the Pacific Northwest Laboratory[11]. Such theories are the only reliable means of extrapolating into the future.

A similar theoretical mass-transfer analysis of time-dependent radionuclide release from a suddenly exposed waste form surrounded by backfill and rock is now used by the basalt project[1]. Although the salt project has based its waste-package release rates on a simple bounding calculation of the rate of brine inflow to an emplacement cavity, multiplied by the individual radioelement solubility, this approach is unrealistic and unnecessarily

conservative because the salt will soon be consolidated against the waste package. More realistically, and now more reliably, one can calculate radionuclide release by calculating the diffusive transport from a brine layer at the waste surface into brine-filled grain boundaries in the surrounding salt[12]. The convective-diffusive mass transfer from the waste surface into interbed flows that may intersect the waste package can also be calculated, similar to the mass-transfer calculations used by Neretnieks[13] to predict container corrosion and waste-package release rates for the KBS project.

C. Some Results of Mass-Transfer Predictions of Release Rates

The profiles of ground water flow and concentration of a dissolved species for a simple waste solid surrounded by porous rock are shown in Figure 1. The diffusion-and-flow calculation by Chambre'[4-9] uses the known distribution of ground water velocities around an infinite cylinder through pores in the surrounding rock. A general solution to the time-dependent dissolution rate of a radioelement with a constant boundary concentration N_i^* at the inner surface of the borehole has been given by Chambre'[7].

1. Steady-state diffusive-convective dissolution rates

The fractional rate of dissolution f_i of the elemental species i and its isotopes from a long waste cylinder of radius R is calculated at steady state to be:

$$f_i = \frac{8 N_i^* (DU)^{\frac{1}{2}} \epsilon}{(\pi R)^{3/2} n_i} , \quad \frac{UR}{D} > 4 \tag{1}$$

where D is the specie diffusion coefficient in pore liquid, U is the pore velocity of ground water before it comes near the waste, ϵ is the porosity of the surrounding rock, and n_i is the bulk density (g/cm^3) of the elemental species i in the waste. For a bounding calculation, N_i is chosen as the saturation concentration. For a waste cylinder of finite length L end effects are accounted for by multiplying the right-hand side of Equation (1) by a correction factor (1 + R/L).

Table I gives estimated values[4,14] of the solubility of silica and the solubilities in water of radioelements in borosilicate glass waste. Also listed are the bulk densities and the calculated fractional release rates for a typical glass waste exposed to groundwater at an approach velocity of 1 m/yr in rock of 1 percent equivalent porosity. The assumed diffusion coefficient of 10^{-5} cm^2/s is typical for an electrolyte in water. It conservatively neglects the effect of tortuosity[15], which in granite can result in more than a 100- to 1000-fold[16-18] reduction in D and more than a 10-fold to 30-fold reduction in estimated dissolution rates. Because the fractional dissolution rates of the low-solubility elements are lower than those of the silica matrix, these elements do not dissolve congruently with the matrix, forming precipitates as the matrix dissolves.

Table I gives values of fractional dissolution rates for silica and for various radioactive elements[19] in borosilicate glass, calculated from experimental data reported from IAEA-type laboratory experiments in which leachant is periodically replaced. For substances of limited solubility, the
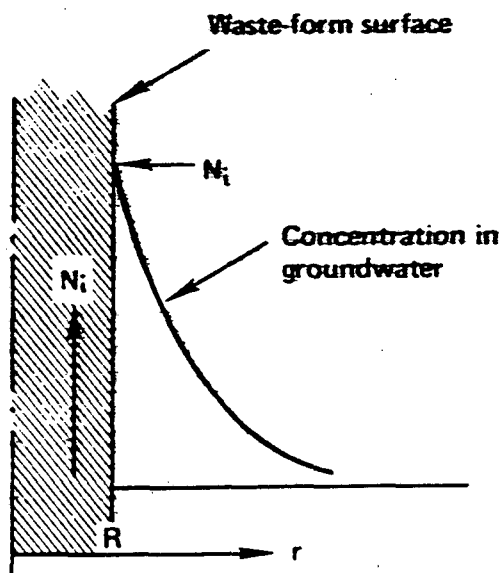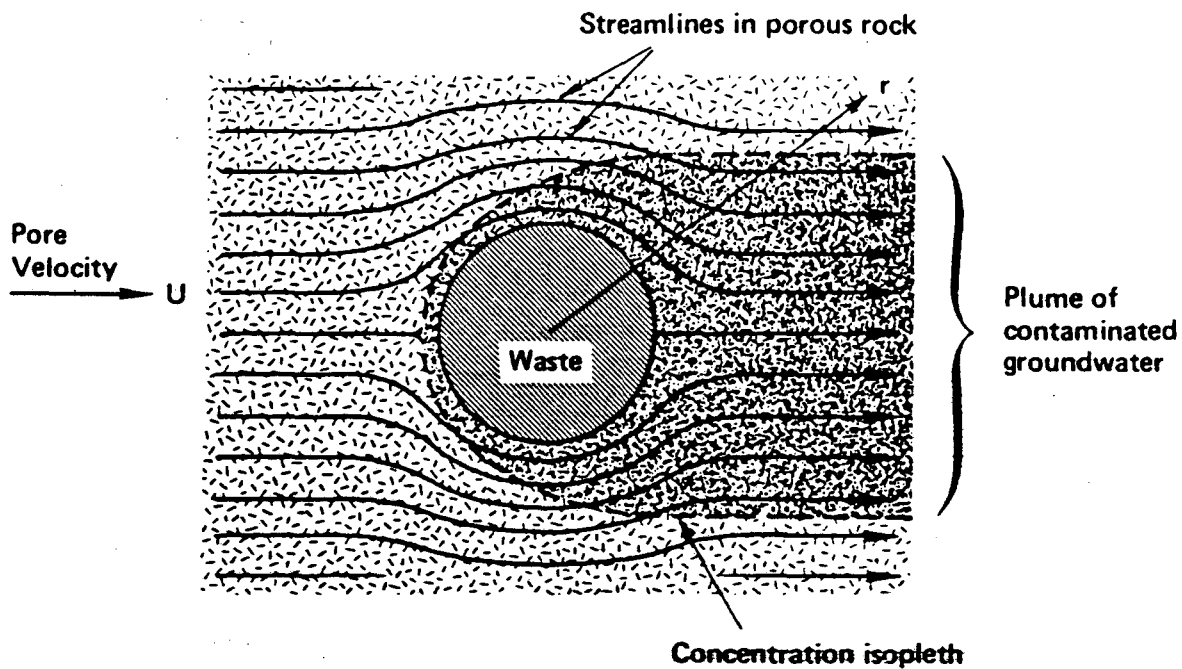
Figure 1

Flow of ground water past a waste cylinder;
concentration profile

TABLE I
Calculated Fractional Dissolution Rates for Commercial Borosilicate Glass Waste

Waste cylinder radius: 0.15 m

length: 2.46 m

Amount of uranium[a] 460 kg

Constituent	Solubility,[b] g/cm^3	Concentration in glass, g/cm^3	Calculated fractional dissolution rate[c] yr^{-1}	Observed fractional dissolution rate[d] yr^{-1}
SiO_2	5×10^{-3}	1.6	1×10^{-6}	2×10^{-3}
U	1×10^{-9}	1.2×10^{-2}	4×10^{-9}	2×10^{-6}
Np	1×10^{-9}	1.9×10^{-3}	2×10^{-8}	7×10^{-4}
Pu	1×10^{-9}	1.1×10^{-4}	4×10^{-7}	3×10^{-5}
Am	1×10^{-10}	3.6×10^{-4}	1×10^{-8}	3×10^{-5}
Se	1×10^{-9}	1.4×10^{-4}	3×10^{-7}	
Sn	1×10^{-9}	9.4×10^{-5}	5×10^{-7}	
Tc	1×10^{-9}	1.9×10^{-3}	2×10^{-8}	

a/ Amount of uranium initially in pressurized water-reactor fuel to produce the radionuclides contained in the waste.

b/ For amorphus SiO_2[14]. Other solubilities are from Krauskopf[4], at 20°C, moderately reducing conditions.

c/ Steady-state dissolution rates calculated from Equation (1) for diffusive-convective mass transfer. Ground water pore velocity = 1 m/yr. D = 3.2 x 10^{-2} m^2/yr.

d/ Data of McVay et al,[19] for IAEA-type leach tests, with periodic replacement of leachant.

TABLE II

Calculated Fractional Dissolution Rates for Commercial Spent Fuel

Waste cylinder radius = 0.43 m

length = 2.46 m

Amount of initial uranium = 2770 kg

Constituent	Concentration in spent fuel, g/cm^3	Fractional dissolution rate,[a] yr^{-1}
U	1.2	2×10^{-12}
Np	6.2×10^{-4}	3×10^{-9}
Pu	1.2×10^{-2}	2×10^{-10}
Am	1.1×10^{-4}	2×10^{-9}
Se	6.4×10^{-5}	3×10^{-8}
Sn	1.5×10^{-4}	1×10^{-8}
Tc	9.5×10^{-3}	2×10^{-10}

[a] Steady-state dissolution rates calculated from Equation (1) for diffusive-convective mass transfer. Ground water pore velocity = 1 m/yr. D = 3.2×10^{-2} m^2/yr. Solubilities from TABLE I.

values of f_i computed from Equation (1) are smaller than those derived from laboratory leach tests, as is expected. For slightly soluble species in waste that has been embedded in a repository rock, the slow diffusion and slow movement of the liquid around the waste containers may be more significant in controlling the net rate of dissolution than the rate at which substances in the waste solid react with the surface liquid. If the solubility is very small, the rate of escape into groundwater will be determined primarily by the solubility, the properties of the porous rock, and the ground water velocity; if the solubility is sufficiently large, the kinetics of the interaction between the solid waste constituents and water may dominate.

In Table II are calculated fractional dissolution rates at steady state for a waste package of commercial spent fuel. Because of the large inventory of uranium, its fractional dissolution rate is much lower than for borosilicate glass and is lower than that calculated for low-solubility fission products and other actinides. Therefore, unless there is a mechanism for waste constituents to be preferentially released from the UO_2 matrix more rapidly than the matrix dissolves, all of the listed species should dissolve congruently at the fractional dissolution rate of uranium.

2. **Steady-state diffusion-controlled dissolution rates.** In most of the repository designs the ground water velocity is so low that the convective component of the release from the waste form is negligible, Equation (1) is not applicable, and an alternate form developed by Chambre′ for a prolate spheroidal waste solid must be used:

$$f_i = \frac{\beta \varepsilon D N_i^*}{n_i}, \qquad U \to 0 \tag{2}$$

where β is a geometrical parameter that can be calculated from the waste-form dimensions:

For a sphere of radius R

$$\beta = \frac{3}{R^2} \tag{3}$$

For a prolate spheroid waste of semiminor axis b and eccentricity e

$$\beta = \frac{3e}{b^2 \ln[\coth \frac{\alpha_s}{2}]}, \qquad \alpha_s \equiv \cosh^{-1}\left(\frac{1}{e}\right) \tag{4}$$

Using the properties listed in Table I, the limiting low-velocity fractional release rates are calculated to be about a fourth of those calculated for a pore velocity of 1 m/yr, which illustrates the nonconservatism (see II A.2) in neglecting diffusional transport at pore velocities of the order of a few millimeters per year.

The time to reach steady state increases from the few years for a pore velocity of 1 m/yr to tens of thousands of years for near-zero velocities[8]. Sorption parameters do not enter these equations for steady-state release of long-lived radionuclides, but sorption increases the transient dissolution rate and the time to reach steady state[8,9].

3. **Extensions of the mass-transfer analysis.** In subsequent studies Chambre' has extended the mass-transfer analyses to consider the effect of a backfill layer between the waste package and rock[20], the increased dissolution rates that can result when the concentration profile is steepened by radioactive decay and sorption[9], the effect of nonlinear sorption characteristics of backfill[21], the effect of repository heating on mass transfer and release rate[22], and the rate of release of species that have already diffused from the UO_2 matrix in spent fuel and are readily accessible as soluble constituents in the fuel voids and fuel-cladding gap.

4. **Use of laboratory leach-rate data.** If one wishes to include the solid-liquid reaction rate as part of a more comprehensive model of waste-package performance in a repository, a concentration-dependent reaction rate should be used as a boundary condition at the waste-form surface, with the concentration in the surface liquid determined by the calculated time-dependent rate of mass transfer into the exterior porous or fractured rock. Zavoshy et al.[10] show that when the boundary condition of constant surface concentration is replaced by an experimentally measured concentration-dependent solid-liquid reaction rate, obtained from laboratory leach data, the calculated dissolution rate approaches that from the simple model of saturation in surface liquid within a few years after emplacement, and the surface concentration at steady state deviates in only a minor way from saturation for the low- solubility components. Therefore, the complication of a reaction-rate boundary condition is not necessary when the low-solubility elements approach saturation in surface liquid at times that are short compared to the times of interest in repository performance analysis, and the reliability of long-term prediction does not suffer from the uncertain extrapolation of laboratory leach-rate data.

5. **Effect of borehole water.** A recent mass transfer analysis by Chambre'[23] shows that the volume of ground water trapped within the borehole and waste package introduces only a short time delay in the rise in concentration of dissolved species at the waste surface. Within the long times important in repository performance analysis, and for the low-solubility waste constituents, the concentration within the borehole liquid approaches saturation and the dissolution rate is controlled by the rate of mass transfer into the backfill or rock. Thus, assuming[30-33] that borehole water represents an equivalent volume of confined leachant to use in applying a laboratory leach correlation (cf. III B.1,2) ignores the important long-term release mechanisms in a repository, and it does not produce a conservative or bounding estimate of release rate. Because of the empirical extrapolation of real-time laboratory data, it cannot be a reliable technique to predict long-term releases.

6. **Reliability and validation.** Although these mass-transfer theories unrealistically assume that all waste solids are suddenly and completely exposed to groundwater, these theories predict compliance with the numerical performance criteria for most of the radioelements in glass and spent fuel. Because the mass-transfer theories are mechanistic, mathematically formulated, exact, and require only a few directly measurable parameters, they are readily

adapted to testing for validity and can be expected to result in reliable predictions of long-term performance, although still conservative and not realistic in all detail that might be desired. As the complexity increases, more phenomena, assumptions, and input data must be validated, and predictive reliability becomes more difficult, as illustrated below.

D. Effect of Partly Failed Protective Waste Containers

Further realism is usually expected to result in lower predicted releases from the waste package. For example, not all of the protective container is expected to fail at once, and releases from the waste solid will likely be reduced by the tortuous pathways through the partly failed outer layers and corrosion products. The multicomponent corrosion products can result in solid phases with low saturation concentration of contained radioelements. The protective features of these more realistic phenomena should be taken into account, where possible. However, in any predictive effort there is a compromise between the increased detail for realism as contrasted with the loss of predictive reliability, when the greater detail invokes additional physical parameters and requires more data and validation than may be possible within available resources and time.

The WAPPA code[24], listed by all of the repository projects as one of their system codes for predicting waste-package performance, predicts release rates by finite-difference calculations of molecular diffusion through backfill. One of the several unjustified approximations[1] made in the WAPPA release-rate calculation is to assume that diffusional transport through holes of known area in the container is given by the diffusional transport from a bare waste solid multiplied by the ratio of hole area to total area. In attempting to be more realistic by taking into account partial container failure, predictive reliability suffers in two ways: (1) data are required on the time-dependent extent of container failure, including the number, size, and spacing of penetrations, and (2) the assumption of release rate proportional to hole area is incorrect when the holes are small.

Chambre''s analytical solution[23] for diffusion through well-separated holes shows that for small holes the area proportionality assumed by WAPPA is not obeyed. As shown in Figure 2, if the equivalent hole radius is 1 mm and if the total hole area is about 0.05 percent of the container area, the rate of diffusive transport through the holes is the same as if no container material were present[25]. This is a consequence of the large concentration gradients and large diffusive fluxes near the hole edges, and it may explain observations by Johnson et al.[26] of large releases of cesium through small apertures in Zircaloy cladding. Of course, the holes could become plugged with corrosion products, or the failure phenomena may be such that containers are penetrated by only a few openings, so that the net release rate could be appreciably lower than that of a bare waste solid. However, even if there are enough container holes for remove the container as an important barrier, the mass-transfer rates will remain low because of the slow diffusive-convective transport through surrounding backfill and rock.

Obtaining sufficient data to reliably predict the effect of partial failure of waste containers on release rate is a challenge to experiment and
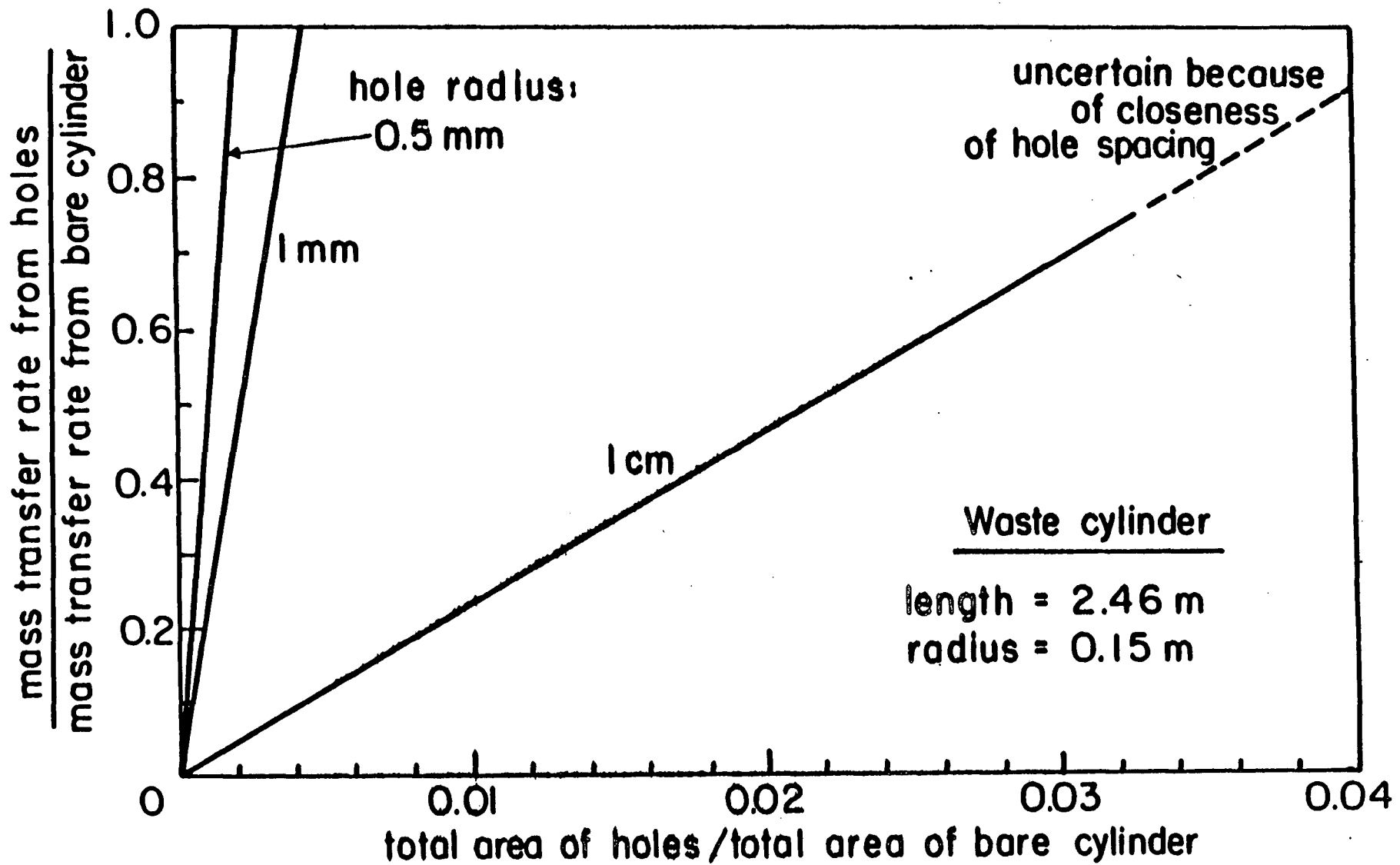
Figure 2. Diffusive mass transfer through holes in waste container

theory.

E. Effect of Statistically Distributed Container Failures

The Nuclear Regulatory Commission requires[27] that the yearly release rate of a radionuclide from engineered barriers in a geologic repository be no greater than 10^{-5} times the 1,000-year inventory of that radionuclide or 10^{-8} times the total curie inventory of all radionuclides at 1,000 years. For the simple analogue of a bare waste solid surrounded by rock, the release rate would equal the dissolution rate estimated by Equations (1) and (2) for steady state or by the analytical solutions for the transient dissolution[7,8,10]. If a backfill is present, the release rate would be the mass-transfer rate calculated at the backfill-rock interface[8,9,20].

If the NRC release-rate criterion is to be applied to the entire ensemble of waste packages in a repository[1], the statistical distribution of waste-package container failures can affect the average release rates for the repository.

At a given time t the average fractional release rate f(t) of the repository inventory of a radionuclide, based on the radionuclide inventory at 1,000 years, is a statistically weighted average of the fractional release rates from the waste packages failed up to time t. At time t the fractional release rate from a package whose container fails at time t′ after emplacement if $f_p(t,t')$, and the failure probability per unit time at time t′ is p(t′). The fraction of containers failing in the time span between t′ and t′ + dt′ is p(t′)dt′, so the repository-average fractional release rate of the radionuclide is given by:

$$f(t) = \int_0^t f_p(t,t')p(t')dt' \tag{5}$$

The repository averaged fractional release rate will not differ much from the single-package fractional release rate for low-solubility long-lived species if waste dissolution continues after all containers have failed. It will be lower than the single-package release rate for soluble long-lived species that are available for rapid dissolution once the waste container fails, such as cesium-135 and iodine-129 in the gap activity in spent fuel.

1. Illustration for cesium-137. Statistically distributed container failures do not necessarily result in repository-average release rates lower than those for individual waste packages. To illustrate, we consider the release of cesium-137 from glass waste[28]. We assume that the cesium dissolves congruently with silica and apply Chambre′′s[23] analytical solution for the time-dependent fractional dissolution rate from a spherical waste surrounded by porous rock, for a silica solubility of 200 g/m^3, and for a waste package containing initially 270 kg of silica and 0.45 kg of cesium-137. The single-package fractional dissolution rate of cesium-137, for a container that fails at the time of emplacement, is shown in Figure 3. Because of the low 1,000-year inventory of 30-year cesium-137, the fractional dissolution rate is very large at early times before cesium-137 has decayed. However, if the container does not fail for 300 years, most of the cesium-137 will have decayed and the single-package fractional dissolution rate will be much smaller than the
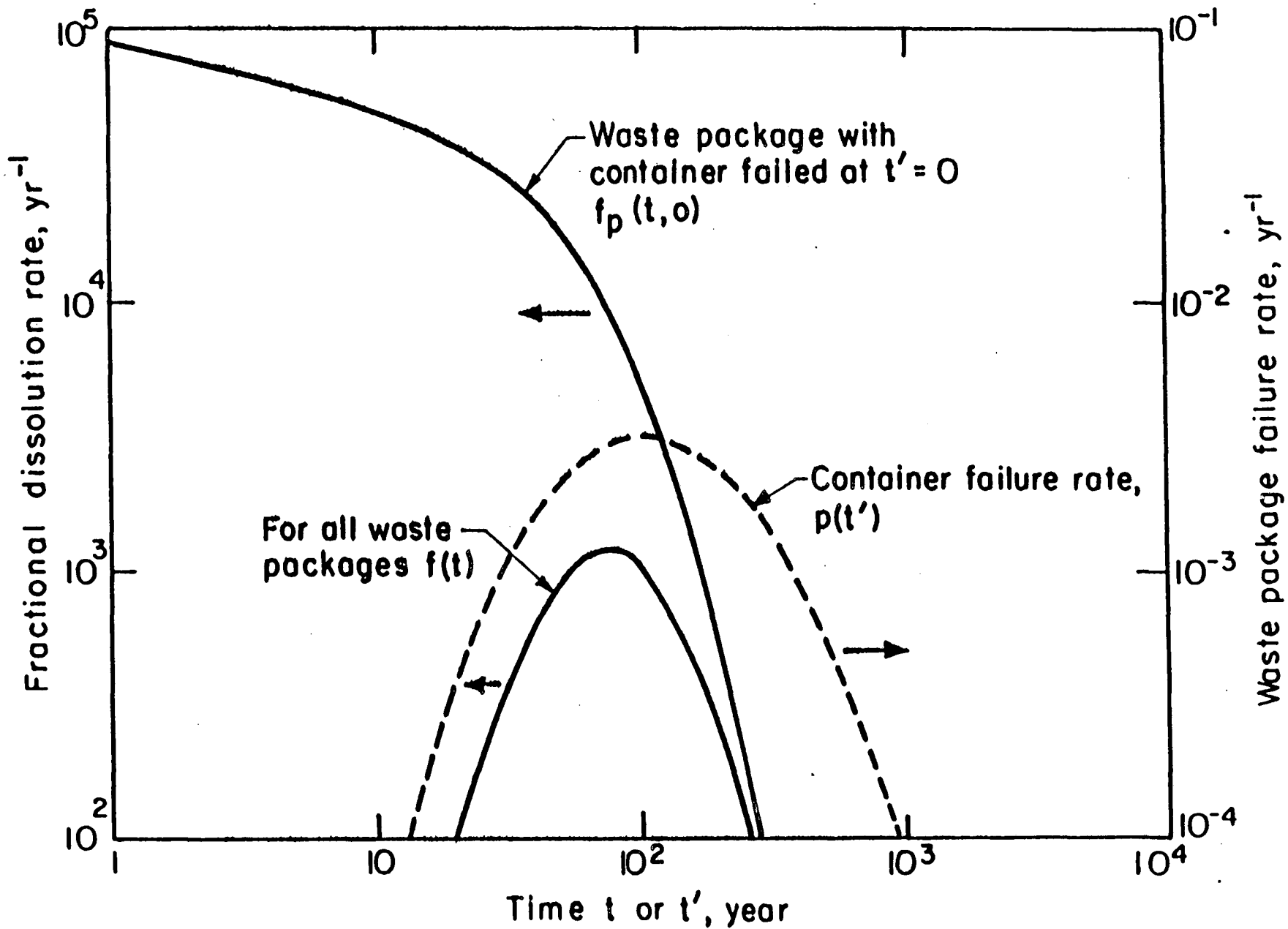
Figure 3. Normalized release rate of cesium-137 from borosilicate glass waste, effect of a XBL857-6385
lognormal distribution of container failures (mean time to failure = 300 years,
deviation = 300 years)

calculated equivalent fractional release limit of 0.02/year.

Assuming that the container failure rate is governed by a log-normal distribution with mean time to failure of 300 years and a deviation of 300 years, we obtain the repository-average fractional dissolution rate of cesium-137 shown in Figure 3. The consequence of a statistical distribution of container failures is to allow earlier container failures and to increase the average normalized dissolution release rate of cesium-137. The calculated release rate of cesium-137 into rock will be much smaller if a sorbing backfill is present or if the low effective solubility (10^{-3} g/m^3) recently measured for cesium in defense glass[29] is considered.

2. Data needed for reliable prediction. Data on the probability distribution of container failures are necessary for reliable prediction of repository-average release rate, placing additional demands on the experiments and performance assessment to establish container failure modes.

III. NONMECHANISTIC ESTIMATES OF WASTE-PACKAGE RELEASE RATE

A. Use of Laboratory Leach Data to Predict Radionuclide Release Rates

Beginning over twenty years ago laboratory leaching experiments have been performed on borosilicate glass and other candidate waste forms. Typically, a small sample of a waste-form material is exposed to a leachant liquid in a vial kept at constant temperature. The leachant is periodically analyzed for the concentration of dissolved constituents. Most data are reported for leach times of about one month, but some leach times of a few years have also been reported. Many publications propose correlations of the rate of dissolution of silica from borosilicate glass, and a few extend the correlations to radioelements contained in glass waste. Some of the correlations are structured in a way to suggest possible mechanisms that control dissolution rate, such as surface films, sorption, etc., but all of the correlations are empirical and include several arbitrary and adjustable parameters that are determined by curve fitting to laboratory data.

In 1980 the Waste Isolation System Panel[4] (WISP) of the National Research Council began a three-year study that included an evaluation of the applicability of these laboratory leach data to predict release rates from waste solids in a geologic repository. In 1981 the panel concluded that (1) there is no reliable basis for extrapolating the empirical correlations of laboratory leach data to predict release rates at exposure times thousands of times longer than encountered in the experiments, and (2) the repository analogue proposed as a means of using the laboratory leach data is a nonmechanistic postulate and is not valid. The analogue problems are discussed in the WISP report and are summarized below.

B. Postulated Repository Analogues for Predicting Releases

The laboratory leach experiments measure the net rate of reaction between the leachant and the solid surface. In the liquid-continuum leachant no appreciable concentration gradients are expected, so the exterior-field diffusive-convective transport processes that control the dissolution rate in a repository environment are not present in the laboratory experiments. The

buildup of corrosion products within the leachant can affect the rate of dissolution of the waste samples, so the ratio S/V of sample surface S to leachant volume V is used as a correlating parameter; a larger S/V results in more rapid increase in concentration of dissolution products in the liquid, more rapid approach to saturation, and a more rapid reduction in leach rate.

1. **Repository S/V based on borehole water.** Various proposals have been made[30-33] to extrapolate the laboratory leach-rate data to repository conditions by adopting the laboratory data taken at the same S/V ratio that is presumed to exist for the waste package in a repository. Although, it has been pointed out that there is no meaning to an equivalent volume of ground water in contact with the surface area of each waste package[4], it is still assumed by some[31,32] that there is a repository analogue of the laboratory leach experiment. The assumption[31-33] that the equivalent repository water volume associated with a waste package is the volume of water in waste-package voids and in the bore-hole annulus leads to a prediction of zero steady-state release, because the concentration in this assumed confined liquid volume will reach saturation.

However, because the borehole liquid is, in fact, not confined, dissolved species will transport into surrounding porous medium by diffusion and convection in pore water, the mechanisms considered in the mass-transfer analyses by Chambre' et al. and others. Release will continue at a finite rate, the solute concentration in the bore-hole liquid will fall slightly below saturation, and solid-liquid reaction at the waste surface will proceed at a steady-state rate equal, for long-lived species, to the rate of diffusive-convective transport into the exterior pores.

2. **Postulates of ground water residence time and volume.** Macedo et al.[30-32] have obtained laboratory leach data for glass waste powder with periodic partial replacement of leachant, simulating a small and continuous leachant flow through a leach-test vial with well-mixed solid and liquid. At early times the dissolution rates are controlled by the solid-liquid reaction rate, which decreases with increasing concentration of solute. At later times the dissolution rate is found to be proportional to the volumetric rate of replacement of leachant, suggesting that an equivalent saturation concentration has been reached and that the release rate is given by the simple bulk-flow saturation-limited calculation discussed in II A above. The diffusive-convective transport mechanisms that control the net release in a repository environment are not present in these experiments. Macedo et al. empirically correlate their leach data with the ratio S/V of powder surface to leachant volume and the average residence time T_r of leachant, the latter determined by dividing the leachant volume by the volumetric replacement rate of leachant.

To apply their empirical correlation of laboratory leach data to predicting waste performance in a repository, Macedo et al.[31,32] propose a repository analogue that has waste fragments well stirred with a specified volume of ground water associated with each waste package, with a specified volumetric flow of ground water through the well-stirred volume. For a waste solid surrounded by a large volume of wet rock, they propose that the leachant

volume be identified as the volume of voids initially inside the waste
container, which will become filled with water when the waste container fails.
Here they do not include water that may be in the gap between the waste
package and rock. They propose that the volumetric flow through this well-
mixed container of waste fragments and void water be identified as the
upstream Darcy velocity of ground water multiplied by the projected cross-
sectional area of the solid waste. They do not consider the effect of any
backfill between the waste package and rock, and they equate NRC's fractional
release rate with the fractional dissolution rate. The expected fractional
dissolution rate when liquid in contact with the waste is at concentration N_i
is then estimated by Macedo et al. to be:

$$f_i = \frac{N_i V}{m_i T_r S} \tag{6}$$

where m_i is the mass of species i in the waste solid per unit surface area of
solid. It is clear that this analogue distorts the physical situation in the
repository. Contrary to the assumptions of Macedo et al., fragmented waste is
not well stirred with void water and with any water that may flow through the
waste. If the waste solid has finite flow permeability, the actual rate of
flow through the waste will depend on the ratio of waste solid permeability to
the permeability of surrounding backfill and rock, and it can depart
considerably, and either direction, from that estimated by Macedo et al.

More importantly, dissolved species can and will diffuse into
surrounding backfill and rock and will be transported by diffusion and
convection into a much larger volume of flowing water than estimated from the
Macedo analogue. If the analogue were correct, Equation (6) would become
identical with the diffusive-convective Equation (1) as the waste permeability
becomes very small, resulting in no volumetric replacement of void water and
an infinite void-water residence time. However, Equation (6) would
incorrectly predict zero dissolution, whereas the dissolution rate from
Equation (1) is finite. As another test, as the volume of void water goes to
zero Macedo's Equation (6) predicts zero dissolution rate. In contrast,
Equation (1) was derived for a waste solid in contact with wet rock and it
correctly predicts finite dissolution rate whether or not void water is
present. Because Equation (1) is for steady-state dissolution rate, it
applies also to a waste package with finite void water, provided that the
radius R is taken as the radius of the bore hole. Also, applying Macedo's
Equation (6) to a repository would overlook the effect of rock porosity, an
important parameter that affects the waste dissolution rate, as shown in
Equation (1). The repository analogue proposed by Macedo et al. for finite
convective flow is unrealistic and results in nonconservative predictions.

Recognizing that exterior-field diffusion can affect the dissolution rate
in a repository, Macedo et al.[31,32] propose that at low ground water flow
rates the equivalent contact time of ground water to be used in Equation (6)
be calculated by:

$$T_r = \frac{d^2}{KD} \tag{7}$$

where d is the waste diameter, K is the retardation coefficient, and D is the coefficient for molecular diffusion in ground water in the rock pores. If Equation (7) were corrected by moving the retardation coefficient to the numerator, T_r would be the the time for a diffusion front to travel a distance d in a sorbing medium. However, it has not been explained why this transient diffusion time should have any connection with the mean residence time for steady-state dissolution, and why it should be related to the mean residence time for Macedo's laboratory experiments, for which Equation (6) was derived. It is not valid to adopt estimates of T_r based on exterior-field diffusion mechanisms to use in adapting correlations of laboratory data which represent dissolution mechanisms not affected by exterior-field diffusion. Different phenomena are involved, and the repository analogue is postulated without demonstrating its causal connection to the laboratory experiments.

The fallacy of the postulated analogue can also be demonstrated by comparing the results predicted by the technique of Macedo et al. with results predicted by Chambre''s Equation (2), which is exact for steady-state dissolution at no flow and without decay. Macedo et al. state that, by using the diffusion estimate for T_r, Equation (6) will predict dissolution rates in a repository when convective effects on dissolution are negligible. In the absence of convection, there can be no finite flow through a fractured waste solid, so Macedo's Equations (6) and (7), derived for steady state dissolution, should agree with the exact steady-state solution in Equation (2). However, Macedo's incorrect repository analogue and his unjustified assumption of a diffusion-limited equivalent residence time introduce the sorption retardation coefficient K, even though sorption cannot affect steady-state dissolution of long-lived species. He fails to predict a functional dependence on rock porosity, which is shown in Equation (2) to be an important parameter in affecting dissolution rate. He incorrectly predicts zero dissolution rate when there is no void water in the waste package, although as explained above (II C.5) water in waste package voids and in the borehole annulus has no affect on the steady-state dissolution rate. Macedo's equations fail to predict the much greater transient dissolution rates that are shown by Chambre's exact solutions to occur over hundreds and thousands of years in a low-flow repository. Neglecting rock porosity and transient diffusion-controlled dissolution results in nonconservative estimates of dissolution rate.

As concluded by the WISP panel[4], such empirical techniques are useful to correlate laboratory leach data, but postulating equivalent values of S/V, volume flow rate per waste package, and T_r in attempting to use these correlations to predict performance in a wet-rock repository is neither valid nor necessary. Predictive reliability is lost by such postulates. Proper mechanistic theories of repository performance exist, and these theories specify the kind of laboratory data, such as saturation concentrations, that are needed for valid and reliable predictions of waste dissolution rates.

3. **Data on natural analogues.** Macedo et al.[31] base their conclusion that solid-liquid reaction rates control dissolution in a repository on a limited number of observations by Berner[34], who studied the dissolution rates of

isolated grains of low-solubility minerals surrounded by a wet porous solid. By observing the temperature dependence of the dissolution rate, Berner concluded that dissolution was controlled by exterior-field diffusion for some mineral grains and by solid-liquid reaction rate for others. Ranking the few samples according to their solubility, he found that the dissolution of most of the low solubility grains was controlled by solid-liquid reaction rate. The observation was empirical and was limited to a small number of mineral samples. It does not justify the unqualified conclusion by Macedo et al.[31] that different materials, e.g., borosilicate glass, and enormously larger solid forms will follow the ranking observed by Berner.

Better insight into the fallacy of generalizing and extrapolating from Berner's data is provided by the analytical solution of Zavoshy et al.[10] for dissolution from a solid sphere of radius R surrounded by a saturated sorbing porous medium. The solid-liquid reaction rate is expressed by a simple first-order reaction, dependent on the concentration of solute in the liquid at the solid surface, is used as a dissolution-flux boundary condition to connect with the mathematical analysis of exterior-field diffusion in the absence of convection. The analytical solution for the time-dependent dissolution rate contains a term ψ, the magnitude of which determines which phenomenon controls dissolution rate at steady state, where:

$$\psi = \frac{\text{forward reaction rate per unit area at R}}{\text{steady-state diffusive mass transfer rate at } r_o} = \frac{kR}{\varepsilon D} \qquad (8)$$

where k is the forward reaction rate constant. When ψ is much larger than unity, steady-state dissolution is controlled by exterior-field diffusion; when ψ is much less than unity, solid-liquid reaction rate controls. Inferring k from early-time leach data for silica from borosilicate glass, assuming a waste sphere 0.44 m in radius, and with $D = 7.7 \times 10^{-2}$ m^2/yr for silicic acid at 90°C and $\varepsilon = 0.01$, we calculate $(SiO_2) = 1240$. For this large glass sphere, silica dissolution is clearly controlled by exterior-field diffusion.

If we make the sphere radius small enough, Equation (8) will predict a small ψ and solid-liquid reaction rate will control. This is what one would expect from the physics of the problem. We know of no causal effect of curvature on the solid-liquid reaction rate, but the high curvature of a small-radius sphere promotes more rapid exterior-field diffusion and can eliminate it as a controlling phenomenon.

Equation (7) demonstrates that it is not valid to apply Berner's conclusions on small mineral grains to large waste solids.

The only physico-chemical property of the solid contained in Equation (7) is the forward reaction rate constant k. The theory shows that the dissolution rate of Berner's small mineral grains should have been ranked according to k, if it were known, instead of solubility. The ranking according to solubility does not demonstrate a causal effect of solubility on first-order dissolution and should not be generalized. Berner observes that the solid-liquid reaction is usually complex, and a higher-order reaction could result in the observed ranking.

There is no valid basis for the conclusion by Macedo et al. that the
dissolution rate of nuclear waste in a repository would be expected to be
controlled by surface reaction mechanisms. Based on the foregoing analysis,
and as demonstrated in Table I, we conclude that for borosilicate glass the
dissolution rate of silica and other low-solubility species in borosilicate
glass waste will be controlled by exterior-field mass transfer and that solid-
liquid reaction rate will not influence the dissolution rate except during the
very early time of exposure to groundwater. This early time is no more than a
few days if the solid-liquid reaction rate is given by the parameters adopted
by Zavoshy et al.[10].

4. **Flow of ground water through fractured waste.** In explaining his
proposed model for predicting waste dissolution rate in a repository,
Macedo[31,32] states that his model considers ground water flowing through a
fractured waste solid, whereas the mass-transfer analytical solutions
presented by Chambre' assume an impermeable waste solid. Glass waste will be
internally fractured from thermal stress. Water is likely to penetrate into
fractured glass, but it will not alter the results of Chambre's mass transfer
analysis if there is no net through flow of liquid through the waste. Solid-
liquid reactions on internal surfaces will only increase the net solid-liquid
reaction rate, which is already sufficiently rapid to maintain near-saturation
concentrations of the low-solubility constituents in surface liquid in a
repository environment.

Net through flow of ground water through the fractured waste is not
included in the present mass-transfer analyses by Chambre', but it can be
added. Because only a portion of the ground water flow can permeate the
fractured waste, parameters appearing in the resulting mass transfer analysis
must include the hydrodynamic permeabilities and porosities of the waste
solid, backfill, and rock. Mass transfer from waste particles to through-
flowing liquid will introduce dimensions of waste fragments and flow
interstices, in addition to the other parameters already appearing in the
mass-transfer analysis. None of these additional parameters appear in
Macedo's proposed method of predicting waste dissolution rate in a repository
because Macedo assumes that all ground water flowing through rock of cross-
sectional area equal to that of the waste solid will flow through the
fractured waste, and he assumes that this permeating ground water is well
stirred with powdered waste, as in his laboratory experiments. Therefore, the
effect of any finite flow of ground water through fractured waste must rest on
a more realistic and mechanistic analysis and cannot be predicted by the
postulates of Macedo et al. The fact that Macedo's experiments include well-
mixed flow through powder samples does not necessarily mean that the same flow
and dissolution process will occur in repository waste.

Theoretical studies of the hydrodynamics and mass transfer in two-region
porous media are underway by Chambre', and extension to include the effects of
flow through fractured waste can be considered.

IV. SUMMARY AND CONCLUSIONS

Predicting rates that radionuclides are released from waste packages cannot rest upon empirical long-term extrapolations of laboratory leach data. Reliable predictions can be based upon simplified assumptions, such as solubility-limited bulk-flow, if the assumed parameters are reliably known or defensibly conservative, but assuming volumetric flow rates through a waste-package cross section is arbitrary and can be nonconservative.

Wherever possible, performance analysis should proceed beyond simple bounding calculations to obtain more realistic—and usually more favorable—estimates of expected performance. Desire for greater realism must be balanced against increasing uncertainties in prediction and loss of reliability. Theoretical predictions of release rate based on mass-transfer analysis are bounding, and the well-established theory is well adapted to verification. The results from the exact analytical solutions can be used to test predictions from numerical techniques and from less mechanistic analogues.

Lower release rates are expected if less than complete failure of waste containers is considered, but data for reliable quantitative predictions are not yet available and will be difficult to obtain. Diffusive transport through small holes and cracks can be much greater than incorrectly predicted on the basis of area proportionality.

Repository-average release rates, taking into account statistical distribution of container failures, can be lower than individual-package release rates for some radionuclides and greater for others, depending upon mean-time to failure and the probability distribution of failures. Data are not yet sufficient for reliable prediction and will be difficult to obtain.

Several efforts to predict waste-package release rates in a repository, utilizing empirical correlations of laboratory leach-rate data, have invoked postulates of repository analogues to simulate the laboratory leach experiments. The postulated analogues are unrealistic, they introduce fictitious repository parameters, such as volume and volumetric flow rate of ground water associated with each waste package and ground water residence time, which are assigned arbitrary values for making predictions. They invoke functional dependence on parameters inconsistent with well-established mass-transfer theory, and they incorrectly assume that the dissolution mechanisms that control release rates observed in laboratory experiments are controlling or important in the repository.

The most useful experimental results from laboratory leach experiments are the saturation concentrations of radioelements released from the waste. Other parameters needed for reliable estimates of release rates in a repository can be directly measured, including rock and backfill porosity and sorption and ground water pore velocity upstream of the waste.

Effects on release rate due to colloids, radiolysis, possible flow through backfill and fractured waste, and grain-boundary diffusion and

interbed flows in salt need to be resolved by theory and experiment.

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