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ACCELERATED LEACH TEST(S) PROGRAM ANNUAL REPORT

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ABSTRACT

This report summarizes the work performed for the Accelerated Leach Test(s) Program at Brookhaven National Laboratory in Fiscal Year 1985 under the sponsorship of the U.S. Department of Energy's Low-Level Waste Management Program (LLWMP).

Programmatic activities were concentrated in three areas, as listed and described in the following paragraphs.

(i) 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. Available mathematical models are based on diffusion as the predominant mechanism. Although numerous factors that affect leaching have been identified, they have been conveniently categorized as factors related to the entire leaching system, to the leachant or to the waste form. A report has been published on the results of this literature survey.

(ii) 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.

(iii) Long-term 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. 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.

PROGRAM SCOPE AND OBJECTIVES

An objective of the U.S. Department of Energy's Low-Level Waste Management Program is to provide support for the disposal of low-level waste in a manner which reduces risks to the public health and safety over both the short and long term. One long-term concern is the release of radionuclides by leaching of solidified LLW after disposal in shallow land burial. To provide a technical basis for understanding leaching behavior and, hence, to allow more realistic prediction of leachability, Brookhaven National Laboratory has initiated investigation(s) to predict long-term leaching behavior of low-level radioactive waste (LLW) forms in their disposal environments.

The objective of this program is to develop an accelerated leach test(s) that can be used to predict the long-term leaching behavior of solidified low-level waste forms. This is to be accomplished through an understanding of the prevailing leaching mechanisms and the factors which control leaching behavior. Leaching mechanims for selected solidification agent/waste types are being determined through a literature survey, by experiment and by data analysis utilizing curve fitting to mathematical models. 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.

The scope of this investigation over the past year has encompassed work in the following three areas:

(i) Compilation of a literature survey of reported leaching mechanisms, available mathematical models and factors that affect leaching of LLW forms.

(ii) Development of a computerized data base of LLW leaching data and mathematical models.

(iii) Experimental investigations including long-term leach tests on portland cement, bitumen and vinyl ester-styrene (VES) polymer waste forms designed to identify and evaluate factors that accelerate leaching without changing mechanisms.

The results of the literature survey have been compiled in a report[1]. The information from Item (i) and Reference 1 provides direction for work in Items (ii) and (iii). Since the results of the literature survey are available[1], only a brief description necessary for continuity with the efforts under Items (ii) and (iii) is given here. Additionally, results obtained under the Leaching Mechanisms Program, which was a short-term effort preceding this program are reported in Reference 2.

1. INTRODUCTION

One of the most important potential initiating events for the return of radioactivity from solidified wastes to man is exposure to water. For this reason, the chemical stability of a waste form is invariably determined by conducting a leach test which involves the direct or indirect measurement of the release of radionuclides to aqueous media. In the absence of national and international agreement on leach test methodology, it is often difficult, if not impossible to compare the results obtained by different groups of workers even for similar waste forms. Although the release of radioactivity from a solidified waste to an aqueous environment is acknowledged to be due to one or more mechanisms such as diffusion, dissolution, corrosion and ion-exchange, most leaching studies have been limited to the early stages of the leaching process, and are insufficient to characterize long-term leachability over hundreds of years. However, the response of an effectively solidified waste to the leaching process is so slow that an extremely long period of time is required to complete one test which will characterize the long-term leachability of a waste form. Therefore, an accelerated test is needed to adequately assess the long-term leaching behavior of solidified radioactive wastes in their disposal environment. This involves an understanding of prevailing leaching mechanisms and factors that affect leaching of waste forms in disposal.

2. SUMMARY OF THE LITERATURE SURVEY

A literature survey of reported leaching mechanisms, available mathematical models and factors that affect leaching of LLW forms has been compiled[1]. Since a similar effort has been completed for the defense high-level waste borosilicate glass waste form[3], the information reported in Reference 3 was reviewed for applicability to the LLW leaching mechanisms program. Although some information from the HLW program was useful, in general it was not applicable because the solidification agents, waste types and disposal environments are different and the time span of concern for LLW is shorter than that for HLW.

Most leaching data obtained from standard leach tests are analyzed using models which assume diffusion with a constant diffusion coefficient in a homogeneous, semi-infinite medium to be the leaching mechanism. Such models are probably inadequate if any of these assumptions are not met in reality. In particular, the semi-infinite medium approximation severely limits the range of validity of such models to real waste forms. Currently available standard leach tests may not be suitable for predicting long-term leaching behavior of waste forms since they do not simulate actual disposal environments.

2.1 Leaching Mechanisms of Several Solidification Agents for LLW

Efforts were concentrated on reporting the leaching mechanisms of portland cement, bitumen, the vinyl ester-styrene copolymer and soda-lime glass. These solidification agents represent four materials types--hydraulic cement, thermoplastic, thermoset and glass, respectively--and are either in use or being considered for solidification of LLW.

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 clays are included in the waste form. Cemented waste forms tend to accumulate carbonate on the surface when either the waste form or leachant is exposed to air. This surface carbonation has been shown to reduce the leachability of strontium. Measurements have been reported which indicate that portland cement itself is a relatively poor sorbent for both cesium and strontium. It has been speculated that both strontium and cobalt slowly react with cement to become part of the hydrated cement matrix. Leaching from bituminized waste forms has been analyzed as resulting from diffusion, from dissolution and from a combination of both mechanisms. Some waste types, including ion exchange resins and sulfate wastes, cause substantial swelling of bituminized waste forms in water which may affect the release mechanism from the waste form. Little information on the leaching mechanisms of polymeric solidification agents has been reported. One study on diffusion of cesium and water through polymer films has been reported. Leaching mechanisms of borosilicate glass have been extensively investigated, reviewed and modeled as part of the defense HLW program. It is not clear how much of the knowledge gained about

borosilicate glass leaching behavior is applicable to the LLW glass which is different both chemically (soda-lime silica versus borosilicate) and physically (the LLW glass is a two-phase system incorporating incinerator ash whereas the HLW glass is single-phase glass) from the HLW glass.

Cement

The mechanism of Cs leaching 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. Additionally, the high solubility of Cs in the typical cement pore water environment suggests that most if not all of the cesium inventory in a cement waste form is free to leach upon contact with water.

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 decreases and 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 reduces the sorbing capacity. Thus, 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 sorptive value of the additive can be lost over time and the long-term leachability can increase. Also, such systems may be very sensitive to the ionic strength of the leachant in that, if more cations are available in the leachant to compete with cesium for the available sorptive capacity, then cesium leachability can increase over that observed in deionized water.

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.

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 preludes 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 tests of up to 80 days duration. Long-term behavior of the LLW glass waste form has not been investigated.

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, none of the available interpretations seems definitive or convincing. Swelling of bituminized waste forms during leaching often complicated data interpretation.

2.2 Factors That Affect Leaching

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 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 affect of creep deformation on the leachability of bituminized waste has apparently not been investigated. There is considerable information available on the effects of irradiation on the leachability of LLW forms. Irradiation should have no effect on glass leachability, based on the HLW glass studies. Cemented LLW, including cemented organic ion exchange resins, showed no effect of irradiation on leachability up to at least 10^9 rad. Both bituminized LLW and vinyl ester-styrene solidified LLW showed no increased leachability up to 10^8 rad.

Leachant factors include the effects of pH, Eh, flow rate or replacement frequency and composition. The solubility of most cations is strongly dependent on pH. The high pH of cement limits the solubility of most radionuclides with the notable exception of cesium. The leachability of glass is near its minimum in neutral pH conditions. Eh controls the oxidation state, and thus the solubility of elements such as cobalt with multiple oxidation states. The

Eh of hydrated cement has been measured and found to be moderately oxidizing. Leachant flow rate or replacement frequency affects the degree of saturation of the leachant with respect to leached material. This not only exerts strong control over leachability but also determines the boundary conditions which need to be accounted for in any modeling analysis of leaching behavior. Leachant composition may affect the leachability of different waste form types in different ways. While demineralized water as leachant often produces higher leach rates than brine or 'tap water,' waste forms containing ion exchange resins or sorbents generally show higher leach rates in brine and leachants which contain exchangeable ions.

Waste form factors include composition, surface condition, porosity and waste form surface area to volume ratio. LLW forms are generally multi-phase systems in which the solidification agents matrix and the incorporated waste are physically and chemically distinct. Waste form composition, including the physicochemical nature of the solidification agent and the waste materials, determines the possibility that these components may react chemically. Cement and glass are both chemically complex and may react with waste components whereas bitumen and VES have been described as inert encapsulants. Surface condition may change as a result of leaching. Glass forms a 'gel layer' upon extended leaching while cemented waste forms are known to accumulate carbonate on the surface from leachants containing carbonates and leachants exposed to air. Porosity in a solid is a major factor affecting diffusion within the solid. Changes in porosity due to dissolution of soluble material or other factors may affect long-term leachability. The surface area to volume ratio of a waste form controls the time required to deplete the waste form of leachable substances. Accordingly, it has been used as an accelerating factor in HLW glass leaching studies. For diffusion as the leaching mechanism, it has been shown that leaching from small-scale samples can predict leaching release from larger waste forms as long as the semi-infinite medium approximation is valid.

2.3 Modeling Considerations and Mathematical Models

Mathematical models which quantify any understanding of leaching are generally regarded as desirable and necessary for long term prediction of leaching behavior. Such models incorporate specific mechanisms into equations and are fit to data using numerical constants or parameters. 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 and changes in porosity in the waste form. The effect of variations in D on leaching behavior are discussed in Reference 1. The initial and boundary conditions assumed for modeling purposes must be met for the model to be a valid representation of the problem. The standard 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 remains negligible during leaching. The stated initial condition is at variance with the fact that real LLW forms are multi-phase systems while the assumed boundary condition is clearly an approximation for slow flow and semi-dynamic leach tests.

Several mathematical models for LLW leaching release are available. All are based on the diffusion equation and all but one assume D constant. Leaching release equations are available in which diffusion is the only mechanism

for both the semi-infinite medium and for realistic geometries such as cylinders. Two different diffusion plus dissolution model equations have been solved and the leaching release equations reported; however, both of these are limited to the semi-infinite medium. In one of these models, the dissolution mechanism is equivalent to corrosion of the surface of the waste form. Models incorporating diffusion plus a specific form of chemical reaction or equilibrium and diffusion plus ion exchange are also available. An empirical equation which was developed for glass leaching may be of some use for analyzing LLW leachability. When models become too complex to solve analytically, in closed form, then numerical solution procedures such as finite element analysis codes may be used to obtain approximate solutions. One such model has been reported for LLW leaching. This model incorporates a concentration-dependent diffusion coefficient plus dissolution, corrosion and radioactive decay. A very sophisticated numerically calculated model, PROTOCOL, for glass leaching in geologic repositories was developed for the HLW leaching mechanisms program[3]. However, it is not clear how this model could be useful for LLW Leaching.

There has been virtually no consideration given to the effect of possible variation in the diffusion coefficient in modeling LLW leaching behavior. The one exception is a numerically calculated model program, which assumes a concentration-dependent diffusion coefficient of the form.

$$D(C) = D_0 \left(1 + a \frac{C}{C_{sat}}\right)$$

$D(C)$ = the value of the diffusion coefficient at concentration, C.

D_0 = the limiting value of the diffusion coefficient at zero concentration.

a = constant

C_{sat} = concentration at saturation.

However, the physiochemical justification for this form of concentration dependence was not clear. There seem to be good reasons to expect that diffusion coefficients in waste forms incorporating soluble wastes would increase with leaching since dissolution of the soluble waste would increase the porosity of the depletion zone. Theoretical equations are available for estimating the variation in D with porosity.

2.4 Summary and Conclusions From The Literature Survey

The Leaching Mechanisms Report reviewed information on leaching mechanisms, models and factors that affect leaching for low-level radioactive waste. Leaching mechanisms are complicated processes which are generally not fully understood.

The literature survey on mechanisms and models for LLW leaching behavior resulted in the following conclusions:

(i) Knowledge of leaching mechanisms and factors that affect leaching is necessary for long-term prediction of leaching behavior.

(ii) The leaching tests currently available may be adequate for short-term comparison of leachability between different waste forms, but are probably not adequate for long-term prediction.

(iii) LLW forms are generally multi-phase systems in which the solidification agent matrix and waste material are physically and chemically distinct. The consequences of this on modeling leaching behavior have not been investigated in more than a very preliminary manner.

(iv) Little information on the long-term aging of LLW forms is available except for irradiation studies. Chemical and physical aging phenomena due to leaching in a disposal environment have been addressed only sparsely.

(v) Although analysis based on diffusion as the principal leaching mechanism has been generally accepted as a standard procedure, no adequate experimental investigation of the validity of this has been reported. Virtually all reported analyses are limited to a small region of fractional release in the early stage of leaching in which the semi-infinite medium approximation may be valid.

(vi) The use of mathematical models to curve fit leaching data requires adherence to conditions during the leach test to comply with the boundary conditions necessary for validity of the mathematical models. Adherence to boundary conditions is generally assumed rather than assured by testing. No systematic studies on the effects of changes in boundary conditions have been reported.

(vii) The problem of scaling to enable data taken from small, laboratory sized samples to be extrapolated to predict leaching from full-scale waste forms has been partially addressed for LLW forms. The reported scaling law is based on diffusion in a semi-infinite medium. The validity of this scaling law has not been investigated beyond the range of validity of the semi-infinite medium approximation.

(viii) Although mathematical models cannot describe all of the complexity of real waste forms in their disposal environment, such models may be used to test hypothetical leaching mechanisms quantitatively.

The literature survey identified several areas in which sufficient information is lacking.

There is an apparent need for a computerized data base on leaching of LLW forms. This information will help in the determination of leaching mechanisms and in radiological assessments of waste disposal. The data base currently being developed by the LLWMP is limited to immediate program needs.

It appears from the literature that there are no "off the shelf" mathematical models which can be utilized for predicting long-term leaching behavior of heterogeneous waste forms in disposal environments. Further model development/modifications of existing models may be necessary.

The information compiled in this report has also indicated that knowledge of leaching mechanisms for LLW is generally incomplete. A major exception to this generality may be for cesium release from cemented waste forms, which has been studied extensively. However, the lack of correlation of mathematical models with data by curve fitting and statistical evaluation to any great degree leaves even this case in some doubt. Overall, quantitative evaluation of data using mathematical models is an area that seems to have been substantially bypassed.

3. DATA BASE DEVELOPMENT

A computerized data base of LLW leaching data and mathematical models is being developed. The Scientific Information Retrieval (SIR)* data base is being used for this purpose. The data base is being developed to assist in model validation by curve fitting and statistical analysis and to assist in evaluating factors which accelerate leaching without changing the mechanism. It is being developed to meet specific program needs and is not intended to be a general compilation of leaching data. Selected literature data as well as data from the experimental part of this program are being included in the data base.

The activities pursued under data base development have included specification of the 'schema' and specification of data selection criteria. The schema provides the framework for data input, manipulation and retrieval. Data selection criteria have been developed based on program requirements for use of the data.

3.1 The Data Base Schema

The schema specifies the organization of the data base and provides the procedures for data input, manipulation and retrieval. 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. Each data point is defined by the sampling time and the fractional release value for one radionuclide or other element or compound of interest in the leaching experiment.

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 used for local identification of leaching experiments performed under this task. The Sample Replicate Number may be used to identify replicate experimental runs.

3.2 Selection Criteria for Literature Data

Although a great deal of leaching data has been reported for LLW in the literature, much of it is not useful for the purposes of this program. The criteria chosen for evaluation of literature data for inclusion in the data base include:

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- Completeness of the experimental description. Information on sample composition and fabrication procedures, leachant composition and leaching procedures must be complete enough that the experiment could be reproduced.

- Replicate experiments are desirable to provide statistical parameters for evaluation of variability and significance of results. Experiments on nominally identical samples provide data on the inherent variability of the process. Such information is necessary to properly evaluate the variations observed between results obtained by different experimenters and results obtained for similar, but somewhat different, sample formulations and fabrication procedures.

- Full-scale waste forms. An objective of the program is to be able to predict leaching behavior of waste forms. Leaching results from full-scale waste forms are needed to evaluate scaling laws which relate results from lab-scale samples to actual waste forms. Two theoretically derived scaling laws and their applications and limitations have been reviewed in Reference 1, pp. 19-21.

- Waste forms incorporating actual waste. The relationship between the leaching of waste forms containing actual waste and those containing simulated waste and/or tracers needs to be established.

- Modelability. In order to gain valid information from curve fitting data to mathematical models, the data must have been obtained in a manner which conforms to model requirements. Conditions which must be obtained for any particular model to be valid include the particular mechanism(s) which the model contains and the initial and boundary conditions. Criteria which are needed to determine compliance with model conditions. Efforts directed toward determining such criteria are presented in the following two subsections.

3.2.1 Mechanistic Parameters and Leaching Models. Leaching mechanisms are generally specified by a parameter, such as the diffusion coefficient, equilibrium constant, rate constant for dissolution, etc. These parameters are typically assumed to be constant. This assumption may or may not be reasonable in a specific leaching system over the time span and range of conditions of the experiment. There are reasons to expect that the diffusion coefficient, D, varies with both concentration of the species of interest and with changing porosity of the waste form. Several implications of D varying with concentration and porosity were discussed in Reference 1.

3.2.2 Leachant Replacement Intervals in Leach Testing. It has been noted that saturation effects which may occur for inadequate leachant replacement frequency can result in questionable data analysis[4-6]. A requirement for model validation is that data used to test the model be obtained under conditions consistent with the model. Leach tests, such as the IAEA[7], ANS 16.1[8] and ISO[9] tests, which call for leachant replacement at specified times, have been widely used due to their simplicity and controllability. Table 1 presents a brief summary of the IAEA, ANS 16.1 and ISO leach tests. Note that, even though these tests have been specified for several different materials, there is one set of leachant replacement intervals in each test. Also, leachant replacement becomes less frequent the longer the test runs.

Although a decreasing frequencey of leachant replacement seems reasonable since leach rates typically decrease with time, none of these tests presents arguments supporting the particular replacement intervals specified.

3.2.3 Partial-Replacement Models. The fundamental characteristics of these models is that leachant flow is simulated by periodic withdrawal of a fraction of the leachate and replacement with fresh leachant. The purpose of these models is to simulate a slow flow of leachant past the waste form. The simulated flow may be slow enough that there is always a significant concentration of leached material in the leachant. Three variations of this model are available:

(i) Case for which all of the species of interest is initially in solution[10].

(ii) Constant leach rate case[11].

(iii) Concentration-dependent leach rate case[11].

Case (i) is clearly the most severe in that all of the species of interest (SOI) is in solution to begin with. In essence, leaching has already occurred into a closed volume and release from this (well stirred) volume occurs by withdrawal of a fraction of the leachate and replacement with fresh leachant. The fractional release of the SOI in any withdrawal-replacement event is equal to the volume fraction replaced. From Reference 10, the incremental fraction released (IFR) in the nth withdrawal-replacement event is:

$$IFR\ (n) = Z(1-Z)^{n-1} \qquad (3.8)$$

Z = fraction of leachate volume withdrawn and then replaced with fresh leachant

The cumulative fraction released (CFR) after n withdrawal-replacement events is shown in Equation (3.9).

$$CFR(n) = \sum_{i=1}^{n} Z(1-Z)^{i-1} \qquad (3.9)$$

The results of the periodic, partial leachant replacement tests for cases (ii) and (iii) are similar. The average concentration at long times from these leach tests is close to, but less than, the concentration that would be expected in the leachant under true-flow conditions. For case (iii), in which the leach rate decreases linearly with concentration, the fact that the average concentration under periodic replacement is less than the steady-state concentration under true-flow conditions results in the average leach rate under periodic-replacement conditions being slightly greater than that under true-flow conditions (Reference 11).

A limitation of the analyses for cases (ii) and (iii) is that no allowance is made for sample depletion. Thus, a semi-infinite medium approximation is an inherent boundary condition for these analyses. Conversely, while the analysis for case (i) accounts for sample depletion, no credit is given for retarded release from the waste form. A realistic analysis of leaching in true-flow, or partial replacement leach tests must account for both retarded release (due to diffusion or other leaching mechanisms and/or a leachate concentration dependence) and sample depletion.

4. EXPERIMENTAL METHODOLOGY

The development of an accelerated leach test will be tested through extensive leaching studies designed to identify and evaluate factors that affect and/or accelerate leaching of waste forms under disposal environments. Results from these tests will be compared to the baseline leaching studies initiated under the Leaching Mechanisms Program[2] and the mathematical models of leaching behavior obtained from the literature. This will provide the basis for the development of an accelerated leach test(s). Trial tests will be conducted to ascertain the effects of various combined acceleration factors on leaching mechanisms. Accelerating factors which do not change the mechanisms will be used to develop the accelerated leach test(s). Ultimately, the model which best fits the data, and which is supported by physicochemical evidence for the mechanisms on which the model is based, will provide the basis for extrapolating leaching data to long times.

Finally, the test methodology will be proposed based on knowledge of leaching mechanisms, the factors which accelerate leaching (without altering the mechanisms) and the results of trial accelerated leach test procedures. Whenever possible, all analyses associated with laboratory experiments will be conducted according to standard methods and practices.

4.1 Fabrication of Test Specimens

4.1.1 Matrix Materials. The solidification agents selected for this study are representative of those currently in use or being considered for use by defense and/or commercial LLW waste generators. They also represent a cross-section of materials properties which may influence the leaching behavior of the waste forms. These materials include portland cement, bitumen, a polymer (vinyl ester-styrene) and glass (soda-lime silica).

4.1.1.1 Hydraulic Cement. Hydraulic cement has been used for many years for the solidification of wet solid wastes. Water in the waste reacts chemically with the cement to form hydrated silicate and aluminate compounds, which interact to form a porous monolithic solid. Waste solids are physically entrapped and act as an aggregate.

4.1.1.2 Vinyl Ester-Styrene. Vinyl ester-styrene is a thermosetting resin marketed by the Dow Chemical Co. for use in solidification of radioactive wastes. The resin is mixed directly with wet solid wastes and subsequently polymerized at room temperature using a promoter-catalyst system. The polymerization reaction is exothermic and a monolithic solid is formed within 30-60 minutes. In this system, the waste and resin are mixed in a container prior to initiating the polymerization reaction.

4.1.1.3 Bitumen. Bitumen (or asphalt) systems are recently being used in the United States for radioactive waste solidification.

Bitumen is a mixture of high molecular weight hydrocarbons obtained as a residue in petroleum or coal tar refining. The two major components are asphaltene compounds, which give bitumen colloidal properties, and malthene compounds, which impart viscous liquid properties. Bitumen is a thermoplastic material which forms a miscible liquid at approximately 120°C. The waste is homogeneously mixed with the molten bitumen which solidifies upon cooling.

4.1.1.4 Soda-Lime Silica Glass. For this study the glass waste form material selected was developed at the Monsanto-Mound Facility in a process that simultaneously incinerates low-level waste and incorporates the ash in glass. The waste form is a non-porous material consisting of two solid phases; the glass matrix in which part of the waste components are dissolved, and the ash residue. The glass phase is comprised primarily of SiO_2 with smaller amounts of oxides of Na, Ca and Mg.

4.2 Sample Preparation

The specimens prepared for conducting the baseline leaching experiments and for evaluating acceleration factors were cylindrical with approximate dimensions of 4.8 cm diameter and 6.4 cm length. Based on past experience, this size sample is convenient for laboratory studies and for compliance with test procedures.

Specimens were prepared individually in separate containers to ensure proper formulation and activity content. Radioactive tracers consisting of Cs-137, Sr-85 and Co-60 were used for the long-term base line samples, whereas, Cs-137, Sr-85 and Co-57 were used in samples to evaluate acceleration factors. The low energy gamma-ray emitted by the short-lived Co-57 isotope is better suited to the automated NaI counting system, used for the short-term tests, than the more energetic gamma-rays of Co-60. Both isotopes have identical chemical behavior. Formulations used to fabricate test specimens are given in Table 4.1.

The soda-lime silicate glass samples, which were produced at the Mound Facility, are smaller in size than the samples normally used for this study. Because these samples were acquired recently, leaching studies using this material have not yet been initiated.

4.3 Leaching Tests

The leachability of the various solidification agents with and without simulated wastes, is being measured by use of several standard leaching tests to obtain the necessary information regarding the leaching mechanisms of waste forms in disposal environments and the factors which control their leach rate. These tests are briefly described below.

4.3.1 ANS 16.1 Leaching Test. The ANS 16.1 Leach Test[8] is a semi-dynamic leaching test in which the leachate is replaced periodically after intervals of static leaching. In this procedure, specimens are placed into the leachant solution in such a way that all external surface area is directly exposed. Specimens are tested in individual containers containing sufficient leachant to provide a leachant/specimen external geometric surface area ratio of 10 cm. Specimen formulations are usually tested in duplicate or triplicate to determine the extent of specimen variation in leaching. Leach test data are expressed as incremental fraction release or a cumulative fraction release to facilitate alternative methods of data treatment.

Table 4.1

Waste Form Compositions

Portland Type I Cement

Component	Weight %	Activity (mCi)
Cement Powder	70	-
Water	30	-
Co-60 or Co-57	-	16.3
Cs-137	-	9.9
Sr-85	-	23.6

Pioneer 321 Bitumen

Component	Weight %	Activity (mCi)
Bitumen	100	-
Co-60 or Co-57	-	13.8
Cs-137	-	8.4
Sr-85	-	20.0

Vinyl Ester-Styrene Emulsion

Component	Weight %	Activity (mCi)
Vinyl Ester-Styrene Monomer	49.2	-
Water	49.5	-
Catalyst	1.26	-
Promoter	0.05	-
Co-60 or Co-57	-	15.4
Cs-137	-	9.3
Sr-85	-	22.3

Vinyl Ester-Styrene

Component	Weight %	Activity (mCi)
Vinyl Ester-Styrene Monomer	97.9	-
Water	0.7	-
Catalyst	1.3	-
Promoter	0.05	-
Co-60 or Co-57	-	13.9
Cs-137	-	8.4
Sr-85	-	20.0

For this study, the ANS 16.1 Leaching Test is primarily used for conducting the baseline leaching tests and for evaluating leach rate controlling factors, described in Sections 5 and 6 of this report.

4.3.2 MCC-3 Leaching Test. The MCC-3 Agitated Powder Leach Test Method[13] is a static leach test developed for determining the solubility limits and the dissolution rates of materials used for the encapsulation of high-level wastes.

This method has been adapted for use with low-level waste materials to determine solubilities of sample components in the leachate. Leachate elemental concentration must be monitored with respect to chemical saturation to eleminate retardation of leach rates or mechanistic variations due to saturation conditions.

4.3.3 MCC-4 Leaching Test. The MCC-4 Low Flow Rate Leach Test Method[14] is a single-pass flow through test which eliminates sampling interval effects and large leachate concentration changes, providing better control over the boundary conditions of leachant composition.

This leaching test was also developed for evaluation of high-level waste forms. Because of the nature of the materials used for this study, some modifications were made in the test procedure, by increasing the flow-rates.

4.4 Leachate Analysis

4.4.1 Radiochemical Analysis. The radiochemical component of the leachate such as Cs-137, Sr-85 and Co-60 (or Co-57) is analyzed by gamma-ray spectroscopy using an intrinsic Germanium detector or a sodium iodide detector in accordance with the methods described in ASTM D3648-78 and ASTM D3649-78.

4.4.2 Chemical Analysis. The analysis of leachate for non-radioactive elements, such as Al, Si, Na, K, Sr, Mg, Cs, Fe and Ca, is determined by atomic absorption spectrophotometry[15].

4.5 Solid Phase Analysis

4.5.1 Scanning Electron Microscopy and Energy Dispersive Spectroscopy SEM/EDS). After leaching, the waste forms are sectioned and analysed by SEM/EDS. Imaging by SEM allows observation of microscopic alterations in the structure of the solid phase due to leaching. Of particular interest are changes in porosity and crystallinity. Chemical analysis of the solid phase by EDS is a semi-quantitative method that can provide ratios of certain elements in the matrix material. Elemental profiles determined with the use of this technique can indicate how elements in solution move through the solid phase.

5. BASELINE LEACHING RESULTS

5.1 Baseline Experiments - Leaching of Radionuclides

The baseline leaching experiments were initiated during the Fiscal Year 1984 and have continued for over 400 days. These studies are based on the ANS 16.1 Leach Test, which has been modified to increase test duration beyond the prescribed 90 days. In addition, the leachant replacement intervals have been increased to minimize the possibility of chemical saturation in the leachate.

The baseline leaching experiments have been conducted in distilled water, using matrix materials with various types of radioactive tracers. The purpose of the baseline leaching study is to:

- provide long-term data for statistical and modeling purposes
- provide leaching data against which accelerating factors can be evaluated
- provide an understanding of the prevailing mechanisms

The leaching results obtained for the baseline experiments are described below.

5.1.1 Portland Cement Leaching. Figure 5.1a shows cumulative fraction releases (CRF) for Cs-137 and Sr-85 leached from a Type I portland cement. Co-60 was not detected in the leachate. However, this is not unusual since cobalt tends to form compounds of low solubility at pH = 10 to 12. The cumulative fraction release for Cs-137 and Sr-85, after 368 days was 73% and 4.4%, respectively. Figures 5.1b and 5.1c show Cs-137 and Sr-85 releases for triplicate cement samples. Reproducibility of the data from the triplicate samples appears relatively good although the statistical analysis has not yet been done.

Figures 5.2a and 5.2b show the leach rates of Cs-137 and Sr-85 plotted against time. The data for Sr-85 in Figure 5.2b is not usable after 160 days. The short half-life of the isotope (64 days) combined with the low fraction release resulted in leachate activity below detection limits beyond 160 days.

5.1.2 Vinyl Ester-Styrene Leaching. Figure 5.3 shows CFR plotted against time for all radionuclides in a vinyl ester-styrene sample. There is little difference in the activity releases between isotopes, indicating that none of the tracers react chemically with the solidification agent. Again, the Sr-85 release falls below those of the other isotopes beyond 160 days because of decay. Figure 5.4a shows Cs-137 release for each of the triplicate samples and Figure 5.4b shows the replicate data for Sr-85. Deviation in released activity at 130 days is about 0.2% of the initial activity in the waste form. Release rates for VES samples are shown in Figures 5.5a, 5.5b and 5.5c. There is some scatter in the low release rate points because the lower rates are susceptable to counting errors as well as small variations in the leach rate itself, which can be attributable to microscopic inhomogeneities in the sample.

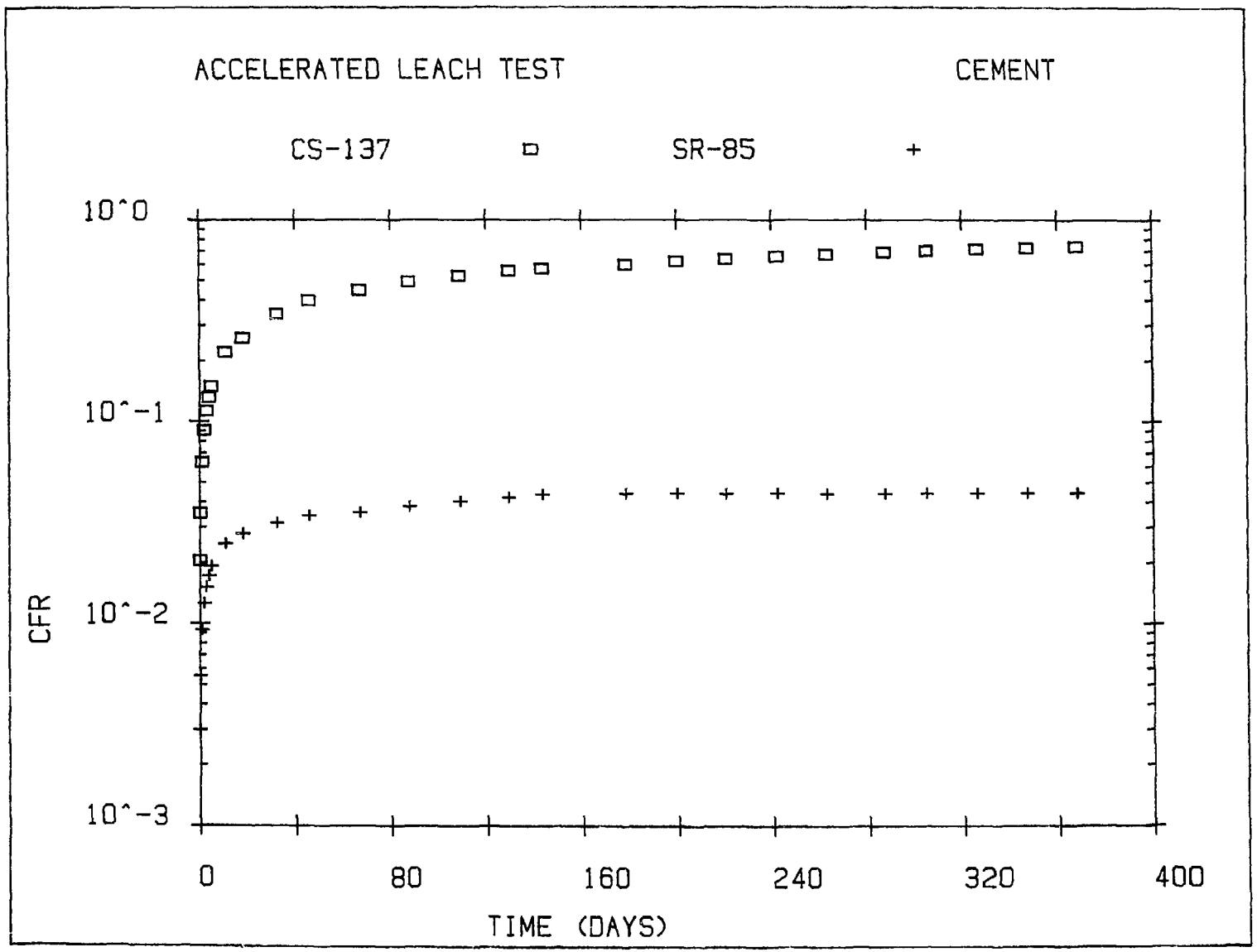

Figure 5.1a. Cumulative fraction release of Cs-137 and Sr-85 from portland type I cement. No Co-60 was observed in the leachate.

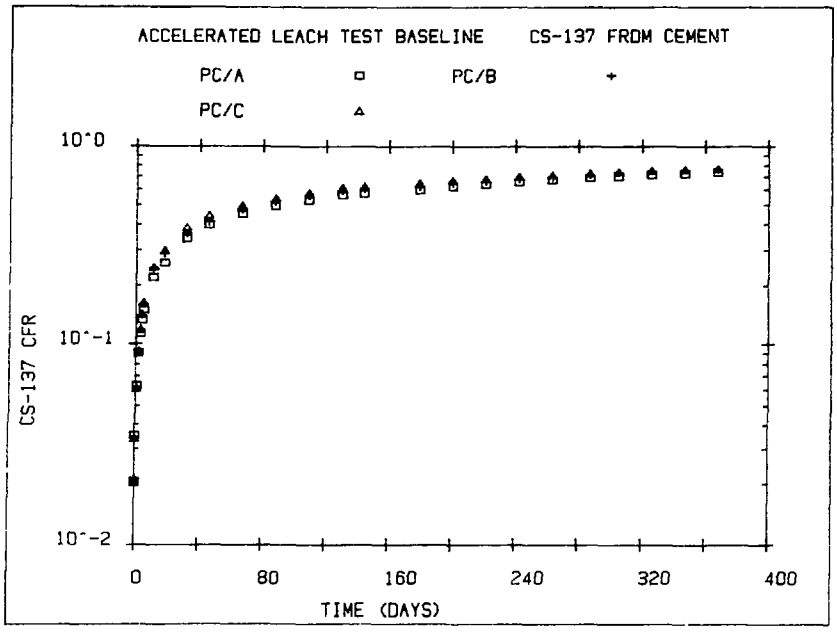

Figure 5.1b. Cumulative Fraction Release of ^{137}Cs from triplicate cement waste forms for the Accelerated Leach Test baseline.

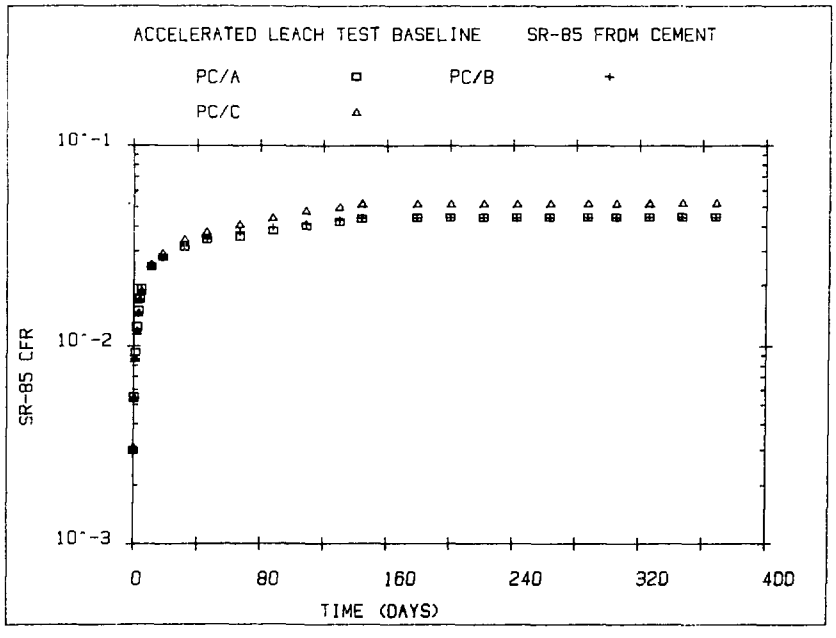

Figure 5.1c. Cumulative Fraction Release of ^{85}Sr from triplicate cement waste forms for the Accelerated Leach Test baseline.

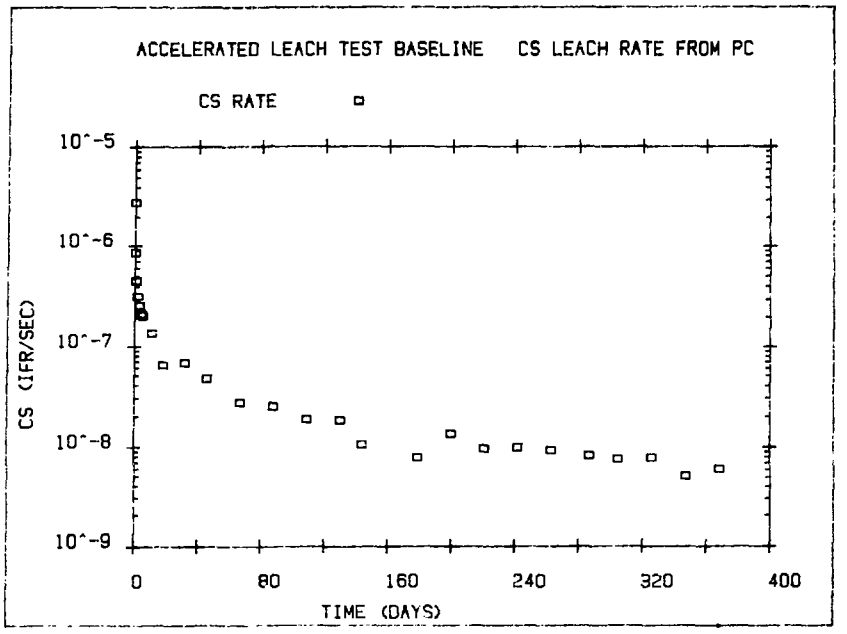

Figure 5.2a. Leach rate (Incremental Fraction Release/Leaching Interval Time) for ^{137}Cs from portland cement.

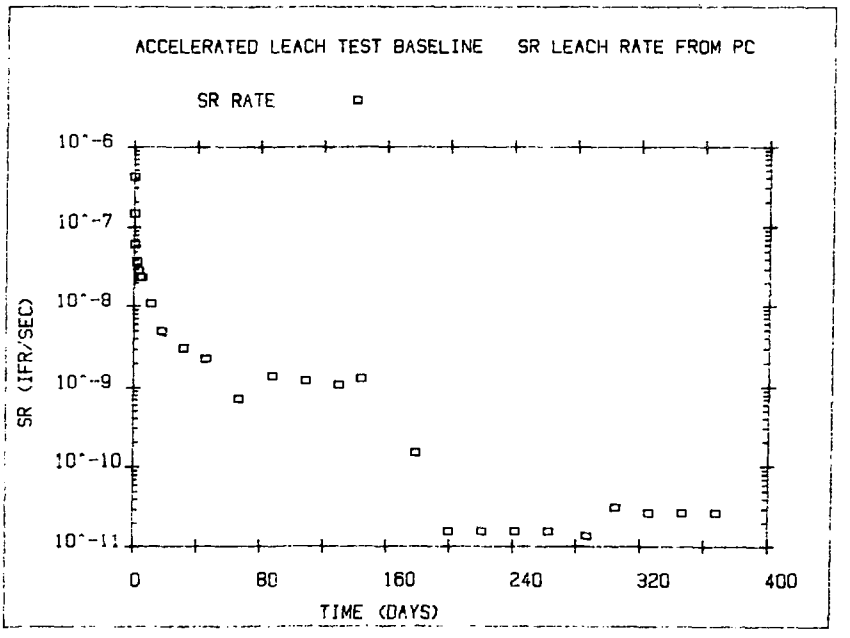

Figure 5.2b. Leach rate (Incremental Fraction Release/Leaching Interval Time) for ^{85}Sr from portland cement.

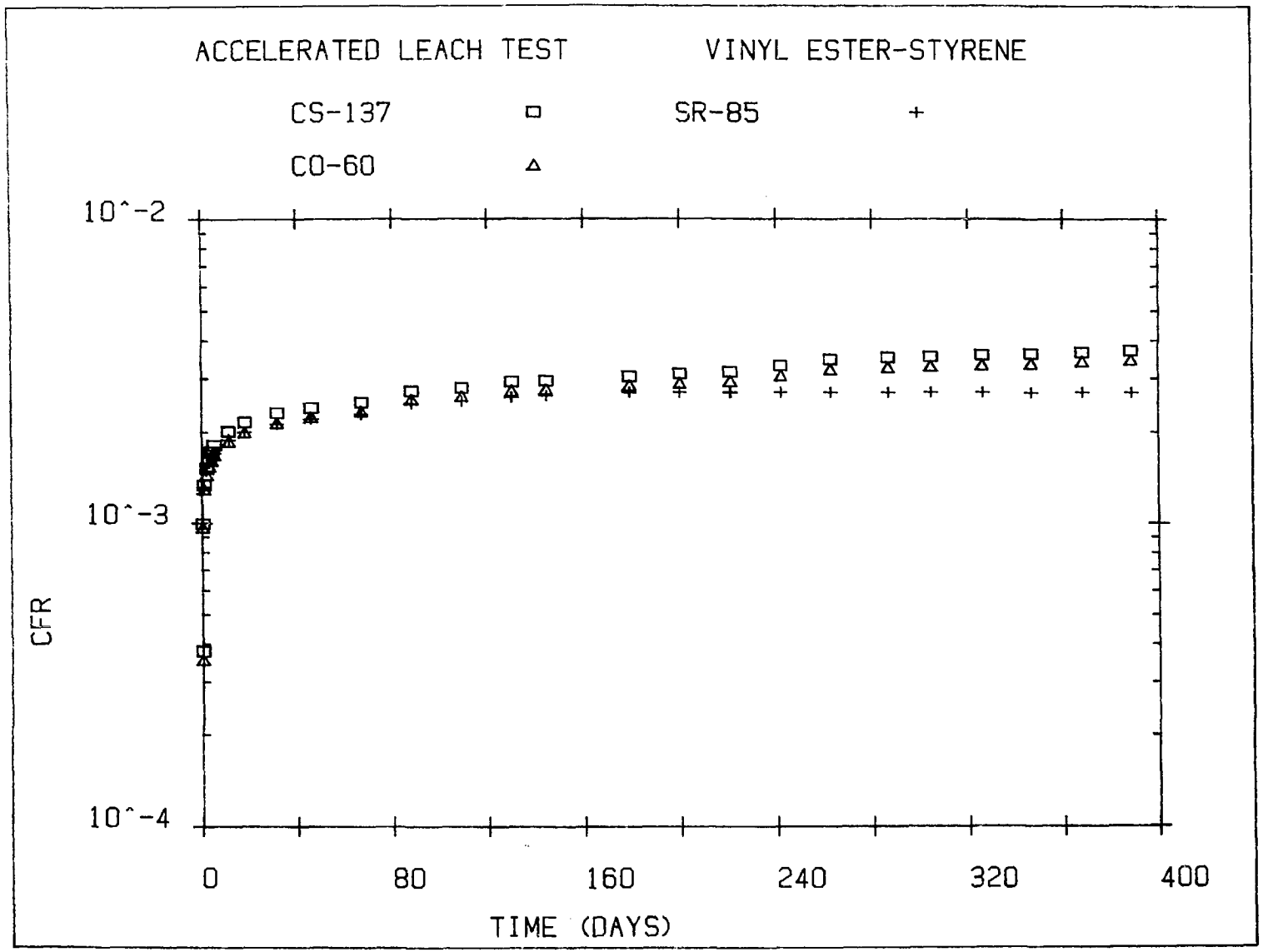

Figure 5.3 Cumulative fraction releases of Cs-137, Sr-85 and Co-60 from vinyl ester-styrene emulsion waste forms.

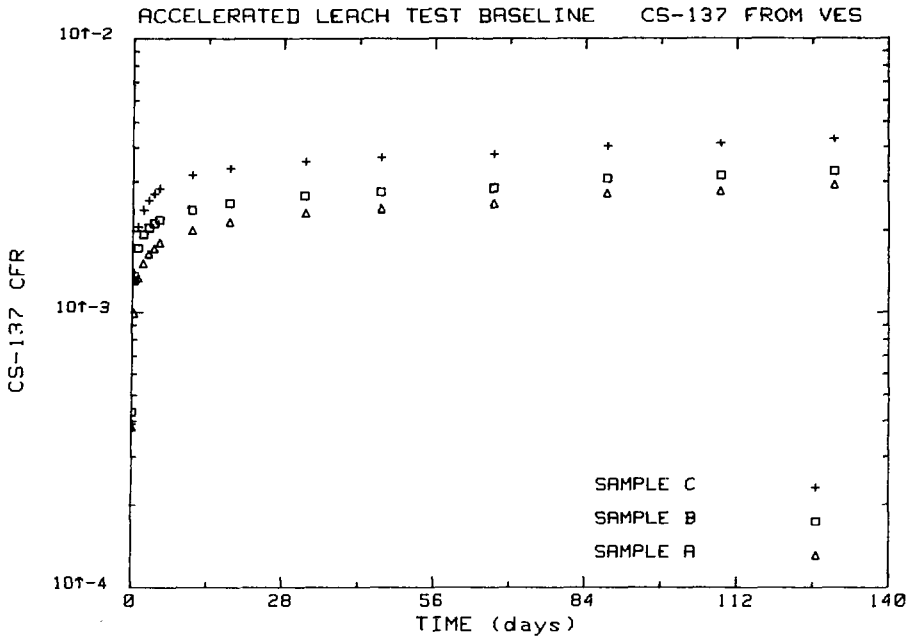

Figure 5.4a. Cumulative Fraction Release of ^{137}Cs, from triplicate VES waste forms.

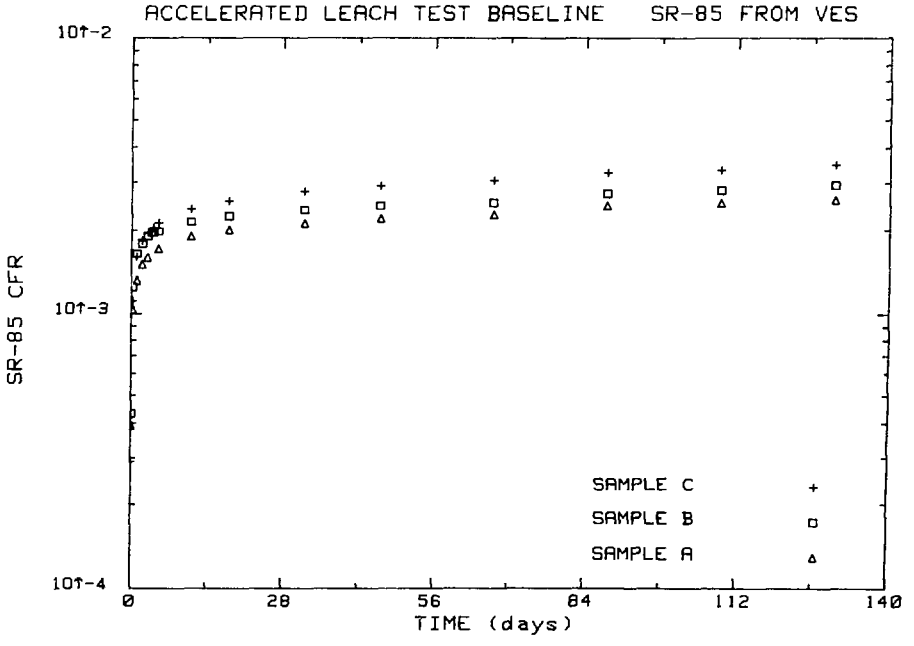

Figure 5.4b. Cumulative Fraction Release of ^{85}Sr, from triplicate VES waste forms.

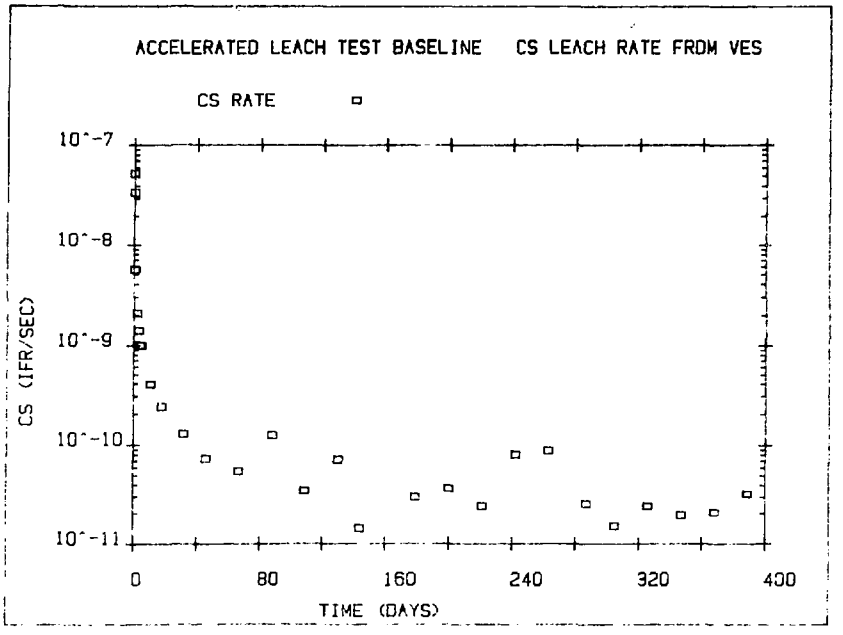

Figure 5.5a. Leach rate (Incremental Fraction Release/Leaching Interval Time) for ^{137}Cs from VES.

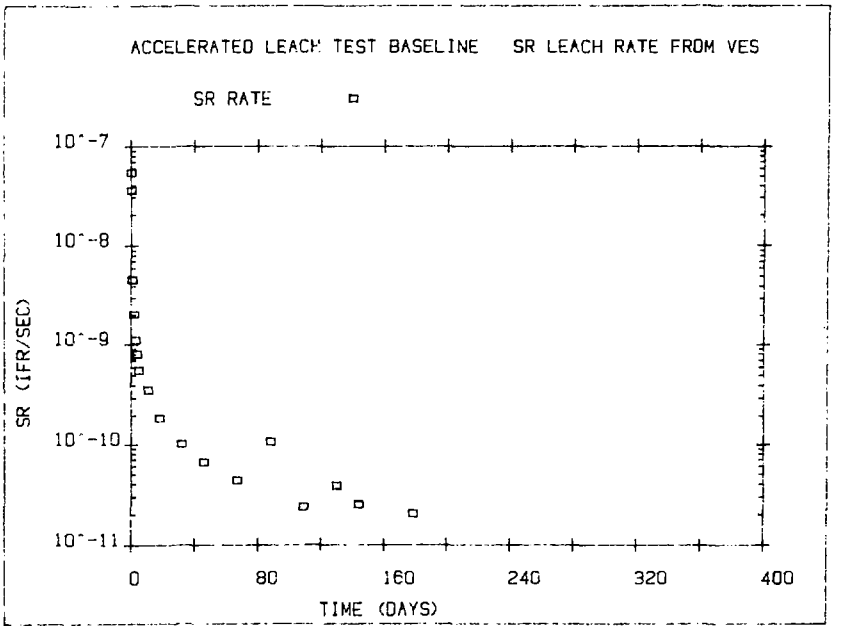

Figure 5.5b. Leach rate (Incremental Fraction Release/Leaching Interval Time) for ^{85}Sr from VES.

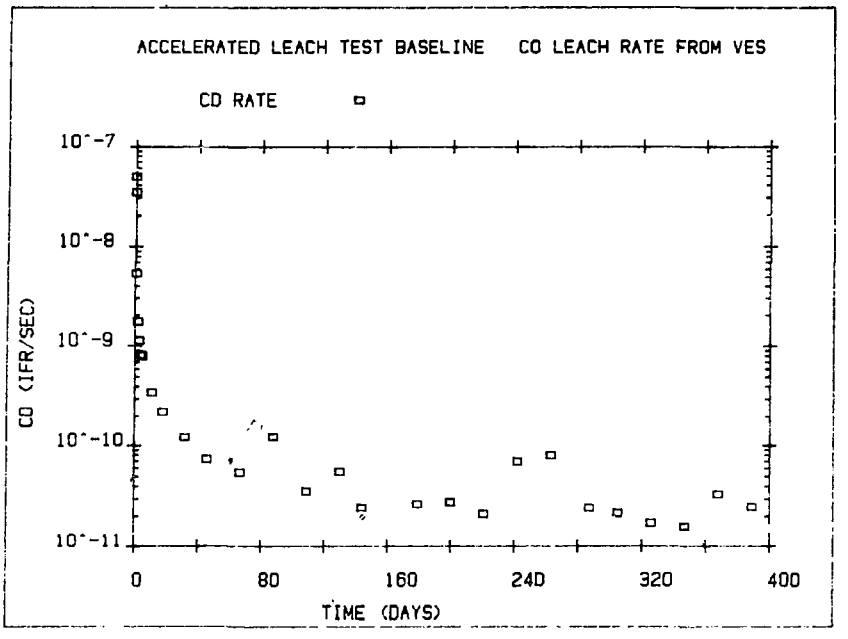

Figure 5.5c. Leach rate (Incremental Fraction Release/Leaching Interval Time) for ^{60}Co from VES.

5.1.3 Bitumen Leaching. Figure 5.6 shows CFR plotted against time for the three radionuclides leached from bitumen. Cumulative fraction releases are slightly lower than those from VES and there is greater variation among the isotopes used.

Replicate variability is shown for a shorter leaching interval in Figures 5.7a and 5.7b. The spread of releases from the three replicates is only slightly smaller than that of the different radionucildes. This implies that the difference in leach curves in Figure 5.6 is due to replicate variability rather than differences in radionuclide leachability.

Leach rates are shown for Cs-137, Sr-85 and Co-60 in Figures 5.8a, 5.8b and 5.8c, respectively. Again note that the Sr-85 leaching was below detection limits after 160 days.

5.2 Baseline Experiments - Leaching of Matrix Components

While the triplicate samples containing radionuclides were being leached similar samples without tracers were also leached. Leachates from these blank samples were analyzed for Si, Al, K, Na, Ca, Mg, Fe, Sr, Cs and alkalinity for all cement and selected VES and bitumen samples. Several VES and bitumen samples were also analyzed for Total Organic Carbon (TOC). In the case of both bitumen and VES, the TOC was less than 1.5 ppm. This indicates that mass loss due to matrix dissolution is insignificant. Similarly, analysis for Si, Al, K, Na, Ca, Mg, Fe, Sr, Cs and alkalinity gave concentrations below detection limits in bitumen and VES samples.

In cement leachates, Cs, Mg and Fe were not detected. However, measurable concentrations of other important elements are given in Table 5.1.

The data listed in Table 5.1 are plotted against the cumulative leaching time to determine the effect of leaching interval in the concentration of elements in the leachate. The data shown in Figures 5.9a-f, indicates that there is a pronounced effect of leaching interval on the elemental concentrations in the leachate. At the beginning of the experiment when the leaching intervals are short, the concentrations rose to a maximum. As the intervals become longer (24 hr), a decrease in concentration was observed. However, at the beginning of the one week interval, concentrations rose to a new maximum, followed by a slow decrease. The significance of this phenomenom in regard to the leaching behavior of waste forms is being investigated.

A similar set of samples was leached using the static MCC-3 Agitated Powder Test, to determine solubility limits of the cement matrix material. These results are shown Table 5.2. Elemental concentrations in leachates from the MCC-3 tests were compared to those from the modified ANS 16.1 tests to determine the degree of chemical saturation achieved by the ANS 16.1 samples. The highest concentration relative to saturation was 16% for Ca, 11.7% for Na, 10.8% for K and 4.1% for Sr. The concentrations of both Si and Al were significantly higher in the ANS 16.1 leachates than in those from the MCC-3 tests, in which these elements were below detection limits. The increased alkalinity in the MCC-3 leachates may have reduced the solubility of these elements relative to those of the ANS 16.1 tests or a back reaction may have developed which resulted in reprecipitation of Al and Si onto the solid sample. Reprecipitation of the mineral tobermorite has been observed in MCC-1 leach tests on cement[16].

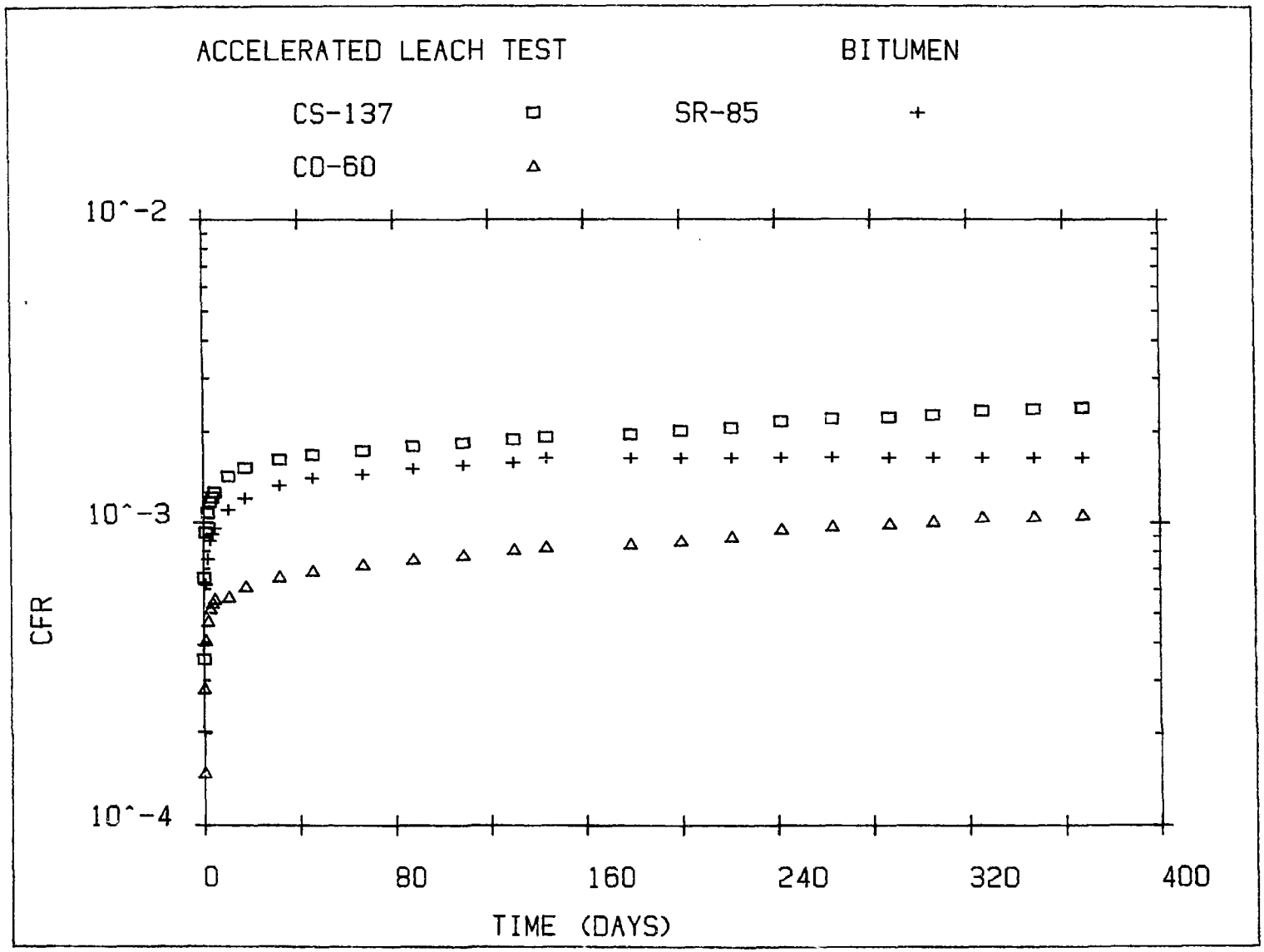

Figure 5.6. Cumulative Fraction Releases of ^{137}Cs, ^{85}Sr and ^{60}Co from bitumen.

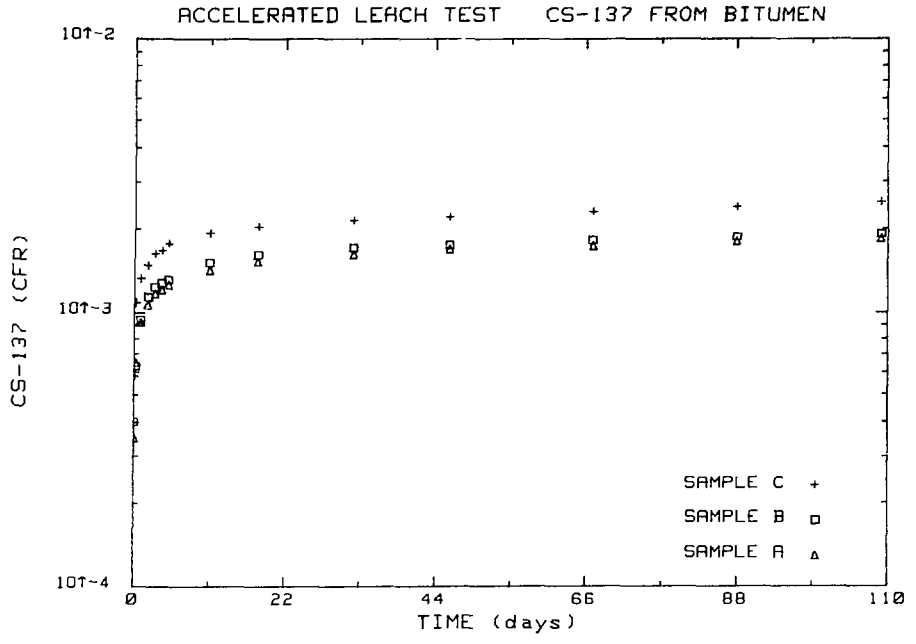

Figure 5.7a. Cumulative Fraction Releases of ^{137}Cs, from triplicate bitumen samples.

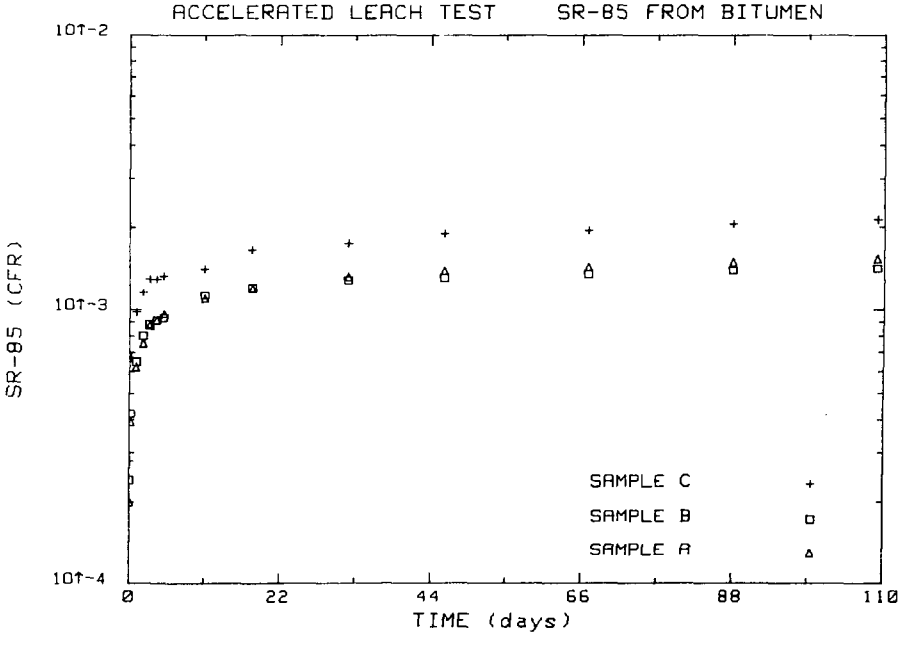

Figure 5.7b. Cumulative Fraction Releases of ^{85}Sr, from triplicate bitumen samples.

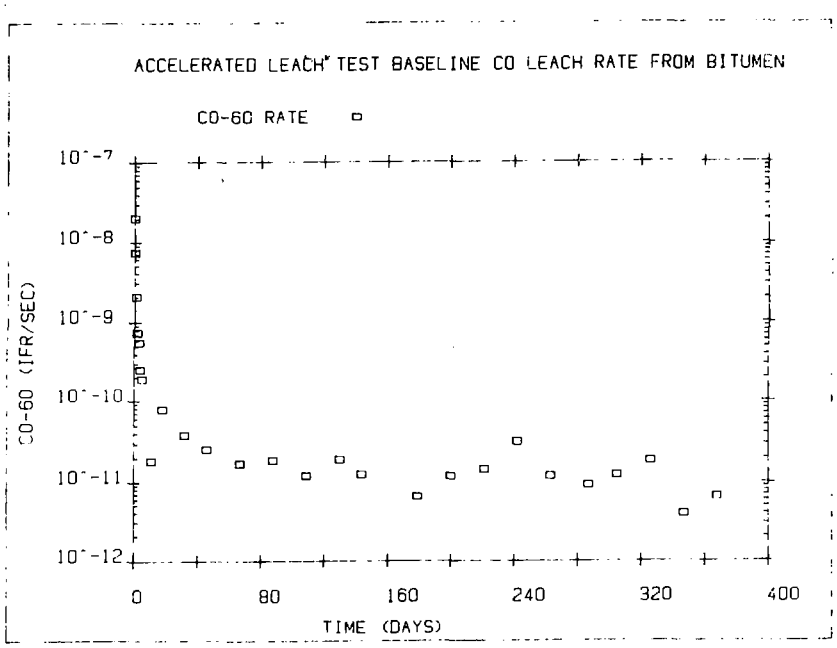

Figure 5.8a. Leach rate (Incremental Fraction Release/Leaching Interval Time) for ^{137}Cs from bitumen.

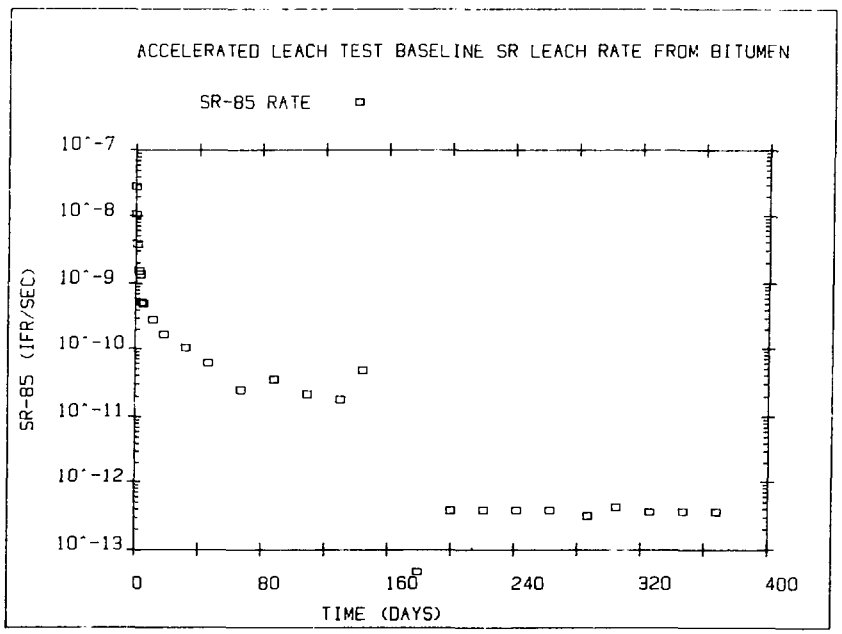

Figure 5.8b. Leach rate (Incremental Fraction Release/Leaching Interval Time) for ^{85}Sr from bitumen.

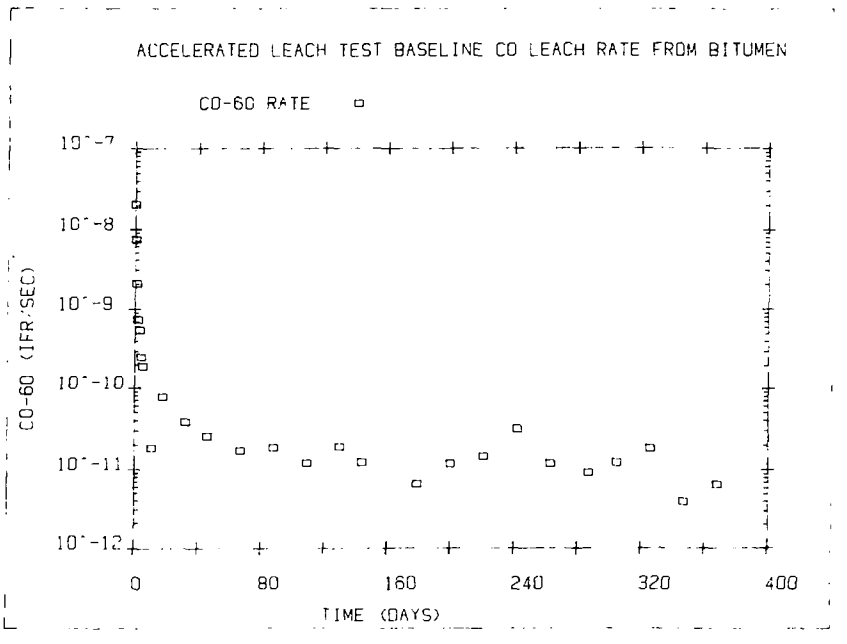

Figure 5.8c. Leach rate (Incremental Fraction Release/Leaching Interval Time) for ^{60}Co from bitumen.

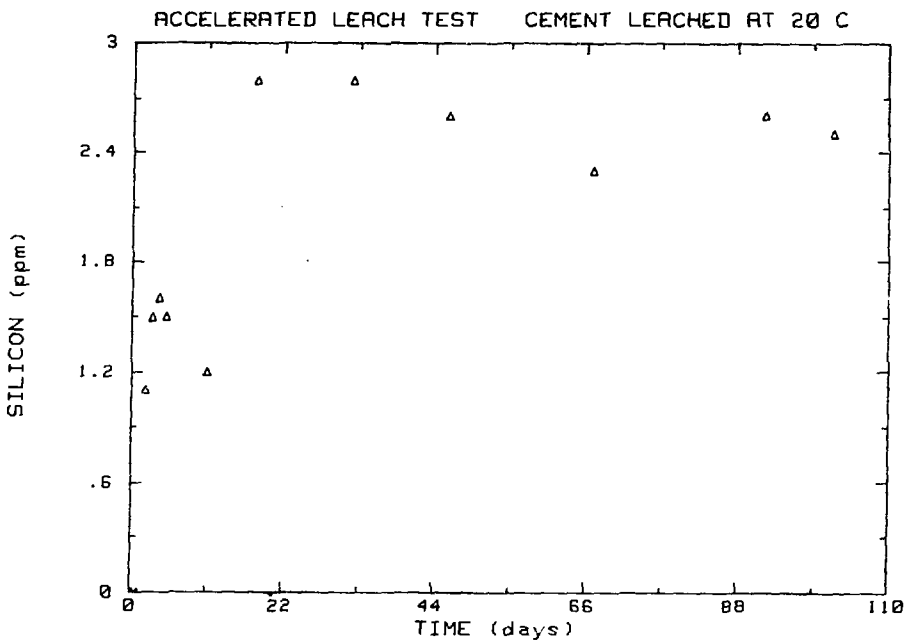

Figure 5.9a. Concentration of silicon in cement leachate for each sampling interval.

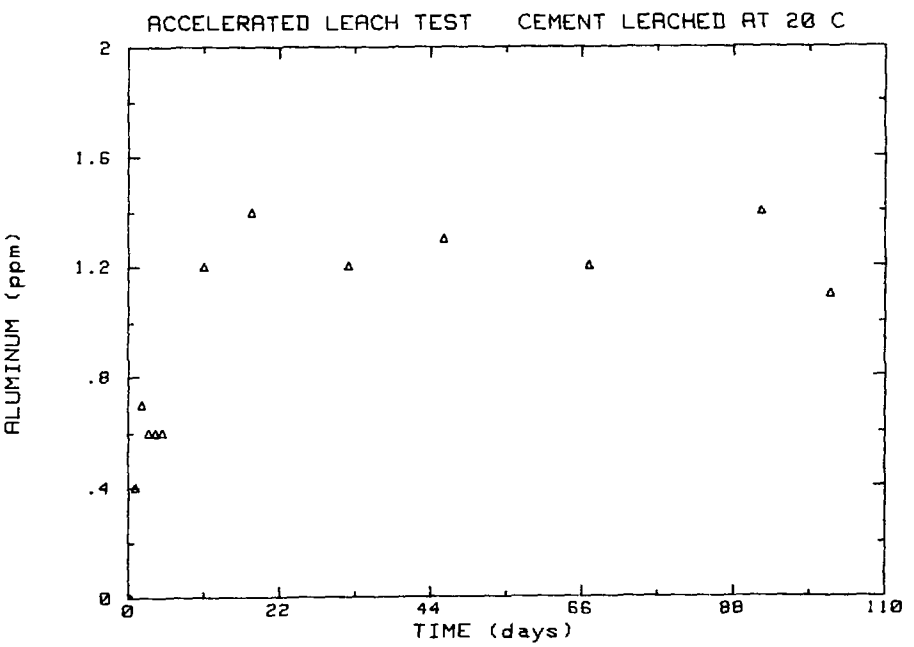

Figure 5.9b. Concentration of aluminum in cement leachate for each sampling interval.

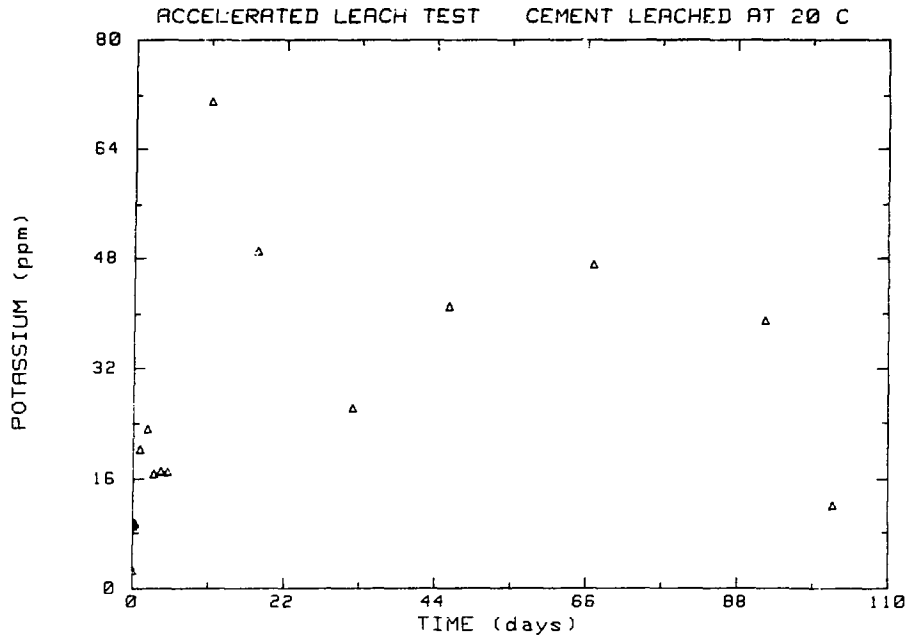

Figure 5.9c. Concentration of potassium in cement leachate for each sampling interval.

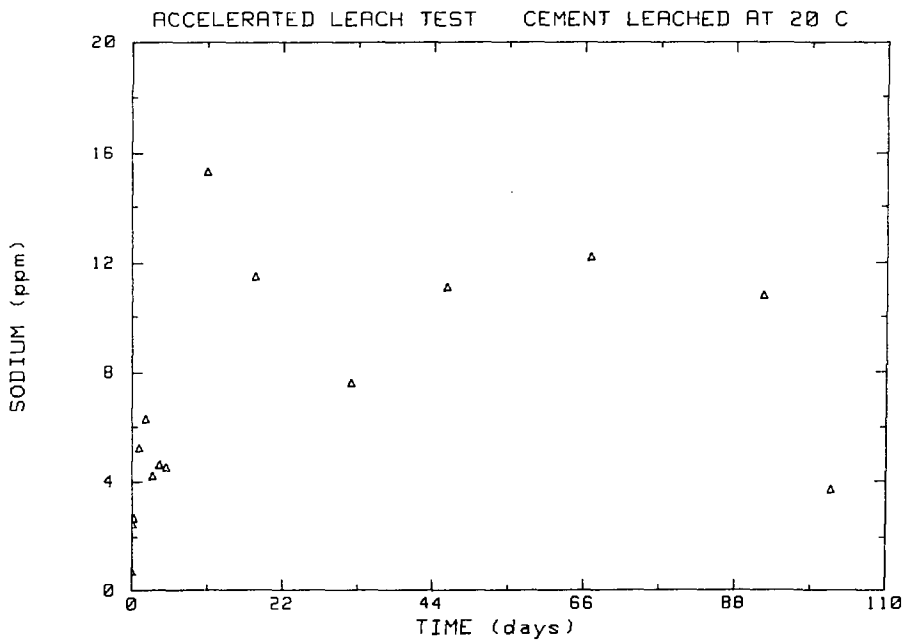

Figure 5.9d. Concentration of sodium in cement leachate for each sampling interval.

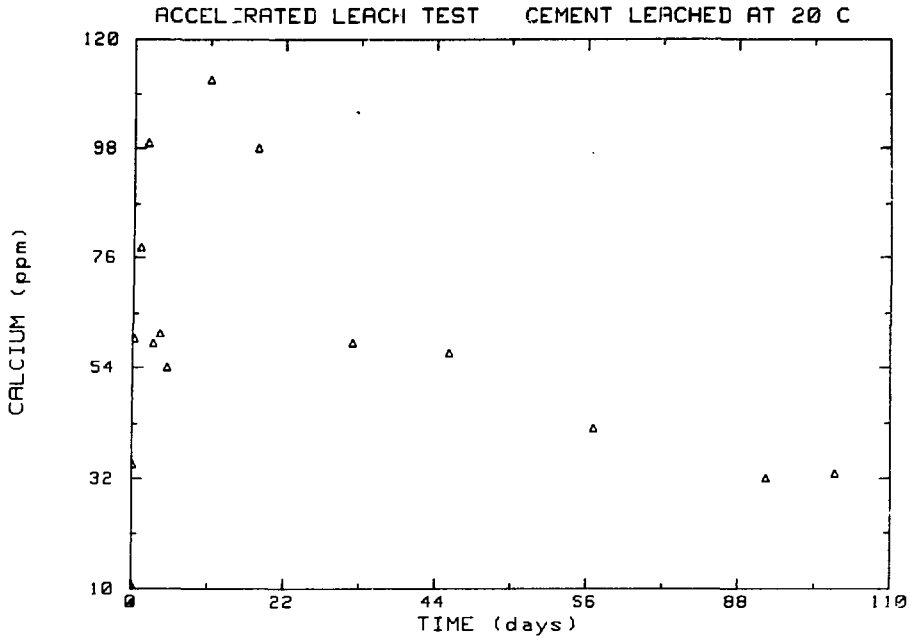

Figure 5.9e. Concentration of calcium in cement leachate for each sampling interval.

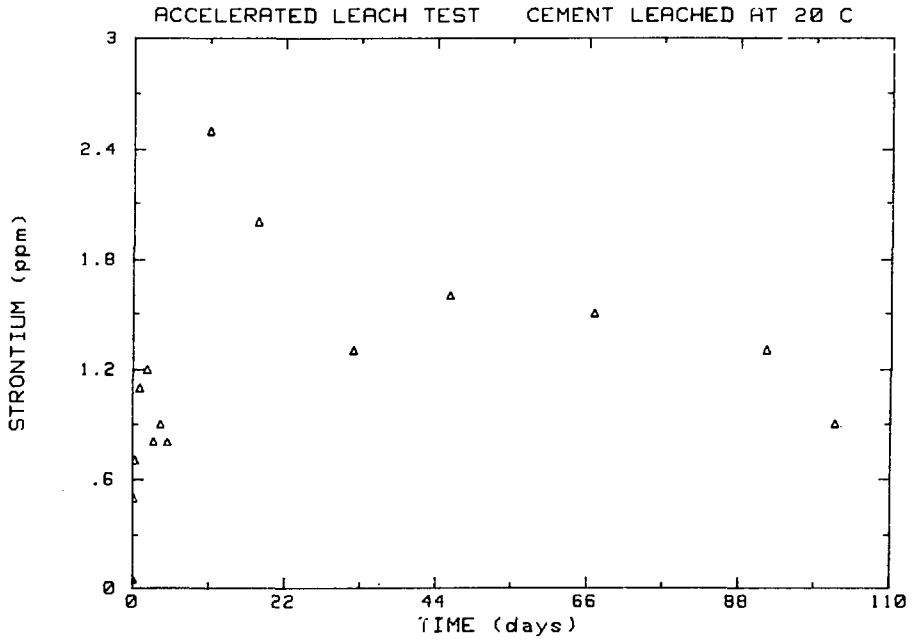

Figure 5.9f. Concentration of strontium (from the matrix material) in cement leachate for each sampling interval.

Table 5.1

Baseline Leaching Experiments
Elemental Analysis of Portland Cement Leachate

Time (days)	Int.	Ca(ppm)	Si(ppm)	Al(ppm)	Na(ppm)	K(ppm)	Sr(ppm)	Alkalinity
0.00	R	11	DL	DL	0.7	2.60	DL	DL
0.08	1	25	DL	DL	2.5	8.90	0.5	0.02
0.29	2	60	DL	DL	2.7	9.30	0.7	0.04
1.0	3	78	DL	DL	5.2	20.3	1.1	0.10
2.0	4	99	DL	0.7	6.3	23.2	1.2	0.10
3.0	5	59	1.5	0.6	4.2	17.7	0.8	0.07
4.0	6	61	1.6	0.6	4.6	17.1	0.9	0.07
5.0	7	54	1.5	0.6	4.5	17.0	0.8	0.05
11	8	112	1.2	1.2	15.3	71.	2.5	0.14
18	9	98	2.8	1.4	11.5	49	2.0	0.11
32	10	59	2.8	1.2	7.6	26	1.3	0.07
46	11	57	2.6	1.3	11.1	41	1.6	0.08
67	12	42	2.3	1.2	12.2	47	1.5	0.06
88	13	32	2.6	1.4	10.8	39	1.3	0.06
109	14	33	2.5	1.1	3.7	12	0.9	0.04

DL=Detection Limit
Alkalinity reported as mg $CaCO_3$/ml

Table 5.2

Baseline Leaching Experiments

MCC-3 Agitated Powder Test for Saturation Limits

Time	Ca(ppm)	Si(ppm)[1]	Al(ppm)[2]	Na(ppm)	K(ppm)	Sr(ppm)	Cs(ppm)[3]	Mg(ppm)[4]	Alkalinity[5]
1	730	DL	DL	129	215	58	DL	DL	1.10
2	695	DL	DL	130	215	61	DL	DL	1.07
3	690	DL	DL	131	214	63	DL	DL	1.05
4	670	DL	DL	133	218	-	DL	DL	1.06

[1]Detection Limit for Si - 1.0 ppm.
[2]Detection Limit for Al - 0.6 ppm.
[3]Detection Limit for Cs - 0.4 ppm.
[4]Detection Limit for Mg - 0.5 ppm.
[5]Results reported as mg $CaCO_3$/ml.

Statistical comparisons of concentrations of radionuclides and cement matrix components in leachates give insight into the relationships among elemental releases. Plotting elemental concentrations against one another provides the comparison in that the more linear the plotted values are, the closer is the relationship between elemental releases. This relationship can also be expressed as R, the correlation coefficient, which approaches 1 as the correlation improves. For example, the plot in Figure 5.10a shows an uncorrelated relationship for K and Si while Figure 5.10b indicates a relatively close correlation between K and Sr releases. Table 5.3 is a correlation matrix in which R values are listed for all combinations of the leachate components.

Correlation coefficents for Al/Si = 0.91, Na/Sr = 0.94, K/Sr = 0.96, K/Na = 0.99 and alkalinity/Ca = 0.92, were determined in this study. Values of R greater than 0.9 typically indicate a significant correlation. It is particularly noteworthy that the correlation between the leaching of the Sr-85 tracer and the nonradioactive Sr contained in the cement is poor; the R value is -0.08. Comparisons of this data with that of matrix elements released under accelerated conditions may help to determine if mechanistic changes are occurring.

5.3 Baseline Leaching Experiments - Solid Phase Analysis

Solid phase analysis of baseline samples can only be performed when the long-term leaching study is terminated. A decision point of December, 1985 has been set to evaluate the leaching results of the experiment. At this time a determination will be made regarding continuation of the leaching tests. Solid phase analysis will begin at termination of the leaching experiments.

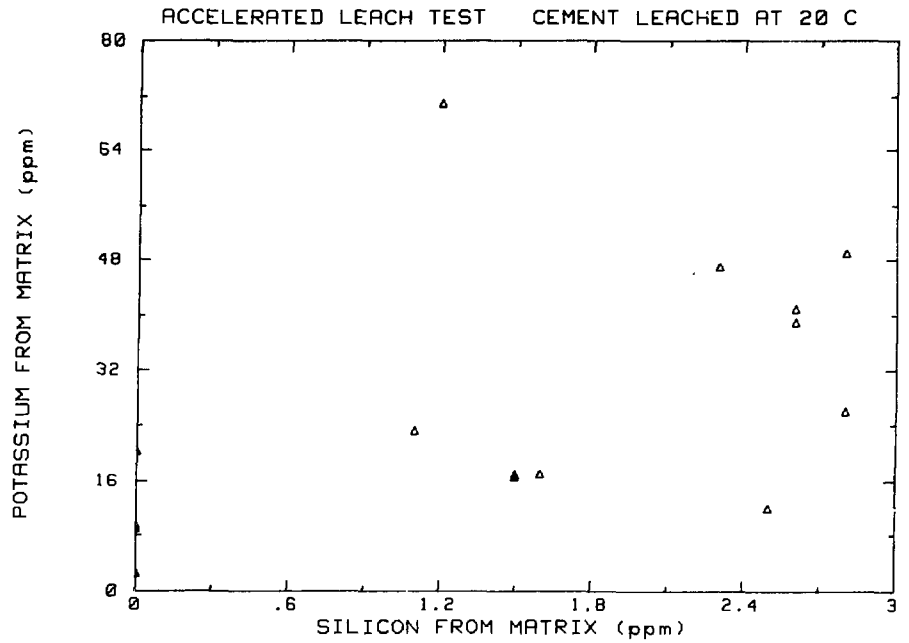

Figure 5.10a. Potassium concentration in cement leachate plotted against silicon concentration. R = 0.50.

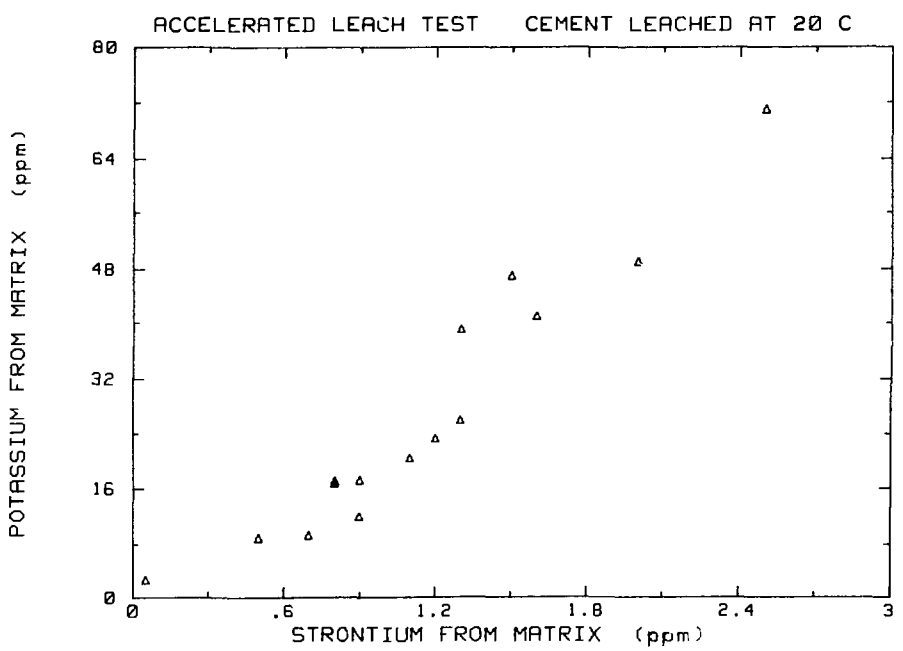

Figure 5.10b. Potassium concentration in cement leachate plotted against strontium leached from cement. R = 0.96.

Table 5.3

Baseline Leaching Experiments

Correlation Matrix of Elemental Releases From Portland Cement Leached at 20°C

	Aluminum	Silicon	Strontium	Sodium	Potassium	^{137}Cs	^{85}Sr	Alkalinity
Calcium	0.29	0.06	0.72	0.51	0.57	0.28	0.18	0.92
Aluminum		0.91	0.79	0.83	0.77	0.59	-0.32	0.56
Silicon			0.53	0.59	0.50	0.61	-0.33	0.29
Strontium				0.94	0.96	0.52	-0.08	0.87
Sodium					0.99	0.50	-0.15	0.73
Potassium						0.48	-0.08	0.76
^{137}Cs							0.44	0.33
^{85}Sr								-0.05

6. TESTING AND EVALUATION OF LEACH RATE CONTROLLING FACTORS

Factors that may accelerate leaching from low-level waste forms have been identified in Reference 1. These include elevated temperature, increased specimen surface area, decreased ratio of waste form surface area to leachant volume, increased flow or replacement frequency and leachant composition.

An experimental program was initiated to investigate the ability of these factors to accelerate leaching, without altering the leaching mechanism. The first potential accelerating factor studied was temperature because it is well understood theoretically. A short term scoping study of temperature was completed, results of which are reported in this section. This study will be followed by a more detailed investigation that will concentrate on those temperatures that were identified in the scoping study to be optimal for the various matrix materials. This expanded work will seek long-term temperature effects not observable in a short-term scoping study.

6.1 Temperature Effects Scoping Study-Radionuclide Leaching Results

6.1.1 Portland Cement. Portland cement samples containing Cs-137, Sr-85 and Co-57 were leached in distilled water at 20°, 30°, 40°, 50° and 70°C for 18 days. Results are presented in Figure 6.1. Releases of Cs-137 increased as temperature increased. After 18 days of leaching at 70°C 86% of the Cs-137 was leached compared to 73% after 368 days at 20°C (see Figure 5.1a). This is more than a twenty-fold acceleration of leaching.

To determine if the leaching mechanisms remain unchanged at elevated temperatures, cumulative fraction release (CFR) from the 20°C leaching curve was plotted against CFR from each of the leaching curves obtained at temperatures above 20°C. Figure 6.2 shows this type of plot for Cs-137 released from cement samples at 20°, 30°, 40°, 50° and 70°C. The 20°C curve is perfectly linear since it is comprised of the 20°C data plotted against itself. The curves for 30°, 40° and 50°C are also linear, suggesting that the leaching mechanism remains unchanged at these temperatures. The slopes of the lines decrease with increasing temperature, indicating that the leach rates have increased. The 70°C curve becomes non-linear above approximately 60% release, at which point the leach rate declines more than expected as leaching continues. This change may be attributed to the depletion of Cs-137 in the sample or it may reflect a change in the leaching mechanism itself. Since the 50°C curve remains linear to a cumulative release of 64%, there is some doubt that depletion is the sole cause for the decrease in leach rate at 70°C. Further work is planned to elucidate this phenomenon.

A further analysis of the data is shown in the Arrhenius plot, Figure 6.3, where the log (base 10) of the final incremental leach rate (the leach rate was taken as the rate between the last two points of each curve on Figure 6.1) is plotted against 1/T; where T is the absolute temperature in degrees Kelvin. If the changes in leach rate result from an activated process, then the points should fall on a straight line. The data in Figure 6.3 shows that this occurs for leaching up to 50°C, whereas, the 70°C point fell significantly off the line. This is consistent with the results shown in Figure 6.2 in which the last two data points for the 70°C curve are clearly not colinear

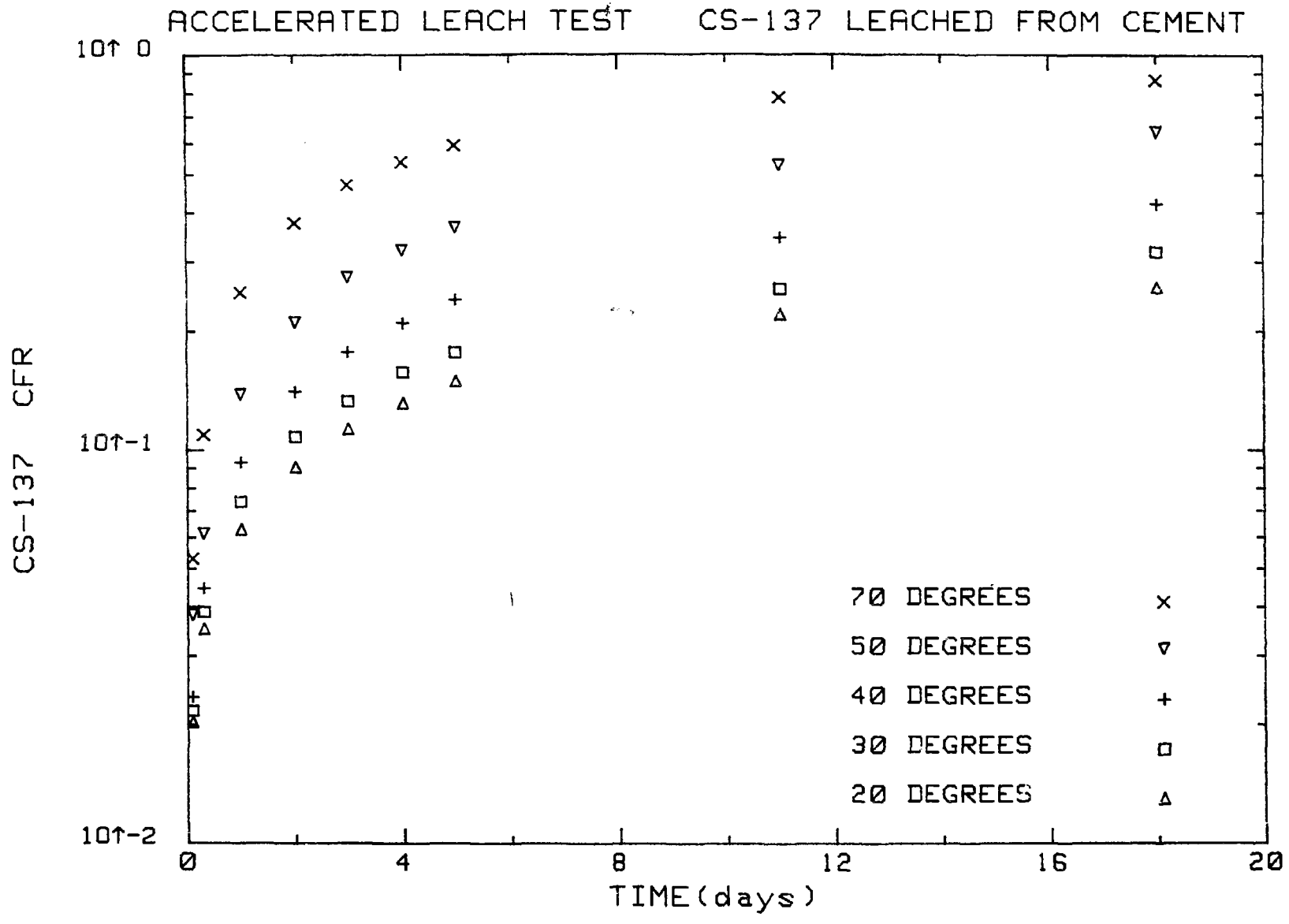

Figure 6.1. Cumulative Fraction Releases (CFR) of ^{137}Cs from cement waste forms leached 20°, 30°, 40°, 50° and $70^{o}C$. Note the $70^{o}C$ curve is not linear.

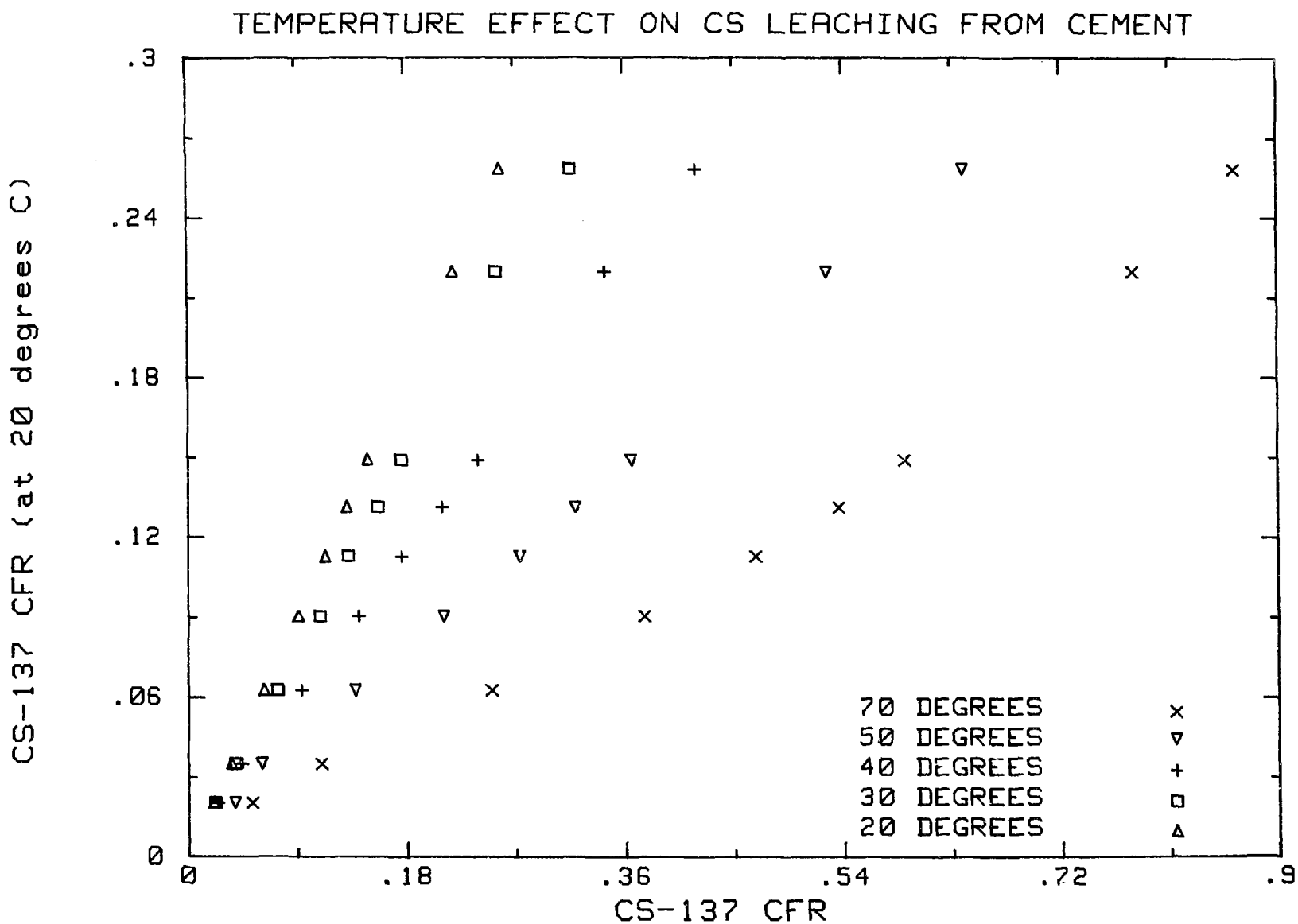

Figure 6.2. Cumulative Fraction Releases (CFR) of ^{137}Cs from portland cement leached at $20^{o}C$ (baseline) is plotted against CFR of samples leached at 20°, 30°, 40°, 50° and $70^{o}C$. Note that the $70^{o}C$ curve is not linear.

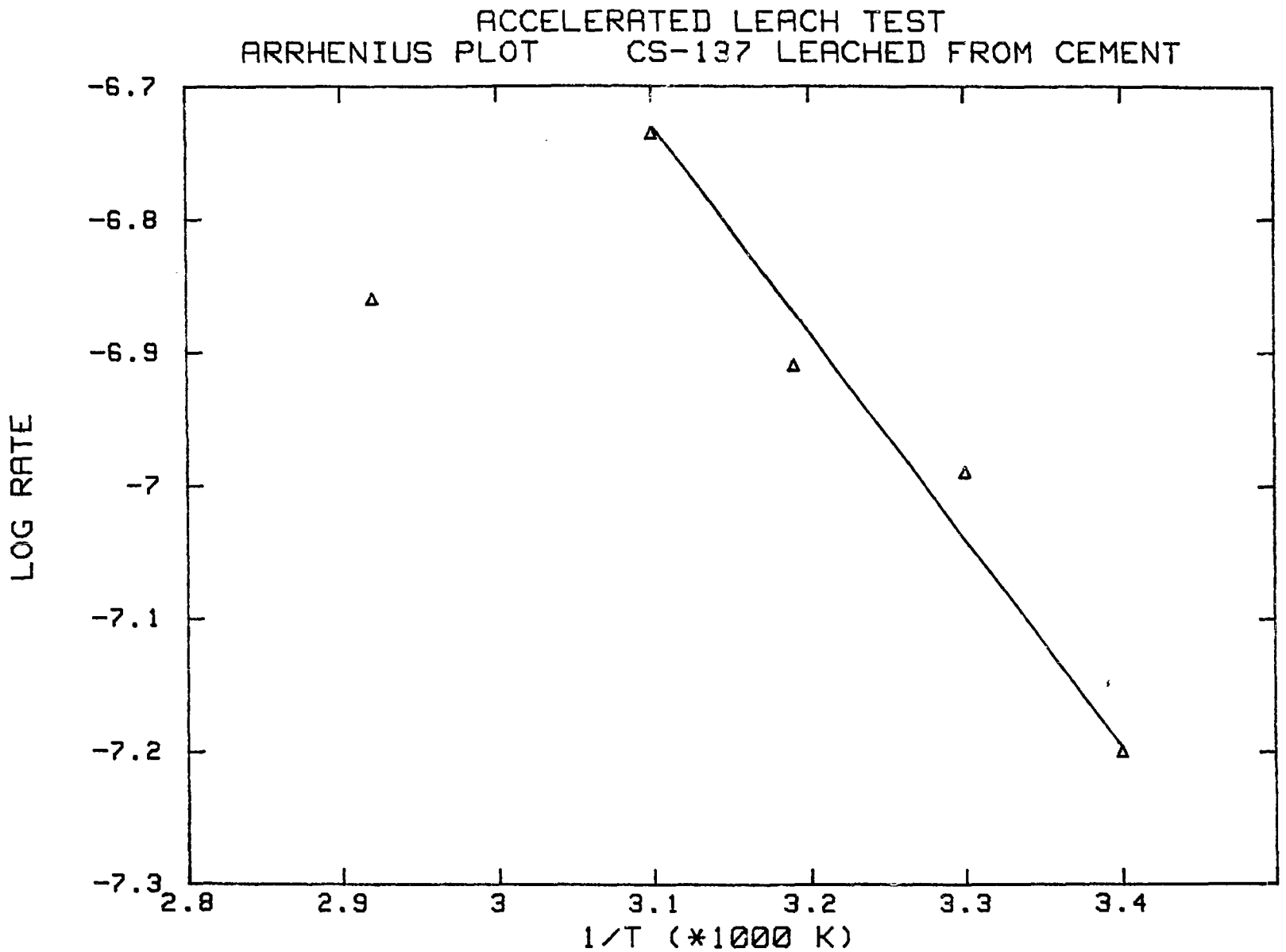

Figure 6.3. Arrhenius plot of the log of the leach rate. The rate was taken between the last two sampling intervals of cement samples leached at 20°, 30°, 40°, 50° and 70°C.

with the rest of the 20°C data. In contrast, all of the data points for the lower temperature curves are colinear. The activation energy calculated from the slope of the line in Figure 6.3 is 16 joules/mole (4.0 kcal/mole) which is similar to values previously reported by other researchers for cement leaching[5,16].

A value of 17-21 joules/mole (4-5 Kcal/mole) is typical for diffusion in aqueous solutions[11]. On this basis, leaching of cesium from cement is consistent with diffusion through the water which permeates the porous cement waste form during leaching.

Leaching of Sr-85 from cement is also accelerated by temperature, as shown in Figure 6.4. After 18 days at 70°C, 8.5% of the Sr-85 was released compared to 4.4% released in 368 days at 20°C. The 20°, 30°, 40° and 50°C curves, Figure 6.4, all show similar CFR's, although the 40°C curve appears anomalously high. Preliminary analysis indicates that the data obtained at 40°C is within the experimental error. This is indicated by noting the spread of the replicate curves in Figure 5.2.

Figure 6.5 shows the Sr-85 data from Figure 6.4 plotted relative to 20°C data. Although an increase in leachability is evident between the 70°C data and those obtained at lower temperatures, the increase is not monotonic as it was for Cs leaching. In contrast to the 70°C Cs plot which showed decreased leaching in the latter part of the experiment, the 70°C Sr plot indicates increased leaching in the latter part of the experiment.

Since the fractional releases for Sr-85 are quite small, the errors inherent to the leaching experiment make interpretation difficult at this point. Preliminary experiments have indicated that leaching of Sr-85 can be accelerated by temperature but, the effect is not as great as that for cesium.

Other workers have found that the effective diffusion coefficient, D, and therefore, the leach rate of cement waste forms increase due to both increased leaching temperature[17] and increased cure temperature[18]. The increase in D during leaching at elevated temperature has been attributed to an irreversible change in the cement pore structure upon heating[18]. Such physical changes should not change the leaching mechanism even though the leach rate is increased. However, it has not been reported whether the leaching at elevated temperature of cement samples cured at elevated temperature results in further changes in pore structure.

Over the temperature range of liquid water, evidence is available that cure temperature has no significant effect on the chemical and physical nature of the hydration products of portland cement[19]. Thus, there may be no limitations imposed by the nature of the cement to the use of increased temperature to accelerate leaching.

6.1.2 Vinyl Ester-Styrene . Release of radionuclides from vinyl ester-styrene emulsion waste forms was affected by temperature in a complex way. Figure 6.6 shows leaching curves for Cs-137 at various temperatures. All samples leached at elevated temperatures show significantly greater releases than did the 20°C baseline samples. However, the variability of cumulative

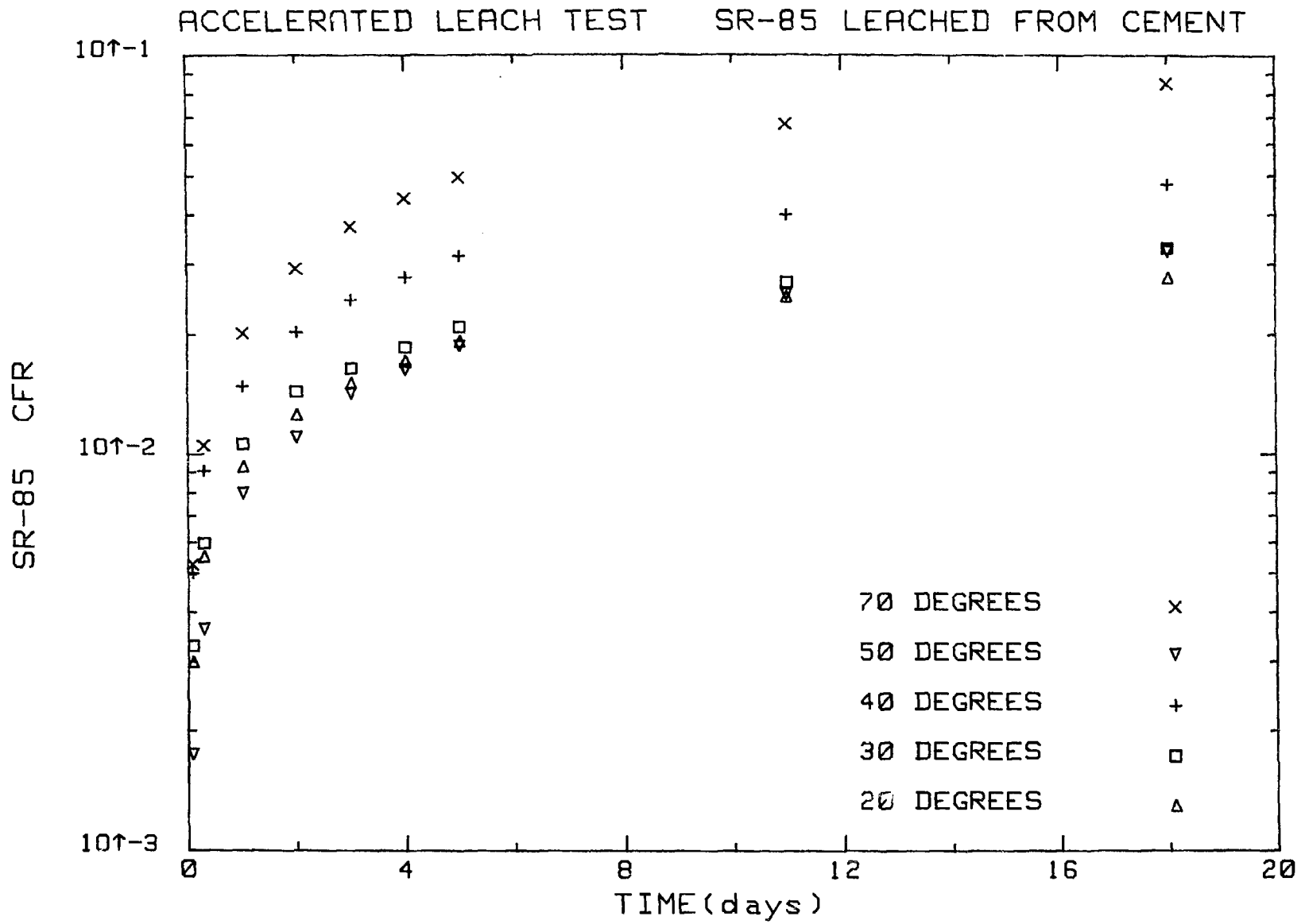

Figure 6.4. Cumulative Fraction Release of ^{85}Sr from cement waste forms at 20°, 30°, 40°, 50° and 70°C.

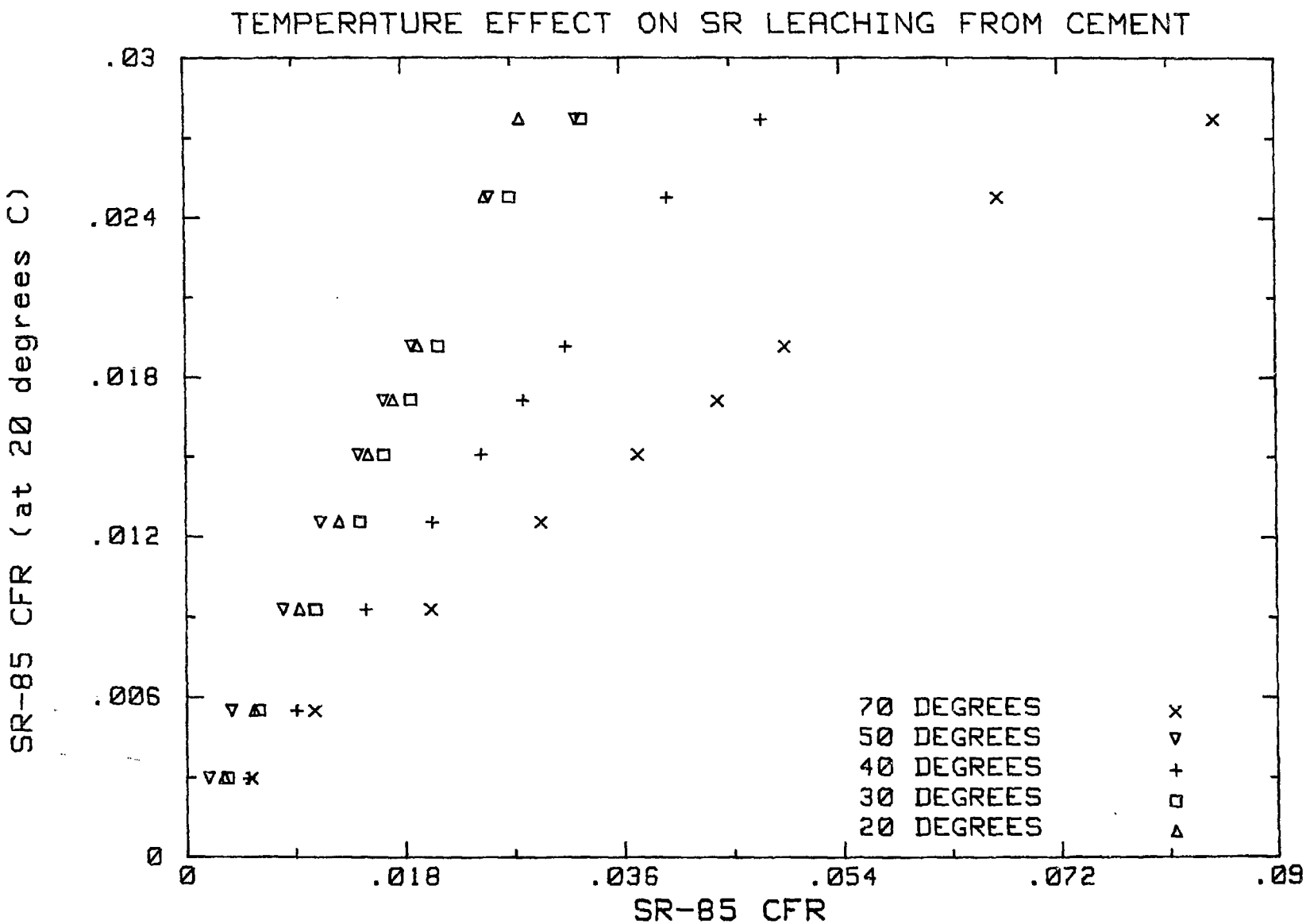

Figure 6.5. Cumulative Fraction Releases (CFR) of ^{85}Sr from portland cement leached at 20°C (baseline) plotted against CFR of samples leached at 20°, 30°, 40°, 50° and 70°C.

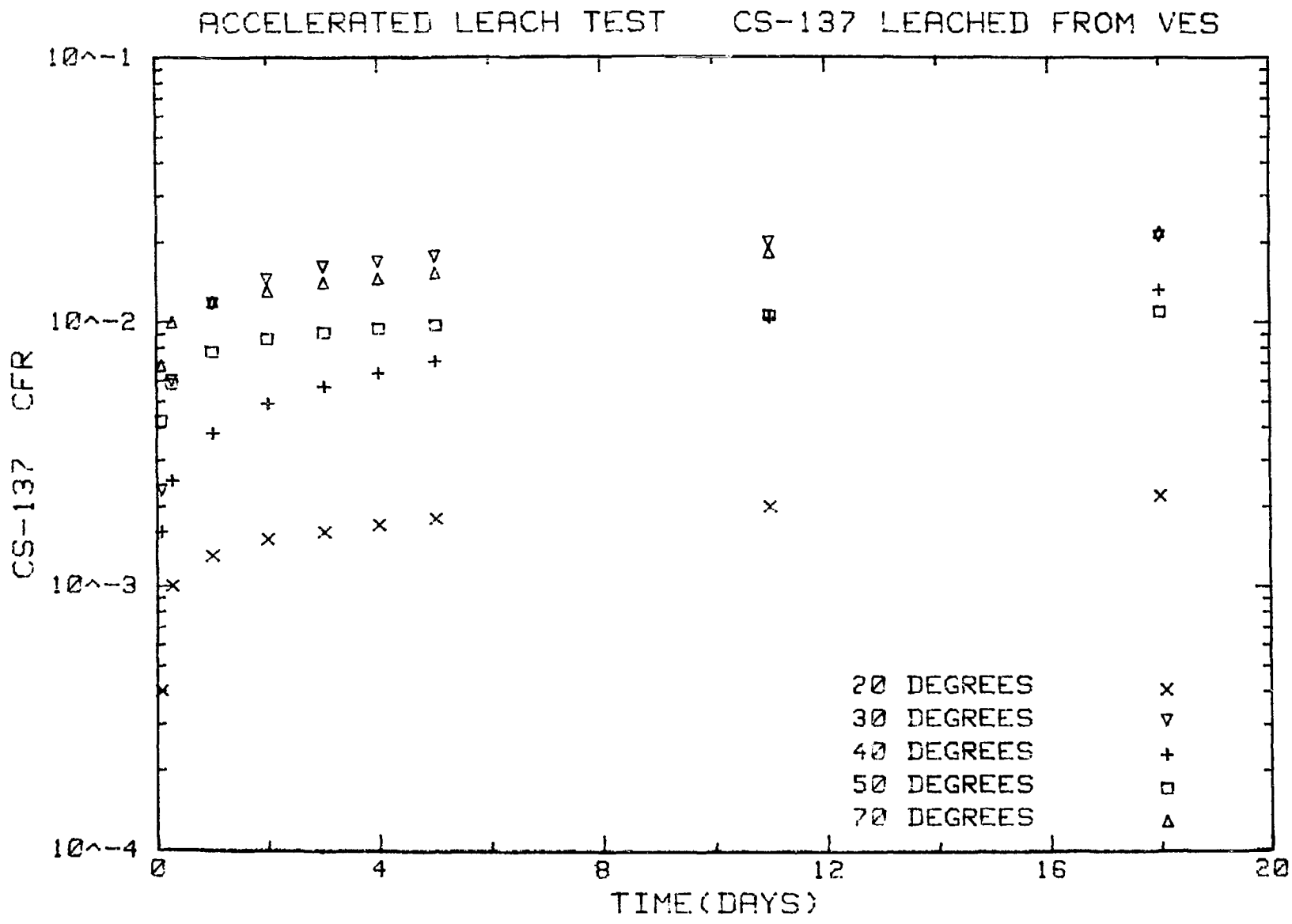

Figure 6.6. Cumulative Fraction Releases of ^{137}Cs plotted against time for samples leached from VES at 20°, 30°, 40°, 50° and 70°C.

fraction releases from replicates is also much greater, making temperature effects on leaching from this material uncertain. The average release from the 30°C samples is just less than the 70°C sample and greater than that of the 40° and 50°C samples. The scatter for Cs-137 and Sr-85 among three samples leached at 50°C is shown in Figure 6.7a and 6.7b. A plot of CFR at 20°C vs CFR at elevated temperature, Figure 6.8, shows no systematic change in the data with the exception that leaching slows down substantially with increasing time.

Releases of Sr-85 from VES are similar to those observed with Cs-137. Leaching is accelerated at temperatures greater than 20°C. Most of the acceleration occurs between 20°C and 30°C with little additional acceleration taking place at higher temperatures. Figure 6.9 shows CFR plotted against time for Sr-85 at 20°, 40°, 50° and 70°C while Figure 6.10 shows CFR at 20°C plotted against CFR at the elevated temperatures. Results for Co releases from VES samples are similar to those of Cs and Sr, as shown in Figures 6.11 and 6.12.

All samples tested at elevated temperatures leached at a slightly greater rate than those in the baseline experiment. However, the large spread between replicate samples and the lack of any monotonic change in leaching with increasing temperature indicate that leaching from VES does not accelerate with increased temperature. This failure to respond to temperature as an accelerating factor may be related to changes induced in the structure of the matrix material caused by elevated temperatures. Pre-treatment of VES samples at some temperature greater than that at which they are leached may be required before the temperature effect, if any, can be seen.

6.1.3 Bitumen. Cumulative fraction releases of Cs-137 from bitumen samples leached at 20°, 30° and 50°C are shown in Figure 6.13. Bitumen was not leached at 70°C because at that temperature it begins to deform severely. As with VES samples, the fraction release is very small compared to the inherent variability in the leaching system. For Cs-137, releases from samples leached at 30°C and 50°C fall on either side of the 20°C baseline data. It appears that temperature has no accelerating effect on Cs leaching from bitumen. Releases of Sr-85 from bitumen, shown in Figure 6.14, are comparable to those of Cs-137 while Figure 6.15 shows cumulative fraction releases for Co-57 from bitumen at 20°, 30°, and 50°C. No leaching acceleration occurred for any of the isotopes used. Cobalt leaching, however, averaged slightly less than that of Sr-137 and Cs-137.

The lack of temperature effect on leaching of bitumen may be attributed to several factors. Radionuclides, even at tracer quantities are presumably held in the bitumen matrix as salt particles, with each particle coated by the matrix. Bitumen has a low permeability to water and this low permeability does not appear to be affected by temperature over the temperature range and time period tested.

6.2 Temperature Effects Scoping Study - Matrix Leaching Results

During leaching not only are the waste components released from the waste form but some portion of the matrix itself is leached. For VES and bitumen this was found to be negligible. The highest value detected for total organic carbon (TOC) was 1.5 ppm. However, significant releases of some elements

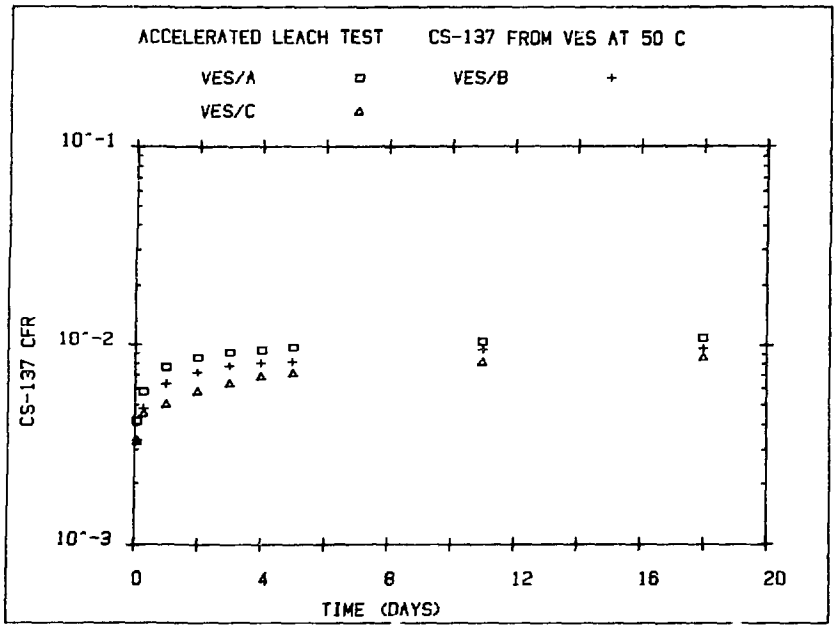

Figure 6.7a. Cumulative Fraction Release of ^{137}Cs from Triplicate VES Samples Leached at 50°C.

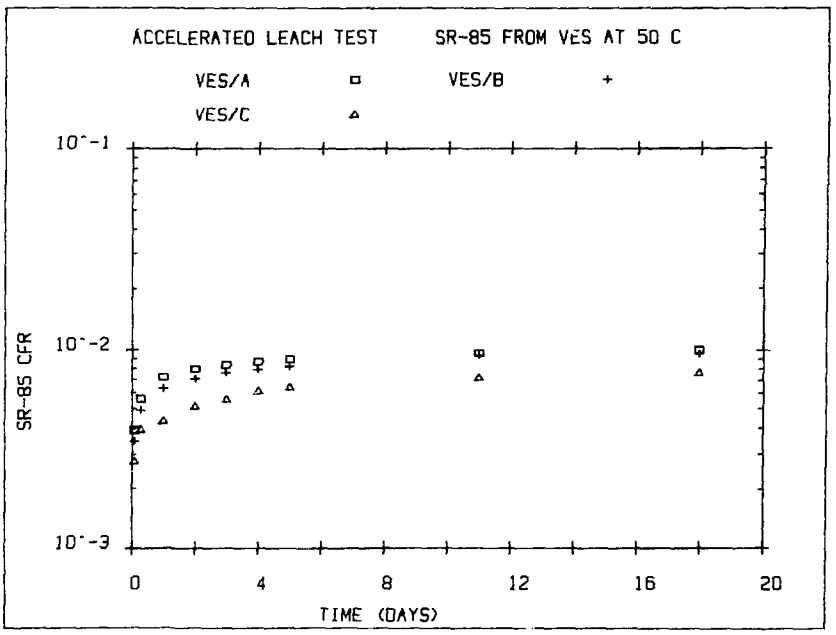

Figure 6.7b. Cumulative Fraction Release of ^{85}Sr from Triplicate VES Samples Leached at 50°C.

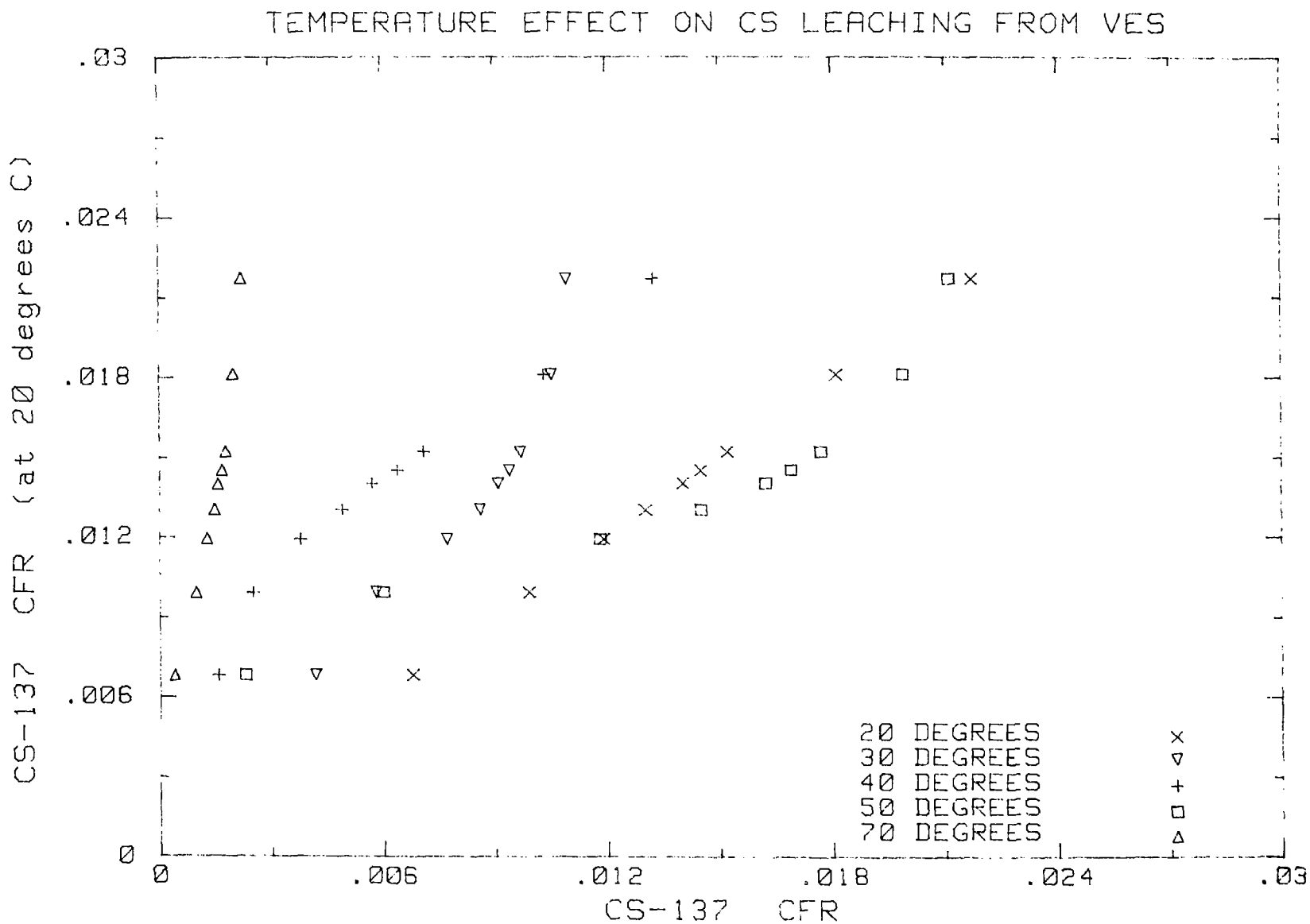

Figure 6.8. Cumulative Fraction Release (CFR) of ^{137}Cs leached from VES at 20°C (baseline) plotted against CFR of samples leached at 20°, 30°, 40°, 50° and 70°C.

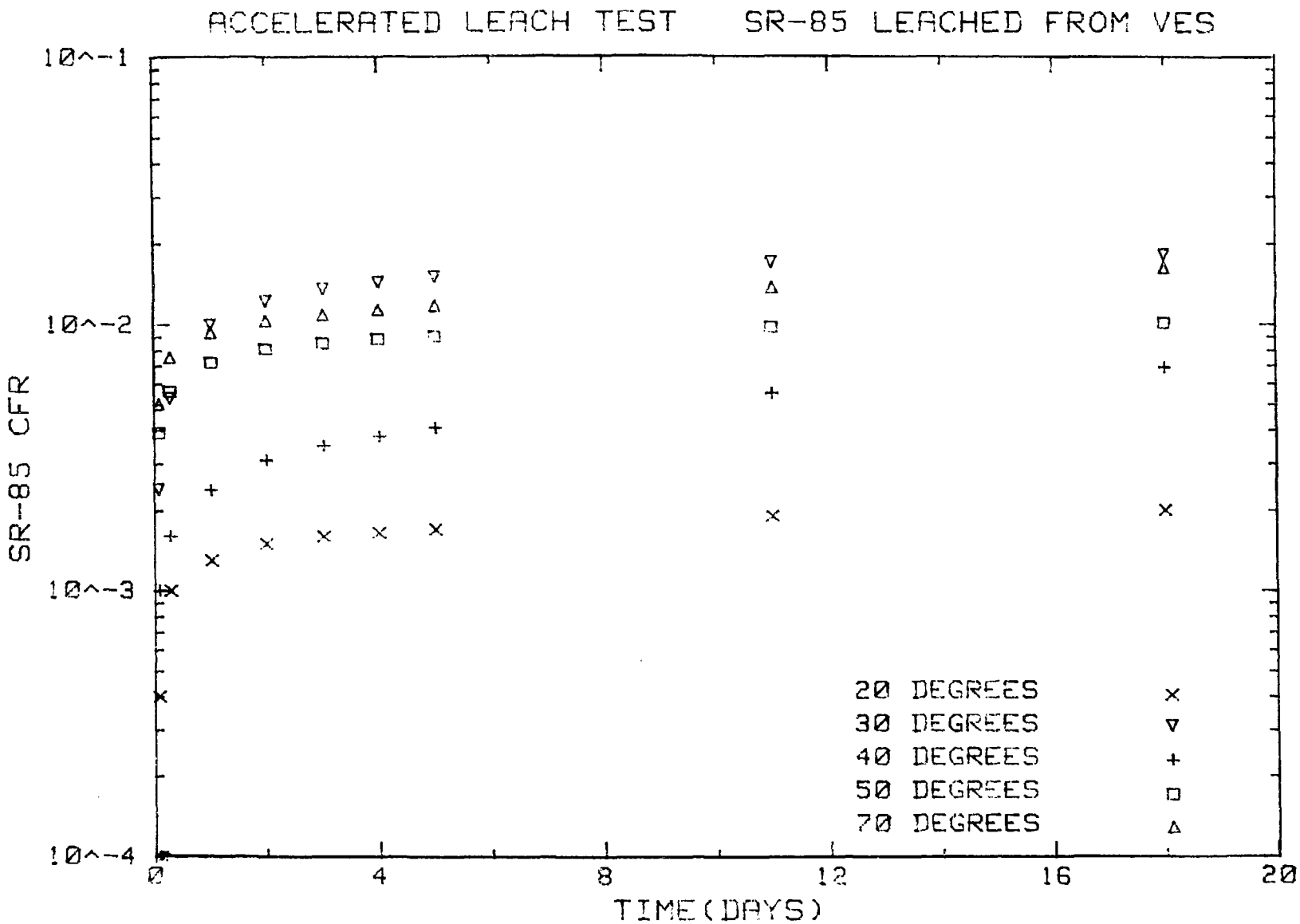

Figure 6.9. Cumulative Fraction Release (CFR) of ^{85}Sr plotted against time for samples leached from VES at 20°, 30°, 40°, 50° and 70°C.

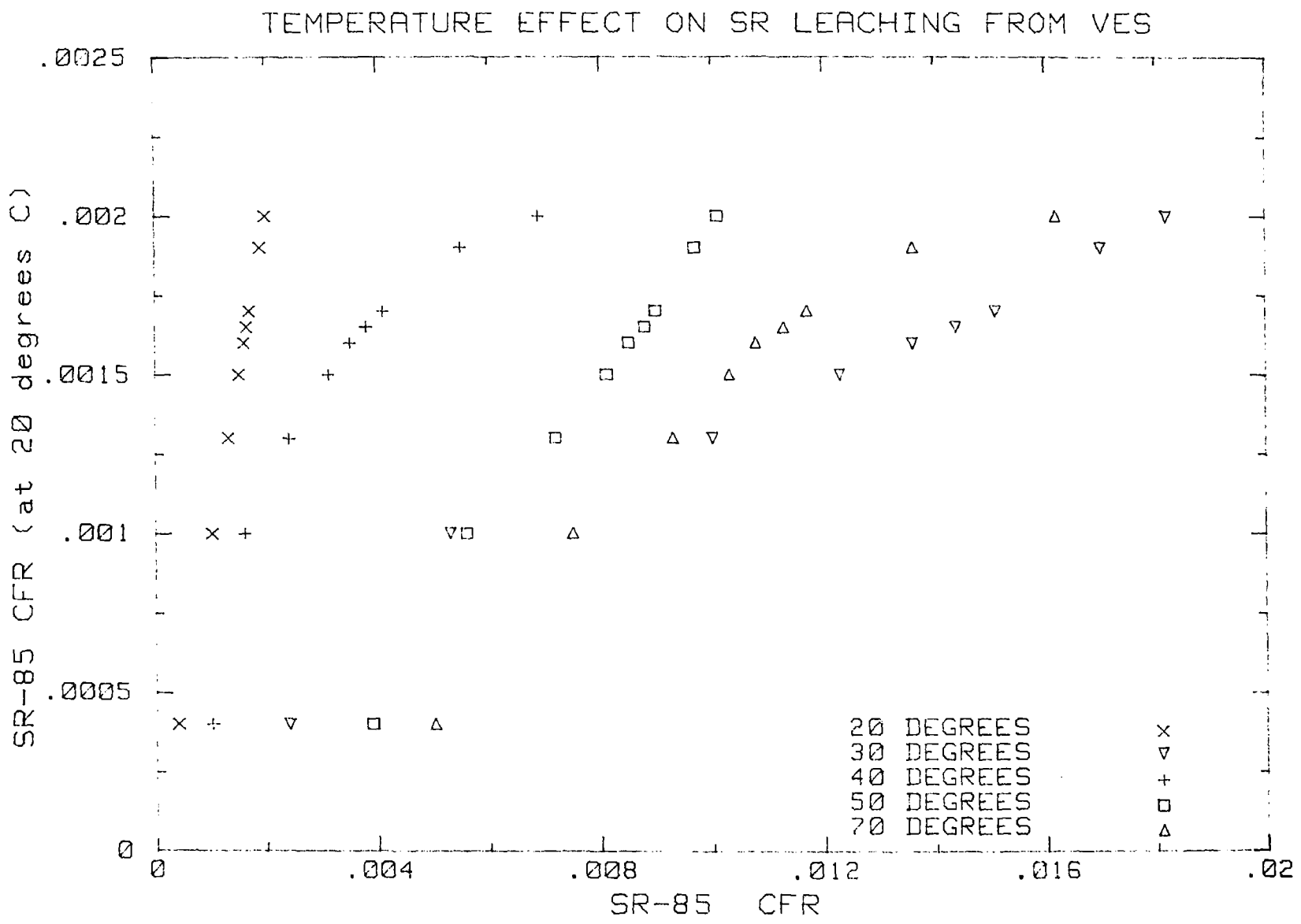

Figure 6.10. Cumulative Fraction Release (CFR) of Sr-85 Leached from VES at 20°C (baseline) Plotted Against CFR of Samples Leached at 20°, 30°, 40°, 50° and 70°C.

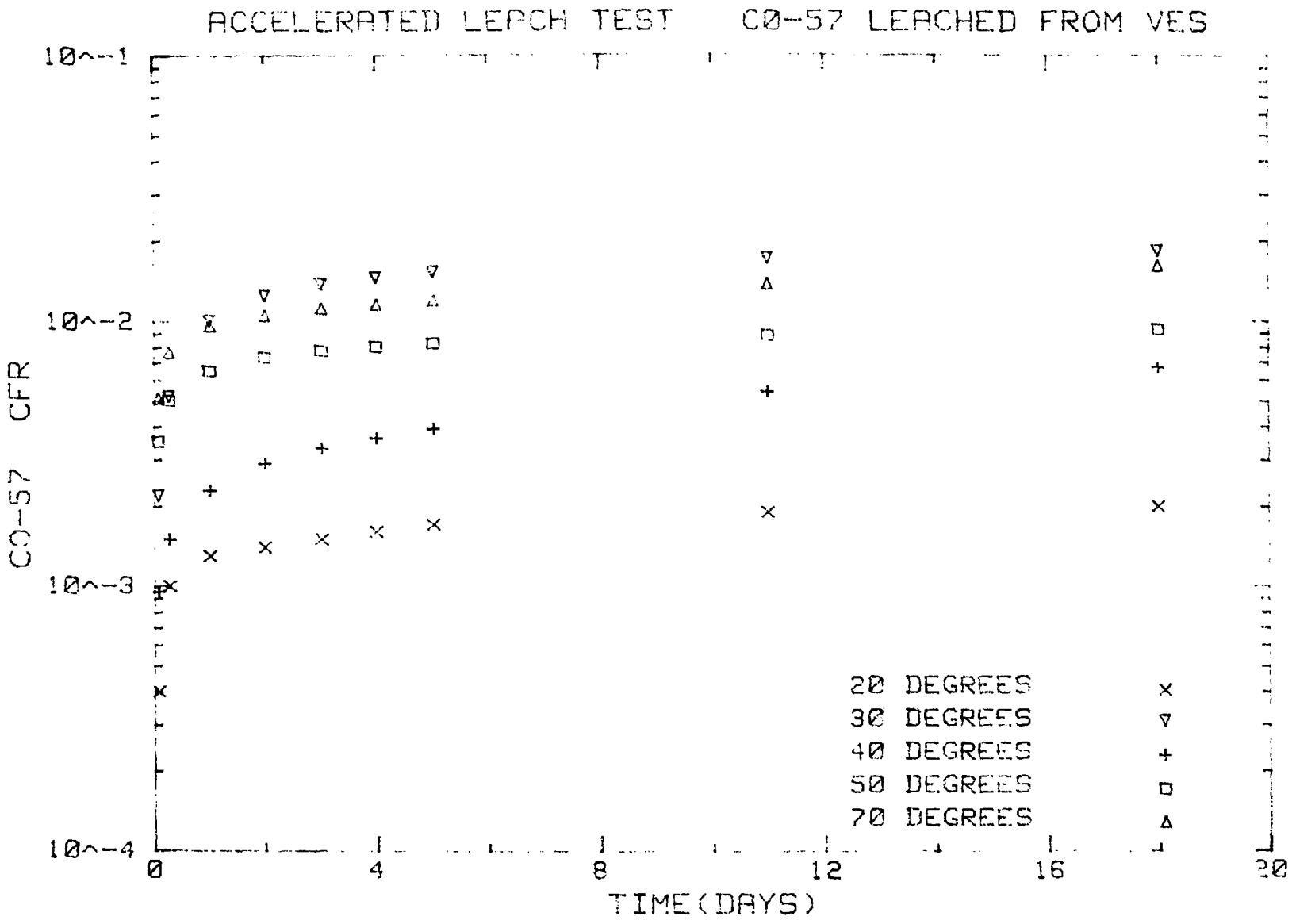

Figure 6.11. Cumulative Fraction Release (CFR) of Co-57 Leached from VES Samples at 20°, 30°, 40°, 50° and 70°C Plotted Against Time.

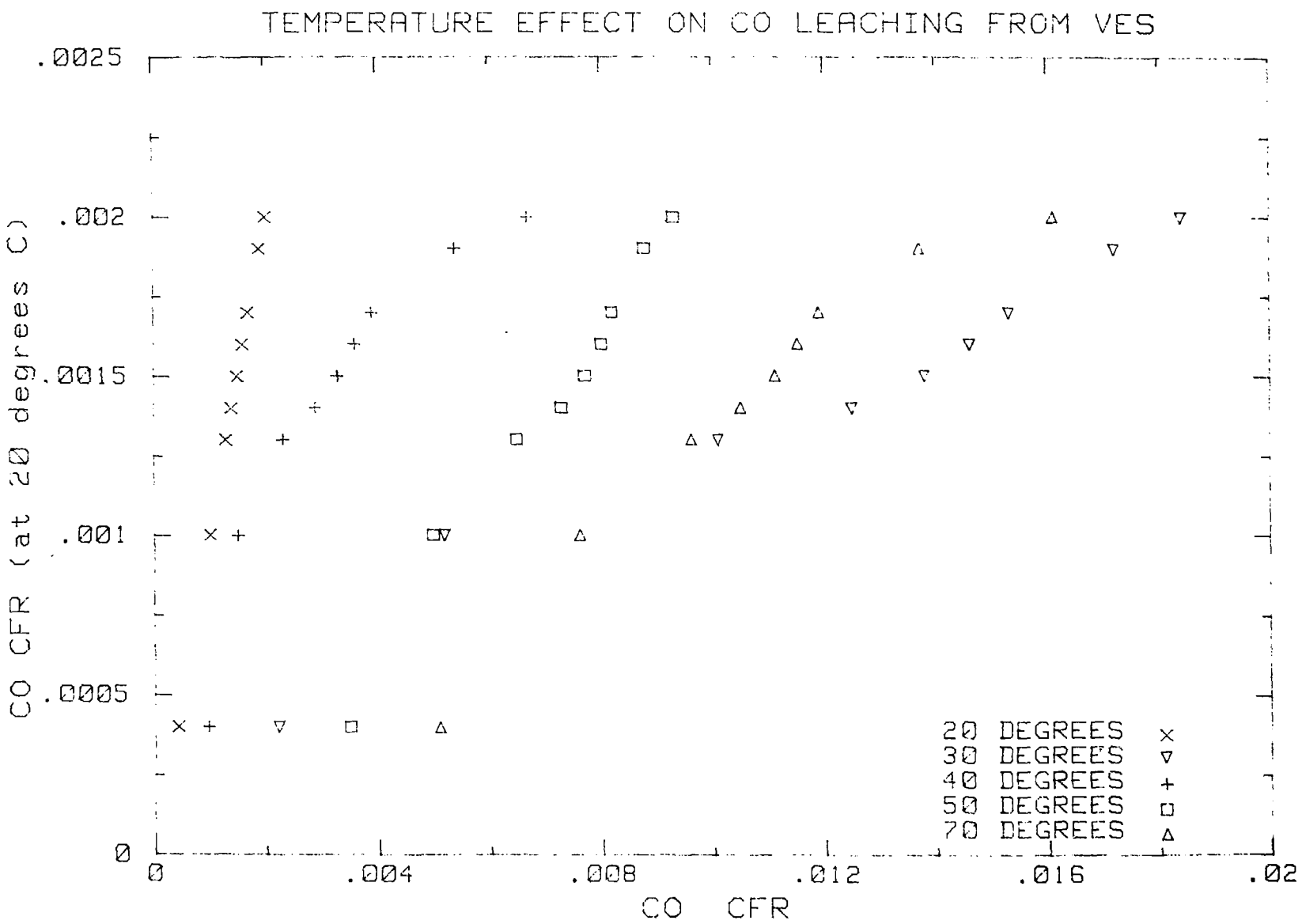

Figure 6.12. Cumulative Fraction Release (CFR) of ^{57}Co Leached from a Sample Leached at 20°C (baseline) Plotted Against CFR of Samples Leached at 20°, 30°, 40°, 50° and 70°C.

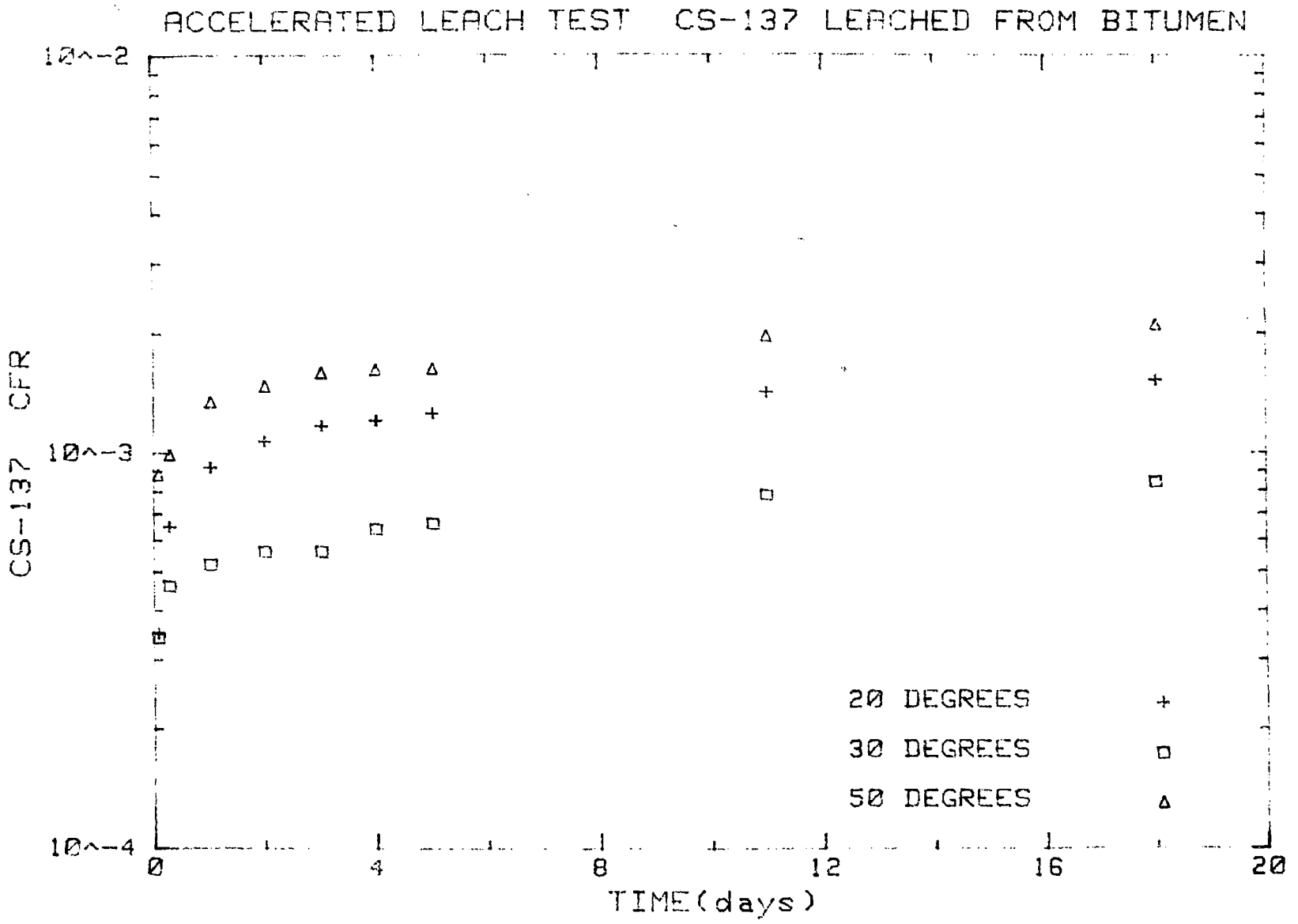

Figure 6.13. Cumulative Fraction Release of Cs-137 from Bitumen Samples Leached at 20°, 30°, and 50°C Plotted Against Time.

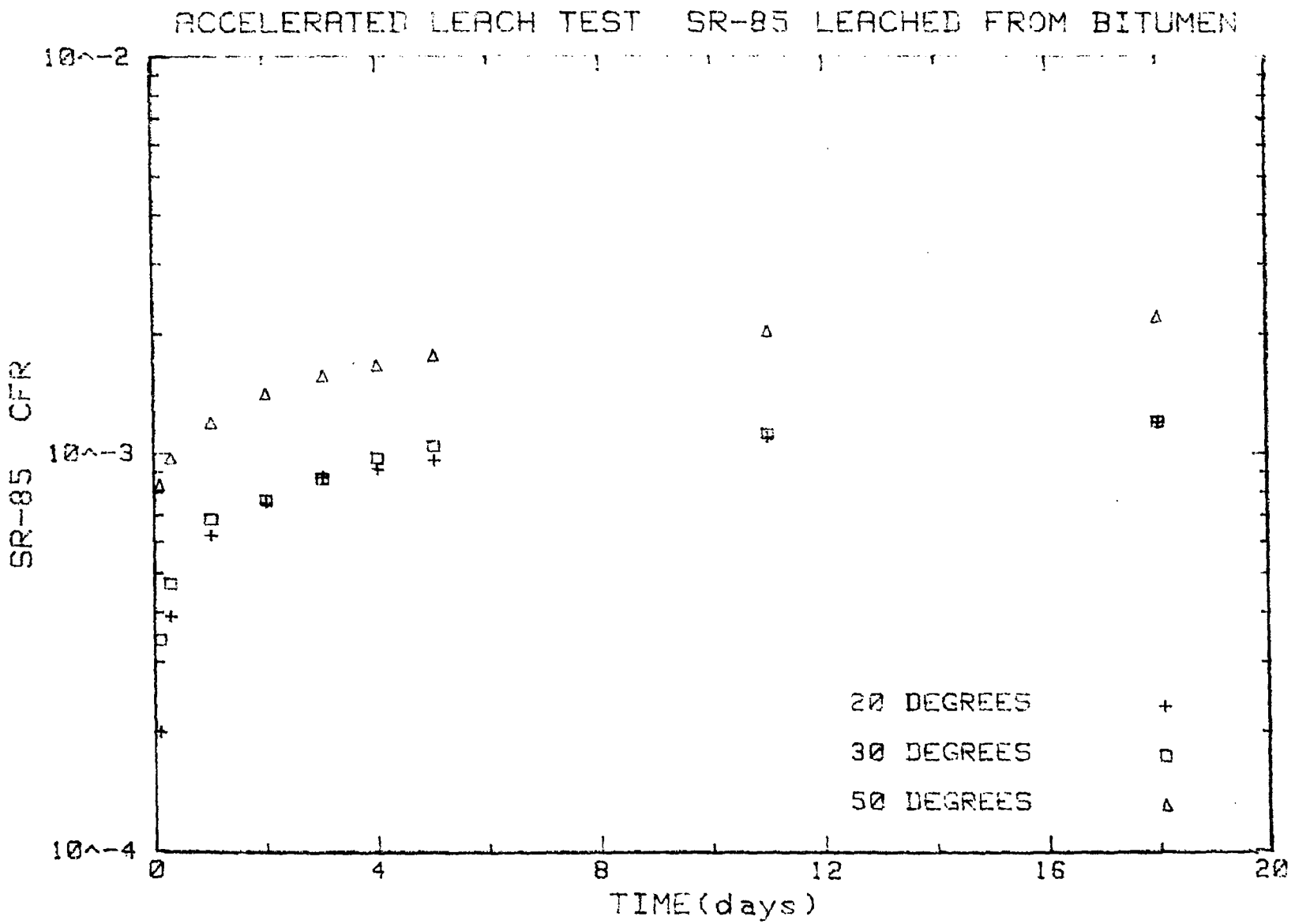

Figure 6.14. Cumulative Fraction Release of Sr-85 from Bitumen Samples Leached at 20°, 30°, and 50°C Plotted Against Time.

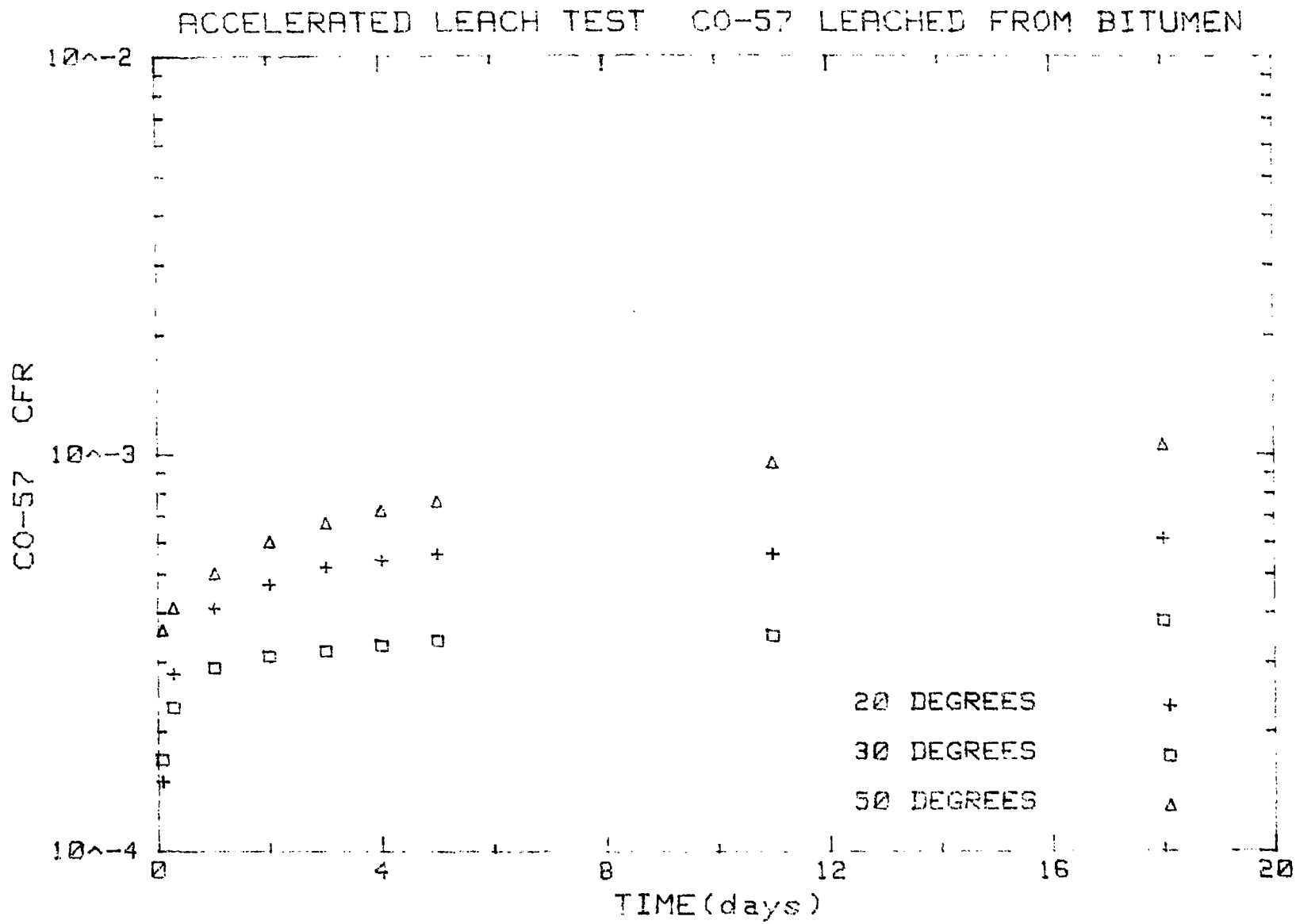

Figure 6.15. Cumulative Fraction Release of Co-57 from Bitumen Samples Leached at 20°, 30°, and 50°C Plotted Against Time.

were detected from cement waste forms. This is expected because of the high solubilities of some components and may provide a useful tool to detect changes in mechanisms as accelerated leaching takes place. In addition it is known that some waste components react with cement but do not appreciably react with VES and bitumen. Therefore, each waste component or radionuclide in cement must be regarded separately as the chemistry of each element reacting with cement may be different.

Tables 6.1 through 6.3 give results of leachate analyses for cement samples leached at 30°, 40° and 70°C. Analysis of samples leached at 50°C is not yet complete. Most elemental concentrations increased with increasing temperature. An exception to this was Si concentration, which increased from 20° to 30°C and then decreased with increasing temperature, possibly because of a back reaction resulting in redeposition of silicon. No silicon was detectable in the 70°C leachate. Aluminum behaved similarly; it increased between 20°C and 40°C and then decreased. Alkalinity increased between 20°C and 30°C, remained the same to 40°C and then fell significantly at 70°C. A similar phenomenon was observed with the MCC-3 baseline experiment where high concentrations of alkaline elements may have reduced Si and Al solubility.

Tables 6.4, 6.5 and 6.6 are correlation matrices for cement leachates at 30°, 40° and 70°C. These can be compared with Table 5.3 which shows correlation coefficients (R) for cement leached at 20°C. As temperature increases so do the R values between many elements suggesting improved correlation. In some cases significant changes occur. For example, correlation coefficients for Sr-85 versus strontium from the matrix and Cs-137 versus K are shown in Table 6.7 for each temperature. Excellent correlations are noted for leaching at 70°C. Scatter plots showing examples of these correlations are given in Figures 6.16a and b. This information is particularly useful for solid phase analysis of waste forms where energy dispersive x-ray spectra are obtained for major components of the matrix material. The change of R for Sr-85 tracer to matrix Sr may be related to an increase in the dissolution rate of the cement matrix between 18°C and 100°C.

Increased temperature clearly had different effects on the various components of the cement matrix. Nevertheless, this incongruent dissolution of the matrix does not appear to have affected ^{137}Cs leachability. Leachability of Sr-85, however, as a function of temperature is not well characterized from these data.

6.3 Temperature Effects Scoping Study - Solid Phase Analysis

To examine the physical and chemical effects of leaching on the waste form itself analysis was performed by SEM/EDS. Both structural changes and chemical changes were observed when comparing data from the outside edge of a cement waste form with that from the center.

Two cement waste forms were analysed by SEM/EDS; one was leached at 30°C and the other leached at 70°C. Compositions of leachates from these samples are shown in Tables 6.1 and 6.3. Both samples showed a qualitative difference between the cement structure at the outside edge of the sample and at the center. Figure 6.17 shows the pore structure in the outer section of the cement at a 100-fold magnification. In comparison, Figure 6.18 shows the relatively unleached center of the waste form. The porosity is greater at the outer edge

Table 6.1

Accelerated Leach Test Cement Leached at 30°C

OBS#	Variable # 1 (DELTA TIME)	Variable # 2 (SIGMA TIME)	Variable # 3 (CALCIUM)	Variable # 4 (ALUMINUM)	Variable # 5 (SILICON)
1	0.00000	0.00000	9.00000	0.00000	0.00000
2	.08000	.08000	47.00000	0.00000	0.00000
3	.21000	.29000	56.00000	0.00000	0.00000
4	.71000	1.00000	84.00000	0.00000	0.00000
5	1.00000	2.00000	83.00000	.90000	0.00000
6	1.00000	3.00000	70.00000	.90000	0.00000
7	1.00000	4.00000	66.00000	1.00000	1.90000
8	1.00000	5.00000	61.00000	1.00000	2.00000
9	6.00000	11.00000	132.00000	2.70000	2.50000
10	7.00000	18.00000	123.00000	2.30000	3.20000

OBS#	Variable # 6 (STRONTIUM)	Variable # 7 (SODIUM)	Variable # 8 (POTASSIUM)	Variable # 9 (CS-137)	Variable #10 (SR-85)
1	.10000	4.00000	6.00000	0.00000	0.00000
2	.60000	5.00000	17.00000	.02200	3.000000E-03
3	.80000	4.00000	12.00000	.01700	3.000000E-03
4	1.30000	8.00000	29.00000	.03500	5.000000E-03
5	1.20000	8.00000	32.00000	.03500	4.000000E-03
6	1.00000	7.00000	24.00000	.02500	2.000000E-03
7	.90000	6.00000	19.00000	.02500	2.000000E-03
8	.90000	5.00000	18.00000	.01900	2.000000E-03
9	2.60000	18.00000	81.00000	.07900	6.000000E-03
10	2.40000	13.00000	55.00000	.06200	6.000000E-03

OBS#	Variable #11 (ALKALINITY)
1	.05000
2	.10000
3	.30000
4	.20000
5	.10000
6	.15000
7	.15000
8	.15000
9	.25000
10	.20000

Time is in days
Cs-137 and Sr-85 is as Incremental Fraction Release
Alkalinity is as mg $CaCO_3$/l.
All other results are as mg/l

Table 6.2

Accelerated Leach Test Cement Leached at 40°C

OBS#	Variable # 1 (DELTA TIME)	Variable # 2 (SIGMA TIME)	Variable # 3 (CALCIUM)	Variable # 4 (ALUMINUM)	Variable # 5 (SILICON)
1	0.00000	0.00000	0.00000	0.00000	0.00000
2	.08000	.08000	61.00000	0.00000	0.00000
3	.21000	.29000	84.00000	0.00000	0.00000
4	.71000	1.00000	126.00000	1.60000	0.00000
5	1.00000	2.00000	115.00000	2.00000	0.00000
6	1.00000	3.00000	93.00000	1.70000	0.00000
7	1.00000	4.00000	86.00000	1.50000	1.90000
8	1.00000	5.00000	75.00000	1.50000	2.20000
9	6.00000	11.00000	141.00000	3.60000	2.10000
10	7.00000	16.00000	106.00000	5.20000	3.10000

OBS#	Variable # 6 (STRONTIUM)	Variable # 7 (SODIUM)	Variable # 8 (POTASSIUM)	Variable # 9 (CS-137)	Variable #10 (SR-85)
1	0.00000	2.00000	3.00000	0.00000	0.00000
2	1.00000	7.00000	25.00000	.02400	5.000000E-03
3	1.10000	5.00000	17.00000	.02100	4.100000E-03
4	1.70000	11.00000	45.00000	.04800	5.700000E-03
5	1.60000	11.00000	46.00000	.04800	5.500000E-03
6	1.30000	8.00000	32.00000	.03600	4.200000E-03
7	1.20000	8.00000	26.00000	.03300	3.400000E-03
8	1.10000	7.00000	22.00000	.03000	3.600000E-03
9	3.00000	21.00000	92.00000	.10500	8.400000E-03
10	2.50000	16.00000	63.00000	.07500	7.800000E-03

OBS#	Variable #11 (ALKALINITY)	Variable #12 (CO-57)
1	.05000	0.00000
2	.10000	9.000000E-05
3	.30000	5.000000E-05
4	.20000	8.000000E-05
5	.10000	8.000000E-05
6	.15000	6.000000E-05
7	.15000	3.000000E-05
8	.15000	6.000000E-05
9	.25000	1.300000E-04
10	.20000	7.000000E-05

Time is in days.
Cs-137 and Sr-85 is as Incremental Fraction Release.
Alkalinity is as mg $CaCO_3$/l.
All other results are as mg/l.

Table 6.3

Accelerated Leach Test Cement Leached at 70°C

OBS#	Variable # 1 (DELTA TIME)	Variable # 2 (SIGMA TIME)	Variable # 3 (CALCIUM)	Variable # 4 (ALUMINUM)	Variable # 5 (SILICON)
1	0.00000	0.00000	0.00000	0.00000	0.00000
2	.08000	.08000	65.00000	0.00000	0.00000
3	.21000	.29000	90.00000	1.70000	0.00000
4	.71000	1.00000	119.00000	2.30000	0.00000
5	1.00000	2.00000	147.00000	2.30000	0.00000
6	1.00000	3.00000	131.00000	1.90000	0.00000
7	1.00000	4.00000	139.00000	1.80000	0.00000
8	1.00000	5.00000	124.00000	1.60000	0.00000
9	6.00000	11.00000	226.00000	2.40000	0.00000
10	7.00000	18.00000	189.00000	1.50000	0.00000

OBS#	Variable # 6 (STRONTIUM)	Variable # 7 (SODIUM)	Variable # 8 (POTASSIUM)	Variable # 9 (CS-137)	Variable #10 (SR-85)
1	0.00000	1.70000	4.70000	0.00000	0.00000
2	1.30000	8.90000	41.00000	.05300	5.300000E-03
3	1.30000	10.50000	51.00000	.05600	5.200000E-03
4	2.60000	27.10000	148.00000	.14100	9.600000E-03
5	3.10000	25.20000	127.00000	.12500	9.100000E-03
6	2.60000	19.00000	86.00000	.09200	8.000000E-03
7	2.30000	15.30000	63.00000	.06800	6.600000E-03
8	2.10000	13.20000	52.00000	.05500	5.600000E-03
9	6.60000	43.40000	210.00000	.18800	.01760
10	5.60000	25.10000	89.00000	.08400	.01800

OBS#	Variable #11 (ALKALINITY)	Variable #12 (CO-57)
1	0.00000	0.00000
2	.05000	8.000000E-05
3	.20000	0.00000
4	.15000	0.00000
5	.05000	1.000000E-04
6	.05000	1.000000E-05
7	.05000	0.00000
8	5.000000E-03	0.00000
9	.20000	3.000000E-05
10	.15000	0.00000

Time is in days.
Cs-137 and Sr-85 is as Incremental Fraction Release.
Alkalinity is as mg $CaCO_3$/l.
All other results are as mg/l.

Table 6.4

Accelerated Leach Test

Correlation Matrix
Portland Cement Leached at 30°C

	Aluminum	Silicon	Strontium	Sodium	Potassium	^{137}Cs	^{85}Sr	Alkalinity
Calcium	0.84	0.65	0.98	0.90	0.92	0.97	0.92	0.57
Aluminum		0.85	0.88	0.88	0.89	0.86	0.61	0.32
Silicon			0.71	0.64	0.65	0.66	0.46	0.31
Strontium				0.95	0.96	0.98	0.90	0.56
Sodium					0.99	0.97	0.81	0.41
Potassium						0.98	0.84	0.44
^{137}Cs							0.90	0.50
^{85}Sr								0.58

Table 6.5

Accelerated Leach Test

Correlation Matrix
Portland Cement Leached at 40°C

	Aluminum	Silicon	Strontium	Sodium	Potassium	^{137}Cs	^{85}Sr	Alkalinity
Calcium	0.63	0.29	0.88	0.82	0.83	0.83	0.87	0.61
Aluminum		0.75	0.85	0.86	0.82	0.86	0.76	0.31
Silicon			0.57	0.57	0.49	0.58	0.45	0.27
Strontium				0.98	0.97	0.98	0.96	0.59
Sodium					0.99	0.99	0.92	0.45
Potassium						0.99	0.92	0.45
^{137}Cs							0.91	0.50
^{85}Sr								0.56

Table 6.6

Accelerated Leach Test

Correlation Matrix
Portland Cement Leached at 70°C

	Aluminum	Silicon	Strontium	Sodium	Potassium	^{137}Cs	^{85}Sr	Alkalinity
Calcium	0.77	-	0.94	0.89	0.80	0.81	0.91	0.52
Aluminum		-	0.60	0.76	0.77	0.79	0.58	0.49
Silicon			-	-	-	-	-	-
Strontium				0.91	0.80	0.78	0.98	0.58
Sodium					0.98	0.97	0.88	0.61
Potassium						0.99	0.78	0.60
^{137}Cs							0.76	0.59
^{85}Sr								0.64

Table 6.7

Change of Correlation Coefficients (R) With Temperature

Temperature	$R(^{85}Sr/Sr)$	$R(^{137}Cs/K)$
20°C	-0.08	0.49
30°C	0.90	0.98
40°C	0.96	0.99+
70°C	0.98	0.99+

of the leached waste form than at the center. In the center of Figure 6.18 is a small air bubble which is shown at 500 times magnification in Figure 6.19. Note the needle like crystal growth along the bubble wall. Close-up views of pores in the cement are shown in Figures 6.20 and 6.21. The blocky appearance of interconnected pores may be associated with water flow while the static conditions in the bubble lead to crystal growth.

Chemical analysis of the solid phase by Energy Dispersive X-ray Spectroscopy provided semi-quantitative elemental analysis of cement samples. These were prepared by sectioning waste forms so that slabs measuring 1 cm by 1 mm thick were obtained. Analysis of a series of these samples gave profiles (with approximately 1 mm increments) of elemental ratios in the solid phase. Figure 6.22 is an x-ray spectrum of the outer edge of a sample leached at 70°C. Another section of the same sample was taken from the center of the waste form. Its spectrum is shown in Figure 6.23. The K peak present in Figure 6.22, is missing in Figure 6.23, indicating movement of this element within the solid.

Figure 6.24 shows ratios of K/Mg in a waste form leached at 30°C. Magnesium is used as a basis for comparison because it is stable in cement and does not leach significantly. Ratios are highest at the outer edge of the waste form, then drop to zero between 11 and 15 mm and increase again at the center of the waste form.

A similar sample leached at 70°C for the same amount of time contains K in the outer 4 mm of the waste form. From 4 mm inward towards the center no K was detected. This is shown in Figure 6.25.

There are distinct differences in the K/Mg ratios in the two waste forms that can be attributed to K depletion due to leaching. In the sample leached at 30°C, K was completely leached to a depth of 15 mm. The high K concentrations present at the outer edge of the waste form may be an artifact of drying after leaching. As the pore fluid evaporates at the surface of the waste form K is left behind and accumulates. It is unclear why the greatest concentration is 7 mm inside the waste form. At 70°C leaching has affected the entire

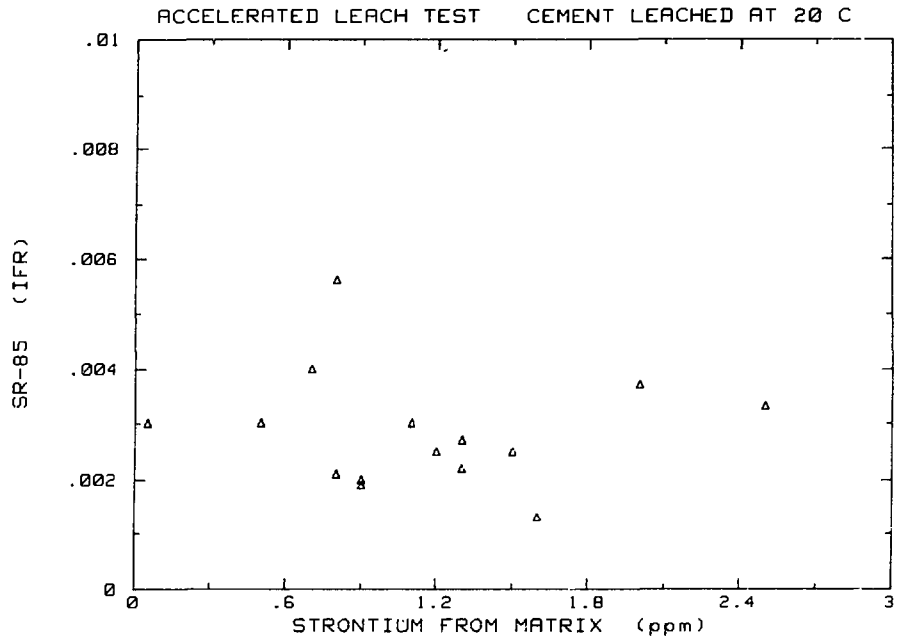

Figure 6.16a. Scatter plot of incremental fraction release (IFR) of Sr-85 tracer plotted against the concentration of Sr released from the portland cement matrix at 20°C. Note the poor correlation. R = -0.08.

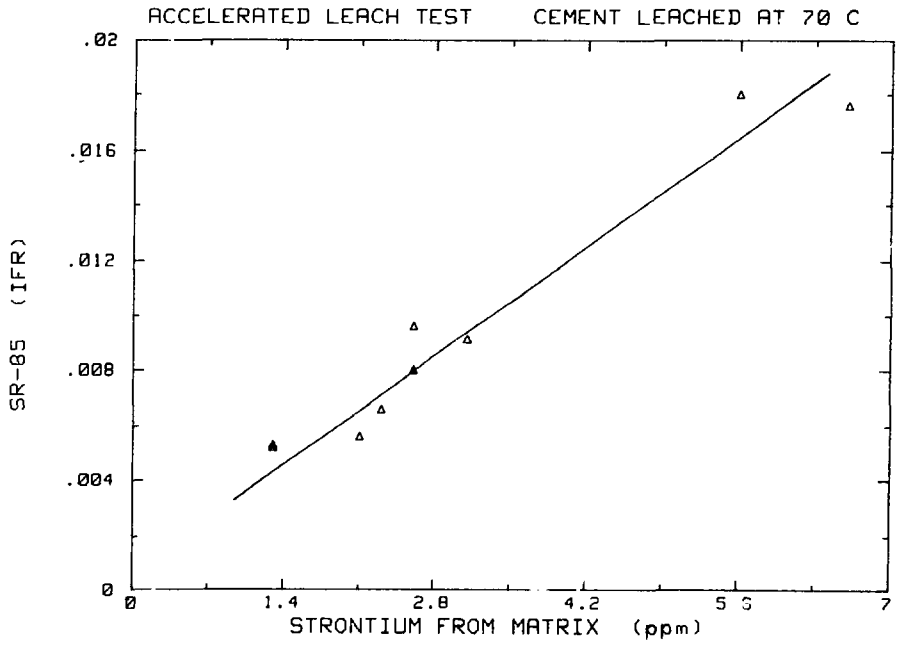

Figure 6.16b. Scatter plot of incremental fraction release (IFR) of Sr-85 tracer plotted against the concentration of Sr released from the portland cement matrix at 70°C. Note the good correlation. R = 0.98.

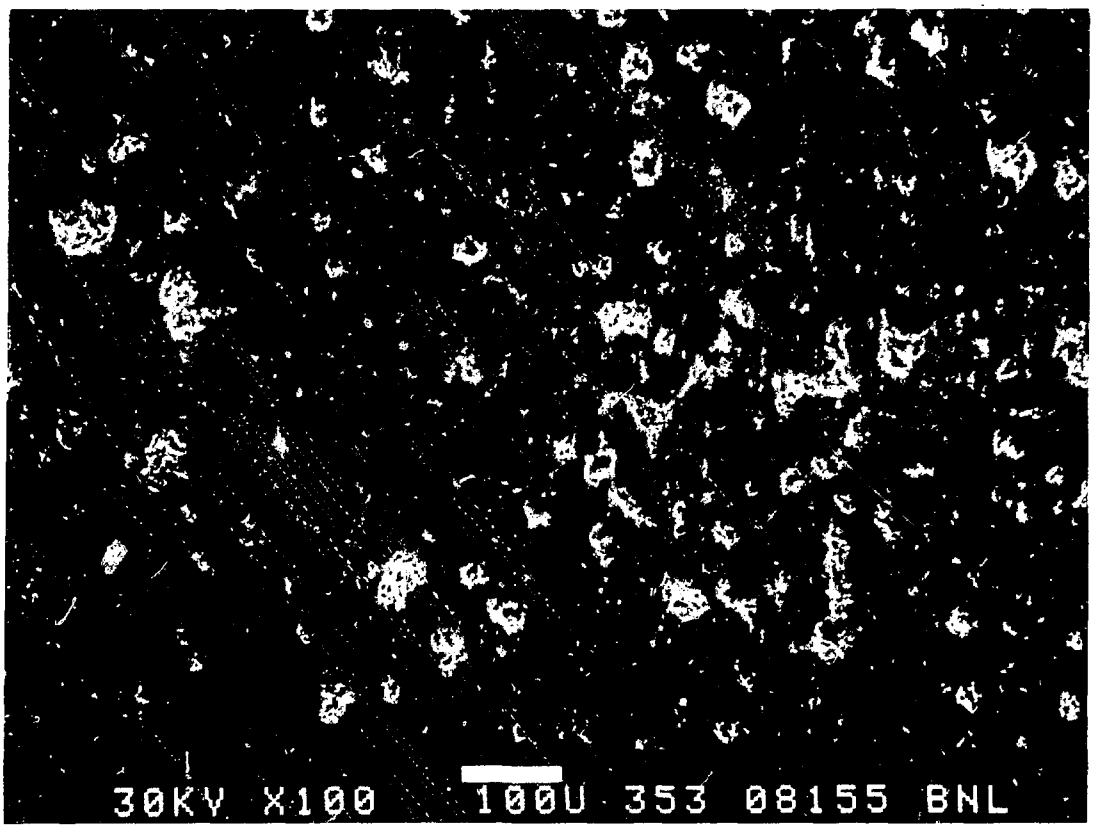

Figure 6.17. An SEM micrograph of portland cement near the outer edge of a waste form after leaching. Porosity is high and pores are connected by fine cracks.

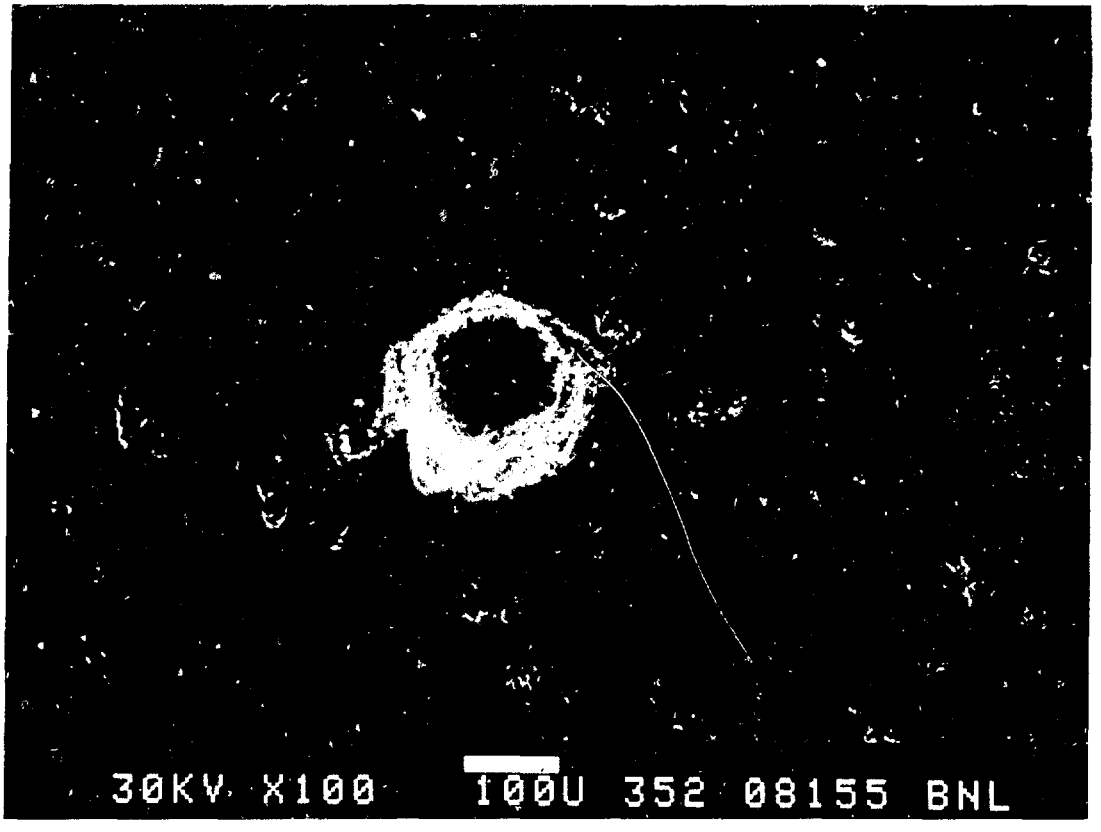

Figure 6.18. An SEM micrograph of portland cement at the center of waste form. The porosity is much less than at the outer edge. An air bubble is in the center of the micrograph.

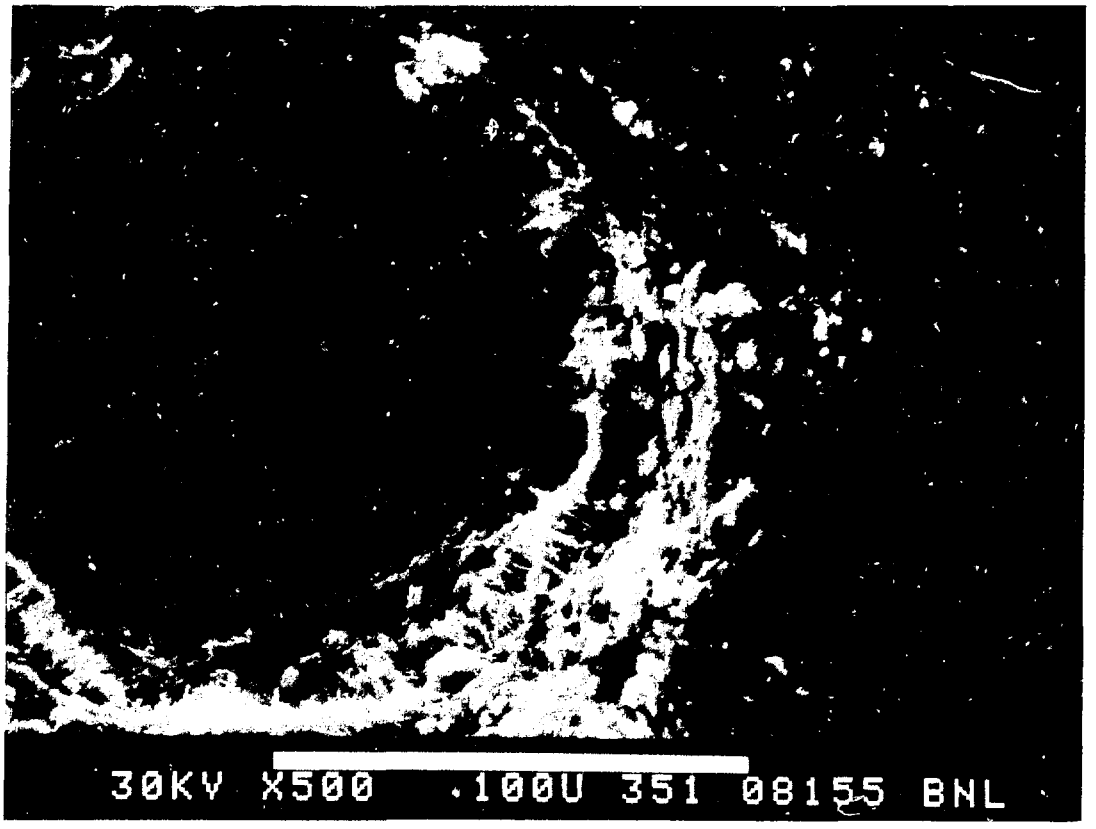

Figure 6.19. The air bubble is shown at 500 times magnification. There is profuse crystal growth along the bubble walls.

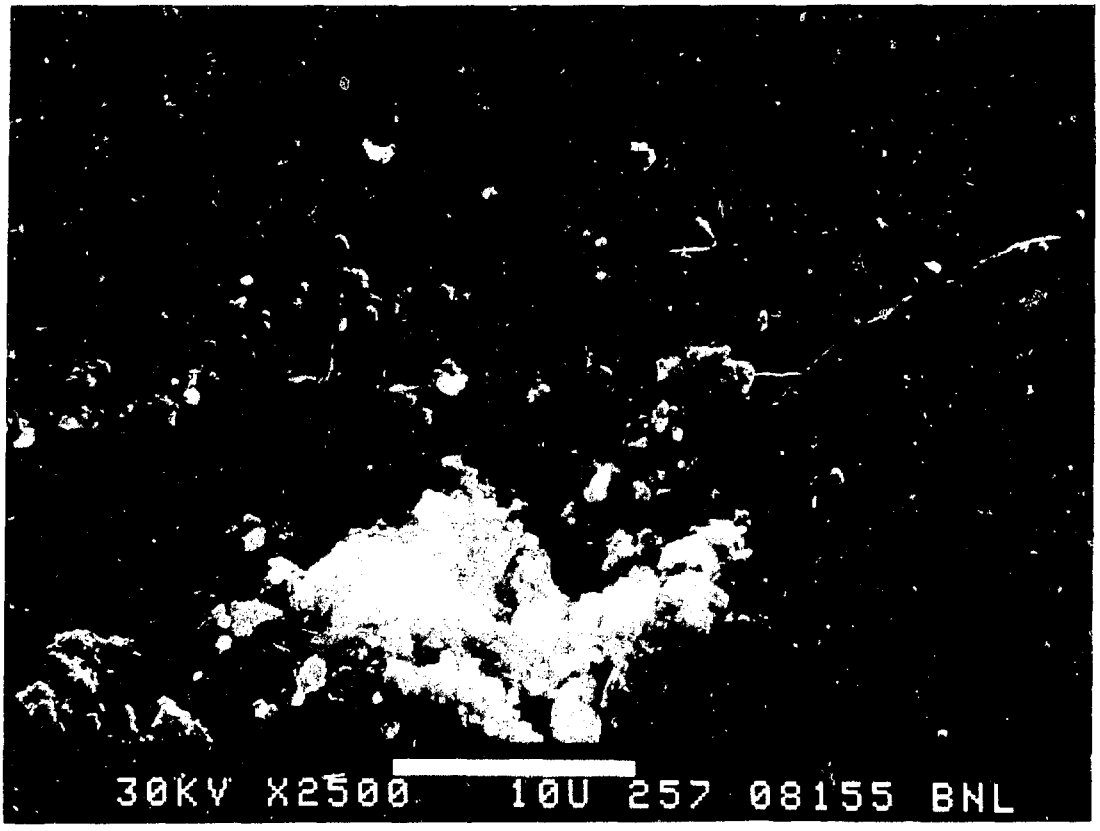

Figure 6.20. A pore in cement after leaching, it has a blocky structure with no crystal growth inside the pore.

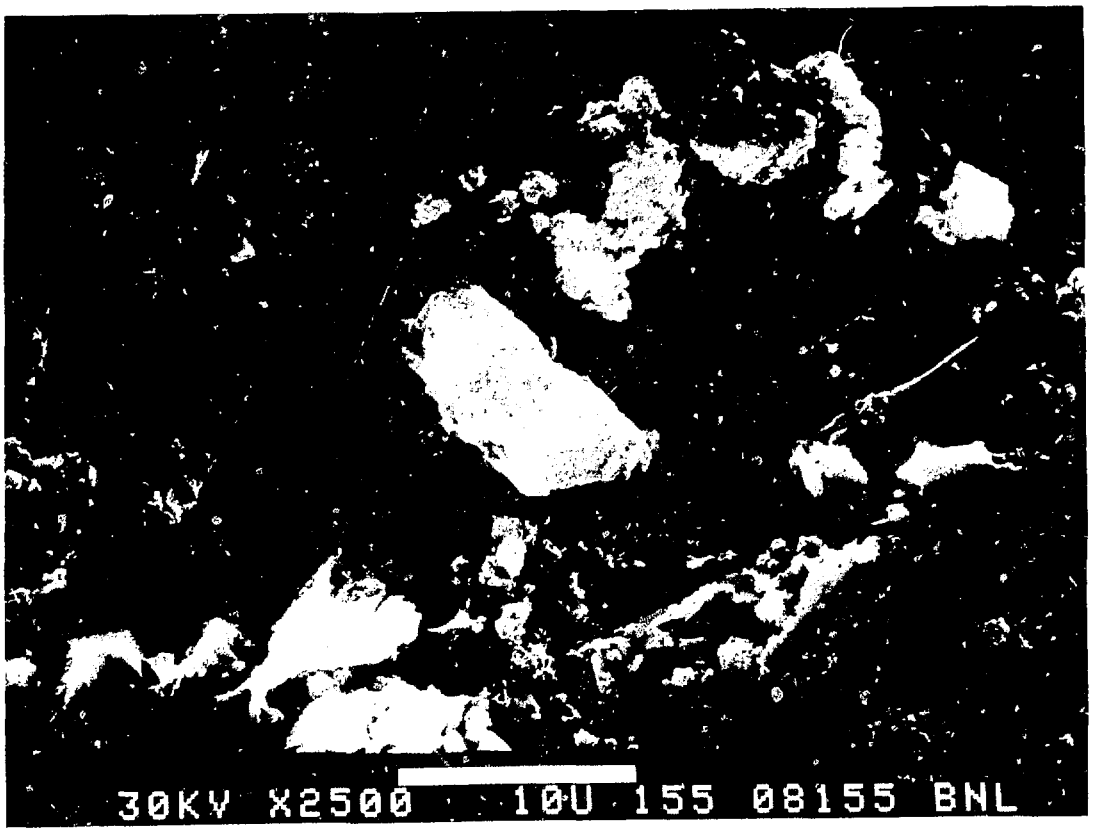

Figure 6.21. Another pore in leached cement showing blocky structure and no crystal growth.

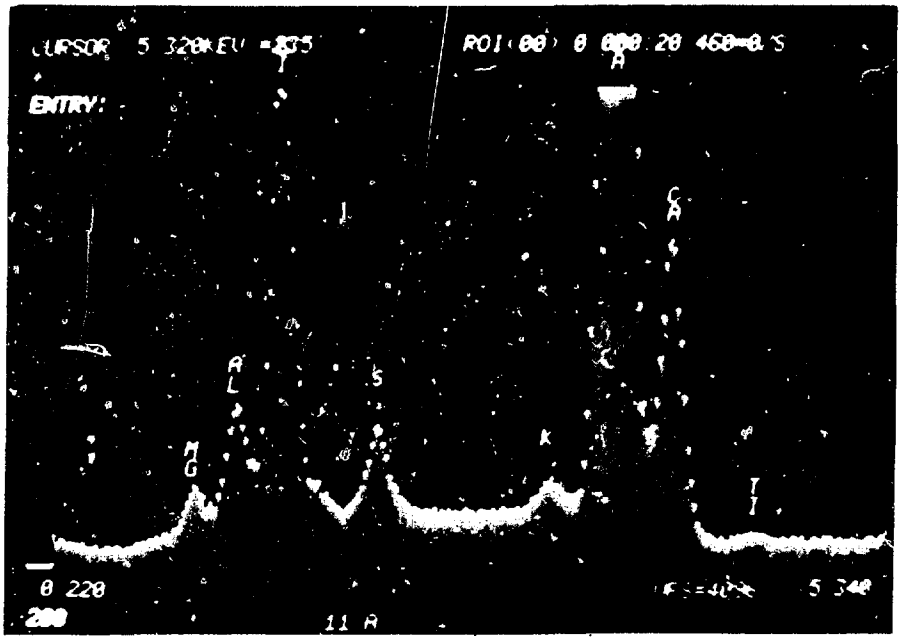

Figure 6.22. X-ray spectrum of the outer edge of a cement waste form leached at 70°C. Note the K peak.

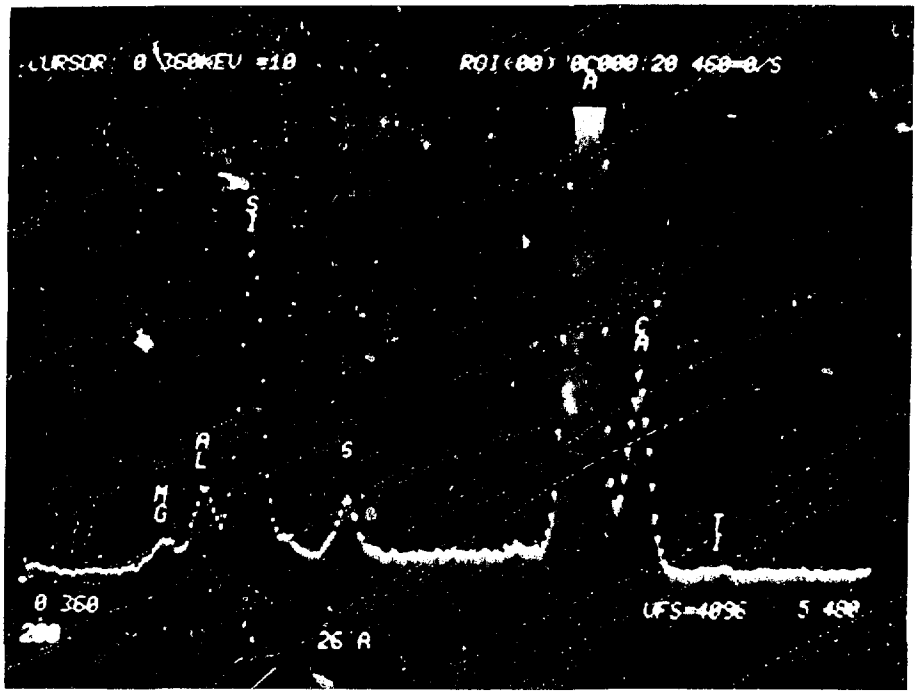

Figure 6.23. X-ray spectrum of the center of a cement waste form. The K peak is below detection limits.

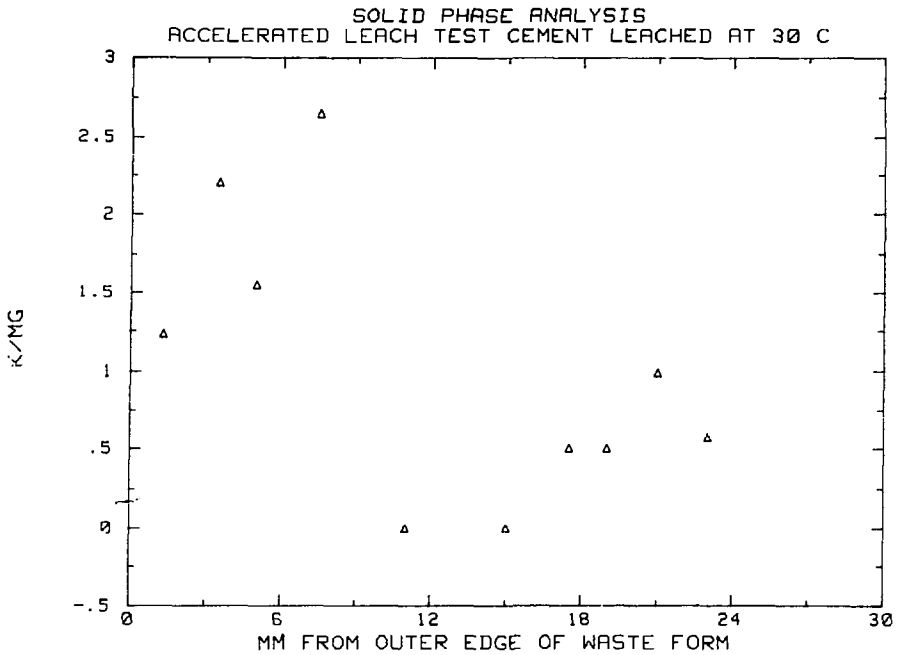

Figure 6.24. Potassium in the solid phase of the waste form after leaching at 30°C for 18 days. The depletion extends 15 mm into the waste form.

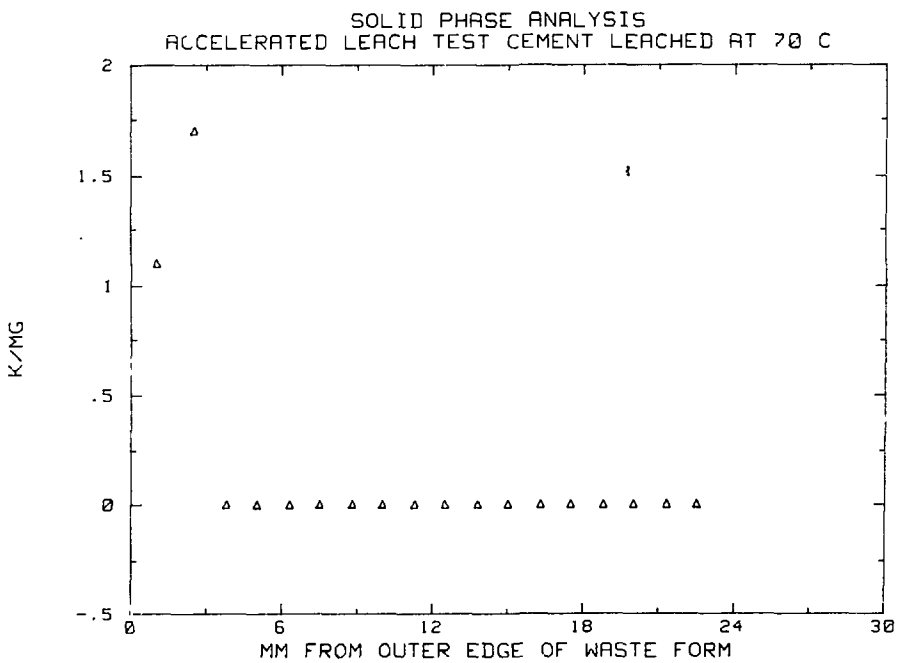

Figure 6.25. Potassium in the solid phase of the waste form after leaching at 70°C for 18 days. Depletion extends all the way through the sample.

waste form and K is depleted throughout. Again, evaporation may have caused some K to accumulate at the edge of the waste form. From the interelemental comparisons discussed earlier, K may be taken as an analog for Cs in this system. The correlation coefficients for K versus Cs-137 at 30°C is 0.98 (see Table 6.4) and at 70°C it is 0.99 (see Table 6.6). Profiles of Cs-137 at 30°C within the waste form probably closely resemble those for K. The process of evaporative transport in a wet waste form as drying takes place has been suggested as an important mechanism for release of radionuclides during wet/dry cycling in shallow land burial. The profiles of K in these waste forms appear to corraborate that hypothesis[20].

7. CONCLUSIONS

(i) Long-term (over 400 days) baseline leaching experiments have provided data against which accelerating factors can be judged.

(ii) Temperatures over the range of 30°C to 70°C showed up to a 20-fold increase in the leach rates for Cs-137 from cement. Under these conditions no significant leaching acceleration was observed for Co-57. Although the Sr-85 showed an increase in leach rate at elevated temperatures, the results were not isotonic, indicating mechanistic alterations.

(iii) No significant acceleration of leach rates were detected for bitumen and vinyl ester-styrene waste forms over the temperature range of 30 to 70°C for a period of 18 days.

(iv) Statistical relationships supporting leaching mechanisms were found for elements leached from the cement solidification agent and for radioactive tracers

8. CURRENT STUDIES

Studies have been initiated to determine:

- the effect of waste materials on the leaching behavior of waste forms
- the effect of disposal environments on leaching behavior of waste forms.
- parameters that effect leaching

The information derived from these studies will provide input into the development of an accelerated leach test(s).

1. Dougherty, D.R. and P. Colombo, Leaching Mechanisms of Solidified Low-Level Wastes: The Literature Survey, Brookhaven National Laboratory, BNL-51899, June, 1985.

2. Dougherty, D.R., M. Fuhrmann and P. Colombo, Leaching Mechanisms Program Annual Report, Brookhaven National Laboratory, BNL-51862.

3. Pacific Northwest Laboratory, Final Report of the Defense High-Level Waste Leaching Mechanisms Program, J.E. Mendel, compiler, PNL-5157, UC-70, August 1984.

4. Moore, J.G., H.W. Godbee, A.H. Kibbey and D.S. Joy, Development of Cementitious Grouts for the Incorporation of Radioactive Wastes, Part I, Leach Studies, ORNL-4962, pg. 28, April 1975.

5. Amarantos, S.G. and J.H. Petropoulos, Certain Aspects of Leaching Kinetics of Solidified "Radioactive Wastes" - Laboratory Studies, Greek AEC, DEMO 81/2, January, 1981.

6. Dayal, R.H., H. Arora and N. Marcos, Estimation of Cesium-137 Release From Waste/Cement Composites Using Data From Small-Scale Specimens, Brookhaven National Laboratory, NUREG/CR-3382, BNL-NUREG-51690, July, 1983.

7. International Atomic Energy Agency, E.D. Hespe, editor, "Leach Testing of Immobilized Radioactive Waste Solids, A Proposal for a Standard Method," Atomic Energy Review, 9, 1971, pp. 195-207.

8. American Nuclear Society, Measurement of the Leachability of Solidified Low-Level Radioactive Wastes, ANS Standards Committee, ANS 16.1, June 20, 1984.

9. International Standards Organization, 5/N 38, Long-Term Leach Testing of Radioactive Waste Solidification Products, ISO/TC 85/SC 5/WG 5/N 38, Berlin, West Germany.

10. Kempf, C.R. "Model for Releases of Cs-137 and Sr-90 from Wastes Shipped by Minnesota Mining and Manufacturing (3M) - Buried at Sheffield Site, 1967-1971, Trenches 1 and 2," Brookhaven National Laboratory, Nuclear Waste Management Division, Memo-to-File, pp. 11-13, December 29, 1983.

11. Seefeldt, W.B., "Review of Simulated-Flow and True-Flow Leach Tests," Fuel Cycle Programs Quarterly Progress Report April-June 1982, Argonne National Laboratory, ANL 82-58, 98-125, December 1982.

12. Pescatore, C., Mechanistic Modeling of Nuclear Waste Form Leaching by Aqueous Solution, Ph.D. Thesis, Nuclear Engineering Department, University of Illinois, Urbana, IL, 1983.

13. MCC-3S Agitated Powder Leach Test Method, Materials Characterization Center, September 30, 1981.

14. MCC-4S Low-Flow-Rate Leach Test Method, Materials Characterization Center, September 30, 1981.

15. General Methods for Atomic Absorption Spectrophotometry, January 1982, Perkin-Elmer Corporation.

16. Jantzen, C.M., "Radioactive Waste-Portland Cement Systems: II, Leaching Characteristics," Journal of the American Ceramic Society, 67(10), 674-78, 1984.

17. Bowerman, B.S., K.J. Swyler, D.R. Dougherty, R.E. Davis, B. Siskind and R.E. Barletta, An Evaluation of the Stability Tests Recommended in the Branch Technical Position on Waste Forms and Container Materials, Brookhaven National Laboratory, NUREG/CR-3829, BNL-NUREG-51784, 35-46, March 1985.

18. Soroka, I., Portland Cement Paste and Concrete, Chemical Publishing Co., Inc., New York, 90-95, 1980.

19. McCulloch, C.E., A.A. Rachman, M.J. Angus, F.P. Glasser and R.W. Crawford, "Immobilization of Cesium in Cement Containing Reactie Silica and Pozzolans," Proceedings of the Second International Symposium on Ceramics in Nuclear Waste Management, G.G. Wil___ and W.A. Ross, editors, 413-428, 1984.

20. Dayal, R., D.G. Schweitzer and R.E. Davis, Wet/Dry Cycle Leaching: Aspects of Release in the Unsaturated Zone, BNL-NUREG-33580, 1983, Brookhaven National Laboratory, Upton, NY 11973.