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ABSTRACT

An accelerated leach test(s) is being developed to predict long-term leaching behavior of low-level radioactive waste (LLW) forms in their disposal environments. As necessary background, a literature survey of reported leaching mechanisms, available mathematical models and factors that affect leaching of LLW forms has been compiled. Mechanisms which have been identified include diffusion, dissolution, ion exchange, corrosion and surface effects. A computerized data base of LLW leaching data and mathematical models is being developed. The data is being used for model evaluation by curve fitting and statistical analysis according to standard procedures of statistical quality control. Long-term leach tests on portland cement, bitumen and vinyl ester-styrene (VES) polymer waste forms are underway which are designed to identify and evaluate factors that accelerate leaching without changing the mechanisms. Initial results on the effect of temperature on leachability indicate that the leach rates of cement and VES waste forms increase with increasing temperature, whereas, the leach rate of bitumen is little affected.

INTRODUCTION

Leaching of low-level radioactive waste (LLW) in the disposal environment is the first step in the release of activity to the surrounding environment. Hence, evaluation of leaching behavior has been considered essential in evaluating LLW forms[1,2]. Since the activity in LLW forms may not decay to innocuous levels for several hundred years, it has been deemed useful to develop an accelerated leach test(s) that can be used to predict the long-term leaching behavior of solidified LLW. This is to be accomplished through an understanding of the prevailing leaching mechanisms and the factors which control leaching behavior. A comprehensive evaluation of the rate controlling factors associated with specific leachant and waste form compositions will establish the basis for the development and validation of an accelerated leach test(s) under a variety of environments.

Activities for the past year have been directed in the following areas:

(i) A literature survey of reported leaching mechanisms, available mathematical models and factors that affect leaching of LLW forms has been compiled. A report documenting the results of the literature survey has been published.

(ii) A computerized data base of LLW leaching data and mathematical models is being developed.

(iii) Experimental investigations on portland cement, bitumen and vinyl ester-styrene (VES) test specimens have been/are being performed to provide data for the data base, for model evaluation and to evaluate factors that accelerate leaching. These studies include long-term leach tests on replicate test specimens, short-term scoping studies, solid phase analyses and statistical correlations of leaching releases.

Various solidification agents for LLW have been used in an effort to produce stable, leach-resistant waste forms[4,5]. The solidification agents under investigation in this program include portland cement, bitumen, vinyl ester-styrene copolymer (DOW process[6]) and the soda-lime-silica glass under development at Mound Laboratory[7]. These solidification agents represent a range of materials types - hydraulic cement, thermoplastic, thermoset and glass, respectively, and are either in use or being considered for LLW solidification.

THE LITERATURE SURVEY

A literature survey on leaching mechanisms, mathematical models and factors that affect leaching from solidified low-level radioactive waste has been compiled from reviews of previous work, pertinent models and information about parameters known to affect leaching[3]. The following is a brief summary of the results of this survey. Fuller accounts of, and references for the statements in this section are provided in Reference 3.

A report[8] on leaching mechanisms of the borosilicate glass high-level waste (HLW) solidification matrix was reviewed for applicability to the LLW leaching mechanisms survey program. Although some information from the HLW program was useful, in general it was not applicable because the solidification agents, waste types, radionuclides of concern and disposal environments are different and the time span of concern for LLW is shorter than that for HLW.

Leaching Mechanisms

Reported leaching mechanisms have included diffusion, dissolution, ion exchange, corrosion and surface effects. Diffusion has traditionally been considered to be the most important leaching mechanism. However, it has been indicated that dissolution is also important for waste containing soluble salts and that ion exchange is important when sorbents such as zeolites or clay are included in the waste form.

Cement

The leaching of cesium from pure portland cement has been shown to closely follow diffusion kinetics by numerous experimenters. This appears to be so because cesium is neither chemically bound by cement nor is it sorbed to any significant extent onto cement. Additives which sorb cesium, such as zeolites, certain clays and silica, can reduce cesium leachability by factors of a hundred or more, depending upon the additive. When sorption is the dominant mechanism of cesium binding in an additive-doped cement waste form, then cesium leachability may be dependent upon displacement of the sorbed cesium by calcium from the cement. In such cases cesium leaching may follow diffusion kinetics, however the actual leaching mechanism (i.e., the rate limiting step) is release from the sorbent. The amount of any such additive is also important to the long-term leachability in that the continued slow reaction of $Ca(OH)_2$ with available silacious material, including zeolites, reduces the sorbing capacity. If the amount of additive is not sufficient to consume all of the $Ca(OH)_2$ liberated by the portland cement in the long term, then the sorption value of the additive can be lost over time and the long-term leachability can increase.

Sr leaching from cemented waste forms does not appear to be simple diffusion. It has been shown to be affected by the presence of CO_2 and by the presence of non-radiostrontium which may be added to waste forms to control Sr release by solubility and dilution considerations. It has been speculated that, over the long term, Sr may be chemically incorporated into cement although no direct evidence for this has been reported.

Cobalt leachability from cemented waste forms appears to be controlled by the low solubility of Co in the high-pH cement environment. Although Co can exist in two oxidation states, no specific effects of Eh on cobalt leachability seem to have been reported. Cobalt readily forms complexes with chelating agents and other complexants which can increase the solubility of the complexed ions.

Bitumen

No definitive mechanistic studies of leachability of bituminized waste forms were found although leach data have been analyzed assuming diffusion, diffusion plus dissolution and dissolution. Swelling of bituminized waste forms during leaching often complicated data interpretation.

Polymers

Mechanistic studies on the leaching of polymer-solidified waste forms appear to be in a preliminary phase of measuring characteristics of permeation through polymer membranes. Such studies are necessary to consideration of the effects of waste loading on leaching behavior.

Glass

The leaching mechanisms and leach rate controlling factors for HLW glass have been intensively studied and extensively reviewed for conditions in a HLW deep-geologic repository. The LLW glass which has been investigated is of a somewhat different composition than the HLW glass and is a two-phase system as opposed to the single-phase HLW glass. These differences do not appear to affect the short term leaching behavior in that the leachabilities of both glass waste form types are reportedly similar in short-term leach tests. Long-term behavior of the LLW glass waste form has not been investigated.

Mathematical Leaching Models

Mathematical models which quantify any understanding of leaching are generally regarded as desirable and necessary for long term prediction of leaching behavior. All of the mathematical models for LLW leaching are derived from solutions to the diffusion equation and most are limited to consideration of a constant diffusion coefficient and a semi-infinite medium. Other mechanistic processes are included as additional terms in the equation. Each additional term represents a mechanistic process and incorporates a parameter which must be assigned a value, either by computation within the model or from independent knowledge. Diffusion coefficients, rate constants and equilibrium constants are common parameters. Although these parameters are generally assumed to be constant, there is reason to expect that the diffusion coefficient, D, varies with both concentration in the waste form and changes in porosity in the waste form. The initial and boundary conditions assumed for modeling purposes must be met for any model to be a valid representation of the problem. The most common initial condition is that of a homogeneous medium with a uniform concentration prior to leaching while a typical boundary condition assumes that the leachant concentration remain negligible during leaching.

Factors That Affect Leaching

Understanding factors that affect leaching is fundamental to any procedure for accelerating leach testing. The accelerated leach test(s) will be based on accelerating factors which do not change the leaching mechanism(s) predominant in the disposal environment.

Factors that affect leaching have been divided into three categories: (i) system factors, (ii) leachant factors and, (iii) composition of the solid waste form.

System factors include time, temperature, pressure, radiation environment and ratio of waste form surface area to leachant volume. Leach rate is a function of time and the functional dependence typically changes over the long term. Any attempt to predict long-term leachability must account for long-term changes in leaching behavior.

Temperature is generally the first parameter to be varied in attempts to analyse rate processes since, if the rate behavior obeys the Arrhenius equation, then an apparent activation energy can be assigned to the process. Correlating apparent activation energies with reasonable physicochemical processes is a traditional tool for analyzing rate processes. Leach rates of some glasses follow Arrhenius behavior. The leachability of cement increases with temperature; however, an irreversible change in the pore structure of cement with increasing temperature which increases leachability complicates any attempted Arrhenius analysis. No definitive trends in the leachability of bituminized waste forms with temperature have been reported.

Pressure effects in near surface burial of LLW may be negligible except for bituminized waste forms, which will probably deform by creep. The effect of creep deformation on the leachability of bituminized waste has apparently not been investigated.

The specific utility of the data base is to provide:

- A convenient compilation of selected data.
- An efficient vehicle for curve fitting data to mathematical models.
- An efficient vehicle for statistical analysis of curve fits for model validation and evaluation of factors that accelerated leaching.

Leaching data from the experimental part of this task plus leach data from the literature are being included in the data base.

Data Base

The data base 'schema' provides the instructions and format for entering the data and other information necessary to provide a complete description of the leach samples. Information on the solidification agent, waste type, sample size, leachant composition, the reference from which the data was taken, plus other information are cataloged for each sample or set of replicate samples. The retrieval programs process the data for curve fitting, plotting, printing out in various formats and other operations. The 'schema' is formatted in pages (i.e., records) of information. The first page contains the sample information on solidification agent, etc., while the leaching data is entered in the following pages, one page for each data point. For leaching data the points are defined by the sampling time and contain fractional release values for one or more radionuclides and/or other elements or compounds of interest in the leaching experiments.

Each set of leach data is assigned a five digit number, the TESTID, and may be further specified by an alphanumeric SAMPLEID. A Sample Replicate Number may also be specified for replicate experiments. The five digit TESTID is subdivided into (2 digits, 1 digit, 2 digits) for organizational purposes. The first two digits are used to designate the literature reference and/or reporter of the data. The third digit is currently unassigned while the last two digits identify individual experiments. The SAMPLEID is currently used for local identification of leaching experiments performed under this task.

Data Selection

Data selection for the data base has been based on the completeness of the experimental description such that the experiment, from test specimen fabrication through leachant replacement intervals, could be duplicated. Of special interest, are data for replicate test specimens, full-scale waste forms and test specimens incorporating real or simulated waste. Replicate test specimens leached in both pure water and brine are of interest since increased leachability in brine indicates that ion exchange may be the dominant leaching mechanism in leachants which contain exchangeable ions.

Since the data are to be curve fitted with mathematical models, the data must also be evaluated for compliance with the boundary conditions of the models. If the data were not obtained in a manner which complies to the boundary conditions under which any particular model is valid, then the data cannot be reliably interpreted by curve fitting to that model. Therefore, it is also necessary to evaluate leach testing procedures for compliance with model boundary conditions. One concern is the leachant flow rate or replacement frequency in the leach test. Leach tests generally specify fixed leachant replacement intervals which are closely spaced at the start of the test and become longer as the test proceeds. The standard boundary condition in leaching models is that leaching takes place into a leachant which has effectively zero concentration of the species of interest. Since experimental evidence of the effect of the leachant replacement interval is seldom reported with leach testing results, a posteriori criteria are being developed to evaluate the adequacy of the leachant replacement interval in any given leach test to meeting model boundary conditions. These criteria are in a preliminary stage of development and are not presented here.

EXPERIMENTAL

Baseline Experiments

A series of leaching experiments designed to provide long-term leaching data for this program have been underway for over 400 days. Triplicate samples of portland type I cement, vinyl ester-styrene and bitumen each containing ^{137}Cs, ^{85}Sr and ^{60}Co tracers are being leached in distilled water. These experiments are based on the ANS 16.1 test but leachant replacement intervals have been added and the test time has been extended. Currently, leachant replacement occurs every 21 days. These tests serve several functions:

- To provide long-term data for modeling.
- To provide leaching data against which accelerated tests can be compared.
- To provide samples and data with which long-term leaching mechanisms, or changes in mechanisms, can be observed.

The examples presented here are limited to ^{137}Cs released from cement. Similar results are available for the other isotopes and solidification agents under investigation.

Figure 1 illustrates the cumulative fraction release of ^{137}Cs from replicate cement specimens. Such replicate tests are needed for statistical evaluation of both the data and the significance of curve fits to models. Statistical analysis for this program is being adapted from basic procedures used for statistical quality control, as detailed in Reference 10.

In addition to radionuclides released from the waste forms, leaching of the matrix material is also being investigated. Cement leachates are being analysed for Ca, Si, Al, Na, K, Cs, Sr, Fe, Mg and alkalinity. A preliminary correlation matrix for the elements detected in the leachate, as well as ^{137}Cs and ^{85}Sr, is shown in Figure 2.

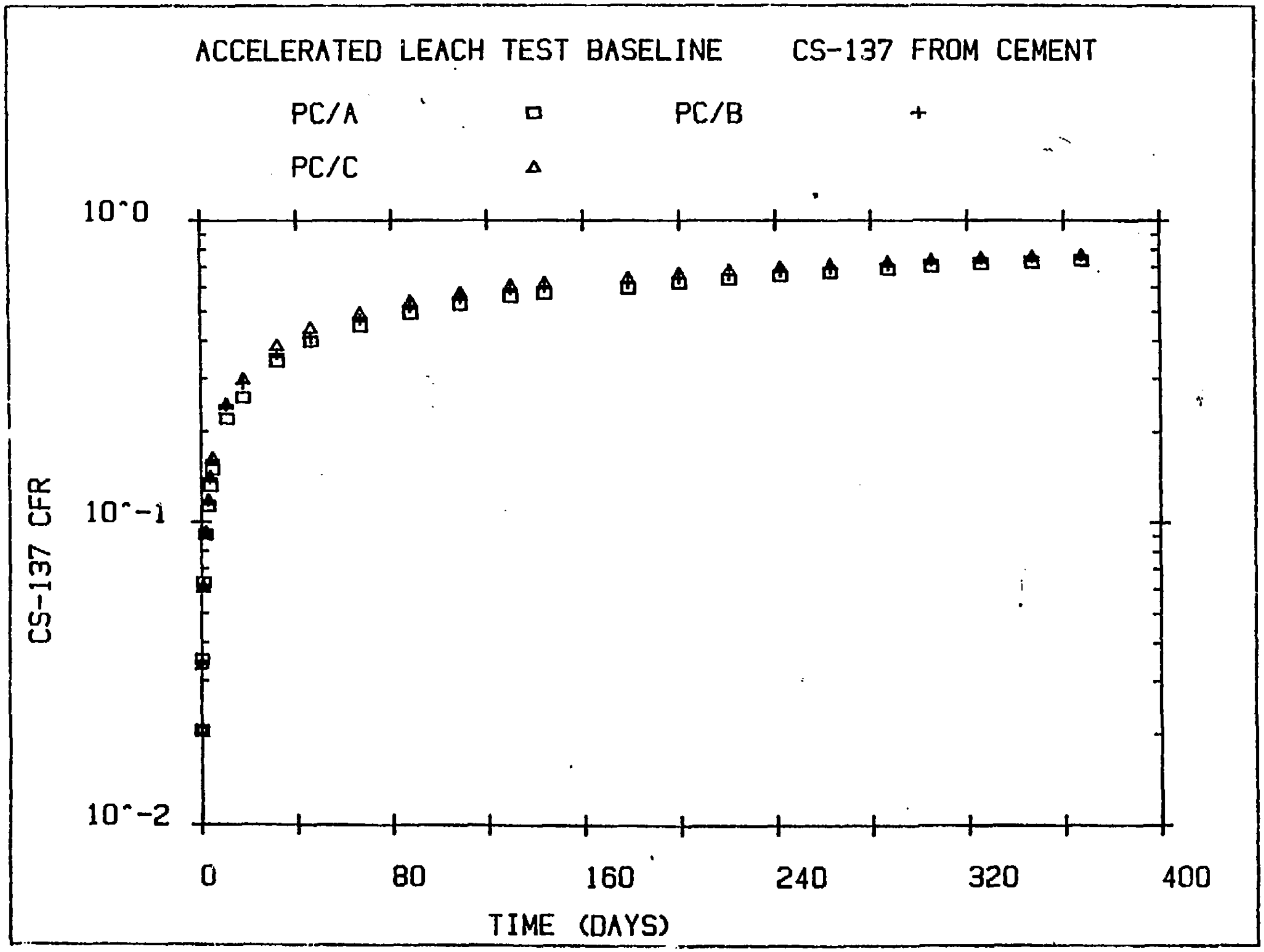

Figure 1. Cumulative fraction release of ^{137}Cs from portland cement showing data from triplicate samples.

SUMMARY STATISTICS
ON DATA SET:
LEACHING MECHANISMS PC-TYPE 1

CORRELATION MATRIX

	CUM TIME	CALCIUM	ALUMINUM	SILICON	STRONTIUM	SODIUM
DELTA TIME	.9006034	-.2489938	.7817969	.7558577	.4156674	.6072055
CUM TIME		-.3746774	.6619373	.6841273	.2223965	.3590613
CALCIUM			.2906097	.0597753	.7218680	.5071462
ALUMINUM				.9143493	.7883335	.8342367
SILICON					.5313083	.5926239
STRONTIUM						.9435285

	POTASSIUM	CESIUM	SR85	ALKALINITY
DELTA TIME	.4943966	.3177659	-.4173600	.0620769
CUM TIME	.2581236	.1765153	-.4492604	-.0963909
CALCIUM	.5737550	.2843229	.1772401	.9175058
ALUMINUM	.7705677	.5943786	-.3151384	.5617204
SILICON	.5011377	.6065448	-.3280959	.2928926
STRONTIUM	.9577601	.5219419	-.0754178	.8710641
SODIUM	.9857689	.5022679	-.1489548	.7257957
POTASSIUM		.4788495	-.0776724	.7630309
CESIUM			.4420875	.3269393
SR85				-.0474840

Figure 2. Correlated matrix for elements released from portland cement. Each correlation coefficient indicates the linear goodness of fit between the element at the top of a column and the element in that row in the column on the left.

This matrix provides an indication of the correlation between the releases of two elements. The closer the correlation coefficient approaches one, the better the correlation between the leaching of the two elements. For example, the correlation coefficient of 0.72 for calcium vs strontium indicates relatively uncorrelated leaching behavior whereas, the coefficient 0.96 for strontium vs potassium indicates stronger correlation, i.e., strontium from the solidification agent is released proportional to potassium. The poor fit of ^{85}Sr tracer to matrix strontium is noteworthy. These elemental relationships will be compared with correlations from future leaching studies to detect differences that may indicate changes in leaching mechanisms.

Temperature Effects

A series of short-term scoping experiments were performed to determine effects of temperature on leaching. Figure 3 shows cumulative fraction released for cement samples leached at 20, 30, 40, 50 and 70°C. As expected, leaching increases with temperature. Approximately 86% of the Cs-137 was released in 18 days at 70°C whereas 73% of ^{137}Cs was released in 368 days at 20°C.

Preliminary analysis was performed by plotting the 30°C, 40°C, 50° and 70°C cumulative fraction releases against the 20°C baseline fraction release. At 20°C, 30°C, 40°C and 50°C the data is linear but with changing slope to reflect accelerated leaching (Figure 4). This suggests that the mechanism remains unchanged over this range of temperature. The 70°C data is not linear. This may be the result of ^{137}Cs depletion in the sample. However, it appears to be more related to the leaching mechanism itself since the sample leached at 50°C does not show any depletion effect, even at 64% release, whereas, by comparison, leaching from the 70°C sample slowed down at 45% release.

A further analysis of the data is shown in the Arrhenius plot, Figure 5, where the log of the incremental leach rate taken between the 11 and 18 day sampling intervals is plotted against 1/T where T is the absolute temperature in degrees Kelvin. The rates for temperatures from 20-50°C appear reasonably linear, whereas that for 70°C is clearly anomalous compared to the lower-temperature data. On this basis it appears that ^{137}Cs leached from cement can be accelerated by temperatures up to approximately 50°C without disturbing the leaching mechanism.

Ongoing investigations include:

- Long-term leaching behavior at the optimum elevated temperature.
- Scoping studies of other accelerating factors.
- Scanning electron microscopy/energy dispersive x-ray spectrometry of the solid phase after leaching.
- Effects of wastes on leaching behavior.

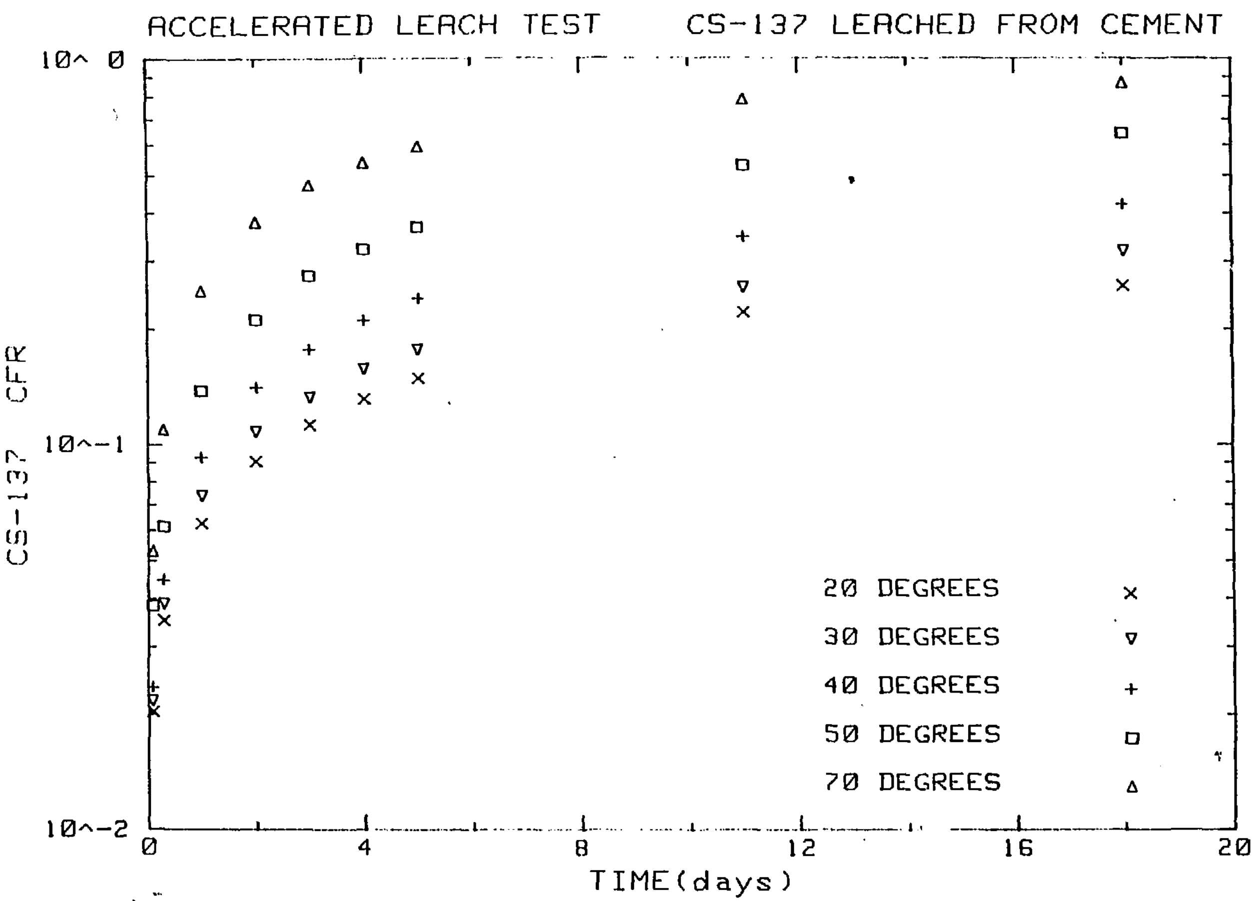

Figure 3. Cumulative fraction release of ^{137}Cs from portland cement samples after leaching 18 days at 20°, 30°, 40°, 50° and 70°C.

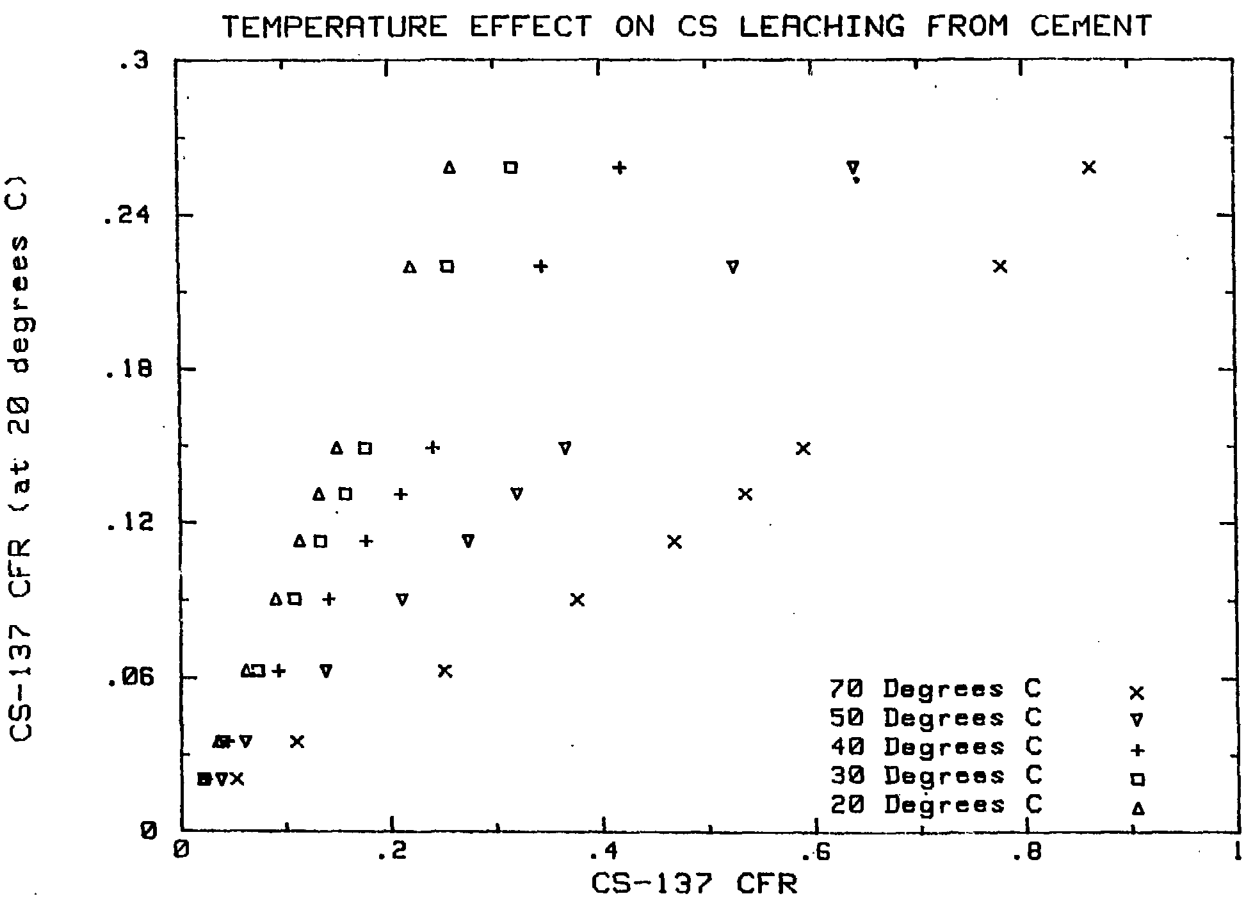

Figure 4. Cumulative fraction release of ^{137}Cs from portland cement. The 20°C release is plotted against the releases at 30°, 40°, 50° and 70°C. Note that the 70°C curve is not linear.

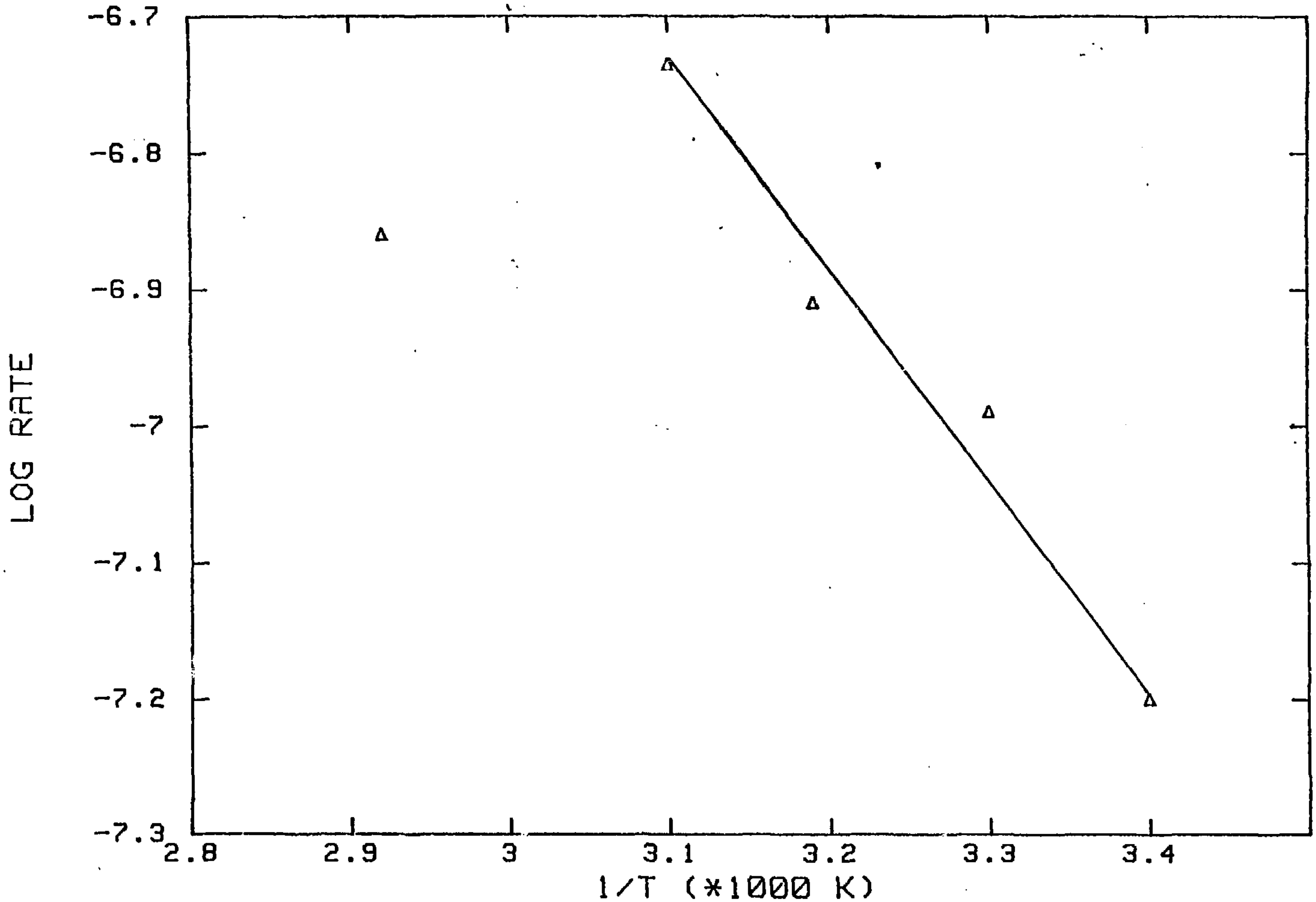

Figure 5. Arrhenius plot of the log of the leach rate taken between the last two sampling intervals of cement samples leached at 20°, 30°, 40°, 50° and 70°C.

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