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UNION CARBIDE CORPORATION
NUCLEAR DIVISION

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ORNL/MIT- 198

DATE: October 21, 1974 COPY NO

SUBJECT: Leaching of Radioactive Nuclides from Cement Grouts, Part II

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MASTER

ABSTRACT

The determination of the leaching rate of radioactive ^{137}Cs from a cement grout should the grout be contacted by water is necessary for environmental protection. The effect of leachant turnover rate on ^{137}Cs leaching rates was evaluated with batch and continuous (modified Soxhlet extractor) modes of experimentation. Three additives (Grundite, potter's clay, and Conasauga shale) were compared in terms of capability of radioactive isotope retention, while two leachants (tap and distilled water) were investigated.

The Soxhlet extractor experiment resulted in the highest rate of leaching, and Conasauga shale was found the best additive for ^{137}Cs immobilization. Tap water used as leachant was more effective than distilled water. Data were analyzed using models involving isotopic diffusion in the grout and involving diffusion plus a time dependent boundary condition at the interface of grout specimen and leachant.

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Contents

1. SUMMARY

The leaching of ^{137}Cs from 80-day cured cement grout specimens was studied to determine the effect of the following factors on leaching rate: (1) type of additive in the grout (Grundite, potter's clay, or Conasauga shale), (2) rate of leachate replacement (continuous replacement, batch replacement at one or two-day intervals, and no replacement), (3) stagnant and stirred leachate, and (4) type of leachant (tap or distilled water). A modified Soxhlet extractor was used to continuously replace the leachate. The experimental data were fitted to a diffusion model for a semi-infinite medium with one of two possible surface concentration boundary conditions: zero concentration or an exponentially decaying concentration with time. Higher rates of leachate replacement resulted in higher leaching rates and effective diffusivities. Infrequent leachate replacement and a resulting approach toward equilibrium saturation, or steady state conditions, inhibited leaching.

Continuous leachate replacement in the modified Soxhlet extractor provided the highest leaching rates and the closest experimental approximation of a zero surface concentration boundary condition. A diffusion model with a time dependent boundary condition provided a better fit to the data than a model with a zero surface concentration boundary condition.

A Conasauga shale grout sample retains cesium better than potter's clay which retains it much better than Grundite. There is about three orders of magnitude difference between the effective diffusivity for Conasauga shale and Grundite based on model parameters. Tap water was found to be a stronger leachant than distilled water. Further studies should be conducted with continuous leachate replacement. Plating and adsorption of ^{137}Cs on the stainless steel and glass equipment should be investigated as a possible source of error. Improved sensitivity in the analysis of cesium content is desired.

2. INTRODUCTION

2.1 Background

Immobilization of radioactive nuclides in a cement grout is currently employed for long-term underground storage of intermediate-level radioactive wastes from nuclear research operations. For environmental protection, it is necessary to know the mass transport rates of the radioactive nuclides from the grout should it come in contact with water (1).

The International Atomic Energy Agency (IAEA) has proposed a standard testing procedure (2) for measuring the rate of leaching of radioisotopes from a variety of storage materials used to immobilize the radioactive waste material. In this method, one end of a cylindrical storage material specimen, characterized by a surface area-to-volume ratio of $\sim 0.2\ cm^{-1}$ for an $\sim 100\ cm^3$ sample, containing the radioisotope is exposed to a fixed volume of leachant, usually water. Samples of the leachate are analyzed to determine the quantity of radioactive material leached from the storage medium as a function of time. Theoretical models for isotopic mass transport in a semi-infinite solid have been developed (1, 3, 4) to analyze leach rate data obtained from these tests. An inherent disadvantage of the IAEA procedure is that it takes a year or more to obtain enough data for interpretation using the theoretical models. Thus, detailed parametric studies are often impractically long.

An alternate test procedure was recently developed by the Chemical Technology Division at ORNL; an MIT Practice School group demonstrated that useful data could be obtained in three weeks (4) using this technique. This test method (hereafter referred to as the ORNL-MIT-194 method) uses a smaller cement sample having a volume of $\sim 4\ cm^3$ and a surface-to-volume ratio of $\sim 3.5\ cm^{-1}$ with the entire cylindrical specimen exposed to the leachant. Semi-infinite geometry models and finite cylinder models have been compared (4). It has been demonstrated that leach rate data obtained using the ORNL-MIT-194 method could satisfactorily be treated using the semi-infinite geometry.

Recent work (3) indicated that the leachant turnover rate (frequency of leachate replacement with fresh leachant) affects the isotopic leaching rate. Hence, the value of the effective mass transport diffusivity and mechanism rate constants, calculated from the theoretical models developed to explain the mass transport phenomena involved in leaching, are also affected. The effects of leachant turnover rate on isotopic leaching rate were investigated to resolve the uncertainty regarding effective diffusivity and rate constants.

2.2 Description of the Models

Two theoretical models of the mass transport process were developed to analyze the data. The first model involves the simple diffusion of cesium from a semi-infinite grout specimen in the leaching medium. In the model, all cesium was assumed to be mobile at the start of the leaching process and the concentration of ^{137}Cs at the surface of the grout is assumed to be zero at all times. The second model also involved diffusion in a semi-infinite medium, but with a time-dependent surface concentration to account for a hypothetical rate of "wash off" of the grout surface by the leachant.

2.3 Objectives and Method of Attack

The objectives were:

1. To determine the effect of leachant turnover rate on the leaching rate of ^{137}Cs from cement grouts of various composition, and hence, to determine the effect on the effective diffusivity, D_e, and other mechanism rate constants calculated from the theoretical models.

2. To ascertain the validity of the various models.

3. To evaluate the testing methods for measurement of leaching rates.

The amount of ^{137}Cs leached from cement grout specimens as a function of time using various leachant turnover rates was experimentally measured for three different grout compositions. A modified Soxhlet extractor was used to effect continuous leachant turnover. Only one Soxhlet extractor was available; consequently only one specimen was tested in this apparatus. Batch experiments were conducted using the ORNL-MIT-194 procedure with leachate replaced at 24-hr and 48-hr intervals. Additional batch experiments were conducted with no leachate replacement.

The theoretical models were fitted to the data obtained in this project and to data previously obtained using the ORNL-MIT-194 method. Values were obtained for the effective diffusivity, D_e, and other mechanism constants for each set of data.

The values of these parameters are compared to the leachant turnover frequency; and, together with a comparison of the theoretical leach rate curves, an evaluation of the validity of the models and the applicability of the testing method for measurement of leaching rates can be made.

3. EXPERIMENTAL APPARATUS AND PROCEDURE

Leaching experiments were conducted with grout specimens containing three different additives: Conasauga shale, Grundite, and potter's clay. The composition and method of preparation of the specimen are discussed in Appendix 10.2. Each specimen was cylindrical with a 1.61-cm diameter, 2-cm length, to give a surface area of 14.2 cm^2, a volume of 4.1 cm^3, and a surface area-to-volume ratio of 3.49 cm^{-1}. Each specimen contained 12.36 μCi of radioactive cesium. The experiments were started after the specimens had been cured 80 days. Two additional experiments were started a week later or after 87 days of curing.

One Conasauga shale grout specimen was contacted with a continuously replaced distilled water leachate in a modified Soxhlet extractor. A schematic diagram of the apparatus is shown in Fig. 1. The evaporator was filled with 300 ml of distilled water which was boiled and then condensed in a shell and tube heat exchanger. The condensate dripped into a

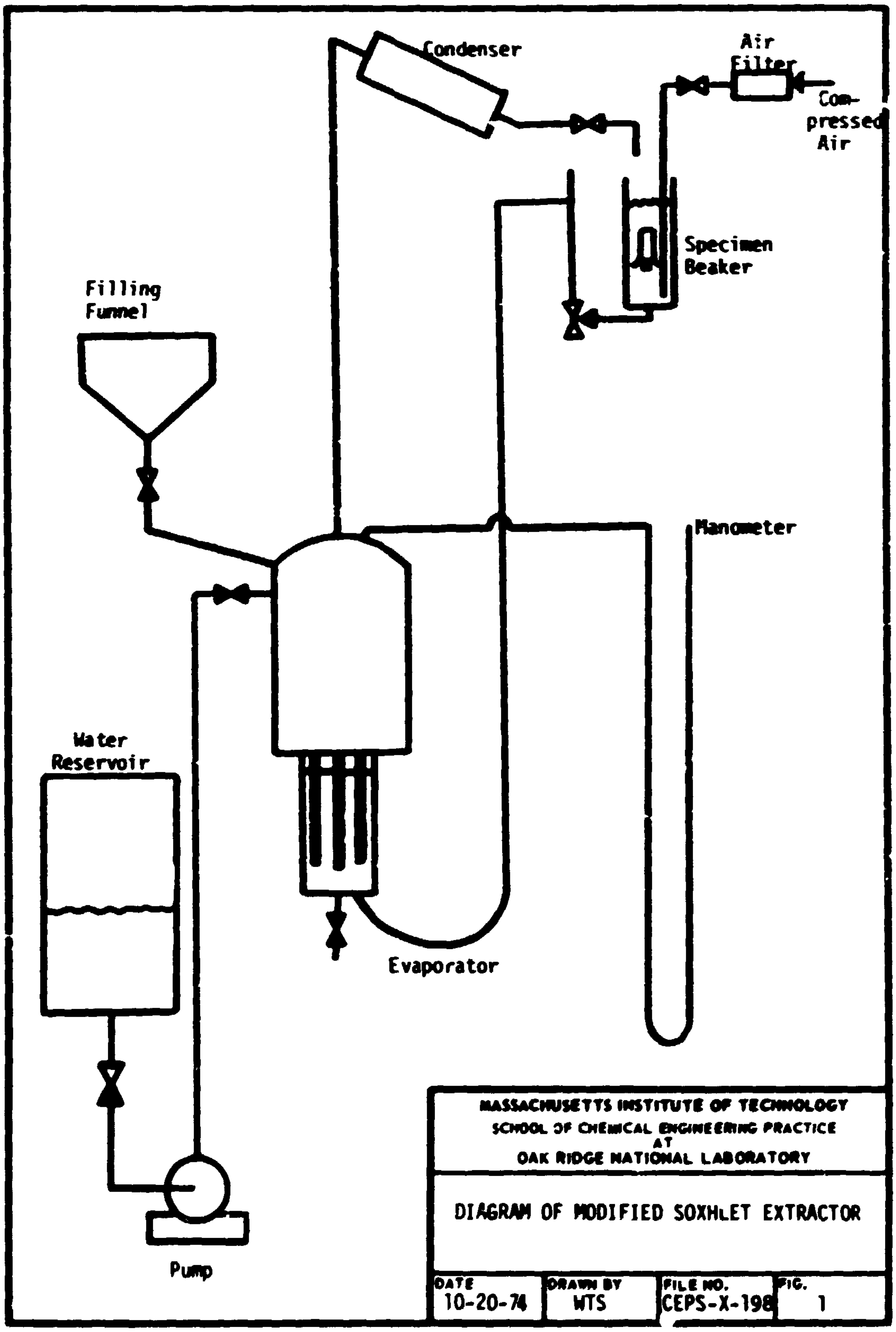

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DIAGRAM OF MODIFIED SOXHLET EXTRACTOR

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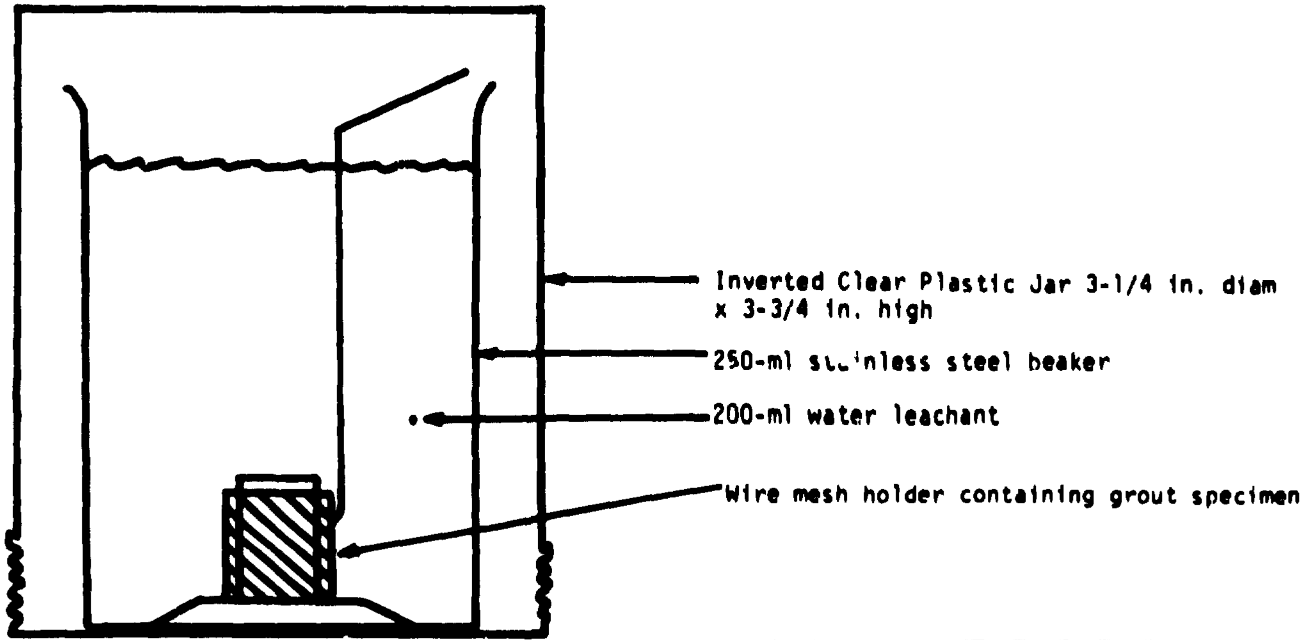
175-ml specimen beaker where the specimen was suspended in a stainless steel wire holder. Filtered compressed air was bubbled through the specimen beaker to provide agitation. A tube siphon between the bottom of the specimen beaker and the bottom of the evaporator carried the leachate to the evaporator. The tube siphon was vented to the atmosphere to maintain the water level in the specimen beaker at a constant level. Three power supplies were adjusted to supply enough power to the evaporator heaters to maintain a 40-ml/min flow rate. Thermocouples indicated a room temperature of 23°C, a leachate temperature of 27°C, and an evaporator liquid temperature of 100°C. Details for the Soxhlet evaporator and the procedure for measuring flow rates are given in Appendix 10.6.

Before a sample was taken from the Soxhlet extractor, the power supplies were turned off. The evaporator was emptied into a stainless steel beaker and the contents cooled to room temperature in an ice bath. The volume of the sample was measured in a 500-ml graduated cylinder, and then a 5-ml sample was taken with a pipette to be analyzed for gamma radiation and pH. The first Soxhlet sample was discarded after measurement and 300 ml of fresh distilled water was put in the evaporator. All samples which followed were returned to the evaporator. Makeup water was added to keep the volume at approximately 300 ml. Five-ml samples of the leachate in the specimen beaker were occasionally taken for a gamma ray count and pH measurement.

Leaching experiments were also conducted with discrete replacement of leachate in batches of 200 ml. By holding all other factors equal in two experiments the effects of the following variables on the amount leached were determined: (1) the time span between leachate replacement: one day, two days, or no leachate replacement, (2) frequency of sampling the leachate. (3) the effect of stirring the leachate, and (4) type of leachant: tap water or distilled water. One experiment in which the leachate was never replaced was run in triplicate to test for reproducibility. Two short-term, two-day experiments were started one week later than the others to obtain additional data on the first two days of leaching. In all these experiments the specimen was held in a stainless steel wire holder and immersed in 200 ml of leachant in a 250-ml stainless steel beaker. In some experiments the specimen was suspended above a magnetic stirring bar; an asbestos pad separated the beaker and the stirring motor to minimize heat transfer from the warm motor. In the unstirred experiments the legs of the wire holder rested on the bottom of the beaker (see Fig. 2). All beakers were enclosed in a plastic jar to minimize losses by evaporation. Leachate was replaced by removing the specimen and its holder, tapping it on the side of the beaker to drain the leachate, and placing it in another beaker with 200 ml of fresh leachant. The old leachate volume was measured in a 250-ml graduated cylinder. In the case of no leachate replacement experiments the leachate volume was measured twice near the end of the experiment. In all experiments, 5-ml leachate samples were taken with a pipette, analyzed for gamma activity and pH, and returned to the rest of the leachate.

A description of the experiments is given in Table 1. The four vertical columns divide the experiments into four grout additive-leachant combinations. On the left side of the table is the description of all experiments



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SCHEMATIC OF LEACH TEST APPARATUS

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Table 1. Summary of Experiments

	Sample-Leachant Combinations			
Leachate Replacement Frequency	Conasauga Shale-Tap Water	Conasauga Shale-Distilled Water	Grundite-Tap Water	Potter's Clay-Tap Water
Continuous		X-S		
Every Day - Unstirred	1-S	1-SD	1-G*	1-P*
- Stirred			1-G(ST)C	
			1-G(ST)*	
Every Two Days - Unstirred	2-S	2-SD	2-GC	2-P*
			2-G*	
None	0-S	0-SD-1	0-G	0-P
		0-SD-2		
		0-SD-3		

*Indicates leachate was sampled between leachate changes in addition to sampling during leachate change.

in terms of leachate replacement rate and stirring. In the horizontal row adjacent to each experiment description are listed the corresponding experiments. The experiments are listed in terms of a phonetic experiment code. The symbols in the codes have the meanings: G = Grundite, P = potter's clay, and S = Conasauga shale, C = control experiment (leachate sampling only when replaced), D = distilled water, ST = short-term experiment (two days), X = Soxhlet, 1 = leachate charge every day, 2 = leachate change every two days, and 0 = no leachate change.

Five ml of each leachate sample was analyzed for gamma radiation with a gamma scintillation counter. Most samples were counted for five 5-min periods and some were counted more times. Initially the activity was measured in the integral mode over the energy range of 0.04 to 1.0 Mev. Many of the integral measurements were not significantly above background. Therefore, all activity measurements were retaken in the differential mode at 662 ± 5 keV.

The procedure for calculation of fraction leached from measured activity is given in Appendix 10.3. Preliminary 1-ml samples were taken from the Soxhlet evaporator to determine when the concentration was high enough to take a full sample for counting. Some dilute samples were concentrated by evaporation. Precautions were taken to prevent cross contamination of the experiments. Leachate sample containers were used once and discarded. Each experiment had separate stainless steel beakers, pipette, and beaker for making pH measurements.

The pH of each sample was read on a Beckman Zeromatic pH meter. In addition, the pH of distilled and tap water were measured each day. The water pH values did not vary and had values of 6.1 for distilled water and 8.0 for tap water.

4. THEORETICAL MODELS

The main interest in the leaching of cesium from cement grouts is the effect of long-term leaching on the environment. A reliable extrapolation of short-term experimental data must be based on a model which closely represents the actual mass transfer in the cement grout. The data accumulated were fitted to two models using an iterative technique developed by Box (5). Both models are based on diffusion in a semi-infinite medium but each has different boundary conditions. The first assumes a zero surfac concentration and the second assumes a time-dependent surface concentration. A close fit using these models had previously been obtained for 60-day cured grout samples. Previous work has shown little difference between the results obtained for the model of diffusion in a semi-infinite medium and diffusion in a finite cylindrical geometry for a 10-day experiment (4).

The mass balance around a differential element in a semi-infinite medium with constant effective diffusivity yields:

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} \qquad (1)$$

where:

C = concentration at any position within the medium

t = time

D_e = effective diffusivity within the medium

x = distance from the surface of the medium

In both models, an initial uniform concentration, C_0, within the medium was assumed and always maintained at an infinite distance from the surface. In the first model, mass transfer external to the grout is assumed to be so rapid relative to the internal transfer that the surface concentration is zero. The boundary and initial conditions are:

$$x > 0, \quad t = 0, \quad C = C_0 \tag{2}$$

$$x = \infty, \quad t > 0, \quad C = C_0 \tag{3}$$

$$x = 0, \quad t > 0, \quad C = 0 \tag{4}$$

Solving the diffusion equation and performing an integration over time gives (see Appendix 10.1 for derivation):

$$\frac{\sum_{i=1}^{n} a_i}{A_0} = \frac{2}{\sqrt{\pi}}\left(\frac{S}{V}\right)\sqrt{D_e t} \tag{5}$$

where:

a_n = radioactivity lost during leaching period n

A_0 = initial radioactivity in the sample

S = surface area of the sample

V = volume of the sample

The second model considers that the surface of the grout may not be instantaneously washed off to a zero concentration. The surface has an initial concentration which decays exponentially with time. The boundary and initial conditions are therefore:

$$x > 0, \quad t = 0, \quad C = C_0 \tag{6}$$

$$x = 0, \quad t > 0, \quad C = \kappa C_0 e^{-\beta t} \tag{7}$$

$$x = \infty, \quad t > 0, \quad C = C_0 \tag{8}$$

Solving the diffusion equation and performing an integration over time yields:

$$\frac{\Sigma a_n}{A_0} = 2\left(\frac{S}{V}\right)\left(\frac{D_e}{\pi}\right)^{1/2}\left[t^{1/2} - \left(\frac{\kappa}{\beta^{1/2}}\right) \mathrm{daw}(\beta t)^{1/2}\right] \tag{9}$$

where daw is Dawson's integral defined as:

$$\mathrm{daw} = e^{-u^2} \int_0^u e^{z^2}\, dz \tag{10}$$

and κ and β are constants.

An equilibrium may exist between mobile and immobile forms of cesium within the grout. Appendix 10.1 describes how the two models account for a direct proportionality of mobile and immobile forms by a redefinition of the effective diffusivity (3).

5. RESULTS

The data obtained from the 80-day cured grout specimens were fitted to the diffusion models using Box's iterative technique (5). The resulting values of the parameters are presented in Table 2. Representative data for the cumulative fraction ^{137}Cs leached as a function of time for experiments with a Conasauga shale grout specimen in the Soxhlet extractor and a potter's clay grout specimen with one-day leachant changes are plotted with the predictions of the diffusion models in Figs. 3 through 6. A plot of the cumulative fraction leached as a function of time for a Grundite grout specimen with no leachant change is shown in Fig. 7. Data for other experiments are given in Appendix 10.5.

6. DISCUSSION OF RESULTS

6.1 Comparison of Leaching Rate with Different Additives

Figure 8 is a plot of the logarithm fraction of ^{137}Cs leached versus time for the daily leachant change experiments with Grundite, potter's clay, and Conasauga shale. The fraction leached from a Grundite specimen using tap water as the leachant is an order of magnitude above that from the other additives. From Table 2, for the simple diffusion model, effective diffusivities of ^{137}Cs in grouts with daily leachant changes and with Grundite, potter's clay, or Conasauga shale additives are $\sim 900 \times 10^{-13}$, $\sim 7 \times 10^{-13}$, and $\sim 1 \times 10^{-13}$ cm^2/sec, respectively.

6.2 Effects of Leachant Stirring on the Cumulative Fraction Leached

Figure 9 shows the short-term concentration history of the fraction leached for a Grundite specimen. The leachant was stirred and changed daily. A control experiment to determine any deviations due to frequent sampling was conducted simultaneously and monitored at leachant changes. No significant differences were noted between the two experiments. However,

Table 2. Parameters for Diffusion Models

Additive	Leachate Replacement	Diffusion Model	Diffusion Model with Time - Dependent Boundary Conditions		
		D_e, cm^2/sec (x 10^{13})	D_e, cm^2/sec (x 10^{13})	κ (x 10)	β, sec^{-1} (x 10^6)
Grundite					
1-G	every day	865	1170	4.15	3.74
1-G(ST)	every day	1070	3900	5.29	1.42
2-G	every 2 days	856	856	0.135	500
Potter's Clay					
1-P	every day	6.91	19.8	7.99	2.29
2-P	every 2 days	5.08	32.7	8.32	0.965
Conasauga Shale					
X-S	continuous	14.3	16.9	10.0	14.5
1-S	every day	1.33	2.94	8.06	2.99
1-SD	every day	0.543	1.32	7.76	2.79
2-S	every 2 days	0.796	1.77	10.0	3.53
2-SD	every 2 days	0.248	0.334	9.8	8.35

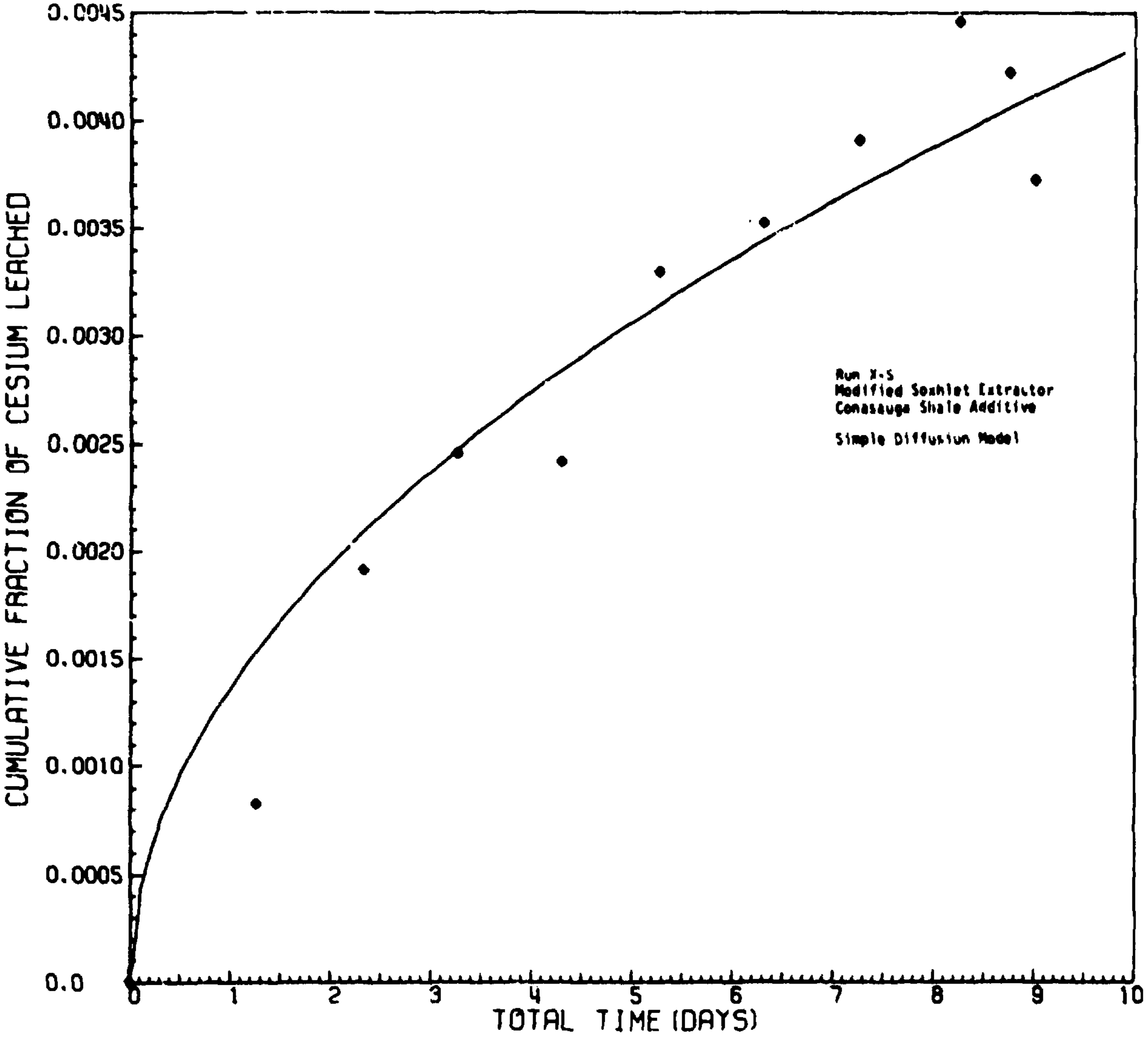


Fig. 3. Cumulative Fraction ^{137}Cs Leached as a Function of Time

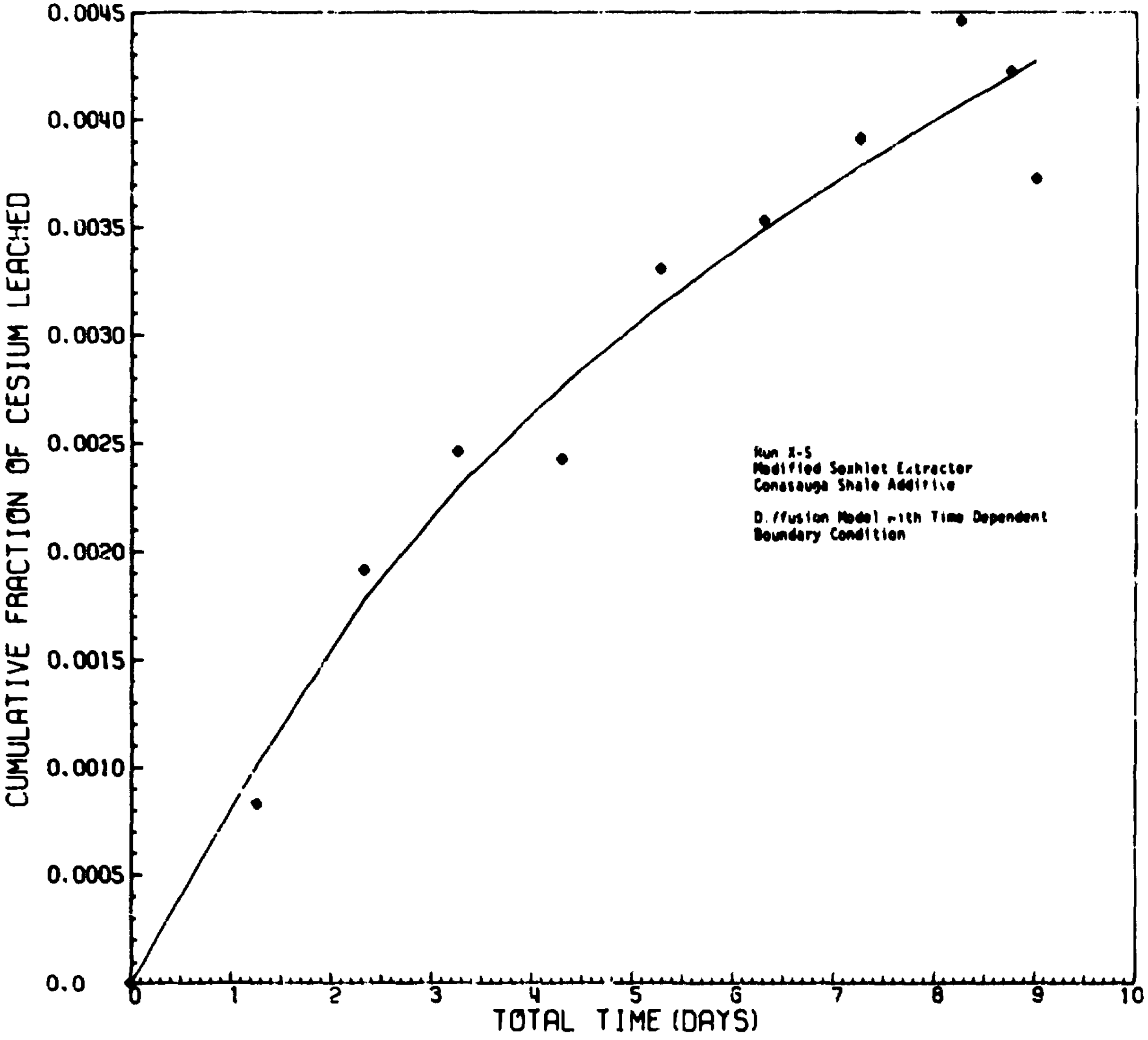


Fig. 4. Cumulative Fraction ^{137}Cs Leached as a Function of Time

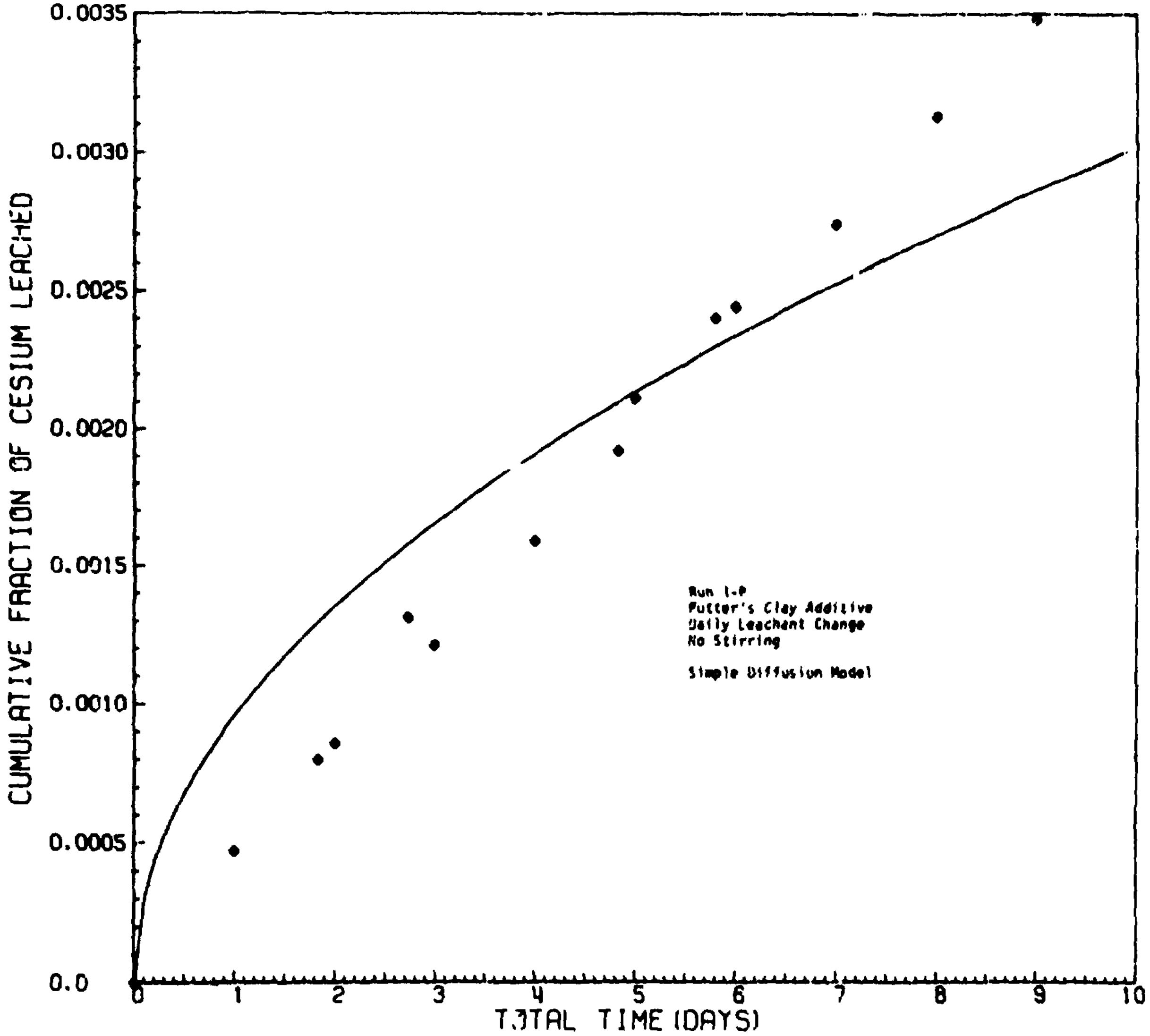


Fig. 5. Cumulative Fraction ^{137}Cs Leached as a Function of Time

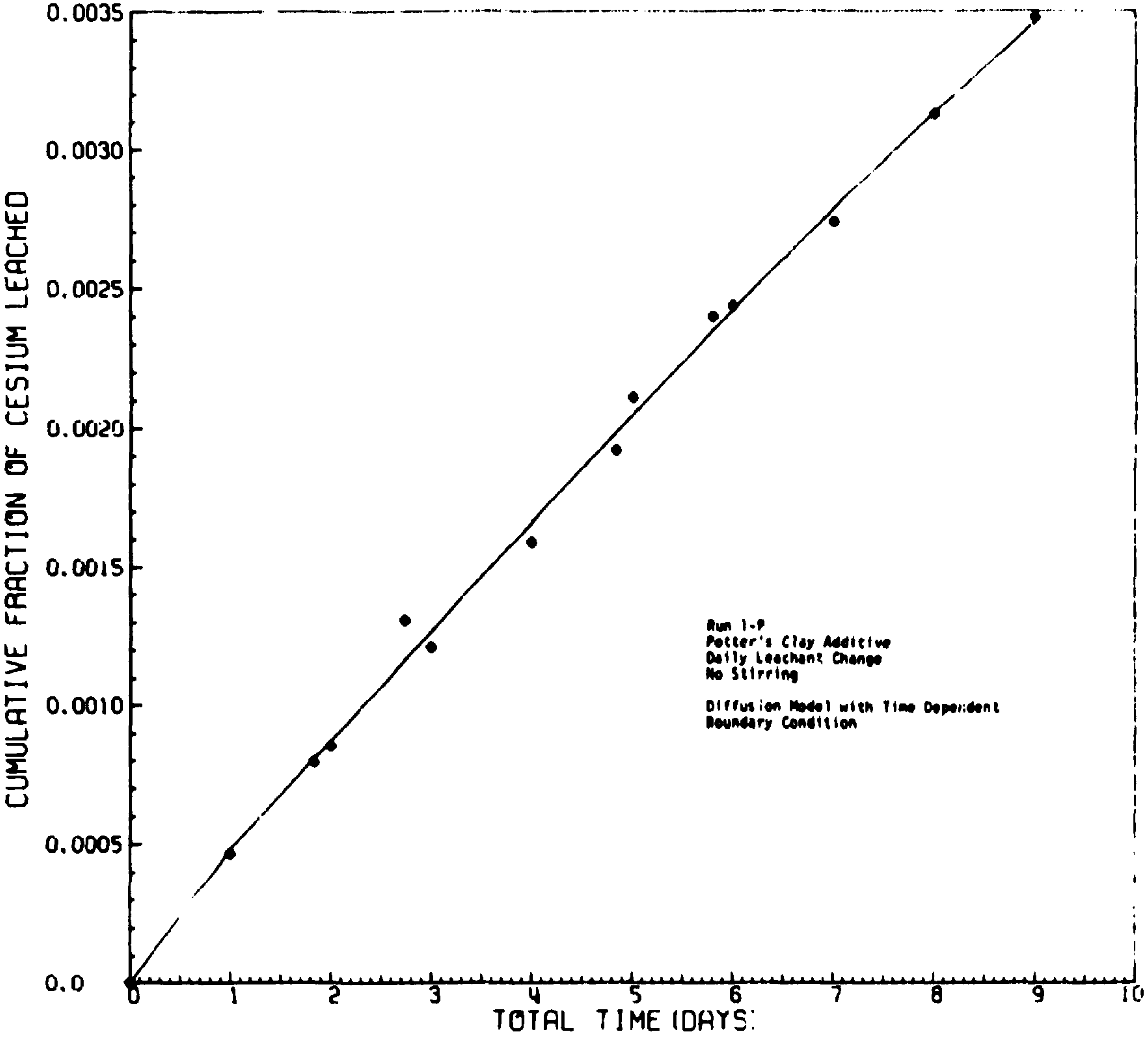


Fig. 6. Cumulative Fraction ^{137}Cs Leached as a Function of Time

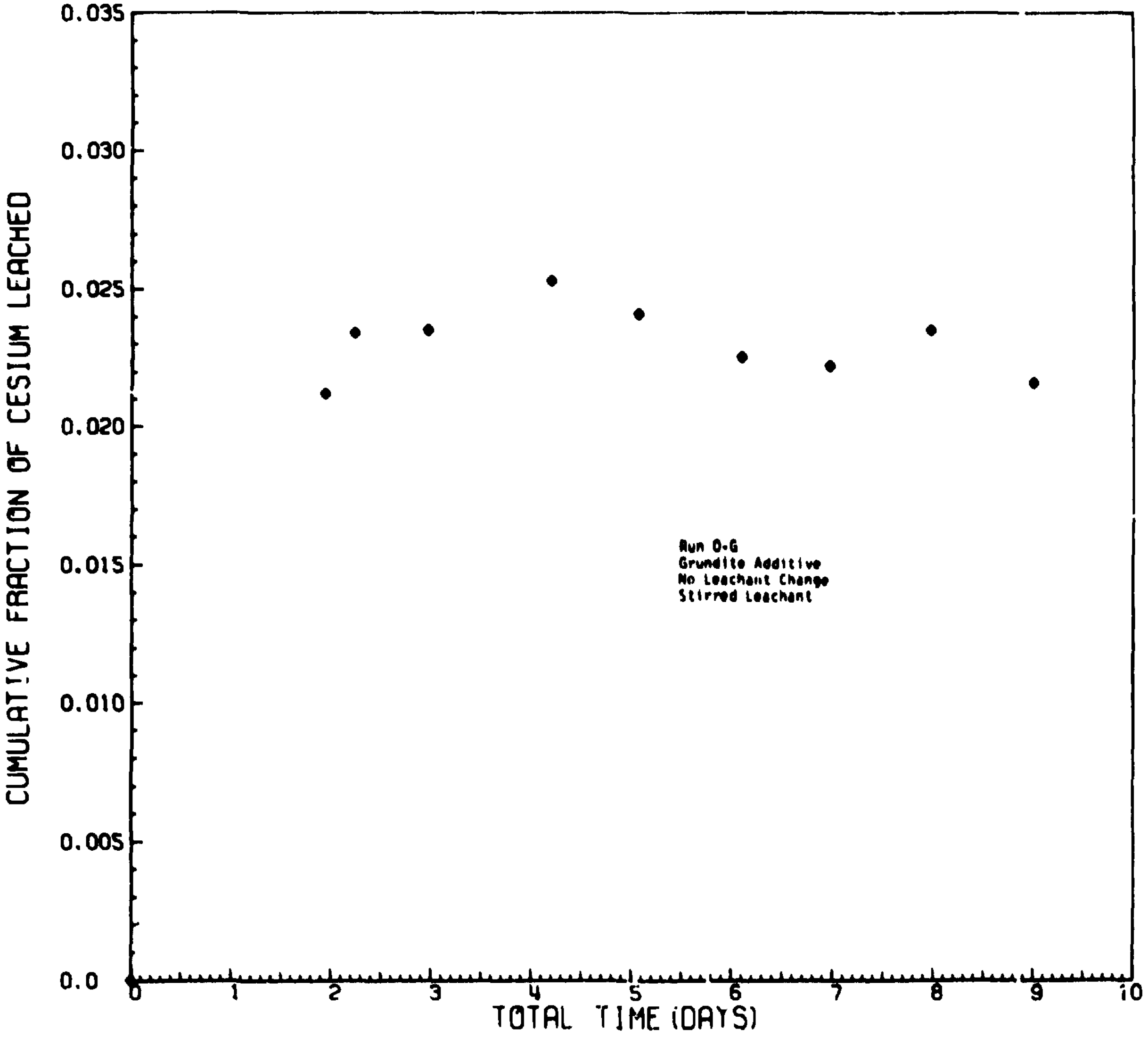
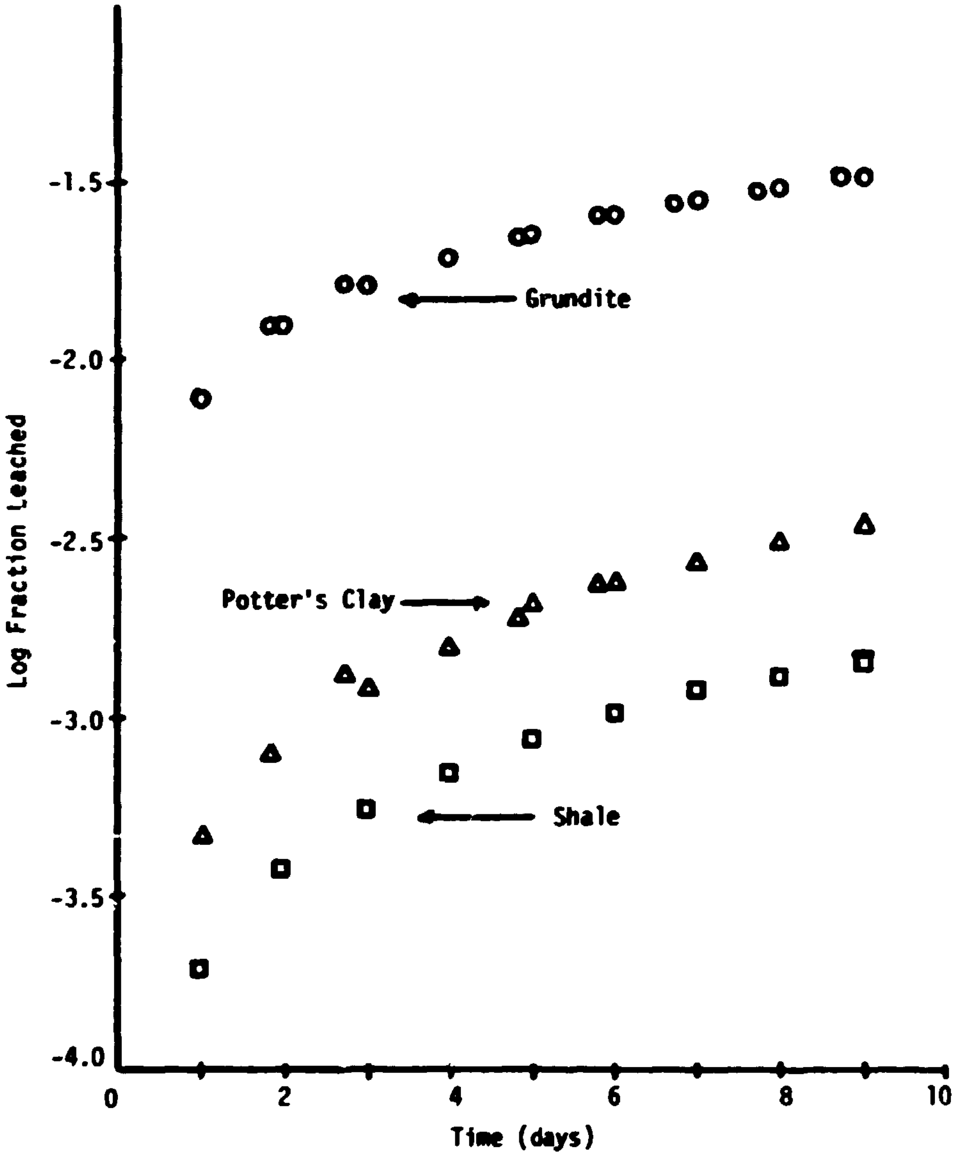


Fig. 7. Cumulative Fraction ^{137}Cs Leached as a Function of Time



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Fraction ^{137}Cs Leached with
Daily Leachant Changes

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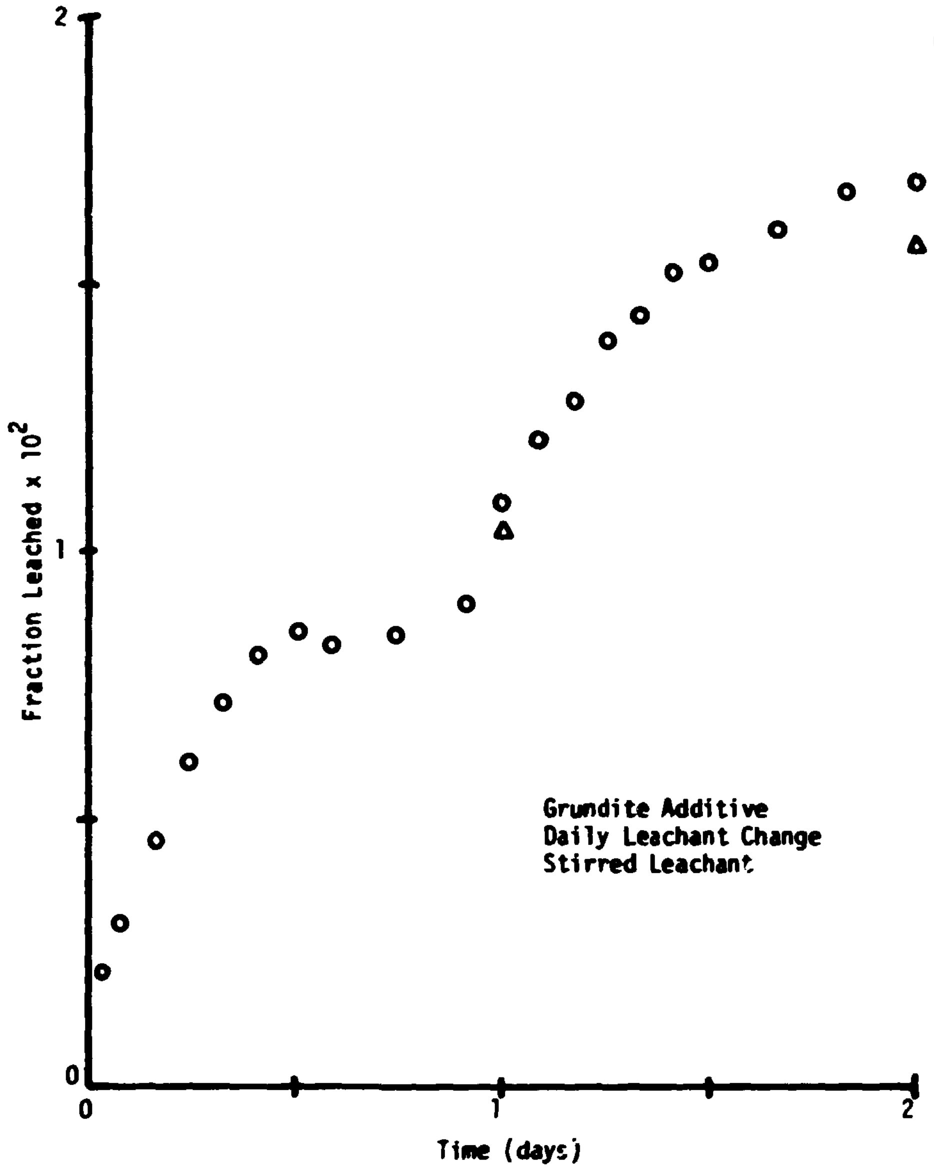

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FRACTION ^{137}Cs LEACHED
AS A FUNCTION OF TIME

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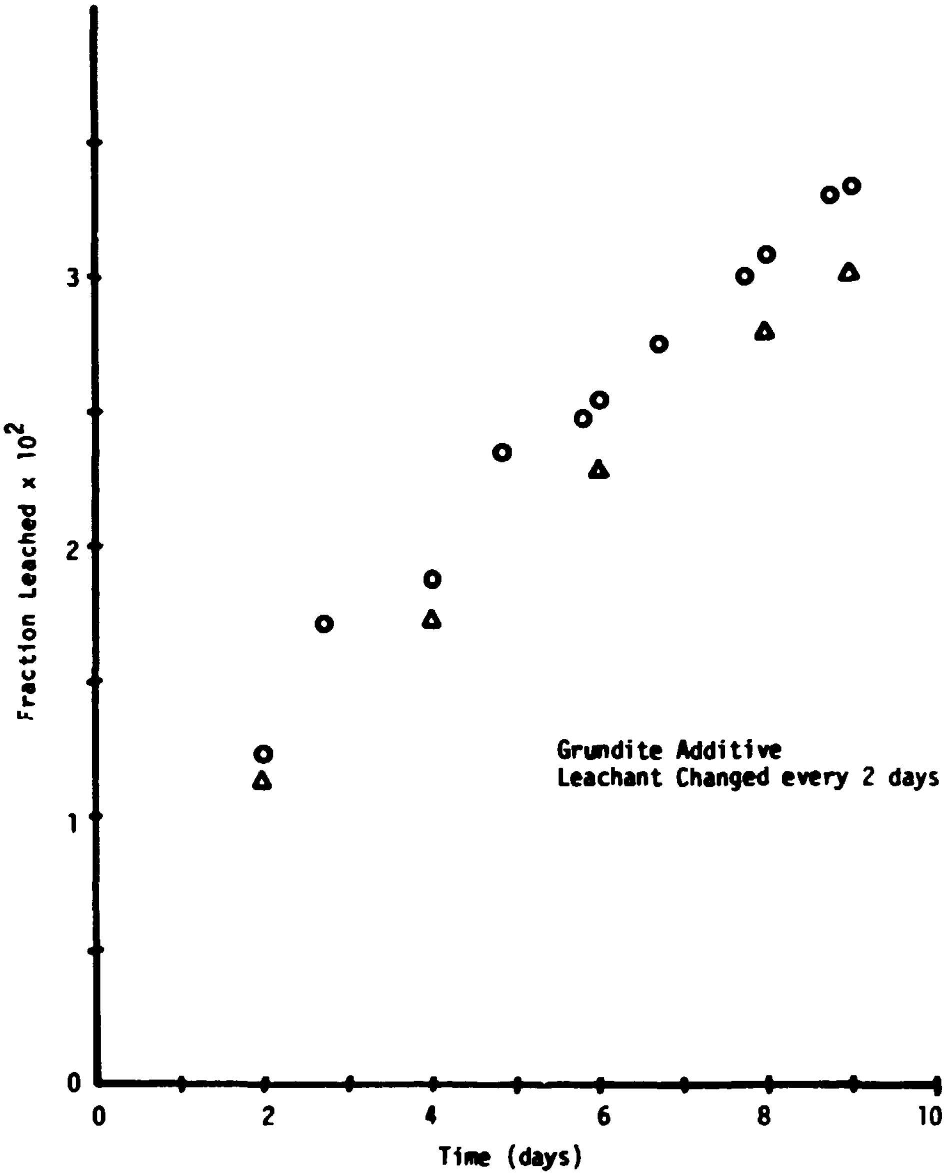
from Table 2, the diffusivity of cesium in a Grundite grout is increased by 15 to 300% depending on the model when the leachate is stirred [compare the experimental results for Runs 1-G and 1-G(ST)]. This difference may be artificial in that the tabulated parameters for Run 1-G(ST) have been fitted to the data shown in Fig. 9 spanning only two days while the parameters for Run 1-G were fitted to data spanning 10 days.

6.3 Effect of Leachant Turnover Frequency

The results of the investigation of the effect of taking samples between leachant changes are depicted in Fig. 10 for the Grundite grout with 2-day leachant changes (Runs 2-G and 2-GC). Sampling between leachant changes may disturb concentration profiles in the liquid increasing the fraction leached as a consequence (see Sect. 6.2). However, differences might also be produced by small departures from uniformity among specimens. These departures are a result of the method of forming and cutting the specimens. The differences observed in Fig. 10 are not significant enough to conclude that additional sampling has any major perturbing effect.

In Fig. 11, a variation in the frequency of leachant change from once a day to once every two days has no noticeable effect on the cumulative fraction leached from a Grundite specimen. For potter's clay and Conasauga shale, a difference does exist. The effect of changing the leachant turnover rate from one to two days is to decrease, except for potter's clay additive, the effective diffusivity determined by either model by at most 50% (as observed in Table 2). However, as the turnover rate is changed from once a day to a nearly continuous rate, the effective diffusivity for grouts with Conasauga shale increases by a factor of 5 to 10, depending on the model used to determine the diffusivity. Clearly, the diffusivity is a stronger function of turnover rate between the continuous and daily turnover rates than between daily and every-other-day turnover rates. In fact, by inspecting Fig. 7 where the data for no leachant changes are presented, the cumulative fraction leached appears to be independent of time.

It is possible that the concentration of cesium species in the leachate may affect the boundary condition at the grout and leachate interface, and consequently affect the rate at which species diffuse from the grout. The models which are currently used to analyze the data have a surface concentration boundary condition which is either zero and independent of time [Eq. (3)] or which will go to zero in the limit as time goes to infinity [Eq. (7)]. These boundary conditions may be suitable for leaching by an infinite volume of leachate, but may not accurately describe the situation of leaching by a finite volume of leachate over a long time span of interest, since the leached species will be allowed to accumulate in the leachant. The current models were not used to analyze the data from the unchanged leachant experiments because the models with their boundary conditions do not adequately represent the phenomena that are occurring.



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FRACTION ^{137}Cs LEACHED
AS A FUNCTION OF TIME

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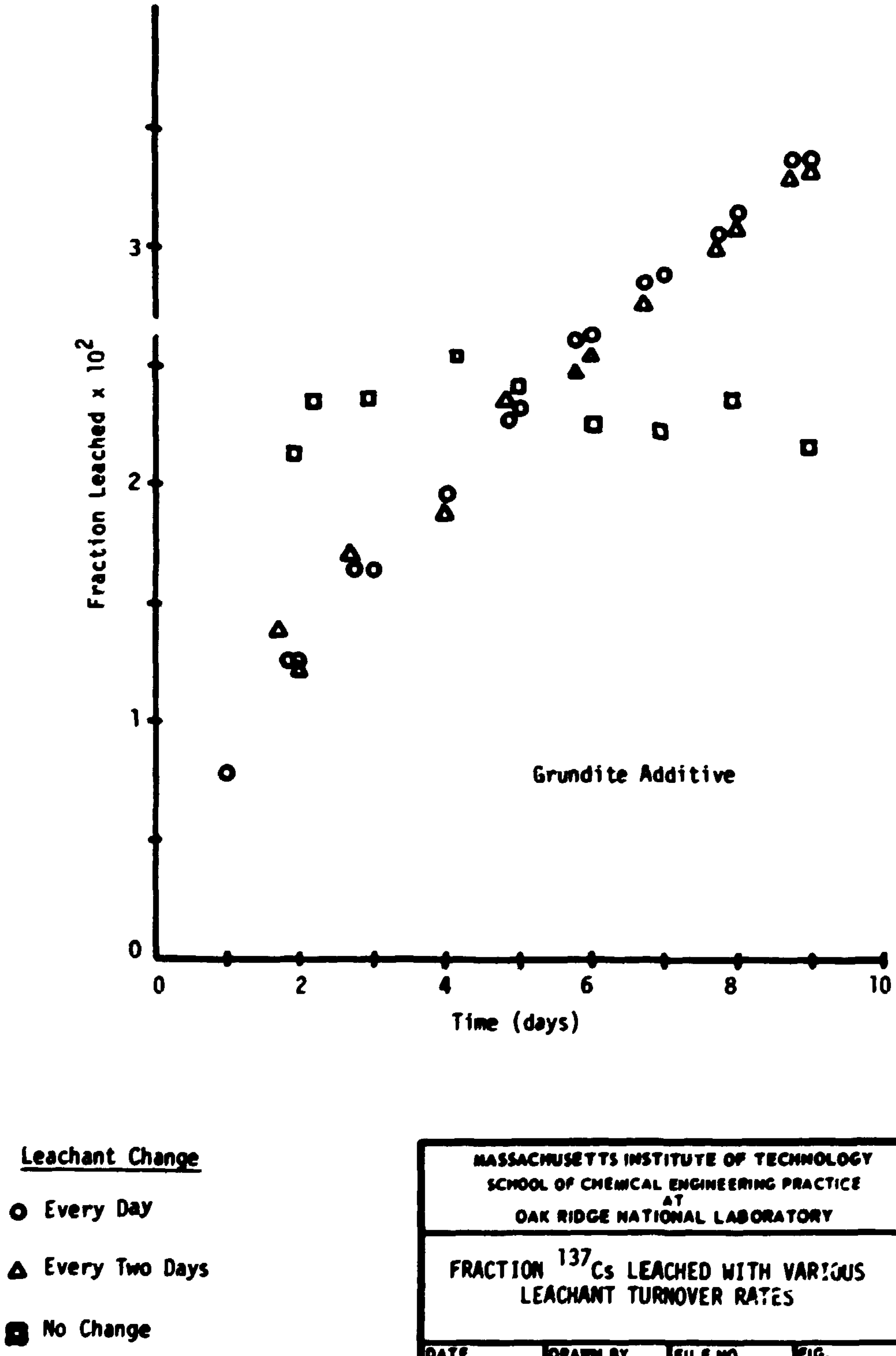

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FRACTION ^{137}Cs LEACHED WITH VARIOUS LEACHANT TURNOVER RATES

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In view of the above, a general trend can be established. Higher leachant turnover rates will result in higher values of the fraction leached at a given time for equivalent extents of stirrings. In the limit, continuous leachant turnover will result in the highest fraction leached at a given time.

6.4 Effects of Tap and Distilled Water

Experiments involving changes of leachant once per day and once every two days were performed on Conasauga shale specimens using both tap and distilled water as leachants. A comparison of the leachants, representative of both sets of data, is shown in Fig. 12 for the daily leachant change (Runs 1-S and 1-SD). The tap water leached considerably more than distilled water. The only known difference between the two agents was the measured pH of 8.0 and 6.1, respectively.

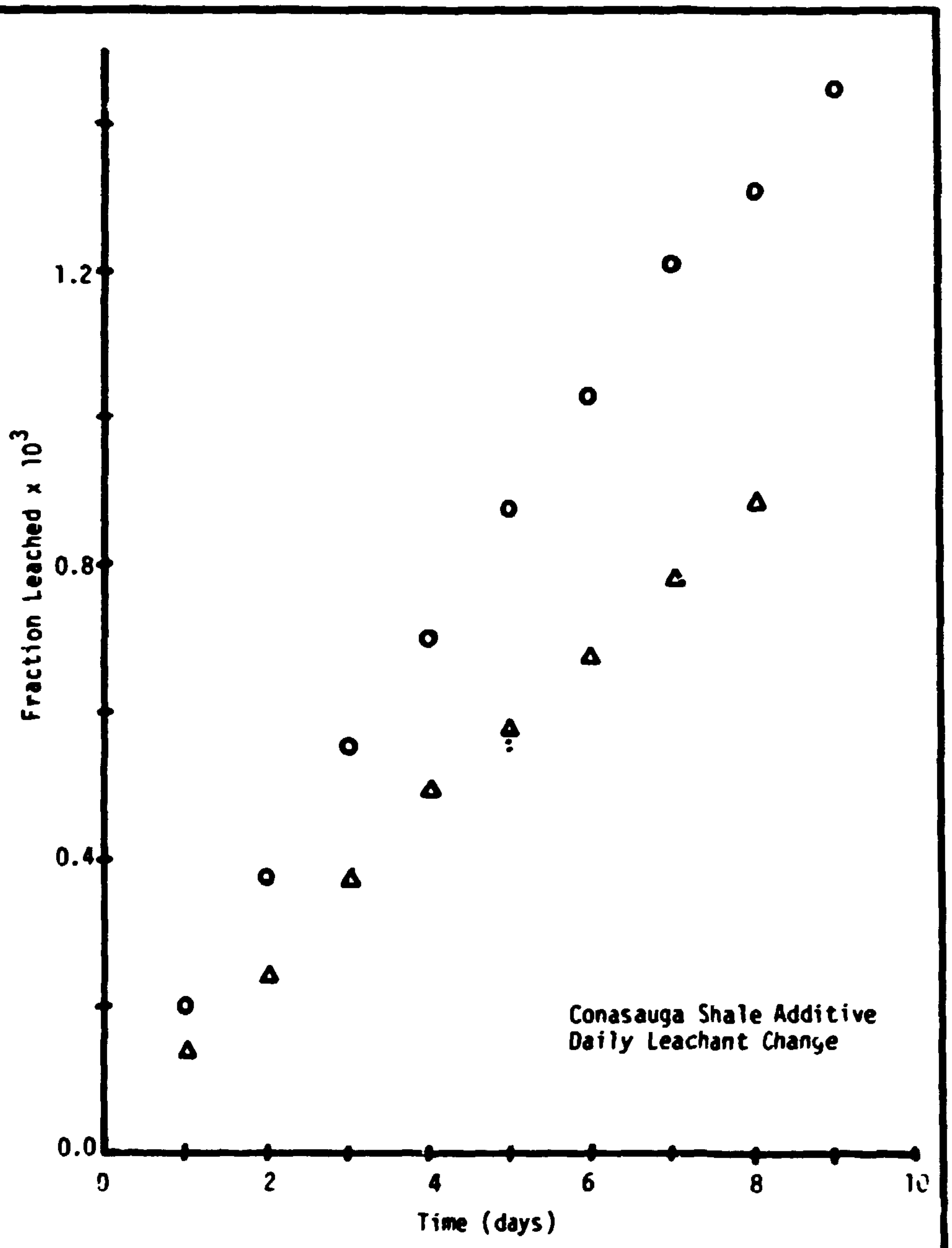
6.5 Modified Soxhlet Extractor

Data for the modified Soxhlet extractor (Run X-S) and batch experiments (Runs 1-SD and 2-SD) with Conasauga shale grouts are compared in Fig. 13. Distilled water was used in the batch experiments since the leachant contacting the specimen in the Soxhlet has been distilled by the equipment (see Sect. 3.1) and significant differences exist between tap and distilled water leaching (see Sect. 6.4). As expected, the rate of leaching (and therefore the amount leached after a given time) is considerably higher than for the batch experiments.

This corroborates that reducing the accumulated ^{137}Cs concentration in the leachant increases the rate of leaching. The scatter of the data is definitely more than could be expected to result from simple experimental error. For a discussion of the possible sources, refer to Appendix 10.4.

6.6 Reproducibility of Results

The batch experiment using Conasauga shale as the additive in grout and distilled water as the leachant (with no replacement) was done in triplicate to determine reproducibility. Figure 14 is a plot of the results obtained. The possible reasons for inconsistent results are the non-homogeneity of shale specimens used due to formation and cutting effects and difficulties encountered with the gamma scintillation counting equipment which are discussed in Appendix 10.4.



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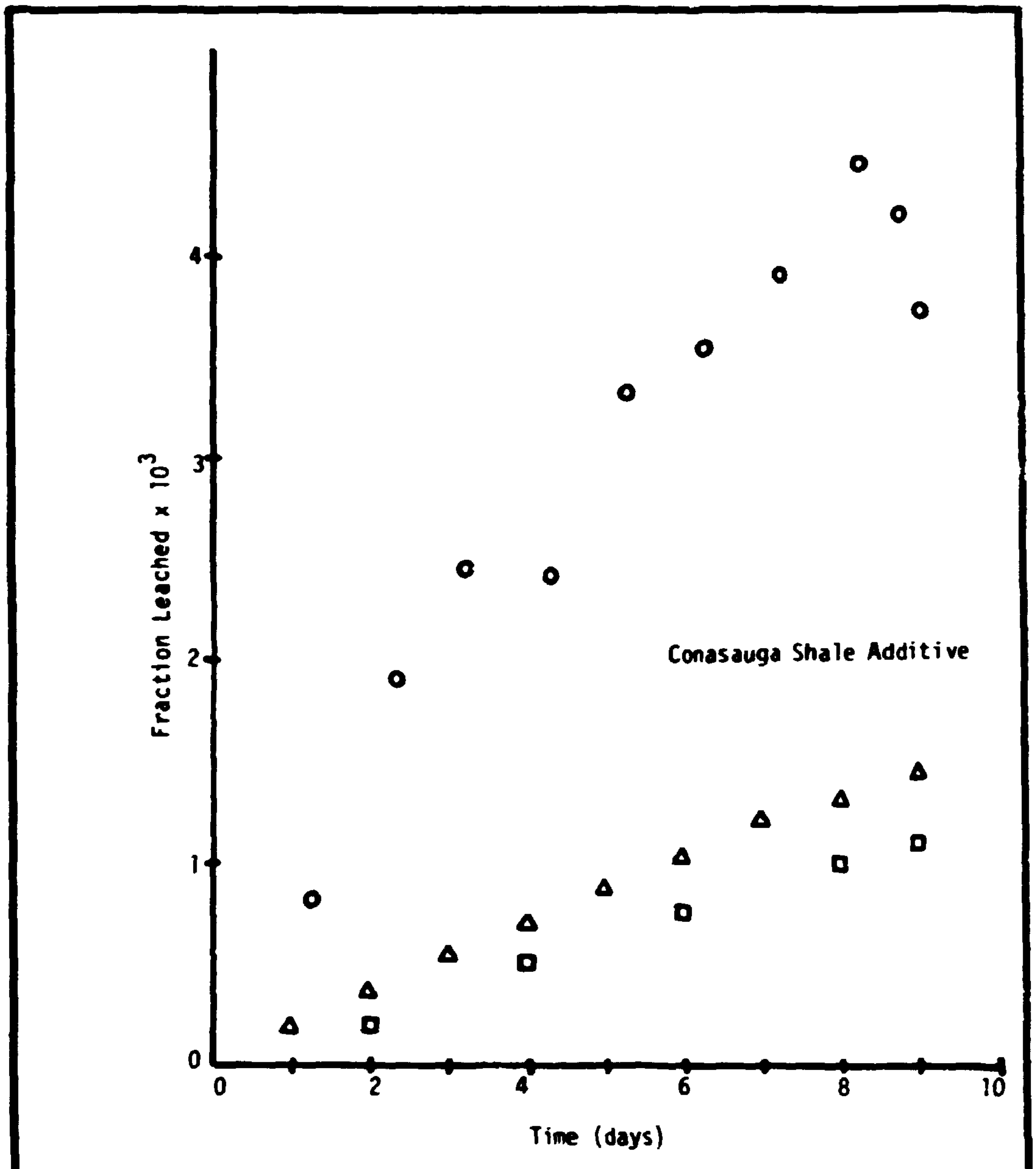
FRACTION ^{137}Cs LEACHED
WITH VARIOUS LEACHANTS

DATE	DRAWN BY	FILE NO.	FIG.
10-20-74	WTS	CEPS-X-198	12



○ Soxhlet Extractor
△ Daily Change
□ Change Every Two Days

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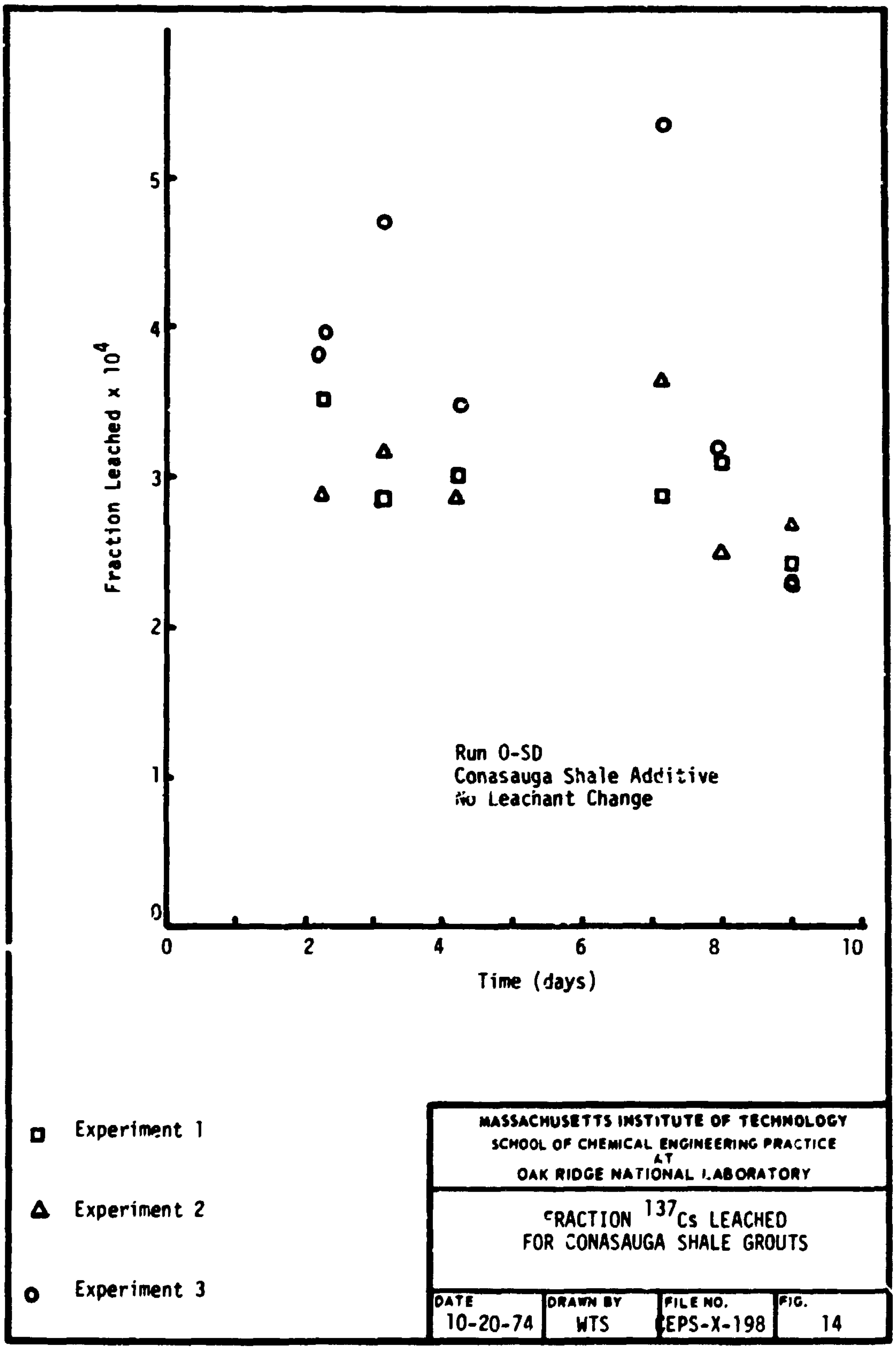
FRACTION ^{137}Cs LEACHED WITH
VARIOUS LEACHANT TURNOVER RATES

DATE	DRAWN BY	FILE NO.	FIG.
10-20-74	WTS	CEPS-X-198	13



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FRACTION ^{137}Cs LEACHED
FOR CONASAUGA SHALE GROUTS

DATE	DRAWN BY	FILE NO.	FIG.
10-20-74	WTS	EPS-X-198	14

6.7 Agreement of Models and Data

An analysis of the values of the parameters of the two models considered here for similar experiments shows that values of the apparent effective diffusivity are nearly three orders of magnitude larger for Grundite than for potter's clay and Conasauga shale (see Table 2). The models used are definitely not applicable to the batch experiments with no change of leachant due to the attainment of significant ^{137}Cs concentrations in the leachant which is not considered in the models.

Values of the parameters for the different experiments with a given additive give an insight as to the validity of the models. For the diffusion model with zero concentration at the interface, the apparent effective diffusivity shows variations of the order of 20%. These variations indicate that leachant turnover rates may have an effect on the computed effective diffusivity. For Conasauga shale the use of the modified Soxhlet extractor increases the value of the effective diffusivity by an order of magnitude.

Values of the parameters obtained are in relatively good agreement with the applicable equivalents from 60-day cured specimen data. As can be seen in Figs. 3 through 6, better agreement with the data is obtained with the diffusion model with the time-dependent boundary condition than with the simple diffusion model.

7. CONCLUSIONS

1. Higher leachant turnover rates result in higher rates of leaching and increased values of the apparent effective diffusivities for the models presented.

2. The modified Soxhlet extractor experiment best fulfills the boundary condition of zero ^{137}Cs concentration at the interface between grout and leachant.

3. The highest rate of leaching observed was obtained in the modified Soxhlet extractor experiment.

4. For the time span and additive materials under consideration, the use of Conasauga shale in cement mixtures provides the lowest leaching rates, and therefore results in the best ^{137}Cs immobilization.

5. The use of Grundite as an additive resulted in cumulative fractions leached an order of magnitude above those for Conasauga shale.

6. The leachant sampling frequency did not significantly effect the leaching rate.

7. Infrequent changes of leachant in the batch procedure inhibit the rate of leaching due to the approach to an equilibrium value of the cumulative fraction leached, or an increase of ^{137}Cs concentration in the leachant. Under the circumstances, the use of a boundary condition requiring zero surface concentration may not be appropriate.

8. The use of a time-dependent boundary condition at the interface results in better agreement of the model and the experimental data.

9. Tap water is a more effective leachant than distilled water.

8. RECOMMENDATIONS

1. Further experimentation should be performed with continuous replacement of leachant.

2. The possibility of developing a model which accounts for the effects of accumulation of ^{137}Cs in the leachant should be investigated.

3. Reproducibility of results should be established.

4. Plating and adsorption of ^{137}Cs on the stainless steel and glass equipment should be investigated in connection with the modified Soxhlet extraction procedure.

5. The use of individual cylindrical molds to insure homogeneity of the specimens is strongly recommended.

6. The effects of stirring the leachant should be examined in experiments of longer duration.

9. ACKNOWLEDGEMENTS

We are indebted to our consultants, H.W. Godbee, J.G. Moore, and D.S. Joy, for their assistance and suggestions throughout the project. Our special thanks are extended to A.H. Kibbey for her assistance.

10. APPENDIX

10.1 Theoretical Models; Solutions of Differential Equations

10.1.1 Derivation of Equations

The mass balance around a differential element in a semi-infinite medium with constant effective diffusivity yields the equation:

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} \tag{1}$$

For boundary and initial conditions:

$$x > 0, \quad t = 0, \quad C = C_o \tag{2}$$

$$x = \infty, \quad t > 0, \quad C = C_o \tag{3}$$

$$x = 0, \quad t > 0, \quad C = 0 \tag{4}$$

the solution of the equation is (4):

$$C = C_o \operatorname{erf} \frac{x}{2\sqrt{D_e t}} \tag{11}$$

where:

$$\operatorname{erf}(u) = \frac{2}{\sqrt{\pi}} \int_0^u e^{-z^2}\, dz \tag{12}$$

From Fick's Law,the flux at the surface is:

$$\left.\frac{dJ}{dt}\right|_{x=0} = D_e \left.\frac{\partial C}{\partial x}\right|_{x=0} = \frac{D_e C_o}{\sqrt{\pi D_e t}} \tag{13}$$

and the total amount leaving the surface is:

$$J = \int_0^J dJ = \int_0^t \frac{D_e C_o dt}{\sqrt{\pi D_e t}} = 2 D_e C_o \left(\frac{t}{\pi D_e}\right)^{1/2} \tag{14}$$

where:

$$J = \frac{\Sigma a_n}{S} \tag{15}$$

$$C_o = \frac{A_o}{V} \tag{16}$$

Substitution of J and C_o from Eqs. (15) and (16) into Eq. (14) gives (4):

$$\frac{\Sigma a_n}{A_o} = \frac{2}{\sqrt{\pi}}\left(\frac{S}{V}\right)\sqrt{D_e t} \tag{5}$$

For the boundary and initial conditions:

$$x > 0, \quad t = 0, \quad C = C_o \tag{6}$$

$$x = 0, \quad t > 0, \quad C = \kappa C_o\, e^{-\beta t} \tag{7}$$

$$x = \infty, \quad t > 0, \quad C = C_o \tag{8}$$

the solution to Eq. (1) is (3):

$$C = C_o\left[\mathrm{erf}\left[\frac{x}{2(D_e t)^{1/2}}\right] + \frac{\kappa e^{-\beta t}}{2}\left[e^{ix\left(\frac{\beta}{D_e}\right)^{1/2}}\mathrm{erfc}\left[\frac{x}{2(D_e t)^{1/2}} - i(\beta t)^{1/2}\right] + e^{ix\left(\frac{\beta}{D_e}\right)^{1/2}}\,\mathrm{erfc}\left[\frac{x}{2(D_e t)^{1/2}} + i(\beta t)^{1/2}\right]\right]\right] \tag{17}$$

where:

$$\mathrm{erfc}(u) = 1 - \mathrm{erf}(u) \tag{18}$$

$$i = (-1)^{1/2} \tag{19}$$

From Fick's Law, the flux at the surface is:

$$\left.\frac{dJ}{dt}\right|_{x=0} = D_e\left.\frac{\partial C}{\partial x}\right|_{x=0} = C_o\,\frac{D_e}{\sqrt{\pi D_e}}\left[t^{-1/2} - \kappa t^{-1/2} - \kappa(\pi\beta)^{1/2}e^{-\beta t}\,\mathrm{erf}[i(\beta t)^{1/2}]\right] \tag{20}$$

and the total amount leached is:

$$J = \int_0^J dJ = \int_0^t \left(D_e \frac{\partial C}{\partial x}\right)_{x=0} dt = 2C_o \frac{D_e}{\sqrt{\pi D_e}}\left[t^{\frac{1}{2}} - \left(\frac{\kappa}{\beta^{\frac{1}{2}}}\right) \mathrm{daw}(\beta t)^{\frac{1}{2}}\right] \tag{21}$$

Substitution of J and C_o from Eqs. (15) and (16) into Eq. (21) gives (3):

$$\frac{\Sigma a_n}{A_o} = 2\left(\frac{S}{V}\right)\left(\frac{D_e}{\pi}\right)^{\frac{1}{2}}\left[t^{\frac{1}{2}} - \left(\frac{\kappa}{\beta^{\frac{1}{2}}}\right) \mathrm{daw}(\beta t)^{\frac{1}{2}}\right] \tag{9}$$

10.1.2 Redefinition of D_e to Account for an Equilibrium between Mobile and Immobile Cesium

The concentration of immobile cesium, F, may be directly proportional to the concentration of mobile cesium, C, with a proportionality constant K (3):

$$F = KC \tag{22}$$

The mass balance for diffusion then yields:

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} - \frac{\partial F}{\partial t} \tag{23}$$

Substitution of F from Eq. (22) into Eq. (23) yields:

$$\frac{\partial C}{\partial t} = \frac{D_e}{1 + K} \frac{\partial^2 C}{\partial x^2} \tag{24}$$

This equation is identical to Eq. (1) if a modified effective diffusivity is defined as (3):

$$\mathcal{D}_e = \frac{D_e}{1 + K} \tag{25}$$

Solving for C in Eq. (24) yields the same answer as for Eq. (1) with D_e replaced by $\mathcal{D}_e$. Thus, Fick's Law equation becomes:

$$\left.\frac{dJ}{dt}\right|_{x=0} = (1 + K)\mathcal{D}_e \left.\frac{\partial C}{\partial x}\right|_{x=0} \tag{26}$$

Therefore, Eq. (14) becomes:

$$J = 2(1 + K)\,\mathcal{D}_e\,C_0\left(\frac{t}{\pi\mathcal{D}_e}\right)^{1/2} \tag{27}$$

and Eq. (21) becomes:

$$J = 2C_0\,\frac{(1 + K)\mathcal{D}_e}{\sqrt{\pi\mathcal{D}_e}}\left[t^{1/2} - \left(\frac{K}{\beta^{1/2}}\right)\mathrm{daw}(\beta t)^{1/2}\right] \tag{28}$$

Equation (16) becomes:

$$C_0 + F_0 = \frac{A_0}{V} = C_0 + KC_0 = (1 + K)C_0 \tag{29}$$

Substitution of both J and C_0 from Eqs. (15) and (29) into each of Eqs. (27) and (28) yields Eqs. (5) and (9), respectively with D_e replaced by $\mathcal{D}_e$. Therefore the diffusion models described show a direct proportionality between mobile and immobile cesium with a redefinition of the effective diffusivity.

10.2 Preparation of Grout Specimens

A 330-ml quantity of each cement grout (Conasauga shale, potter's clay, and Grundite) was prepared by mixing 251.4 ml of radioactive feed solution with 179.7 gm of dry mix (see Table 3). The radioactive feed solution consisted of 250 ml of simulated W-7 waste solution (see Table 4), 0.1 ml tributylphosphate used as a surfactant, 0.3 ml d-gluconolactone (300 mg/ml) added to retard setting, and 1 ml of radioactive CsCl solution. The CsCl solution was prepared by dissolving 10 mCi in 0.05 ml 1.0-N hydrochloric acid (a concentration of ∿6.7 mg/ml) and diluting with 10 ml 0.1-N HCl.

The dry mix was added to the waste solution over a 15-sec interval in a Waring blender operating at 5000 rpm. The mixing was continued for an additional 15 sec, then poured into 20-ml plastic test tubes. The tubes were placed in a closed container partially filled with water and allowed to cure 80 days at room temperature. The grouts were prepared July 12, 1974. The cured samples were cut with a saw to the desired 2-cm lengths (1.61-cm diameter) (6).

Table 3. Composition of Dry Mix Used in Grout Preparation

Constituent	Weight %
Portland Cement Type I	38.5
Fly Ash[1]	38.5
Attapulgite-150[2]	15.4
Additive[3]	7.7

[1] Fly ash was obtained from the coal-fired Kingston Steam Plant, Kingston, Tenn.

[2] Attapulgite-150 is the tradename of a clay product from the Polygorskite group of clay minerals. It is used to disperse the cement when mixed with water and to stop phase separation.

[3] Either Conasauga shale, potter's clay or Grundite. Grundite is the tradename of a clay product from the Illite group of clay minerals from Grundy County, Ill.

Table 4. Composition of Simulated W-7 Waste Solution[1]

Component	Concentration (gmole/liter)
$NaOH$	0.18
$Al(NO_3)_3 \cdot 9H_2O$	0.0074
NH_4NO_3	0.003
$NaNO_3$	0.81
$NaCl$	0.093
Na_2SO_4	0.094
Na_2CO_3	0.19

[1] Components were dissolved in distilled water.

10.3 Calculation of Fraction ^{137}Cs in Leachate

The fraction of ^{137}Cs in the leachate is defined as a_n/A_0 where a_n is the activity of ^{137}Cs leached from the specimen (µCi) in time elapsed since preceding leachant change and A_0 is the total initial activity of the specimen. A_0 is determined by the preparation procedure (see Appendix 10.2). One milliliter of CsCl with an activity of 995 µCi/ml was used to make 330 ml of grout. Each specimen had a volume of 4.1 cm^3. Therefore, the total initial activity was

$$A_0 = \frac{(995\ \mu\text{Ci/ml})(1\ \text{ml})(4.1\ \text{ml})}{330\ \text{ml}} = 12.4\ \mu\text{Ci}$$

The activity in the leachate is determined by comparing the number of net counts in the leachate sample to the number of net counts in a sample of the waste feed solution of known activity, then multiplying this ratio by the volume of the leachate.

The feed solution sample was 25 µl of the waste solution made up to 5 ml. The total activity in the feed solution samples was therefore:

$$\frac{995\ \mu\text{Ci}}{251\ \text{ml waste}}(0.025\ \text{ml waste}) = 9.91 \times 10^{-2}\ \mu\text{Ci}$$

The activity in the leachate is calculated as follows:

$$a_n = \left[9.91\text{x}10^{-2}\ \frac{\mu\text{Ci}}{5\ \text{ml feed sample}}\right]\left[\frac{C_G - C_B\ \frac{\text{counts}}{5\ \text{min}\cdot 5\ \text{ml leachate}}}{C_F - C_B\ \frac{\text{counts}}{5\ \text{min}\cdot 5\ \text{ml feed sample}}}\right]$$

$$\text{x (V ml of leachate)}$$

$$= 9.91 \times 10^{-2}\ \left(\frac{C_G - C_B}{C_F - C_B}\right)\left(\frac{V}{5}\right)\mu\text{Ci} \qquad (30)$$

The fraction leached is a_n/A_0.

$$\frac{a_n}{A_0} = \frac{\left[1.98 \times 10^{-2}\left(\frac{C_G - C_B}{C_F - C_B}\right)V\right]}{12.36} = 1.6 \times 10^{-3}\left(\frac{C_G - C_B}{C_F - C_B}\right)V \qquad (31)$$

The cumulative fraction leached, $\bar{f}$, is therefore given by,

$$\bar{f} = \frac{\sum_{i=1}^{N} a_i}{A_0} = 1.6 \times 10^{-3} \sum_{i=0}^{N} \left(\frac{C_{G_i} - C_B}{C_F - C_B}\right) V_i \qquad (32)$$

10.4 Error Analysis

10.4.1 Statistical Analysis

The determination of the mean of the population of counts for a given sample is subject to statistical error. To estimate the effect of these errors in the values of the fraction leached, an estimation of the confidence intervals for the latter was made.

For a given sample, statistical parameters were computed as:

$$\bar{C}_j = \frac{\sum_{i=1}^{n_j} C_{ji}}{n_j} \qquad (33)$$

$$s^2(C_j) = \frac{\sum_{i=1}^{n_j} (C_{ji} - \bar{C}_j)^2}{n_j - 1} \qquad (34)$$

$$s^2(\bar{C}_j) = \frac{s^2(C_j)}{n_j} \qquad (35)$$

$$\ell_{0.05}(\bar{C}_j) = t_{0.05,\nu_j} s(\bar{C}_j) \qquad (36)$$

A program for computation of these statistics was developed for use with a Hewlett-Packard 9810A.

The equation for computing the fraction leached from observed data can be written as:

$$\bar{f} = (1.6 \times 10^{-3}) \sum_{i=1}^{N} \frac{(\bar{C}_{G_i} - \bar{C}_B)}{(\bar{C}_F - \bar{C}_B)} V_i \qquad (37)$$

If the error is assumed to be in C_{G_i}, C_B, and C_F, the variance of f can be expressed as (7, 8, 9):

$$S^2(\bar{f}) = \left(\frac{\partial f}{\partial \bar{C}_{G_i}}\right)^2 S^2(\bar{C}_{G_i}) + \left(\frac{\partial f}{\partial \bar{C}_F}\right)^2 S^2(\bar{C}_F) + \left(\frac{\partial f}{\partial \bar{C}_B}\right)^2 S^2(\bar{C}_B) \qquad (38)$$

Substituting the derivatives from Eq. (36) and recognizing that $\bar{C}_F >> \bar{C}_B$, the expression for $S^2(\bar{f})$ becomes:

$$S^2(\bar{f}) = (1.6 \times 10^{-3})^2 \sum_{i=1}^{N} \left(\frac{V_i}{\bar{C}_F}\right)^2 \left[S^2(\bar{C}_{G_i}) + \frac{(\bar{C}_{G_i} - \bar{C}_B)^2}{\bar{C}_F{}^2} S^2(\bar{C}_F) + \frac{(\bar{C}_{G_i} - \bar{C}_F)^2}{\bar{C}_F{}^2} S^2(\bar{C}_B) \right] \qquad (39)$$

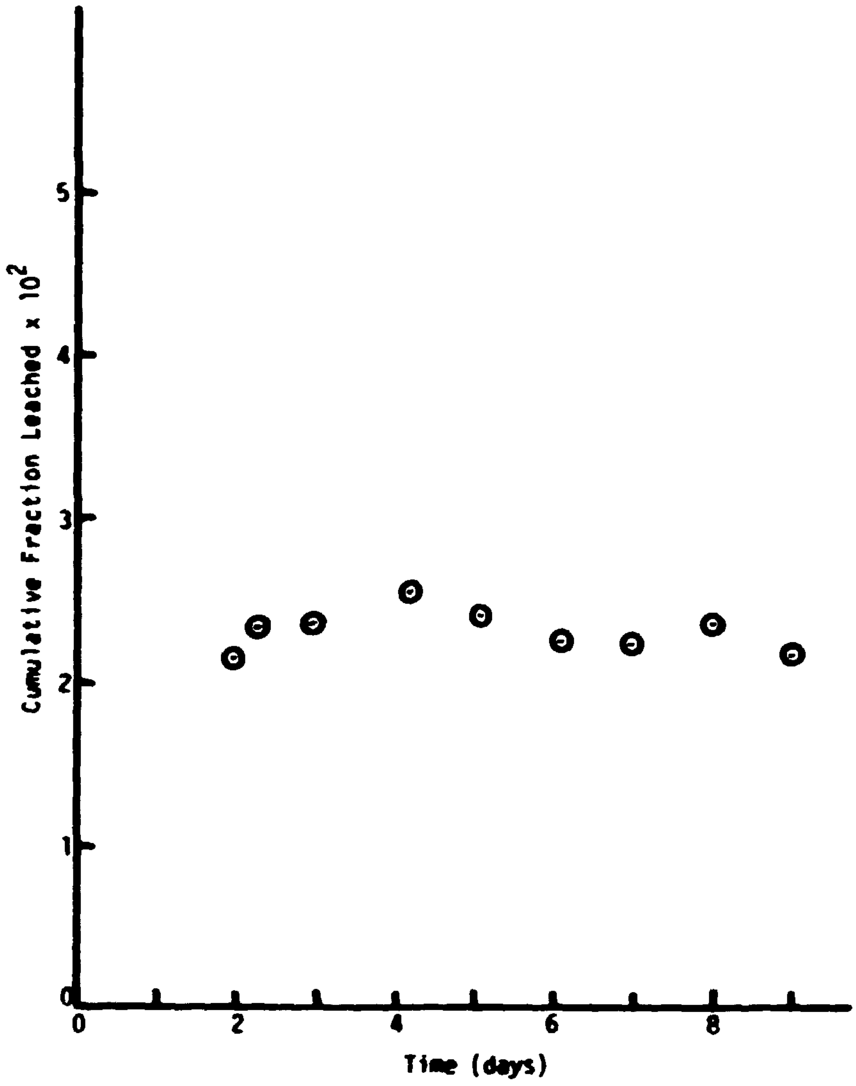
Once $S^2(f)$ is obtained, the approximate number of degrees of freedom in the estimation can be obtained from (7, 8, 9):

$$\nu_f = \frac{S^4(\bar{f})}{(1.6\times10^{-3})^2 \sum_{i=1}^{N} \left(\frac{V_i}{\bar{C}_F}\right)^4 \left[S^4(\bar{C}_{G_i}) + \frac{(\bar{C}_{G_i} - \bar{C}_B)^4}{\nu_F \bar{C}_F{}^4} S^4(\bar{C}_F) \frac{(\bar{C}_{G_i} - \bar{C}_F)}{\nu_B \bar{C}_F{}^4} S^2(\bar{C}_B) \right]} \qquad (40)$$

Confidence limits on $\bar{f}$ can then be defined by:

$$\Delta_{0.05}(\bar{f}) = t_{0.05,\nu_f} S(\bar{f}) \qquad (41)$$

The calculated 95% confidence interval for the modified Soxhlet extractor experiment and an experiment involving no replacement of the leachate for a Grundite additive specimen were approximately ± 6% of the actual value of the cumulative fraction leached. Hence, the limits of the 95% confidence intervals are contained within the symbols shown in Figs. 15 and 16. The



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CONFIDENCE INTERVALS FOR EXPERIMENT O-G

DATE	DRAWN BY	FILE NO.	FIG.
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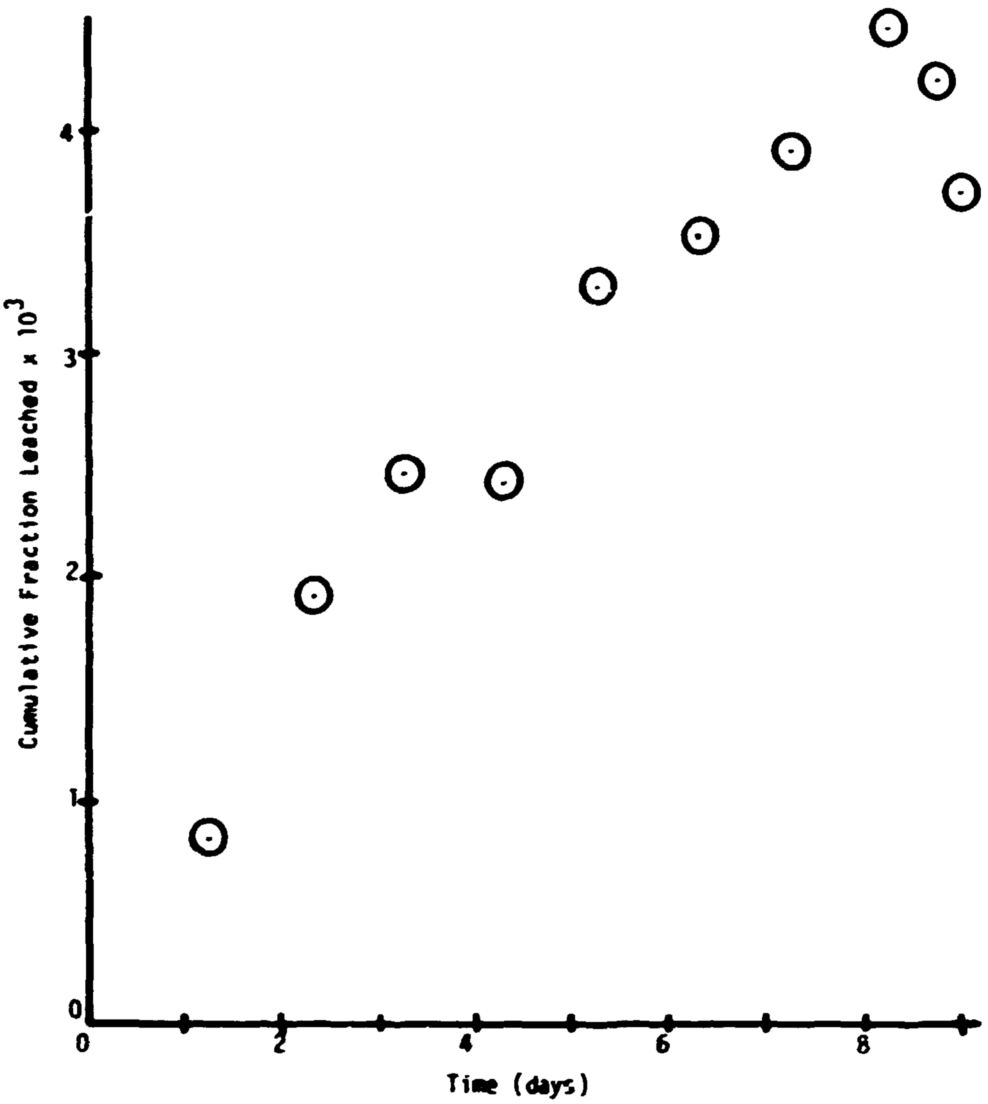

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CONFIDENCE INTERVALS FOR EXPERIMENT X-S

DATE	DRAWN BY	FILE NO.	FIG.
10-21-74	WTS	CEPS-X-198	16

confidence intervals for these two experiments are representative of the confidence intervals for other experiments.

10.4.2 Sources of Error

Unpredictable variations in instrument readings of the order of 20-30% which do not appear to be of a random nature were observed in the gamma scintillation counter. These apparent shifts in mean readings did not seem to fit a normal drift pattern and may well be the source of further variability in the apparent behavior of the fraction leached.

A further source of error was detected in the modified Soxhlet extractor. When the last leachate sample was collected and the grout specimen was removed, the apparatus was loaded again with distilled water. The Soxhlet was then operated as before to determine the presence of ^{137}Cs in it. After 30 hr of operation, an amount of ^{137}Cs equivalent to about 1/3 of the total fraction leached at the end of the original experiment was measured in the liquid. The appearance of ^{137}Cs was possibly due to the removal of plated ^{137}Cs on the stainless steel heaters or other parts of the boiler.

10.5 Additional Data

Data that were not presented in Sects. 5 and 6 are presented in Figs. 17 through 26. The cumulative fraction of ^{137}Cs is plotted as a function of time with results from the simple diffusion model when applicable.

10.6 Details of Soxhlet Evaporator and Flow Rate Measurement

10.6.1 Soxhlet Evaporator

The Soxhlet evaporator consisted of a 3-in.-ID x 6-in.-high glass evaporator pot topped by a 6-in.-ID x 8-in.-high stainless steel flash chamber. Three 1-in.-diam stainless steel tubes ran vertically down the length of the evaporator. Within each tube at the bottom was a 7/8-in.-OD x 5-in.-high 500-W stainless steel electric heater. A controller shut off the power supplies if the heater temperatures exceeded 175°C to prevent coil burnout. A manometer was connected to the flash chamber to vent it in case of pressure buildup.

10.6.2 Soxhlet Flow Rate Measurement

Condensate from the heat exchanger was collected in a 100-ml graduated cylinder for 2 min. Makeup distilled water was pumped for 2 min at 40 ml/min into the evaporator to bring the water level back to ∿300 ml.

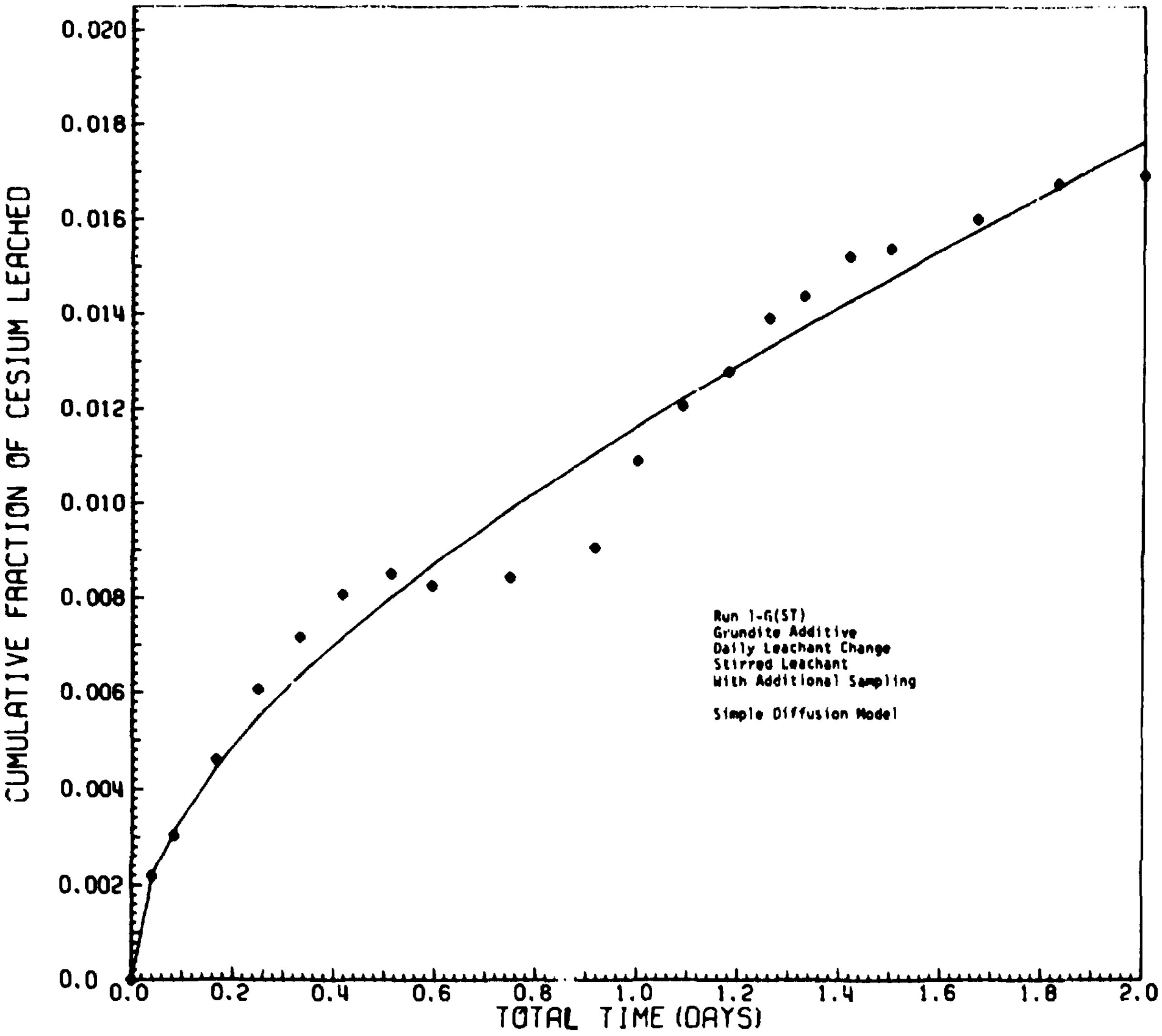

Fig. 17. CUMULATIVE FRACTION ^{137}Cs LEACHED WITH TIME

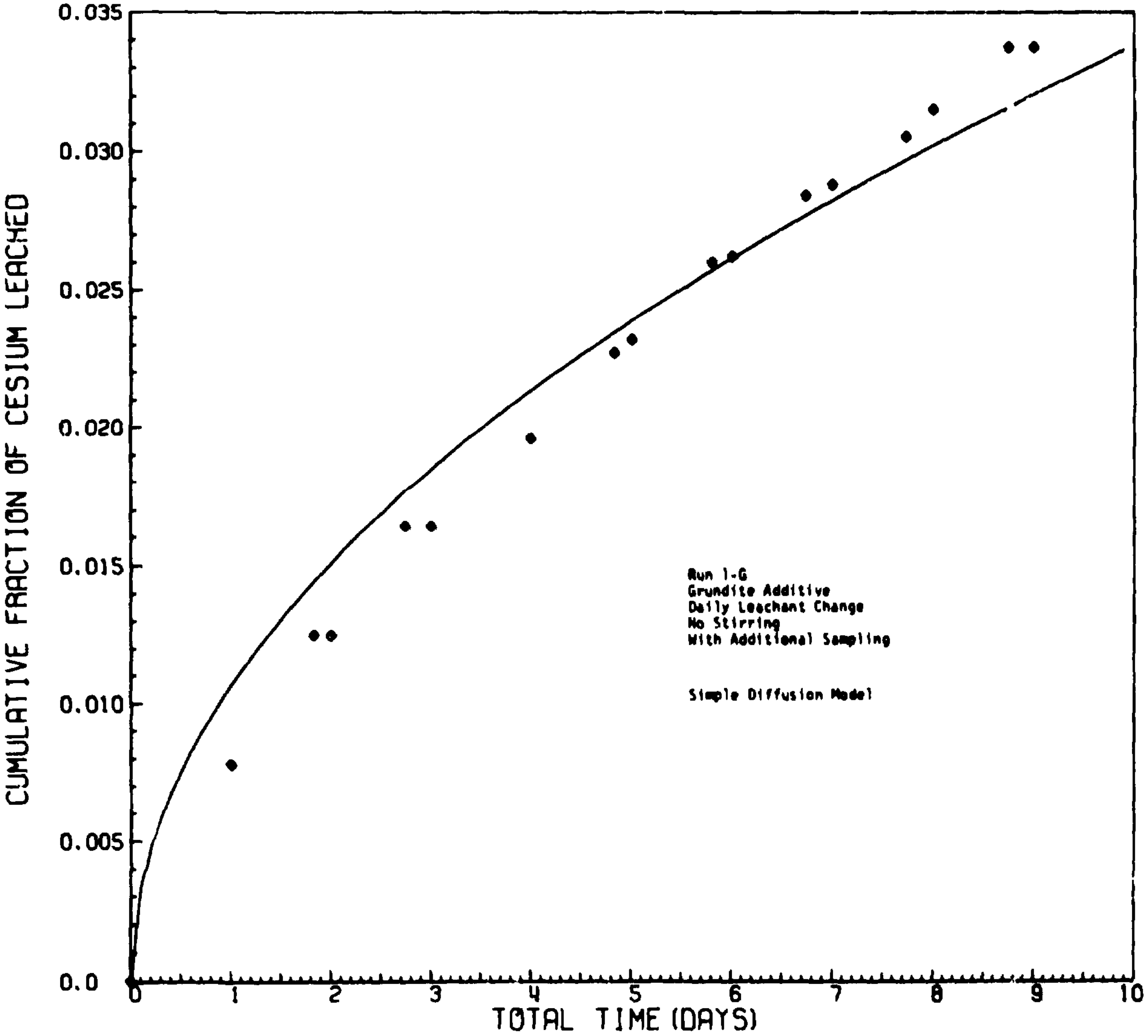

Fig. 18. CUMULATIVE FRACTION ^{137}Cs LEACHED WITH TIME

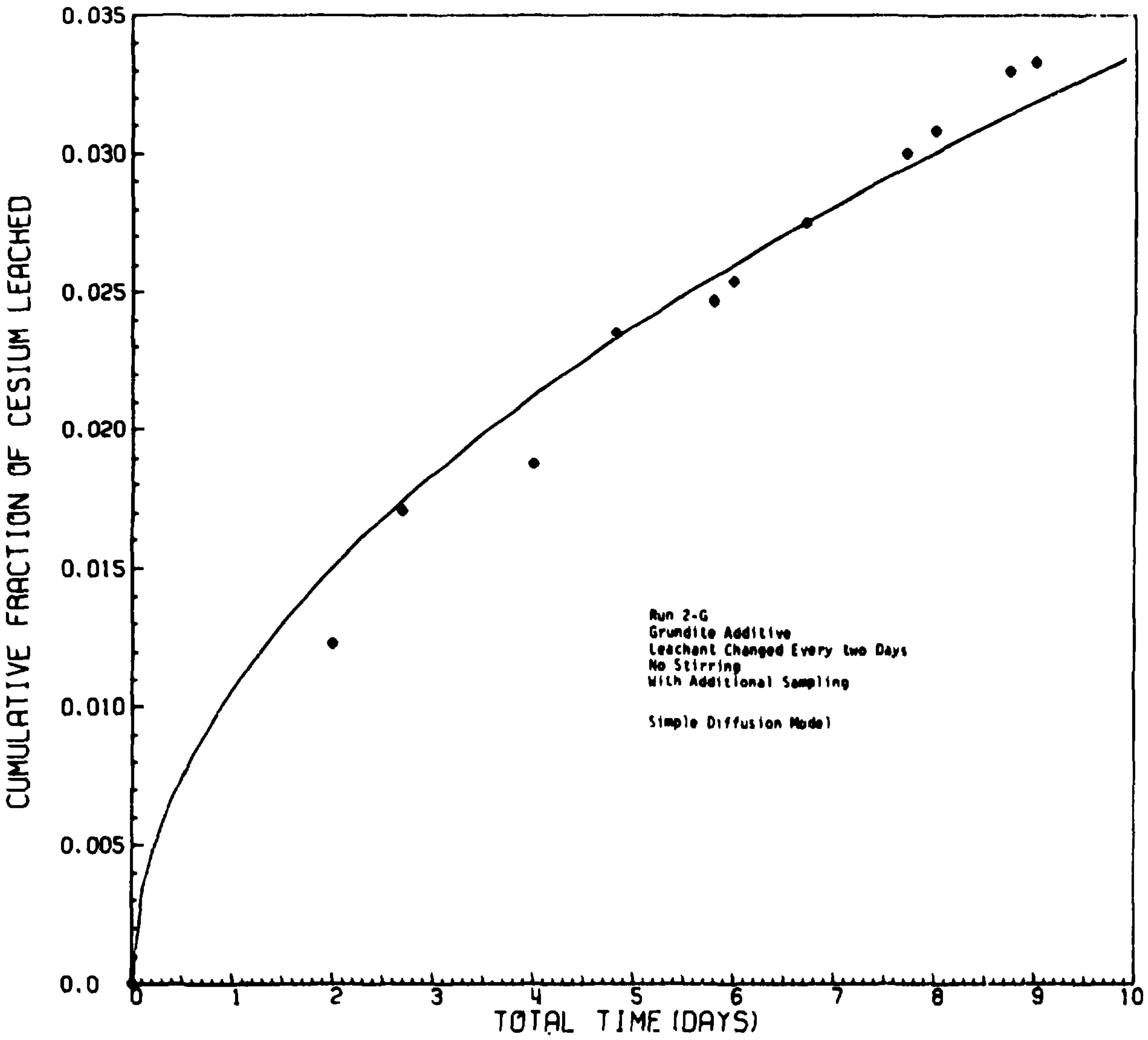

Fig. 19. CUMULATIVE FRACTION ^{137}Cs LEACHED WITH TIME

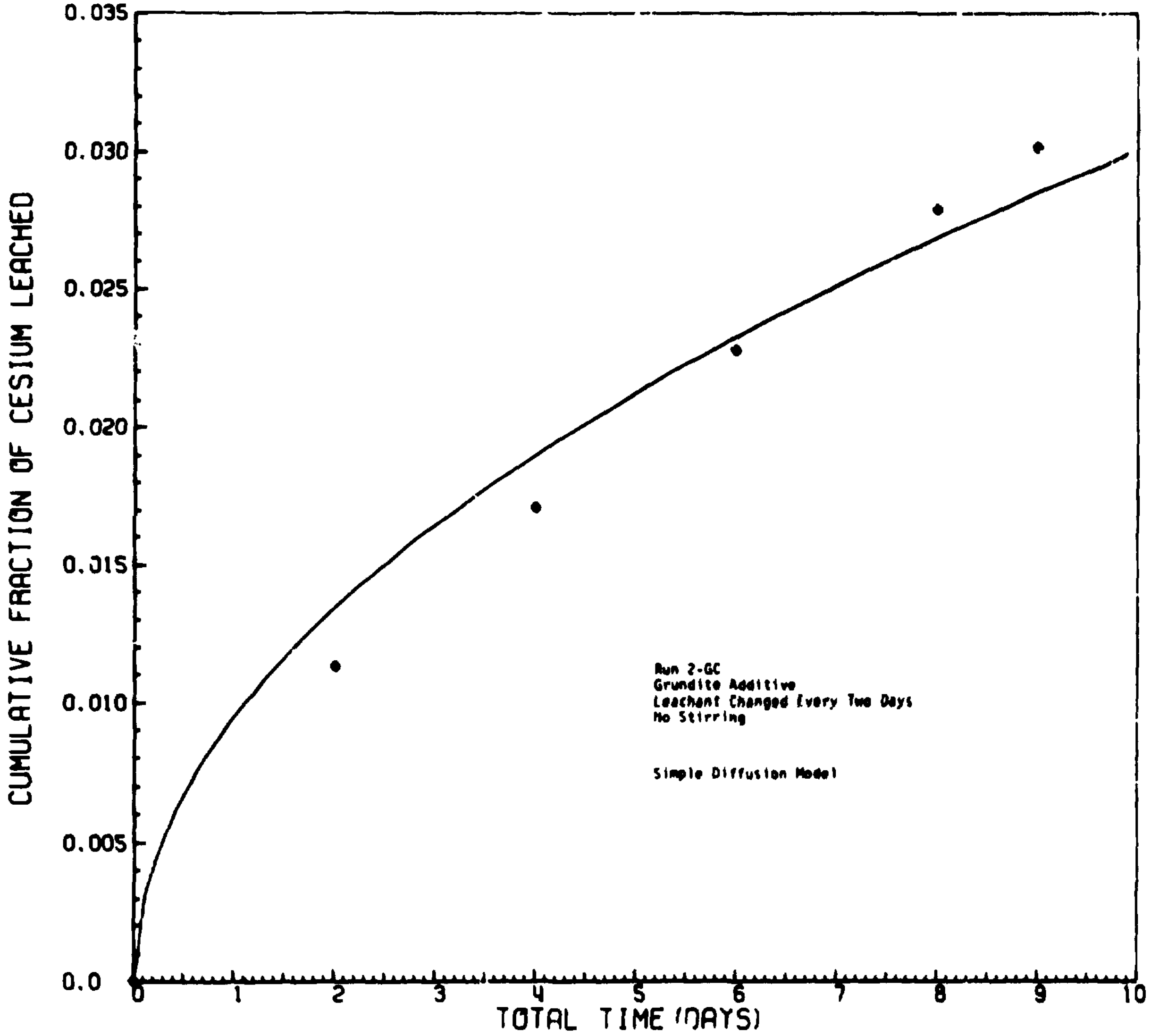

Fig. 20. CUMULATIVE FRACTION ^{137}Cs LEACHED WITH TIME

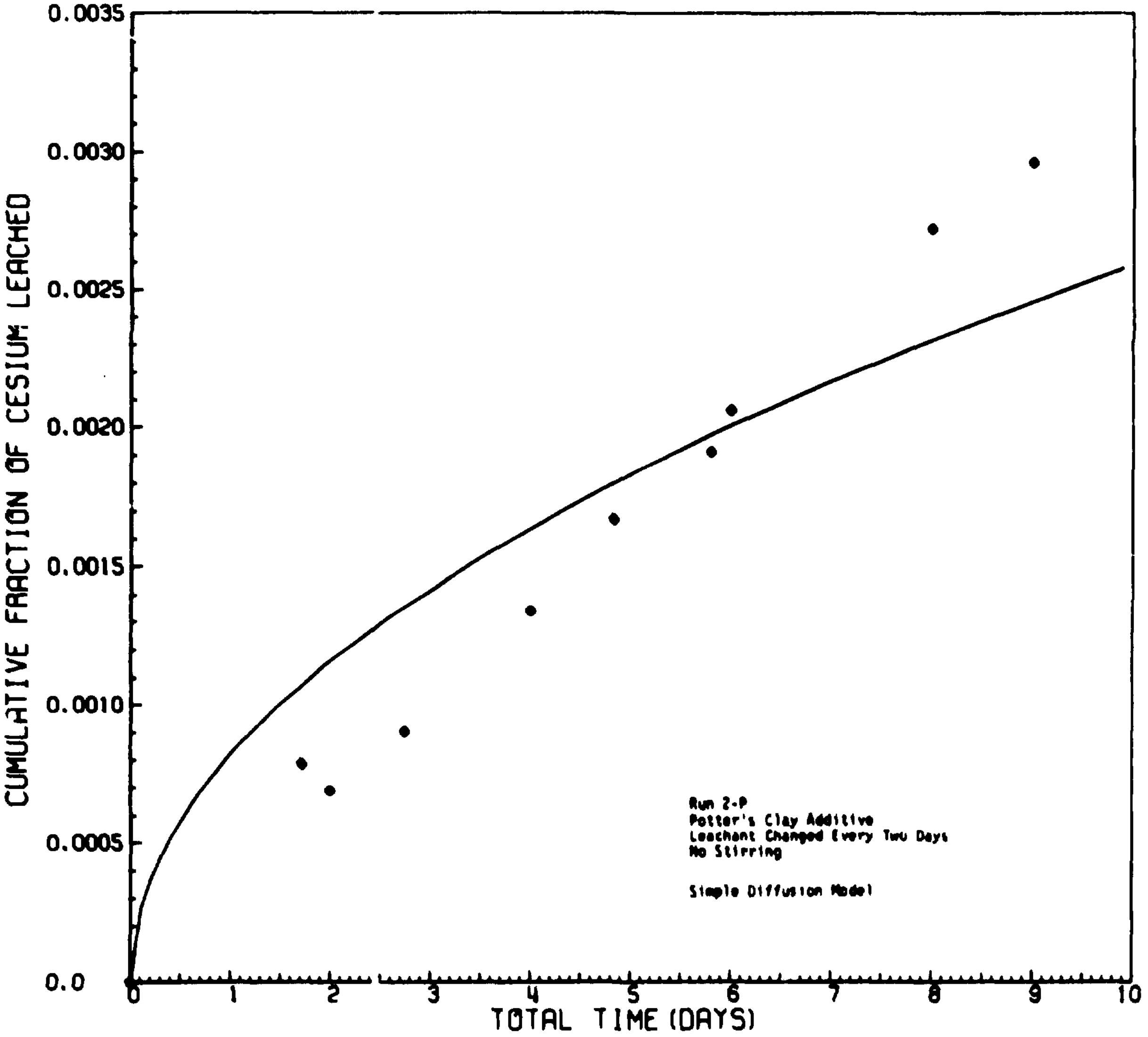

Fig. 21. CUMULATIVE FRACTION ^{137}Cs LEACHED WITH TIME

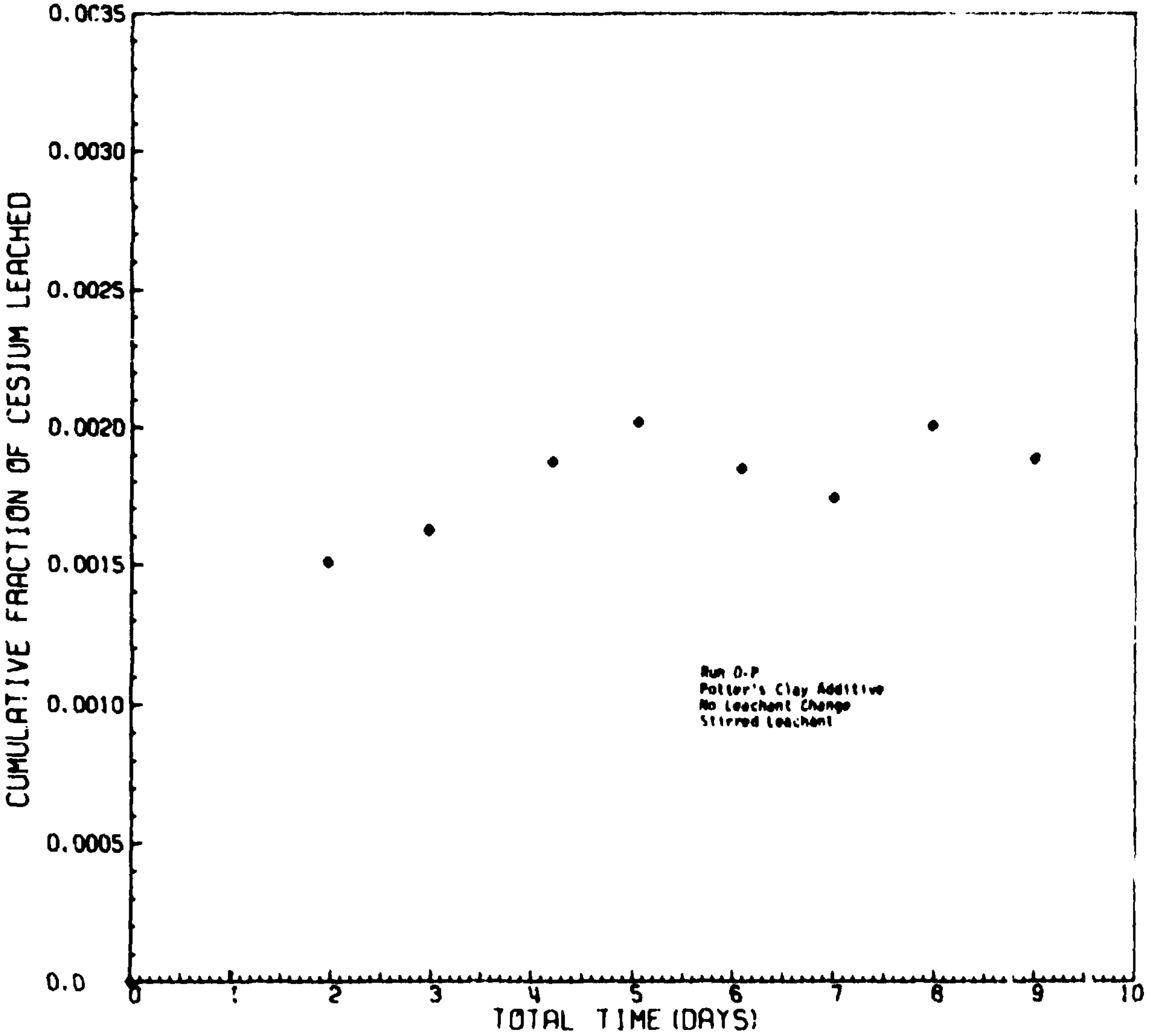

Fig. 22. CUMULATIVE FRACTION ^{137}Cs LEACHED WITH TIME

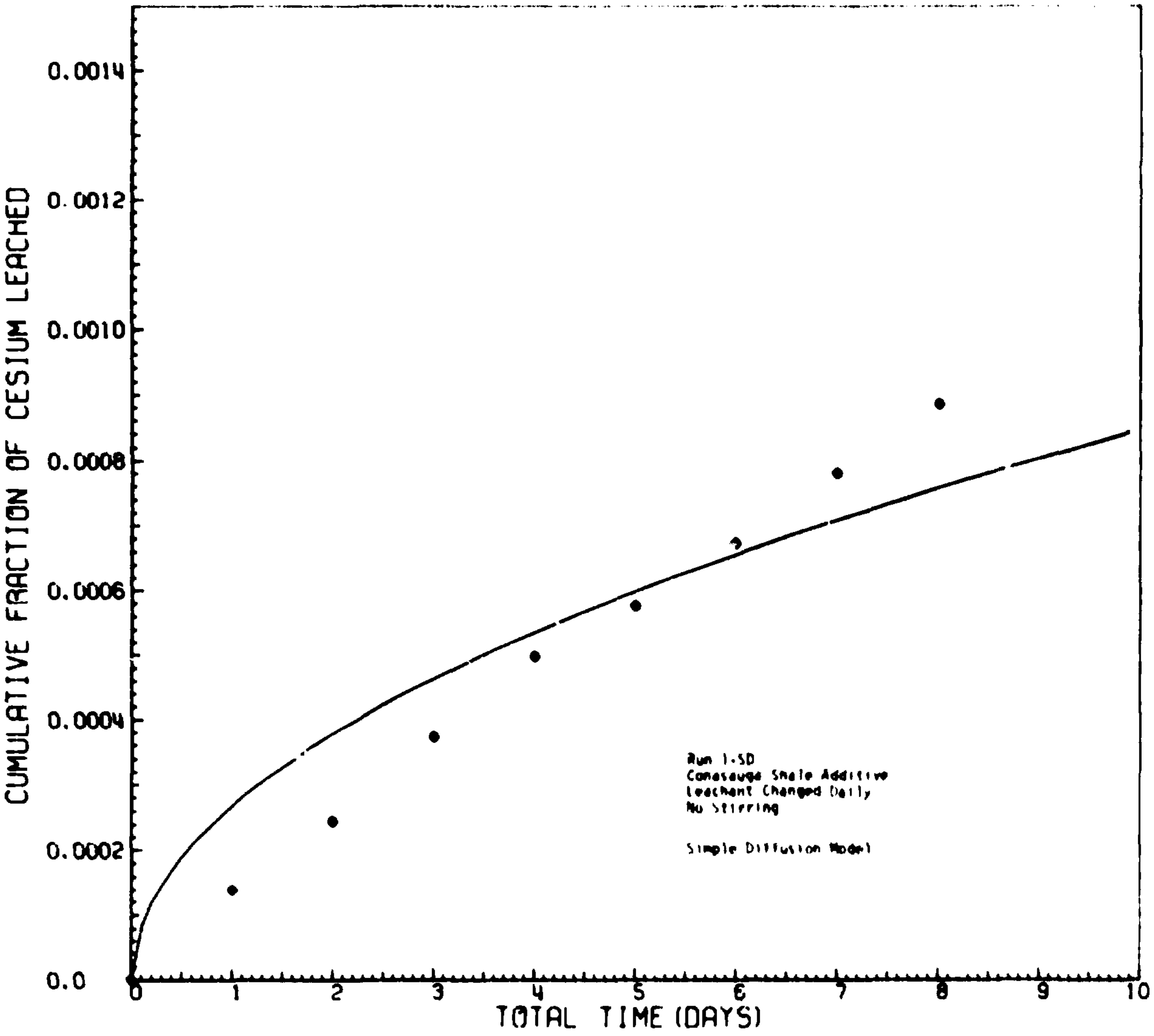

Fig. 23. CUMULATIVE FRACTION ^{137}Cs LEACHED WITH TIME

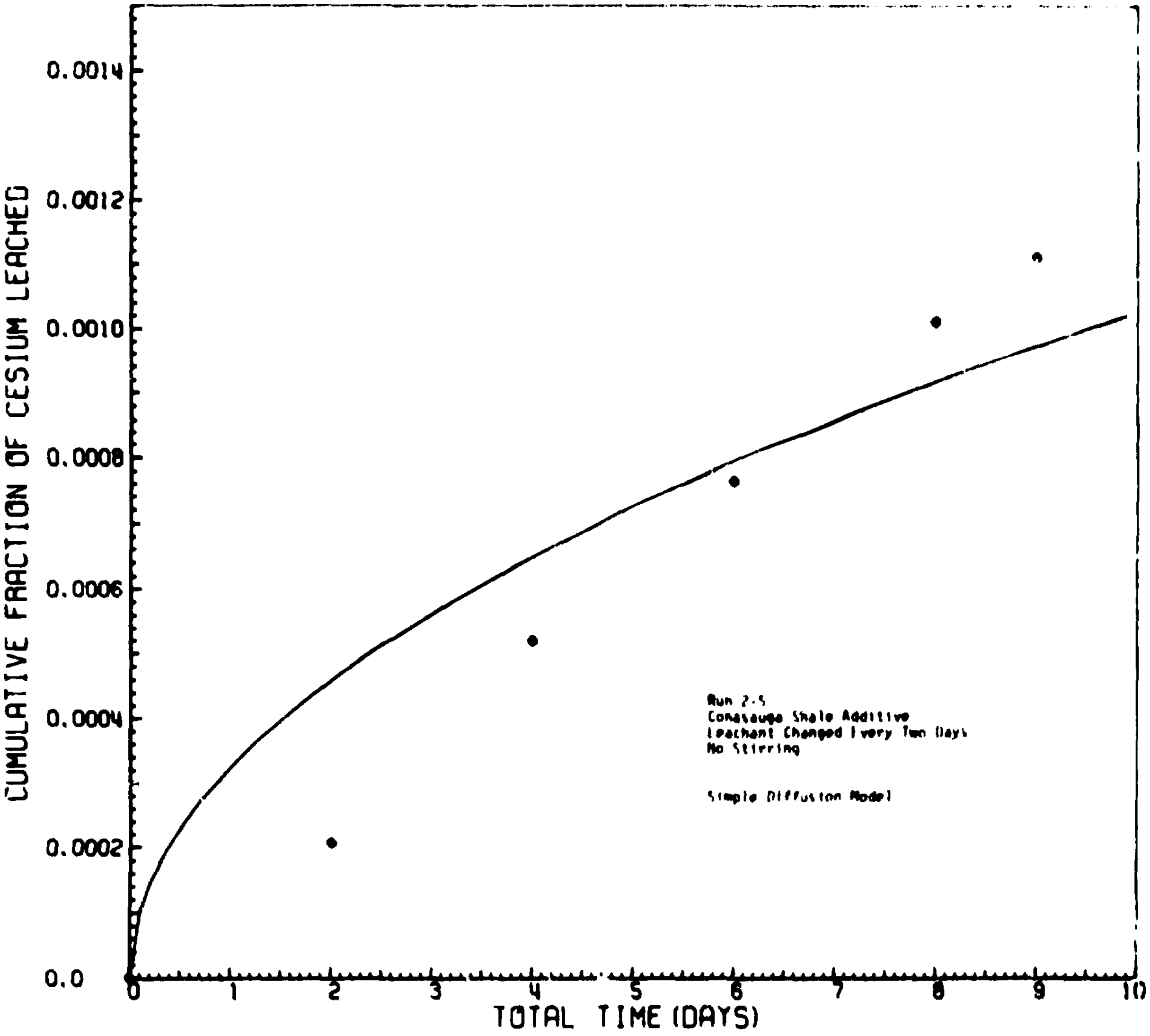

Fig 24. CUMULATIVE FRACTION ^{137}Cs LEACHED WITH TIME

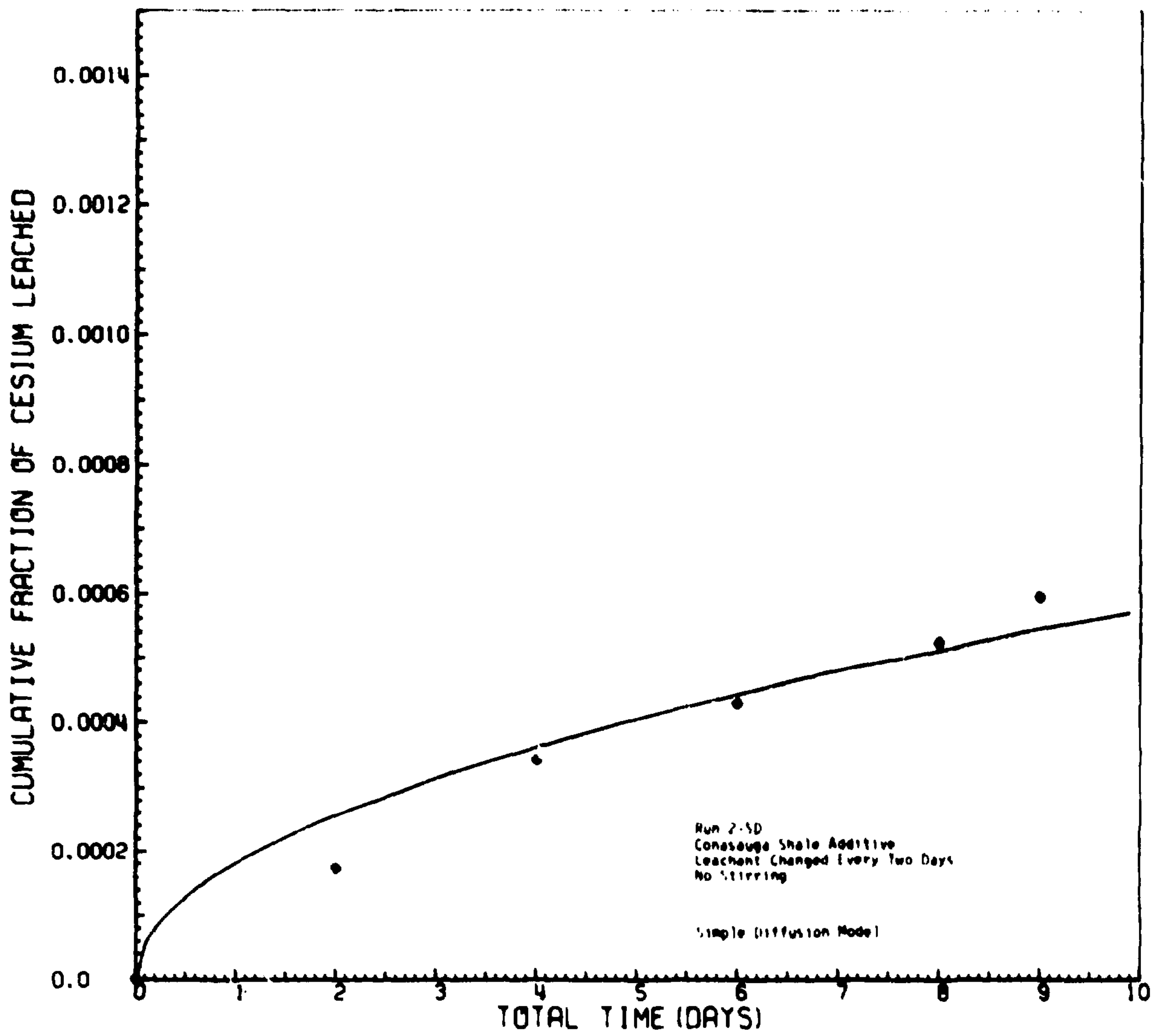

Fig. 25. CUMULATIVE FRACTION ^{137}Cs LEACHED WITH TIME

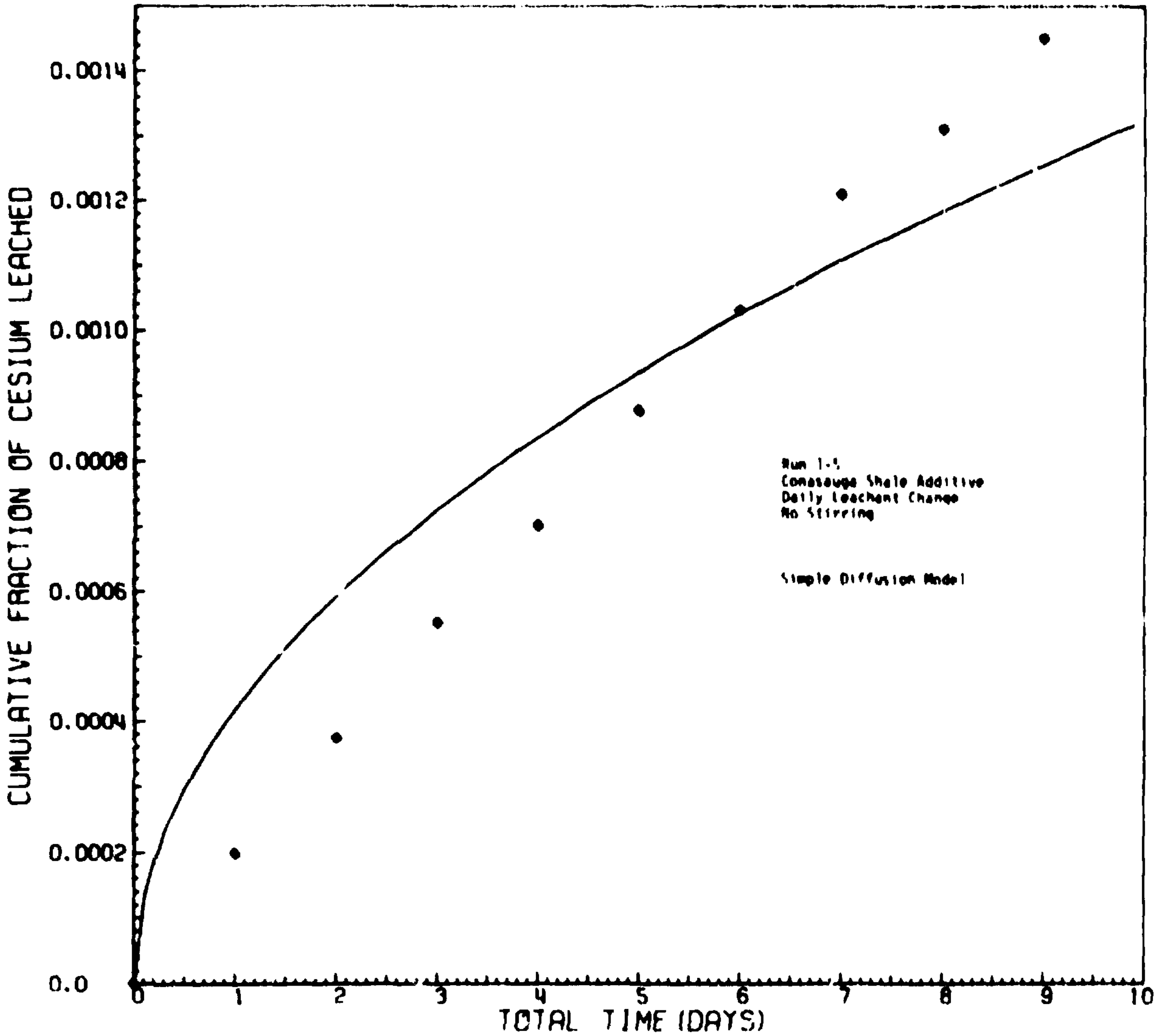

Fig. 26. CUMULATIVE FRACTION ^{137}Cs LEACHED WITH TIME

10.7 Location of Original Data

The original data are located in ORNL Databooks A-7221-G and A-6980-G on file at the MIT School of Chemical Engineering Practice, Bldg. 3001, ORNL.

10.8 Nomenclature

a_n	radioactivity lost during leaching period n, counts/5 min
A_0	initial radioactivity in specimen, counts/5 min
C	concentration in the specimen at any position and time, counts/min/ml
C_B	background counts/5 min
C_F	counts of specimen feed solution, counts/5 min for 5 ml
C_G	gross counts of the leachate, counts/5 min for 5 ml
$\bar{C}_j$	estimated mean number of counts per 5 min for 5 ml of sample j
C_{ji}	i^{th} reading of the counts per 5 min for 5 ml of sample j
C_0	total initial concentration in specimen, counts/min/ml
daw	Dawson's integral
D_e	effective diffusivity, cm^2/sec
$\mathcal{D}_e$	$\frac{D_e}{1+K}$
erf(u)	error function of u
erfc(u)	complementary error function [1 - erf(u)]
$\mathcal{F}$	cumulative fraction of initial cesium that is leached
F	concentration of immobile cesium, counts/min/ml
J	cumulative cesium lost per unit surface area at time t, counts/min/cm^2
K	proportionality constant between mobile and immobile cesium
$\ell_\alpha(\bar{C}_j)$	interval above and below $\bar{C}_j$ in which there is $(1 - \alpha)$ confidence that the true mean is contained

$\Delta_\alpha(\bar{f})$	confidence interval of $(1 - \alpha)$ for $\bar{f}$
n_j	number of readings taken for sample j
N	number of leachant changes made up to the sampling time plus one
S	specimen surface area, cm^2
$S^2(C_j)$	estimated variance of the population of readings for sample j
$S^2(\bar{C}_j)$	estimated variance of the mean counts for sample j when the mean is computed using n_j readings
$S^2(\bar{f})$	estimated variance of the computed $\bar{f}$
t	time, days, hours
t_{α,ν_c}	value of the student's t distribution for ν_c degrees of freedom and a $(1 - \alpha)$ confidence interval
V	volume of specimen, cm^3
V_i	volume of leachate at time of sampling or changing, ml
x	distance from specimen surface, cm

Greek Symbols

α	level of t test
β	time constant in time dependent boundary condition, sec^{-1}
ν_f	estimated degrees of freedom in the computation of $\bar{f}$
ν_j	number of degrees of freedom returned in the estimation of $\bar{C}_j$
κ	constant in time dependent boundary condition

10.9 Literature References

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