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CLOSED-SYSTEM POSTULATES FOR PREDICTING WASTE-PACKAGE PERFORMANCE
IN A GEOLOGIC REPOSITORY

an Addendum to

RELIABLE PREDICTIONS OF WASTE PERFORMANCE IN A GEOLOGIC REPOSITORY

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I. INTRODUCTION **

In a recent paper [A] we reviewed the need for reliable theory and experiment in making long-term predictions of waste performance in a geologic repository. We discussed uncertainties in postulated techniques of applying closed-system laboratory leach data to predicting the dissolution of waste solids in a geologic repository, and we discussed the use of mass-transfer analysis to unify theory and experiment and to provide a clear theoretical basis for long-term prediction.

Comments on our recent paper by Drs. Macedo and Montrose [B] provide a welcome opportunity to clarify several issues related to predicting waste performance. Their comments help illustrate the need for reliable and sound theories for predicting waste performance in the long-term future, and they help focus the fundamental differences between waste dissolution in laboratory leach experiments and dissolution in a repository. To aid better understanding and resolution of the differences between mass transfer in the closed systems considered by Macedo et al. and others and mass transfer in the open systems of waste repositories considered in our mass transfer analyses, we comment here in some detail.

Our mass-transfer theory of waste-package performance has been developed with the objective of unifying theory and experiment to achieve reliable long-term predictions. A theory is adequate if it derives from well-understood and properly formulated governing equations, if it contains well-defined parameters that can be determined by experiment, if it survives tests and verification, and if it can relate experiment to the mechanistic processes that affect performance in a repository. The comments by Macedo and Montrose help illustrate these issues.

** References listed in our earlier paper are shown here as numerical superscripts. Additional references listed at the end of this response are indicated by letter references in square brackets, e.g., [A].
II. NEED FOR DATA ON SATURATION CONCENTRATIONS

Macedo and Montrose have correctly observed that the simplest and bounding application of mass-transfer theory requires, for low solubility species, data on saturation limits in the complicated chemical environment near a waste package. Data on effective saturation concentrations obtained in laboratory leach experiments, including the valuable experiments of Macedo and Montrose, are useful in applying the mass-transfer theory for predicting waste performance in a repository.

Macedo and Montrose question the saturation concentrations of soluble constituents, such as boron, to be used in applying mass-transfer theory. No such saturation concentrations are needed, other than to verify that the constituent is highly soluble. Our publications have stated that the theory of solubility-limited mass transfer does not apply to highly soluble species whose dissolution rate may not be limited by a solubility-limited dissolution rate of the waste matrix. Boron is evidently one such species in borosilicate glass waste. Here we would use the more general analysis, summarized in section III-B-3 of our paper and derived in a separate paper, wherein solid-liquid reaction rate is used as a boundary condition rather than saturation concentration.

In other publications we apply mass transfer theory to the transient dissolution of highly soluble species, such as the "gap activity" of spent fuel, that can dissolve rapidly when exposed to ground water. Saturation concentrations are not required for that calculation.

III. WATER FLOW THROUGH WASTE FORMS IN A REPOSITORY

Macedo and Montrose correctly observe, as is also pointed out in our paper [A], that the particular form of the mass-transfer equations that we have published does not apply if there is flow of ground water through a highly fractured waste package. Dissolution with flow through fractured waste and with diffusion and flow in the surrounding nondissolving media would require a reformulation of the mass-transfer analysis.

In the U.S. repository projects the expected ground-water flow is so low that mass-transfer rates are evidently controlled by diffusion from the outer surfaces of the waste package into the surrounding media. If any of the projects should expect appreciable flow through a fractured waste package in a repository, the mass-transfer analysis should be reformulated. We also note that in Sweden's waste disposal project, which predicts greater ground-water flows than in the U.S. projects, net flow through the waste package is not expected.

However, even if there is sufficient flow through the waste form to affect release rate from the waste form in a repository, there will remain open-system pathways for diffusion and convection from the waste form's exterior surface into the pore water in the surrounding media. The questions on the validity of the Macedo-Montrose proposed extrapolation of closed-system laboratory data to a waste package in the open system of a repository remain and are unanswered.

Also, if there is appreciable flow of ground water through a waste solid surrounded by porous or fractured rock, the actual flow rate through the waste must depend upon permeabilities of the waste solid and the surrounding
rock, as pointed out in our paper. These parameters do not enter the equations proposed by Macedo. If the waste is more permeable than the rock, the volume flow rate through the waste can be greater than that estimated by Macedo's prescription of multiplying the approach Darcy velocity by the cross sectional area of the waste. The conclusion by Macedo and Montrose that their prescription gives the correct volumetric flow rate contradicts the known hydrodynamics of this problem.

IV. AN INVALID TEST OF THE PUBLISHED THEORY

Macedo and Montrose adopt a statement by B. L. Cohen [C] that our published mass-transfer theory "...has been shown to be replete with shortcomings when used to describe dissolution under geologic conditions", and that "...for rock of a depth of 600 m the theory overestimates the dissolution of SiO2 by a factor of 10^7". Evidently Macedo and Montrose were not aware of a 1984 publication [D] by members of the National Research Council's Waste Isolation System Panel that had already analyzed each of Cohen's claims in detail and showed that Cohen has made an invalid test of the published equation for dissolution rate from a single dissolving object.

Cohen argued that natural grains of siliceous rock dissolve much more slowly than predicted by our equations, even if it is assumed that the rock has long existed with water slowly flowing between the grains. Cohen made two fundamental errors: (1) he applied our equation derived for release from isolated dissolving objects spaced far from each other and surrounded by a nondissolving porous medium, to individual small "grains" of ore that touch each other, forming the pores through which ground water flows through ore bodies, and (2) he failed to allow for the rapid approach to saturation of ground water as it permeates an ore body. In Cohen's ore body all of the grains surrounding a given dissolving grain are also dissolving, whereas our published mass-transfer equations apply to a single dissolving object surrounded by a porous medium of nondissolving grains. The governing equations for diffusive-advective transport must apply also to the ore body, but they are of different form than those used in our analysis. The resulting analytical solutions will be different. We expect that in Cohen's ore body the water between dissolving grains would soon reach saturation, and the net rate of dissolution would be far less than predicted by Equation (1).

Cohen did not consider dissolution rates from the outer boundaries of a dissolving ore body into surrounding nondissolving porous media, so his proposed test should be applied to a closed-system analysis. Therefore, the data reported by Cohen are not a valid test of our mass-transfer equations.

Macedo and Montrose do not credit the dissolution tests conducted by McGrail et al.12 in an open system, where they measured diffusive-convective mass transfer from a single dissolving object surrounded by a nondissolving porous medium, confirming Equation (1) of our paper.

V. VOLUME OF GROUND WATER ASSOCIATED WITH A WASTE PACKAGE

Part III-B-2 of our paper discusses proposals by Macedo and others to extrapolate leach-rate data, obtained in laboratory experiments with no continuous diffusive-convective transport across the container boundaries, to the open system of a waste package in a repository by assuming some finite volume of ground water associated with each waste package. The fallacies of assuming some ill-defined water volume were outlined in a National Research
Council report. Macedo and Montrose have not responded to the technical issues pointed out therein. Their statement that there is a definite void volume within the waste canister and that the surrounding rock and backfill have a specified porosity does not answer the question of what water volume per package is the analogue of the laboratory closed-system experiment. They have not shown what is the appropriate water volume associated with the rock and backfill porosity, nor have they shown that either the canister void water or the pore water, or both, is the appropriate analogue for the water volume in their closed-system experiment with well-mixed waste solid and water.

As a test, consider a limiting case of a nonporous solid waste form in direct contact with infinite porous rock through which ground water is flowing. Our exact analytical solution (Equation (1)) predicts a finite steady-state dissolution rate limited by diffusion and convection in pore water. However, the total ground water volume in rock pores associated with this single waste package is infinite. This, together with a finite surface area of waste, results in zero ratio of waste surface S to water volume V. If one now adopts zero as the proper S/V ratio to obtain appropriate dissolution rates from laboratory closed-system experiments, the predicted repository dissolution rate would be the forward rate of solid-liquid reaction measured in laboratory experiments, i.e., the rate of solid-liquid reaction in the absence of dissolved waste constituents in the reacting liquid. The forward reaction rate has been shown in both Table I of our paper and by our more detailed analysis to be far greater than the maximum value of the steady-state convection-diffusion-limited dissolution rate of low-solubility species such as silica that is predicted from the exact analytical solution (Equation (1)). Therefore, the postulated S/V analogue fails. The S/V postulate fails other tests described in III-B-2 of our paper.

Macedo and Montrose's reference [7] is an interesting application of their S/V postulate to connect closed-system laboratory leach data for powdered minerals mixed in water to the dissolution rate of rock into ground water in the rock interstices. Evidently there are no nearby outer surfaces of the rock formation for diffusion and convection of dissolving rock into surrounding nondissolving porous media. Therefore, their natural analogue appears to be a closed system, similar to that in Macedo's laboratory experiments. Unfortunately, the successful comparison by Macedo et al. of their laboratory data with this natural analogue does not answer the questions of how to apply their closed-system laboratory data to the open system of a waste package surrounded by the exterior nondissolving medium of a repository.

For other closed-system natural analogues, we suggest that Macedo and Montrose consider Cohen's data on rock grains dissolving into interstitial ground water. There are as yet few natural-analogue data for testing the mass-transfer theories for open-system dissolution. We urge the test of open-system mass-transfer theories with open-system experiments, such as those of McGrail et al. [11].

VI. DISSOLUTION RATE AT LOW VELOCITIES

Our equations show that for very low groundwater velocities, characteristic of expected conditions in U.S. repositories, convection has little effect on dissolution rate, and the rate of mass transfer from waste to ground water can be analyzed by calculating molecular diffusion of dissolved species into pore water. In Equation (2) we presented the exact analytical
solution for the steady-state mass transfer rate as an example of a reliable theory. Governing equations, boundary conditions, and derivation were referenced to earlier publications. We then examined the equations proposed by Macedo et al. for dissolution rates at low velocities, presented as Equations (6) and (7), having determined that they were indeed the equations proposed by Macedo et al. Macedo and Montrose state that "substituting Equation (7) in Equation (6) leads to Equation (2), apart from a trivial geometrical factor of order unity."

We find that Equations (6) and (7) combine to yield:

\[ f = \frac{NVKD}{md^2S} \]  

(after Macedo and Montrose)

Functionally, Equation (9) is markedly different from the exact analytical solution (Equation (2) in our paper). Equation (9) does not contain the rock porosity \( \varepsilon \), which must be present because of the boundary condition that joins the waste dissolution rate to the exterior-field mass transfer rate. Omitting the porosity introduces an error of two to four orders of magnitude for some emplacement rocks in the U.S. program. Equation (9) incorrectly contains the retardation coefficient \( K \). The governing transport equation shows that \( K \) cannot be a parameter affecting dissolution rate at steady-state for long-lived species. These two differences were pointed out in III-B-2 of our paper. Evidently Macedo and Montrose have not recognized these points.

Equation (9) also contains the postulated ratio \( S/V \) of waste surface to ground water volume. The fallacy outlined above in attempting to define \( S/V \) for the open system of a repository also occurs here.

The view of Macedo and Montrose that ground water flows appreciably through the waste form does not affect the comparison of their Equations (6) and (7) to the exact solution, Equation (2), because there is no flow in this problem. Nonflowing permeation of a waste form by ground water does not affect the applicability of Equations (1) and (2) \(^4\).

We understand from the publications of Macedo, and from the comments by Macedo and Montrose, that the surface area \( S \) in (9) is intended to be the surface area of the individual grains of waste solid, i.e., the surface area of the particles of glass powder in their laboratory experiments and the surface area of particles of fractured waste in their repository analogue. The quantity \( m \) has been defined as the mass of reacting species per unit area of reacting surface of the waste particles. Macedo and Montrose consider their repository waste form to behave as waste fragments well stirred and mixed with water. Thus, the product \( mS \) is the total inventory of the reacting species in the waste. For a spherical waste form of overall radius \( R \) in a repository, the inventory of a dissolving species is also given by the product of the species density \( \rho \) and the waste volume, so that equation (9) of Macedo and Montrose can be transformed to the form of Equation (2) by:

\[ mS = 4\pi \rho \frac{R^3}{3} \]  

Also, from Macedo's qualitative description of Equation (7), we understand the diameter \( d \) to be \( 2R \) for a spherical waste in a repository. Substituting
Equation (10) and \( d = 2R \) into Equation (9) of Macedo and Montrose, we obtain:

\[
f = \frac{3NVKD}{16\pi R^5 n_i} \text{ (after Macedo and Montrose)}
\]

whereas Equation (2) for a sphere is:

\[
f = \frac{3eDN^*}{n_i R^3} \text{ (exact solution)}
\]

If one postulates a repository volume of water given entirely by the waste-package void water volume, as in a closed system, then \( V \) would be proportional to the waste volume and Equation (11) would give the same functional dependence on \( R \) as does Equation (2). However, Macedo and Montrose state that in this low-flow case the greatest contribution to \( V \) is from pore water in the rock surrounding the waste. For a waste form directly surrounded by a large amount of porous rock, the Macedo-Montrose prescription for \( V \) becomes the volume of pore water in the surrounding rock, in addition to the small amount of void water in the waste package. For a large amount of rock per waste package, \( V \) is mainly the pore water in the rock and is affected little by waste radius. The resulting incorrect \( R^5 \) dependence in Equation (11) is a consequence of the unjustified assumption that the ratio \( S/V \) is a meaningful and correct parameter for the repository and the incorrect assumption that the size of individual waste particles affects net diffusion rates from the outer surface of the waste into the surrounding rock.

Macedo and Montrose state that in this low-flow condition there is "rather thorough mixing" of pore water in the surrounding rock with the solid waste, creating a well-stirred condition analogous to their closed-system laboratory experiments. The mechanisms of such mixing of pore water throughout the considerable amount of rock associated with each waste package have not been described, nor have the mechanisms of mixing of that pore water with the waste solid. Macedo and Montrose speak of rapid exchange of pore water with the reaction volume of the waste particles by diffusion, evidently visualizing the result equivalent to a well-stirred mixture of waste particles and pore water. However, the "exchange" is only outward from the waste package. It is the concentration gradients of dissolved species in ground water in rock pores, as shown in Figure 1 of our paper, that create the barriers to mass transfer that are so effective in a repository. The "diffusive mixing" envisioned by Macedo and Montrose to create the same concentration throughout rock pores as in the liquid at the waste surfaces, equivalent to the spatially uniform concentration in closed-system laboratory experiments, cannot occur.

Finally, Macedo and Montrose have not answered the test of their Equation (6) discussed in our paper.

The principal point being made in our paper is that reliable theories must have a clear theoretical basis, and they must specify well-defined parameters for their application. No derivation of Macedo's Equation (7) has been presented. Since learning in 1984 of Macedo's proposed equations for predicting repository performance, we have sought [8] on several occasions his help in deriving Equation (7), but without success. Regardless of numerical constants, Equation (7) does not produce the correct and physically necessary
functional relationship for the parameters that are shown, by exact mathematical solutions, to control steady-state release rates in a repository.

The technical points at issue here can be best resolved by such tests, using the tools of mathematics and governing equations.

VII. WHEN DOES EXTERIOR-FIELD DIFFUSION CONTROL DISSOLUTION?

Part III-B-3 of our paper refers to a more detailed analytical solution of the mass transfer rate from a spherical waste form, wherein solid-liquid reaction rate is used as an interface boundary condition. The analysis assumes a simple expression for the solid-liquid reaction rate, linearly dependent on the concentration of dissolved species and with experimentally determined rate constants, similar to a reaction-rate equation assumed by Macedo. The results of the exact time-dependent solution tell us under what conditions mass-transfer rate is limited by chemical reaction rate and under what conditions it is limited by exterior-field diffusion.

This analytical solution provides a tool for assessing Macedo's conclusion that Berner's data on dissolution of small mineral grains surrounded by a nondissolving porous medium show that solid-liquid reaction rates control waste dissolution in a repository. Our exact analytical solutions show that wherein solid-liquid reaction rates may control dissolution of some small ore grains surrounded by nondissolving material, exterior-field mass transfer can control for the same species in large solids similar to the repository waste forms. We do not "assert that exterior-field mass transfer processes are completely dominant," for we show under what conditions solid-liquid reaction rate can control.

We cite our earlier paper to provide the full details and derivation and for a detailed numerical calculation, from the exact analytical solution, of the time-dependent concentration of silica in ground water adjacent to a glass waste package. It is shown that the steady-state surface concentration of dissolved silica is within 0.1 percent of the saturation concentration, and it is shown that the solid-liquid reaction rate controls silica dissolution rates only during the first few days or months of exposure to groundwater, depending on the retardation coefficient for dissolved silica.

The simple comparison in Table I of our paper between exterior-field mass transfer rates and solid-liquid reaction rates shows clearly that the latter do not control steady-state dissolution rates for low-solubility constituents in a repository waste package, a conclusion reached by the WISP Panel and endorsed by its reviewers. The more detailed analysis described in III-B-3 predicts the rapid build-up of dissolved species in surface liquid and the rapid transition from chemical reaction controlling, at early times, to exterior-field mass transfer controlling for low-solubility species such as silica.

VIII. THE REPETITION OF FOUR-YEAR-OLD MASS-TRANSFER ANALYSES

Macedo and Montrose conclude that "the first half of the paper gives a summary version of what is essentially the same diffusion-convection mass transfer analysis that they [Pigford and Chambre'] have been presenting for roughly the past four years." Mere repetition of our 1982 publication of the simple steady-state equations for mass-transfer in a geologic repository would be adequate for our paper, which is to emphasize the need for careful
development and evaluation of means for predicting future performance. However, our paper goes further. It summarizes continued refinement and generalization of the mass-transfer theory during the last four years, and some new results are presented in our paper. Based on our more extensive work on mass-transfer in a repository, we caution readers from using the simple steady-state equations to predict waste-package performance. Steady-state is reached soon in some convective conditions, but our referenced work shows that the higher mass-transfer rates accompanying the approach to steady state are important for the U.S. repositories. We do not understand how Equations (6) and (7) postulated by Macedo et al. could be expected to predict mass-transfer rates in either steady state or during the long-duration transient.

IX. MASS TRANSFER THROUGH BACKFILL

Macedo and Montrose criticize the analysis of mass transfer from a waste package through backfill and into surrounding rock, stating that the nature of the backfill has not been determined and that it is more conservative to determine the dissolution rate at the waste-package surface. Evidently they mean that release rates into the rock are always more conservatively predicted if it is assumed that no backfill is present and that the waste form is surrounded directly by rock. Their proposal to ignore backfill in predicting release rates into rock is indeed more conservative for radionuclides that are short lived and that would otherwise decay in backfill before reaching the rock. However, for the more important long-lived radionuclides the steady-state release rates into rock with backfill present will be greater, and hence more conservative, if the backfill is of greater porosity than the rock that it replaces. One of the U.S. projects now specifies backfill with porosity greater than that of the surrounding rock. Therefore, it is timely to consider the effect of backfill, and, for the more important radionuclides, it would not always be more conservative to neglect backfill and consider a waste solid surrounded directly by rock.

One of our tasks is to develop correct analytical solutions and design equations to be used as tools by repository and waste-package designers in assessing what benefits can or cannot be achieved by incorporating backfill in waste packages. We urge that designers use these tools before decisions are made that determine the nature of the backfill to be used, if any.

X. THE USE OF MASS-TRANSFER ANALYSIS IN REPOSITORY PROGRAMS

Macedo and Montrose misinterpret our observation that mass-transfer theory is the only reliable means of extrapolating waste-package performance into the future. Mass-transfer theory relies on detailed and careful application of the governing equations that describe the mechanistic processes of transport of material between and within phases. It is applicable to all situations in which transport occurs. The form of the mass-transfer theories that are finally used may not be the same as the simple steady-state equations presented in this paper to illustrate results of mass-transfer analysis. However, a point of this paper is to illustrate the pitfalls of waste-performance predictions based on heuristic assumptions and plausibility.

Used correctly, mass transfer theory is a valuable and necessary tool for developing reliable predictions. Its use by Sweden's nuclear waste disposal project has been reviewed and endorsed by international peer review, including two reviews by panels of the National Research Council.
XI. ADEQUACY OF DATA ON SATURATION CONCENTRATIONS (SOLUBILITIES)

Macedo and Montrose conclude that the data on solubilities given in Table I, used to illustrate the prediction of diffusive-convective-limited dissolution rates, "imply a ground water composition that is unlike anything to be encountered in a geologic repository." We understand this to mean that none of these solubilities is appropriate for any of the repository projects. Certainly the local chemical environment is likely to depend on many conditions that may not have been present in the laboratory experiments from which solubilities were derived. However, that all the solubility data are so unrealistic is not yet apparent. The solubility data on silica, neptunium, and plutonium from borosilicate glass were suggested by saturation data from leaching experiments at Battelle's Pacific Northwest Laboratory. The data on actinide and fission product solubilities were recommended in a 1982 study by Krauskopf, from his analysis of the expected stable phases in reducing conditions.

The repository projects are seeking new and more realistic solubility data. Some new data have been published. We also find that one project is still using Krauskopf's data on an interim basis. We find that many--but not all--of the newer solubility data from the projects are similar to those listed in Table I. For some species, such as uranium, higher values should be used in an oxidizing environment, but the higher values now suggested do not invalidate the applicability of the mass transfer equations to these constituents in the waste.

We do not know the basis for the Macedo-Montrose comment that none of the concentrations in Table I of our paper could occur in a repository. For those saturation concentrations in Table I that are appropriate to the repository environment, our detailed analysis shows that these limiting concentrations will be approached soon within a repository. For example, the steady-state concentration of dissolved silica, from borosilicate glass, is predicted to be within 0.1 percent of saturation.

We continue to seek unification of theory and experiment for reliable prediction of waste performance. Macedo's measurements of saturation concentrations can contribute to that unification.

XII. ADDITIONAL COMMENTS

The term "nonmechanistic" used to characterize the postulates discussed in part III-A,B of our paper was adopted from Macedo's published description of his own work.

We thank Drs. Macedo and Montrose for their helpful and constructive comments, and we thank Dr. Harry Burkholder, technical editor of these proceedings, for providing the opportunity to resolve these issues and to bring them to the attention of the technical community. We welcome further comments.

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XIII. REFERENCES


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