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LEACHING MECHANISMS OF SOLIDIFIED LOW-LEVEL WASTE THE LITERATURE SURVEY

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ABSTRACT

A literature survey on leaching mechanisms, available mathematical models and factors that affect leaching from solidified low-level radioactive waste (LLW) has been compiled. Physicochemical mechanisms which have been identified include diffusion, dissolution, ion exchange, corrosion and surface effects. Diffusion has been generally considered to be the predominant mechanism in LLW leachability with the other processes playing relatively minor roles. However, this hierarchy of importance has been strongly questioned for waste forms containing soluble salts and has been shown to be invalid for waste forms incorporating sorbents which control the release of radionuclides by ion exchange. Leaching behavior has been modeled both mathematically for curve fitting to leaching data and by consideration of physical and chemical interactions within and between solidification agents, waste materials and additives, if any. Detailed descriptions of chemical reactions in cement including interactions with silica-containing additives and cesium are available. Physicochemical analyses of bitumen and polymer solidification agents have considered them to be inert encapsulants with limited water permeability. All of the mathematical models are derived from solutions to the diffusion equation and most are limited to consideration of a constant diffusion coefficient and a semi-infinite medium. Other mechanistic processes are included as additional terms in the equation. Each additional term represents a mechanistic process and incorporates a parameter which must be assigned a value, either by computation within the model or from independent knowledge. No comprehensive evaluations of mathematical models for LLW based on curve fitting to data were found in the literature. Factors that affect leaching have been categorized as system factors, leachant factors and waste form factors. System factors include temperature, pressure, radiation, time and the ratio of waste form area to leachant volume. Leachant factors include pH, Eh, flow or replacement frequency and composition while waste form factors include composition, surface condition, porosity and surface area to volume ratio. Information obtained from the literature is reported for each of these factors.

EXECUTIVE SUMMARY

A literature survey on leaching mechanisms and factors that affect leaching from solidified low-level radioactive waste (LLW) has been compiled from reviews of previous work, pertinent models and information about parameters known to affect leaching.

1. Introduction

The final report on the leaching mechanisms of the high-level waste (HLW) borosilicate glass waste form 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. Standard leach tests currently available are more suited for formulation development and quality control than for long-term prediction of leaching behavior.

2. 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 clay 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.

3. 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 analyze rate processes since, if the rate behavior obeys the Arrhenius equation, then an apparent activation energy can be assigned to the process. Correlating apparent activation energies with reasonable physicochemical processes is a traditional tool for analyzing rate processes. Leach rates of some glasses follow Arrhenius behavior. The leachability of cement increases with temperature; however, an irreversible change in the pore structure of cement with increasing temperature which increases leachability complicates any attempted Arrhenius analysis. No definitive trends in the leachability of bituminized waste forms with temperature have been reported. Pressure effects in near surface burial of LLW may be negligible except for bituminized waste forms, which will probably deform by creep. The effect of creep deformation on the leachability of bituminized waste has apparently not been investigated. 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 agent matrix and the incorporated waste are physically and chemically distinct. Waste form composition, including the physicochemical natures 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.

4. 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. 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 remain 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. The dissolution mechanism in one of the models 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 of 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. However, it is not clear how this model could be useful for LLW Leaching.

5. Summary and Conclusions

This report has 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 except possibly for the case of cesium release from cement. This is because most experimental and modeling efforts have concentrated on cesium release from cemented waste forms. However, definitive conclusions on leaching mechanisms and models are substantially limited by the lack of curve fitting and evaluation of complete, or near complete, leaching curves since virtually all modeling of cesium release has been based on analysis of a relatively small fraction of the total release in the initial stages of leaching. Cesium is also unique in cement in that it may be the only radionuclide of concern in LLW management which does not have at least the possibility of chemical reaction with cement (technetium in some chemical forms may be another although this was not addressed in this report). Reported leaching mechanisms for bitumen have included diffusion and dissolution alone and in combination. However, none of the work on bitumen appears to be really convincing. Mechanistic studies on polymer solidification agents appear to be in an early phase of development and have been limited to investigating the permeation properties of the polymer solidification agents themselves.

1. INTRODUCTION

This report documents the results of a literature survey on the leaching mechanisms of solidified low-level radioactive waste. The information presented in this report includes reviews of previous experimental work and pertinent mathematical models which have been used to analyze leaching data. Also included is information on parameters which may affect leaching, such as the physicochemical properties of various solidification agents, waste types, environmental conditions and waste form properties. Finally, the effects of the environmental and waste form parameters and their interactions with postulated leaching mechanisms are correlated with leach testing. The question with regard to leach testing is whether long term performance can be predicted with confidence from short term testing. The answer to this question must be based on knowledge of leaching mechanisms and interactions between the waste form and disposal environmental conditions over both the short and long term. In sum, the objective of this report is to document the current state of knowledge of the leaching mechanisms of solidified low-level radwaste and to relate this knowledge to the goal of long-term performance assessment.

The Low-Level Waste Program has initiated a program to evaluate leaching mechanisms with emphasis on predictive capabilities and accelerated testing. Leaching mechanisms research will better allow investigators to understand the performance of the waste form for low-level waste (LLW) and allow modelers to take credit for the waste form in performance assessments. Understanding factors that affect leach rates without changing the mechanisms will allow development of accelerated test procedures. The results of investigations of the leaching mechanisms of borosilicate glass systems similar to that to be used for high-level waste (HLW) solidification have been reported¹. Although the borosilicate glass studies provide some guidance for the LLW leaching mechanisms studies, the details of the high-level waste systems and those of LLW systems are significantly different. Some of these differences are:

- The time span of concern for LLW is on the order of a few hundred years as compared to thousands of years for HLW. The radionuclides of concern in LLW are relatively short-lived fission and activation products, whereas the very long-lived transuranic elements are the radionuclides of primary concern in HLW.
- The trench water in LLW shallow land burial (SLB) sites has much different characteristics than the groundwater in HLW deep geologic repositories. HLW repositories (except in salt) have been postulated to be flooded with slow moving, anoxic groundwater which will be in chemical equilibrium with the host rock and, eventually, with the HLW form as well¹. Conversely, SLB trench water may range from aerobic to anaerobic and will contain organic products from biodegradation and other constituents picked up during runoff and seepage into the trench. Conditions in a trench may vary from saturated to dry depending on climate and seasonal variations in precipitation.

- Activity in SLB trenches, once leached from the waste form, is potentially directly available to the environment. Transport out of the trench can occur via downward movement to groundwater, by lateral movement toward the disposal site boundary or by movement to the surface via plants whose roots have penetrated into the trench.

Qualitatively, the basis for leaching of solidified LLW is release of radionuclides from the waste form upon contact with water. The mechanism for leaching has been assumed to be diffusion, or diffusion dominated, by virtually all researchers. The analytical basis for the diffusion mechanism has been the linearity of plots of cumulative-fraction-released (CFR) vs the square-root-of-time over some selected range of experimental leaching data. The procedure has generally included three steps:

- (i) Discard the initial data from the leaching experiment as atypical due to surface effects. For example, in the ANS 16.1 Leachability Test a 30 second wash is specified which is then subtracted from the source term. The general consensus is that the initial surface wash occurs by a different mechanism from the long-term data and so should be treated separately.
- (ii) Use the linear (more or less) region of the data on the CFR vs. $(\text{time})^{1/2}$ plot which remains after discarding the short-time data to calculate an effective diffusion coefficient.
- (iii) Often, leaching data at 'long' times does not remain linear vs. $(\text{time})^{1/2}$. Depending on conditions this has been attributed to source term depletion, to leachant saturation effects and to surface effects changing with time. If the leaching release becomes linear with time, dissolution or corrosion have been cited as having superseded diffusion as the predominant leaching mechanism.

This procedure may be adversely affected by any or all of several possibilities. If diffusion is not the only important mechanism controlling mass transport out of the waste form, then a problem would arise from attempting to fit a wrong or incomplete functional description to the data. Other potential problems may arise from the following possibilities:

- The diffusion coefficient, which has generally been assumed to remain constant during leaching, may vary significantly with varying concentration in the waste form, waste form porosity and leaching time.
- Conditions in laboratory leaching experiments may be significantly different than leaching conditions in a burial trench.
- Waste forms, being real rather than hypothetical materials, may change their leaching characteristics due to the leaching process itself.

Numerous solutions to the diffusion equation (equivalently, the heat equation) for various boundary and initial conditions have been documented²⁻⁴. Boundary conditions include the shape of the waste form, surface conditions and leachant composition while initial conditions specify the radionuclide distribution within the waste form prior to leaching. With certain restrictions, the solution to the semi-infinite medium problem can be applied to any diffusion problem over part of the data range, e.g., the first

20% or so of the CFR according to Nestor's analysis of diffusion from cylinders⁵. Solutions to the diffusion equation for other geometries are also available²⁻⁴. The solution for cylindrical waste forms has been used in a procedure developed by the American Nuclear Society to quantify diffusional leaching in terms of a leaching index and to account for source-term depletion due to the finiteness of real waste forms⁶. Solutions of the diffusion equation for realistic geometries allow quantitative comparison of data to a diffusion model. The goodness-of-fit of the model to the data should provide a measure of the applicability of the diffusion-only model to the problem of LLW leaching. One aspect of this program is to determine the applicability of the diffusion model to leaching data for several types of solidified LLW.

One condition must always be met for real systems: the leach rate at long time must approach zero as the diffusant is leached out. Other restrictions may apply because of the initial and boundary conditions which apply to specific situations and because of the nature of the mathematical analysis. These restrictions are discussed in later sections of this report.

1.1 Leach Testing and Long-Term Leaching Behavior

The standard leach tests currently available were designed to be used for relative comparison of formulations, quality control or for meeting regulatory requirements, not for long term prediction of leaching behavior. Some reasons for this are listed as follows:

- (i) No account of actual burial conditions over the long term is taken. Specifically, the actual composition of trench water, including aerobic vs. anaerobic conditions, the presence of carbonates and natural organic complexing agents from biodegradation in trench water and other factors have not been accounted for.
- (ii) Not enough account is taken in the standard leach tests of boundary condition requirements. The leachant replacement frequency in all semi-dynamic leach tests may be inadequate, especially for cement. Alternatively, it is not clear that such tests adequately mimic long-term conditions in a burial trench.
- (iii) Source term depletion in the waste form is accounted for in only one test procedure--the ANS 16.1 Leach Test Procedure⁶.
- (iv) Diffusion with a constant diffusion coefficient has been the only leaching mechanism considered in the standard leach tests. The adequacy of this assumption has been questioned, especially for waste forms incorporating soluble waste, but has never been adequately tested^{8,59,60}.
- (v) Solidified LLW forms are generally heterogeneous systems. The solidification agent matrix is normally physically and chemically distinct from the waste material. In such systems one phase often exerts much more control over leaching behavior than the other phase. Some of the mathematical problems of modeling diffusion in two-phase systems have been reviewed².

The knowledge to be developed in this task will be directed toward the goal of long-term prediction of leaching behavior. This is to be accomplished through knowledge of: (i) leaching mechanisms for each radionuclide in each solidification agent and, (ii) waste form leaching characteristics in the burial site environment. Factors which influence leaching have been discussed in the literature and some have been investigated experimentally⁷⁻²². This report documents information reported on leaching mechanisms of low-level waste and factors which affect leaching and includes both experimentally supported and speculatively proposed mechanisms.

2. LEACHING MECHANISMS OF SEVERAL SOLIDIFICATION AGENTS FOR LLW

This section documents reported leaching mechanisms for several solidification agents used for solidification of LLW. Leaching mechanisms in any specified disposal environment are largely dependent on waste form characteristics. These, in turn, are dependent upon the solidification agent, the type of waste which is solidified and processing parameters such as temperature, homogeneity, waste-to-binder ratios, etc. Portland cement has been by far the most common solidification agent with bitumen gradually increasing in use. Polymer solidification agents have been used to only a very limited extent because of cost and other problems associated with interactions with waste components. The use of soda-lime glass as a possible solidification agent for low-level waste has been experimentally investigated by Mound Laboratory²³.

Leaching results from mass transport of substances within as well as out of a waste form. Mass transport processes which have been identified as occurring in solidified waste forms include diffusion, dissolution, ion exchange, corrosion and surface effects. Diffusive transport out of the solidified waste form has traditionally been credited as being the principal leaching mechanism. The other factors have often been assumed to be relatively minor compared to diffusion. Although the validity of this assumption has been questioned, little by way of review and evaluation of the relative importance of mechanistic factors in LLW leaching is available. Figure 2.1 pictures schematically the traditional view of the relative importance of mass transport processes in LLW leaching.

2.1 Portland Cement

Portland cement solidifies as the result of a hydration process with water. Cement leachability is affected not only by the type and quantity of waste but also by the amount of water used to set the cement^{15,30}. Sorbents such as vermiculite and other additives are often added to the cement-waste mixture. These additives also influence the leachability of the waste form. Portland cement and the hydrated chemical components that constitute solidified portland cement have been shown to exhibit very limited sorption for cesium²⁴⁻³⁰. A somewhat greater, but still very limited, sorption for strontium onto hydrated portland cement has also been reported²⁹⁻³¹.

Neilson and Colombo²⁹ reported distribution ratios (Rd) for portland cements and other materials which were under consideration as additives for cement-based waste forms. The distribution ratio is defined as the ratio of the activity sorbed onto a solid sorbent per unit weight divided by the activity, per unit volume, remaining in solution.

$$Rd = \left(\frac{A_s}{W_s} \right) / \left(\frac{A_l}{V_l} \right) \quad (2.1)$$

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

Figure 2.1 Traditional view of the relative importance of mass transport terms in the leaching of low-level radioactive waste.

Rd = distribution ratio

A_s = activity associated with the solid

W_s = weight of dry solid

A_l = activity remaining in liquid

V_l = initial volume of liquid

The data from Reference 29 is reproduced in Table 2.1. These are single-point data based on the results of sorption experiments at room temperature for 0.5 g of powdered (< 63 μm) solid agitated for three days in 20 ml of liquid which originally contained 1.0 μ Ci of radionuclide in solution. Results were expressed as distribution ratio rather than distribution coefficient, K_d, since the experiments were not continued to determine if equilibrium was attained. These data indicate that portland cement is a relatively poor sorbent for cesium, whereas the synthetic zeolites (Ionsiv 1E-95 and Ionsiv A-51) are relatively strong sorbents for cesium. The reduced sorption by the zeolites in saturated calcium hydroxide solution compared to pure water was attributed to competition with the calcium ions.

Atkinson, et al.³⁰, investigated cesium and strontium leaching from two types of cement waste forms and reported the leaching mechanisms which they deduced from mechanistic modeling of data from leaching and sorption experiments. The two types of waste forms which they studied were described as:

- (i) a 'homogeneous' wasteform produced by mixing an aqueous solution of radionuclide with ordinary portland cement (OPC).
- (ii) a 'heterogeneous' wasteform produced by mixing granuals of a contaminated zeolite ion-exchange (clinoptilolite) with OPC.

Atkinson, et al.³⁰, also performed sorption experiments, which they allowed to proceed to apparent equilibrium, at several concentrations using portland cement and zeolite materials. They fitted the data to a Langmuir adsorption isotherm to quantify the sorption versus concentration behavior. The form of the Langmuir adsorption isotherm they used to fit the data is shown in Equation (2.2).

$$C_{ads} = \gamma C_l / (1 + \gamma C_l / C_{sat}) \quad (2.2)$$

C_{ads} = concentration of adsorbed species on solid

C_{sat} = maximum adsorption possible on solid (i.e., all adsorption sites filled)

C_l = concentration in the liquid

γ = constant for the specific adsorbent/liquid system

Table 2.1

Measured Distribution Ratios for Selected Candidate Additive Materials for Cement Waste Forms

Material	DISTRIBUTION RATIO (Rd)							
	CESIUM		STRONTIUM		COBALT		CERIUM	
	D.W. ^a	Ca(OH) ₂ ^b	D.W. ^a	Ca(OH) ₂ ^b	D.W. ^a	Ca(OH) ₂ ^b	D.W. ^a	Ca(OH) ₂ ^b
Thixojel ~ 1	900	600	240	1,200	280	42	24,000	19,000
Limonite	5.0	3.0	39	3.0	-	-	-	-
Glauconite	60	83	63	25	-	-	-	-
Attaflow-350	140	98	350	20	-	-	-	-
Attasorb-LVM	310	150	820	270	59,000	49	26,000	2,100
Mineral Colloid BP	59	540	17	1,300	20	25	110	26,000
Thixojel ~ 3	490	790	99	1,000	290	19	290	Very High
Tuff	18	7.0	160	6.0	-	-	-	-
Alumina	17	7.0	32,000	560	150,000	390	710,000	20,000
Silica	3.0	1.0	13	0	-	-	-	-
Bauxite	19	8.0	210	26	-	-	-	-
Unmilled Incinerator Ash	5.0	11	-	-	-	-	-	-
Ball-milled Incinerator Ash	8.0	8.0	-	-	-	-	-	-
Volcanic Ash	11	2.0	-	-	-	-	-	-
Illitic Slate	53	21	-	-	-	-	-	-
Ionsiv IE-95	89,000	37,000	-	-	-	-	-	-
Ionsiv A-51	9,700	2,400	-	-	-	-	-	-
Coal Fly Ash	1.5	4.8	-	-	-	-	-	-
Portland Cement Type I	1.0	0	6.0	15	-	-	-	-
Portland Cement Type III	0	2.0	10	11	-	-	-	-
High Alumina Cement	2.0	0	36	32	-	-	-	-

^aDemineralized Water^bSaturated Ca(OH)₂ Solution

Values of γ and C_{sat} for adsorption onto hardened portland cement and values of γ for desorption from clinoptilolite (a natural zeolite) derived from the curve fits by Atkinson, et al.³⁰, are listed in Tables 2.2 and 2.3., as reproduced from Reference 30. These parameters indicate that, at 30°C, sorption of cesium and strontium by hardened portland cement is very limited compared to that of a known strong sorbent for these ions.

Table 2.2

Parameters Describing the Absorption of Cs and Sr onto Hardened Cement Paste

Element	γ	C_{sat} (mole l ⁻¹)
Cs	4.2	0.002
Sr	10	0.64

Table 2.3

The Desorption Partition Coefficient Between a Simulated Waste Clinoptilolite and Various Liquids

Liquid	pH	γ (Cs)	γ (Sr)
Distilled water	7.3	$2.6 (+0.9) \times 10^5$	$2(+1) \times 10^5$
Saturated Ca(OH) ₂	12.4	$2.1 (+0.6) \times 10^4$	$5(+3) \times 10^4$
OPC equilibrated water	12.4	$2.2 (+0.6) \times 10^4$	$6(+3) \times 10^4$
Equilibrium leach test on clinoptilolite/OPC wasteform		$1.8 (+0.4) \times 10^4$	$5(+1) \times 10^3$

Leach data for the 'homogeneous' type waste forms were taken from the literature³¹. The 'heterogeneous' type waste forms were fabricated and leach tested by the authors. Both static and dynamic leach tests were performed. The static leach tests were performed to determine steady state concentrations between sample and leachant. The dynamic tests used distillation recycling of water past the sample as in a Soxhlet procedure. The flow rate was approximately 3 ml min^{-1} to ensure that leachant concentrations remained well below saturation.

Mechanistic modeling of leaching release from the OPC and OPC - clinoptilolite simulated waste forms specifically considered diffusion as the mass transport mechanism and adsorption/desorption from both the OPC and zeolite materials as possible release mechanisms for the Cs and Sr radionuclides. Adsorption parameters were derived from the sorption experiments which were analyzed assuming a Langmuir adsorption isotherm. Diffusion parameters were derived both from leaching data and from permeation experiments which provided independent estimations of diffusion coefficients of ions through water-saturated cement³².

The mechanistic interpretation deduced by Atkinson, et al.³⁰, from this work are summarized below for the two waste form types.

For the OPC waste form:

- For Cs, diffusion through the water-saturated cement matrix is the principal release mechanism. A weak, reversible adsorption onto the cement matrix is the only additional process which occurs. Although, this reversible adsorption tends to slow the release, the effect is small.
- For Sr, the release-controlling mechanism does not appear to be simple diffusion from the waste form. Chemical binding in the waste form was given as the most probable reason for this. Possibilities for chemical binding were said to include: Sr replacing Ca in the calcium silicate hydrate during setting; coprecipitation with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or ettringite (a calcium aluminum sulfate hydrate) since this specific waste form contained a lot of sulfate salts or, the Sr may be incorporated in precipitated carbonates as a result of CO_2 dissolving in the leachant.

For the OPC - clinoptilolite waste forms:

- For both Cs and Sr, the controlling release mechanisms were indicated to be desorption from the zeolite ion-exchange and diffusion. The driving force for Cs release was said to be ion exchange between Cs and Ca ions. Modelling results were less conclusive for Sr release via the mechanism of ion exchange for Ca. This was said to possibly be due to the participation of another ion in the Sr exchange.

For both waste form types:

- Leaching release for the first several days was greater than could be accounted for by the diffusion-ion exchange mechanism.
- A conclusion which was implied, but not directly stated, was that the release mechanism(s) of Sr from these waste form types has not been well enough characterized for reliable modeling.

2.2 Bitumen

The function of bitumen in the solidification of LLW is generally considered to be that of an adhesive coating agent. As such, the waste content of bituminized waste does not significantly change the mechanical properties of the solidified form until the waste loading exceeds approximately 60 wt%^{16,18}. Conversely, the strength of a cement form depends on waste loading and reportedly decreases substantially at salt loadings greater than 130 g per Kg of cement product (i.e., 13 wt% of waste form)¹⁵. According to a 1970 report on bituminized low-level waste, "The mechanisms of leaching of isotopes from bituminous mixtures has not yet been precisely established"¹⁸. Analysis of data based on two postulated mechanisms has been reported^{16,19}. In one analysis¹⁹, diffusion was presumed to be the mass transport process, whereas in the other¹⁶ the solubility of the activity was presumed to control the leaching. Functionally, the diffusion-mechanism would result in a release rate proportional to $t^{-1/2}$ while the solubility controlled mechanism would result in a constant rate of activity release from the waste form. These different analyses may not be incompatible since the bitumens used for solidification, the waste and the process used to incorporate the wastes into the bitumens were different.

2.3 Polymers

There is almost a complete dearth of reported information on the leaching mechanism(s) of VES. Structurally, the solidified emulsified material has been reported to consist of droplets of waste enveloped in polymer. However, no physical evidence, such as photomicrographs are available to support this hypothetical structure. Only a limited amount of information has been reported on leaching mechanisms of polymeric solidification agents¹³. The postulated mechanism for two thermosetting polymers under study in Europe, which included a chemically crosslinked epoxy and a chemically crosslinked polyester-styrene copolymer, is that these polymers form a low permeability barrier from which radionuclides are leached by diffusion [Reference 13, 47-55]. Measured diffusion coefficients from these studies¹³ on thin membranes of the two polymers were approximately 7×10^{-13} cm²/sec for Cs-137 and 3×10^{-9} cm²/sec for water in both materials.

2.4 Glass

Leaching mechanisms for glass have been comprehensively investigated and reviewed in Reference 1. Although this work concentrated on the HLW defense glass solidification matrix, the review and experimental work appear to be general enough to address the long-term leachability of most glasses based on

silica as the primary network former. Glass leachability is sensitive to temperature, leachant pH and flow rate and glass composition. Initially, the leaching is dominated by release of soluble species such as alkali metals and boron (in borosilicate glasses). The leaching of these elements typically follows diffusion kinetics until the depleted surface layer, which is composed of the less soluble material such as silica, begins to affect the leaching release. In a hard-rock HLW repository, the slow flow of groundwater through the repository and the development of a surface layer which includes precipitated crystalline species of lower solubility than glass was said to ultimately control the leachability of HLW glass waste forms under the expected conditions.

The LLW glass²³ investigated by Mound Laboratory has different physical and chemical characteristics than the HLW borosilicate glass. Chemically, the LLW glass is ordinary soda-lime silica glass rather than the borosilicate glass used for HLW solidification. Physically, the LLW glass is a two-phase system since some incinerator ash which has not been totally oxidized is incorporated in the glass. Short term leach tests on the LLW glass²³ show no greater leachability than a typical HLW glass.

3. FACTORS THAT AFFECT LEACHING

In 1981, Stone⁷ provided a brief, qualitative overview of factors affecting leachability from a review of the literature. Factors which need be considered in any comprehensive analysis of leaching behavior were listed under three categories: (i) system factors, (ii) leachant factors and, (iii) composition of the solid waste form. System factors included time, temperature, pressure, radiation environment and ratio of waste form surface area to leachant volume. Leachant factors included composition, pH, Eh and flow or replacement frequency. Waste form factors were said to include composition, surface condition and porosity. These factors plus others are discussed in this chapter and quantitative models of the effects of these factors are included, where available.

3.1 System Factors

3.1.1 Time. Leachability is a function of time in the sense that the functional relationship of leach rate to time typically changes over the long term. The exact dependence of leachability with time depends on the leaching mechanism(s) operative at the time and may also be affected by other conditions. A common empirical function which fits cumulative fraction released versus time for several types of glass is:^{33,34}

$$F = at^{1/2} + bt \quad (3.1)$$

where F is cumulative fraction released, a and b are constants with a larger than b . Thus, at short times the fraction released is linear with $t^{1/2}$, which would be expected for a diffusion mechanism, while at long times the fraction released becomes linear with t .

Godbee and Joy⁵⁹ have reviewed the relationship of the empirical Equation 3.1 to proper solutions of mass transport equations incorporating diffusion with a constant diffusion coefficient plus dissolution as the release mechanisms. Two types of dissolution were considered: (i) concentration dependent dissolution of waste which occurs throughout the waste form and, (ii) surface dissolution only. It appears that the shapes of the curves given by Equation 3.1 compared to the proper solutions to the mass transport equation may be similar in the short term ($at^{1/2} \gg bt$), but not when both terms make significant contributions to the overall release. They also show that, if dissolution of radionuclides of limited solubility is not accounted for, the leaching release of activity assuming diffusion can underestimate that which actually occurs at long time.

3.1.2 Temperature. Temperature is usually the first variable considered in attempts to change and/or analyze rate processes. This is so because: (i) relatively small changes in temperature often lead to relatively large changes in the observed rates of many processes and (ii) the variation of the rate with temperature is often well represented by the Arrhenius equation,

$$R(T) = A \exp (-E_a/RT) \quad (3.2)$$

where $R(T)$ is the rate at (absolute) temperature T , A is a constant, R is the gas constant and E_a is the 'apparent activation energy' of the rate process. Upon taking the logarithm of Equation 3.2,

$$\log R(T) = \log A - \left(\frac{E_a}{RT} \right) \quad (3.2a)$$

it is seen that plotting the log of the rate parameter versus $(1/T)$ results in a straight line of slope $(-E_a/R)$ for an activated process. A change of slope on these plots is indicative of a change in activation energy associated with a change in mechanism.

The leach rates of some high-level waste glasses have shown Arrhenius behavior^{35,36}. Such relationships have also been observed for some cemented LLW forms, but not for bituminized LLW forms. Leaching of cemented cesium sulfate salts (simulated sulfate evaporator wastes) has indicated an approximate Arrhenius relation with an apparent activation energy of 4-6 Kcal/mole in the early stages of leaching^{8,10}. These data were from approximately room temperature to 70°C and were said to be consistent with a diffusion mechanism. However, at longer times at the high temperature the apparent activation energy increased to 8-11 Kcal/mole which was said not to be consistent with diffusion⁸. Additionally, upon lowering the temperature again, the leach rate remained high, indicating that irreversible changes occurred at the higher temperature⁸. This last observation may be explained at least in part from the observations by Atkinson and Nickerson³² that the pore structure of cement becomes more permeable at higher temperatures. Thus, for cesium, the leach rate increase at higher temperature appears to arise from at least two contributing processes: (i) the increase due to temperature normally associated with an activated process and, (ii) the irreversible increase resulting from the effect of an increase in temperature on the pore structure of the cemented waste form.

Leaching data for strontium over the same temperature range resulted in little increased release at 70°C compared to 30°C⁸. The reproducibility of duplicate leach test results on the $SrSO_4$ salt in cement was also poor. However, it was noted that these results for Sr may have been influenced by solubility limitations since a relatively large quantity of $SrSO_4$ salt (6.6% by weight) was solidified in the cement waste form samples. Conversely, leach tests on $Sr(NO_3)_2$ salts incorporated in trace amounts in cement (which would be more typical of LLW concentrations) showed a large temperature effect on leachability³⁷. Thus, it appears that temperature effects on Sr leachability may be influenced by solubility limitations and that any analysis of Sr leachability versus temperature must take solubility into account.

Bituminized samples containing the cesium and strontium sulfate salts showed no consistent trend in leaching behavior with temperature⁸. It was stated that further testing was needed before any conclusions could be shown concerning the effect of temperature on the leachability of bituminized waste forms.

3.1.3 Pressure. The effect of pressure under shallow land burial should be negligible for rigid waste forms such as cement and glass. Test results under hydrothermal conditions such as occur under deep geologic burial for high-level waste disposal are not applicable to LLW forms.

The overburden load of approximately 20-50 psi in shallow land burial may affect bituminized waste forms and some types of VES waste forms³⁸⁻⁴⁰. Bituminized waste forms are known to deform by creep in this load range and, over the long term, this can lead to substantial deformation. One can speculate that if the deformation by creep results in cracking of the bituminized waste form then the increased surface area could lead to an increase in leachability. However, this speculation has no basis in experimental results since leach tests on bituminized waste forms have not been performed under load to our knowledge.

3.1.4 Radiation. Irradiation of LLW forms results primarily from β, γ activity, since the TRU content of LLW is normally limited to less than 100 nCi/g. The effects of radiation on the mechanical integrity and leachability of cement, bitumen and VES as solidification agents for LLW have been reviewed in a report prepared for the U.S. Nuclear Regulatory Commission⁴¹.

Cement exhibits excellent radiation resistance and is used for both shielding and construction of reactors and other radiation facilities. Cement-solidified ion exchange resins have been irradiated to 10^9 rad with no noticeable effect on the leachability or mechanical integrity⁴².

Similarly, irradiation of cement-solidified sodium nitrate salt to 10^{10} rad showed no significant increase in leachability for loadings up to 30 wt% salt⁴³.

Although bitumin evolves gas and swells upon irradiation, no significant increases in leachability have been reported for doses up to 10^8 rad for bituminized simulated wastes⁴⁴ and to 10^9 rad for bituminized sludge wastes^{18,61}.

VES solidified wastes from a BWR showed little change in leachability up to a dose of 10^8 rad^{62,72}. Above 10^8 rad the leachability appeared to increase with increasing dose and by 6×10^8 rad the fraction leached was approximately double that at 10^8 rad.

For glass, no effect on leachability due to irradiation from LLW is expected, based on leach studies on HLW glass following irradiation [Reference 1, Chapter 5].

3.1.5 Ratio of Waste Form Area to Leachant Volume. The ratio of waste form surface area to leachant volume affects how fast the leaching system can approach steady state as the leachant becomes saturated with leached material. This factor is clearly not independent of leachant flow rate or replacement frequency (Section 3.2.3) and is also not independent of the surface area to volume ratio of the waste form (Section 3.3.4). Given this, we will include consideration of this point with Section 3.2.3 (Flow or Replacement Frequency) and Section 3.3.4 (Surface Area to Volume Ratio).

3.2 Leachant Factors

3.2.1 pH Effects on LLW Leaching. Since LLW forms are typically two phase systems, pH effects result from the interaction between the leachant, waste and solidification agent. Percolate water from rain and runoff may be expected to be close to neutral, depending on dissolved atmospheric gases such as carbon dioxide and interaction with the overburden soil.

Neutral conditions, pH 5-9, give the lowest leach rates for glass with leachability rising as pH becomes more acidic than 5 or more basic than 9^{1,65-67}. Glasses with high concentrations of soda (Na_2O) and other soluble basic oxides cause the leachant to become basic, which then causing leaching to increase. However, at room temperature the leachability of glass is generally so low that this may not be a problem.

The pH of hydrated portland cement is approximately 12.5, based on the presence of a saturated solution of $\text{Ca}(\text{OH})_2$ in the pore fluid. This value varies somewhat depending on the water to cement ratio and the quantity of alkali metal oxides, Na_2O and K_2O , in the cement powder. Addition of silica or silacious material which reacts with calcium hydroxide may reduce the pH to approximately 11. This high pH limits the solubility of most cations with the exception of the alkali metal cations.

3.2.2. Eh. Several elements of concern in LLW management exhibit more than one chemical oxidation state, e.g., Co, U, Pu and Tc. The solubility of these elements depends (in the absence of chelation complexes) on the chemical oxidation state which is a function of Eh. For cobalt the +2 state is generally more soluble than the +3 state for the common anions such as hydroxide, chloride and sulfate. Conversely, for uranium, the lower oxidation state, +4 is less soluble than the +6 state. For elements with only one oxidation state, such as Cs and Sr, Eh conditions probably have little effect on solubility.

Glasser, et al.¹¹, have reported Eh data for portland cement from measurements on pore fluid squeezed from set cement and from direct measurements in situ from electrodes placed in the cement before setting. Results from both of these techniques indicated moderately oxidizing conditions in the set cement with Eh values from 80-181 for setting times from 7 days to 14 months. Pore fluid measurements on portland cement containing additives including silica, pozzolan and blast furnace slag indicated no noticeable change in Eh after 14 months setting time. It was also noted that, while the Eh in portland cement is inherently oxidizing, it is of limited poisoning capacity so that addition of even relatively small amounts of materials active in redox reactions may alter the normally moderately oxidizing Eh.

3.2.3 Flow or Replacement Frequency. Leachant flow rate or, presumably equivalently, replacement frequency of a specific volume of leachant in semi-dynamic leach tests is a major factor in determining leachability and also determines the boundary conditions which apply to any data analysis. The subject of boundary conditions in data analysis and modeling is described in Section 4.1.2.

Static leach tests, such as the MCC-1⁶³, ideally are of sufficient duration to allow the leachant and sample to attain equilibrium. Information available from static tests includes solubility limits for the specific leachant-waste form system under the conditions of the test and kinetic data if the approach to equilibrium is followed. Knowledge of both saturation levels and the kinetic approach to saturation are important not only for static leaching but also for estimating adherence to boundary conditions in flowing and semi-dynamic tests. By repeating static leach tests on the same sample it should be possible to determine the minimum amount of leachant required to remove a substance from the sample. Such successive leaching would not be needed if the leaching process itself does not significantly alter the leaching behavior of the system due to, for instance, depletion of a soluble constituent of the waste form.

Flowing and semi-dynamic leach tests ideally maintain the leachant at such low concentrations of leached substances that redeposition onto the sample is not significant. However, this is seldom assured since the fixed schedule of leachant replacement in most leach tests is seldom varied by experimenters, and no specific test procedures are included to assure that concentration effects are not significant. This problem would seem to be of more concern for cemented waste forms than for bitumen, VES and glass waste forms which are generally less leachable than cement-solidified waste forms. One case has been reported in which leach rates from weekend leachant replacements were lower than those from daily replacement⁶⁴. Such retardation of leachability in tests may be of little significance as long as the effect is small and the shape of leach curve is not affected. However, evidence is needed to establish under what conditions of concentration the effect remains small.

3.2.4 Leachant Composition. Standard leachants include demineralized water (DIW) and brine although leach testing is also done with tap water, whose composition may or may not be specified, and other aqueous solutions. DIW generally results in higher leach rates than brine except for ion exchange resin wastes in which the cationic radionuclides on the resin are readily exchanged for cations in the brine.

3.3 Waste Form Factors

Waste form factors which affect leachability include composition, surface condition, porosity and the ratio of the surface area to volume of the waste form. The relative importance of these factors varies substantially depending upon composition.

3.3.1 Waste Form Composition. The fundamental nature of a waste form, including its physicochemical properties and the mechanism of leaching is determined by its composition. A waste form consists of some type and quantity of waste fixed in a solidification agent. Other materials such as sorbents are often added to cemented waste forms to improve performance in specific ways. The nature of the waste also affects the selection of the solidification agent. The waste stream may need treatment to become compatible with a solidification process. Such treatments may include pH and/or water content adjustments or, in the case of glass, incineration.

Low-level waste forms are generally two or more phase systems in which the solidification agent matrix is physically and chemically distinct from the incorporated waste. This is unlike the case for the HLW glass in which the waste components are required to become part of the glass itself. Phase separation, or devitrification, of HLW glass has been considered to be undesirable. Because LLW forms are inherently not 'one substance' there is the possibility of interaction between waste and solidification agent.

Cement is chemically complex and the interactions of each radionuclide of concern with hydrated cement must be considered individually during solidification and subsequent leaching. Cesium has been shown not to react with and to sorb only weakly onto hydrated portland cement (Section 2). Also, the inherently high pH of hydrated cement does not limit the solubility of Cs. Thus, pure portland cement acts to limit the leachability of cesium only by physical restriction, not by chemical reaction. Strontium has also been shown to sorb relatively weakly onto hydrated portland cement. However, Sr has been postulated to chemically react with cement during solidification and over time following solidification²². This speculation was based in part on several observations in which Sr leachability from cemented waste forms decreased with increasing cure time²⁰⁻²² and, in part, on the fact that small amounts of Sr can substitute for Ca in calcium-containing minerals²². An alternative interpretation of reduced Sr leachability from cemented waste forms with length of cure and/or extended leaching time is also available⁸. In this interpretation, it is carbonation of the surface which results in reduced Sr leachability (see also Section 3.3.2). In support of this latter interpretation Amarantos and Petropoulos⁸ presented results in which the leachability of Sr did not decrease with time when carbon dioxide (from air) was rigidly excluded from the leaching system. The high-pH cement environment also limits the solubility of Sr in cemented waste forms. The high-pH of cement also severely limits the solubility of cobalt in cemented waste forms.

Bitumen has been thought to be an essentially inert, adhesive coating of low permeability to water. Waste incorporated into bitumen must be dry or de-watered during bituminization, which is done at elevated temperature. Although bitumen has been thought to be generally unreactive toward radwaste components, it has been reported that Sr leachability is reduced at bituminization processing temperatures above 205°C¹⁸. Also, in a leach test employing tap water as leachant of a bituminized waste form containing reprocessing sludges, the total salinity of the leachate was reported to be lower than that of the leachant even though water absorption by the waste form increased its weight by 3% [Reference 13, pp. 42-43]. This observation was not explained although the reduced salinity presumably resulted from sorption by the bitumen and/or the sludge. These observations may indicate that under some conditions chemical reactivity and/or sorption may affect the leachability of bituminized wastes.

3.3.2 Surface Condition. Waste form surface conditions often change as a result of leaching. The alteration layer which may form on glass as a result of leaching has been shown to have a significant effect on the leachability of glassified high-level waste¹. Carbonation of the surfaces of cement LLW forms from CO₂ dissolving in the leachant has been shown to reduce Sr leachability^{8,13}. No similar surface carbonation of bituminized sludge wastes was observed under conditions similar to those in which it was observed

with cement waste forms [Reference 13, p. 43]. The elemental composition of the surface of a cement waste form has also been reported to have changed due to leaching¹⁷. Specifically, the relative concentration of silicon (silica) increased compared to that of calcium in the surface layer.

3.3.3 Porosity. An inert matrix which is physically porous can only retard the leachability of other substances embedded in the matrix compared to simply exposing the substances to the leachant directly. This is not equivalent to the effect of porosity acting to increase surface area because of microscopic surface roughness, as has been found to be important for glass^{1,7}. Porous LLW forms in which the waste and solidification agent matrix are distinguishable may be better described by formally considering the effect of the porous matrix rather than considering the effect of porosity as simply increasing surface area.

The physical considerations necessary to account for the effect of porosity on diffusion in a porous matrix along with mathematical models incorporating these considerations have been reviewed by Van Brakel and Heertjes⁶⁸. In general, the diffusibility, Q , of a porous matrix is described as

$$Q = \frac{PC}{T^2} \quad (3.3)$$

where P is the porosity, C is the constrictivity and T is the tortuosity. P and T depend only on the porous matrix whereas C depends on both the porous matrix and the diffusant since the relative sizes of porosity and diffusing species are important. Q is defined as the ratio of the effective diffusion coefficient in the porous medium to the diffusion coefficient in the absence of the porous medium.

Atkinson and Nickerson³⁰, have applied this concept of porosity-dependent diffusion to the problem of leachability of cemented LLW forms. Analysis of leaching data plus other data led them to conclude that the pore structure of cement is best characterized as one in which relatively large pores are connected through much finer pores. They also indicated that the pore structure was irreversibly changed upon heating from 30°C to 60°C. Cesium leachability from a sample which had been heated and then cooled was greater than from the sample prior to heating.

3.3.4 Surface Area to Volume Ratio. It has been stated that, when certain conditions are met, increasing the sample surface area to volume ratio may be useful as an accelerating factor in leach testing. Different requirements have been stated for leaching which is diffusion-controlled or corrosion-controlled. The argument for corrosion-controlled leaching is contained in [Reference 1, 1.11-1.12]. Briefly, this conclusion proceeded from the following argument. The concentration of species, i , in the leachant, C_i , may be related to the leach rate, L_i , the fraction of species in the waste form, f_i , the surface area to volume ratio of the waste form, (S/V) , and the contact time of the leachant with the waste form, T , as in Equation (3.4).

$$C_i = L_i f_i (S/V) T \quad (3.4)$$

L_1 depends on the chemical composition of the leachant and may also be a function of time and/or (S/V) explicitly⁴⁵. If L_1 depends only on leachant composition and Equation (3.5) holds, then increasing (S/V) will effectively shorten the time required to reach a given concentration level in the leachant, thus accelerating the leaching process.

$$(S/V)_1 T_1 = (S/V)_2 T_2 \quad (3.5)$$

The subscripts 1 and 2 in Equation (3.5) indicate different conditions of (S/V) and T. The validity of Equation (3.5) for glass leaching has been experimentally demonstrated once the leach rate has become linear with time^{1,46-48}. No such similar investigations on low-level waste forms have been reported to our knowledge.

Alternatively, under diffusion-controlled conditions, the following argument has suggested that leach test results on small samples may be used to predict the leaching that would occur from full-size waste forms^{49,50}. The relationship of the cumulative release leached from different sized samples, which are otherwise identical and are leached under identical conditions, has been stated to be

$$\left(\frac{\sum a_n}{A_0} \right)_1 \left(\frac{V}{S} \right)_1 = \left(\frac{\sum a_n}{A_0} \right)_2 \left(\frac{V}{S} \right)_2 \quad (3.6)$$

a_n = amount of substance of interest leached in interval n

A_0 = total amount of substance of interest originally present

$\frac{\sum a_n}{A_0}$ = cumulative fraction leached through interval n.

where subscripts 1 and 2 indicate the different sized samples. This conclusion is based on the solution to the problem of diffusional release from the semi-infinite medium [Reference 2, p. 32], which may be stated as in Equation (3.7).

$$\left(\frac{\sum a_n}{A_0} \right) \left(\frac{V}{S} \right) = 2 \left(\frac{Dt}{\pi} \right)^{1/2} \quad (3.7)$$

For samples which are nominally identical, except for size, D should be the same. If they are leached under similar conditions for the same length of time, t, then the right-hand-side of Equation (3.7) is the same for both samples and Equation (3.6) follows. Experimental evidence has been reported

in support of Equation (3.6)⁴⁹⁻⁵¹. However, the leaching results used to support the validity of Equation (3.6) were limited to a relatively small range of fractional release early in the leach test such that the semi-infinite medium approximation might be valid. Rearrangement of Equation (3.6) to the form of Equation (3.8)

$$\left(\frac{\Sigma a_n}{A_o} \right)_{fs} = \left(\frac{\Sigma a_n}{A_o} \right)_{ss} \left(\frac{V}{S} \right)_{ss} \left(\frac{S}{V} \right)_{fs} \quad (3.8)$$

was said to allow prediction of cumulative release from a full-scale (fs) waste form from data obtained from a small scale (ss) sample⁴⁹.

To summarize, it has been shown based on diffusion theory and supported by experimental results that leaching from small-scale test samples can be used to predict leaching release of larger waste forms under certain conditions⁴⁹⁻⁵¹. The complete set of conditions under which this result may be valid include the conditions set forth above plus those which lead to Equation (3.7) as the quantitative expression of cumulative release versus the square root of time². These include:

- Diffusion is the mass transport mechanism and the diffusion coefficient is constant.
- The diffusant is uniformly distributed throughout an effectively homogeneous medium prior to leaching.
- The leachant and the surface of the waste form are maintained at effectively zero concentration with respect to the diffusant during leaching.

If test conditions on small scale samples can be controlled to effectively simulate actual burial conditions and Equation (3.7) holds, then it should be possible to use Equation (3.8) to predict long-term leaching release for the specified conditions. Under these conditions, small scale tests would provide an accelerating factor to estimate long-term release. The validity of Equation (3.8) is based on the applicability of Equation (3.7) to the leaching behavior. Since Equation (3.7) describes the release by diffusion the concurrence of leaching mechanisms other than diffusion may invalidate the utility of Equation (3.8) for long-term prediction. Also, Equation (3.7) applies to a semi-infinite medium. The validity of Equation (3.6) was not investigated beyond the range of validity of the semi-infinite approximation.

4. MODELING CONSIDERATIONS AND MATHEMATICAL MODELS

One approach to investigate the leaching mechanisms of radioactive waste has been based on curve fitting data to mathematical models incorporating an assumed mechanism, or mechanisms, plus initial and boundary conditions as seem reasonable or as simplification to make the mathematics more tractable.

Empirical and semi-empirical model equations are sometimes included for convenience and because theoretically-derived model equations are often approximated by simpler expressions for convenient, albeit, approximate calculation. Empiricism may also be introduced into theoretically-derived models by allowing certain parameters to 'relax'. For example, an exponent specified as 0.5 in the precise model equation may be allowed to vary to the optimal value for a specific curve fit. Optimization is a valuable tool for several reasons. First, it provides a sensitivity estimate of variation for specific parameters. Second, real systems are generally more complex than the model, therefore, one can often include only the most important aspects of the real system.

The mathematical problem of radionuclide release from solidified LLW forms has traditionally been approached as a diffusion problem or as a modified diffusion problem in which the diffusion equation is modified by including terms representing other mechanistic processes such as dissolution, corrosion, ion exchange, surface effects, etc. In this section, various mathematical models which have been used to analyze leaching data are presented following some discussions of general modeling considerations. Such considerations include the specifications which any real system must meet for the model to be applicable to that system. These are often expressed in the initial condition and boundary conditions of the model. Also, every model contains parameters such as diffusion coefficients, equilibrium constants and rate constants, which may be obtained from curve fitting to leach data or from other sources independent of leach data. The most valuable and reliable parameters are those which are independently verifiable from different sources.

4.1 Modeling Considerations

A leaching mechanism may be expressed or implied. Often, an analysis is made using a standard model or procedure without any specific reference to the mechanism inherent in the procedure. In such cases, the mechanism inherent in the procedure is the mechanism implied by the analysis. In any curve fitting procedure utilizing theoretically derived equations, a very specific mechanism, or set of mechanisms, is involved and a good fit to the data is a necessary, but not a sufficient condition, to validate the model. Confirmatory physical and/or chemical evidence for specific mechanisms is required to be able to justifiably assert that a particular mechanism obtains in a given set of leaching circumstances.

Leach data is often plotted as CFR vs $\sqrt{t}$ based on the assumption that diffusion is the predominant mechanism in LLW leaching. Following an initial release which is of relatively short duration and typically greater than can be accounted for by the diffusion mechanism assumption based on data following the period of initial release, the CFR vs $\sqrt{t}$ plot often becomes linear for some limited time and then falls below the extrapolated linear region. This behavior has been rationalized in several ways. First, there is source term

depletion. This can be calculated using the actual geometry of the waste form to calculate CFR vs time for any selected mass transport mechanism. Defining a basic 'simple system' as having diffusion as the only mass transport mechanism, the incorporation of geometric boundary conditions based on waste form geometry then allows curve fitting to establish to what degree depletion accounts for decreased leachability. Such data characterization would be most useful on complete leaching curves (i.e., leach until CFR = 1) and analyses of a statistically significant number of data curves could allow a meaningful assessment of the applicability of the pure-diffusion model. Secondly, leachant replacement interval changes to longer time intervals, which is common practice in semi-dynamic leach tests as the test progresses, have been suspected of retarding the measured leachability due to saturation effects in the leachant at the longer replacement intervals. A significant aspect of this is that the appropriateness of assumed leachant boundary conditions in leaching models may be affected by concentration effects in the leachant. Few studies of leachant replacement interval effects have been reported. Third, incorporation of a variable diffusion coefficient in place of a constant coefficient has reportedly allowed one model to better fit data over a longer CFR range⁶⁰. For glass, the diffusion-coefficient has been shown to vary across the surface layer which is formed after prolonged immersion (leaching)⁵². A similar effect may be expected to occur in LLW if significant chemical and/or physical changes occur in the waste form or on its surface.

4.1.1 The Effective Diffusion Coefficient. Strictly speaking, the effective diffusion coefficient, D , is not generally constant but may be expected to vary with the concentration of diffusant, porosity and other factors^{53,54}. However, it may be adequate, and is computationally much simpler, to assume the constancy of D and to limit consideration to a sufficiently narrow concentration range that any variation in D over this concentration range is negligible. For low-level waste the concentration of radionuclides is small for most wastes to begin with and approaches zero as leaching progresses. If there is a significant concentration of non-radioactive isotopes of any of the radionuclide elements of interest, then the constant- D approximation may be suspect. For example, portland cement typically contains a few tenths weight percent of Sr which will leach along with any radioactive Sr from the waste and will cause a much larger (absolute) decrease in concentration than the radiostrontium isotope alone. From a mechanistic viewpoint, it would be useful to know if the leaching profile of the radiostrontium from the waste and that of the Sr initially in the cement powder parallel each other. No such correlative studies appear to be available at the moment.

The effective diffusion coefficient may also vary because of changes in the waste form during leaching. Dissolution of soluble salts from the waste form would tend to change D by increasing porosity. Selective dissolution of parts of the solidification agent matrix may affect D by a change in the chemical nature of the matrix as well as by a change in porosity of the waste form.

The effect of variation in D with the concentration of diffusant in the waste form has been reported in the literature⁵³. The conclusions listed below were drawn from a list of general conclusions stated by Crank⁵³ for the case of leaching by diffusion in which the magnitude of D varies with concentration in the waste form, but does not depend on any other variable.

- (i) In the early stages, when diffusion takes place effectively in a semi-infinite medium, the amount leached is directly proportional to the square root of time. When D increases with concentration in the waste form decreasing, the linear behaviour may extend beyond 50 per cent of the final release.
- (ii) When they cease to be linear, the leaching curves plotted against $(\text{time})^{1/2}$ become concave towards the $(\text{time})^{1/2}$ axis, and steadily approach the final release value. It is reasonable to conclude that this is a quite general result though no satisfactory general proof has yet been produced.
- (iii) When D decreases as concentration in the waste form decreases, the shape of the leaching curve is sensitive to the form of the diffusion coefficient and is often significantly different from the corresponding curve for constant D . If D increases as concentration in the waste form decreases, then the leaching curve will approximate that for a constant diffusion coefficient (see also Item (i)).
- (iv) When D decreases with concentration in the waste form decreasing throughout the relevant range of concentration, leaching slows in the later stages beyond that which would occur in the case of constant D .

Nestor⁵ has shown that for the finite cylinder, deviation from the semi-infinite medium, constant D diffusion model becomes significant beyond approximately 20% fractional release. However, a concentration dependence in D may significantly change the point of deviation, as discussed by Crank⁵³ in Items (i), (iii) and (iv). Table 4.1 summarizes the changes in a diffusional leaching curve resulting from either an increase or a decrease in D with concentration compared to the reference case of constant D .

The shapes of leach curves for test samples compared to those expected for the case of diffusion with constant D in the actual geometry of the samples may offer evidence for the adequacy of the constant D hypothesis for the diffusion model. In fact, experimental results are available which suggest that, for waste forms incorporating readily soluble waste, the constant diffusion coefficient model may not be adequate. Specifically, leach data has been reported for cement-solidified sodium nitrate wastes in which the nitrate release was linear with $(\text{time})^{1/2}$ to approximately 50% release⁴³. This may be a case in which the diffusion coefficient was increasing as concentration was decreasing since, as the nitrate salts dissolved, the porosity of the waste form almost certainly increased while the concentration of nitrate in the waste form pore water remained relatively constant until depletion occurred due to dissolution of the salt crystals.

4.1.2 Initial and Boundary Conditions. In general, it has been found that the higher the leachant flow rate (or the more often the leachant is replaced) the greater is the mass loss or activity loss from the waste form vs time. This is expected since the leaching rate is greatest when the concentration of diffusant in the leachant is zero and the leach rate approaches zero at saturation when the system reaches steady-state. The approach to steady-state is a function of concentration and may, or may not, be significantly affected by a relatively small concentration of diffusant in the leachant.

Table 4.1

Tabulated Behavior of the Shape of Leaching Behavior Presented as Fractional Release vs $(\text{time})^{1/2}$ for D Remaining Constant, Increasing or Decreasing with Concentration in the Waste Form According to General Conclusions (i), (iii) and (iv) From Crank [Reference 53].

Variation of D as Concentration in the Waste Form Decreases	(i)	(iii)	(iv)
D Increases as Concentration in the Waste Form Decreases	linear region of CFR vs $(\text{time})^{1/2}$ may extend well beyond 20% of total release	desorption curve may approximate that for constant D; see Item (i)	desorption faster than reference case
D Remains Constant	linear region of CFR vs $(\text{time})^{1/2}$ extends to about 20% of total release	reference case	reference case
D Decreases as Concentration in the Waste Form Decreases	linear region of CFR vs $(\text{time})^{1/2}$ may not extend to 20% of total release	desorption curve sensitive to form of D, may deviate substantially from reference case	desorption slower than reference case

For the case of pure diffusion, the semi-infinite model may be applied to finite systems provided that concentration changes near the boundaries are negligible [Ref. 54, pg. 21].

Moore, et al.⁵⁶, indicated that the ideal boundary conditions of negligible concentration maintained in the leachant were not met during a set of leach tests on hydrofracture grout. It also seems likely that the boundary conditions may not be adequately met for other cementitious waste forms in standard leach tests. The question then becomes to what extent this affects analysis and can any effects be accounted for quantitatively. The evidence of Moore, et al.⁵⁶ indicated that the measured diffusion coefficient decreased. This may well be the totality of the effect for small deviations from the specified ideal boundary conditions. However, it seems unlikely that the results would be so simple for a large deviation from the specified boundary conditions.

Waste form leaching in SLB may be affected by the waste form container as well as by the leaching characteristics of the waste form itself. If the container leaks or corrodes so as to hold water, then a saturated solution, or 'bath', may be in contact with the waste form. If the waste form swells upon contact with this water due to, say, hydration of salts or other waste components, then interaction between container and waste may occur. In one case [Reference 13, pp. 60-61] reported as part of leaching studies using the IAEA Leach Test⁵⁸ on cemented nitrate salts, the container cracked after approximately 60 days of leaching. Following cracking of the container the leach rate increased dramatically and far more than could be explained by a simple increase in exposed surface. The same effect was also observed upon removal of the container on another sample following approximately the same duration of leaching. This result was dramatically different from leaching typically seen from samples which are removed from their containers prior to leaching.

4.2 Models Based on Diffusion

Models in which diffusion with constant D is the only mass transport mechanism and which consider the waste form to be a homogeneous medium may be divided into two subsets for purposes of discussion: (i) those which use the semi-infinite medium approximation and (ii) those which incorporate the actual, or appropriate, geometry of the waste form into the boundary conditions. The semi-infinite medium approximation may be accurate to approximately 20% release, depending on other factors as discussed in Section 4.1, before source term depletion begins to decrease the leachability.

4.2.1 Semi-Infinite Approximation. The solution to the transport equation for diffusion in a homogeneous, semi-infinite medium [Reference 2, 32] has become the most general analytical relation to explain the leaching release of radionuclides from solidified waste forms. The differential equation from which this model derives is shown in Equation (4.1).

$$\frac{dC}{dt} = D \nabla^2 C \quad (4.1)$$

C = concentration of diffusant

t = time

D = diffusion coefficient (constant)

∇^2 = Laplacian Operator $\left(\frac{d^2}{dz^2}\right)$ in one dimension)

Limiting consideration to a one dimensional, semi-infinite medium in which the diffusant is uniformly distributed prior to leaching ($t \leq 0$) and for which the surface concentration drops to zero upon initiation of leaching leads to the following initial and boundary conditions:

$$C(z,0) = C_0, \quad z > 0$$

$$C(\infty,t) = C_0, \quad t \geq 0 \quad (4.2)$$

$$C(0,t) = 0, \quad t > 0$$

Godbee and Joy [Reference 59, 13-16] have reviewed this equation and other equations which have a similar form as applied to LLW leaching. Section 3.3.4 of this report reviews other aspects of the semi-infinite model to LLW leachability and scaling effects. The great virtue of this model is its simplicity compared to other models which incorporate other mechanisms as well as diffusion or which account for the actual geometry of real waste forms. The release equation for this model is shown in the first line of Figure 4.1. Bell⁶⁹ has reviewed the use of this model for evaluating leaching along with other relevant factors, including radioactive decay and the ultimate amount of activity released from a waste form.

4.2.2 Finite Geometry. Leaching of real waste forms leads to depletion, which must be accounted for in any realistic model of leaching behavior. Considerable mathematical complexity is introduced into the analytical solutions for diffusion in any finite medium. The solution to the problem of diffusion in finite cylinders, which is relevant to LLW leaching, has been reported⁵ and is reproduced in the second line of Figure 4.1. Equation (4.1) is also the differential equation solved for diffusion in a finite geometry. Accounting for the cylindrical geometry in the boundary conditions leads to the increased complexity of the solution in line 2 of Figure 4.1.

4.3 Models Incorporating Diffusion Plus Other Processes

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. However, other processes including dissolution, corrosion, ion exchange and/or surface effects also affect the leaching behavior of LLW forms. This section presents analytical model equations which incorporate these other processes along with diffusion.

The effect of radioactive decay on leaching release has been addressed by Bell⁶⁹ and by Godbee and Joy⁵⁹. Although radioactive decay affects all leaching releases over long enough time periods, it is easily accounted for and is not considered as a mechanism for the purposes of this report.

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

* a_n = amount of substance of interest leached in interval n ; A_o = total amount of substance of interest originally present; (V/S) = volume to surface ratio; t = time; D = diffusion constant; k = dissolution rate constant; erf = error function; $R = U^2/4D$ where U = velocity on the moving boundary. J_{om} = m^{th} positive zero of the zeroth order Bessel function; r = radius of cylinder; h = height of cylinder.

Figure 4.1 Mass transport models that have been used to describe leaching from LLW forms.

4.3.1 Diffusion Plus Equilibrium. Theoretically, the leaching behavior of a system in which the species of interest is in equilibrium between a mobile, leachable form and a fixed form is indistinguishable from the case of diffusion, using the semi-infinite medium boundary conditions for both cases⁶⁴. The differential equation plus the ancillary equilibrium specification are shown in Equation (4.2).

$$\frac{dC}{dt} = D \nabla^2 C - \frac{dF}{dt} \quad (4.2)$$

$$F = KC$$

F = concentration of the fixed species

K = equilibrium constant

The release equation from Equation (4.2) is identical in form to that listed in line 1, Figure 4.1, except that the diffusion constant is

$$D_e = \frac{D}{1 + K}$$

as a result of the equilibrium condition. For this reason it is not listed separately in Figure 4.1.

The use of this equation of analyzing leach data from grouted waste forms is reported in Reference 64 and the detailed solution to Equation (4.2) is shown in Appendix B, Reference 64.

4.3.2 Diffusion Plus Dissolution. The importance of dissolution as a leaching mechanism has been pointed out for waste forms incorporating soluble wastes^{8,56,59}. Two analytical mathematical models incorporating both diffusion and dissolution are available and have been used to analyze LLW leach data^{56,59}. However, these models are based on the semi-infinite medium and the effects of depletion due to the finiteness of real waste forms is not addressed. Both of these models modify the diffusion equation by adding a term which represents a dissolution process. The models are different due to the different mechanistic natures of the two posited dissolution processes. These are:

- (i) Concentration dependent dissolution.
- (ii) Dissolution of the surface at a constant rate of penetration into the waste form (i.e., a moving boundary).

The differential equation which models diffusion plus concentration-dependent dissolution is

$$\frac{dC}{dt} = D\nabla^2 C + k(C_s - C) \quad (4.3)$$

k = dissolution rate constant

C_s = saturation concentration of mobile species under conditions in the waste form.

The release equation for this model is shown in line 3 of Figure 4.1. Godbee and Joy⁵⁹ have fit Equation 4.3 to leach data and reviewed the applicability of this equation to LLW leaching. The detailed derivation of the release equation shown in line 3 of Figure 4.1 from Equation (4.3) is presented in Reference 59, Appendix A.

For the model incorporating diffusion plus surface dissolution the differential equation is

$$\frac{dC}{dt} = D\nabla^2 C + u\nabla C \quad (4.4)$$

u = rate of surface dissolution (velocity of moving boundary).

The release equation for this model is shown in line 4, Figure 4.1. The detailed derivation of this equation is not available since the report in which it was to appear was not published. The release equation listed in line 4, Figure 4.1, is reported in Reference 21 and is used to theoretically predict ($Cs-137$) leaching from borosilicate glass.

Pescatore⁷⁰ has reviewed the use of Equation (4.4) as a model for glass leaching and concludes that it provides a basis to develop a predictive model for glass leaching. The predictive model which he developed using Equation (4.4) as a basis is published in Reference 70 and includes the effect of leachant composition as the concentration of leached material builds up in the leachant. The possibility of using this equation for LLW leaching modeling was presented in Reference 71.

4.3.3 Diffusion Plus Ion Exchange. The effect of diffusion plus ion exchange on leaching of cement-based waste forms has been investigated both theoretically and experimentally³⁰. The conclusions deduced from this work are listed in Section 2.1 of this report. Two alternative models for evaluating the effect of ion exchange on the diffusion of Cs and Sr through cemented waste forms containing a zeolite additive were discussed in Reference 30. The applicability of those models depended upon the microstructure of the waste form which, in turn, was determined by whether or not the hydrated cement gel penetrated the zeolite granules.

4.4 Other Analytical Models

A power series equation, the BIKO equation, was reportedly developed to fit and extrapolate leach data empirically⁷³. The acronym "BIKO," which was reportedly chosen for purposes of reference, apparently is not shorthand for a

descriptive phase although the letters B, I and O are the first letters of the last names of three of the four authors of the report. The BIKO equation is shown in Equation (4.5).

$$f = \sum_{i=0}^n \frac{z_i k_i t^{1/2}}{1 + k_i t^{1/2}} \quad \text{for } n=2,3,\dots \quad (4.5)$$

f = fraction leached

Z_i = fraction of ions leachable by the i th "mechanism"

k_i = rate constant for the i th "mechanism"

t = time

Griffing⁵⁷ reviewed the mechanistic interpretation of the BIKO equation and concluded that, "Although there are similarities between the second and third terms of the BIKO equations to diffusion and (chemical) reaction, they are sufficiently different from the derived equations as to be invalid for reliably extrapolating leach data."

In Reference 57 Griffing also solves the equations for leaching from a sphere with diffusion plus a reversible, first order source term. The differential equations (4.6) which express the mechanisms of this model are

$$\begin{aligned} \frac{dC_1}{dt} &= D\nabla^2 C_1 - k_1 C_1 + k_2 C_2 \\ \frac{dC_2}{dt} &= k_1 C_1 - k_2 C_2 \end{aligned} \quad (4.6)$$

C_1 = concentration of mobile ions

C_2 = concentration of fixed ions

t = time

k_1 = rate constant for fixing ions

k_2 = rate constant for mobilizing ions

The solution to this equation is extremely complex and was not obtained in final form. Additionally, since there are three parameters, D , k_1 and k_2 , in the equation, one would need a good initial idea of the values of at least two of these to be able to effectively use the solution to this model.

4.4.1 Non-Homogeneous Waste Forms. Low-level waste forms are typically inhomogeneous, whereas most mathematical analysis procedures and models assume homogeneity. The only example we have found to date of modeling which specifically accounts for inhomogeneity is that reported by Atkinson⁷⁴. The model was described theoretically and compared to simple diffusion models, but was not used for data analysis.

The Atkinson model⁷⁴ assumes a three-phase, semi-infinite waste form consisting of a radiophase (i.e., the phase which initially contains the radionuclides), a conductive phase and an inert phase. The mechanisms of radionuclide release from the radiophase is diffusion with a constant diffusion coefficient. The radiophase consist of uniformly distributed spherical particles of radius, R , which comprise volume fraction, V_1 , of the waste form. Diffusion within each of the spheres is characterized by diffusion constant, D_1 . Phase 2 has volume fraction, V_2 , is continuous, having both the radiophase spheres and the inert phase embedded in it, and provides the high diffusivity path to the surface of the waste form. The diffusivity of phase 2, D_2 , is much greater than D_1 . Phase 3 is an inert phase which occupies the remaining volume.

Two conclusions were reported from applications of the model to a series of hypothetical systems in which model conditions were varied.

- (i) Although the model considered is intrinsically complicated, the release of radionuclide at times greater than the characteristic diffusion time for a single sphere of radiophase (D_1/R^2) can be described simply in terms of an effective diffusion coefficient. The concept of the effective diffusion coefficient was originally developed by Hart⁷⁵ (in considering grain boundary diffusion in polycrystalline solids) and was believed to apply only at times many orders of magnitude greater than D_1/R^2 . The computed results show that the concept is valid even for relatively short times.
- (ii) At times shorter than D_1/R^2 the exponent of time for the leaching kinetics is > 0.5 . Therefore, exponents of time other than 0.5 measured in leaching experiments do not necessarily show that the release is not diffusion controlled.

Typical waste form types said to be potentially modelable using this procedure included ion-exchange resins and fuel cladding material embedded in cement.

4.5 Models Utilizing Approximate Numerical Solution Procedures

The number of problems which have been solved analytically using Fickian or modified Fickian analysis is extensive²⁻⁴. If a problem involving diffusion plus other well defined mass transport effects can be determined to hold in a particular case, then that particular case is, in principle, exactly modellable for the specified set of conditions. Approximate methods are used when the detailed mechanisms are not known or the complete equation cannot be solved analytically (or is not worth the effort of solving exactly).

Numerical solution is the most popular form of approximate solution. A weakness of numerical methods occurs when the results of a previous approximate solution is then used as input for another approximate calculation. Such situations arise in projecting numerical solutions in time where each time step calculation is used as input for the next time step. Eventually, the buildup of error from the successive approximation may become unacceptably large. Griffing⁵⁷ reported that such error-buildup in numerical calculations led him to revert to seeking analytical solutions to problems for long-term projection of leaching of glass waste forms.

A numerical model for LLW leaching which includes provision for a concentration-dependent effective diffusion coefficient has recently been reported⁶⁰. The concentration dependence of D is expressed in Equation (4.7).

$$D(C) = D_0 \left(1 + a \frac{C(t)}{C_{sat}} \right) \quad (4.7)$$

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

D_0 = the value of the diffusion coefficient at $t = 0$.

a = constant

t = time

$C(t)$ = the concentration of the species of interest at time, t.

C_{sat} = the concentration of the species of interest at saturation.

The most thorough computational model for glass leaching was developed as part of the Defense High-Level Waste Leaching Mechanism Program. This numerically computed model, named PROTOCOL, is far more sophisticated than the other models discussed in this report in that it is specifically designed to extrapolate experimental rate data to very long times in a repository environment. Since PROTOCOL was programmed to model condition in a HLW repository and addresses the borosilicate glass waste form, it is not clear that this program would be of value for predicting releases from LLW glass in a shallow-land burial environment. A description of PROTOCOL and information on access for potential users is contained in Chapter 7 of Reference 1.

5. SUMMARY AND CONCLUSIONS

The literature survey on mechanisms and models for LLW leaching behavior has 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.

Mechanistic and other information gained in this literature survey are summarized in the following paragraphs.

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 even though several models are available.

Cement

The mechanisms 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 silicious 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 sorption 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 sorption 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.

Modeling Considerations

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 the numerically calculated model program, DIFMOD⁶⁰, which assumes a concentration-dependent diffusion coefficient of the form (see Section 4.5).

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

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.

REFERENCES

1. Pacific Northwest Laboratory, Final Report of the Defense High-Level Waste Leaching Mechanisms Program, J.E. Mendel, compiler, PNL-5157, UC-70, August 1984.
2. Crank, J., The Mathematics of Diffusion, 2nd Edition, Clarendon Press, Oxford, 1975.
3. Carslaw, H.S. and J.C. Jaeger, Conduction of Heat in Solids, Second Edition, Clarendon Press, Oxford, 1959.
4. Jost, W., Diffusion in Solids, Liquids, Gases, Academic Press, New York, 1960.
5. Nestor, C.W., Jr., Diffusion From Solid Cylinders, Oak Ridge National Laboratory, ORNL/CSD/TM-84, January 1980.
6. American Nuclear Society, Measurement of the Leachability of Solidified Low-Level Radioactive Wastes, ANS Standards Committee, ANS 16.1, June 20, 1984.
7. Stone, J.A., "An Overview of Factors Affecting the Leachability of Nuclear Waste Forms," Nuclear and Chemical Waste Management, Vol. 2, Pergamon Press, Ltd., 113-118, 1981.
8. 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.
9. Glasser, F.P., A.A. Rahman, R.W. Crawford, C.E.C. McCulloch and M.J. Angus, Immobilization of Radioactive Waste in Cement-Based Matrices, Department of the Environment and Commission of the European Communities, DOE/RW/84.050, CEC Contract No: 300.83.13, March, 1984.
10. N. Moriyama, N.H. Matsuzuru, S. Dojiri and Y. Wadachi, Analytical Evaluation on the Leaching of Radionuclides from Waste Solids. JAERI-M 6302 (Nov. 1975).
11. Glasser, F.P., A.A. Rahman, D. Macphree, C.E.C. McCulloch and M.J. Angus, Immobilization of Radioactive Waste in Cement-Based Matrices, Department of the Environment, Commission of the European Communities, DOE/RW/84.159, CEC Contract No: 300.83.13, 31 October 1984.
12. McCulloch, C.E., R.W. Crawford, M.J. Angus, F.P. Glasser and A.A. Rahman, "Sorption of Radiocesium by Active Silica," Health Physics, Vol. 46, No.5, 1095-1100, May 1984.
13. Sambell, R.A.J., R. De Batist, P. Van Iseghem, W. Timmermans and K. Brodersen, Characterization of Low- and Medium-Level Radioactive Waste Forms, Commission of the European Communities, PB84-212976, EUR 8663 EN, 1983.

REFERENCES (Cont.)

14. Westik, J.H., Jr., C.O. Harvey, F.P. Roberts, W.A. Ross and R.E. Thornhill, "Comparison of 200 Liter and 40 Milliliter Leach Tests," Scientific Basis for Nuclear Waste Management VI, North-Holland, D.G. Brookins, editor, 243-249, 1983.
15. Peltonen, E.K., J.U. Heinonen and J. Kuusi, "Incorporation of Radioactive Wastes from Nuclear Power Plants Into Concrete and Bitumen," Management of Radioactive Wastes From the Nuclear Fuel Cycle, II, IAEA-SM-207/5, 97-105, 1976.
16. Blanco, R.E., W. Davis, Jr., H.W. Godbee, L.J. King, J.T. Roberts and W.C. Yee, "Recent Developments in Treating Low- and Intermediate-Level Radioactive Waste in the USA," Practices in the Treatment of Low- and Intermediate-Level Radioactive Wastes, IAEA and ENEA-(SM-71/26), 793-839, 1966.
17. Dougherty, D.R., M. Fuhrmann and P. Colombo, Leaching Mechanisms Program Annual Report, Brookhaven National Laboratory, BNL-51862, September 1984.
18. International Atomic Energy Agency, Bituminization of Radioactive Wastes, IAEA Technical Reports Series No. 116, 69-89, 1970.
19. Dejonghe, P., L. Baetsle, N. Van de Voorde, W. Maes, P. Staner, J. Pyck and J. Souffriau, "Asphalt Conditioning and Underground Storage of Concentrates of Medium Activity," Proc. Int. Conf. Peaceful Uses Atom. Energy, 14, UN, New York, 343, 1964.
20. McDaniel, E.W., M.T. Morgan, J.G. Moore, H.E. Devaney and L.R. Dole, "Strontium Leachability of Hydrofracture Grouts for Sludge-Slurries," ORNL/TM-8198, 1982.
21. Moore, J.G., H.W. Godbee and A.H. Kibbey, "Leach Behavior of Hydrofracture Grout Incorporating Radioactive Wastes," Nuclear Technology, 32, 39-52, 1977.
22. Dayal, R., D.G. Schweitzer and R.E. Davis, "Wet and Dry Cycle Leaching: Aspects of Releases in the Unsaturated Zone," NRC Nuclear Waste Geochemistry '83, D.H. Alexander and G.F. Birchard, editors, U.S. Nuclear Regulatory Commission, NUREG/CP-0052, 1983.
23. Armstrong, K.M., and L.M. Klingler, Evaluation of a Processing Technique for Immobilization of Low-Level Radioactive Waste, Mound Laboratory, MLM-3149, UC-70, July 13, 1984.
24. Anderson K., B. Torstenfeld and B. Allard, "Sorption and Diffusion Studies of Cs and I in Concrete," Chalmers University of Technology, Goteborg, Sweden, 1981.
25. Glasser, F.P., A.A. Rahman, R.W. Crawford, C.E. McCulloch and M.J. Angus, "Immobilization and Leaching Mechanisms of Radwaste in Cement-based Matrices," First half yearly progress report, DOE/RW 82.050,61, March 1982.

REFERENCES (Cont.)

26. Glasser, F.P., A.A. Rahman, R.W. Crawford, C.E. McCulloch and M.J. Angus, "Immobilization and Leaching Mechanisms of Radwaste in Cement-based Matrices," Second half yearly progress report, DOE/RW 82.108,106. November 1982.
27. Komarnerni, S. and D.M. Roy, "Mechanisms of Immobilization of Nuclear Waste Elements by Cement Minerals, Cement and Mortar," Cem. Conc. Res. 11, 789, 1981.
28. H. Matsuzura, N. Moriyama, Y. Wadachi and A. Ito, "Leaching Behavior of Cesium-137 in Cement-waste Composites," Health Phys., 32, 529, 1977.
29. Neilson, R.M., Jr., and P. Colombo, "Waste Form Development Program Annual Progress Report," Brookhaven National Laboratory, BNL-51517, October 1980-September 1981, 80-85, January 1982.
30. Atkinson, A., A.K. Nickerson and T.M. Valentine, "The Mechanisms of Leaching From some Cement-Based Nuclear Wasteforms," United Kingdom Atomic Energy Authority, Harwell, AERE-R10809, June 1983.
31. Matsuzuri, H. and A. Ito, "Effect of Dimension of Specimen on Amounts of Cesium-137, Strontium-90 and Cobalt-60 Leached from Matrix of Hardened Cement Grout," J. Nuclear Science and Tech., 15, 296-301, 1978.
32. Atkinson, A. and A.K. Nickerson, The Diffusion of Ions Through Water Saturated Cement, UKAEA, Harwell, AERE-R10952, October 1983.
33. Douglas, R.W. and T.M.M. EL-Shamy, "Reactions of Glasses with Aqueous Solutions," J. Am. Ceram. Soc., 50, 1-8, 1967.
34. Heimerl, W., H. Heine, L. Kahl, H.W. Levi, W. Lutze, G. Malow, E. Schiewer and P. Schubert, Research on Glasses for Fission Product Fixation, Hahn-Meitner-Institut Berlin GmbH, Report No. HMI-B 109, September 1971.
35. Westsik, J.H., Jr., J.W. Shade and G.L. McVay, "Temperature Dependence for Hydrothermal Reactions of Waste Glasses and Ceramics," Scientific Basis for Nuclear Waste Management, Vol. 2, C.J.M. Northrup, Jr., ed., Plenum, New York, 239, 1980.
36. Flynn, K.F., I.J. Jardine and M.J. Steindler, "Resistance of High-Level Waste Materials to Dissolution in Aqueous Media," Scientific Basis for Nuclear Waste Management, Vol. 2, C.J.M. Northrup, Jr., Plenum, New York, 103, 1980.
37. Koster, G.R.R., Stoffliche Untersuchungen Zur Verfestigung Mittelaktiver Abfallösungen Mit Zement: Auslaugbarkeit Von Cesium Und Strontium, Kfk 2842, August 1979.
38. Colombo, P. and R. Neilson, Jr., "Properties of Radioactive Wastes and Waste Containers, First Topical Report," NUREG/CR-0619, BNL-NUREG-50957, Brookhaven National Laboratory, August 1979.

REFERENCES (Cont.)

39. Piciulo, P.L. and S.F. Chan, "Thermal Stability of Low-Level Waste Forms," Draft Report, BNL-NUREG-32337, Brookhaven National Laboratory, December 1982.
40. Piciulo, P.L., C.E. Shea and R.E. Barletta, "Biodegradation Testing of Solidified Low-Level Waste Forms," Draft Report, BNL-NUREG-32557, Brookhaven National Laboratory, February 1983.
41. 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.
42. Barletta, R.E., K.J. Swyler, S.F. Chan and R.E. Davis, "Solidification of Irradiated Epicor-II Waste Products," NUREG/CR-2969, May 1983.
43. Colombo, P., A. Auskern, J. Pruzansky, W. Becker and W. Horn, Development of Durable Long-Term Radioactive Waste Composite Materials, Progress Report No. 5, October-December, BNL-18652, 1973.
44. Blanco, R.E., et al., Recent Developments in Treating Low- and Intermediate-Level Radioactive Waste in the United States, Oak Ridge National Laboratory, ORNL-TM-1289, 1965.
45. Machiels, A.J. and C. Pescatore, "The Functional Dependence of Leaching on the Surface Area-to-Solution Volume Ratio." Scientific Basis for Nuclear Waste Management, Vol. VI, ed. D.G. Brookins, North-Holland, New York, pp. 209-216, 1983.
46. Ethridge, E.C., D.E. Clark and L.L. Hensch, "Effects of Glass Surface Area to Solution Volume Ratio on Glass Corrosion." Phys. Chem. Glasses 20:35-40, 1978.
47. Oversby, V.M., "Leach Testing of Waste Forms: Interrelationship of ISO and MCC Type Tests." Materials Characterization Center Workshop on Leaching Mechanisms of Nuclear Waste Forms, ed. J.E. Mendel. May 19-21, 1982, Gaithersburg, Maryland. PNL-4382, 1982.
48. Pederson, L.R., C.Q. Buckwalter, G.L. McVay and B.L. Riddle, "Glass Surface Area to Solution Volume Ratio and Its Implications to Accelerated Leach Testing." Scientific Basis for Nuclear Waste Management, VI, ed. D.G. Brookins, North-Holland, New York, pp. 47-54, 1983.
49. Matsuzuru, H. and A. Ito, "Effect of Dimension of Specimen on Amounts of ^{137}Cs , ^{90}Sr and ^{60}Co Leached from Matrix of Hardened Cement," J. Nucl. Sci. Tech., 15, 296-301, 1978.
50. Matsuzuru, H. and A. Ito, Annals of Nucl. Energy, 4, 465-470, 1977.
51. Speranzini, R.A. and L.P. Buckley, "Treatment of Spent Ion-Exchange Resins for Disposal," AECL - 7411, September 1981.

REFERENCES (Cont.)

52. Johansson, G., B. Karlberg and A. Wikby, "The Hydrogen-ion Selective Glass Electrode." Talanta, 22:953-966, 1975.
53. Crank, J., The Mathematics of Diffusion, 2nd Edition, Clarendon Press, Oxford, pg. 4 and Chapters 9-11, 1975.
54. Jost, W., Diffusion in Solids, Liquids, Gases, Academic Press, New York, 2-4, 1960.
55. International Atomic Energy Agency, Conditioning of Low-and Intermediate-Level Radioactive Wastes, IAEA Technical Reports Series No. 222, 97-122, 1983.
56. 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.
57. Griffing, D.E., Progress Report on the Development of Models for the Description of Radionuclide Transport in Solids, ARH-SA-190 REV, August, 1974.
58. Hespe, E.D., editor, "Leach Testing of Immobilized Radioactive Waste Solids, A Proposal for a Standard Method," Atomic Energy Review, 9, 195-207, 1971.
59. Godbee, H.W. and D.S. Joy, Assessment of the Loss of Radioactive Isotopes From Waste Solids to the Environment, Part I, Background and Theory, ORNL-TM-4333, Oak Ridge National Laboratory, February, 1974.
60. Kienzler, B., E. Korthaus, R. Koster, Modellrechnungen Zum Korrosions-Und Auslaugverhalten Von Zementierten Abfallprodukten, KfK 3612, November 1983.
61. Burtes, R.G., "Solidification of Low- and Intermediate-Level Wastes." AERE, United Kingdom, Atomic Energy Reviews, 9, 647-599, 1971.
62. Filter, H., "The Dow System for Solidification of Low-Level Radioactive Waste From Nuclear Power Plants," Dow Chemical Company, Midland, Michigan, June 1978.
63. Materials Characterization Center, MCC-1 Static Leach Test, Pacific Northwest Laboratory, August 1980.
64. 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, Oak Ridge National Laboratory, 1975.
65. Wiley, J.R. and J.J. LeRoy, "Long-term Leach Rates of Glasses Containing Actual Waste," Ceramics in Nuclear Waste Management, T.D. Chikalla and J.E. Mendel, eds., p. 284. CONF790420, U.S. Department of Energy, Technical Information Center, Oak Ridge, TN, 1979.

REFERENCES (Cont.)

66. Bradley, D.J., C.O. Harvey and R.F. Turcotte, Leaching of Actinides and Technicium from Simulated High-level Waste Glass, PNL-3152, Pacific Northwest Laboratory, Richland, WA, 1979.
67. Boulton, K.A., J.T. Dalton, A.R. Hall, A. Hough and J.A.C. Marples, "The Leaching of Radioactive Storage Glasses," Ceramics in Nuclear Waste Management, T.D. Chikalla and J.E. Mendel, eds., p. 248. CONF-790420, U.S. Department of Energy, Technical Information Center, Oak Ridge, TN, 1979.
68. Van Brakel, J. and P.M. Heertjes, "Analysis of Diffusion in Macroporous Media in Terms of a Porosity, a Tortuosity and a Constrictivity Factor," Int. J. Heat and Mass Transfer, Vol. 17, 1093-1103, 1974.
69. Bell, M.J., An Analysis of the Diffusion of Radioactivity From Encapsulated Wastes, Oak Ridge National Laboratory, Contract No. W-7405-eng-26, February, 1971.
70. Pescatore, C., Mechanistic Modeling of Nuclear Waste Form Leaching by Aqueous Solution, Ph.D. Thesis, Nuclear Engineering Department, University of Illinois, Urbana, IL, 1983.
71. Pescatore, C., S.A. Simson and A.J. Machiels, "Predictive Modeling of Long-Term Leaching Behavior," Waste Management '82, Vol. III, 323-332, 1980.
72. Phillips, D.C., D.I. Johnson, S.G. Burnay and J.W. Hitchon, "The Effects of Radiation on Organic Matrix Waste Forms," Testing, Evaluation and Shallow Land Burial of Low and Medium Radioactive Waste Forms, W. Krischer and R. Simon, editors, Harwood Academic Publishers, 183-199, 1984.
73. Brownell, L.E., R.E. Isaacson, W.E. Ogren and D.E. Griffing, Durability Evaluation of Radioactive Wastes in Ceramic Form, Atlantic Richfield Hanford, ARH-SA-178, April 1974.
74. Atkinson, A., "Mathematical Modeling of Leaching from Porous Nuclear Waste Forms," Radioactive Waste Management and the Nuclear Fuel Cycle, 3(3-4), 371-385, June 1983.
75. Hart, E.W., Acta Met., 5, 597, 1957.