FORECAST OF RADIONUCLIDES RELEASE FROM ACTUAL WASTE FORM GEOMETRIES

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ABSTRACT

The complete understanding of the leaching mechanism of radionuclides from solid cementitious waste forms is still far from being reached. Much effort has been devoted, however, to identify and explain the main components which contribute to the dispersal of radionuclides out of the waste form to the environment. This is of prime importance when short term results are extrapolated into the future.

The diffusion coefficient evaluation, based on experimental leaching data obtained from samples produced from the same batch was performed using the exact diffusion formulation applied to real geometric sample shape.

The laboratory obtained diffusion coefficients are not constant in time nor are they the same for the different samples assayed precluding the use of laboratory scale leaching experiments to forecast the behavior of large scale samples.

INTRODUCTION

Knowledge of the release mechanism of radionuclides from an immobilization matrix by the action of water is important to forecast the long term behavior of the radionuclides when buried in geological strata, and the rate to reaching the biosphere.

The leaching rate of radionuclides immobilized in matrices by the water action is one of the parameters utilized to evaluate the durability of the engineered barriers used in repositories for low and medium level wastes.

Much effort has been devoted to identify and explain the main components which contribute to the dispersal of radioactivity out of the waste form when in contact with water. In spite of this a complete understanding of the leaching mechanisms of radionuclides from solid waste products is far from being reached.

The understanding of leaching is of prime importance when short term results are extrapolated into the future, especially since long term leach rates can not be measured directly and must be predicted through developing mathematical models.

It is observed from the literature that many authors of papers related to leaching mechanism studies try to adjust their data to the $t^{\frac{1}{2}}$ law obtained when one considers the simple diffusion from a semi-infinite plane source. Since this law does not fit the experimental data, some extrapolations to explain the discrepancy are made.

Other leaching mechanisms exist such as chemical reactions, concentration dependent dissolution etc, which compete with the diffusion process. According to the radionuclide involved one or the other processes can be dominant. This discussion will be centered, however, in the diffusion

process responsable for the majority of the leaching behavior reported till now.

As can be observed from any experimental leaching curve plotted the cumulative leached fraction versus the square root of time is linear only for short time periods. Several authors concluded that the semi-infinite geometry, from which the $\sqrt{t}$ law is obtained, is applicable to finite geometry samples provided that the cumulative fraction to be leached is less than 20% of the total. For higher cumulative fraction values a different formulation has to be applied. All attempts to fit combined formulas expressing different mechanisms of leaching have no actual basis.

Assuming that diffusion is the most important process of leaching and using an exact mathematical formulation (1) for the actual sample dimensions it is possible to obtain the diffusion coefficient from experimental data. As can be observed from the data, the diffusion coefficient is not constant. To the contrary, it decreases rather rapidly in the beginning of the leaching experiment and then decrease slowly to an apparent constant value.

Leach tests were conducted with specimens of various geometries in order to confirm that the diffusion coefficient behavior with time is the same for all geometries. This would prove that a sample withdraw from a full size waste form could act as a fingerprint of the waste provided that the release of radioactivity to the environment can be predicted by using the diffusion coefficient, evaluated from leaching experiments, of the sample and the exact formulation.

This simple way of predicting the cumulative fraction of radioisotopes released from full size waste forms, from laboratory specimens (2,3), is not valid even for small values of the cumulative fraction. This is due to the fact that the diffusion coefficient is not constant with time.

The objective of the present work was to verify the validity of the use of small scale samples in laboratory experiments in order to evaluate the amount of radioactive material released from full size waste forms.

EXPERIMENCAL PROCEDURES

Sample preparation

The simulated waste form samples were prepared by using a simple ordinary Portland cement, OPC, and all were in the form of right cylinders ranging from 20 cm^3 to about 20,000 cm^3. The mixing of all components was done using standard procedure(4) and a planetary paddle mixer. The reported data represent the average of two samples used for each geometry assayed with the exception of the largest sample with 20,000 cm^3 for which there was a single sample. Inactive cesium in the chemical form of nitrate was used as a tracer together with sodium nitrate to simulate a nitrate waste stream. The sample composition is given in Table I.

Table I

Components	% wt
Cement	71.4
$NaNO_3$	3.1
$CsNO_3$	0.5
Water	25.0

After casting and setting for 24 hours, the samples were air/moist cured for 28 days at room temperature before the leaching process.

The leaching tests, using international standard procedure(5), were carried out in closed plastic bottles using distilled water as the leaching fluid and using a water volume to specimen area ratio of 10 cm. The water was renewed at frequent intervals and the concentration of stable cesium leached, during each interval, was determined by wavelength dispersive X-ray fluorescence spectrometry.

The schedule of water renewal was established so that the assumption used for the transport equation solution was valid, that is, the concentration of the tracer in the water is practically zero.

X-ray analysis

Inactive cesium concentration in each leachate sample was determined by wavelength dispersive X-ray fluorescence technique described elsewhere (5,6). The equipment used was a Rigaku Denki spectrometer Model 405/A0 with their parameters selected for measurement of the CsL_{α} analytical line as follows:

Tube	:	Chromium (2.0 kW)
Tube settings	:	40 mA and 40 kV
Analyzing crystal	:	PET (002)
Collimator (mm)	:	0.15
Detector	:	FPC(gas flow counter)

Eight sets of standard aqueous solutions were prepared from spectropure $CsNO_3$. The cesium concentration was varied in the range of 2×10^{-5} to 1×10^{-4} g cm^{-3}. Triplicate samples were prepared for each leachate sample and standard solution.

DIFFUSION COEFFICIENT EVALUATION

The immobilization materials are usually porous enabling the leaching kinetics to be explained as a diffusion controlled process.

As long as the dissolution of the matrix can be neglected when compared with the diffusion, the time dependence (t) of the leached fraction F(t) for cylindrical waste forms with radius and half height equal to R and H respectively is given by :

$$F(t) = 1 - \frac{2}{R^2} \sum_{n=1}^{\infty} \frac{e^{-\alpha_n^2 (D/R^2) t}}{\alpha_n^2} \cdot \frac{4}{\sum_{m=1}^{\infty} \frac{1}{(m-\delta)^2}} \cdot \frac{1}{(m-\delta)^2} \qquad (1)$$

where α_n equals the roots of the Bessel function of zero order

$$J_0(\alpha_n) = 0$$

D is the effective diffusion coefficient and t is the time elapsed after water immersion.

Most authors use a first approximation of that expression corresponding to the solution of the transport equations for a semi-infinite medium of uniform initial concentration for mobile species with the surface concentration equal to zero for time greater than zero.

The expression (1) reduces to:

$$F(t) = 2 (S/V) (Dt/\pi)^{1/2} \qquad (2)$$

where S is the surface area of the wastes form and V is the volume.

This equation suggest that the experimental data, when multiplied by (V/S), becomes independent of the geometry of the samples. Therefore, the experimental data are usually presented as (V/S)F(t) versus t or $\sqrt{t}$.

As can be seen from figure 1 any short term extrapolation from small laboratory sample to a full scale waste form has to be made carefully, otherwise large errors can result.

It is also observed that the rate of leaching is especially high in the beginning of leaching and this was attributed to surface wash off. Some authors try to overcome this by adjusting their data to a more general expression:

$$[(V/S)F(t)] = [(V/S)F(t)]_0 + 2(Dt/\pi)$$

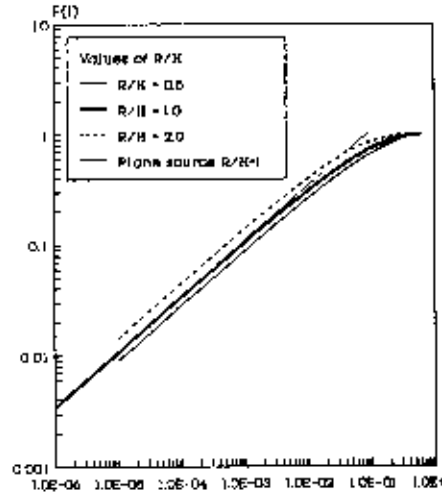

Fig. 1 Theoretical relationship between F(t) and Dt/R^2 for some H/R values.

where $[(V/S)F(t)]_0$ represents the amount of radionuclides that are readily washed off over a relatively short period of time.

Making use of these expressions it is possible to evaluate the diffusion coefficients for different geometries. In Figure 1 a comparison between the exact formulation given by expression (1) for three geometries: R/H equal to 0.5, 1.0 and 2.0, and the first order approximation, that is, the solution for a semi-infinite plane source as given by expression (2) for the geometry R/H equal to 1.0 is given.

All these formulations assume that the diffusion coefficient is constant in time. That is not the case however, because the diffusion of ions and the permeability of fluids across a porous cementitious matrix are related to the volume of pores and the size and interconnection of these pores (2). The size of these pores and channels between them vary with time as long as the hydration of cement continues.

Using expression (1), it is possible to evaluate the diffusion coefficient for a given geometry and elapsed time from the experimental value obtained for the cumulative leached fraction.

Special care has to be taken however

when evaluating the cumulative fraction for larger samples in the early stages of leaching since the amount of cesium able to be leached is less than the total incorporated in the sample. This is due to the delay time for the water to diffuse into the volume of the sample. This delay time is related to the permeability of the sample and varies according to the hydraulic pressure under which the sample is submitted.

EXPERIMENTAL RESULTS

Leach experiments were carried out on six sample geometries with average volumes equal to 30, 60, 170, 950, 3,500, and 20,800 cm^3. Two sets of samples had S/V equal to 0.48 and another set had this ratio equal to 1.74. The volume to surface ratio varied from 0.56 to 4.97. The correspondence among the sample volume and their respective S/V values is given in Table II.

Table I

Sample volume (cm^3)	S/V
30	1.60
60	0.48
170	0.48
950	1.74
3,500	1.00
20,800	1.00

The aim of this work was to verify the general hypothesis that it is possible to forecast the behavior of full scale waste forms from the leaching experiments of a sample withdrawn from the waste form, which would act as a fingerprint. Previous experiments indicate the possibility that the diffusion coefficient varies with time due perhaps to the competition between the leaching of the matrix components (corrosion) and the continued hydration of cement.

In Figure 2 the averaged cumulative fraction of the samples assayed versus the leaching time is given. In Figure 3 the data are presented as the cumulative fraction corrected for the first order geometric effect versus the square root of time. This representation of data should appear as a single straight line if the diffusion coefficient were constant in time and equal for all the samples. The difference among the samples clearly indicates that the hypothesis used to evaluate the time dependence of leaching is wrong.

In Figure 4 the cumulative fraction versus (t/R^2) is given. If the diffusion coefficient was constant for the samples, the curves should resemble the Figure 1 except

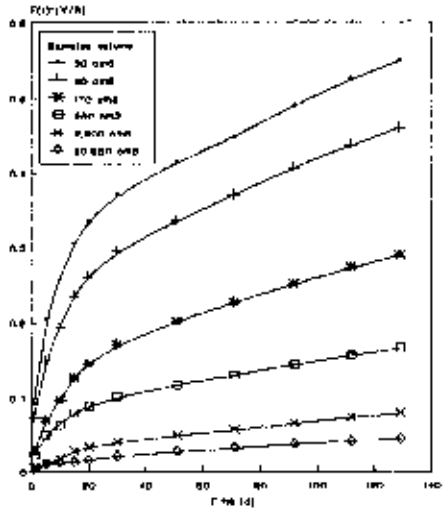

Fig.2 Effect of samples geometry on cumulative leaching fraction.

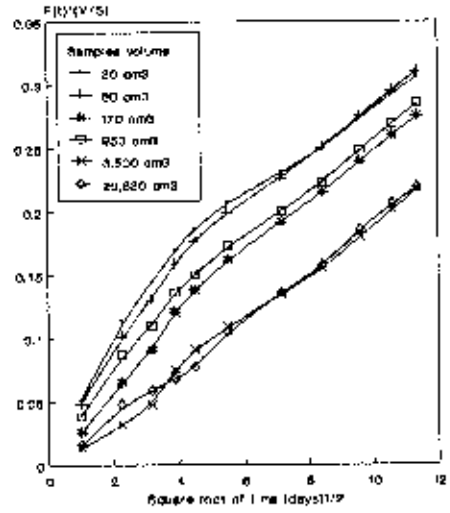

Fig.3 Cumulative leaching fraction corrected for geometry in first order approximation plotted against t.

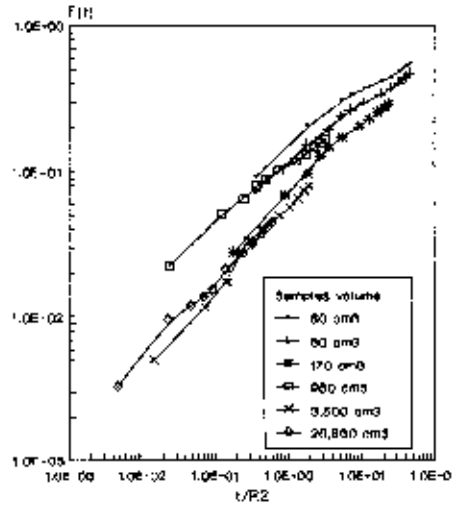

Fig.4 Cumulative leaching fraction plotted versus t/R^2.

for a constant additive value. On contrary, the obtained values scarcely keeps the same trend indicating the weakness of the simple diffusion hypothesis as the main mechanism responsible for the leaching of cesium from the samples.

Figure 5 gives the values of the average diffusion coefficient evaluated out of the experimental data and for each sample assayed. As can be observed diffusion varies quickly with time till it stabilizes to some value which differs for each pair of samples.

CONCLUSIONS

The realized leaching tests with different size samples showed that after 130 days the data obtained do not allow for a definitive conclusion. It was expected that the diffusion coefficient behavior would be the same for all the samples, but that was not the case. So, the correlation of data obtained from small samples to that of full scale waste form is poor. Therefore, the extrapolation of short term small sample data to longer periods of time is questioned until more accurate conclusions can be extracted from the experiments.

The mathematical model has to be improved to consider the time dependence of

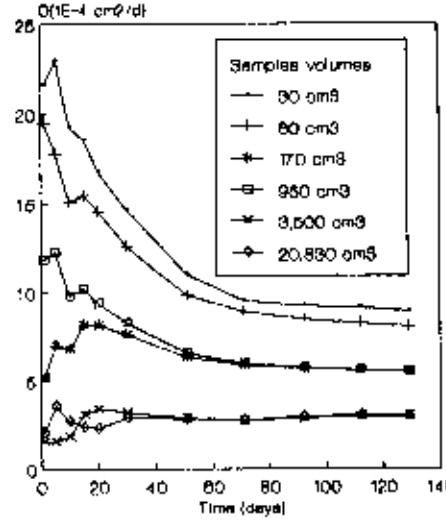

Fig.5 Diffusion coefficient variation with time, for different geometries.

the diffusion coefficient.

The possibility remains however, for the use of the leaching experiment as a tool to decide among which immobilizing matrices is the best.

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