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ASSESSMENT OF THE LOSS OF
RADIOACTIVE ISOTOPES FROM
WASTE SOLIDS TO THE ENVIRONMENT.
PART I: BACKGROUND AND THEORY

H. W. Godbee
D. S. Joy

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ORNL-TM-4333

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

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FEBRUARY 1974

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Oak Ridge, Tennessee 37830
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UNION CARBIDE CORPORATION
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U.S. ATOMIC ENERGY COMMISSION

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ASSESSMENT OF THE LOSS OF RADIOACTIVE ISOTOPES FROM WASTE SOLIDS
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ABSTRACT

Assessments of the amounts of radioactivity from waste solids that enter the environment are needed for engineering, economic, and safety evaluations of proposed waste treatment, storage, transport, and disposal systems. Nearly all programs on the incorporation of radioactive wastes in solid media have included studies to determine the time dependency of losses from the products formed. Frequently, recourse has been made to empirical and semiempirical relations in order to transpose the experimental data to a broad spectrum of real situations and to extrapolate these results. However, too much reliance on empirical and semiempirical relations tends to obscure an understanding of the fundamental mass transport processes taking place in waste solids, and often leads to the conclusion that mass transport through waste solids is hopelessly complicated and not amenable to treatment by established mass transport theory.

In view of the foregoing, this report presents several theoretical expressions based on mass transport phenomena that relate the radioactivity escaping from such solids to diffusion, dissolution processes, surface conditions, and radioactive decay. Representative available data for radioactive waste solids incorporated in cement, asphalt, ceramic, and glass media are analyzed using the theoretical expressions presented. These analyses show that an expression taking into account diffusion and concentration-dependent dissolution gives good agreement with the data for most of the products considered. In the main, these products can be categorized as waste solids of low solubility incorporated in inert matrices. The effective diffusivities obtained are in the range of mid 10^{-17} to mid 10^{-12} cm^2/sec , the dissolution rate constants are in the range of high 10^{-9} to low 10^{-7} sec^{-1} , and the surface transfer constants are in the range of low 10^{-4} to low 10^{-3} sec^{-1} for the products analyzed. Once determined, such parameters can be used to compare various waste products and to estimate releases from these products, in particular, long-term releases.

1. INTRODUCTION

Estimation of the quantities of radioisotopes that are removed from waste solids as a function of time and enter the environment is an important consideration in the assessment of a waste treatment, short-term storage, transportation, or long-term disposal program. It strongly influences the amount of additional treatment, containment, and surveillance that is required. Radioactive wastes have been incorporated in cements, plastics, asphalts, ceramics, and glasses¹⁻⁴ in attempts to prepare solid products that will hold virtually all radioactivity for long periods of time and prevent contamination of the environment. To determine how effectively this goal may be achieved, the radioactivity that is leached from the solid by water is usually measured as a function of time. Recently revised International Atomic Energy Agency (IAEA) regulations for the safe transport of radioactive materials include such leach rates among the criteria for the shipment of low-level solid and special form radioactive material.⁵

To permit intercomparison of various products from different processes or different installations, the IAEA has proposed a standard method⁶ of measuring and reporting the leaching, by water, of the radioactive components in solid waste products. The removal of radioactivity by air, steam, and other fluids at temperatures that might be encountered during treatment, storage, transport, and long-term disposal must also be considered in the full assessment of a waste management program. For example, the removal of tritiated water vapor and radioactive noble gases, such as krypton and radon, by air currents is an important consideration in some situations even though the environment is dry.

Most radioactive waste solids are heterogeneous, and mass transfer in heterogeneous materials is complicated by the numerous processes that can occur simultaneously. Transport is possible along many paths: inside crystal lattices, along crystal grain boundaries, through pore volumes or intraparticle voids, along pore surfaces, through interparticle voids, etc. Chemical reactions, vaporization-condensation, dissolution-precipitation, etc., may be taking place also to affect the transport, and the mobile species may be moving in either the solid, liquid, or gaseous state.

When transport is known to occur via several mechanisms, use^{7,8} is made of an "effective diffusivity," D_e , in the mass transport equation. This usage is analogous to that of "effective thermal conductivity" in the heat transport equations.⁷ Generally, effective diffusivity and effective thermal conductivity must be determined experimentally and the question of the diffusion mechanism is not belabored. The only assumption made in such usage is that the transport equations can adequately represent the system. Solutions of the mass transport equations for many cases of practical interest for diffusion, diffusion plus convection, diffusion plus chemical reaction, diffusion plus heat transfer, etc., with various initial and boundary conditions are given in books such as refs. 7-13. Solutions for other cases of diffusion or for diffusion plus other mechanisms for mass transport, with different initial and boundary conditions, are frequently tractable using the methods and suggestions given by such books. In design calculations on proposed systems for long-term disposal, the present lack of effective diffusivity data for most waste solids of interest makes it necessary to use estimated D_e 's, or extrapolated values¹⁴ of leach rates determined in short-term leaching tests. To illustrate these points, representative data for asphalt, cement, ceramic, and glass products are examined to determine the behavior with time. These data were chosen not only because they meet the present need but also because they were obtained from sufficiently well-characterized systems and are presented in a most usable form (i.e., tabular).

The main purpose for incorporating radioactive wastes in asphalt, cement, glass, or similar materials and measuring the amounts of radioactivity that are lost from the resulting products is to obtain data that will permit the assessment of any potential hazard that the short-term storage, transport, and long-term disposal of such products may pose to man. The aim of this report is to illustrate, by looking at several waste products, the use of data gathered over short periods of time to assess the release of radioactivity to the environment, in particular, over long periods of time. Toward this end, the results of measurements made over periods of time ranging from a few months to several years are utilized to determine mechanisms for time dependency of losses and to

predict losses for several centuries. Obviously, such extrapolation presupposes that a system maintains its integrity and that the mechanism for time dependency of losses from the system, as determined from short-term data, holds for the longer span of time.

2. GRAPHICAL METHODS FOR REPORTING THE RESULTS OF LEACH TESTS AS A FUNCTION OF TIME

Various methods for measuring the quantities of radioisotopes that are removed from radioactive waste solids as a function of time, and several ways of expressing these results, have been developed in laboratories in different countries.¹⁻³ The IAEA concluded⁶ that,

"This has led to difficulties in applying the data obtained in one set of circumstances to another set of circumstances; and to difficulties in communication with consequent confusion and wastage of effort and time."

To improve this situation, the IAEA has proposed specific leach test methods and ways for expressing and reporting the results.

The IAEA recommends⁶ that leach test results be reported as a plot of the quantity, [(cumulative fraction of the radioactivity leached from the specimen) x (specimen volume-to-exposed surface ratio)], as a function of the total time of leaching,

$$\left(\frac{\sum a_n}{A_0} \right) \left(\frac{V}{S} \right) \text{ versus } \sum t_n, \quad (1)$$

or cumulative fraction leached as a function of the square root of the total time of leaching,

$$\left(\frac{\sum a_n}{A_0} \right) \text{ versus } \left(\sum t_n \right)^{1/2}, \quad (2)$$

where

- a_n = radioactivity lost during leaching period n ,
- $\sum a_n$ = sum of radioactivity lost during all leaching periods,
- A_0 = initial radioactivity,
- V = volume of specimen in cm^3 ,
- S = exposed surface area of specimen in cm^2 ,

t_n = duration of leachant renewal period, and
 Σt_n = sum of all leaching periods.

Leach results reported as $(\Sigma a_n/A_o)$ are peculiar to the sample since $(\Sigma a_n/A_o)$ depends on the surface-to-volume ratio of the sample. Thus, values of S and V (or their ratio) must be reported along with $(\Sigma a_n/A_o)$ if meaningful comparisons and mathematical treatments of the data are to be made. In addition to one of the above plots, the IAEA states that results may also be expressed as a plot of the incremental leaching rate, R_n , as a function of time, that is,

$$\left(\frac{a_n}{A_o}\right) \left(\frac{V}{S}\right) \left(\frac{1}{t_n}\right) \text{ versus } (t - t_n/2), \quad (3)$$

where

$$\left(\frac{a_n}{A_o}\right) \left(\frac{V}{S}\right) \left(\frac{1}{t_n}\right) = R_n = (\text{fraction leached})(\text{cm})(\text{day}^{-1}), \quad (4)$$

t is the elapsed time in days = Σt_n , and $(t - t_n/2)$ signifies that the value of R_n should be plotted at a time representing the middle of the leaching period.

In the past, leaching data have been reported using variously defined leach rates. One is an incremental leach rate based on the mass of the specimen,

$$\left(\frac{a_n}{A_o}\right) \left(\frac{M}{S}\right) \left(\frac{1}{t_n}\right) \text{ versus } (t - t_n/2), \quad (5)$$

where

$$\left(\frac{a_n}{A_o}\right) \left(\frac{M}{S}\right) \left(\frac{1}{t_n}\right) = r_n = (\text{fraction leached})(\text{g/cm}^2)(\text{day}^{-1}), \quad (6)$$

M = mass of specimen in g.

The division of expression (4) by (6) shows that

$$R_n = r_n \left(\frac{V}{M}\right) = \frac{r_n}{\rho}, \quad (7)$$

where

$$\rho = \frac{M}{V} = \text{density of the specimen in g/cm}^3.$$

Another is an incremental leach rate based on the mass of waste solids incorporated in the specimen, i.e.,

$$\left(\frac{a_n}{A_o} \right) \left(\frac{m}{S} \right) \left(\frac{1}{t_n} \right) \text{ versus } (t - t_n/2), \quad (8)$$

where

$$\left(\frac{a_n}{A_o} \right) \left(\frac{m}{S} \right) \left(\frac{1}{t_n} \right) = \bar{r}_n = (\text{fraction leached})(\text{g/cm}^2)(\text{day}^{-1}), \quad (9)$$

m = mass of waste solids in the specimen in g.

The division of expression (4) by (9) shows that

$$R_n = \bar{r}_n \left(\frac{V}{m} \right) = \bar{r}_n \left(\frac{V}{M} \right) \left(\frac{M}{m} \right) = \frac{\bar{r}_n}{\rho\phi}, \quad (10)$$

where

$$\phi = \frac{m}{M} = \text{mass fraction of waste solids in the specimen.}$$

Thus, r_n is converted to R_n by means of the density of the specimen while \bar{r}_n is converted to R_n through the density and the mass fraction of waste solids in the specimen. This comparison of several leach rates lends support to the IAEA recommendation relative to the reporting of leach test results, namely, that information concerning the sample should be reported along with the results of leach tests. Information such as A_o (for each nuclide leached), V , S , M , m , and composition allows manipulation of units, as above, and more meaningful comparisons of leach results and products. The use of incremental leach rates that do not clearly stipulate the substance to which the gram unit refers (viz., the incorporated waste solids or the total waste product), the nuclide to which A_o refers, or how they are averaged with time, has caused some confusion in the interpretation of leaching results.

Data for an asphalt-sludge product¹⁵ and a cement-sludge product¹⁶ are plotted as $(\sum a_n/A_o)(V/S)$ vs t in Fig. 1, as $(\sum a_n/A_o)$ vs $t^{1/2}$ in Fig. 2, and as $(a_n/A_o)(V/S)(1/t_n)$ vs $(t - t_n/2)$ in Fig. 3. The data, as $(a_n/A_o)(M/S)(1/t_n)$ as a function of time, are given for the asphalt-sludge product in ref. 15 and as $(a_n/A_o)(m/S)(1/t_n)$ as a function of time for the cement-sludge product in ref. 16. The asphalt sludge product contained 39 wt % dry waste solids plus 61 wt % asphalt and had a density of 1.47 g/cm³. The sample had a volume of 1.8×10^5 cm³; the surface area in contact with water was 1.7×10^4 cm². The cement-sludge product contained 9 wt % dry waste solids, 43 wt % water, and 48 wt % dry cement. The sample had a volume of 10^4 cm³; the surface area exposed to water was 619 cm². The density of the cement-sludge product was not reported, but a value of 2 g/cm³ seems reasonable for such a product and is therefore assumed in this study. The asphalt-sludge product and the cement-sludge product contained 3.7×10^{-2} $\mu\text{Ci}/\text{cm}^3$ and 2.2×10^{-2} $\mu\text{Ci}/\text{cm}^3$ respectively. The radioactive content of these products was a mixture of aged fission products, for which a half-life of about 30 years should be representative. Thus, over the time span of data collection in these tests, radioactive decay would make no noticeable difference in the results. However, in leach tests with products containing isotopes with half-lives that are short in comparison with the sampling period, radioactive decay for each isotope which occurs in the specimen and also in the leachant must be taken into account individually if the leaching mechanism is to be correctly interpreted. Of course, when results from leaching tests are extrapolated to times that are several orders of magnitude greater than the half-life of an isotope, radioactive decay becomes increasingly important in assessing the amount of the isotope that has been leached and is in the environment (see Sect. 4).

The amount of radioactivity removed from the specimen at any time during the test is readily obtained from Fig. 1 or 2. Data presented in the manner of Fig. 2 can be misleading, as they are in this case, if the effect of different surface-to-volume ratios is not kept in mind. Data presented as in Fig. 1 or Fig. 2 are monotonic with time, a fact that facilitates comparison. A disadvantage of using "cumulative fraction

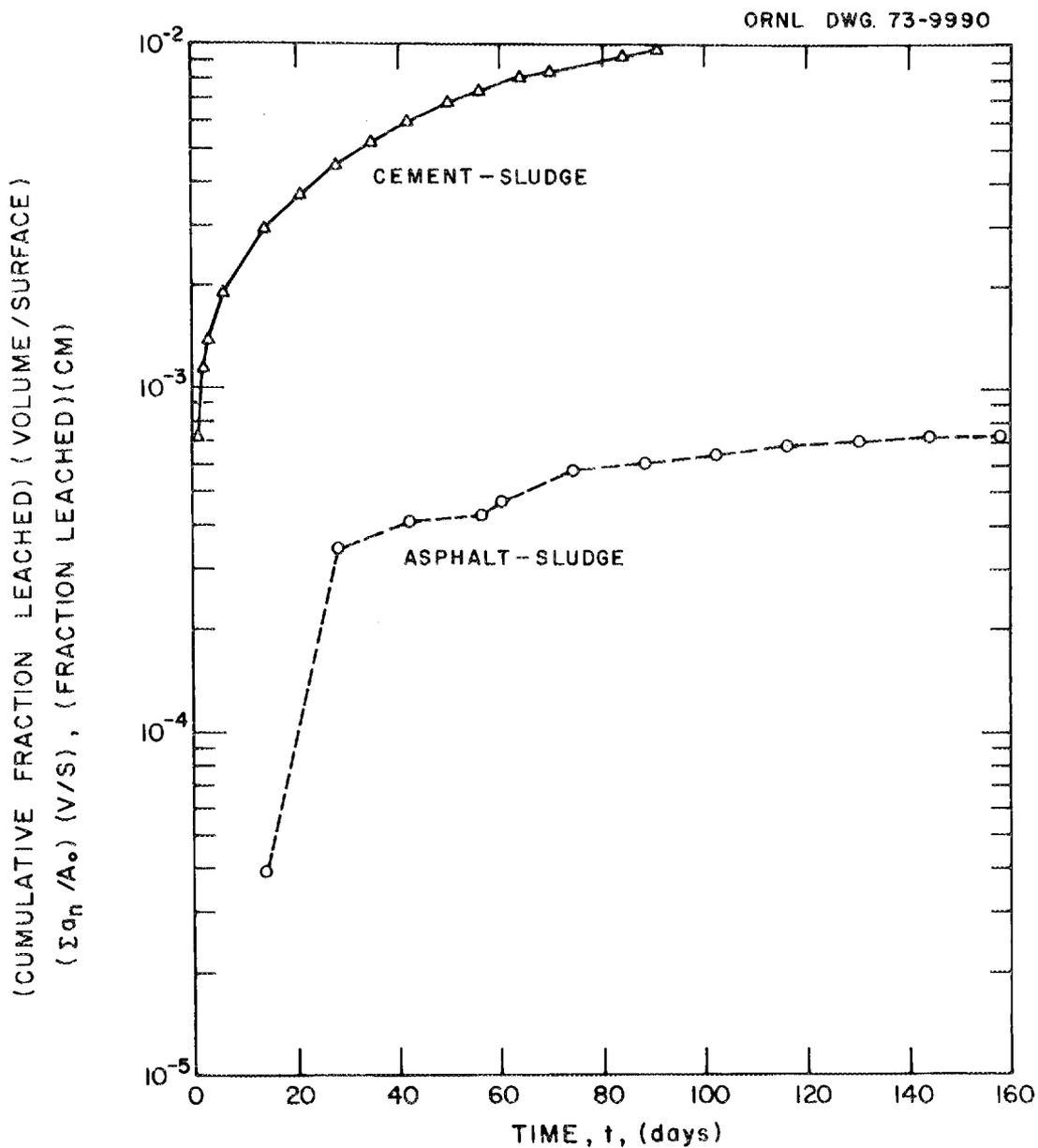


Fig. 1. Cumulative Fraction Leached Multiplied by the Volume-to-Surface Ratio Plotted Against Time for an Asphalt-Sludge Product (Ref. 15) and a Cement-Sludge Product (Ref. 16).

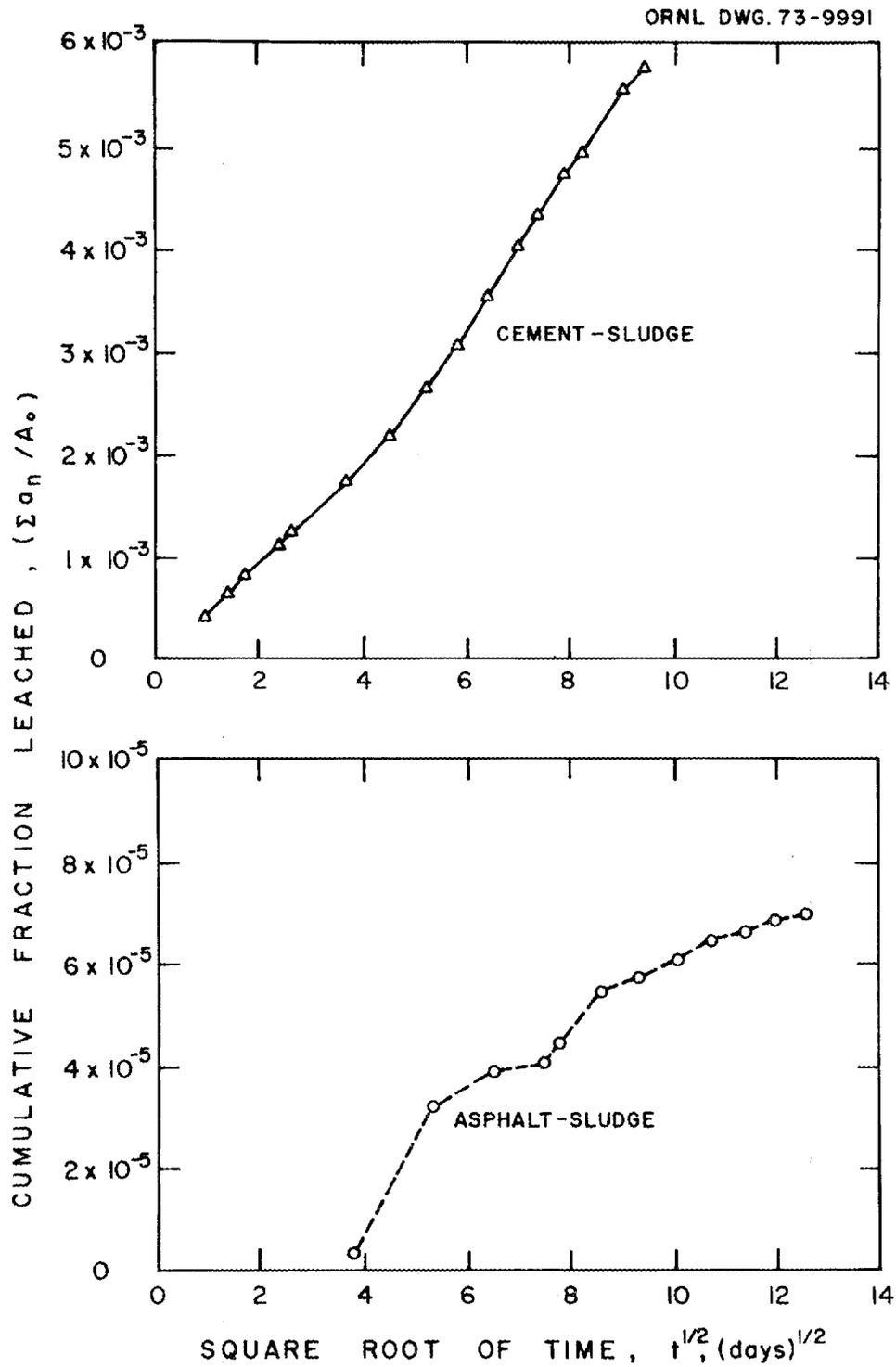


Fig. 2. Cumulative Fraction Leached Plotted Against the Square Root of Time for an Asphalt-Sludge Product (Ref. 15) and a Cement-Sludge Product (Ref. 16).

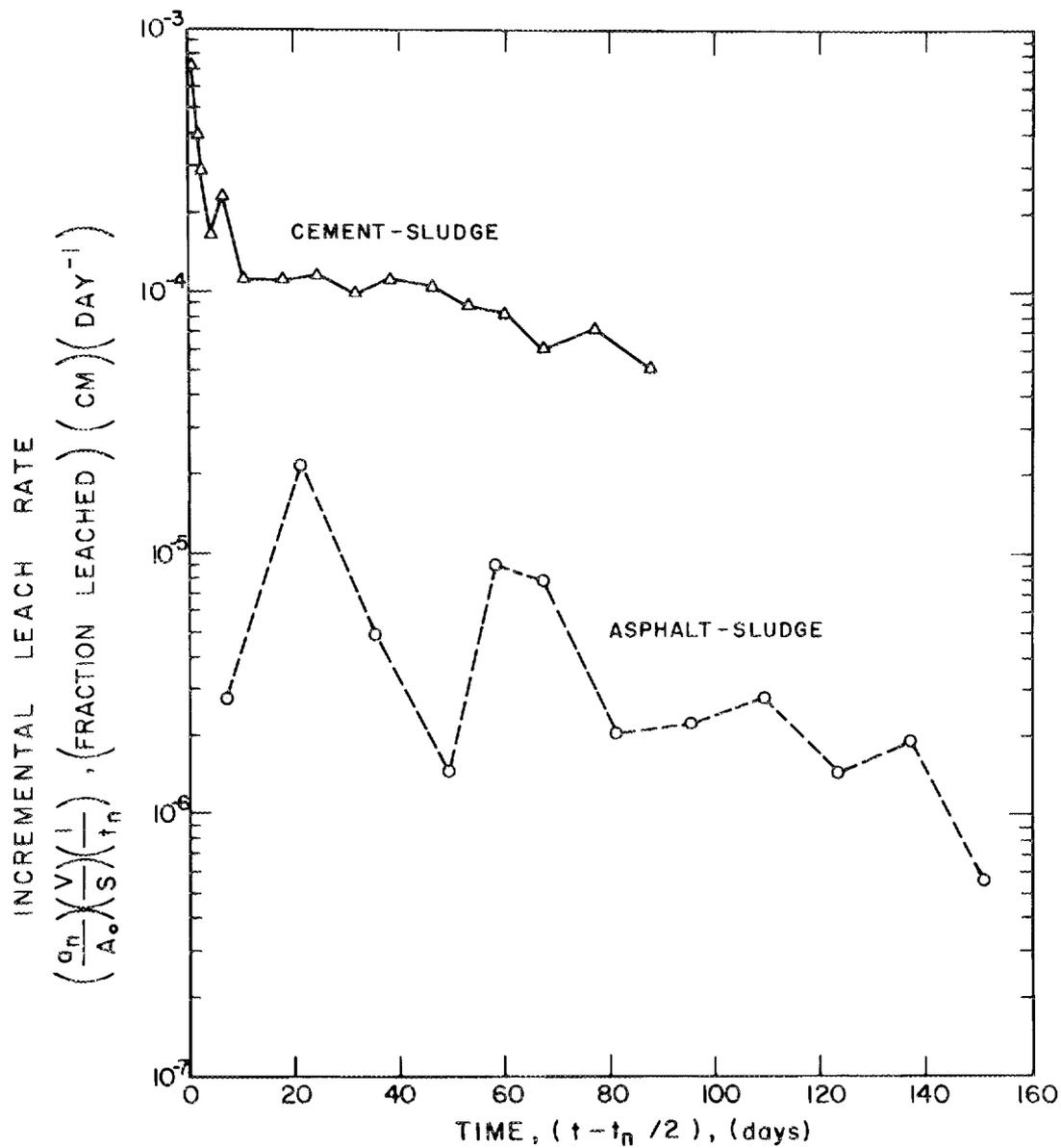


Fig. 3. Incremental Leach Rate Plotted Against Time for an Asphalt-Sludge Product (Ref. 15) and a Cement-Sludge Product (Ref. 16).

leached" is that the data points are coupled. In other words, any error or bias in a given data point is carried by the summing process into all subsequent data points.

An advantage of presenting "incremental fraction leached," as in Fig. 3, is that the data points are not coupled; that is, any error or bias in a data point is not carried into subsequent data points. The true average curve for each of the sets of data points shown in Fig. 3 is monotonic. However, such is not always the case for leach rates vs time (e.g., see ref. 17). In addition, graphical or numerical integration is usually required to obtain the amount of activity removed from a specimen when the results are available only as a plot of incremental leach rate as a function of time. For example, if only the average curves for the sets of data points in Fig. 3 were available, the radioactivity leached from the products at any time, θ , would be obtained from an expression of the form

$$\frac{\sum a_n}{A_0} = \frac{S}{V} \int_0^{\theta} R_n dt \quad . \quad (11)$$

The value of the integral in Eq. (11) would, in most cases, be obtained by graphical integration. Care should be exercised in using values of leach rate to compare waste solids since, as pointed out, they may not clearly indicate the substance to which the gram unit and A_0 refer and how they are averaged with time; in addition, they may not be monotonic with time. As Eq. (11) brings out, they must be integrated over time to achieve full significance, namely, to reveal how much total radioactivity was leached before a given R_n was obtained.

3. ANALYTICAL METHODS FOR REPORTING AND EXTRAPOLATING THE RESULTS OF LEACH TESTS AS A FUNCTION OF TIME

As mentioned, estimates of the quantities of radioactivity from waste solids that enter the environment over long periods of time are needed for engineering, economic, and safety evaluations of proposed waste treatment, storage, transportation, and disposal systems. One

method used for estimating the amount released from a solid over periods of time that are much longer than the span over which the data were taken is to fit the data with various functions and intuitively extrapolate the results. A better way is to attempt to model the system using mass transport equations with data obtained over a period of time sufficient to establish the validity of the model. Such results may be extrapolated with a greater degree of confidence.

3.1 Empirical Curve Fitting

A linear least-squares regression of the asphalt-sludge data plotted in Fig. 1 to an equation of the form

$$Y = \alpha_0 X^{1/2} , \quad (12)$$

where α_0 is a constant, gives

$$\left(\frac{\sum a_n}{A_0} \right) \left(\frac{V}{S} \right) = 6.14 \times 10^{-6} t^{1/2} , \quad (13)$$

where the constant is expressed in the units (fraction leached)(cm)(day^{-1/2}). A similar regression of the cement-sludge data plotted in Fig. 1 to an equation of the form

$$Y = \alpha_1 X^{\alpha_2} , \quad (14)$$

where α_1 and α_2 are constants, gives

$$\left(\frac{\sum a_n}{A_0} \right) \left(\frac{V}{S} \right) = 7.07 \times 10^{-4} t^{0.574} , \quad (15)$$

where α_1 has the dimensions (fraction leached)(cm)(day^{-0.574}). Of course, the fits to the data given by Eqs. (13) and (15) are not unique since, as in any curve-fitting problem, the data can be fitted to other functions, with more constants, and by other techniques than used above. Also, it should be borne in mind that equations obtained in the manner of (13) and (15) generally have not properly considered radioactive decay and will not correctly account for the actual geometry of a system if the finite size becomes important. In addition, extrapolation of such fits beyond

the data bounds can give misguided results. The purpose of this strictly mathematical treatment is not to encourage empiricism but to point out that this approach may, of necessity, be needed for data that seem to fit no valid model based on transport phenomena.

3.2 Modeling with Transport Equations

Several models based on transport phenomena are presented in the following sections to describe the leaching of radioactivity from waste solids. Concentration changes in the solid due to diffusion, dissolution, and a surface condition are considered. In all cases, the solids are treated as semi-infinite media and the effective diffusivity as a constant. Explicitly, for a given product, the effective diffusivity and dissolution rate constant are considered to be independent of position but dependent on the nuclide leached and the temperature while the surface condition is considered to be dependent on the thickness and effective diffusivity of the surface film.

3.2.1 Diffusion

To explain the amount of material leaving per unit surface from the asphalt-sludge product, Dejonghe et al.¹⁵ employed the solution¹⁸ of the transport equations for a semi-infinite medium of uniform initial concentration of mobile species with the surface concentration equal to zero for time greater than zero, namely,

$$\left(\frac{\sum a_n}{A_0} \right) \left(\frac{V}{S} \right) = 2 \left(\frac{D_e}{\pi} \right)^{1/2} t^{1/2} , \quad (16)$$

where D_e is defined as effective diffusivity. This solution also applies to the case of diffusion with simultaneous conversion of a less mobile form of the species to a more mobile form (the inverse of this case is given in ref. 19) where the concentrations of the two forms are directly proportional. That is, if the concentrations of the less and more mobile forms are P and C, respectively, the relationship between them is $P = KC$. The constant of proportionality, K, is included in the D_e of Eq. (16). In this context, it is worth noting that the initial amount of a species

that is free to diffuse at time zero may or may not be equal to the total amount of that species. In any event, the initial amount which is mobile at time zero, A_{om} , may be expressed as a fraction, β , of the total amount of that species, A_o , in the sample at time zero (i.e., $A_{om} = \beta A_o$). It is concentration based on the amount free to diffuse at time zero which is an initial and boundary condition in solving the transport equations. As shown in Appendixes A and B, the fraction can be included in D_e , as well as other parameters of the solution, and need not be of concern unless the concentration of the mobile species as a function of position and time within the sample is needed.

The IAEA has emphasized this square-root relationship of time.^{3,6} A fact that should be equally emphasized is that this square-root relationship for the amount leaving per unit surface from a semi-infinite medium of uniform initial concentration does not hold if other initial and boundary conditions (e.g., a rate of change of surface concentration) are imposed or if other processes (e.g., nonlinear sorption-desorption and chemical reaction) are taking place in the medium.²⁰

If the slope of Eq. (13), 6.14×10^{-5} , is equated to the slope of Eq. (16), $2(D_e/\pi)^{1/2}$, and the resulting expression is solved for D_e , a value of 3.0×10^{-9} cm²/day is obtained for D_e . The same value of D_e was obtained in ref. 15 by a different curve-fitting technique. This value is equivalent to 3.5×10^{-14} cm²/sec. With regard to this change from cm²/day to cm²/sec as the units for expressing diffusivity, it is worth noting that, traditionally, diffusivities are given in cm²/sec in the standard works of the field such as refs. 9-12, engineering textbooks such as refs. 7 and 8, and in engineering handbooks such as ref. 21.

A pertinent observation made in ref. 22 concerning the square-root-of-time relationship is that effective diffusivities have been reported that were obtained from data which, though linear with the square root of time, did not go through the origin as required by Eq. (16). This is tantamount to fitting the data to a more general equation

$$\left(\frac{\sum a_n}{A_o} \right) \left(\frac{V}{S} \right) = \left[\left(\frac{\sum a_n}{A_o} \right) \left(\frac{V}{S} \right) \right]_o + 2 \left(\frac{D_e}{\pi} \right)^{1/2} t^{1/2} , \quad (17)$$

where the y-intercept, $[(\sum a_n/A_o)(V/S)]_o$, is not zero. Speaking broadly, a positive $[(\sum a_n/A_o)(V/S)]_o$ could represent an amount of radioactivity (due perhaps to factors such as an especially active, contaminated, or nonrepresentative surface) that is leached or readily washed off over a relatively short period of time. A negative $[(\sum a_n/A_o)(V/S)]_o$ would correspond to a time (the value of a x-intercept) that represents a delay or lag in the leaching due perhaps to factors such as a passive surface or the filling of voids. In many cases, $[(\sum a_n/A_o)(V/S)]_o$ represents a small fraction¹⁵ of the total leached during the experiments, or the time lag is a small portion²² of the total time of the experiment. However, if the initial amount leached is a significant portion²³ of the total amount leached or the time lag is a significant portion of the total time, these phenomena cannot be ignored and an attempt to account for them is necessary. This would also apply to any solution of the transport equations.

The flux (amount transferred per unit surface per unit time) at the surface of the medium for this model is¹⁸

$$\left. \frac{dq}{dt} \right|_{x=0} = \left(\frac{A_o}{V} \right) \left(\frac{D_e}{\pi} \right)^{1/2} t^{-1/2}, \quad (18)$$

where q is the amount leaving per unit surface. The intensive property, q , of the semi-infinite medium can be expressed in terms of extensive properties of the finite sample, as follows:

$$q = \frac{a}{S}, \quad (19)$$

where a is the amount removed at any time t . If the leachant renewal periods are sufficiently short or the leach rate is reasonably linear over the leachant renewal period, then

$$\frac{a_n}{t_n} = \lim_{\Delta t \rightarrow 0} \left(\frac{\Delta a}{\Delta t} \right) = \frac{da}{dt} \quad (20)$$

is a good approximation. If a_n/t_n is taken to be at the middle of the leachant renewal period, that is, at time

$$T = (t - t_n/2) , \quad (21)$$

the substitution of Eqs. (19)-(21) into Eq. (18) gives

$$\left(\frac{a_n}{A_o} \right) \left(\frac{V}{S} \right) \left(\frac{1}{t_n} \right) = \left(\frac{D_e}{\pi} \right)^{1/2} T^{-1/2} . \quad (22)$$

Thus, incremental leach rates that satisfy the above restraints can approximate the flux at the surface of the sample and can be used to evaluate D_e . For the most part, cumulative fraction leached as a function of time has been used to evaluate D_e for waste solids in the past and will be used in this report. However, for each model presented, the incremental leach rate representation for the flux at the surface is given so that this method of treating leach data may be evaluated.

3.2.2 Diffusion with a Concentration-Dependent Dissolution Rate

The model of diffusion with concentration-dependent dissolution suggested in ref. 22 seems plausible to explain the amount of material leaving per unit surface from the cement-sludge product¹⁶ and is considered here. The initial concentration of mobile forms of a species may be at a level representing saturation for these forms in the matrix. The rate at which less mobile forms of the species are converted to more mobile forms can be considered to be proportional to the difference in concentration between this saturation concentration and the average concentration of mobile species at any time. That is, the rate can be expressed as $k(C_s - C)$, where k is a dissolution rate constant, C_s is the concentration of mobile species at saturation, and C is the concentration of mobile species at any time.

Solution (Appendix A) of the transport equations for a semi-infinite medium with a uniform initial concentration of the mobile species, with the mobile species being produced at a rate $k(C_s - C)$ per unit volume per unit time for time >0 , and with the surface concentration of mobile species maintained at zero for time >0 , gives

$$\left(\frac{a_n}{A_o} \right) \left(\frac{V}{S} \right) \left(\frac{1}{t_n} \right) = (D_e k)^{1/2} \left[\text{erf} (kT)^{1/2} + \frac{e^{-kT}}{(\pi k T)^{1/2}} \right] \quad (23)$$

for the incremental leach rate at the surface, and

$$\left(\frac{\sum a_n}{A_o} \right) \left(\frac{V}{S} \right) = (D_e k)^{1/2} \left[\left(t + \frac{1}{2k} \right) \text{erf} (kt)^{1/2} + \left(\frac{t}{\pi k} \right)^{1/2} e^{-kt} \right] \quad (24)$$

for the total amount leached. In these equations,

k = a dissolution rate constant, sec^{-1} and

$$\text{erf } u = \frac{2}{\pi^{1/2}} \int_0^u e^{-z^2} dz .$$

Properties and tabulated values of the error function (erf) are given in refs. 10-12 and comprehensive mathematical handbooks such as ref. 24.

The data for the cement-sludge product given in Fig. 1 were fitted by a searching or successive iteration technique with Eq. (24) to give a D_e of 5.5×10^{-12} cm^2/sec and a k of 1.5×10^{-7} sec^{-1} . A comparison of the experimental values with the amounts leached as predicted by Eqs. (15) and (24) are shown in Table 1. For the most part, the results predicted by Eqs. (15) and (24) agree well with the data. As a general rule, the extrapolation of an empirical equation such as Eq. (15) beyond the data bounds is a questionable operation. On the other hand, theoretical relations such as Eq. (24) are based on well-established principles and suggest techniques that might be investigated systematically for corroboration. One corroborative experiment in this case might be an independent determination of the dissolution rate constant, k , for the sludge solids alone. If the physicochemical properties of the sludge are largely unaltered by the incorporation in cement, k would be expected to be essentially the same before and after incorporation. A corroborative procedure suggested by Eq. (24) is to determine the rate of approach of the data to the asymptote required by the model; namely, when kt is large so that $\text{erf}(kt)^{1/2}$ approaches unity, Eq. (24) becomes²⁵

Table 1. Comparison of the Amounts Leached from a Cement-Sludge Product^a at Ambient Temperatures to Those Predicted by an Empirical Equation and an Equation Based on Transport Phenomena

$\left(\frac{\sum a_n}{A_o}\right) \left(\frac{V}{S}\right)$, (fraction leached)(cm)				
Time (days)	Data ^a	Predicted by		Approach to Asymptote ^d (%)
		Empirical Eq. (15) ^b	Transport Eq. (24) ^c	
1	7.2×10^{-4}	7.1×10^{-4}	7.8×10^{-4}	23
2	1.1×10^{-3}	1.1×10^{-3}	1.1×10^{-3}	35
3	1.4×10^{-3}	1.3×10^{-3}	1.4×10^{-3}	43
6	1.9×10^{-3}	2.0×10^{-3}	2.0×10^{-3}	54
7	2.1×10^{-3}	2.2×10^{-3}	2.1×10^{-3}	59
14	2.9×10^{-3}	3.2×10^{-3}	3.1×10^{-3}	70
21	3.7×10^{-3}	4.1×10^{-3}	3.9×10^{-3}	79
28	4.5×10^{-3}	4.8×10^{-3}	4.6×10^{-3}	86
35	5.2×10^{-3}	5.4×10^{-3}	5.3×10^{-3}	90
42	6.0×10^{-3}	6.0×10^{-3}	5.9×10^{-3}	95
50	6.8×10^{-3}	6.7×10^{-3}	6.6×10^{-3}	98
56	7.4×10^{-3}	7.1×10^{-3}	7.1×10^{-3}	100
64	8.0×10^{-3}	7.7×10^{-3}	7.8×10^{-3}	99
70	8.4×10^{-3}	8.1×10^{-3}	8.3×10^{-3}	99
84	9.4×10^{-3}	9.0×10^{-3}	9.5×10^{-3}	98
91	9.8×10^{-3}	9.4×10^{-3}	1.0×10^{-2}	96

^aData from ref. 16 converted to the above units assuming the density of the cement-sludge product = 2 g/cm³.

^bThe constant in Eq. (15) is 7.07×10^{-4} (fraction leached)(cm)(day^{-0.574}).

^cEquation (24) with $D_e = 5.5 \times 10^{-12}$ cm²/sec and $k = 1.5 \times 10^{-7}$ sec⁻¹.

^d[Data/Eq. (25)] x 100 with $D_e = 5.5 \times 10^{-12}$ cm²/sec and $k = 1.5 \times 10^{-7}$ sec⁻¹.

$$\left(\frac{\sum a_n}{A_o} \right) \left(\frac{V}{S} \right) \approx (D_e k)^{1/2} \left[(t + 1/2k) \right]. \quad (25)$$

The amount leached from the product approaches within 70% of this asymptote at 14 days and remains within 95 to 100% during the interval from 42 to 91 days (Table 1). If data had been collected for several more months and still remained near the asymptote, it would tend to confirm more forcefully that the model describes the behavior of the sample. Leach rate data fitted with Eq. (24) for other cement- and asphalt-sludge products described in ref. 16 gave equally good agreement between observed and calculated values. Solutions of the transport equations used to describe the results of leach tests are based most often on linear flow in a semi-infinite solid or in the solid bounded by two parallel planes. Parametric studies that compare these solutions with solutions for actual geometries can be carried out in the manner illustrated by ref. 26 (for the case of diffusion). Such studies can provide valuable insight that aids in the design and evaluation of leach tests as well as in the extension of these results to actual disposal conditions.

Naturally, the question arises why the product discussed by Smith,¹⁶ which incorporates a sludge of low solubility, seems to follow Eq. (24) while the product of Dejonghe et al.,¹⁵ also incorporating a sludge of low solubility, seems to follow Eq. (16) given in Sect. 3.2.1. The answer may be that the latter sludge is of even lower solubility than the former and that the data of Dejonghe et al. do fit Eq. (24), which for very small kt approaches Eq. (16). This may be demonstrated in the following discussion. When kt is small, Eq. (24) becomes²⁵

$$\left(\frac{\sum a_n}{A_o} \right) \left(\frac{V}{S} \right) \approx 2 \left(\frac{D_e}{\pi} \right)^{1/2} \left[\left(1 + \frac{1}{2}kt \right) t^{1/2} \right]. \quad (26)$$

For small k at small t , Eq. (26) approaches Eq. (16) and, for $k = 0$, reduces to Eq. (16). To illustrate this point, the data for the asphalt-sludge product of Dejonghe et al. were fitted with Eq. (24) by a searching technique. The amounts leached from the asphalt-sludge product as given by the data, and as predicted by Eq. (16) with a D_e of 3.5×10^{-14} cm²/sec

and by Eq. (24) with a D_e of 3.3×10^{-14} cm²/sec and a k of 7.2×10^{-9} sec⁻¹, are shown in Table 2. The table also shows the approach of the data to the asymptote. This approach is much slower with the asphalt-sludge product than with the cement-sludge product (Table 1) because of the lower k for the asphalt-sludge product. Over the time span shown, the results predicted by Eqs. (16) and (24) agree equally well with the data. However, when extrapolated to much longer times, Eq. (24) predicts a larger fraction leached than does Eq. (16), for example, about 58% more at 10 years and a factor of 4.2 more at 100 years (Table 2). This difference effectively illustrates a point made in ref. 22, namely, that extrapolations concerning the leaching of sparingly soluble solids based on Eq. (16) should be viewed with reserve. Consideration of the $l/2$ kt term in Eq. (26) shows that long leaching periods (a year to several years) are needed to discern k when its value is small ($\sim 10^{-8}$ to 10^{-9} sec⁻¹).

The leaching of commercial glasses by aqueous solutions has been studied extensively using a wide variety of experimental techniques and conditions.²⁷⁻²⁹ Many of these tests are carried out in a manner such that the results are specific with regard to the sample, technique, and conditions. However, a purely empirical expression^{29,30} that explains much of the leaching results, especially silicate glasses, is of the form

$$F = b t^{1/2} + ct \quad , \quad (27)$$

where F is the total fraction leached and b and c are empirical constants, with b always considerably larger than c . Equation (27) shows that the total fraction leached varies with the square root of time at short times and becomes linear with time at longer times. The differentiation of Eq. (27) with respect to time gives

$$\frac{dF}{dt} = (b/2)t^{-1/2} + c \quad , \quad (28)$$

which shows that the rate of leaching varies with the reciprocal of the square root of time at short times and approaches a constant value at long times. This is the behavior predicted by Eq. (24) for sparingly

Table 2. Comparison of the Amounts Leached from an Asphalt-Sludge Product^a at Ambient Temperatures to Those Predicted by Equations Based on Transport Phenomena without^b and with^c a Concentration-Dependent Dissolution Term

Time (days)	Data ^a	Predicted by		Approach to Asymptote ^d (%)
		Transport Eq. (16) ^b	Transport Eq. (24) ^c	
14	3.97×10^{-5}	2.32×10^{-4}	2.25×10^{-4}	4
28	3.45×10^{-4}	3.28×10^{-4}	3.20×10^{-4}	31
42	4.13×10^{-4}	4.02×10^{-4}	3.93×10^{-4}	37
56	4.34×10^{-4}	4.64×10^{-4}	4.54×10^{-4}	38
60	4.71×10^{-4}	4.81×10^{-4}	4.71×10^{-4}	41
74	5.82×10^{-4}	5.34×10^{-4}	5.25×10^{-4}	50
88	6.11×10^{-4}	5.82×10^{-4}	5.74×10^{-4}	51
102	6.42×10^{-4}	6.26×10^{-4}	6.20×10^{-4}	53
116	6.82×10^{-4}	6.68×10^{-4}	6.63×10^{-4}	56
130	7.03×10^{-4}	7.07×10^{-4}	7.03×10^{-4}	57
144	7.30×10^{-4}	7.45×10^{-4}	7.42×10^{-4}	58
158	7.38×10^{-4}	7.80×10^{-4}	7.80×10^{-4}	58
	End of Data			
365		1.10×10^{-3}	1.24×10^{-3}	
3650		3.75×10^{-3}	5.92×10^{-3}	
36500		1.19×10^{-2}	4.97×10^{-2}	

^aData from ref. 15 converted to the units indicated.

^bEquation (16) with $D_e = 3.5 \times 10^{-14}$ cm²/sec.

^cEquation (24) with $D_e = 3.3 \times 10^{-14}$ cm²/sec and $k = 7.2 \times 10^{-9}$ sec⁻¹.

^d[Data/Eq. (25)] x 100 with $D_e = 3.3 \times 10^{-14}$ cm²/sec and $k = 7.2 \times 10^{-9}$ sec⁻¹.

soluble substances. At short times, the amount leached is given by Eq. (26) which, for very small kt , follows a square-root-of-time relationship. For very long times, the amount leached is given by Eq. (25), which follows a linear relationship with time. The differentiation of Eq. (26) with respect to time when kt is very small yields

$$d \left[\left(\frac{\sum a_n}{A_0} \right) \left(\frac{V}{S} \right) \right] / dt \approx \left(\frac{D_e}{\pi} \right)^{1/2} t^{-1/2} , \quad (29)$$

and the differentiation of Eq. (25) with time yields

$$d \left[\left(\frac{\sum a_n}{A_0} \right) \left(\frac{V}{S} \right) \right] / dt \approx (D_e k)^{1/2} . \quad (30)$$

Equation (29), which is applicable at short times, predicts a leach rate that varies with the reciprocal of the square root of time; Eq. (30), which is applicable at long times, predicts a leach rate that is constant with time. Of course, these results for the leach rate can be obtained directly from Eq. (23) by evaluation at small kt and large kt , respectively. The time variations given by Eqs. (29) and (30) are the same as given by Eq. (28).

A phosphate-glass product³¹ (PG-1) with a density of 2.8 g/cm³ was chosen to illustrate data fitted with Eq. (24) for this type of glass. It was composed nominally of the following constituents (in wt %):

P ₂ O ₅ , 67.9	Cr ₂ O ₃ , 0.5	MoO ₃ , 3.5
SiO ₂ , 0.2	NiO, 0.6	RuO ₂ , 0.1
Na ₂ O, 4.4	U ₃ O ₈ , 0.8	Co ₃ O ₄ , 0.2
K ₂ O, 0.6	RE ₂ O ₃ , 5.9	SrO, 0.5
Fe ₂ O ₃ , 11.5	ZrO ₂ , 2.5	BaO, 0.9

The chief reason for selecting this product to analyze in detail is that long-term leaching data for it are available. Mendel and McElroy³¹ have clearly stated that these results are for phosphate-glass products which are cooled rapidly (called "grab" samples³¹), that these products devitrify when cooled slowly, and that the leachability of these devitrified phosphate products is increased by a factor of roughly a thousand. The leach

rate data for most of the other products given in ref. 31 were also studied and were found, in general, to follow Eq. (24) reasonably well. The few exceptions were for data that covered the shorter periods of time and had the most pronounced scatter, as well as for data yielding the higher values of D_e and lower values of k .

Data for the leaching of ^{137}Cs from the phosphate-glass PG-1 were fitted with Eq. (24) by a searching technique to give a D_e of 6.2×10^{-17} cm^2/sec and a k of 4.7×10^{-8} sec^{-1} . The amounts leached from the product, as given by the data and predicted by Eq. (24) with the D_e and k given above, are shown in Table 3 and Fig. 4. Within the scatter of the data, the results predicted by Eq. (24) agree well with the observed values. The approach of the data to the asymptote (given in Table 3) indicates that the amount leached appears to be following the asymptote (within about $\pm 7\%$) throughout the period beginning after approximately four months and continuing to the end of the reported data at 31 months. In experiments carried out for this length of time, the decay of ^{137}Cs begins to have an effect on the results (see Sect. 4). A linear least-squares regression of the PG-1 data to Eq. (16) gives a D_e of 1.5×10^{-18} cm^2/sec . A comparison of the data with the amounts leached as predicted by Eq. (16) with this D_e is given in Table 3 and shows that the predicted amounts are greater than the experimental results at short times and less than the experimental results at long times.

A borosilicate-glass product³¹ (SS-12) with a density of 3.0 g/cm^3 was chosen as the product to illustrate this type of glass. It was composed nominally of the following constituents (in wt %):

SiO_2 , 22.5	ZnO , 10.5	MoO_3 , 5.3
B_2O_3 , 25.2	CaO , 1.4	RuO_2 , 0.2
Na_2O , 5.9	MgO , 0.7	Co_3O_4 , 0.2
K_2O , 4.5	U_3O_8 , 0.6	CuO , 0.1
Fe_2O_3 , 2.3	RE_2O_3 , 10.3	SrO , 2.3
Cr_2O_3 , 0.2	ZrO_2 , 4.0	BaO , 2.9
NiO , 0.9		

Table 3. Comparison of the Amounts of ^{137}Cs Leached from a Phosphate-Glass Product^a at 25°C to Those Predicted by an Equation Based on Transport Phenomena without^b and with^c a Concentration-Dependent Dissolution Term

$\left(\frac{\sum a_n}{A_0} \right) \left(\frac{V}{S} \right)$, (fraction leached)(cm)				
Time (days)	Data ^a	Predicted by		Approach to Asymptote ^d (%)
		Transport Eq. (16) ^b	Transport Eq. (24) ^c	
7	5.5×10^{-6}	1.1×10^{-6}	7.0×10^{-6}	29
14	9.0×10^{-6}	1.5×10^{-6}	9.9×10^{-6}	44
21	1.2×10^{-5}	1.9×10^{-6}	1.2×10^{-5}	56
28	1.4×10^{-5}	2.2×10^{-6}	1.4×10^{-5}	63
35	1.5×10^{-5}	2.4×10^{-6}	1.6×10^{-5}	64
42	1.7×10^{-5}	2.7×10^{-6}	1.8×10^{-5}	70
49	1.8×10^{-5}	2.9×10^{-6}	1.9×10^{-5}	71
56	2.1×10^{-5}	3.1×10^{-6}	2.1×10^{-5}	79
63	2.2×10^{-5}	3.3×10^{-6}	2.2×10^{-5}	80
70	2.4×10^{-5}	3.4×10^{-6}	2.4×10^{-5}	84
77	2.6×10^{-5}	3.6×10^{-6}	2.5×10^{-5}	88
84	2.7×10^{-5}	3.8×10^{-6}	2.7×10^{-5}	88
91	2.9×10^{-5}	3.9×10^{-6}	2.8×10^{-5}	92
98	3.0×10^{-5}	4.1×10^{-6}	2.9×10^{-5}	92
105	3.1×10^{-5}	4.2×10^{-6}	3.0×10^{-5}	92
112	3.3×10^{-5}	4.4×10^{-6}	3.2×10^{-5}	95
119	3.4×10^{-5}	4.5×10^{-6}	3.3×10^{-5}	95
126	3.5×10^{-5}	4.6×10^{-6}	3.4×10^{-5}	95
168	4.2×10^{-5}	5.3×10^{-6}	4.1×10^{-5}	98
196	4.5×10^{-5}	5.8×10^{-6}	4.5×10^{-5}	96
224	5.0×10^{-5}	6.2×10^{-6}	5.0×10^{-5}	98
252	5.5×10^{-5}	6.5×10^{-6}	5.4×10^{-5}	99
280	5.8×10^{-5}	6.9×10^{-6}	5.9×10^{-5}	98
364	7.7×10^{-5}	7.9×10^{-6}	7.1×10^{-5}	107
448	8.4×10^{-5}	8.7×10^{-6}	8.4×10^{-5}	100
532	9.0×10^{-5}	9.5×10^{-6}	9.6×10^{-5}	93
616	1.03×10^{-4}	1.02×10^{-4}	1.09×10^{-4}	94
672	1.14×10^{-4}	1.07×10^{-4}	1.17×10^{-4}	96
756	1.28×10^{-4}	1.13×10^{-4}	1.30×10^{-4}	99
854	1.43×10^{-4}	1.20×10^{-4}	1.44×10^{-4}	99
938	1.65×10^{-4}	1.26×10^{-4}	1.56×10^{-4}	105

^aData (Product PG-1)³¹ converted to the units indicated.

^bEquation (16) with $D_e = 1.5 \times 10^{-16}$ cm²/sec.

^cEquation (24) with $D_e = 6.2 \times 10^{-17}$ cm²/sec and $k = 4.7 \times 10^{-8}$ sec⁻¹.

^d[Data/Eq. (25)] x 100 with $D_e = 6.2 \times 10^{-17}$ cm²/sec and $k = 4.7 \times 10^{-8}$ sec⁻¹.

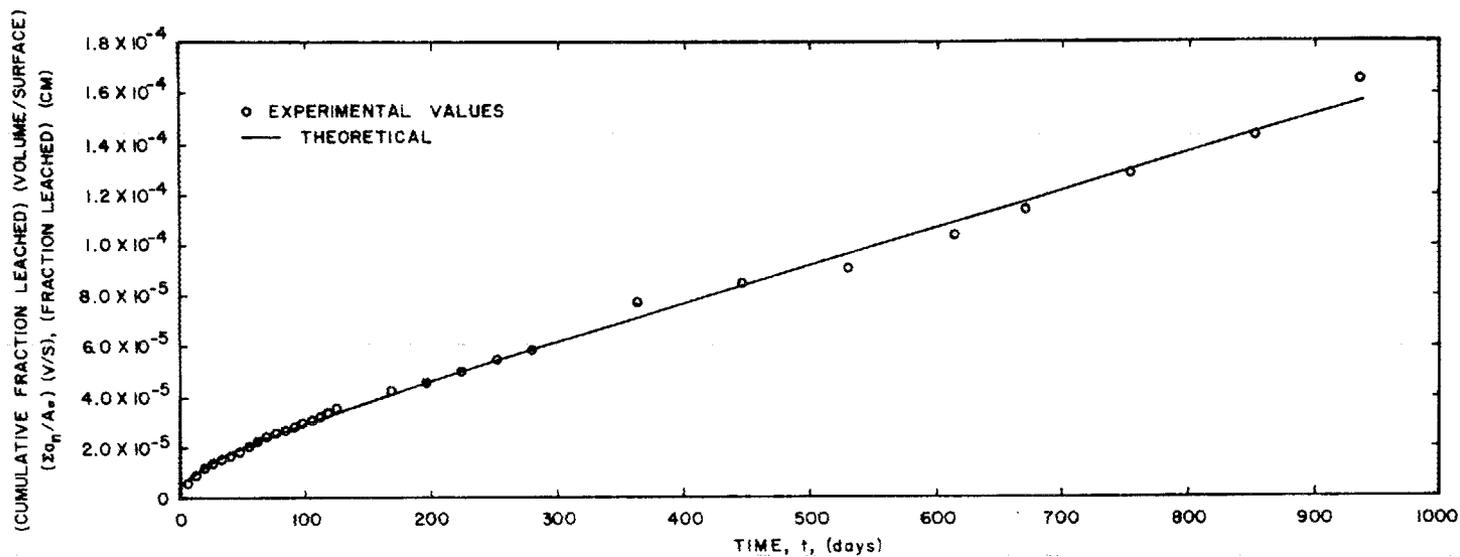


Fig. 4. Comparison of the Amounts of ^{137}Cs Leached from a Phosphate-Glass Product at 25°C to Those Predicted by an Equation Based on Transport Phenomena with a Dissolution Term. [Experimental values from ref. 31 for product PG-1. Theoretical curve calculated using Eq. (24) with $D_e = 6.2 \times 10^{-17} \text{ cm}^2/\text{sec}$ and $k = 4.7 \times 10^{-8} \text{ sec}^{-1}$.]

The borosilicate-glass products (called core-drilled samples³¹) were not cooled rapidly and had time-temperature treatments (long periods of time at high temperature) closely simulating those envisaged for the products obtained by solidification of high-level radioactive wastes.

The parameters in Eq. (24) for the borosilicate-glass product are a D_e of 8.4×10^{-15} cm²/sec and a k of 1.1×10^{-7} sec⁻¹. The amounts leached from the product, as given by the data and predicted by Eq. (24), are shown in Table 4 and Fig. 5 and are in good agreement. The data appear to be following the asymptote after about three months (Table 4).

3.2.3 Diffusion with a Concentration-Dependent Dissolution Rate and Linear Surface-Transfer

Frequently, the surface of a body has or develops a condition or film which can affect the rate of transfer of diffusing substance. An assumption commonly made, which often represents the facts quite well,^{9,10,32} is that the rate of transfer across the surface is directly proportional to the difference in concentration between the surface of the body and the surrounding medium. In heat transfer, this relationship is sometimes referred to as "Newton's law of cooling." Speaking broadly, the effect of surface films of low diffusivity can be very marked for materials of high diffusivity, while it is much less important for materials of low diffusivity.

Solution (Appendix B) of the transport equations for a semi-infinite medium with a uniform initial concentration of the mobile species, with the mobile species being produced at a rate $k(C_s - C)$ per unit volume per unit time for time >0 , and with linear mass transfer at the surface gives

$$\left(\frac{a_n}{A_0} \right) \left(\frac{V}{S} \right) \left(\frac{l}{t_n} \right) = \frac{l(D_e k)^{1/2}}{l - k} \left[\operatorname{erf} (kT)^{1/2} + \left(\frac{l}{k} \right)^{1/2} e^{(l-k)T} \operatorname{erfc} (lT)^{1/2} - (k/l)^{1/2} \right] \quad (31)$$

for the incremental leach rate at the surface, and

Table 4. Comparison of the Amounts of ^{137}Cs Leached from a Borosilicate-Glass Product^a at 25°C to Those Predicted by an Equation Based on Transport Phenomena with a Concentration-Dependent Dissolution Term

Time (days)	$\left(\frac{\sum a_n}{A_0}\right)\left(\frac{V}{S}\right)$, (fraction leached)(cm)		
	Data ^a	Predicted by Transport Eq. (24) ^b	Approach to Asymptote ^c (%)
1	2.6×10^{-5}	3.0×10^{-5}	18
7	7.4×10^{-5}	8.2×10^{-5}	47
14	1.19×10^{-4}	1.19×10^{-4}	68
21	1.56×10^{-4}	1.48×10^{-4}	81
28	1.91×10^{-4}	1.75×10^{-4}	90
56	2.64×10^{-4}	2.66×10^{-4}	93
84	3.30×10^{-4}	3.48×10^{-4}	92
112	4.21×10^{-4}	4.26×10^{-4}	97
140	5.09×10^{-4}	5.02×10^{-4}	101
168	5.82×10^{-4}	5.77×10^{-4}	100
196	6.50×10^{-4}	6.52×10^{-4}	100
	End of Data		
3,650		9.76×10^{-3}	
36,500		9.64×10^{-2}	
365,000		9.62×10^{-1}	

^aData (Product SS-12)³¹ converted to the units indicated.

^bEquation (24) with $D_e = 8.4 \times 10^{-15} \text{ cm}^2/\text{sec}$ and $k = 1.1 \times 10^{-7} \text{ sec}^{-1}$.

^c[Data/Eq. (25)] x 100 with $D_e = 8.4 \times 10^{-15} \text{ cm}^2/\text{sec}$ and $k = 1.1 \times 10^{-7} \text{ sec}^{-1}$.

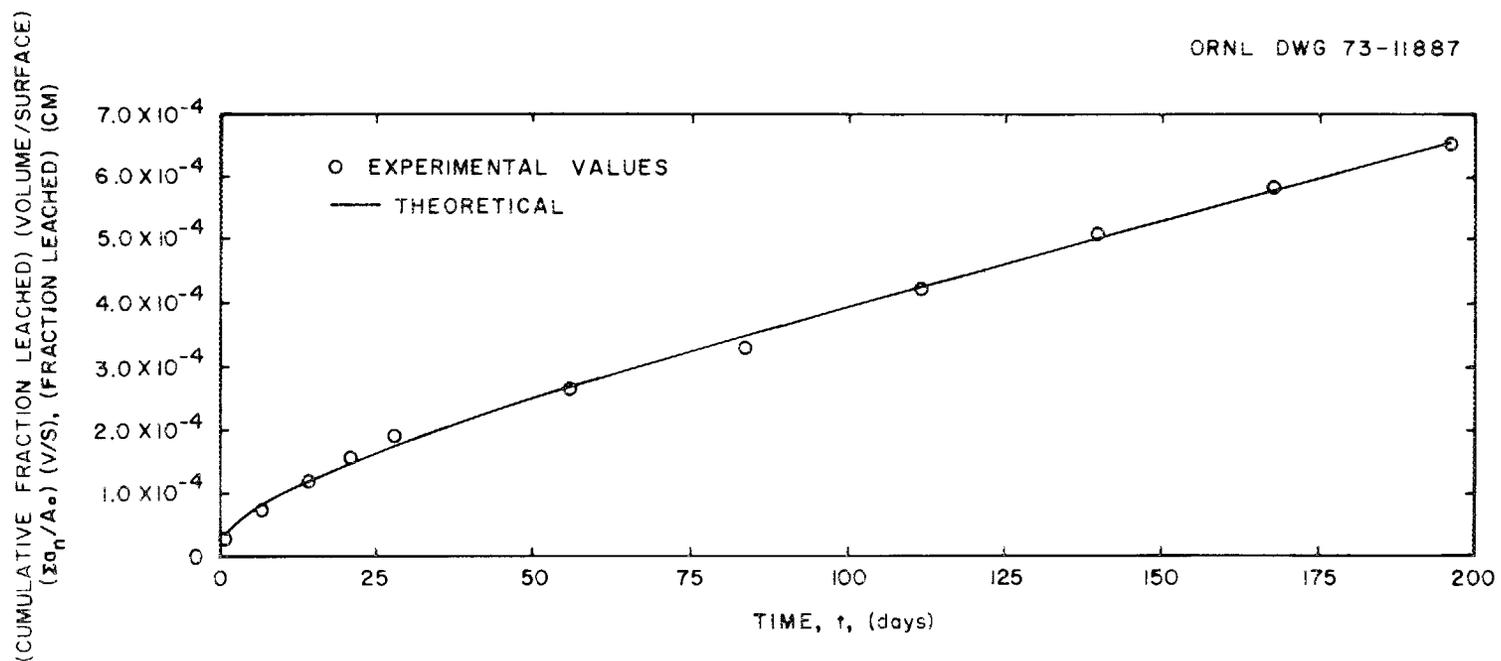


Fig. 5. Comparison of the Amounts of ¹³⁷Cs Leached from a Borosilicate-Glass Product at 25°C to Those Predicted by an Equation Based on Transport Phenomena with a Dissolution Term. [Experimental values from ref. 31 for product SS-12. Theoretical curve calculated using Eq. (24) with $D_e = 8.4 \times 10^{-15}$ cm²/sec and $k = 1.1 \times 10^{-7}$ sec⁻¹.]

$$\begin{aligned}
\left(\frac{\sum a_n}{A_0} \right) \left(\frac{V}{S} \right) &= \frac{\ell(D_e k)^{1/2}}{\ell - k} \left[\left\{ t + \frac{\ell}{k(\ell - k)} - \frac{1}{2k} \right\} \operatorname{erf}(kt)^{1/2} \right. \\
&+ \frac{\ell}{(\ell - k)(k\ell)^{1/2}} e^{(\ell-k)t} \operatorname{erfc}(\ell t)^{1/2} + \left(\frac{t}{\pi k} \right)^{1/2} e^{-kt} \\
&\left. - \left(\frac{k}{\ell} \right)^{1/2} t - \frac{\ell}{(\ell - k)(k\ell)^{1/2}} \right] \quad (32)
\end{aligned}$$

for the total amount leached. In Eqs. (31) and (32),

ℓ = a surface transfer constant, sec^{-1} , and
 $\operatorname{erfc} u = 1 - \operatorname{erf} u$.

The solution is valid for both positive and negative $(\ell - k)$ but not for $(\ell - k)$ equal to zero.

The data for the phosphate-glass³¹ (PG-1) were fitted by a searching technique with Eq. (32) to yield a D_e of $6.5 \times 10^{-17} \text{ cm}^2/\text{sec}$, a k of $4.5 \times 10^{-8} \text{ sec}^{-1}$, and an ℓ of $3.7 \times 10^{-4} \text{ sec}^{-1}$. The amounts leached from the product, as given by the data and predicted by Eq. (32) with the parameters above, are shown in Table 5. As seen, the values are in good agreement. The values predicted for PG-1 by Eqs. (24) and (32) are very nearly the same and show that the surface film has no significant affect on the amount leached (cf. Table 3 with Table 5). The values of $[(\sum a_n/A_0)(V/S)]$ are 5.57×10^{-4} , 5.40×10^{-3} , and 5.39×10^{-2} as predicted by Eq. (24), and are 5.54×10^{-4} , 5.37×10^{-3} , and 5.35×10^{-2} as predicted by Eq. (32) at 10, 100, and 1,000 years, respectively.

The data for the borosilicate-glass³¹ (SS-12) were fitted by a searching technique with Eq. (32) to yield a D_e of $8.6 \times 10^{-15} \text{ cm}^2/\text{sec}$, a k of $1.1 \times 10^{-7} \text{ sec}^{-1}$, and an ℓ of $2.7 \times 10^{-3} \text{ sec}^{-1}$. The amounts leached from the product, as given by the data and predicted by Eq. (32) with these parameters, are shown in Table 6. As seen, the predicted values and the data are in good agreement. The amounts leached from SS-12 as predicted by Eq. (24) are less than 0.5% greater than those predicted by Eq. (32) at 10, 100, and 1,000 years (cf. Table 4 and

Table 5. Comparison of the Amounts of ^{137}Cs Leached from a Phosphate-Glass Product^a at 25°C to Those Predicted by an Equation Based on Transport Phenomena with a Dissolution Term plus a Surface Condition

Time (days)	$\left(\frac{\sum a_n}{A_0}\right) \left(\frac{V}{S}\right)$, (fraction leached)(cm)		
	Data ^a	Predicted by Transport Eq. (32) ^b	Approach to Asymptote ^c (%)
7	5.5×10^{-6}	6.7×10^{-6}	28
14	9.0×10^{-6}	9.8×10^{-6}	44
21	1.2×10^{-5}	1.2×10^{-5}	55
28	1.4×10^{-5}	1.4×10^{-5}	62
35	1.5×10^{-5}	1.6×10^{-5}	63
42	1.7×10^{-5}	1.8×10^{-5}	69
49	1.8×10^{-5}	1.9×10^{-5}	70
56	2.1×10^{-5}	2.1×10^{-5}	78
63	2.2×10^{-5}	2.2×10^{-5}	79
70	2.4×10^{-5}	2.4×10^{-5}	83
77	2.6×10^{-5}	2.5×10^{-5}	87
84	2.7×10^{-5}	2.7×10^{-5}	87
91	2.9×10^{-5}	2.8×10^{-5}	91
98	3.0×10^{-5}	2.9×10^{-5}	91
105	3.1×10^{-5}	3.0×10^{-5}	91
112	3.3×10^{-5}	3.2×10^{-5}	94
119	3.4×10^{-5}	3.3×10^{-5}	94
126	3.5×10^{-5}	3.4×10^{-5}	95
168	4.2×10^{-5}	4.1×10^{-5}	97
196	4.5×10^{-5}	4.6×10^{-5}	95
224	5.0×10^{-5}	5.0×10^{-5}	97
252	5.5×10^{-5}	5.4×10^{-5}	99
280	5.8×10^{-5}	5.9×10^{-5}	97
364	7.7×10^{-5}	7.1×10^{-5}	107
448	8.4×10^{-5}	8.4×10^{-5}	100
532	9.0×10^{-5}	9.6×10^{-5}	93
616	1.03×10^{-4}	1.09×10^{-4}	95
672	1.14×10^{-4}	1.17×10^{-4}	97
756	1.28×10^{-4}	1.29×10^{-4}	99
854	1.43×10^{-4}	1.44×10^{-4}	100
938	1.65×10^{-4}	1.56×10^{-4}	106

^aData (Product FG-1)³¹ converted to the units indicated.

^bEquation (32) with $D_e = 6.5 \times 10^{-17} \text{ cm}^2/\text{sec}$, $k = 4.5 \times 10^{-8} \text{ sec}^{-1}$, and $\ell = 3.7 \times 10^{-4} \text{ sec}^{-1}$.

^c[Data/Eq. (33)] x 100 with $D_e = 6.5 \times 10^{-17} \text{ cm}^2/\text{sec}$, $k = 4.5 \times 10^{-8} \text{ sec}^{-1}$, and $\ell = 3.7 \times 10^{-4} \text{ sec}^{-1}$.

Table 6. Comparison of the Amounts of ^{137}Cs Leached from a Borosilicate-Glass Product^a at 25°C to Those Predicted by a Equation Based on Transport Phenomena with a Dissolution Term Plus a Surface Condition

$\left(\frac{\sum a_n}{A_o}\right)\left(\frac{V}{S}\right)$, (fraction leached)(cm)			
Time (days)	Data ^a	Predicted by Transport Eq. (32) ^b	Approach to Asymptote ^c (%)
1	2.6×10^{-6}	2.9×10^{-6}	18
7	7.4×10^{-6}	8.1×10^{-6}	47
14	1.19×10^{-4}	1.18×10^{-4}	68
21	1.56×10^{-4}	1.48×10^{-4}	81
28	1.91×10^{-4}	1.74×10^{-4}	90
56	2.64×10^{-4}	2.66×10^{-4}	92
84	3.30×10^{-4}	3.48×10^{-4}	92
112	4.22×10^{-4}	4.26×10^{-4}	97
140	5.09×10^{-4}	5.02×10^{-4}	100
168	5.82×10^{-4}	5.77×10^{-4}	100
196	6.50×10^{-4}	6.52×10^{-4}	99
	End of Data		
3,650		9.72×10^{-3}	
36,500		9.60×10^{-2}	
365,000		9.58×10^{-1}	

^aData (Product SS-12)³¹ converted to the units indicated.

^bEquation (32) with $D_e = 8.6 \times 10^{-15}$ cm²/sec, $k = 1.1 \times 10^{-7}$ sec⁻¹, and $l = 2.7 \times 10^{-3}$ sec⁻¹.

^c[Data/Eq. (33)] x 100 with $D_e = 8.6 \times 10^{-15}$ cm²/sec, $k = 1.1 \times 10^{-7}$ sec⁻¹, and $l = 2.7 \times 10^{-3}$ sec⁻¹.

Table 6). These results obtained with SS-12 show that the surface film has no significant effect on the amount leached.

When kt is large so that $\text{erf}(kt)^{1/2}$ approaches unity and ℓt is large so that $e^{-(\ell-k)t} \text{erfc}(\ell t)^{1/2}$ approaches zero (a series approximation for $e^u \text{erfc} u^{1/2}$ will show this for $\ell > k$, while the limit is obvious for $k > \ell$), Eq. (32) becomes

$$\left(\frac{\sum a_n}{A_0} \right) \left(\frac{V}{S} \right) \approx \frac{\ell(D_e k)^{1/2}}{\ell - k} \left[\left\{ 1 - (k/\ell)^{1/2} \right\} t + \frac{1}{2k} \left\{ \frac{1 - (k/\ell)^{1/2}}{1 + (k/\ell)^{1/2}} \right\} \right]. \quad (33)$$

Inspection of Eq. (33) shows that for small values of k/ℓ the equation reduces to Eq. (25), which is the asymptote for this case without a surface condition. The approach of the data for the phosphate-glass PG-1 to this asymptote is given in Table 5 and for the borosilicate-glass SS-12 in Table 6.

The expressions based on transport phenomena presented in Sects. 3.2.1, 3.2.2, and 3.2.3 above do not give predicted values that are in good agreement with the data for several of the phosphate-ceramic products (viz. SS-1, -2, -5, -6, -7, -9, and -10) described in ref. 31. This suggests that an expression taking into account a mechanism, or combination of mechanisms, other than those presented should be considered to explain the leaching of these products.

Solutions of the mass transport equations that take into account diffusion, concentration-dependent dissolution, linear surface-transfer, and a moving boundary are presented in ref. 33.

4. ACCOUNTING FOR RADIOACTIVE DECAY

In the foregoing considerations, the isotope being removed from the waste product has been considered to be a stable one. Solutions of the mass transport equations accounting for radioactive decay of an isotope escaping from a product are obtained readily from solutions for stable isotopes, as shown in ref. 26.

The amount of an isotope which has escaped from a waste solid where decay of the isotope in the source (waste product) is taken into account, but where the isotope is considered to be stable after it is released to the environment (leachant), is described, for the model with diffusion plus concentration-dependent dissolution, by the following equation:

$$\left(\frac{\sum a_n}{A_0} \right) \left(\frac{V}{S} \right) = \left(\frac{D_e}{k + \lambda} \right)^{1/2} \left[\operatorname{erf} [(k + \lambda)t]^{1/2} + \frac{k}{\lambda} \left\{ \operatorname{erf} [(k + \lambda)t]^{1/2} - \left(\frac{k + \lambda}{k} \right)^{1/2} e^{-\lambda t} \operatorname{erf} (kt)^{1/2} \right\} \right], \quad (34)$$

where

$$\lambda = \ln 2/t_{1/2} = \text{radioactive decay constant, sec}^{-1} \text{ and}$$

$$t_{1/2} = \text{half-life of isotope, sec.}$$

The derivation of Eq. (34) is presented in Appendix A. In many instances, Eq. (34) represents the manner in which experiments are conducted with isotopes having relatively short half-lives as compared with the total time of the leach test. For example, consider a leach test with ^{144}Ce (half-life of about 284 days) that is carried out for approximately a year with leachant renewal periods of a few days. Radioactive decay in the leachant for each renewal period is essentially negligible. The activity in each leachant may be considered "frozen," or fixed, when removed. Thus, it may be summed with the activity of subsequent leachants (similarly considered frozen at the time of removal). However, over the time span of the experiment, decay of ^{144}Ce in the waste product is significant and must be taken into account. This is the situation with respect to radioactive decay that is represented by Eq. (34).

The amount of a radioactive isotope which has escaped from a waste product where decay of the isotope in the source and in the environment has been taken into account for the model with diffusion plus concentration-dependent dissolution is given by

$$\left(\frac{\sum a_n}{A_0} \right) \left(\frac{V}{S} \right) = (D_e k)^{1/2} \left[\left(t + \frac{1}{2k} \right) \operatorname{erf} (kt)^{1/2} + \left(\frac{t}{\pi k} \right)^{1/2} e^{-kt} \right] e^{-\lambda t}. \quad (35)$$

The derivation of Eq. (35) is presented in Appendix A and may be considered trivial when Eq. (35) is compared to Eq. (24) since the result is intuitively obvious.

Solution for the total amount of radioactivity that escapes from the source (waste product) and enters the environment (leachant), taking into account decay that occurs in the environment but considering the isotope to be stable in the source, seems to be of little practical value and is not presented.

The amounts of ^{137}Cs (half-life of about 30 years) that Eqs. (24), (34), and (35) predict would be leached from a phosphate-glass product (PG-1)³¹ and would enter the environment are shown in Table 7 as a function of time. The waste product is considered to be in the form of a 2-ft-diam x 8-ft-long right circular cylinder ($V = 7.12 \times 10^5 \text{ cm}^3$) with all surfaces ($S = 5.25 \times 10^4 \text{ cm}^2$) continuously exposed to fresh water. The fraction leached, as predicted by Eq. (24), increases from about 5.3×10^{-6} at one year to about 1.2×10^{-2} at 3000 years (Table 7), and will continue to increase with time for a stable isotope escaping from a semi-infinite medium. The fraction leached, as predicted by Eq. (34), increases from about 5.2×10^{-6} at one year to an approximately constant value of 1.7×10^{-4} after about 200 years (Table 7), indicating that decay in the product has become the controlling factor in the amount leached. The fraction leached, as predicted by Eq. (35), increases from about 5.1×10^{-6} at one year to about 6.0×10^{-5} between 30 and 60 years and then decreases to about 9.4×10^{-33} at 3000 years (Table 7). The maximum fraction of the ^{137}Cs activity in the environment for this product, as predicted by Eq. (35), is about 6.4×10^{-5} at 43 years. Relationships such as Eq. (35), derived to account for the actual geometry of the solid if necessary, can give values needed for determining the environmental impact of a waste product.

The above solutions apply to independent activities in the product, that is, radioactive decay but not production. Solution for a case

Table 7. Comparison of the Amounts of ^{137}Cs Leached from a Phosphate-Glass Product^a at 25°C and in the Environment as Predicted by Equations Based on Transport Phenomena Considering No Decay, Decay of the Product, and Decay of the Product and the Amount Leached

Time		$\left(\frac{\sum a_n}{A_0}\right)$, (fraction leached)		
(days)	(Years)	No Decay in Product or Leachant, Eq. (24) ^b	Decay in Product But No Decay in Leachant, Eq. (34) ^c	Decay in Product and Decay in Leachant, Eq. (35) ^d
91	1/4	2.05×10^{-6}	2.05×10^{-6}	2.04×10^{-6}
182	1/2	3.19×10^{-6}	3.18×10^{-6}	3.16×10^{-6}
365	1	5.27×10^{-6}	5.22×10^{-6}	5.14×10^{-6}
3,650	10	4.10×10^{-6}	3.68×10^{-6}	3.26×10^{-6}
5,475	15	6.09×10^{-6}	5.17×10^{-6}	4.30×10^{-6}
10,950	30	1.20×10^{-4}	8.72×10^{-6}	6.02×10^{-6}
21,900	60	2.40×10^{-4}	1.30×10^{-4}	5.99×10^{-6}
32,850	90	3.59×10^{-4}	1.52×10^{-4}	4.48×10^{-6}
43,800	120	4.78×10^{-4}	1.62×10^{-4}	2.99×10^{-6}
54,750	150	5.97×10^{-4}	1.68×10^{-4}	1.87×10^{-6}
65,700	180	7.16×10^{-4}	1.70×10^{-4}	1.12×10^{-6}
76,650	210	8.35×10^{-4}	1.72×10^{-4}	6.52×10^{-6}
87,600	240	9.54×10^{-4}	1.72×10^{-4} (e)	3.73×10^{-6}
98,550	270	1.07×10^{-3}	1.73×10^{-4} (e)	2.10×10^{-6}
109,500	300	1.19×10^{-3}	1.73×10^{-4} (e)	1.16×10^{-6}
1,095,000	3,000	1.19×10^{-2}	1.73×10^{-4} (e)	9.40×10^{-33}

^aValues of D_e and k obtained from the leach results in ref. 31 by fitting the data for PG-1 to Eq. (24). The waste product is considered to be in the form of a 2-ft-diam x 8-ft-long right circular cylinder ($V = 7.12 \times 10^5 \text{ cm}^3$) with all surfaces ($S = 5.25 \times 10^4 \text{ cm}^2$) continuously exposed to water.

^bEquation (24) with $D_e = 6.2 \times 10^{-17} \text{ cm}^2/\text{sec}$ and $k = 4.7 \times 10^{-8} \text{ sec}^{-1}$.

^cEquation (34) with $D_e = 6.2 \times 10^{-17} \text{ cm}^2/\text{sec}$, $k = 4.7 \times 10^{-8} \text{ sec}^{-1}$, and $t_{1/2}$ of $^{137}\text{Cs} = 30$ years.

^dEquation (35) with $D_e = 6.2 \times 10^{-17} \text{ cm}^2/\text{sec}$, $k = 4.7 \times 10^{-8} \text{ sec}^{-1}$, and $t_{1/2}$ of $^{137}\text{Cs} = 30$ years.

^eRounding off obscures the slight increase in these numbers.

including a parent and daughter in secular equilibrium is given in ref. 33.

The nature of the correction suggested by the IAEA⁶ for radioactive decay during leaching seems obscure. Apparently, it is intended to describe the situation with respect to radioactive decay represented by Eq. (34) for the model considered in this section.

5. CONCLUSIONS AND RECOMMENDATIONS

Many different methods have been used for expressing the results of leach tests on radioactive wastes incorporated in solid media. The IAEA has recommended that such results be reported as a plot of the quantity $(\Sigma a_n/A_o)(V/S)$ or the quantity $(a_n/A_o)(V/S)(1/t_n)$ vs time. Solutions of mass transport equations lead readily to expressions which give these quantities as functions of effective diffusivity as well as other physicochemical parameters of the system and time. In addition to having theoretical significance, these quantities are unambiguous with respect to units, and wider use of $(\Sigma a_n/A_o)(V/S)$ and $(a_n/A_o)(V/S)(1/t_n)$ vs time is encouraged for reporting the results of leach tests. While graphical presentation of data is valuable for showing a large number of tests and qualitative trends concisely, tabular presentation makes data readily available for precise mathematical treatment. Consequently, where feasible, more tabular presentation of leach data is recommended.

Models based on established transport phenomena appear to offer a means for achieving improved understanding of the basic processes governing the amount of radioactivity escaping from waste solids. A theoretical relation based on data taken over a period of time sufficient to establish the validity of the model may be extrapolated with a greater degree of confidence than an empirical or semiempirical relation. In addition, theoretical relations allow parametric studies to be made. Such studies can provide valuable insight that aids in the design and evaluation of leach tests as well as in the extension of these results to actual disposal conditions.

Several theoretical expressions based on mass transport phenomena that relate the radioactivity escaping from waste products to diffusion and dissolution processes, surface conditions, and radioactive decay were evaluated with representative available data. In the main, these products can be categorized as waste solids of low solubility incorporated in inert matrices - cement, asphalt, ceramic, and glass. The analyses show that an expression taking into account diffusion and concentration-dependent dissolution gives good agreement with the data for most of the products considered. The expressions presented in this report do not give good agreement with several of the phosphate-ceramic products considered. Expressions taking into account mechanisms, or combinations of mechanisms, other than those presented should be considered for these products.

These results indicate that systematic application of mass transport theory to leach data (from well-characterized systems and tests carried out for sufficient time to establish long-term trends) for radioactive waste products can yield significant information concerning the suitability of these products in waste management programs. Included in this information are physicochemical properties, such as effective diffusivity and dissolution rate constant, for each isotope in the product. These properties are useful when comparisons are made of several products. Coupled with solutions of mass transport equations, they provide a way to estimate the amount of each isotope escaping from a product as a function of time, taking into account actual geometries and decay of radioactive isotopes. Relationships similar to Eqs. (24) and (32) provide theoretically sound rationale for establishing loss-of-radioactivity criteria for waste products.

6. ACKNOWLEDGMENTS

Thanks are due H. C. Claiborne and I. L. Thomas, of the Oak Ridge National Laboratory (ORNL), for their many valuable suggestions and helpful discussions during the preparation of this manuscript. Comments and suggestions on the various models by J. T. Bell, K. J. Notz, Jr.,

and W. W. Pitt, of ORNL, are sincerely appreciated. A. H. Kibbey, of ORNL, gave significant assistance in the editing of the manuscript. Gratitude is expressed to H. F. Soard, of ORNL, for programming and computational assistance.

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8. NOMENCLATURE

ENGLISH ALPHABET

- A = amount of radioactivity; expressed in atoms, curies, or grams as required for dimensional consistency
- A_0 = initial total radioactivity of a species
- A_{om} = initial portion of a species that is mobile
- a = amount of radioactivity lost at any time t
- a_n = radioactivity lost during leaching period n
- Σa_n = sum of radioactivity lost during all leaching periods
- b = empirical constant in Eq. (27) with the units (fraction leached) ($\text{time}^{-1/2}$)
- C = concentration (amount per unit volume) of mobile species
- Ci = curie, the quantity of any radioactive material in which the number of disintegrations per sec is 3.7×10^{10}
- C_0 = initial total concentration of a species (A_0/V)
- C_{om} = initial concentration of that portion of a species which is mobile at time zero (A_{om}/V)
- C_s = concentration at a saturation point
- c = empirical constant in Eq. (27) with the units (fraction leached) (time^{-1})
- cm = centimeter
- D_e = unmodified [Eqs. (A-1a) and (B-1a)] effective diffusivity (cm^2/sec)
- D_e = modified [Eqs. (A-14) and (B-13)] effective diffusivity with the units cm^2/day or cm^2/sec as required for dimensional consistency
- d = differential operator
- diam = diameter
- e = base of natural logarithms, 2.7182818 . . .

erf u = error function; defined as $\frac{2}{\sqrt{\pi}} \int_0^u e^{-z^2} dz$

erfc u = complementary error function; defined as $1 - \text{erf } u$

exp u = representation for e^u

F = fraction leached in Eq. (27)

f = concentration (amount per unit volume)

f' = concentration (amount per unit volume) in Eq. (B-5)

g = gram

h = linear surface-transfer constant (cm^{-1}) in Eqs. (B-1d) and (B-3d)

J'_0 = flux at the surface without a first-order process, used in Eq. (B-4)

K = constant of proportionality (dimensionless)

k = dissolution rate constant (sec^{-1})

lim = limit

ln = natural logarithm (base e)

l = surface transfer constant (sec^{-1}) defined by Eq. (B-8)

M = mass of specimen (g)

m = mass of waste solids in specimen (g)

n = non-negative integer

P = concentration (amount per unit volume) of a less mobile form of a species

Q = integrated amount lost per unit of surface in time t

q = amount lost per unit of surface at any time t

$R_n = \left(\frac{a_n}{A_0}\right)(V/S)(1/t_n)$; an incremental leach rate with the units (fraction leached)(cm)(day $^{-1}$)

$r_n = \left(\frac{a_n}{A_0}\right)(M/S)(1/t_n)$; an incremental leach rate with the units (fraction leached)(g/cm 2)(day $^{-1}$), based on the mass of the specimen

- $\bar{r}_n = (a_n/A_o)(m/S)(1/t_n)$; an incremental leach rate with the units (fraction leached)(g/cm²)(day⁻¹), based on the mass of waste solids in the specimen
- S = exposed surface area of specimen (cm²)
- sec = second
- T = designation for time representing the median of successive leachant renewal periods $(t - t_n/2)$ in days or sec
- t = elapsed time in days or seconds as required for dimensional consistency
- t_n = duration of leachant renewal period (days or sec)
- Σt_n = sum of all leaching periods
- $t_{1/2}$ = half-life of an isotope in years, days, or sec as required for dimensional consistency
- u = a variable
- V = volume of specimen (cm³)
- X = a variable
- x = length (cm) and a space coordinate (x-axis)
- Y = a variable
- z = a variable

GREEK ALPHABET

- $\alpha_o = \text{empirical constant in Eq. (13); } 6.14 \times 10^{-5} \text{ (fraction leached)}$
(cm)(day^{-1/2})
- $\alpha_1 = \text{empirical constant in Eq. (15); } 7.07 \times 10^{-4} \text{ (fraction leached)}$
(cm)(day^{-0.574})
- $\alpha_2 = \text{empirical constant in Eq. (15); } 0.574$
- $\beta = \text{fraction of total species which is mobile at time zero}$
(A_{om}/A_o)
- $\gamma = \text{ratio of saturation concentration to initial total concentration}$
(C_s/C_o)

Δ = finite change

θ = time (days)

∂ = partial differential operator

λ = $\ln 2/t_{1/2}$, defined as radioactive decay constant (sec^{-1})

μ = micro-, the factor 10^{-6}

π = 3.141592 . . .

ρ = density of specimen (g/cm^3)

Σ = summation

τ = time (sec)

ϕ = m/M , mass fraction of waste solids in specimen

APPENDIX A. SOLUTION OF MASS TRANSPORT EQUATIONS FOR THE CASE OF DIFFUSION WITH A CONCENTRATION-DEPENDENT DISSOLUTION RATE

For a semi-infinite medium with a uniform initial concentration of mobile species equal to C_s , with mobile species being produced at a rate $k(C_s - C)$ per unit time per unit volume for time greater than zero, and with the surface concentration of mobile species maintained at zero for time greater than zero, the law of conservation of mass equation (from a mass balance across a differential section) to be solved is:

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} + k (C_s - C) , \quad (\text{A-1a})$$

with the initial and boundary conditions

$$x > 0, t = 0, C = C_s \quad (\text{A-1b})$$

$$x = 0, t > 0, C = 0, \text{ and} \quad (\text{A-1c})$$

$$x = \infty, t > 0, C = C_s . \quad (\text{A-1d})$$

If the variable

$$f(x,t) = C_s - C(x,t) \quad (\text{A-2})$$

is introduced and substituted into Eqs. (A-1), the transformed equation is

$$\frac{\partial f}{\partial t} = D_e \frac{\partial^2 f}{\partial x^2} - kf , \quad (\text{A-3a})$$

with the initial and boundary conditions

$$x > 0, t = 0, f = 0 \quad (\text{A-3b})$$

$$x = 0, t > 0, f = C_s, \text{ and} \quad (\text{A-3c})$$

$$x = \infty, t > 0, f = 0 . \quad (\text{A-3d})$$

The solution²⁵ of Eqs. (A-3) is:

$$f = \frac{C_s}{2} \left\{ \exp \left[-x \left(\frac{k}{D_e} \right)^{1/2} \right] \operatorname{erfc} \left[\frac{x}{2(D_e t)^{1/2}} - (kt)^{1/2} \right] \right. \\ \left. + \exp \left[x \left(\frac{k}{D_e} \right)^{1/2} \right] \operatorname{erfc} \left[\frac{x}{2(D_e t)^{1/2}} + (kt)^{1/2} \right] \right\}, \quad (\text{A-4})$$

where

$$\exp u = e^u, \quad (\text{A-5})$$

$$\operatorname{erfc} u = 1 - \operatorname{erf} u, \text{ and} \quad (\text{A-6})$$

$$\operatorname{erf} u = \frac{2}{\pi^{1/2}} \int_0^u e^{-z^2} dz. \quad (\text{A-7})$$

Properties and tabulated values of the error function (erf) and complementary error function (erfc) are given in refs. 10-12 and comprehensive mathematical handbooks such as ref. 24. Substitution of Eq. (A-4) into Eq. (A-2) gives

$$C = C_s \left\{ 1 - \frac{1}{2} \exp \left[-x \left(\frac{k}{D_e} \right)^{1/2} \right] \operatorname{erfc} \left[\frac{x}{2(D_e t)^{1/2}} - (kt)^{1/2} \right] \right. \\ \left. - \frac{1}{2} \exp \left[x \left(\frac{k}{D_e} \right)^{1/2} \right] \operatorname{erfc} \left[\frac{x}{2(D_e t)^{1/2}} + (kt)^{1/2} \right] \right\} \quad (\text{A-8})$$

for the concentration of the mobile species in the medium as a function of position and time.

Differentiation of Eq. (A-8) with respect to x , evaluation of this concentration gradient at $x = 0$, and insertion of this gradient into Fick's law give

$$\frac{dq}{dt} \Big|_{x=0} = C_s (D_e k)^{1/2} \left[\operatorname{erf} (kt)^{1/2} + \frac{e^{-kt}}{(\pi kt)^{1/2}} \right] \quad (\text{A-9})$$

for the flux at the interface.

Integration of Eq. (A-9) over time t gives

$$Q = C_s (D_e k)^{1/2} \left[\left(t + \frac{1}{2k} \right) \operatorname{erf} (kt)^{1/2} + \left(\frac{t}{\pi k} \right)^{1/2} e^{-kt} \right], \quad (\text{A-10})$$

where Q is the total amount of species that has left the medium per unit of surface in time t .

The intensive properties, q , Q , and C_s , of the semi-infinite medium can be expressed in terms of extensive properties of the finite sample, viz.,

$$q = \frac{a}{S} \quad (\text{A-11})$$

$$Q = \frac{\sum a_n}{S}, \text{ and} \quad (\text{A-12})$$

$$C_s = \frac{\gamma A_0}{V}, \quad (\text{A-13})$$

where γ is a constant representing the ratio of the concentration at saturation to the initial total concentration of the species. By definition, let

$$D_e = \gamma^2 D_e. \quad (\text{A-14})$$

If

$$\frac{a_n}{t_n} = \lim_{\Delta t \rightarrow 0} \left(\frac{\Delta a}{\Delta t} \right) = \frac{da}{dt} \quad (\text{A-15})$$

is a good approximation and if a_n/t_n is taken to be at time

$$T = (t - t_n/2), \quad (\text{A-16})$$

the substitution of Eqs. (A-11), (A-13), (A-14), (A-15), and (A-16) into Eq. (A-9) yields

$$\left(\frac{a_n}{A_0} \right) \left(\frac{V}{S} \right) \left(\frac{1}{t_n} \right) = (D_e k)^{1/2} \left[\operatorname{erf} (kT)^{1/2} + \frac{e^{-kT}}{(\pi kT)^{1/2}} \right] \quad (\text{A-17})$$

for the leach rate representation of the flux at the surface for a sparingly soluble material at time T . The substitution of Eqs. (A-12), (A-13), and (A-14) into Eq. (A-10) yields

$$\left(\frac{\sum a_n}{A_0} \right) \left(\frac{V}{S} \right) = (D_e k)^{1/2} \left[\left(t + \frac{1}{2k} \right) \operatorname{erf} (kt)^{1/2} + \left(\frac{t}{\pi k} \right)^{1/2} e^{-kt} \right] \quad (\text{A-18})$$

for the total amount of the material which has left the medium in time t .

The initial quantity, γA_0 , is not generally known (or needed) for waste products. However, if an expression [e.g., Eq. (A-8)] based on transport equations relating the concentration of the mobile species to position and time within the product were used, it would require the unmodified effective diffusivity \mathcal{D}_e - not the modified effective diffusivity D_e .

The treatment above applies to a stable isotope. However, solutions accounting for radioactive decay of an isotope of mean or average life, $1/\lambda$, are readily obtained from solutions for stable isotopes as shown in ref. 26.

Solutions for the total amount of radioactivity that is removed from a waste solid and is in the environment, taking into account radioactive decay that occurs in the waste solid but considering the isotope to be stable once it is in the environment, can be obtained²⁶ by multiplying the flux out of the solid for a stable isotope [Eq. (A-9) in this case] by $e^{-\lambda t}$ and integrating the resulting expression with time. Since

$$\left. \frac{dq}{dt} \right|_{x=0} = C_s (\mathcal{D}_e k)^{1/2} \left[\operatorname{erf} (kt)^{1/2} + \frac{e^{-kt}}{(\pi kt)^{1/2}} \right] e^{-\lambda t}, \quad (\text{A-19})$$

then

$$\int_0^Q dq = C_s (\mathcal{D}_e k)^{1/2} \int_0^t \left[\operatorname{erf} (kt)^{1/2} + \frac{e^{-kt}}{(\pi kt)^{1/2}} \right] e^{-\lambda t} dt, \quad (\text{A-20})$$

and

$$Q = C_s \left(\frac{D_e}{k + \lambda} \right)^{1/2} \left[\operatorname{erf} [(k + \lambda)t]^{1/2} + \frac{k}{\lambda} \left\{ \operatorname{erf} [(k + \lambda)t]^{1/2} - \left(\frac{k + \lambda}{k} \right)^{1/2} e^{-\lambda t} \operatorname{erf} (kt)^{1/2} \right\} \right]. \quad (\text{A-21})$$

Substitution of Eqs. (A-12), (A-13), and (A-14) into Eq. (A-21) yields

$$\left(\frac{\sum a_n}{A_o} \right) \left(\frac{V}{S} \right) = \left(\frac{D_e}{k + \lambda} \right)^{1/2} \left[\operatorname{erf} [(k + \lambda)t]^{1/2} + \frac{k}{\lambda} \left\{ \operatorname{erf} [(k + \lambda)t]^{1/2} - \left(\frac{k + \lambda}{k} \right)^{1/2} e^{-\lambda t} \operatorname{erf} (kt)^{1/2} \right\} \right]. \quad (\text{A-22})$$

Equation (A-22) then represents the amount of the isotope which has left the waste solid in time t , where decay of the isotope in the source (waste product) has been taken into account but where the isotope is considered to be stable after it is in the environment. This amount is sometimes referred to as the amount of activity "discharged" from a source in time t .

Solution for the total amount of radioactivity that is removed from a waste solid and is in the environment, taking into account radioactive decay that occurs in the solid and in the environment, can be obtained by computing the instantaneous flux with decay out of the solid [Eq. (A-19) in this case] at time τ , computing the activity remaining at some later time, t , and integrating τ from zero to t :

$$Q = C_s (D_e k)^{1/2} \int_0^t \left\{ \left[\operatorname{erf} (k\tau)^{1/2} + \frac{e^{-k\tau}}{(\pi k \tau)^{1/2}} \right] e^{-\lambda \tau} \right\} e^{-\lambda(t - \tau)} d\tau, \quad (\text{A-23})$$

$$Q = C_s (D_e k)^{1/2} \left[\left(t + \frac{1}{2k} \right) \operatorname{erf} (kt)^{1/2} + \left(\frac{t}{\pi k} \right)^{1/2} e^{-kt} \right] e^{-\lambda t}. \quad (\text{A-24})$$

Substitution of Eqs. (A-12), (A-13), and (A-14) into Eq. (A-24) yields

$$\left(\frac{\sum a_n}{A_o} \right) \left(\frac{V}{S} \right) = (D_e k)^{1/2} \left[\left(t + \frac{1}{2k} \right) \operatorname{erf} (kt)^{1/2} + \left(\frac{t}{\pi k} \right)^{1/2} e^{-kt} \right] e^{-\lambda t} . \quad (\text{A-25})$$

Equation (A-25) represents the total amount of a sparingly soluble isotope that has been removed from a waste solid and is in the environment at time t , where decay of the isotope in the source and in the environment is taken into account. Equation (A-25) could have been obtained immediately from Eq. (A-18) by multiplying by $e^{-\lambda t}$. However, the integration is presented to emphasize the difference between Eq. (A-22) and Eq. (A-25).

Solution for the total amount of radioactivity that escapes from the source (waste product) and is in the environment (leachant), taking into account decay that occurs in the environment but considering the isotope to be stable in the source, seems to be of little practical interest and is not presented.

APPENDIX B. SOLUTION OF MASS TRANSPORT EQUATIONS FOR THE CASE OF
DIFFUSION WITH A CONCENTRATION-DEPENDENT DISSOLUTION RATE AND
LINEAR SURFACE-TRANSFER

For a semi-infinite medium with a uniform initial concentration of mobile species equal to C_s , with mobile species being produced at a rate $k(C_s - C)$ per unit time per unit volume for time greater than zero, and with linear mass transfer at the surface into another medium containing none of the mobile species (i.e., with $\partial C/\partial x = hC$ at the surface where h is a constant), the law of conservation of mass equation (from a mass balance across a differential section) to be solved is

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} + k (C_s - C) \quad , \quad (\text{B-1a})$$

with the initial and boundary conditions

$$x > 0, t = 0, C = C_s \quad (\text{B-1b})$$

$$x = \infty, t > 0, C = C_s, \text{ and} \quad (\text{B-1c})$$

$$x = 0, t > 0, \frac{\partial C}{\partial x} = hC \quad . \quad (\text{B-1d})$$

If the variable

$$f(x,t) = C_s - C(x,t) \quad (\text{B-2})$$

is introduced and substituted into Eqs. (B-1), the transformed equation is

$$\frac{\partial f}{\partial t} = D_e \frac{\partial^2 f}{\partial x^2} - kf \quad , \quad (\text{B-3a})$$

with the initial and boundary conditions

$$x > 0, t = 0, f = 0 \quad (\text{B-3b})$$

$$x = \infty, t > 0, f = 0, \text{ and} \quad (\text{B-3c})$$

$$x = 0, t > 0, -\frac{\partial f}{\partial x} = h(C_s - f) \quad . \quad (\text{B-3d})$$

The flux at the interface for the above case can be obtained readily using the method developed in ref. 32; viz.,

$$\left. \frac{dq}{dt} \right|_{x=0} = k \int_0^t J'_0 e^{-k\tau} d\tau + J'_0 e^{-kt}, \quad (\text{B-4})$$

where J'_0 is the flux at the interface for the same boundary conditions [Eqs. (B-3b), (B-3c), and (B-3d)] without a first-order process. The solution³⁴ for Eqs. (B-3) without the first-order process (kf) is:

$$f' = C_s \left[\operatorname{erfc} \frac{x}{2(\mathcal{D}_e t)^{1/2}} - e^{(hx + h^2 \mathcal{D}_e t)} \operatorname{erfc} \left\{ \frac{x}{2(\mathcal{D}_e t)^{1/2}} + h(\mathcal{D}_e t)^{1/2} \right\} \right], \quad (\text{B-5})$$

where $\operatorname{erfc} u = 1 - \operatorname{erf} u$. Properties and tabulated values of the error function (erf) and complementary error function (erfc) are given in refs. 10-12 and comprehensive mathematical handbooks such as ref. 24. Differentiation of Eq. (B-5) with respect to x , evaluation of this concentration gradient at $x = 0$, and insertion of this concentration gradient at $x = 0$ into Fick's law give

$$J'_0 = C_s \left[h \mathcal{D}_e e^{(h^2 \mathcal{D}_e t)} \operatorname{erfc} \left\{ h(\mathcal{D}_e t)^{1/2} \right\} \right]. \quad (\text{B-6})$$

Substitution of Eq. (B-6) into Eq. (B-4) and integration of the resulting expression yields

$$\left. \frac{dq}{dt} \right|_{x=0} = \frac{h \mathcal{D}_e C_s}{h^2 \mathcal{D}_e - k} \left[h(\mathcal{D}_e k)^{1/2} \operatorname{erf} (kt)^{1/2} + h^2 \mathcal{D}_e e^{(h^2 \mathcal{D}_e - k)t} \operatorname{erfc} \left\{ h(\mathcal{D}_e t)^{1/2} \right\} - k \right] \quad (\text{B-7})$$

for the flux of f into the medium, which is the flux of C out of the medium.

By definition, let

$$l = h^2 \mathcal{D}_e, \quad (\text{B-8})$$

where l is called a surface transfer constant (with the units sec^{-1}).

Integration of Eq. (B-7), with l substituted for $h^2 D_e$, over time t gives

$$Q = \frac{l(D_e k)^{1/2} C_s}{l - k} \left[\left\{ t + \frac{l}{k(l - k)} - \frac{1}{2k} \right\} \text{erf}(kt)^{1/2} + \frac{l}{(l - k)(kl)^{1/2}} e^{(l-k)t} \text{erfc}(kt)^{1/2} + \left(\frac{t}{\pi k} \right)^{1/2} e^{-kt} - \left(\frac{k}{l} \right)^{1/2} t - \frac{l}{(l - k)(kl)^{1/2}} \right], \quad (\text{B-9})$$

where Q is the total amount of species that has left the medium per unit of surface in time t .

The intensive properties, q , Q , and C_s , of the semi-infinite medium can be expressed in terms of extensive properties of the finite sample, as follows:

$$q = \frac{a}{S} \quad (\text{B-10})$$

$$Q = \frac{\sum a_n}{S}, \text{ and} \quad (\text{B-11})$$

$$C_s = \frac{\gamma A_0}{V}, \quad (\text{B-12})$$

where γ is a constant representing the ratio of the concentration at saturation to the initial total concentration of the species. By definition, let

$$D_e = \gamma^2 D_e. \quad (\text{B-13})$$

If the relationship

$$\frac{a_n}{t_n} = \lim_{\Delta t \rightarrow 0} \left(\frac{\Delta a}{\Delta t} \right) = \frac{da}{dt} \quad (\text{B-14})$$

is a good approximation and if a_n/t_n is taken to be at time

$$T = (t - t_n/2) \quad , \quad (B-15)$$

the substitution of Eqs. (B-8), (B-10), (B-12), (B-13), (B-14), and (B-15) into Eq. (B-7) yields

$$\left(\frac{a_n}{A_0} \right) \left(\frac{V}{S} \right) \left(\frac{1}{t_n} \right) = \frac{l (D_e k)^{1/2}}{l - k} \left[\operatorname{erf} (kT)^{1/2} + \left(\frac{l}{k} \right)^{1/2} e^{(l-k)T} \operatorname{erfc} (lT)^{1/2} - \left(\frac{k}{l} \right)^{1/2} \right] \quad (B-16)$$

for the leach rate representation of the flux at the surface for a sparingly soluble material at time T. The substitution of Eqs. (B-11), (B-12), and (B-13) into Eq. (B-9) yields

$$\left(\frac{\sum a_n}{A_0} \right) \left(\frac{V}{S} \right) = \frac{l (D_e k)^{1/2}}{l - k} \left[\left\{ t + \frac{l}{k(l - k)} - \frac{1}{2k} \right\} \operatorname{erf} (kt)^{1/2} + \frac{l}{(l - k)(kl)^{1/2}} e^{(l-k)t} \operatorname{erfc} (lt)^{1/2} + \left(\frac{t}{\pi k} \right)^{1/2} e^{-kt} - \left(\frac{k}{l} \right)^{1/2} t - \frac{l}{(l - k)(kl)^{1/2}} \right] \quad (B-17)$$

for the total amount of the material which has left the medium in time t. The solutions are valid for both positive and negative (l - k) but not for (l - k) equal to zero.

The initial quantity, γA_0 , is not generally known (or needed) for waste products. However, if an expression [e.g., Eq. (B-9)] based on transport equations relating concentration of the mobile species with position and time within the product were used, it would require the unmodified effective diffusivity D_e - not the modified effective diffusivity D_e .

The treatment above applies to a stable isotope. However, solutions accounting for radioactive decay of an isotope of mean or average life, $1/\lambda$, are readily obtained from solutions for stable isotopes as shown in ref. 26 and illustrated in Appendix A.

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