

LEACHING MECHANISMS PROGRAM

ANNUAL REPORT

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ABSTRACT

This report summarizes the work performed for the Leaching Mechanisms Program at Brookhaven National Laboratory in FY 1984 under the sponsorship of the U.S. Department of Energy's Low-level Waste Management Program (LLWMP). The primary goal of this work is to determine the leaching mechanisms of a variety of matrix materials either in use or being considered for the solidification of low-level radioactive wastes by defense and commercial waste generators.

Since this program is new and did not formally begin until May of FY 84, the results reported here are few and preliminary. Efforts were concentrated in the following activities:

- (i) The literature search for leaching data and proposed leaching models and mechanisms for low-level waste.
- (ii) Data base development for leaching data being compiled from the literature and from the leaching experiments in this program.
- (iii) The selection of solidification agents for the experimental part of the program.
- (iv) Fabrication of leach samples and initiation of leach testing.

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1. PROGRAM SCOPE AND OBJECTIVES

One 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 from 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 in the disposal environment, Brookhaven National Laboratory has initiated an investigation of leaching mechanisms of solidified LLW.

The overall objective of this study is to determine the leaching mechanisms of a variety of matrix materials either in use or being considered for the solidification of low-level radioactive wastes by defense and commercial waste generators. Specific goals include validation of mathematical leaching models, identification of controlling material properties which influence leaching mechanisms and, if possible, providing a methodology for predicting leaching behavior from materials properties.

The scope of this investigation encompasses the following three areas: (i) A literature survey to compile leaching data, postulated mechanisms and proposed models for LLW; (ii) Experimental work including leach tests and other analyses to validate leaching mechanisms for selected solidification agents and, (iii) Development of a data base of LLW leaching data from the literature survey and the data generated in the experimental part of this investigation. This study also includes a survey of solidification agents to assure that a broad range of materials properties are represented in those solidification agents selected for experimental investigation.

2. SELECTION OF SOLIDIFICATION AGENTS FOR EXPERIMENTAL INVESTIGATION

An understanding of the prevailing leaching mechanisms of a variety of matrix materials will not only provide a basis for predicting the long-term behavior of the waste forms in disposal environments but may also provide guidance on the use and choice of solidification materials, the treatment of

waste streams prior to solidification, the waste/binder ratios and the suitability of waste form containers. For this reason the selection of solidification agents must encompass several materials exhibiting sufficiently different characteristics that their leaching mechanisms can be discerned.

This section identifies the solidification agents selected for the experimental part of the leaching mechanisms study and the reasons for selecting them.

To provide a basis for this selection, a survey of solidification agents for LLW was conducted and a set of selection criteria was chosen which seemed to provide the best compromise for covering solidification agents in current usage and for providing information which may be of value for solidification agents which may come into use in future.

2.1 Selection Criteria

The choice of solidification agents for this task was based on the following criteria, which reflect the intention to provide information that can be applied to contemporary solidification materials and to matrix materials which may be adopted for use in the future. The criteria are:

- The materials should be those which have been used or have been considered for use by either commercial or defense generators of low-level radioactive wastes.
- The group of materials chosen should represent a cross-section of chemical and physical properties that may affect leaching mechanisms.

2.2 Survey of Solidification Agents

A survey of materials that have been considered for use and/or have been used to solidify low-level radioactive waste was conducted. Previous reviews 2.1, 2.2 of solidification agents for LLW are available and the results of these reports formed much of the basis for the current effort. Solidification agents such as urea-formaldehyde and high alumina cement which have been

previously investigated but are now deemed unacceptable for use in the U.S. have not been considered in this survey. The materials that were reviewed represent a broad range of materials with varying physical and chemical characteristics. They are listed below according to their general material type.

Hydraulic Cements

Portland cement

Masonry cement

Gypsum cement

Thermosetting Materials

Vinyl ester-styrene

Epoxy

Thermoplastic Materials

Bitumen

Polyethylene

Sulfur cement

Glass

Soda-lime silica glass

Fusion slag

Solidification of hydraulic cement occurs through a hydration reaction with water and may involve other chemical reactions. In portland cements the hydration reaction is accompanied by the release of calcium hydroxide from part of the cement mixture and its reaction with another part of the setting cement. Masonry cement is a one to one mixture of lime (calcium oxide) or slaked lime (calcium hydroxide) with portland cement. The solidification of masonry cement generally involves the same reactions as occur in portland cement. Gypsum cement solidifies from the hydration of calcium sulfate hemihydrate to form calcium sulfate dihydrate. These chemical and/or hydration reactions occurring in the solidifying cement binders offer the possibility of chemical reaction with waste materials as well as physical encapsulation.

Thermosetting materials also undergo chemical reaction to solidify. For both the vinyl ester-styrene copolymer and the epoxy material this reaction is polymerization following mixing with the waste. Only limited chemical reaction between the waste and unpolymerized binder can occur or the mixture will not solidify.

Incorporating waste into thermoplastic solidification agents generally requires heating to liquify the mixture of binder and waste. The mixture solidifies upon cooling. Thermoplastic binders serve to physically encapsulate waste and undergo little, if any, chemical reaction with waste materials.

Solidification in glass involves high temperatures and incineration of wastes. The incineration process volatilizes radionuclides of non-metals while metallic radionuclides are captured in the molten glass as oxides. Glassification of wastes typically results in substantial volume reduction due to the incineration step.

Further discussion of these materials as solidification agents for LLW is available in References 2.1 and 2.2.

2.3 Solidification Agents Selected for Experimental Investigation

Based upon the survey of solidification agents and the selection criteria, the following materials were chosen for the experimental leaching mechanism(s) study:

- Type I portland cement
- Bitumen
- Vinyl ester-styrene (VES)
- Soda-lime silica glass

Cement:

Portland type I cement has been chosen for the experimental part of this study because of its widespread use for radioactive waste solidification. The use of cement as a solidification agent by most waste processors make this material a useful subject for the leaching mechanisms study. A large body of information is available on its physical and chemical properties. 2.3-2.7 There are five types of portland cement. The various portland cements are similar in that they are composed of the same chemical constituents, but the relative proportions are changed to produce the different types of cement. These compounds and some of their properties are given in Table 2.1.

Table 2.1

Characteristics of Portland Cement

Principal Compounds Present in Portland Cements

<u>Compound</u>	<u>Formula</u>	<u>Abbreviation</u>
Tricalcium silicate	$3\text{CaO}\cdot\text{SiO}_2$	C ₃ S
Dicalcium silicate	$2\text{CaO}\cdot\text{SiO}_2$	C ₂ S
Tricalcium aluminate	$3\text{CaO}\cdot\text{Al}_2\text{O}_3$	C ₃ A
Tetracalcium aluminoferrite	$4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$	C ₄ AF

Compound Composition of Portland Cements (%)

<u>Type of Cement</u>	<u>C₃S</u>	<u>C₂S</u>	<u>C₃A</u>	<u>C₄AF</u>
I. Normal	45	27	11	8
II. Modified	44	31	7	13
III. High early strength	53	19	10	7
IV. Low heat	20	52	6	14
V. Sulfate resistant	38	43	4	8

Behavior of Principal Compounds in Portland Cement^{2.6}

<u>Property</u>	<u>C₃S</u>	<u>C₂S</u>	<u>C₃A</u>	<u>C₄AF</u>
Rate of reaction	medium	slow	fast	slow
Heat liberated	medium	small	small	small
Cementing value:				
Early	good	poor	good	poor
Ultimate	good	good	poor	poor

The setting and curing processes that occur in cement are complex as they involve several primary compounds and many reaction products. The solidification process can be described as proceeding through three stages.^{2.5,2.6}

The initial stage occurs as the cement powder is mixed with water and the hydration reaction forms a coating of a silicate gel around the powder particles. These hydration reactions are exothermic and cause heating of the cement after it is mixed with water.

As the reaction continues calcium hydroxide precipitates and fibrils and sheets of tobermorite begin to form an interlocking network which gives strength to the cement. The third stage, curing, consists of continued slow fibril growth and drying. In actuality the three stages continue indefinitely at very slow rates as moisture enters the cement causing additional hydration.

Bitumen:

Solidification of radioactive waste with bitumen is widely practiced in Europe and Japan. For example the centralized waste processing facility of CEN/SCK at Mol, Belgium, annually processes 28 tons of sludge with bitumen. An additional 1300 m³ of "Intermediate-level Waste" has been bitumenized at the Eurobitumen facility at Mol.^{2.8} Only recently has bitumen been used commercially as a solidification agent in the United States.

Bitumen is a mixture of high molecular weight hydrocarbons that is derived as a residue in petroleum or coal tar refining. As a thermoplastic material it behaves mechanically as either a viscous liquid or as a solid, depending on the temperature. Bitumen products are characterized primarily by softening point, penetration at a defined temperature and ductility at a defined temperature.

Current methods of solidifying radioactive waste with bitumen employ its thermoplastic properties to allow simultaneous mixing and drying of waste slurries. Generally, no chemical reaction occurs between radionuclides and bitumen, although it has been reported that releases of strontium may be reduced by processing at temperatures greater than 205°C.^{2.9}

Bitumen is of interest for the Leaching Mechanisms Program for the following reasons:

- It is hydrophobic and readily adhesive to most materials.
- It has relatively low porosity.
- Waste is normally contained within bitumen as dry particles.

The bitumen chosen for the Leaching Mechanisms Program is Pioneer 321 Industrial Asphalt (Witco Chemical Corporation, Lawrenceville, Illinois). This material is recommended by Waste-Chem Company for their radioactive waste solidification system. This material is described by Witco in their technical data sheet^{2.10} as "an all-purpose, tough, medium softening point asphalt for use in laminating paper, foil-to-paper, as a base pigment for paint and varnishes and in the manufacture of sealers and adhesives." Its physical characteristics are reproduced in Table 2.2.

VES:

Polymer thermosets have been investigated for use as low-level waste solidification agents. One commercial polymer system, vended by the DOW Chemical Company, uses vinyl ester-styrene (VES) to solidify low-level waste slurries.^{2.11}

Polyester resins, such as the vinyl ester used in the Dow material, are liquid at room temperature but polymerize to form a hard solid. Vinyl esters are typically diluted with styrene to reduce the viscosity of the liquid vinyl ester monomer. This system is in the class of thermosetting polymers since, once polymerized, it cannot be liquified without destroying the material.

The vinyl ester-styrene material, as marketed by Dow, is water extensible, that is, it can solidify even when emulsified with water. It is this property that is exploited for the waste solidification process. The monomer is blended with liquid waste under high shear mixing to form an emulsion.

Table 2.2

Physical Characteristics of Pioneer 321 Bitumen^{2.10}

Softening Point	190-200°F ASTM D-36
Penetration @ 77°C	20-28 DMM. ASTM D-5
Ductility @ 77°C	2.5-3.5 CMS. ASTM D-113
Solubility CCL ₄	99.5% + ASTM D-2042
Flash Point (C.O.C.)	559°F Min. ASTM D-92
Weight Per Gallon	8.34 Lbs.
Use Temperature	400°F ± 25°
Viscosity @ 400°F	95 Secs. ASTM D-88
@ 375°F	174 Sec. ASTM D-88
@ 350°F	360 Secs. ASTM D-88
Loss on Heating at 325° (for 5 hours)	0.1% Max. ASTM D-6
Loss by volatilization when held at 212° for 1 hour	None
Oliensis Test (AASHTO T-102)	Negative ASTM D-1370

Upon addition of initiators the monomer polymerizes trapping the liquid waste in microscopic cells. This unique structure is of interest for the Leaching Mechanism Program because the waste is retained as individual droplets in the solidified waste form.

Vinyl ester-styrene can also be used to solidify dispersible solids, such as incinerator ash or ion exchange resins, without forming an emulsion. The properties of this solid, relatively non-porous material may be significantly different than those of the emulsion. The non-emulsified VES is also being investigated in this study.

Glass:

This material was chosen for the Leaching Mechanisms Program for several reasons. Vitreous materials have been examined in great detail by high-level waste programs. This solidification agent provides a point of comparison to that body of work. It should be noted however that the high-level waste glass, being a borosilicate, is different from that under investigation in this program. Glass also provides another structure within which radionuclides are held providing another potential mechanism for comparison.

The use of glass as a solidification matrix for low-level waste has been the subject of only limited investigation. Of note are the slagging incineration process, such as the one developed at the Eurochemic facility at Mol, Belgium,^{2.8} and the glass furnace under development at the Mound facility.^{2.12} It is the product of the latter process that has been chosen for the Leaching Mechanisms Program.

The Mound facility glass furnace incorporates incineration of low-level radioactive waste within the furnace. Combustible waste is introduced into a glass melter that is maintained at approximately 1400°C. The waste is incinerated in the space above the molten glass and the residue falls into the melt, where it is mixed into the glass by convection in the heated melt.

The waste form produced by this process is a soda-lime silica glass containing particles of ash interspersed throughout the material. Radionuclides are contained as oxides, often within the glass itself. The nominal composition of the glass is given in Table 2.3. It forms a non-porous solid with very high compressive strength.

Table 2.3

Composition of Mound Facility Glass^{2.12}

<u>Component</u>	<u>Weight Percent</u>
SiO ₂	74.8
Na ₂ O	14.4
CaO	6.2
MgO	3.8

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3. LEACHING MECHANISMS PROGRAM

Although the release of radioactivity from a waste form to an aqueous environment is recognized to be due to one or more mechanisms such as diffusion, dissolution, corrosion or ion exchange, the mechanisms of leaching and the factors which control the mechanisms for waste form matrices are not fully understood.^{3.1} For this reason, a series of leaching experiments using a range of solidification agents is being conducted to provide a basis for understanding leaching mechanisms. An understanding of the prevailing leaching mechanisms for the various matrix materials will not only provide a basis for predicting the long-term behavior of the waste forms in disposal environments but may also provide guidance on the use and choice of solidification materials, the treatment of waste streams prior to solidification, the waste/binder ratios and the suitability of waste form containers.

The overall objective of this task is to determine the leaching mechanism(s) of a variety of matrix materials either in use or being considered for the solidification of low-level radioactive wastes by defense and commercial waste generators. To accomplish this objective the program effort for FY 84 was divided into three subtasks: (1) The literature survey, (2) An experimental effort which involved sample fabricating for leach test and, (3) Development of a leaching data base. Each of these subtasks is described in the following sections.

3.1 Subtask 1: Literature Survey

Under the literature survey, published LLW leach data and leaching models are being compiled.

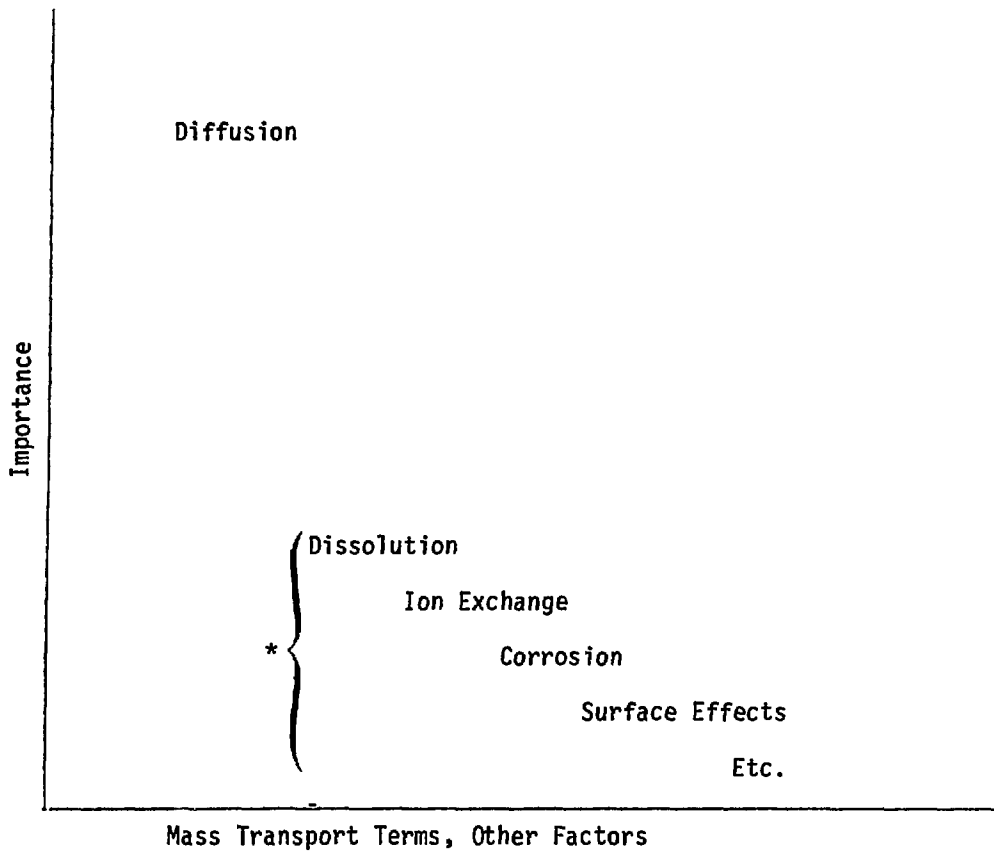
3.1.1 Leaching Data: Leaching data on all published solidification agents are being compiled, not just those which are under experimental investigation in Subtask 2 (i.e., portland cement, bitumen, vinyl ester-styrene and soda-lime glass). Of particular interest are data on replicate samples, where some measure of statistical variation in the data is available, and data on nominally identical samples of varying size, from which scaling effects can be gauged. The most relevant data are for actual solidified waste

and it is of interest to compare these leach data with those of simulated waste and tracer experiments. Appropriate leaching data compiled from the literature search are being screened for inclusion in the data base, which is described in Section 3.3. References 3.2-3.9 list those data which have been selected for inclusion in the data base to date.

3.1.2 Mass Transport Leaching Models for LLW: Leaching models for LLW generally proceed from the assumption that diffusion is either the only, or most important process, controlling the release of radionuclides from the waste form. Figure 3.1 illustrates schematically the general perception of the relative importance of terms which may be included in a mass transport equation. The release equation representing diffusion from a semi-infinite medium into a leachant maintained at infinite dilution provides the simplest leaching model.^{3.10,3.11} Considering the finiteness of actual waste forms in a diffusion-only model results in substantially increased complexity of the release equation.^{3.12,3.13} Finally, including terms in the mass transport equation which account for processes such as dissolution, corrosion, ion exchange or surface effects also results in increased complexity of the release equation.^{3.14-3.16} Figure 3.2 illustrates the increase in complexity introduced into the release equation for semi-infinite media resulting from including a dissolution term in the mass transport equation. The equation for diffusional release from a finite cylinder is also included and shows the complexity introduced by depletion effects from the finiteness of waste forms. The equation incorporating diffusion plus concentration-dependent dissolution may represent soluble waste in an insoluble matrix whereas the equation incorporating diffusion plus surface dissolution may represent soluble waste in a soluble matrix or a matrix which, upon dissolution of the waste, is extremely porous.

3.2 Subtask 2: Fabrication of Test Specimens and Experimental

Leaching experiments are being conducted on low-level radioactive waste solidification agents to provide long term baseline information for both the Leaching Mechanisms Program and the Accelerated Leach Test Program to follow in FY 85. While much of the information being used for the leaching mechanisms data base is drawn from the literature, a series of leaching tests is



*Relative importance may vary with waste type, solidification agent and elapsed leach time.

Figure 3.1 Traditional view of the relative importance of mass transport terms in the leaching of low-level radioactive waste.

<u>Model Description</u>		Release Equation for the Mobil Species ^a (Cumulative Fractional Release)
Medium	Transport Mechanism	
semi-infinite, homogeneous, chemically inert	diffusion	$\frac{\sum a_n}{A_0} * \frac{V}{S} = 2 \left(\frac{Dt}{\pi} \right)^{1/2}$
finite cylinder, homogeneous, chemically inert	diffusion	$\frac{\sum a_n}{A_0} = 1 - \frac{32}{\pi^2} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{\exp\left[-\left(\frac{J_{0m}}{r}\right)^2 Dt\right]}{J_{0m}^2} \cdot \frac{\exp\left\{-\left[\frac{(2n-1)\pi}{h}\right]^2 Dt\right\}}{(2n-1)^2}$
semi-infinite, uniform initial, concentration	diffusion + concentration-dependent dissolution	$\frac{\sum a_n}{A_0} * \frac{V}{S} = (kD)^{1/2} \left[\left(t + \frac{1}{2k}\right) \text{erf}(kt)^{1/2} + \left(\frac{t}{\pi k}\right)^{1/2} e^{-kt} \right]$
semi-infinite, uniform initial, concentration	diffusion + surface dissolution (moving boundary)	$\frac{\sum a_n}{A_0} * \frac{V}{S} = (RD)^{1/2} \left[\left(t + \frac{1}{2R}\right) \text{erf}(Rt)^{1/2} + \left(\frac{t}{\pi R}\right)^{1/2} e^{-Rt} + t \right]$

^a(V/S) = volume to surface ratio; t = time; D = diffusion constant; k = dissolution rate constant; erf = error function; R = U²/4D where U = velocity on the moving boundary. J_{0m} = mth positive zero of the zeroth order Bessel function; r = radius of cylinder; h = height of cylinder.

Figure 3.2 Some selected mass transport models.

necessary to provide a measure of the overall statistical variability of leaching experiments on the pure matrix materials. Rarely do literature sources discuss the experimental spread of leach tests. Therefore, it is often unclear, when comparing results from two sets of experiments, whether differences have actual mechanistic implications or are simply due to the inherent variability of the experiments. Moreover, very few leaching studies have been conducted for sufficiently extended times to resolve dominant long-term trends. The experimental task in this program is intended to begin to fill these two gaps.

A simple system of solidification agent/radionuclide tracers/distilled water was chosen to eliminate extraneous variables that may obscure results. The solidification agents used, as discussed earlier, were chosen because they provide a variety of material characteristics and because they all have either been used or are being considered for use for low-level waste solidification.

3.2.1 Waste Form Fabrication: Laboratory scale waste forms were prepared with portland type I cement, Pioneer 321 bitumen, vinyl ester-styrene/water emulsion and vinyl ester-styrene without water. Formulations of these products are given in Table 3.1. The glass samples, as described in Section 2.3, are being supplied by Mound Laboratory.

The waste forms produced measure approximately 4.8 cm by 6.5 cm. Homogeneity of samples has been assured either by the production technique itself or by gamma spectroscopy of subsamples taken prior to solidification of the waste form.

3.2.2 Preliminary Leach Test Results: Leach tests are being conducted in triplicate using the ANS 16.1 (February 8, 1984) protocol. The test has been modified to include extra samplings and by extension of the duration of the test. Leachate samples have been taken at 30 seconds (rinse), 2 and 7 hours, 1, 2, 3, 4, 5, 11, 14, 28 and 42 days and every 21 days thereafter. The leachant is 1300 ml of distilled water. Leachate samples are being analyzed for radionuclides, pH and chemical species that reflect dissolution of the solidification agent itself.

Table 3.1

Waste Form Compositions (weight %)

Portland Type I Cement

Cement	70%
Water	30%

Pioneer 321 Bitumen

Bitumen	100%
---------	------

Vinyl Ester-Styrene Emulsion

Vinyl Ester-Styrene Monomer	49.2%
Water	48.6%
Tracer	0.9%
Polymerization Initiator	1.3%

Vinyl Ester-Styrene

Vinyl Ester-Styrene Monomer	97.4%
Tracer	0.7%
Polymerization Initiator	1.9%

Preliminary results of the leach tests for ^{137}Cs , ^{85}Sr and ^{60}Co are shown in Figures 3.3, 3.4 and 3.5 respectively. Each figure shows the cumulative fraction released of a single isotope for the three solidification agents being tested. Cesium releases for cement are higher by two orders of magnitude than releases from vinyl ester-styrene/water emulsion or bitumen waste forms. Strontium releases for VES and bitumen are similar to those for cesium. Release of strontium from cement is an order of magnitude lower than cesium release from cement. Leachabilities of cobalt from VES and bitumen are again similar to those of other radionuclides. Activities of ^{60}Co in the cement leachate was below the detection limits of the equipment used. These leachates are currently being analyzed with more efficient detectors.

3.2.3 Solid Phase Analysis: Two nominally identical portland cement samples were sectioned and analyzed by Scanning Electron Microscopy (SEM) and Energy-Dispersive Spectroscopy (EDS). EDS is a method of solid phase analysis that provides a quantitative estimate of elemental concentration. One sample had been leached while the other was unleached. To prepare specimens for analysis the two cylindrical (2cm x4cm) portland cement samples were sectioned, removing a thin, circular slice from the center of each cylinder. The specimens were dewatered in a vacuum and given a thin coating of carbon for electrical conductivity.

Each sectioned waste form was analyzed at various points along a radius for calcium, silicon, aluminum and magnesium. Generally, several spectra were made at each location encompassing a sample area of approximately 0.09 mm^2 for each analysis.

Figure 3.6 illustrates changes that occurred in the portland cement matrix (neat cement) upon leaching for 120 days in distilled water. The differences in relative peak heights between the SEM/EDS spectra of the leached specimen (top) compared to that of the unleached specimen (bottom) indicate changes in elemental composition of the surfaces of the two specimens. Changes apparent in the spectrum of the leached sample surface compared to that of the unleached sample include:

- Increases in the relative concentration of magnesium (Mg) and silicon (Si).

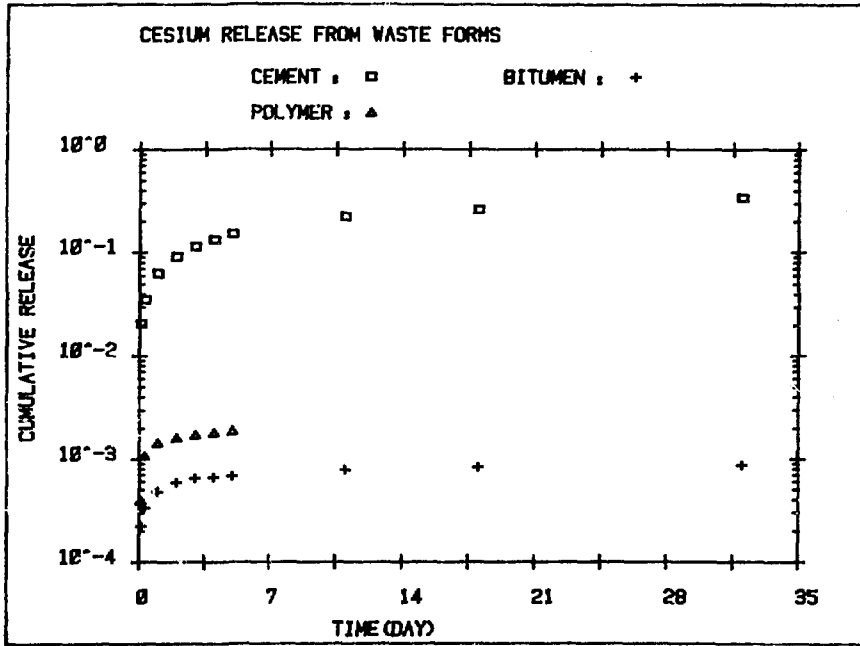


Figure 3.3 Cumulative fraction release of cesium-137.

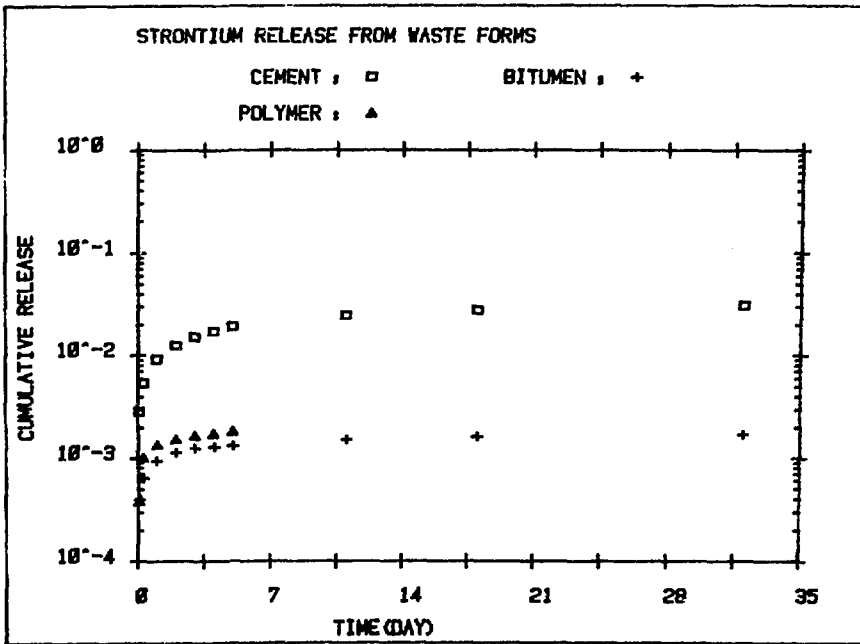


Figure 3.4 Cumulative fraction release of strontium-85.

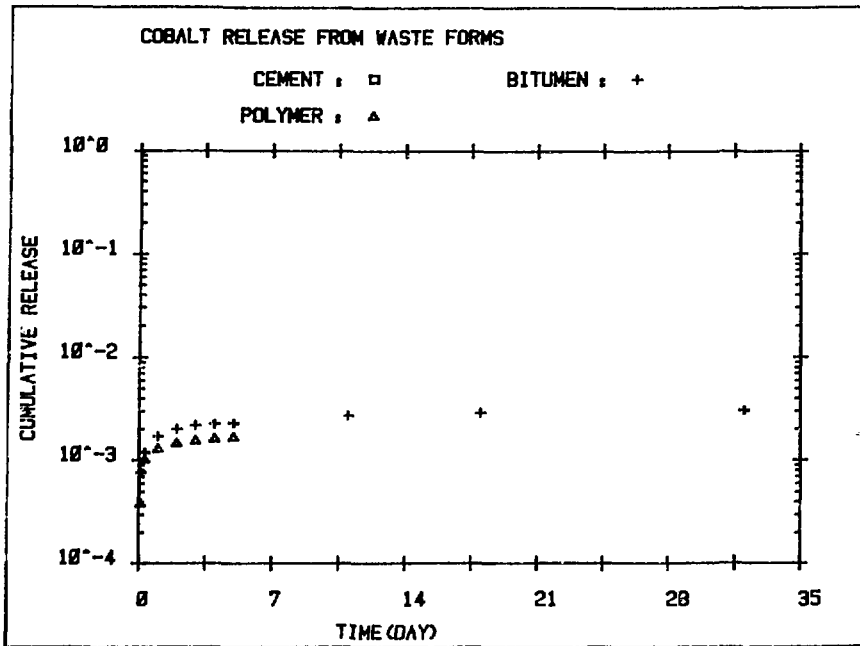


Figure 3.5 Cumulative fraction release of cobalt-60. Release for cement waste forms were below detection limits and are being re-analyzed.

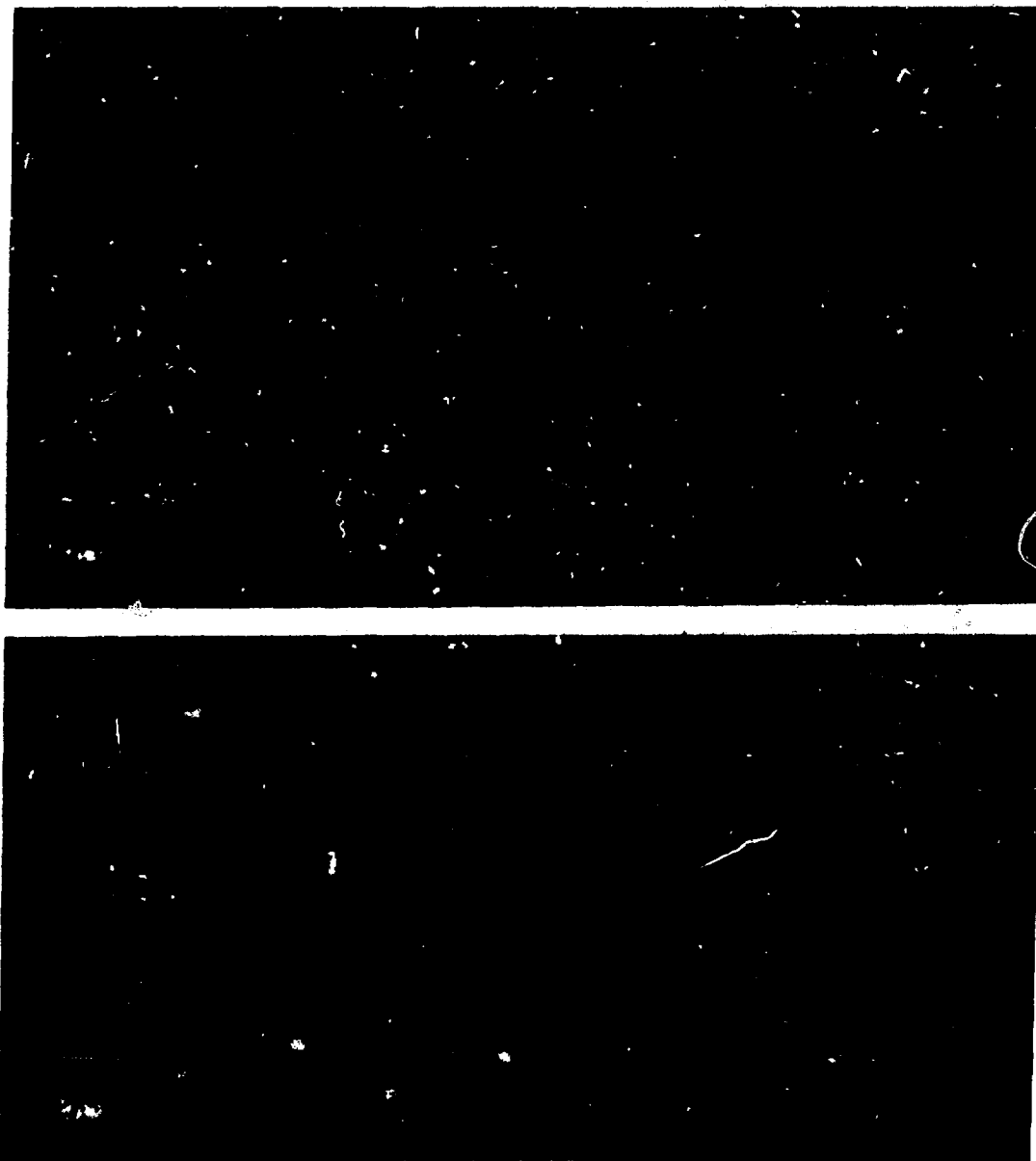


Figure 3.6 SEM/EDAX spectra of the surfaces of two nominally identical portland cement samples. The top spectrum of a sample leached for 120 days in distilled water shows increases in the concentrations of Mg and Si relative to Ca and the disappearance of the K peak.

- The disappearance of the potassium (K) peak.
- The appearance of two peaks between Si and calcium (Ca). These peaks correspond to chlorine and sulfur and indicate that chloride and sulfate anions are accumulating on the surface of the leached samples.

These differences in the spectra of the leached and unleached samples indicate changes in chemical composition which may affect leachability.

Figure 3.7 shows the ratio of silicon to calcium in the leached and unleached sample cross-sections. The ratio remained constant through the unleached sample. However, for the leached waste form the surface of the cylinder had a significantly higher ratio than the unleached sample. This effect was not observed 0.5 cm into the sample. Analysis of interior locations of the leached sample show silicon to calcium ratios that are similar to the unleached specimen. Surface depletion of calcium relative to the much less soluble silicon in the cement accounts for this effect. Further analysis will better define the shape of the depleted zone.

3.3 Subtask 3: Development of a Leaching Data Base

Leaching data from the experimental part of this task plus leach data from the literature are being input into a data base to facilitate analysis. The Scientific Information Retrieval (SIR)* data base is being used for this purpose. Although data input is underway, the major effort involved with the data base has been developing the 'schema' and the retrieval programs. The 'schema' provides the instructions and format for entering the data and other information necessary to provide a complete description of the leach samples. Information on the solidification agent, waste type, sample size, leachant composition, the reference from which the data was taken, plus other information are cataloged for each sample or set of replicate samples. The retrieval

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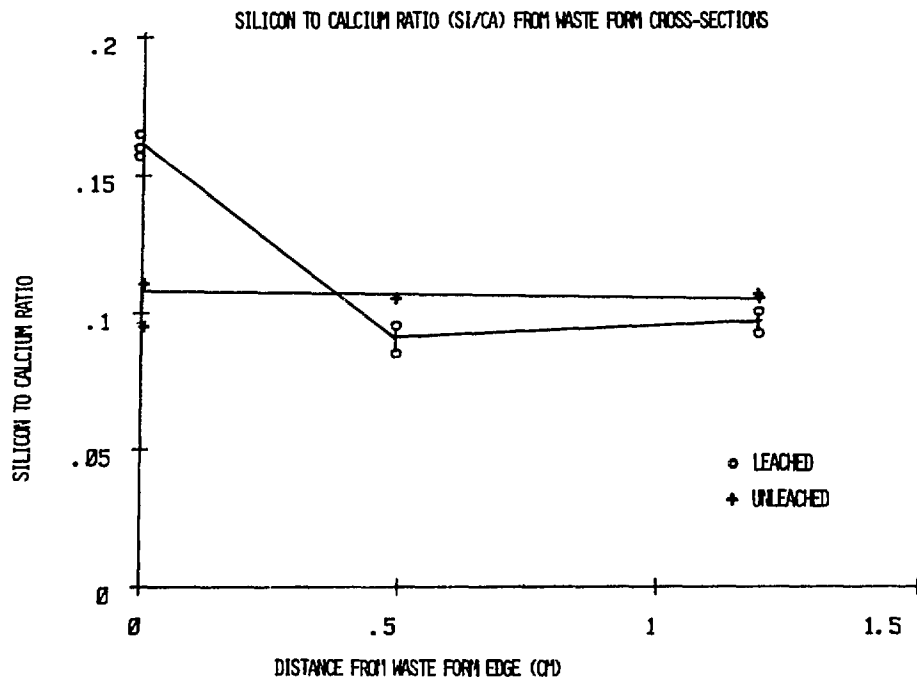


Figure 3.7 Silicon to calcium ratios for three positions along cross-section radii of leached and unleached portland cement cylinders. Depletion of calcium at the edge that was exposed to water caused the increase in Si/Ca ratio.

programs process the data for curve fitting, plotting, printing out in various formats and other operations. Although the schema is still undergoing revision, retrieval procedures and curve fitting programs using the equations listed in Figure 3.3 and other equations have been written and are being tested on data in the data base.

The 'schema' is formatted in pages (i.e., records) of information. The first page contains the sample information on solidification agent, etc., while the leaching data is entered in the following pages, one page for each data point. For leaching data the points are defined by the sampling time and contain fractional release values for one or more radionuclides and/or other elements or compounds of interest in the leaching experiments.

Each set of leach data is assigned a five digit number, the TESTID, and may be further specified by an alphanumeric SAMPLEID. A Sample Replicate Number may also be specified for replicate experiments.

The five digit TESTID is subdivided into (2 digits, 1 digit, 2 digits) for organizational purposes. The first two digits are used to designate the literature reference and/or reporter of the data. The third digit is currently unassigned while the last two digits identify individual experiments. The SAMPLEID is currently used for local identification of leaching experiments performed under this task. It will be redefined when the indexing system for the data base is developed. The Sample Replicate Number may be used to identify replicate experimental runs. All of these numbers may be redefined as the data base is modified from user experience. Figures 3.8 and 3.9 show trial Sample Information and Data pages.

TESTID
 SAMPLEID
 COMMENTS
 SAMPLE DESCRIPTION
 DATA UNIT-COUNT(1), FRAC REL(2)
 SAMPLE COUNT MULTIPLIER
 FRAC RELEASE MULTIPLIER
 WASTE TYPE
 SOLIDIFICATION AGENT
 SAMPLE WEIGHT(G)
 SAMPLE SURFACE AREA(CM**2)
 SAMPLE VOLUME(CM**3)
 SAMPLE DIAMETER(CM)
 SAMPLE HEIGHT(CM)
 DATE SAMPLE WAS MADE
 LEACHANT TYPE
 LEACHANT VOLUME(CM**3)
 LEACHANT TEMPERATURE(C)
 LEACHANT PH
 DATA REPORTED BY
 TITLE
 JOURNAL
 START DATE
 START TIME
 CS-137, SOURCE TERM
 CS-134, SOURCE TERM
 SR-85, SOURCE TERM
 CD-60, SOURCE TERM
 CE-144, SOURCE TERM
 STMN54
 RN07 SOURCE TERM
 RN08 SOURCE TERM
 RN09 SOURCE TERM
 RN10 SOURCE TERM
 RN07 LABEL
 RN08 LABEL
 RN09 LABEL
 RN10 LABEL
 CHEM01
 CHEM02

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Figure 3.8 Trial Sample page for the leaching data base.
 The Sample Page lists physico-chemical information,
 the reference from which the data was taken and
 other information.

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TESTID
NUMBER
SAMPLE REPLICATE NUMBER

COMMENTS
SAMPLING DATE
SAMPLING TIME
COUNTING VOLUME(ML)
CUMULATIVE TIME(DAYS)

CS137
CS134
SR85
CO60
CE144
MN54
RN07
RN08
RN09
RN10

Figure 3.9 Trial Data Page for the leaching data base. The Page lists fractional release at a given time in the experiment for the radionuclides and/or other chemical species of interest.

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