Reprinted from ANALYTICAL CHEMISTRY, Vol. 50, Page 564, April 1978

Determination of the Leachability of Solids

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A novel method for measuring the leachability of homogeneous solids is reported using as examples radioactive tracers incorporated in plastics and concrete. Theoretical treatment of the data using simple diffusion theory is able to reduce the experimental information to a single "leachability constant" for the material and permits the calculation of the leaching behavior as a function of time for any size regular-shape object made of it.

The leachability of a material is frequently measured by experiments which either use Soxhlet extraction equipment to ascertain zero concentration of the leachant at all times or involve immersion of the solid until an equilibrium concentration is reached in the liquid (*1*, *2*).

Such experiments generally follow protocols specifying a certain specimen size and shape and are carried out at elevated temperatures to hasten the leaching process (*3*). These test protocols and their results stand by themselves and serve as yes-no criteria for quality control and legislation etc. (*4*). They do not yield insight into the leaching process nor do they represent the real world. In particular, they do not answer the often most important question: what is the amount of noxious substance leached from an object made of the tested material during the object's use time. For example, it is not

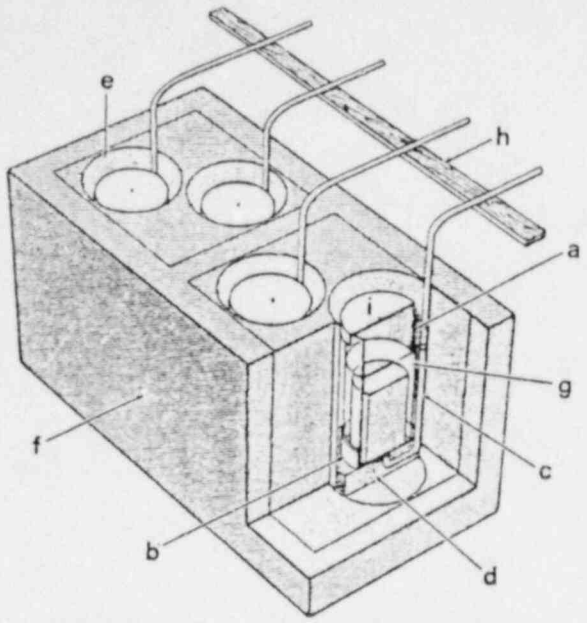

Figure 1. Schematic of leach test equipment: (a) Leaching vessel, (b) Rubber septum, (c) Thin plastic tubing, (d) Plastic foam support plug, (e) Drywell liner (empty beverage can) embedded in concrete, (f) Concrete building block, (g) Leaching liquid, (h) Loading board, (i) Cap with vent hole

important to know how much of a monomer can be leached from a specimen of plastic, but rather how much is leached into the soft drink while the liquid is in a bottle made of the material. And this quantity may be orders of magnitude different than the amount leached under extreme conditions.

It is the purpose of this report to introduce a new and inexpensive approach to leachability measurement which is both fast and applicable to ambient conditions and determines a "leachability parameter" specific for the material being tested. Its significance is readily interpreted by theory and can be extrapolated to arbitrary specimen size and shape as a function of time.

EXPERIMENTAL

The experimental investigation addressed itself to the leaching of radioactive isotopes from cylinders prepared by the solidification of simulated rad-waste in plastics and concrete (5). The study included the solidification of true solutions as well as of suspensions or slurries of ion-exchange resins. The experiments were performed in multiples using different specimens cast from the same preparations by the same, or supposedly same, procedure.

The dimensions of the specimens were kept small to limit the amounts of radioactive material involved and to enhance the leaching process. The leaching was carried out with relatively small amounts of leachant in contact with the specimen in order to minimize dilution and render most of the leached radioactivity accessible to measurement in the counting aliquots.

The apparatus shown in Figure 1 consists of a leaching vessel made of plastic tubing (a) cut to the right length to contain the specimen and the leaching aliquot. This tubing is closed at the bottom with a septum (b) through which penetrates a 1-mm diameter plastic tubing, 1 or 2 ft long (c). This "vessel" is mounted on a plastic-foam plug (d) provided with a cut-in recess to receive the septum and guide the small tubing in a 180° turn.

The mounted vessel is inserted into a beverage can without lid (e) which in turn is cast into a concrete building block (f) using portland cement. Four such beverage cans can be mounted in one building block as seen in the figure.

An array of leaching vessels was constructed of these concrete blocks. Other concrete blocks served both as the supports and the biological shielding surrounding the radioactive experiments. The thin plastic tubings were brought out toward the front of the structure and lined up on a "loading board" (h) consisting of a wooden lath onto which the tubings were fastened and labeled with the number of the respective leaching vessel.

To initiate the experiments, the radioactive specimens were prepared, counted, weighed, and their dimensions measured with calipers. They were then placed into the leaching vessels. Each leaching vessel was covered with a cap (i) provided with a small vent hole, and the biological shielding was put into place.

The parallel experiments used both deionized water and a commercially available formulation simulating ocean water as leachants.

The leaching experiments were carried out in the following manner.

For each experiment a 10-mL plastic syringe was provided with a plastic tip such as used with 0.1-mL disposable pipets. The syringes were labeled and kept in sequence in an appropriate rack.

After loading each specimen, 10 mL of leach solvent was injected through the tube into the vessel by means of a dispensing pipet and immediately withdrawn with the syringe. This served as an initial rinse. A second 10-mL portion was then injected and left in contact with the specimen for the desired length of time.

After the leach interval, the leach solvent was withdrawn. Five milliliters of the solution was transferred to a counting vial while the rest was discarded. Quantitative recovery of the leach aliquot was thus not required.

In order to prepare for the subsequent leach interval, 10 mL of solvent was again injected into the vessel and immediately withdrawn and discarded. This operation assured the removal of any leachate remaining from the preceding time interval. A second charge of 10 mL of the leachant was then introduced into the vessel and remained there for the next leaching interval.

The experimental run described was carried out with 54 such leaching experiments performed simultaneously. From the theoretical considerations, it appeared that initial leaching would be significant. The leaching time intervals were thus kept short at first and followed each other in relatively rapid succession. In order to accomplish this, a rigid time schedule was followed for the initial phase of the experiments.

Leaching started with a 0.5-h interval which was followed by a 1.5-h interval and subsequently by 3-h, 6-h, 18-h, and 24-h leach intervals. After this, leaching times of 1 day were in order excepting weekends and holidays, when, after the initial week of operation, up to 96-h leach intervals were tolerated. It was assumed that the accumulation of dissolved material in the leach solution would not significantly affect the theoretical assumption of having zero-concentration leachant present at all times. The total amount of radioactivity present in the solutions for these experiments was kept to below 20% of the original radioactivity present in the specimen.

The run was subdivided into three sets so that 18 experiments in groups of six could be started together on one day. The second 18 followed the next day, and the third 18 were started the day after. In this way there was only one, and on the subsequent days two 0.5-h periods during which more than six leach changes had to be performed. This schedule permitted the operation to be carried out by one person.

The radioactivity of the 5-mL aliquots in the counting vials was crudely measured by holding them in front of a Geiger-tube laboratory monitor and comparing the approximate counting rates with that of a comparison standard. In case the aliquot exceeded this counting rate, a 1:5 dilution was prepared. The counting vials were then sealed and counted in a 3 in. × 3 in. well-type NaI(Tl) detector of a γ-ray spectrometer capable of handling up to 100 samples per counting run.

Many of the investigations were carried out using both ^{137}Cs and ^{60}Co tracers in the same specimens. In the present context, this was done merely to obtain twice as much data from the same experiments. The fact that different behavior of the tracers was observed in certain matrixes demonstrated the dependence of the leachability on the chemical nature of the species and the matrix material. A detailed study of this subject will have to wait for a later time.

γ-Ray spectrometry was used to distinguish between the two isotopes, so that their individual leaching rates could be followed. In order to ensure consistency of the counting data, the measurements were carried out relative to standards which were used throughout the counting experiments. The counting data were obtained in units of these counting standards. The radioactivity originally present in the specimens was also determined relative

to these counting standards by counting both with a low-sensitivity Ge(Li) γ spectrometer. In this way the selection of the γ-spectrometer window widths was not critical from day to day and week to week.

One set of experiments was carried out with tritium as the radioactive species. The initial loading of the tritium-containing specimens was determined from their weights and the specific activity of the formulation from which they were prepared. A small piece of the plastic was weighed, burned in oxygen, and the resulting tritiated water was counted with a liquid-scintillation counter. The leach aliquots from the tritium-leaching experiments were similarly counted with the liquid-scintillation counter.

DISCUSSION AND THEORY

An evaluation of the results of these leaching experiments was found possible with reference to simple diffusion theory (6–8). A mathematical model could be derived for the case of the leaching of homogeneous solids of regular shape, assuming no chemical interaction between leachant and the material being leached. It was assumed that diffusion through the matrix is the rate-limiting process.

The general diffusion equation:

$$\frac{\partial c}{\partial \theta} = k\nabla^2 c \tag{1}$$

describes the rate of change of concentration at a given location in the diffusion medium in terms of the size- and shape-dependent Laplacian operator and a diffusivity constant k characteristic of the material. Solutions of the general diffusion equation are thus shape- and size-dependent. They can be derived by various techniques well known to mathematicians.

To provide a needed base for the present discussion, the following equations are given which describe the diffusion behavior of simple bodies progressing from the "infinite slab", the "parallelepiped", the "sphere", and the "infinitely-long cylinder" to the cylinder of finite length.

For specific cases the integrals of the diffusion equation are conveniently presented in the form (9):

$$\frac{c - c_1}{c_0 - c_1} = \frac{\text{the difference between the concentration at a point and the concentration in the liquid at time } \theta}{\text{the initial uniform concentration in excess of the concentration of the leach liquid at time } \theta} \tag{2}$$

where c is the concentration of the leachable substance in the solid, c_0 is the concentration in the initially homogeneous solid and c_1 is the equilibrium concentration in the leachate at time θ.

Equation 3 represents the leaching behavior of an infinite slab of thickness $2a$:

$$\frac{c - c_1}{c_0 - c_1} = \frac{4}{\pi}\left\{\cos\frac{\pi x}{2a}\exp\left(-k\theta\left(\frac{\pi}{2a}\right)^2\right) - \frac{1}{3}\cos\frac{3\pi x}{2a}\exp\left(-9k\theta\left(\frac{\pi}{2a}\right)^2\right) + \frac{1}{5}\cos\frac{5\pi x}{2a}\exp\left(-25k\theta\left(\frac{\pi}{2a}\right)^2\right) - \ldots\right\} \tag{3}$$

Equation 4, in analogy to Equation 3, describes the parallelepiped.

$$\frac{c - c_1}{c_0 - c_1} = (\text{Series A})\,(\text{Series B})\,(\text{Series C}) \tag{4}$$

Series A is that given in Equation 3. In series B and C, the thickness $2a$ is replaced with the corresponding thicknesses in the other two dimensions.

The equivalent equation describing the diffusion behavior of the sphere, Equation 5 contains a similar series:

$$\frac{c - c_1}{c_0 - c_1} = \frac{2\mathrm{r}}{\pi r}\left\{\sin\frac{\pi r}{\mathrm{r}}\exp\left(-k\theta\left(\frac{\pi}{\mathrm{r}}\right)^2\right) - \frac{1}{2}\sin\frac{2\pi r}{\mathrm{r}}\exp\left(-4k\theta\left(\frac{\pi}{\mathrm{r}}\right)^2\right) + \frac{1}{3}\sin\frac{3\pi r}{\mathrm{r}}\exp\left(-9k\theta\left(\frac{\pi}{\mathrm{r}}\right)^2\right) - \ldots\right\} \tag{5}$$

where r is the radius of the sphere.

Equation 6 describes the instantaneous concentration at a distance (r) from the axis of an initially homogeneous, infinitely long cylinder of radius (r) at the time θ after the beginning of the diffusion process:

$$\frac{c - c_1}{c_0 - c_1} = 2\left[\frac{J_0\left(\frac{R_1}{\mathrm{r}}r\right)}{R_2 J_1\left(\frac{R_1}{\mathrm{r}}\mathrm{r}\right)}\exp\left(-k\theta\left(\frac{R_1}{\mathrm{r}}\right)^2\right) + \frac{J_0\left(\frac{R_2}{\mathrm{r}}r\right)}{R_2 J_1\left(\frac{R_2}{\mathrm{r}}\mathrm{r}\right)}\exp\left(-k\theta\left(\frac{R_2}{\mathrm{r}}\right)^2\right) + \ldots\right] \tag{6}$$

The right side of this equation we will denote as "Series R", in which:

$$J_0(x) = 1 - \frac{x^2}{2^2} + \frac{x^4}{2^2 4^2} - \frac{x^6}{2^2 4^2 6^2} + \ldots \tag{7}$$

and

$$-J_1(x) = \frac{\mathrm{d}(J_0(x))}{\mathrm{d}x} = -\left[\frac{x}{2} - \frac{x^3}{2^2 4} + \frac{x^5}{2^2 4^2 6} - \ldots\right] \tag{8}$$

For the finite cylinder of length ($2a$) and radius (r) the flow is described by:

$$\frac{c - c_1}{c_0 - c_1} = (\text{Series R})\,(\text{Series A}) \tag{9}$$

Integration of these equations permits the determination of the total transport from the surface of the specimen into the surrounding liquid as a function of time. One can thus calculate both the leaching rate at a given time and the fraction of the unleached constituent still remaining in the solid.

For the present purpose, it is sufficient to be able to calculate the average residual concentration in the solid relative to the initial loading. The equations then take on the form (9, 10):

$$\frac{w - c_1}{c_0 - c_1} = \frac{\text{average concentration in excess of } c_1}{\text{initial uniform concentration in excess of } c_1} \tag{10}$$

where $w - c_1$ is the average concentration of the leachable substance in the solid at some given time θ in excess of the concentration in the leachate.

The corresponding equations are the following. For the slab:

$$\frac{w - c_i}{c_0 - c_i} = \frac{8}{\pi^2}\left[\exp\left(-\left(\frac{k\theta}{a^2}\right)\left(\frac{\pi}{2}\right)^2\right) + \frac{1}{9}\exp\left(-9\left(\frac{k\theta}{a^2}\right)\left(\frac{\pi}{2}\right)^2\right) + \frac{1}{25}\exp\left(-25\left(\frac{k\theta}{a^2}\right)\left(\frac{\pi}{2}\right)^2\right) + \ldots\right] \quad (11)$$

For the sphere:

$$\frac{w - c_i}{c_0 - c_i} = \frac{6}{\pi^2}\left[\exp\left(-\left(\frac{k\theta}{r^2}\right)\pi^2\right) + \frac{1}{4}\exp\left(-4\left(\frac{k\theta}{r^2}\right)\pi^2\right) + \frac{1}{9}\exp\left(-9\left(\frac{k\theta}{r^2}\right)\pi^2\right) + \ldots\right] \quad (12)$$

For the cylinder:

$$\frac{w - c_i}{c_0 - c_i} = 4\left[\frac{1}{R_1^2}\exp\left(-\left(\frac{k\theta}{r^2}\right)R_1^2\right) + \frac{1}{R_2^2}\exp\left(-\left(\frac{k\theta}{r^2}\right)R_2^2\right) + \ldots\right] \quad (13)$$

and for the finite cylinder:

$$\frac{w - c_i}{c_0 - c_i} = 4\left[\frac{1}{R_1^2}\exp\left(-\left(\frac{k\theta}{r^2}\right)R_1^2\right) + \frac{1}{R_2^2}\exp\left(-\left(\frac{k\theta}{r^2}\right)R_2^2\right) + \ldots\right] \times \frac{8}{\pi^2}\left[\exp\left(-\left(\frac{k\theta}{a^2}\right)\left(\frac{\pi}{2}\right)^2\right) + \frac{1}{9}\exp\left(-9\left(\frac{k\theta}{a^2}\right)\left(\frac{\pi}{2}\right)^2\right) + \frac{1}{25}\exp\left(-25\left(\frac{k\theta}{a^2}\right)\left(\frac{\pi}{2}\right)^2\right) + \ldots\right] \quad (14)$$

Equation 14 for the finite cylinder has two parts, one stemming from the equation of the infinite cylinder or radius (r) the other from the slab of thickness ($2a$). These dimensions are the size parameters for our cylinder. The equation contains as additional parameter the leachability (= diffusivity) constant k[cm^2 s^{-1}] for the material. The terms R_1, R_2, etc. represent the roots of the zero-order Bessel function of the first kind (11), $J_0(r)$, and θ is the time elapsed since the beginning of the leaching process.

It was found that the two mathematical series making up Equation 14, each representing one of the simpler geometrical shapes that constitute the finite cylinder, converge very slowly for small values of $k\theta/a^2$ or $k\theta/r^2$. For reasonable accuracy, calculations must thus consider a large number of terms in each series. This virtually requires that the calculations be carried out with a computer or programmable calculator. For the range of interest in this discussion, it is necessary to include between 100 and 200 terms of the series to arrive at meaningful leaching rates for the initial phases of the leaching process.

The Equations 11, 12, 13, and 14 give the average concentration of the leachable substance in the solid after a given time θ as a fraction of the initial loading. The fraction leached during an interval of interest is thus computed as the difference of the fractions remaining in the solid at the beginning and the end of the leaching interval.

RESULTS

The experimental data from several of the specimens investigated are presented as plots in Figures 2, 3, and 4. The theoretical curves were calculated with the aid of the described model for the finite cylinder of the dimensions of the respective specimens and estimated "leachability constant" (k) to fit the data.

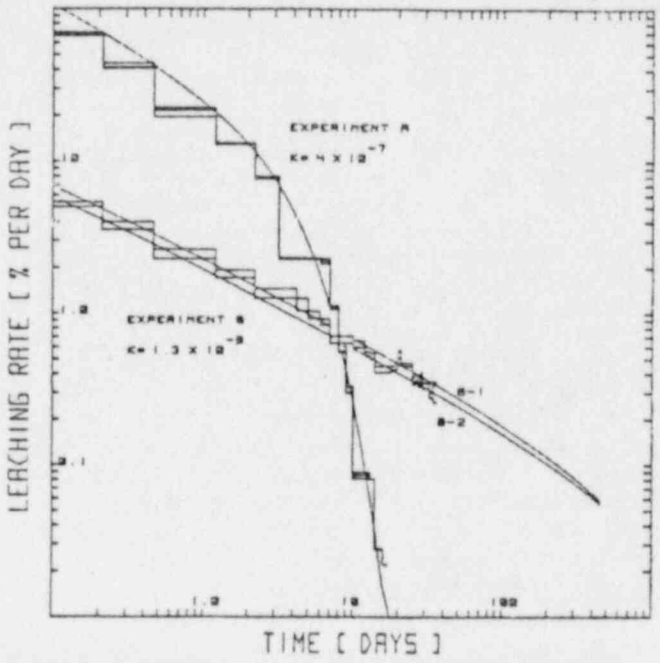

Figure 2. Experiment A: ^{137}Cs leaching data of three cylinders, 5 cm long and 1.28-cm diameter made of a portland cement-simulated liquid rad-waste formulation. Deionized water used as leachant. Experiment B: Tritiated water leaching data from 5 cm long, 1.19-cm diameter and 1.42-cm diameter cylinders made of a plastic formulation. Deionized water used as leachant. The theoretical curves are calculated with an estimated leachability parameter, k, to fit the experimental data. B-1 and B-2 are calculated for the two sizes of cylinders used in experiment B, made of the same material for which $k = 3 \times 10^{-9}$ cm^2 s^{-1}

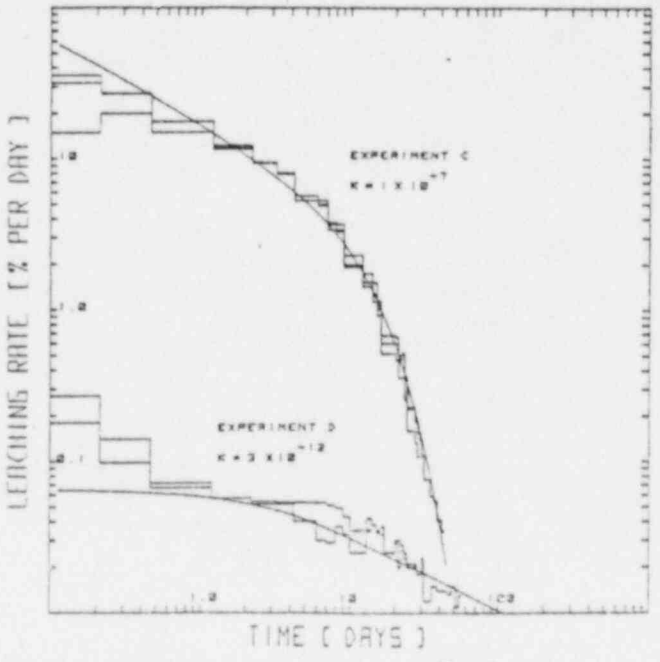

Figure 3. Experiment C: Leaching data of ^{137}Cs from 5 cm long, 1.19-cm diameter cylinders made of a different type plastic formulation. Simulated ocean water used as leachant. Experiment D: Leaching data of ^{60}Co from two cylinders made of yet another plastic formulation. Deionized water used as leachant

The deionized-water leaching rates determined for ^{137}Cs from three identical specimens made of a formulation of simulated rad-waste and portland cement are plotted in Figure 2 as "experiment A". The cylindrical specimens were 5 cm

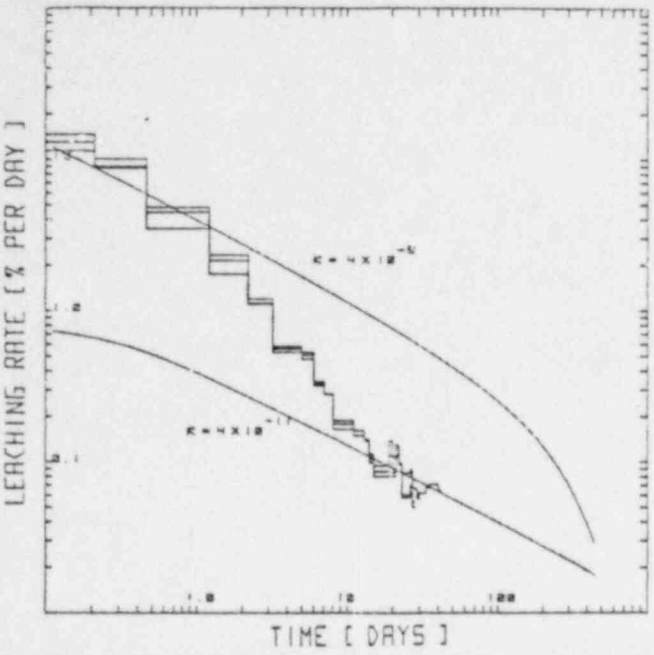

Figure 4. Ocean-water leaching rates of ^{137}Cs from two cylinders 4.9 cm long and 1.18-cm diameter made of an inhomogeneous material containing ion-exchange beads

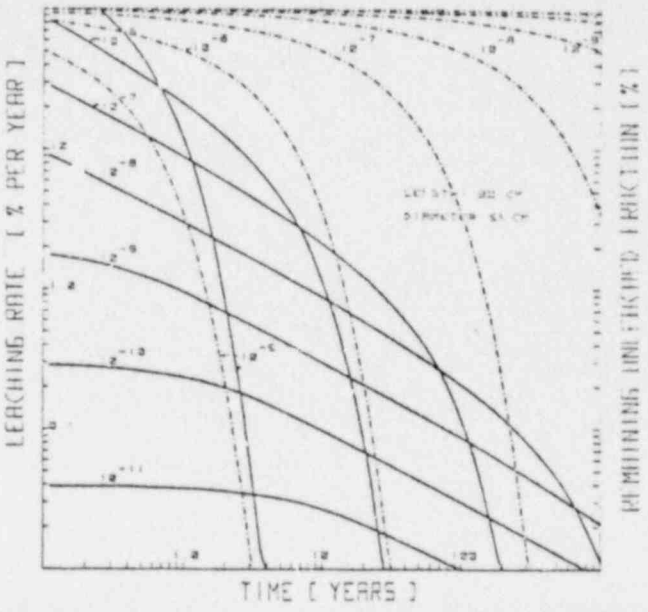

Figure 5. Calculated leaching rates for barrel-size cylindrical ingots of 90-cm height and 55-cm diameter as function of time for materials with different values of the leachability parameter k [$cm^2\ s^{-1}$]. The dotted curves represent the fractional amounts of leachable material left in the solid as a function of leaching time

long and 1.28 cm in diameter. The resulting histogram is fit well by the model prediction using $k = 4 \times 10^{-7} cm^2\ s^{-1}$ as the leachability constant of the material.

The two histograms representing the data from "experiment B" are also plotted in Figure 2. The tracer, tritiated water, was solidified in a plastic formulation as two different-size ingots. Both were 5 cm long, one had a diameter of 1.19 cm, the other of 1.42 cm. As predicted by the model, the leaching rates obtained with deionized water for the smaller cylinder remained higher than those of the larger cylinder throughout the experiment. The theoretical curves, B-1 and B-2, calculated with $k = 1.3 \times 10^{-9}\ cm^2\ s^{-1}$ for the two sizes have about the same distance as the corresponding histograms.

In Figure 3 the results of "experiment C" are well matched by the model using $k = 1 \times 10^{-7}\ cm^2\ s^{-1}$ as the material parameter. This experiment involved the ocean-water leaching of ^{137}Cs tracer from another plastic formulation.

The model also accommodated the much lower leaching rates found for ^{60}Co leached by deionized water from yet another plastic formulation. The leachability constant in this case was only $k = 3 \times 10^{-12}\ cm^2\ s^{-1}$.

The leachability parameter introduced here is a function of the matrix as well as of the leachant and the species being leached. For different leachable species present in the same solid, one would thus expect to obtain different values for the respective leachability constants.

It is apparent that the experimental results are generally in good agreement with the model. For each case studied, it is thus possible to describe the results by a single number, k, representing the material and with its aid calculate the expected leaching behavior as a function of time for any regular-shaped body made of the material.

Figure 5 is presented to facilitate the extrapolation of experimental data, obtained with small specimens in a few days, to the 55-gallon drum size ingots customary in radioactive-waste burial operations. The figure includes the expected leaching rates for materials of different "leachabilities" for times up to 1000 years. It also includes, as dotted curves, the predicted fractional amounts of leachable material left in the solid as a function of the leaching time.

Whenever nonhomogeneous leach specimens are investigated the leaching data obtained deviates from the theoretical model. Figure 4 presents the data of a ^{137}Cs leaching experiment using ingots made of ion-exchange resin beads solidified in a plastic matrix and ocean water as leachant. The surfaces of the two specimens were formed in part by exposed resin beads which showed an enhanced leaching rate relative to the average composite.

Porous materials and specimens with rough surfaces also exhibit initially higher leaching rates, since their surface-to-volume ratios are greater than for a regular body (cf. Figure 3, experiment D).

After the surface layer is depleted to some depth, the relative effects of the surface irregularities and micro-inhomogeneities are overcome or averaged out and the theoretical leaching curve is approached (Figure 4). Due to the higher surface-to-volume ratio, such irregularities are more pronounced in experiments using small ingots. They become less important as the size is increased.

The assumption that the diffusion across the solid–liquid interface is rapid relative to the diffusion in the solid is given its most severe test at the beginning of the leaching experiments with high-k materials, where relatively high leaching rates are encountered. The effect of surface-diffusion limitation is thus seen only in Figure 3, experiment C for the $k = 1 \times 10^{-7}\ cm^2\ s^{-1}$ material during the first day of the run. The experimental data there definitely stayed below the prediction of the simple model.

In case a chemical interaction between the leachant and constituents of the solid causes changes which affect the characteristics of the material, i.e., the diffusivity etc. or causes the leachable material to precipitate and change chemically in the solid, we expect deviations from the model.

CONCLUSION

The leachability of solidified low-level radioactive waste forms is one of the critical parameters determining the quality of the product and its acceptability for burial (*12*). The present work provides a simple procedure to measure this parameter in a few days of experimentation and supplies a mathematical model able to predict the leaching behavior of waste forms made of the material. As an extension of the reported approach, the method might find application in the quality assurance testing of materials used for beverage

containers etc. to measure and predict the amounts of noxious materials leached during their actual use.

ACKNOWLEDGMENT

The writers are indebted to H. Filter, K. Roberson, and W. Strom for providing the molded radioactive specimens and to I. Takahashi for providing the tritium tracer and performing the tritium counting.

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RECEIVED for review June 6, 1977. Accepted January 5, 1978.