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Effects on Radionuclide Concentrations by Cement/Ground-Water Interactions in Support of Performance Assessment of Low-Level Radioactive Waste Disposal Facilities

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Abstract

The U.S. Nuclear Regulatory Commission (NRC) is developing a technical position document that provides guidance regarding the performance assessment of low-level radioactive waste (LLW) disposal facilities. This guidance includes considerations associated with the chemical environment of the vault disposal system and the effects this system may have on the release and mobility of radionuclides. Because the disposal system will contain cementitious materials as structural, waste form, and/or backfill materials, the geochemical properties of pore waters buffered by reactions with cement will be very different from those waters associated with the local soil and geology. This environment therefore needs to be considered within the source term calculations if credit is taken for solubility limits and/or distribution coefficients for dissolved radionuclide concentrations within disposal units. Geochemical modeling may be used to assess potential chemical conditions in concrete vault disposal units and associated effects on aqueous speciation, solubilities, and sorption of radionuclides that are released from the waste form.

In support of NRC's development of this technical position, two literature reviews were done on information related to the chemical environments associated with the interaction of water with cementitious materials. One review was conducted on methods and associated solid-phase assemblages used to model the composition of pore water resulting from reaction with cementitious materials used in a disposal vault. This literature review also included related information on experimental studies of cement/water systems, natural analogue studies of cement and concrete, and radionuclide solubilities experimentally determined in cement pore fluids.

Based on the results of this review, geochemical modeling was used to demonstrate the calculation of conservative maximum concentrations for dissolved americium, neptunium, nickel, plutonium, radium, strontium, thorium, and uranium with respect to key geochemical input parameters for two ground-water environments associated with the disposal system. These environments include 1) a cement buffered system, wherein the leachate pH is controlled at values above 10 by the effective buffering capacity of the concrete; and 2) a ground-water buffered system, wherein the leachate pH and related solution parameters are dominated by the local ground-water system.

Another literature review was completed on the available data for the sorption potential of selected LLW radionuclides onto "fresh" cement/concrete where the expected pH of the cement pore waters will equal or exceed 10. The review included data for the radionuclides americium, inorganic carbon, chlorine, iodine, lanthanide elements, niobium, nickel, neptunium, plutonium, radium, strontium, technetium, thorium, and uranium. Based on information gleaned from the literature, a database was developed of preferred minimum distribution coefficient (K_d) values for these radionuclides. The K_d values are specific to the chemical environments associated with the evolution of the compositions of cement/concrete pore waters.

Contents

Figures

Tables

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NUREG/CR-6377 is not a substitute for NRC regulations, and compliance is not required. The approaches and/or methods described in this NUREG/CR are provided for information only. Publication of this report does not necessarily constitute NRC approval or agreement with the information contained herein.

Abbreviations/Acronyms

A	when used in a cement formula, symbol for the Al_2O_3 component in the cement phase
(act)	description for a microcrystalline solid
(am)	descriptor for an amorphous solid
ANS	American Nuclear Society
(aq)	descriptor for neutral aqueous species
BFS	blast furnace slag
BFS-FA	blast furnace slag fly ash
BTP	Branch Technical Position
C	Symbol for the element carbon or, when used in a cement formula, the CaO component in the cement phase
C-S-H	calcium silicate hydrogel
C/S	calcium/silicon
D_a	apparent diffusion coefficient
D_f	diffusion coefficient
D_i	"intrinsic" diffusion coefficient
DoE	UK Department of the Environment
DOS	Disk Operating System
DTA	differential thermal analysis
Eh	Electrical potential relative to the standard hydrogen electrode in volts or millivolts
EPA	U.S. Environmental Protection Agency
EPC	Expansive Portland Cement
EPMA	electron probe microanalysis

F	Symbol for the element fluorine or, when used in a cement formula, the Fe_2O_3 component in the cement phase. Although "F" might be included in a cement formula, the iron content of some phases may be very low and thus be neglected in their chemical formula.
$\Delta G^\circ_{f,298}$	Gibbs energy of formation from the elements for the specified compound at 298 K
$\Delta G^\circ_{r,298}$ and $\Delta G^\circ_{r,T}$	Change in Gibbs energy of formation for the specified reaction at 298 K and temperature T
H	Symbol for the element hydrogen or, when used in a cement formula, the H_2O component in the cement phase
HLW	high-level radioactive waste
$\Delta H^\circ_{f,298}$	Enthalpy or heat of formation from the elements for the specified compound at 298 K
$\Delta H^\circ_{r,298}$ and $\Delta H^\circ_{r,T}$	Change in enthalpy or heat for the specified reaction at 298 K and temperature T
IAEA	International Atomic Energy Agency
ISO	International Standards Organization
K	Temperature in degrees Kelvin
$K^\circ_{r,298}$ and $K^\circ_{r,T}$	Equilibrium "activity" constant for the specified reaction at 298 K and temperature T
K_d	Mass-related distribution coefficient, describing the equilibrium partitioning of a solute between solid and liquid phases due to sorption $K_d = C_S/C_L$ where C_S and C_L are the concentrations of solute in the solid and liquid phases, respectively
K_{sp}	solubility product
LLW	low-level radioactive waste
ln	Natural logarithm to the base e = 2.7183 . .
log	Common logarithm to the base 10
M	Molarity, moles of solute per liter of solution
m	Molality, moles of solute per 1000 g of solvent
$_m$	Subscript "m" when used in a cement formula referes to mono-sulfate.
mol	Mole, quantity of substance that is equal to its gram formula weight
MW	molecular weight

NRC	U.S. Nuclear Regulatory Commission
OPC	ordinary Portland cement
PA	performance assessment
PAM	performance assessment methodology
PC	personal computer
PFA	pulverized fuel ash
pH	Negative log of the activity of H^+
PNNL	Pacific Northwest National Laboratory
ppm	Concentration in parts per million, which is equivalent to milligrams of solute per 1000 grams of solvent
R	Gas constant, 1.9872 cal/K·mol
R_d	Sorption constant calculated from R_d (ml/g) = $v/m\{(C_0 - C_f)/C_f)\}$ where v is the volume of solution in ml, m is the mass of solid in g, C_0 is the initial adsorbate concentration in Bq/ml, and C_f is the final adsorbate concentration in Bq/ml
S	Symbol for the element sulfur or, when used in a cement formula, the SiO_2 component in the cement phase
$\bar{S}$	When used in a cement formula, symbol for the SO_3 component in the cement phase
SCSSS	Standard Canadian Shield Saline Solution
SEM	scanning electron microscopy
SRPC	sulfate resistant Portland cement
T	Temperature in degrees Kelvin, unless otherwise noted as degrees celsius
t	Subscript "t" when used in a cement formula refers to tri-sulfate.
TGA	thermal gravimetric analysis
TMS	trimethylsilylation
UK	United Kingdom
V	Volt

XRD	x-ray diffraction
298	Signifies 298.15 K (25.0°C)
	Signifies degrees temperature or a compound that is in its standard state at 1 atmosphere (atm) pressure (1 atm = 1.013 bars = 1.013×10^5 Pascals)
Σ	Summation

1 Introduction

The U.S. Nuclear Regulatory Commission (NRC) is developing a Branch Technical Position (BTP) document that provides guidance regarding the performance assessment (PA) of low-level radioactive waste (LLW) disposal facilities. This guidance includes considerations relative to modeling the release of radionuclides from LLW disposal units as a function of time. The literature reviews and calculations described in the following report were completed as technical support to the source-term component of NRC's development of the LLW performance assessment methodology (PAM) and associated test case analysis.

1.1 Background

The NRC considers PA essential to the licensing process for LLW disposal facilities. The performance objectives and technical requirements for LLW land disposal facilities are specified in Subparts C and D of 10 CFR Part 61. Performance assessment calculations may be used to help provide reasonable assurance that the required performance objectives will be met. The performance objectives for LLW land disposal facilities include "protection of the general population from release of radioactivity" (§ 61.41), "protection of individuals from inadvertent intrusion" (§ 61.42), "protection of individuals during operations" (§ 61.43), and "stability of the disposal site after closure" (§ 61.44).

1.1.1 NRC Branch Technical Position on LLW Performance Assessment

The NRC is developing a BTP on PA for LLW disposal systems. The draft BTP was released for public comment in May 1997. The public comment period ended August 23, 1997. Finalization of the BTP on PA for LLW disposal systems and documentation of associated test case analyses are dependent on satisfactory resolution of public comments and final commission approval.

The BTP provides guidance for regulatory authorities and developers with regard to a suggested strategy and associated technical issues for conducting an assessment of a facility's post-closure performance for protection of the general public from release of radioactivity (10 CFR Part 61.41). The BTP includes discussions of the following topics:

- need and development of the PA process
- overall approach for completing a PA
- NRC positions on technical issues, such as site considerations, roles of engineered barriers, time frames, uncertainty and sensitivity analyses, and roles of operational and closure periods with respect to PA analyses
- issues and recommended analytical approaches for PA modeling.

The PAM described in the BTP addresses issues and recommended approaches for modeling the following processes

- water infiltration at the disposal unit and transport to the ground-water system
- behavior and physical characteristics of engineered barriers as a function of time
- releases of radionuclides (i.e., source term) from the disposal unit as a function of time

- transport of radionuclides by ground-water, surface-water, and air pathways as a function of time
- potential doses to humans from radioactivity released from the LLW disposal system.

The source-term component of a PA provides estimates of the release of radionuclide concentrations from the LLW disposal unit. These calculations require input from the water infiltration and engineered barrier calculations to determine the flux of water that may pass through the disposal unit, contact and react with the waste forms and containers, and possibly lead to the release of radionuclides. Results from the source-term calculations then become input data for the transport calculations involving the potential for radionuclide migration by ground-water, surface-water, and air pathways.

Source-term modeling needs to consider the anticipated inventories of radionuclides associated with the LLW disposal system and identify those radionuclides that are most important to meeting the 10 CFR Part 61.41 performance objective. The source-term model should address the mechanisms and rates of failure of the waste containers, if the containers are believed to delay the release of any radionuclides. Once the waste containers are breached, some gaseous radionuclides, such as ^{14}C, ^{85}Kr, ^{222}Rn, and ^{3}H, may be released from the waste forms immediately along air pathways. Other radionuclides will be released as a result of chemical reactions that will occur when the infiltrating water contacts the waste forms. These reactions will be affected by the composition of the infiltrating water as modified by the chemical environment associated with the waste disposal facility. This environment includes cement, metal, and other materials present in the engineered structure as well as in the waste forms, containers, and any backfill materials used in the facility.

The NRC BTP suggests an iterative approach to LLW PA. From this perspective, initial source-term calculations of radionuclide release via interactions of infiltrating water with LLW may be based on fairly conservative models, such as rinse release models. For certain radionuclides to meet the performance objective, additional constraints may need to be placed on the release of radionuclides from the disposal unit. These constraints may include the use of solubility limits for certain radionuclide elements in the aqueous phase or retardation coefficients for sorption in the disposal unit. Because disposal units are expected to contain significant quantities of cementitious materials, the composition of the aqueous solution leaching the LLW will be modified significantly, especially in terms of pH, by reactions between the infiltrating water and cement phases. The chemical environment resulting from the water/cement reactions must therefore be considered when determining solubility limits and sorption potentials for radionuclides.

1.1.2 LLW PA Test Case

The NRC is completing a test case modeling exercise to assist the development and evaluation of the guidance described in its BTP for LLW PA. Another goal of the test case analysis is to determine the sensitivity of the calculated releases to the input values. The input database and preliminary results have been presented in Campbell and McCartin (1994), Cady and Thaggard (1994), Campbell (1994), and at workshops like that conducted by the NRC at its headquarters in Rockville, Maryland, on November 16-17, 1994. The database used for the performance test case is for a hypothetical, below-ground, concrete vault LLW disposal system located on a sub-humid coastal plain. The vaults are overlain by a multi-layer cover. An analysis of daily water balance from 29 years of historical weather data is used to estimate ranges of infiltration to the multi-layer cover. The composition of the ground water infiltrating the disposal vaults is given in Chapter 3 of our report. Information for the LLW form and inventory used in the NRC LLW PA test case was taken from the "Richland '89" data given in Roles (1990).

Cady and Thaggard (1994) summarize the modeling approaches used in the NRC LLW PA test case. As listed by Cady and Thaggard, the PA includes

- infiltration of water to and percolation through the multi-layered cover

- percolation of water into the concrete vaults
- breaching of the waste containers and leaching of the LLW forms
- migration of radionuclides along air and water pathways within the concrete vaults and their subsequent movement vertically to the water table and horizontally in the ground water
- discharge of radionuclides at an adjacent well or eventually to surface water
- exposure of humans through ingestion of water or food contaminated with radionuclides.

To determine the sensitivity of the predicted releases of radionuclides to the input data, the system code used by NRC incorporates Latin-Hypercube sampling of the distributions of parameter values to do stratified Monte-Carlo analyses of the sample values.

The source term model for the LLW considers radionuclide release by either rinse release, diffusion, or dissolution mechanisms. Suitable ranges of radionuclide solubility limits [e.g., Krupka et al. (1994)] and retardation coefficients are included in the calculations of radionuclide release from the disposal vaults. Because large amounts of cementitious material are present in various components of the disposal vault system, interactions between the infiltrating water and the concrete are expected to have a strong buffering effect on the chemical environment in and near the disposal vault system. A description of the rinse release model, the most conservative of the three source-term release models, and radionuclide concentrations calculated by NRC for vaults containing Class A and B/C wastes for the LLW PA test case are given in Chapter 4 of our report. The rinse component of the model assumes that quantitative transfer of radionuclides can occur from the waste to the aqueous phase. It is used in the test case for radionuclides that are not modeled either with diffusion release (e.g., cement solidified waste) or dissolution release (e.g., metallic waste forms). The amount of a radionuclide released into the aqueous phase from any of the three source term models, however, is limited by the thermodynamic equilibrium solubility of the radionuclide. The classification of LLW wastes for near-surface disposal is described in detail in 10 CFR Part 61.55 (Waste Classification). Class A wastes are characterized by low concentrations of radionuclides, such as contaminated protective clothing, paper, and laboratory trash. Class B wastes contain higher concentrations of radionuclides, such as resins and filters from nuclear power plants. Class C wastes have the highest concentrations of radionuclides, and typically include nuclear reactor components, sealed sources, and industrial waste with high radioactivity.

1.2 Purpose and Objectives

The purpose of this study was to provide technical support to issues associated with the concrete-buffered chemical environment considered in the source-term component of the NRC BTP and test case analysis for LLW PA. Information collected during our study has been used by NRC for some of their source-term performance calculations. In addition, our report serves as an information base for others involved with PA studies of the disposal of LLW and other contaminants in facilities containing cementitious materials.

The specific objectives of our study were to

- review the available literature that describes
  - computerized modeling methods used to predict the chemical evolution of pore fluids resulting from the interactions of water and cementitious materials

  - laboratory phase equilibrium and leaching studies related to the hydration of cement phases and the associated evolution of pore-fluid compositions
  - natural analogue studies of aged or ancient cementitious materials.

- use geochemical modeling methods to calculate maximum solubility limits for selected radionuclide elements for a range of pH values that includes the chemical environments buffered by the high pH conditions of the cementitious disposal vaults and the local ground-water system in the test case
- review the available literature that describes adsorption studies of selected radionuclides on cement and concrete materials
- determine a preferred conservative database of distribution coefficient (K_d) values for selected radionuclide elements based on the information gleaned from the literature review.

The geochemical modeling calculations were also designed to illustrate some geochemical considerations that are important to determine radionuclide solubility limits that serve as input to PA source-term calculations. Radionuclide elements considered in the solubility limit calculations include americium, carbon as ^{14}C, iodine, neptunium, nickel, niobium, plutonium radium, strontium, technetium, thorium, and uranium.

As noted in the NRC BTP for LLW PA, proper selection and use of K_d values that are most germane to the physicochemical system (e.g., cement-containing disposal vault) being modeled is an important concern to the technical adequacy and defensibility of PA calculations. The extent of adsorption studies pertaining to radionuclides on cement and concrete materials is generally considered to be limited. Our literature review of radionuclide adsorption studies was conducted to determine the true extent of this literature and to provide an information base that is a starting point for more detailed analysis by those requiring these data. The elements considered in the adsorption literature include americium, carbon as ^{14}C, chlorine, iodine, lanthanides, neptunium, nickel, niobium, plutonium, radium, strontium, technetium, thorium, and uranium.

1.3 Report Organization

The main body of our report contains

- an overview of the chemical environment resulting from the interactions between water and cementitious materials and the subsequent evolution of the pore-fluid compositions
- a description of the conceptual model, input data, and MINTEQ geochemical code (or computerized model) used to calculate the maximum solubility limits for the selected radionuclide elements
- the results of the geochemical modeling calculations of radionuclide solubility limits as a function of pH for the cement- and ground-water-buffered environments
- the preferred database of distribution coefficient (K_d) values for selected radionuclides on cementitious materials and the results of the literature review of adsorption studies that support the selection of these preferred values.

The overview of water/cement interactions is a brief summary based on the literature review. The overview describes the scope of the computerized literature review. References identified during the course of the literature review on cement modeling studies, laboratory phase equilibrium and leaching studies, and natural analogue studies are described, respectively, in Appendices A, B, and C.

The thermodynamic database used to calculate maximum concentration limits for the radionuclide elements is described and listed in Appendix D. The reader is cautioned that our modeling calculations were based on a thermodynamic database available for the MINTEQ code and supplemented by our own experience in this field. Our study was not designed to be a critical review of the existing thermodynamic data for radionuclides. Development of "the" best thermodynamic database for radionuclide aqueous species and solids was beyond the scope of this study. Because new measurements of thermodynamic data for radionuclide compounds are constantly being published, those conducting geochemical modeling calculations as part of a PA must factor in their own review of the most appropriate database at the time of their calculations.

Appendix E describes an approach reported by Atkinson (1983), Atkinson et al. (1986), and Atkinson and Nickerson (1988) for estimating K_d values from radionuclide diffusion measurements. Given the limited extent of adsorption measurements available for many radionuclides, it has been suggested that this analysis method could be used to augment the available K_d data.

The main body of the report and each appendix contain extensive reference lists. Readers are encouraged to inspect these lists for material most appropriate to their individual PA needs. For many situations, references cited in this report may include additional references in their own bibliographies that have information relevant to the readers' PA needs.

2 Chemical Environment of Cement/Water Interactions

Cementitious materials have several important uses in low-level radioactive waste (LLW) disposal facilities. These include the use of cement as a waste form (i.e., solidification) for LLW as well as its use as backfill and construction material for the LLW storage vault. The formulations of these cements are expected to contain substantial amounts of Portland cement. Therefore, the long-term behavior of hydrated cements and their constituent phases in natural ground waters is important to the performance assessment (PA) of LLW disposal systems and the potential release of radionuclides.

Useful background information on cement systems and nomenclature related to this technical field are given by the International Atomic Energy Agency's (IAEA) technical report on improved cement solidification of low- and intermediate-level radioactive wastes (IAEA 1993). Although cement solidification of low and intermediate level radioactive wastes is the focus of the IAEA report, sections that summarize the types of cements and their properties, chemical and mineral admixtures, cement solidification processes, and chemical stability of cements will be useful for any reader seeking an overview of cement systems.

2.1 Computerized Literature Review

A computerized literature review of modeling and experimental studies pertaining to the prediction of pore-water composition resulting from the dissolution of cement was completed as part of this study. Details of the execution of the computerized literature review are given at the beginning of Appendix A. References pertaining to the following topics are summarized in the first three appendices of this report:

- Appendix A - approaches to modeling cement pore-water compositions
- Appendix B - experimental studies of cement/water interactions
- Appendix C - natural analogue studies of cementitious materials.

A series of 13 papers published in a single issue of *Waste Management* (1992, Volume 12, Numbers 2/3) is particularly noteworthy. This issue focuses on cementitious materials in radioactive waste management, and several of the papers contain background reviews of relevant information. Several of the papers published in this issue of *Waste Management* are cited in this report and summarized in Appendices A and B.

The reader should also be aware of three extensive literature reviews published in the United Kingdom (UK), where a substantial research and development program in the use of cementitious materials for radioactive waste disposal is being conducted. These literature reviews include studies published in the UK and the international community on speciation and solubility (Smith-Briggs 1992a,b,c), sorption (Berry 1992a,b,c), and colloid formation (Tipping and Higgo 1992a,b,c) relative to the release and transport of radionuclides in the near and far field. Each literature review was published as three reports, and each of the nine total reports contains a chapter on studies related to cement systems. The first report of each literature review summarizes studies funded by the UK Nirex and Department of the Environment (UK DoE) that pertain to the subject area. The second report contains an extensive bibliography, including reference citations and complete abstracts, of UK and international publications on the subject area. The third report compares the objectives and approaches used in studies funded by Nirex and UK DoE to those in related studies undertaken by the international community.

2.2 Cement/Water Interactions

The composition of pore water that evolves during the degradation of cement in water has been studied extensively in the laboratory and with computer modeling techniques. The composition of hydrated cement generally consists of the following (Berner 1992):

- 40-50 wt% calcium silicate hydrogel (C-S-H)
- 20-25 wt% portlandite [$Ca(OH)_2$]
- 10-20 wt% ettringite [$Ca_6Al_2O_6(SO_4)_3$], monosulfate [$Ca_4Al_2O_6SO_4$], and ferric phases
- 10-20 wt% pore solution
- 0-5 wt% minor components, such as NaOH, KOH, and $Mg(OH)_2$.

As used above for the calcium silicate hydrogel (C-S-H), a convention has been adopted by researchers in cement science to name cement phases. This terminology includes the use of the following abbreviations for components in the cement phases: $C \equiv CaO$, $S \equiv SiO_2$, $A \equiv Al_2O_3$, $F \equiv Fe_2O_3$, $H \equiv H_2O$, and $\bar{S} \equiv SO_3$. The formula of a particular cement phase is then expressed as the appropriate stoichiometric combination of these initials. Subscripts "m" and "t," as in F_m, are sometimes used to note mono- and tri-sulfate, respectively. For example, portlandite [$Ca(OH)_2$], gibbsite [$Al(OH)_3$], and hydrogarnet [$Ca_3Al_2(OH)_{12}$] are abbreviated as CH, AH_3, and C_3AH_6, respectively. This convention will also be used throughout this report to refer to cement components. Although "F" might be included in a cement formula, the iron content of some phases may be very low and thus neglected in their chemical formula.

2.2.1 Chemical Environment of Cement Pore Fluids

The chemical reactions associated with the hydration of cement are described in detail in IAEA (1993), Atkins and Glasser (1992), Reardon (1992), and references cited therein. Because pH is one of the most important chemical parameters affecting the solubility of radionuclides, understanding the pH conditions of the cement pore fluids is particularly important to the PA of cementitious materials in LLW disposal systems. The change of pH resulting from the reaction of cement and water is shown schematically as a function of time in Figure 2.1. The dissolution of the C-S-H and portlandite phases, which may constitute as much as 75 wt% of the cement, has an important role in buffering the pH of the resulting pore fluids. As ground water reacts with the cement, dissolution of the alkali hydroxide phases, present in relatively minor amounts, results initially in high pH values of approximately 13.5. As these phases are leached from the cement, the pore fluid pH is then buffered near 12.5 by the dissolution of free portlandite in the cement.

Eventually the portlandite is depleted and the pore fluid pH decreases to approximately 10.5 where it is controlled by the incongruent dissolution of the C-S-H. Because of its importance as a pH control, extensive research has been conducted to develop a thermodynamic model to calculate the solubility properties of C-S-H which vary as a function of its calcium/silicon ratio. When the dissolution of C-S-H is complete, the pH of the cement pore fluid will continue to decrease to a value buffered by the host ground water. This pH change will also be affected to a limited extent by the dissolution of any calcite that precipitated at the high pH conditions during the early stages of cement dissolution.

The timeframe over which the pH of the pore solution changes from 13.5 to that of the ground water is determined by the rate at which water migrates through the cement system. For radioactive waste disposal systems being considered in the UK, studies by Atkinson et al. (1989) indicate that the pH of the near-field pore water would remain above 10.5 for several hundred thousand years.

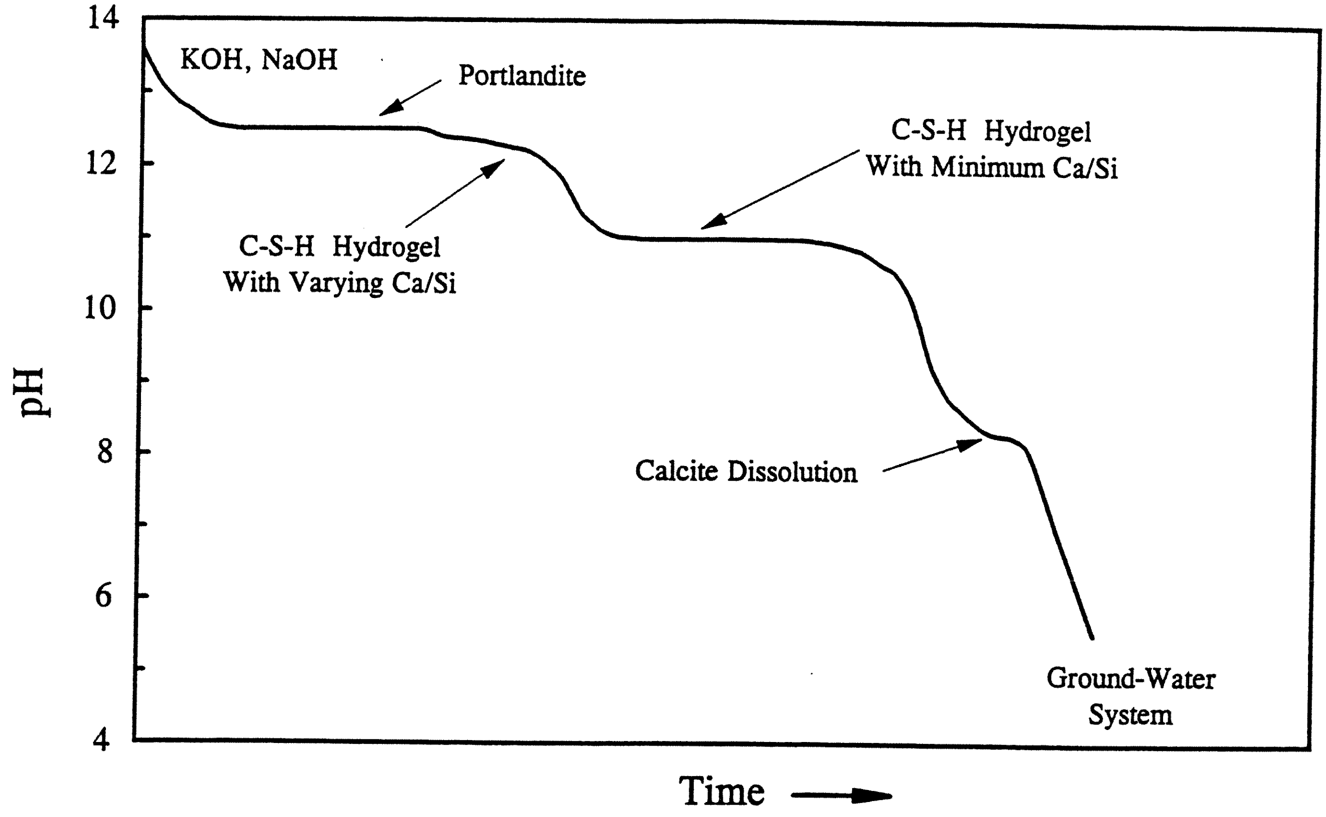

Figure 2.1 **Schematic diagram illustrating the change of pore fluid pH resulting from the progressive aqueous dissolution of cement**

2.2.2 Approaches to Modeling Compositions of Cement Pore Fluids

Numerous studies have been conducted with regard to the development of modeling approaches to predict the final mineral assemblage and composition and pH of pore solutions resulting from the hydration of cement. References describing the various modeling approaches are reviewed in Appendix A. The development of an incongruent dissolution model for the C-S-H phase by Berner (1992) is of particular importance given its significance in affecting the pH, silica, and calcium concentrations of cement pore fluids.

Many of the modeling approaches use existing computerized geochemical models, such as EQ3/EQ6, PHREEQE, MINTEQ, and others, to derive the composition of cement pore fluids. A conceptual model based on an assemblage of cement-related phases is typically used in conjunction with a series of mass transfer calculations to predict the compositions of the cement pore fluids. Characterization data from laboratory studies of cement hydration and cement/water dissolution are used to develop the conceptual models and/or partially validate the modeling results. The cement mineral assemblages used for the conceptual models are identified with the relevant references in Appendix A. Many sources also list and explain the derivation of the thermodynamic data that the investigators used for these cement mineral assemblages. Some of the modeling approaches also involve auxiliary computer codes that have been developed to predict the solid-phase assemblage of a cement paste based on the initial cement composition.

2.2.3 Laboratory Studies of Cement Hydration and Pore Fluids

All of these modeling approaches are based to some extent on the results of laboratory studies of cement-phase equilibria. These studies were designed to identify and characterize the reaction products and/or determine the composition of pore fluids resulting from cement/water reactions. The results of these experiments were in turn used to identify the assemblages of stable phases and their associated compositions resulting from the progressive aqueous dissolution of cement. Many of these studies were identified during the course of our literature review. Because the results of many of these studies are the technical basis for model development, these references have been summarized in Appendix B.

Because this literature review focuses on studies published during the last ten years, the references in Appendix B do not provide a complete summary of all cement/water phase equilibria studies completed to date. Many of the cited studies are based on previous experimental phase equilibria studies that have been extended to more complex composition systems and/or higher temperatures. Readers should examine references cited in the studies summarized in Appendix B for a more comprehensive understanding of the extent of experimental studies of cement/water equilibria available.

2.3 Natural Analogue Studies of Cement and Concrete Materials

Natural analogue studies provide unique opportunities to study chemical and physical processes that occur over historical or geologic timescales not possible in laboratory or field experiments. During the past 20 years, the scientific community has conducted a broad spectrum of natural analogue studies that help us understand the long-term behavior of materials that may be used for waste forms, containers, engineered barriers, and construction materials for storing radioactive waste.

References describing natural analogue of cementitious materials and disposal systems are reviewed in Appendix C. These studies fall into the following two categories:

- studies pertaining to the physical stability of cement hydration compounds
- studies related to the chemical interactions between cement, rock, and ground water

Data from these studies have been used to test conceptual and computerized models used for PAs of cement-containing disposal facilities for radioactive waste.

Samples of industrial and ancient concretes and mortars have been studied as possible analogues to the physical degradation of cementitious materials, including cement hydration mineral phases. These materials have included, for example,

- Portland cement taken from an 80-year-old concrete sea wall at a dockyard in Scotland
- hardened cement that was part of a consignment of cement paste found in barrels in an 1848 ship wreck
- cement samples from Britain's first multi-story reinforced concrete framed building and first reinforced concrete marine structure
- concrete from a 800-year-old wall of the Reading Abbey in England
- mortar and concrete from several Gallo-Roman thermal baths
- 1700-year-old mortar from Hadrian's Wall in northern England

- lime-soil mix from the Great Wall, China
- cementitious material from a 2500-year-old water tank in Kamiros on the island of Rhodes
- mortar from the Great Pyramid, Giza, Egypt.

Ground waters from two field sites have also been studied as natural analogues to the chemical evolution of pore waters resulting from cement/rock/ground water interactions. These include studies of hyperalkaline waters at sites in northern Oman and northern Jordan. Because of their high pH values (≥11 at the Oman site and ≥12.5 at the Maqarin site) and the presence of portlandite [$Ca(OH)_2$], these ground waters are considered possible analogues to cement pore waters. The emphasis of these studies has been on the determination of the solubility and speciation of radionuclides, and the verification testing of geochemical models and associated thermodynamic databases.

3 Application of Geochemical Modeling to Estimating Solubility Limits for Radionuclide Elements

Conservative maximum concentration limits for dissolved americium, nickel, neptunium, plutonium, radium, strontium, thorium, and uranium were determined for the ground-water conditions being considered in the NRC LLW PA test case. The concentration limits are based on equilibrium thermodynamic solubilities calculated using the geochemical equilibrium code MINTEQA2. The conceptual model used for the solubility calculations is based on the geochemical conditions for the source-term component of the test case that NRC is using to demonstrate PA methodologies for LLW disposal facilities.

3.1 Conceptual Model

Two chemical environments are being considered for the source term in the NRC LLW PA test case. In one environment, the composition of the leachate migrating from the disposal vault is assumed to be controlled by the dissolution of the cement hydrate phases (i.e., "cement buffered" case). As noted in Chapter 2, this environment would be characterized by high pH values from 10.5 to 12.5. These conditions would correspond to the initial stages of water infiltration into the LLW disposal system where the pore volume of water is small compared to availability of reactive concrete hydrate phases. In the second environment, the leachate composition is assumed to be controlled by reactions with the site soils and therefore equivalent to the local ground-water composition (i.e., "ground-water buffered" case). This case would correspond to an advanced state of degradation of the LLW disposal system when the availability of reactive concrete phases is insufficient to affect pore fluid compositions. The ground-water buffered case also corresponds to conditions in the far field where the ground-water composition would not be affected by cementitious materials in the disposal system. The rate at which the leachate composition changes from the cement to ground-water buffered conditions will depend on the physical properties (e.g., fractures, porosity) of the cementitious materials being leached, rate of infiltration, and related hydrologic properties of the disposal system.

The radionuclide concentration limits were calculated for the range of pH and redox (Eh) conditions defined by the cement and ground-water buffered environments. The pH/Eh values specified by the NRC were 1) pH = 12.5 and Eh = +200 mV for the cement buffered system, and 2) pH = 5.8 and Eh = +500 mV for the ground-water buffered system. The effects of pH on the solubility of each radionuclide were demonstrated by calculating the radionuclide solubilities at 0.5 pH-unit increments over the pH range 4.0 to 12.5. A minimum pH value of 4.0 was specified for the modeling calculations in order to include the complete range of pH values considered for the ground-water composition used in the NRC LLW PA test case. The Eh values used for the solubility calculations were assumed to vary linearly as a function of pH between the pH/Eh conditions of the cement- and ground-water buffered systems. The Eh values corresponding to pH values between 4.0 and 12.5 were calculated from the following equation:

$$\text{Eh (mV)} = -44.78\ \text{pH} + 760 \tag{3.1}$$

The above equation was derived from the pH/Eh values specified by the NRC for the cement- and ground-water buffered systems.

As a conservative limit, the concentrations of dissolved carbonate, an important complexing ligand for many radionuclides, in the leachate were fixed between pH values of 4.0 and 8.0 by assuming equilibrium with 0.003 atm CO_2 (gas), which is frequently used as the reference level of CO_2 (gas) in soils (Lindsay 1979). For pH values greater than 8.0 up to 12.5, concentrations of dissolved carbonate were constrained by assuming equilibrium with the solubility of calcite ($CaCO_3$). Calcite is known to precipitate as a result of carbonation reactions occurring with the dissolution of cement (Criscenti and Serne 1990; Duerden et al. 1990; Reardon and Dewaele 1990; Smith and Walton 1991). The concentrations of dissolved calcium were also constrained in the pH range from 8.5 to 12.5 by assuming the leachate is in equilibrium with the solubility of calcite.

To simplify the modeling calculations, the concentrations of the other dissolved, non-radionuclide constituents in the leachate were fixed at the concentrations specified for the average ground-water compositions listed in Table 3.1. This rather dilute ground-water composition is used in the NRC LLW PA test case. This assumption was justified given the general absence of thermodynamic data, except for the data available for some uranium solids, for radionuclide-containing solids containing cationic constituents other than the radionuclide element of interest. This simplification also assumes that the ground water is the major source for dissolved fluoride, chloride, nitrate/nitrite, sulfate, and phosphate which may form aqueous complexes with some radionuclides. Cement contains measurable quantities of sulfate and minor amounts of

Table 3.1 Composition of ground water used in the NRC LLW PA test case

Variable	Average value	Range
Temperature	18.6°C	16-22°C
pH	5.8	4.5-7.3
Eh (mV)	500	350-700
Conductivity (µmho/cm)	50	10-250
Dissolved Oxygen (ppm)	6	5-10
TDS (ppm)	13	10-20
DOC (ppm)	6	
Silica (SiO_2) (ppm)	5.8	0.1-12
Alkalinity ($CaCO_3$) (ppm)	14.1	
Cations (ppm)		
Na	3.2	<1-17
K	1.3	0.2-10
Ca	4.0	<0.1-40
Mg	0.4	<0.01-3
Fe	0.118	0.010-1.600
Mn	0.052	0.005-0.780
Ba	0.2	0-1
Sr	0.1	0-0.5
Anions (ppm)		
F	0.07	0-0.4
Cl	3.0	0.5-16
NO_3+NO_2	0.6	0.02-4
SO_4	2.6	0.2-20
PO_4	0.1	0.03-2.2

chloride phases that could increase the concentrations of these ligands in the pore fluids. However, at the high pH conditions (>10) associated with cement dissolution, complexation of radionuclides by dissolved sulfate or chloride is not important.

A electrical neutrality was not maintained for the charge balance of the speciated radionuclide-containing water compositions calculated with MINTEQA2 (Chapter 4). Because these are bounding-type calculations, the lack of a charge balance constraint should not significantly increase the uncertainties in the modeling results given the low concentrations predicted for most radionuclides and the inherent uncertainties already associated with the conceptual models for the cement and ground-water buffered systems for the NRC LLW PA test case. The lack of this constraint does, however, invalidate the high solubilities calculated for neptunium, nickel, and strontium at pH values less than 6. Moreover, these high concentrations, as noted in Chapter 4, are unrealistic and not observed in nature.

Because the cement-buffered pore fluids exiting at the outer edge of a vault would be diluted to some unknown extent by infiltrating ground water, the leachates leaving the facility were assumed to have a moderate to low ionic strength. The ion activities used to calculate the solubility products were therefore corrected for ionic strength using the Davies or extended Debye-Hückel equations in the MINTEQA2 code (Allison et al. 1991). High ionic strength corrections using, for example, Pitzer-type ion interaction parameters were therefore not applied to these simplistic solubility calculations. This approach would be invalid for modeling chemical interactions in water within the cement matrix, especially during the early stages of cement dissolution. During this period, the cement pore waters have pH values greater than 12 and high solute concentrations due to the dissolution of NaOH and KOH. Andersson et al. (1989) analyzed the compositions of pore fluids that were pressure extracted from pastes of seven cements (see discussion of this study in Appendix B of our report). The pH and the ionic strength values of the analyzed pore fluids ranged from 12.4 to 13.5 and 0.03 to 0.29 M, respectively. At high ionic strength conditions, a model, such as that described by Reardon (1992), that uses Pitzer's ion interaction approach to calculate ion activity corrections, is more accurate. Some examples of applications where the Pitzer model might be needed include the modeling of chemical interactions associated with the degradation and longevity of cement materials used as waste forms, structural material, or backfill components.

The radionuclide solubilities were calculated using both the average and maximum concentrations of anions listed in Table 3.1. The objective of these two sets of modeling calculations was to demonstrate the possible importance of complexation by anionic constituents in estimating the concentration limits for radionuclides in the ground water included in the NRC LLW PA test case.

3.2 MINTEQA2 Geochemical Code

The radionuclide solubilities and associated aqueous speciation were calculated using a personal computer (PC) version of the chemical equilibria code MINTEQA2 (Version 3.10) compiled to execute in the DOS computer operating system. The PC version of the MINTEQA2 code was obtained from the Center for Exposure Assessment Modeling at the U.S. Environmental Protection Agency (EPA) in Athens, Georgia. The MINTEQA2 code and its predecessor versions have been described by Felmy et al. (1984, MINTEQ), Peterson et al. (1987, MINTEQ), Brown and Allison (1987, MINTEQA1), and Allison et al. (1991, MINTEQA2). The code was originally constructed by combining the mathematical structure of the MINEQL code (Westall et al. 1976) with the thermodynamic database and geochemical attributes of the WATEQ3 code (Ball et al. 1981).

The MINTEQ code is used in conjunction with a thermodynamic database to calculate complex chemical equilibria among aqueous species, gases, and solids, and between dissolved and adsorbed states. The use of thermodynamic principles to calculate solubility equilibria in aqueous systems is described in detail in Garrels and Christ (1965), Lindsay (1979), Morel (1983), Nordstrom and Munoz (1985), and Stumm and Morgan (1981). The MINTEQ calculations include aqueous speciation, solubility and saturation state (i.e., saturation index), adsorption, oxidation-reduction, gas phase equilibria, and precipitation/dissolution of solid phases. The MINTEQ code incorporates a Newton-Raphson iteration scheme to solve the set of mass-action and mass-balance expressions, and uses the Davies and extended Debye-Hückel equations to calculate activity coefficients for aqueous ions.

The reader is referred to the references and user guides listed above for details regarding the use of MINTEQ code, types and examples of geochemical equilibria calculations possible with this code, and the basic equations on which the model is based.

3.3 MINTEQA2 Thermodynamic Database

The thermodynamic data used to calculate radionuclide solubilities include the database originally supplied with MINTEQA2 by the EPA and modifications completed during the course of this study. During its development, the MINTEQ database has undergone numerous modifications as described by Krupka and Morrey (1985) as well as references cited by Felmy et al. (1984), Peterson et al. (1987), Brown and Allison (1987), and Allison et al. (1991).

The EPA MINTEQA2 thermodynamic database was augmented for aqueous species and solids containing the radionuclide elements of interest to the NRC LLW PA test case using database supplements provided by D. Turner at the Center for Nuclear Waste Regulatory Analyses at the Southwest Research Institute in San Antonio, Texas. These database additions included MINTEQ-formatted reactions, associated thermodynamic data (i.e., log $K^{\circ}_{r,298}$ and $\Delta H^{\circ}_{r,298}$) and ancillary information (e.g., identification number, formula, charge, mass, reaction stoichiometry) for americium, neptunium, plutonium, radium, technetium, thorium, and uranium. Additional revisions to the MINTEQ thermodynamic database for radionuclide elements were identified and added during the course of our study. These changes are discussed in the subsequent sections that discuss the calculated solubility limits for the individual radionuclides.

The aqueous species and solids included in the MINTEQA2 thermodynamic database for radionuclides elements considered in this study are described in Appendix D.

4 Radionuclide Solubility Limits for NRC Performance Assessment Test Case

Conservative maximum concentration limits for dissolved americium, nickel, neptunium, plutonium, radium, strontium, thorium, and uranium were calculated using the geochemical equilibrium code MINTEQA2 and the associated thermodynamic data for their aqueous speciation and solubility reactions. Solubility limits could not be determined for other radionuclides of interest to the NRC LLW PA test case, such as ^{14}C, ^{36}Cl, ^{129}I, niobium, and technetium. Results of the solubility calculations and the reasons why such calculations were not possible for some radionuclides are discussed in the individual sections later in this chapter. It should be noted that information from the modeling and laboratory studies described in Appendices A and B, respectively, was not required to do the modeling calculations described in this chapter. Therefore, there was no need to choose one modeling method versus another relative to predicting the evolution of cement pore water.

The concentration limits are based on selected equilibrium solubility controls for each of the dissolved radionuclide elements. Selection of the most appropriate solubility control(s) from solids contained in the MINTEQ thermodynamic database was based on phase-stability information given in published studies and the experience that project staff have with the geochemistry of radionuclide aqueous systems. Solubility controls selected for each radionuclide are identified in subsequent sections that report the results of the modeling calculations.

The radionuclide solubility limits described in this chapter are being used as input to the NRC LLW PA test case and were calculated for physicochemical conditions that are specific to the NRC test case. The NRC LLW PA test case uses a rinse release model for radionuclides that are not modeled either with diffusion release (e.g., cement solidified waste) or dissolution release (e.g., metallic waste forms). The rinse component of the model assumes that quantitative transfer to the aqueous phase can occur. The amount of a radionuclide released into the aqueous phase from any of the three source term models, however, is limited by the thermodynamic equilibrium solubility of the radionuclide. The radionuclide may be quantitatively transferred to the aqueous phase, if the solubility limit allows a greater amount of a radionuclide into the aqueous phase than the total inventory available for release. The details of this approach are described in Sullivan (1991, 1993) and Sullivan and Suen (1989). Once released into the aqueous phase, the radionuclides may sorb onto cementitious materials or other solid phases (e.g., clays, iron oxyhydroxides) in the vault.

The "rinse release model" is the most conservative release model for the LLW source term. In a real disposal system, both chemical factors (e.g., solubility limits, sorption, dissolution kinetics) and physical factors (e.g., matrix diffusion, limited water contact with the waste) provide constraints on the total amount of a radionuclide that can actually be released to water in a vault. For many radionuclides, quantitative transfer of all of the radionuclide into the aqueous phase would not be possible due to constraining factors, such as mass balance, electro-neutrality, and chemical complexation. The solubility-limited rinse release model also does not take kinetic effects into account. While chemical equilibrium models can provide an upper limit to solution concentrations, they provide no information about the reaction rate to reach those concentrations. In addition, physical constraints on the distribution of radionuclides in waste packages and the vault, assumptions concerning the degradation of the waste containers, and the distribution of moisture within a vault further constrain the probability of release. However, in a case where the solubility is high (e.g., ^{36}Cl) and the inventory is concentrated in a limited volume within the vault (e.g., in a single waste package), the rinse release model may represent a realistic scenario. In a number of cases, the total inventory available for rinse release is less than a solubility limit (e.g., neptunium). The sorption parameter (K_d) provides a further constraint on the total amount of radionuclide that can be released from the waste packages and the facility.

In the text, figures, and tables that follow in this chapter, the vault inventory limited "rinse release model" concentrations are derived from water flux and inventory parameters from the NRC LLW PA test case. The rinse release model values calculated prior to application of solubility limits or sorption parameters are listed in Table 4.1. In the different solubility figures, the horizontal lines labeled as "Class A" and "Class B/C" vaults correspond to concentrations that would occur if the entire inventory of a radionuclide in a particular vault is quantitatively transferred into 1,000 cubic feet of water. This volume corresponds to about the 10th percentile of the total range for the calculated annual volume flux of water through a vault in the NRC LLW PA test case, which ranges from about 100 to 20,000 ft^3/yr. Thus there is a 90% probability that the volume flux of water through a test case vault, after complete degradation of engineered features, is higher than this volume of water. Therefore the inventory-limited concentration could be as much as approximately an order of magnitude lower than this value (one log unit on the vertical axis scale in the figures).

It should be noted that the LLW PA test case corresponds to a specific natural site and a hypothetical facility design and inventory. The specifications and the results of the LLW PA test case analyses are likely to differ from potential State/ Compact LLW disposal facility PAs in a number of important aspects. Nevertheless, the NRC's LLW PA test case methodology is generally applicable to concrete vault disposal in humid environments. Documentation of the NRC LLW PA test case parameters and calculations are in preparation at the NRC.

4.1 Americium

4.1.1 Calculated Solubilities

The solubility limits calculated for dissolved americium for the range of pH/Eh conditions limited by the cement- and ground-water buffered systems are listed in Table 4.2. The tabulated solubilities are based on the average ground-water composition used in the NRC LLW PA test case. These results are not significantly different than those based on the ground-water composition containing the maximum concentrations of the anionic components listed in Table 3.1.

Preliminary modeling calculations indicated that two solids, $AmOHCO_3$ and $Am(OH)_3$ (am), might control the concentrations of dissolved americium over different pH ranges between 4.0 and 12.5. At pH values less than 9.5, the predicted solubility control for americium was $AmOHCO_3$. For the pH range from 9.5 and 11.0, the MINTEQ results indicated that two americium solids, $AmOHCO_3$ and $Am(OH)_3$ (am), could coexist and control the solubility of dissolved americium. At pH values greater than 11.0, the predicted solubility control is $Am(OH)_3$ (am). The final MINTEQ runs were set up to include these phase constraints, and the results listed in Table 4.2 reflect these multiple solubility controls for americium fo the pH ranges listed above.

The modeling results indicate that the dominant valence form of americium dissolved at these pH/Eh conditions would be +3. The aqueous speciation calculated from the available thermodynamic data shows a complex assemblage of uncomplexed, hydrolytic, carbonate, and fluoride aqueous species of Am^{III}. The distribution, given as the percent of total mass of dissolved Am^{III}, of the dominant Am^{III} aqueous species for the modeling results based on the average ground-water composition are listed below for several pH values:

- pH = 4.0 Am^{3+} (99.9%), other Am^{III} species (0.1%)
- pH = 5.8 Am^{3+} (87.6%), $AmSO_4^+$ (5.7%), AmF^{2+} (4.3%), $AmCO_3^+$ (2.0%), other Am^{III} species (0.4%)
- pH = 9.0 $AmCO_3^+$ (31.0%), $AmOH^{2+}$ (28.7%), Am^{3+} (24.4%), $Am(OH)_2^+$ (15.0%), other Am^{III} species (0.9%)
- pH = 12.5 $Am(OH)_3^\circ$ (aq) (86.9%), $Am(OH)_2^+$ (13.1%).

Table 4.1 Radionuclide concentrations calculated by the NRC using a rinse release model for its LLW PA test case

	Class A vault		Class B/C vault	
	Volume flux of Water through Vault		Volume flux of Water through Vault	
	1,000 ft³/yr	20,000 ft³/yr	100 ft³/yr	6,000 ft³/yr
Isotope	mol/l			
^{241}Am	4.98×10^{-10}	2.49×10^{-11}	1.94×10^{-7}	3.24×10^{-9}
^{243}Am	1.79×10^{-11}	8.96×10^{-13}	nc[(a)]	nc
^{59}Ni	9.49×10^{-8}	4.74×10^{-9}	4.27×10^{-3}	7.12×10^{-5}
^{63}Ni	1.58×10^{-7}	7.90×10^{-9}	9.76×10^{-4}	1.63×10^{-5}
^{237}Np	4.58×10^{-8}	2.29×10^{-9}	4.25×10^{-8}	7.08×10^{-10}
^{236}Pu	1.94×10^{-16}	9.72×10^{-18}	nc	nc
^{238}Pu	1.73×10^{-11}	8.67×10^{-13}	2.32×10^{-8}	3.86×10^{-10}
^{239}Pu	1.15×10^{-8}	5.76×10^{-10}	1.63×10^{-5}	2.72×10^{-7}
^{240}Pu	8.40×10^{-10}	4.20×10^{-11}	1.33×10^{-6}	2.22×10^{-8}
^{241}Pu	2.90×10^{-10}	1.45×10^{-11}	3.38×10^{-7}	5.63×10^{-9}
^{242}Pu	9.91×10^{-9}	4.95×10^{-10}	4.23×10^{-8}	7.06×10^{-10}
^{90}Sr	1.67×10^{-9}	8.36×10^{-11}	9.87×10^{-4}	1.64×10^{-5}
^{99}Tc	7.37×10^{-6}	3.68×10^{-7}	2.43×10^{-3}	4.04×10^{-5}
^{226}Ra	2.21×10^{-8}	1.11×10^{-9}	5.47×10^{-6}	9.12×10^{-8}
^{228}Ra	1.33×10^{-12}	6.63×10^{-14}	nc	nc
^{228}Th	5.03×10^{-12}	2.52×10^{-14}	2.91×10^{-13}	4.85×10^{-15}
^{229}Th	4.96×10^{-13}	2.48×10^{-14}	nc	nc
^{230}Th	1.52×10^{-9}	7.61×10^{-11}	nc	nc
^{232}Th	8.07×10^{-1}	4.03×10^{-2}	nc	nc
^{232}U	2.45×10^{-15}	1.23×10^{-16}	nc	nc
^{233}U	1.18×10^{-7}	5.89×10^{-16}	nc	nc
^{234}U	2.49×10^{-5}	1.25×10^{-6}	4.67×10^{-7}	7.78×10^{-9}
^{235}U	9.27×10^{-3}	4.64×10^{-4}	1.40×10^{-4}	2.33×10^{-6}
^{236}U	2.87×10^{-8}	1.44×10^{-9}	nc	nc
^{238}U	$2.06 \times 10^{+0}$	1.03×10^{-1}	1.48×10^{-2}	2.47×10^{-4}

(a) nc = not calculated. Concentrations were not calculated, because Roles (1990) reported no data for isotope in B/C waste.

Table 4.2 Maximum concentration limits calculated for dissolved americium for the NRC LLW PA test case

pH	Eh (mV)	Average ground-water composition mol/l
4.0	581	4.0×10^{-2}
4.5	558	4.0×10^{-2}
5.0	536	2.1×10^{-2}
5.5	514	1.0×10^{-4}
5.8	500	1.3×10^{-5}
6.0	490	3.4×10^{-6}
6.5	470	1.5×10^{-7}
7.0	450	2.0×10^{-8}
7.5	420	6.0×10^{-9}
8.0	400	3.6×10^{-9}
8.5	380	1.4×10^{-9}
9.0	360	6.5×10^{-10}
9.5	340	4.8×10^{-10}
10.0	310	9.7×10^{-11}
10.5	290	3.6×10^{-11}
11.0	270	4.4×10^{-11}
11.5	250	1.8×10^{-11}
12.0	220	2.9×10^{-12}
12.5	200	1.9×10^{-12}

The Am^{III} solubilities calculated using the ground-water composition containing the maximum concentrations of the anionic components (right most column in Table 3.1) are not significantly different from those determined for the average ground-water composition. These differences are due primarily to the increase in the mass of the aqueous species $AmSO_4^+$ and AmF^{2+} calculated using the larger concentrations of dissolved sulfate and fluoride, respectively. The distributions of dominant Am^{III} aqueous species calculated using the maximum anion concentrations at pH values of 5.8 and 9.0, respectively, are

- Am^{3+} (57.4%), $AmSO_4^+$ (25.2%), AmF^{2+} (14.9%), $AmCO_3^+$ (1.2%), other Am^{III} species (1.3%)
- $AmCO_3^+$ (30.4%), $AmOH^{2+}$ (28.1%), Am^{3+} (23.9%), $Am(OH)_2^+$ (14.6%), AmF^{2+} (2.0%), other Am^{III} species (1.0%)

The differences between Am^{III} solubilities calculated for the average ground-water composition and one containing the maximum concentrations of the anionic components are minor. However, as will be shown for some of the other radionuclides, the differences between the modeling results based on the two sets of anion concentrations can be significant (e.g., several orders of magnitude).

The concentrations of dissolved americium based on the average ground-water composition in Table 3.1 are plotted as a function of pH as the thick solid line in Figure 4.1.

4.1.2 Published Solubility Data

Ewart et al. (1986, 1992) experimentally determined the concentrations of dissolved americium resulting from the equilibration of cement-equilibrated waters that were oversaturated with dissolved Am^{III}. Values estimated from data reported graphically by Ewart et al. (1992, Figure 6) are plotted as filled circles in Figure 4.1 for comparison to the values calculated in our study by computer modeling.

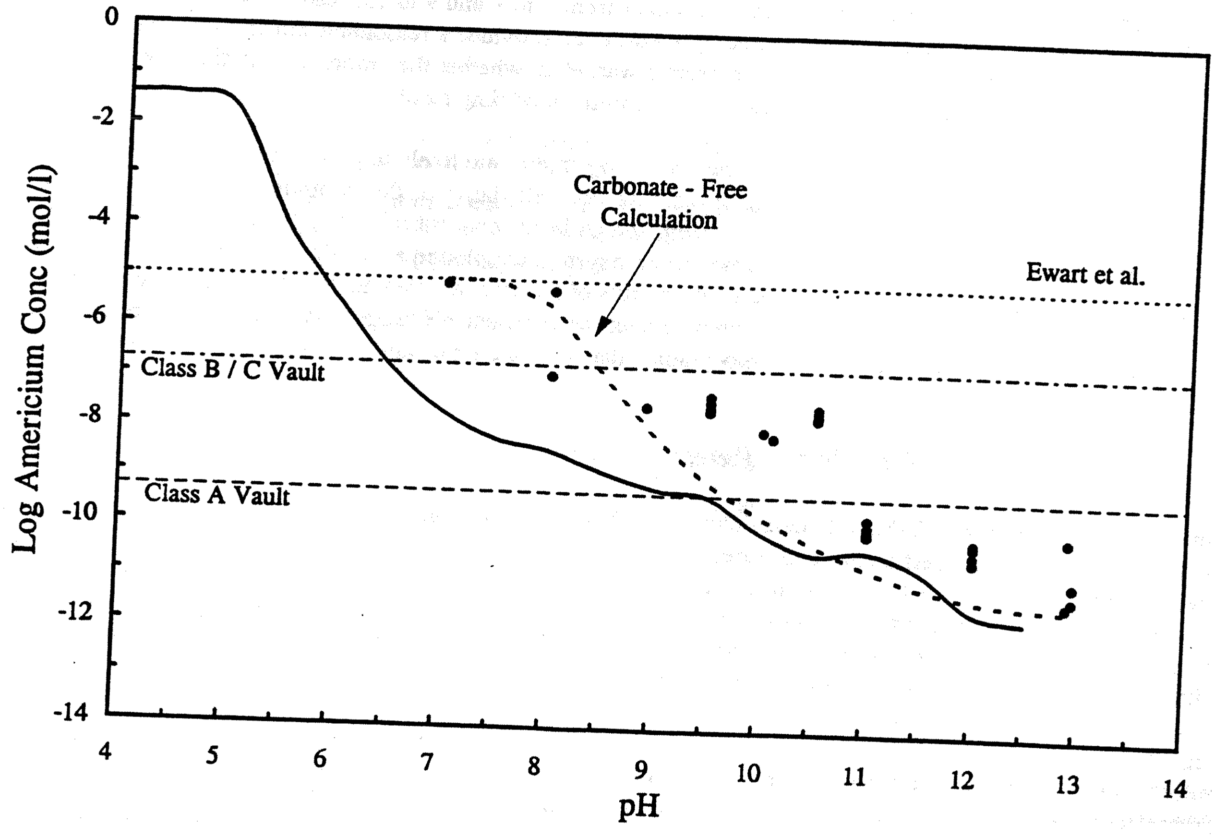

Figure 4.1 Concentration limits for dissolved americium

[Thick solid and dashed curves represent values calculated in our study for carbonate and carbonate-free systems, respectively. Filled circles represent values estimated from data presented in Ewart et al. (1992). The thin dotted horizontal line shows the initial concentration of total dissolved americium used in experiments by Ewart et al. The thin dashed and dashed-dotted horizontal lines show the americium concentrations calculated by the NRC using the rinse release model and water volume fluxes of 1,000 ft^3/yr for Class A and 100 ft^3/yr for B/C vaults, respectively.]

The experiments of Ewart et al. (1992) involved the addition of Am^{III} chloride solutions to cement equilibrated waters in controlled atmosphere chambers with low CO_2 contents. Sufficient americium solution was added to obtain an initial concentration of 10^{-5} M dissolved americium. The pH of the resulting mixtures was adjusted with sodium hydroxide or hydrochloric acid. The measured redox potential in the americium experiments was 200 mV (Ewart et al. 1986). Aliquots of the equilibrated mixtures were taken and filtered using the technique of Rai (1984). Americium concentrations in the filtered solutions were determined by liquid scintillation counting. By monitoring the concentrations of americium in filtered solution samples as a function of time, the equilibration period was determined to be 30 min (Ewart et al. 1986).

The agreement between the experimental measurements of Ewart et al. (1992) and the concentrations calculated in our study is poor at pH values less than 11. As noted by Ewart et al. (1992), modeling calculations for americium solubilities in this pH/Eh region are sensitive to the concentrations used for dissolved carbonate and the thermodynamic data selected for americium aqueous species given their importance in this pH range. Ewart et al. (1992) also thermodynamically modeled the results of their americium solubility studies. Their conceptual model involved the use of two solubility-controlling solids to match their measured concentrations of dissolved americium. The model included $AmOHCO_3$ and $Am(OH)_3$ as solubility controls for dissolved americium for the pH ranges from 7 to 9 and 9 to 13, respectively (Ewart et al. 1986, 1992). The combination of solubility controls used by Ewart et al. provided a reasonable match to the trend of their measured americium concentrations. It was unclear from Ewart et al. whether they modified any thermodynamic data for americium aqueous species or solid phases to achieve the reported modeling results.

The concentrations of dissolved carbonate used in our modeling studies are likely to be significantly greater than those present in the experiments by Ewart et al. (1992). Thus, a second calculation of the solubility of $Am(OH)_3$ (am) was completed from pH 7 to 13 assuming a carbonate-free system and an initial concentration of 10^{-5} mol/l total dissolved americium. The calculated solubilities for the carbonate-free system are plotted as the thick dashed curve in Figure 4.1. Although these values are a better fit to the trend of the results of Ewart et al., they underestimate the experimentally determined solubilities by at least an order of magnitude over the complete pH range from 7 to 13. The residual differences may be partially due to inadequacies in the thermodynamic data for americium aqueous complexes at these high pH conditions.

4.1.3 NRC LLW PA Test Case Rinse Release Model

The americium concentrations (Table 4.1) calculated by the NRC using the rinse release model (prior to application of solubility limits or sorption coefficients) and water volume fluxes of 1,000 ft^3/yr for ^{241}Am in Class A and 100 ft^3/yr for B/C vaults are plotted in Figure 4.1 as thin dashed and dashed-dotted horizontal lines, respectively. The values derived for these fluxes were selected for plotting purposes because they represented the highest radionuclide concentrations of the results provided to Pacific Northwest National Laboratory (PNNL) by the NRC. For the Class A vault scenario, only the solubilities calculated for pH values above 9.5 are less than americium concentrations determined from the rinse release model and the physicochemical conditions specified for the NRC LLW PA test case. For the Class B/C vault scenario, the concentration limits calculated for americium from solubility considerations are less than the rinse release model values at pH values above 6.5. Given the conservative nature of the rinse release model, concentrations of dissolved americium that are greater than 1.9 x 10^{-7} mol/l are unreasonable for the conditions considered for the NRC LLW PA test case. A solubility model may provide a more accurate constraint on the maximum concentrations of dissolved americium at pH values greater than 9.5 and 6.5 for the NRC LLW PA test case for Class A and B/C vaults, respectively.

4.2 Inorganic Carbon (^{14}C)

The precipitation of calcite ($CaCO_3$), as a result of carbonation reactions at the high pH conditions of the cement pore-fluid dominated system, will attenuate to some degree the concentrations of ^{14}C released from the waste form. Dayal (1995) discusses the role of cementitious materials in the disposal of ^{14}C. Serne et al. (1992), Allard et al. (1981), Dayal and Klein (1988), Hietanen et al. (1985), and Bayliss et al. (1988) show almost complete removal of ^{14}C added as bicarbonate or carbonate to waters contacting cementitious materials. The mechanism cited by all researchers is the incorporation of ^{14}C in calcite that precipitates within the pores of the cement or on the surfaces of the test specimens immersed in the water. Dayal and Reardon (1992) also describe how the calcium silicate hydrogel (C-S-H) and some of the other cement weathering products can also react with dissolved inorganic carbon species to form insoluble calcite. The micro-environment near the cement surface and within the internal pores is very basic and saturated with calcium ions from the dissolution of portlandite [$Ca(OH)_2$]. At pH values above 12, calcite is more insoluble than portlandite and any carbonate molecules present in the solution will combine with the enriched calcium to form a carbonate precipitate.

The concentrations of ^{14}C will also be reduced by isotopic exchange with the natural ^{12}C present in the aqueous, gaseous, and solid phases that exist in the soil/water system. The reader is referred to the papers in Fritz and Fontes (1980) for discussions on the topic of isotopic exchange. Calculation of isotopic exchange of ^{14}C for ^{12}C in ground-water systems is possible with a modified version of the PHREEQE geochemical code described by Cheng and Long (1984).

4.3 Chlorine (^{36}Cl)

Chloride is very mobile in soil/ground-water environments. The concentrations of dissolved chloride will not be controlled in soil/water environments by solubility. Dissolved chloride may be controlled to a very limited extent by coprecipitation and/or sorption processes but the amount of attenuation is not expected to be significant. In evaporite environments, chloride-containing salt minerals may precipitate from brine solutions. These types of environments, however, are not expected to be important in the disposal of commercial LLW, except where such disposal may occur in an evaporite basin (e.g., Salt Lake Basin, Utah).

4.4 Iodine (^{129}I)

As is the case for chloride dissolved in ground water, the concentrations of dissolved iodide will not be controlled by solubility considerations. Iodide can be mobile in the soil/ground-water and cement/concrete (see Section 5.3.4) environments.

4.5 Neptunium

4.5.1 Calculated Solubilities

Concentration limits calculated for dissolved neptunium for the range of pH/Eh conditions constrained by the cement- and ground-water buffered systems are listed in Table 4.3. The tabulated solubilities are based on the average ground-water composition used in the NRC LLW PA test case. These results are not significantly different than those based on the ground-water composition containing the maximum concentrations of the anionic components listed in Table 3.1.

The solubility control selected for dissolved neptunium at these environmental conditions was the amorphous (am) solid $NpO_2(OH)$. At the pH/Eh conditions used in our calculations (see Columns 1 and 2 in Table 4.3), the modeling results indicate that the dominant valence form of dissolved neptunium would be +5. The distributions, given as the percent of total mass of dissolved Np^V, of the dominant Np^V aqueous species for the modeling results based on the average ground-water composition are listed below for several pH values:

Table 4.3 Maximum concentration limits calculated for dissolved neptunium for the NRC LLW PA test case

		Average ground-water composition
pH	Eh (mV)	mol/l
4.0	581	$2.0 \times 10^{+1}$
4.5	558	$5.7 \times 10^{+0}$
5.0	536	$2.5 \times 10^{+0}$
5.5	514	8.4×10^{-1}
5.8	500	4.1×10^{-1}
6.0	490	2.5×10^{-1}
6.5	470	7.2×10^{-2}
7.0	450	2.1×10^{-2}
7.5	420	6.7×10^{-3}
8.0	400	2.3×10^{-3}
8.5	380	1.1×10^{-3}
9.0	360	6.9×10^{-4}
9.5	340	5.7×10^{-4}
10.0	310	4.9×10^{-4}
10.5	290	3.5×10^{-4}
11.0	270	1.9×10^{-4}
11.5	250	7.5×10^{-5}
12.0	220	2.5×10^{-5}
12.5	200	8.9×10^{-6}

- pH = 4.0 and 5.8 — NpO_2^+ (~100.0%)
- pH = 9.0 — $NpO_2CO_3^-$ (77.5%), NpO_2^+ (22.4%), other Np^V species (0.1%)
- pH = 12.5 — $NpO_2CO_3^-$ (79.0%), $NpO_2(OH)_2^-$ (14.2%), $NpO_2(OH)^{\circ}$ (aq) (5.6%), other Np^V species (1.2%).

The concentrations of dissolved neptunium in Table 4.3 based on the average ground-water composition are plotted as a function of pH as the solid line in Figure 4.2.

It should be noted that the predicted solubility for dissolved neptunium at pH values less than 6 are probably too high and not realistic. A different solid or another reaction process, such as sorption or coprecipitation, will likely control the solubility of neptunium at pH values less than 6 to concentrations lower than those in Figure 4.2. Moreover, the modeling calculations that predicted the high solubilities for dissolved neptunium are probably not valid given the lack of a charge balance constraint as noted in Section 3.1.

4.5.2 Published Solubility Data

Ewart et al. (1986, 1992) experimentally determined the concentrations of dissolved neptunium resulting from the equilibration of cement-equilibrated waters that were oversaturated with dissolved Np^{V} and Np^{IV}, respectively. Values estimated from data reported graphically for dissolved Np^{V} by Ewart et al. (1986, Figure 3) and dissolved Np^{IV} by Ewart et al. (1992, Figure 4) are plotted as filled circles and triangles, respectively, in Figure 4.2 for comparison to the values calculated in our computer modeling study.

The experiments of Ewart et al. (1986, 1992) involved the addition of neptunium chloride solutions to cement equilibrated waters in a controlled atmosphere chamber with low CO_2 contents. Sufficient neptunium solution was added to obtain initial concentrations of dissolved neptunium of 10^{-5} M and 3×10^{-7} M in the Np^{V} (Ewart et al. 1986) and Np^{IV} experiments, respectively. These initial concentrations are plotted as thin dotted and dash-dotted lines in Figure 4.2. The pH of the resulting mixtures was adjusted with sodium hydroxide or hydrochloric acid. Reducing conditions were maintained in the Np^{IV} experiments by the addition of sodium hydrosulfite solution. The measured redox potentials in the Np^{V} and Np^{IV} experiments were 200 mV (Ewart et al. 1986) and less than -400 mV (Ewart et al. 1992), respectively. Aliquots of the equilibrated mixtures were taken and filtered using the technique of Rai (1984). Neptunium concentrations in the filtered solutions were determined by liquid scintillation counting. By monitoring the concentrations of neptunium in filtered solution samples as a function of time, the equilibration period was determined to be 30 min (Ewart et al. 1986).

The agreement between the experimental measurements of dissolved neptunium by Ewart et al. (1986, 1992) and the concentrations calculated from solubility considerations in our study is poor. The solubility calculations from pH 8.5 to 12.5 match the general trend of the Np^{V} experimental data, but overestimate the experimentally determined neptunium concentrations by approximately two orders of magnitude. These differences may be due to inadequacies in the thermodynamic value and/or solubility control used for our solubility calculations. Concentration limits for dissolved neptunium were also calculated assuming solubility equilibrium with $NaNpO_2CO_3$. These concentrations were greater than those reported in Table 4.3 for the solubility of $NpO_2(OH)$ (am) for the pH range from 9.0 to 12.5.

Ewart et al. (1986, 1992) also thermodynamically modeled the results of their neptunium solubility experiments. In the Np^{V} solubility studies, Ewart et al. (1986) used the solid NpO_2OH to model their measured concentrations. To match the trend of their experimentally measured concentrations, Ewart et al. excluded the Np^{V} hydrolytic species from their thermodynamic calculations. To model the Np^{IV} data, Ewart et al. (1992) used the solid $Np(OH)_4$ with a modified equilibrium constant as the solubility controlling phase for dissolved Np^{IV}. Ewart et al. also excluded the anionic hydrolytic species for Np^{IV} from their thermodynamic calculations to achieve agreement between their experimental and modeling results.

4.5.3 NRC LLW PA Test Case Rinse Release Model

The neptunium concentrations (Table 4.1) calculated by the NRC using the rinse release model (prior to application of solubility limits or sorption coefficients) and water volume fluxes of 1,000 and 100 ft^3/yr are approximately the same, respectively, for ^{237}Np in Class A and B/C vaults. They are plotted as the single thin dashed horizontal line in Figure 4.2. The values derived for these fluxes were selected for plotting purposes, because they represented the highest radionuclide concentrations of the results provided to PNNL by the NRC.

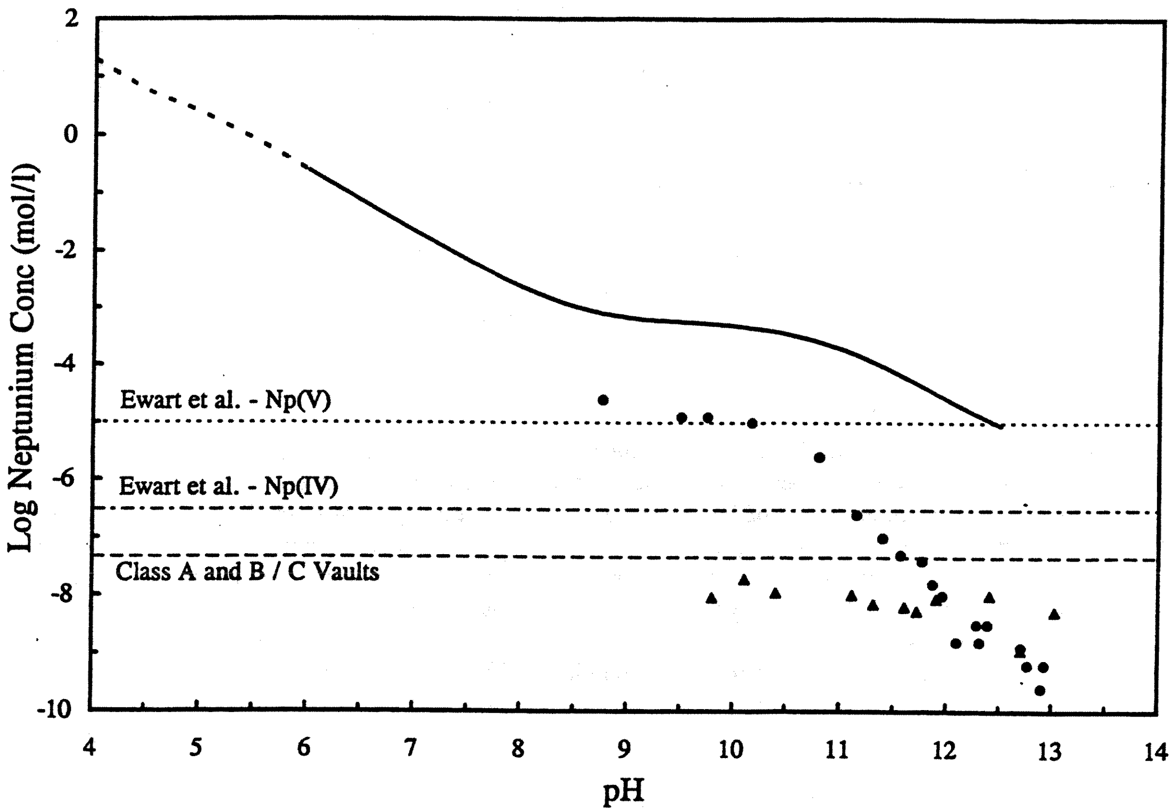

Figure 4.2 Concentration limits for dissolved neptunium

[Solid line represents values calculated in our study. Filled triangles and circles represent concentrations of Np^{IV} and Np^{V} estimated from data plotted in Ewart et al. (1992; 1986), respectively. The thin dotted and dash-dotted horizontal lines show the initial concentrations of total dissolved neptunium used in Np^{V} and Np^{IV} experiments by Ewart et al., respectively. The thin dashed horizontal line shows the neptunium concentrations calculated by the NRC using the rinse release model and water volume fluxes of 1,000 ft^3/yr for Class A and 100 ft^3/yr for B/C vaults.]

For both vault scenarios, the rinse release model concentration limits for dissolved neptunium are lower than those determined from solubility calculations. For the conditions considered in the NRC LLW PA test case, solubility considerations do not provide a better constraint on the maximum concentrations of dissolved neptunium for the pH range 4.0 to 12.5.

4.6 Nickel

4.6.1 Calculated Solubilities

Concentration limits calculated for dissolved nickel for the range of pH/Eh conditions constrained by the cement- and ground-water buffered systems are listed in Table 4.4. The tabulated solubilities are based on the average ground-water composition used in the NRC LLW PA test case. These results are not significantly different than those based on the ground-water composition containing the maximum concentrations of the anionic components listed in Table 3.1.

Table 4.4 Maximum concentration limits calculated for dissolved nickel for the NRC LLW PA test case

		Average ground-water composition
pH	Eh (mV)	mol/l
4.0	581	$2.6 \times 10^{+2}$
4.5	558	$2.6 \times 10^{+1}$
5.0	536	$2.6 \times 10^{+0}$
5.5	514	6.1×10^{-1}
5.8	500	2.0×10^{-1}
6.0	490	5.9×10^{-2}
6.5	470	3.2×10^{-3}
7.0	450	3.9×10^{-4}
7.5	420	1.1×10^{-4}
8.0	400	3.9×10^{-5}
8.5	380	1.5×10^{-5}
9.0	360	5.6×10^{-6}
9.5	340	2.0×10^{-6}
10.0	310	6.7×10^{-7}
10.5	290	1.7×10^{-7}
11.0	270	3.3×10^{-8}
11.5	250	1.2×10^{-8}
12.0	220	2.5×10^{-8}
12.5	200	7.5×10^{-8}

The solubility control selected for dissolved nickel at these environmental conditions was the solid $Ni(OH)_2$. The distribution, given as the percent of total mass of dissolved nickel, of the dominant nickel aqueous species for the modeling results based on the average ground-water composition are listed below for several pH values:

- pH = 4.0 Ni^{2+} (100%)
- pH = 5.8 Ni^{2+} (99.7%), other nickel species (0.3%)
- pH = 9.0 $NiCO_3^\circ$ (aq) (91.4%), $Ni(CO_3)_2^{2-}$ (8.2%), other nickel species (0.4%)
- pH = 12.5 $Ni(OH)_3^-$ (97.2%), $Ni(OH)_2^\circ$ (aq) (2.7%)

The concentrations of dissolved nickel in Table 4.4 based on the average ground-water composition are plotted as a function of pH as a solid line in Figure 4.3.

It should be noted that the predicted solubility for dissolved nickel at pH values less than 6 are probably too high and not realistic. A different solid or another reaction process, such as sorption or coprecipitation, will likely control the solubility of nickel at pH values less than 6 to concentrations lower than those in Figure 4.3. Moreover, the modeling calculations that predicted the high solubilities for dissolved nickel are probably not valid given the lack of a charge balance constraint as noted in Section 3.1.

4.6.2 Published Solubility Data

Pilkington and Stone (1990) conducted several experiments to determine the concentrations of dissolved nickel resulting from the equilibration of cement-equilibrated waters that were oversaturated with dissolved nickel. These experiments

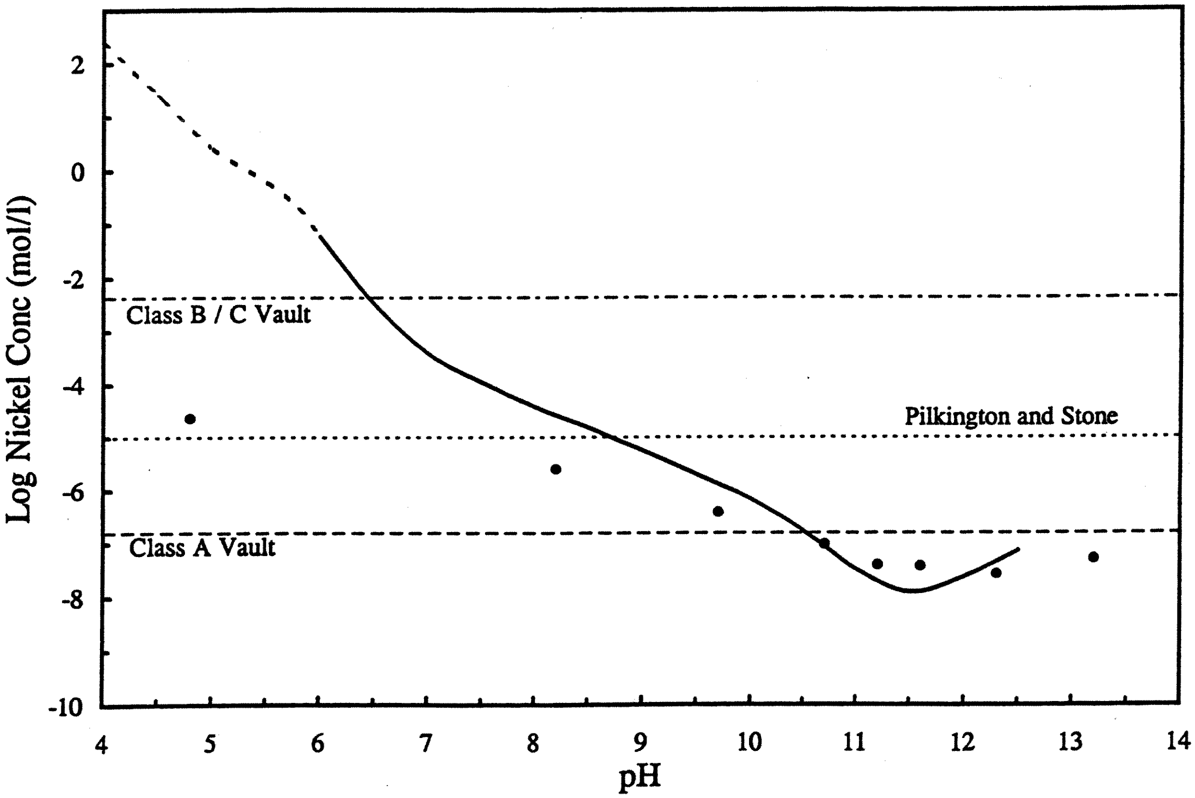

Figure 4.3 Concentration limits for dissolved nickel

[Solid line represents values calculated in our study. The filled circles represent concentrations of nickel reported in over-saturation experiments measured as function of pH by Pilkington and Stone (1990). The thin dotted horizontal line shows the initial concentration of total dissolved nickel used in experiments by Pilkington and Stone. The thin dashed and dashed-dotted horizontal lines show the nickel concentrations calculated by the NRC using the rinse release model and water volume fluxes of 1,000 ft^3/yr for ^{63}Ni in Class A and 100 ft^3/yr for ^{59}Ni in Class B/C vaults, respectively.]

included evaluation of the effects of solution composition (e.g., organic degradation products and salinity), sample filtration, equilibration time, and pH on the measured solubility of nickel. One set of results from Pilkington and Stone (1990, Table 12) are plotted as filled circles in Figure 4.3 for comparison to the values calculated in our computer modeling study.

The solubility experiments of Pilkington and Stone (1990) involved the addition of nickel chloride solutions to cement equilibrated waters to approach nickel solubilities from oversaturated conditions. For the experimental results plotted in Figure 4.3, sufficient nickel solution (spiked with ^{63}Ni) was added to obtain initial concentrations of dissolved nickel of 10^{-5} M (thin dotted line in Figure 4.3). The pH of the resulting mixtures was adjusted with sodium hydroxide or hydrochloric acid. Aliquots of the equilibrated mixtures were taken and filtered using 0.45-µm membrane filters. Nickel-63 concentrations in the filtered solutions were determined by liquid scintillation counting. The equilibration time for these experiments was one week.

For the pH range 9.5 to 12.5, the agreement between the experimental measurements of dissolved nickel by Pilkington and Stone (1990) and the concentrations calculated in our study is generally good. The nickel concentration reported at pH 4.8 is essentially equal to the initial concentration of 10^{-5} M used for their experiments. If the solubility-limited concentration of dissolved nickel is greater than 10^{-5} M, as the modeling results suggest, then the concentration measured at pH = 4.8 represented undersaturated conditions and not a solubility-limited value. Given the very high concentrations predicted for dissolved nickel from solubility considerations, concentrations of dissolved nickel will most likely be controlled in natural environments at lower values by coprecipitation and/or adsorption processes.

Pilkington and Stone also thermodynamically modeled the results of their nickel solubility experiments using $Ni(OH)_2$ as a solubility control. Pilkington and Stone adjusted the stability constants for the nickel hydrolytic species and the solid $Ni(OH)_2$ to adequately model their experimental data. Their modeling calculations, however, did not include reactions for the nickel-carbonate aqueous species.

4.6.3 NRC LLW PA Test Case Rinse Release Model

The nickel concentrations (Table 4.1) calculated by the NRC using the rinse release model (prior to application of solubility limits or sorption coefficients) and water volume fluxes of 1,000 ft^3/yr for ^{63}Ni in Class A and 100 ft^3/yr for ^{59}Ni in Class B/C vaults are plotted in Figure 4.3 as thin dashed and dashed-dotted horizontal lines, respectively. The values derived for these fluxes were selected for plotting purposes, because they represented the highest radionuclide concentrations of the results provided to PNNL by the NRC. For the Class A vault scenario, only the solubilities calculated for pH values above 11.0 are less than nickel concentrations determined from the rinse release model and the physicochemical conditions specified for the NRC LLW PA test case. For the Class B/C vault scenario, the solubility limits calculated for nickel are less than the rinse release model values at pH values greater than 6.5. Given the conservative nature of the rinse release model, concentrations of dissolved nickel that are greater than 4.3 x 10^{-3} mol/l are unreasonable for the conditions considered for the NRC LLW PA test case. A solubility model may provide a more accurate constraint on the maximum concentrations of dissolved nickel at pH values greater than approximately 10.5 and 6.5 for the NRC LLW PA test case for Class A and B/C vaults, respectively.

4.7 Niobium

The absence of thermodynamic data (especially Gibbs free energy of formation values at 25°C) for aqueous species and solids containing niobium as well as knowledge regarding solubility controls for niobium in low-temperature aqueous systems precluded any geochemical modeling of solubility controls for dissolved niobium.

4.8 Plutonium

4.8.1 Calculated Solubilities

Concentration limits calculated for dissolved plutonium for the range of pH/Eh conditions limited by the cement- and ground-water buffered systems are listed in Table 4.5. The solubility control selected for dissolved plutonium at these environmental conditions was the amorphous solid $PuO_2 \cdot H_2O$ (am).

Table 4.5 Maximum concentration limits calculated for dissolved plutonium for the NRC LLW PA test case

		Average ground-water composition	Maximum anion concentrations
pH	**Eh (mV)**	**mol/l**	
4.0	581	2.9×10^{-9}	3.5×10^{-6}
4.5	558	8.4×10^{-10}	3.5×10^{-6}
5.0	536	6.5×10^{-10}	3.5×10^{-6}
5.5	514	5.7×10^{-10}	3.4×10^{-6}
5.8	500	5.2×10^{-10}	3.4×10^{-6}
6.0	490	4.8×10^{-10}	3.3×10^{-6}
6.5	470	3.2×10^{-10}	3.2×10^{-6}
7.0	450	1.6×10^{-10}	2.3×10^{-6}
7.5	420	1.0×10^{-10}	7.6×10^{-7}
8.0	400	9.5×10^{-11}	3.4×10^{-8}
8.5	380	9.5×10^{-11}	4.2×10^{-10}
9.0	360	9.5×10^{-11}	9.9×10^{-11}
9.5	340	9.5×10^{-11}	9.5×10^{-11}
10.0	310	9.5×10^{-11}	9.5×10^{-11}
10.5	290	9.5×10^{-11}	9.5×10^{-11}
11.0	270	9.5×10^{-11}	9.5×10^{-11}
11.5	250	9.5×10^{-11}	9.5×10^{-11}
12.0	220	9.5×10^{-11}	9.5×10^{-11}
12.5	200	9.3×10^{-11}	9.3×10^{-11}

All plutonium redox couples were included in the solubility calculations for the average and maximum anion ground-water compositions. The modeling results for the average ground-water composition indicate that essentially 100 percent of the dissolved plutonium at pH values greater than 6.0 would be present in the +4 valence state. Below pH 6.0, the dissolved plutonium would consist of quantities of the +3, +4, and +5 valence states.

For the average ground-water composition, the speciation calculations indicate that approximately >99 percent of the dissolved Pu^{IV} at pH values greater than 7.5 would be the neutral aqueous (aq) species $Pu(OH)_4^{\circ}$(aq). At lower pH values, a significant mass of the dissolved plutonium would be present as Pu^{IV}-phosphate and other-hydroxyl aqueous species. The distributions; given as the percent of total mass of dissolved Pu^{IV}, of the dominant plutonium aqueous species for the modeling results based on the average ground-water composition are listed below for several of the pH values:

- pH = 4.0 $Pu(HPO_4)_4^{4-}$ (54.9%), $Pu(OH)_3^{+}$ (22.6%), $Pu(OH)_4^{\circ}$ (aq) (11.4%), $Pu(HPO_4)_3^{2-}$ (6.2%), $Pu(OH)_2^{2+}$ (2.7%), $Pu(HPO_4)_2^{\circ}$ (1.8%), other plutonium species (0.4%)
- pH = 6.5 $Pu(HPO_4)_4^{4-}$ (70.1%), $Pu(OH)_4^{\circ}$ (aq) (29.7%), other plutonium species (0.2%)
- pH = 7.5 $Pu(OH)_4^{\circ}$ (aq) (94.6%), $Pu(HPO_4)_4^{4-}$ (5.3%), other plutonium species (0.1%)

For the pH range 4.0 to 7.0, the concentrations of dissolved plutonium (right most column in Table 4.5) calculated using $PuO_2 \cdot H_2O$ (am) as a solubility control and the maximum anion concentrations are several orders of magnitude greater than those calculated from the average ground-water composition. This increase is due to the higher concentrations of dissolved phosphate (0.1 versus 2.2 ppm) in the maximum-anion ground-water composition and the resulting complexation of dissolved plutonium with phosphate to form the aqueous species $Pu(HPO_4)_4^{4-}$. Because of the large stoichiometric factors associated with the dominant Pu^{IV}-phosphate complexes [e.g., four and three for $Pu(HPO_4)_4^{4-}$ and $Pu(HPO_4)_3^{2-}$, respectively], the factor of twenty-two difference between the total phosphate concentrations of the average and maximum anion ground-water compositions results in a greater difference in calculated plutonium solubility. Based on the thermodynamic database used in this study, at least 99 percent of the dissolved mass of Pu^{IV} is present at pH values between 4.0 and 8.0 as $Pu(HPO_4)_4^{4-}$. Given the potential importance of Pu^{IV}-phosphate complexation, as indicated by our modeling calculations, additional laboratory studies need to be conducted to validate the importance of Pu^{IV}-phosphate aqueous species and solid phases.

The concentrations of dissolved plutonium based on the average ground-water composition in Table 4.5 are plotted as a function of pH as the thick solid line in Figure 4.4.

4.8.2 Published Solubility Data

Ewart et al. (1992) experimentally determined the concentrations of dissolved plutonium resulting from the equilibration of cement-equilibrated waters that were oversaturated with dissolved Pu^{IV}. Values estimated from data reported graphically by Ewart et al. (1992, Figure 5) are plotted as filled circles in Figure 4.4 for comparison to the values calculated in our computer modeling study.

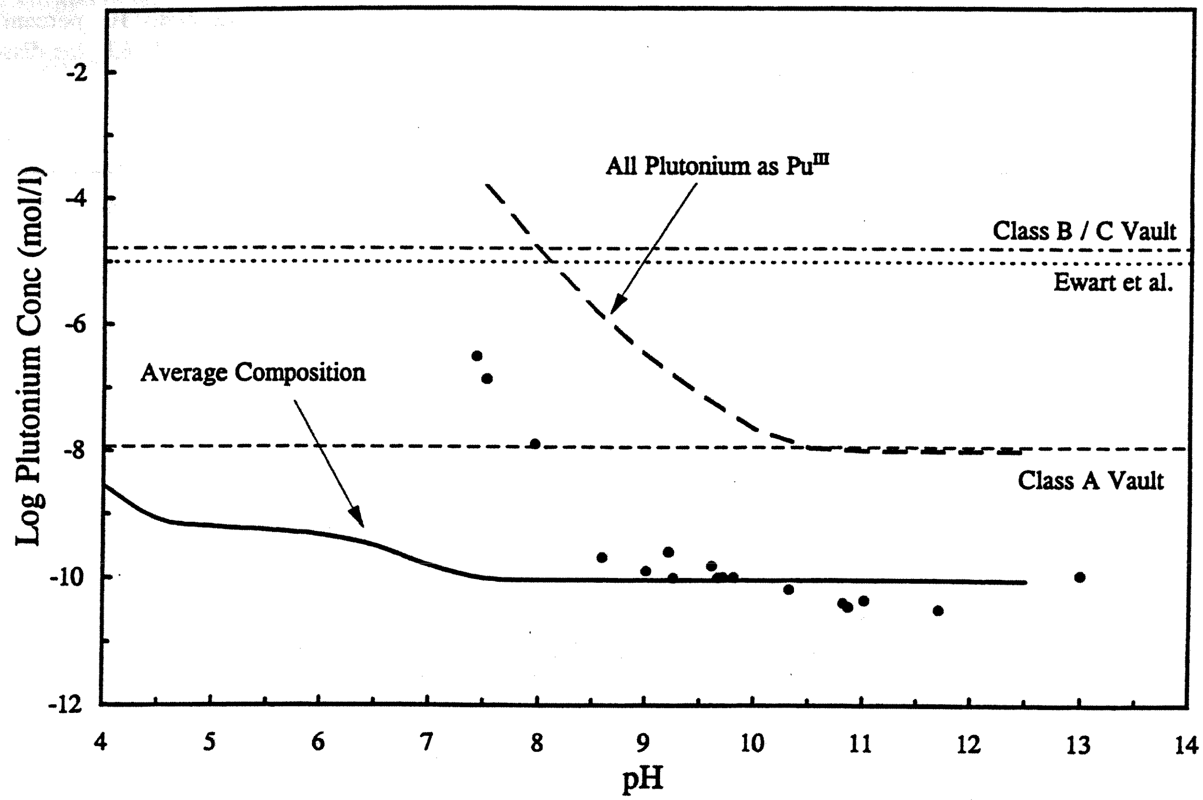

Figure 4.4 Concentration limits for dissolved plutonium

[The thick solid line represents values calculated in our study using $PuO_2 \cdot H_2O$ (am) as the solubility control and the average ground-water composition. The thick dashed line shows the concentrations of dissolved plutonium calculated assuming that all plutonium was present as Pu^{III} and using $Pu(OH)_3$ as the solubility control and the average ground-water composition. Filled circles represent values estimated from data presented in Ewart et al. (1992). The thin dotted horizontal line shows the initial concentration of total dissolved plutonium used in experiments by Ewart et al. The thin dashed and dashed-dotted horizontal lines show the plutonium concentrations calculated by the NRC using the rinse release model and water volume fluxes of 1,000 and 100 ft^3/yr for ^{239}Pu in Class A and B/C vaults, respectively.]

The experiments of Ewart et al. (1992) involved the addition of Pu^{III} chloride solutions to deoxygenated cement equilibrated waters. Because Pu^{III} oxidizes to Pu^{IV} at high pH values, Ewart et al. assumed that the dissolved plutonium would exist as Pu^{IV} in the experiments. Sufficient plutonium solution was added to obtain an initial concentration of 10^{-5} M dissolved plutonium (thin dotted horizontal line on Figure 4.4). The pH of the resulting mixtures was adjusted with sodium hydroxide or hydrochloric acid. The measured redox potential in the plutonium experiments was -300 mV (Ewart et al. 1986). Aliquots of the equilibrated mixtures were taken and filtered using the technique of Rai (1984). Plutonium concentrations in the filtered solutions were determined by liquid scintillation counting. By monitoring the concentrations of plutonium in filtered solution samples as a function of time, the equilibration period was determined to be 30 min (Ewart et al. 1986).

At pH values greater than 8.5, the concentrations of dissolved plutonium calculated in our study using $PuO_2 \cdot H_2O$ (am) as a solubility control are in good agreement with the experimental measurements of Ewart et al. (1992). The agreement with the three experimental values at pH values between 7.0 and 8.0, however, is poor. If the plutonium spikes used by Ewart et al. had not yet oxidized from Pu^{III} to Pu^{IV} in their solubility experiments between pH values of 7.0 to 8.0, then comparison of our equilibrium modeling calculations to these three data points would not be valid. To test this assumption, an additional set of solubility calculations was completed in which 1) all of the dissolved plutonium was assumed to be in the +3 valence state and 2) the solid $Pu(OH)_3$ was assumed to be the solubility control. These Pu^{III} calculations are shown as the thick dashed line in Figure 4.4. Although our Pu^{III} solubility calculations reproduce the general trend of the low-pH experiments of Ewart et al., the resulting concentrations of dissolved plutonium are approximately two orders of magnitude greater than those measured by Ewart et al. This offset between the modeling results for dissolved Pu^{III} and the laboratory data may be due to errors in one or more of the thermodynamic constants used in the Pu^{III} solubility calculations.

4.8.3 NRC LLW PA Test Case Rinse Release Model

The plutonium concentrations (Table 4.1) calculated by the NRC using the rinse release model (prior to application of solubility limits or sorption coefficients) and water volume fluxes of 1,000 and 100 ft^3/yr for ^{239}Pu in Class A and B/C vaults, respectively, are plotted in Figure 4.4 as thin dashed and dashed-dotted horizontal lines, respectively. The values derived for these fluxes were selected for plotting purposes, because they represented the highest radionuclide concentrations of the results provided to PNNL by the NRC. For both vault scenarios, the calculated solubility-limited concentrations of dissolved plutonium (thick solid line in Figure 4.4) based on the average ground-water composition are less than the concentrations determined from the rinse release model and the physicochemical conditions specified for the NRC LLW PA est case. Maximum concentration limits based on solubility considerations may therefore provide a more accurate contraint, especially at pH values greater than 8.0, on the maximum concentrations of dissolved plutonium at these conditions.

4.9 Radium

4.9.1 Calculated Solubilities

Concentration limits calculated for dissolved radium for the range of pH/Eh conditions limited by the cement- and ground-water buffered systems are listed in Table 4.6. The solubility control selected for dissolved radium at these environmental onditions was the solid $RaSO_4$. For the pH range 4.0 to 12.5, the total mass of dissolved radium is present as the aqueous species Ra^{2+}, which is the only radium aqueous species in the thermodynamic database used for these calculations.

he modeling results indicate that the radium concentrations calculated with the average ground-water compositions are pproximately an order of magnitude greater than those calculated with the maximum anion concentrations. This is caused y the differences in the concentrations of sulfate, which are 2.6 ppm (2.7×10^{-5} mol/l) and 20 ppm (2.1×10^{-4} mol/l), espectively, in the average and maximum-anion ground-water compositions (see Table 3.1). The solubility product for olid $RaSO_4$ can be expressed as

$$Ra^{2+} + SO_4^{2-} \Leftrightarrow RaSO_4 \qquad \text{Log } K^{\circ}_{r,298} = 10.4499 \tag{4.1}$$

$$\{Ra^{2+}\}\{SO_4^{2-}\} = 10^{-10.4499} \tag{4.2}$$

here "{}" denote activities of the indicated aqueous species. As indicated in Equation 4.2, if the concentration of disolved sulfate is increased, then the concentration of dissolved radium in equilibrium with $RaSO_4$ must correspondingly ecrease. Because the difference in the two sulfate concentrations is approximately an order of magnitude, the calculated oncentrations of dissolved radium will change by the same amount.

Table 4.6 Maximum concentration limits calculated for dissolved radium for the NRC LLW PA test case

		Average ground-water composition	Maximum anion concentrations
pH	Eh (mV)	mol/l	
4.0	581	1.3×10^{-6}	1.7×10^{-7}
4.5	558	1.3×10^{-6}	1.7×10^{-7}
5.0	536	1.3×10^{-6}	1.6×10^{-7}
5.5	514	1.3×10^{-6}	1.6×10^{-7}
5.8	500	1.3×10^{-6}	1.6×10^{-7}
6.0	490	1.3×10^{-6}	1.7×10^{-7}
6.5	470	1.3×10^{-6}	1.7×10^{-7}
7.0	450	1.3×10^{-6}	1.7×10^{-7}
7.5	420	1.3×10^{-6}	1.7×10^{-7}
8.0	400	1.3×10^{-6}	1.7×10^{-7}
8.5	380	1.4×10^{-6}	1.7×10^{-7}
9.0	360	1.4×10^{-6}	1.8×10^{-7}
9.5	340	1.4×10^{-6}	1.8×10^{-7}
10.0	310	1.4×10^{-6}	1.8×10^{-7}
10.5	290	1.5×10^{-6}	1.9×10^{-7}
11.0	270	1.6×10^{-6}	2.0×10^{-7}
11.5	250	1.7×10^{-6}	2.1×10^{-7}
12.0	220	1.9×10^{-6}	2.4×10^{-7}
12.5	200	2.5×10^{-6}	3.2×10^{-7}

The concentrations of dissolved radium in Table 4.6 for the average and maximum anion ground-water compositions are plotted as a function of pH as thick solid and dashed lines in Figure 4.5, respectively.

4.9.2 Published Solubility Data

Bayliss et al. (1989) attempted to experimentally determine the solubility limits for dissolved radium equilibrated in cement-equilibrated waters. Our results are consistent with, but not validated by, their results. The experiments by Bayliss

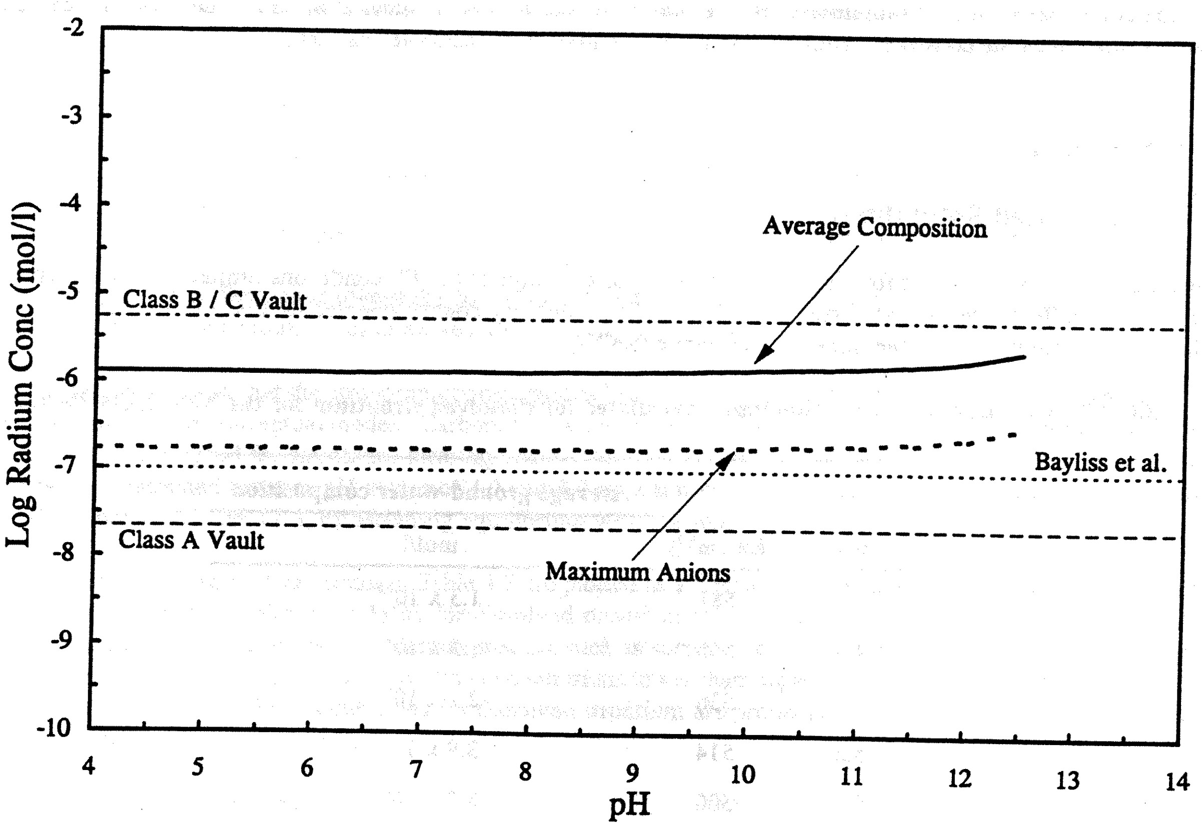

Figure 4.5 Concentration limits for dissolved radium

[The thick solid and dashed curves represent values calculated in our study using $RaSO_4$ as the solubility control for the average and maximum-anion ground-water compositions, respectively. The thin dotted horizontal line shows the initial concentration of total dissolved radium used in experiments by Bayliss et al. (1989). The thin dashed and dashed-dotted horizontal lines show the radium concentrations calculated by the NRC using the rinse release model and water volume fluxes of 1,000 and 100 ft^3/yr for ^{226}Ra in Class A and B/C vaults, respectively.]

et al. indicated that radium stayed in solution (i.e., undersaturated conditions) at an initial concentration of dissolved radium of 10^{-7} M (thin dotted line in Figure 4.5). Hazards from a high dose rate of gamma radiation precluded them from conducting experiments using higher concentrations of dissolved radium.

4.9.3 NRC LLW PA Test Case Rinse Release Model

The radium concentrations (Table 4.1) calculated by the NRC using the rinse release model (prior to application of solubility limits or sorption coefficients) and water volume fluxes of 1,000 and 100 ft^3/yr for ^{226}Ra in Class A and B/C vaults, respectively, are plotted in Figure 4.5 as thin dashed and dashed-dotted horizontal lines, respectively. The values derived for ^{226}Ra at these fluxes were selected for plotting purposes, because they represented the highest radionuclide concentrations of the results provided to PNNL by the NRC. The radium concentrations derived using the rinse release model for the Class A vault scenario are lower than those based on solubility considerations. For the Class B/C vault scenario, the solubility limits calculated for radium are less than the rinse release model values at all pH values from 4.0 to 12.5 and may provide a more accurate constraint on the maximum concentrations of dissolved radium.

4.10 Strontium

4.10.1 Calculated Solubilities

Concentration limits calculated for dissolved strontium for the range of pH/Eh conditions limited by the cement- and ground-water buffered systems are listed in Table 4.7. The solubility control selected for dissolved strontium at these environmental conditions was the mineral strontianite ($SrCO_3$).

Table 4.7 Maximum concentration limits calculated for dissolved strontium for the NRC LLW PA test case

		Average ground-water composition
pH	**Eh (mV)**	**mol/l**
4.0	581	$1.3 \times 10^{+2}$
4.5	558	$1.3 \times 10^{+1}$
4.9	536	$2.1 \times 10^{+0}$
5.5	514	3.9×10^{-1}
5.8	500	8.7×10^{-2}
6.0	490	2.3×10^{-2}
6.5	470	1.4×10^{-3}
7.0	450	1.3×10^{-4}
7.5	420	3.5×10^{-5}
8.0	400	9.8×10^{-6}
8.5	380	2.5×10^{-6}
9.0	360	7.3×10^{-7}
9.5	340	2.5×10^{-7}
10.0	310	1.1×10^{-7}
10.5	290	6.6×10^{-8}
11.0	270	5.3×10^{-8}
11.5	250	5.1×10^{-8}
12.0	220	5.6×10^{-8}
12.5	200	7.2×10^{-8}

The distribution, given as the percent of total mass of dissolved strontium, of the dominant strontium aqueous species for the modeling results based on the average ground-water composition are listed below for several pH values:

- pH = 4.0 and 5.8 Sr^{2+} (100%)
- pH = 9.0 Sr^{2+} (97.4%), $SrCO_3^\circ$ (aq) (2.2%), other strontium species (0.4%)
- pH = 12.5 Sr^{2+} (69.4%), $SrCO_3^\circ$ (aq) (22.0%), $SrOH^+$ (7.9%), other strontium species (0.7%)

There are no significant differences between the solubility-limited concentrations of dissolved strontium calculated with the average and maximum concentrations of dissolved anions as listed in Table 3.1.

However, it should be noted that the strontium concentrations listed in Table 4.7 are very sensitive to the carbonate equilibria assumed in the conceptual model. Carbonate is a component of the strontianite solubility product and is also an important complexing ligand for strontium, forming aqueous species such as $SrCO_3^\circ$ (aq). The concentrations of dissolved carbonate were constrained between pH values of 4.0 and 8.0 by assuming equilibrium with 0.003 atm CO_2 (gas) and between pH values of 8.0 and 12.5, by assuming equilibrium with the solubility of calcite ($CaCO_3$).

The concentrations of dissolved strontium in Table 4.7 are plotted as a function of pH as the thick solid line in Figure 4.6. It should be noted that the predicted solubility for dissolved strontium at pH values less than 6 are probably too high and not realistic. A different solid or another reaction process, such as sorption or coprecipitation, will likely control the solubility of strontium at pH values less than 6 to concentrations lower than those in Figure 4.6. Moreover, the modeling calculations that predicted the high solubilities for dissolved strontium are probably not valid given the lack of a charge balance constraint as noted in Section 3.1.

4.10.2 Published Solubility Data

Based on the literature reviewed to date, no published experimental studies of strontium solubility in cement-equilibrated water have been identified. These data will be needed for validation testing of the calculated solubility limits for strontium.

4.10.3 NRC LLW PA Test Case Rinse Release Model

The strontium concentrations (Table 4.1) calculated by the NRC using the rinse release model (prior to application of solubility limits or sorption coefficients) and water volume fluxes of 1,000 and 100 ft^3/yr for ^{90}Sr in Class A and B/C vaults, respectively, are plotted in Figure 4.6 as thin dashed and dashed-dotted horizontal lines, respectively. The values derived for ^{90}Sr at these fluxes were selected for plotting purposes, because they represented the highest radionuclide concentrations of the results provided to PNNL by the NRC. The strontium concentrations derived using the rinse release model for the Class A vault scenario are lower than those based on solubility considerations for the pH range from 4.0 to 12.5. For the Class B/C vault scenario, the solubility limits calculated for strontium are less than the rinse release model values at all pH values greater than approximately 6.5 and may provide a more accurate constraint on the maximum concentrations of dissolved strontium.

4.11 Technetium

A solubility control could not be identified for dissolved technetium at the oxidizing conditions used in our conceptual model for the solubility calculations (see Chapter 3). A limited set of chemical equilibria calculations were completed at pH values of 5.8 and 12.5 to determine the redox conditions at which a solubility control might limit the concentrations of

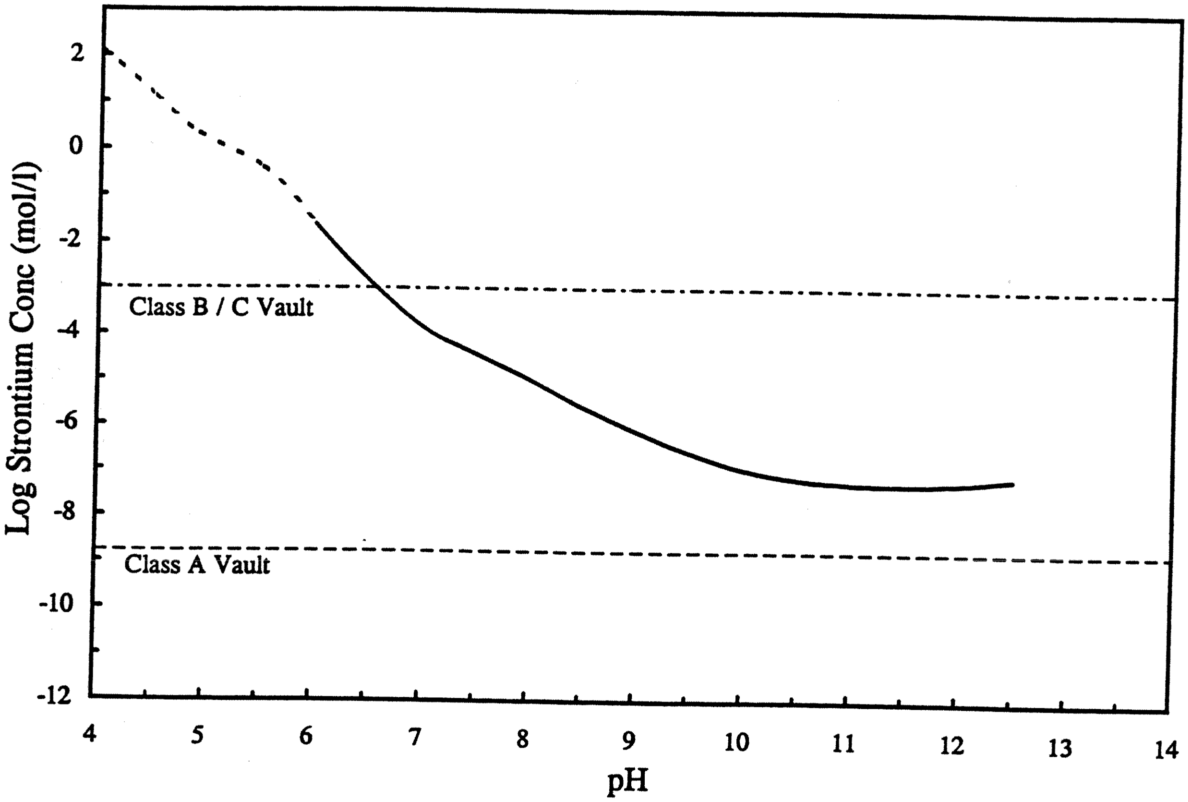

Figure 4.6 Concentration limits for dissolved strontium

[Solid line represents values calculated in our study using strontianite ($SrCO_3$) as the solubility control. The thin dashed and dashed-dotted horizontal lines show the strontium concentrations calculated by the NRC using the rinse model and a water volume flux of 1000 ft^3/yr for ^{90}Sr in Class A and B/C vaults, respectively.]

dissolved technetium. Using an arbitrary initial concentration of total dissolved technetium of 6.2 x 10^{-6} mol/l [1 ppm Tc(total) as TcO_4^-], the calculations indicate that the Eh values must decrease from +500 to +211 mV at pH 5.8 before the solubility of a technetium solid (e.g., Tc_3O_4) is exceeded. At pH 12.5 and the same initial concentration of dissolved technetium, the redox conditions must decrease from +200 to -267 mV before the solubility of Tc_3O_4 is exceeded. This starting concentration for dissolved technetium [1 ppm TcO_4^-(total)] is similar to the concentration estimated by the NRC using the rinse release model for a Class A vault disposal scenario at a water flux of 1,000 ft^3/yr. At any given pH, the Eh value at which solubility equilibrium is reached decreases with decreasing initial concentrations of dissolved technetium.

4.12 Thorium

4.12.1 Calculated Solubilities

Concentration limits calculated for dissolved thorium for the range of pH/Eh conditions limited by the cement- and groundwater buffered systems are listed in Table 4.8. The solubility control selected for dissolved thorium at these environmental

Table 4.8 Maximum concentration limits calculated for dissolved thorium for the NRC LLW PA test case

		Average ground-water composition		Maximum anion concentrations
	Eh	Without Th-CO_3 species	With Th-CO_3 species	Without Th-CO_3 species
pH	(mV)		mol/l	
4.0	581	9.9×10^{-5}	9.9×10^{-5}	2.3×10^{-4}
4.5	558	1.1×10^{-5}	1.1×10^{-5}	4.2×10^{-5}
5.0	536	2.6×10^{-6}	2.6×10^{-6}	1.9×10^{-5}
5.5	514	7.7×10^{-7}	7.8×10^{-7}	1.0×10^{-5}
5.8	500	5.3×10^{-7}	5.5×10^{-7}	8.5×10^{-6}
6.0	490	4.5×10^{-7}	4.8×10^{-7}	8.1×10^{-6}
6.5	470	3.3×10^{-7}	4.3×10^{-7}	7.7×10^{-6}
7.0	450	2.5×10^{-7}	5.0×10^{-7}	7.4×10^{-6}
7.5	420	1.2×10^{-7}	4.8×10^{-7}	6.8×10^{-6}
8.0	400	9.0×10^{-9}	4.4×10^{-7}	4.7×10^{-6}
8.5	380	9.8×10^{-10}	5.4×10^{-7}	7.4×10^{-7}
9.0	360	7.0×10^{-10}	6.0×10^{-7}	9.9×10^{-9}
9.5	340	6.5×10^{-10}	5.9×10^{-7}	7.1×10^{-10}
10.0	310	6.3×10^{-10}	4.8×10^{-7}	6.3×10^{-10}
10.5	290	6.2×10^{-10}	2.9×10^{-7}	6.2×10^{-10}
11.0	270	6.2×10^{-10}	1.3×10^{-7}	6.2×10^{-10}
11.5	250	6.2×10^{-10}	4.6×10^{-8}	6.2×10^{-10}
12.0	220	6.2×10^{-10}	1.5×10^{-8}	6.2×10^{-10}
12.5	200	6.1×10^{-10}	4.7×10^{-9}	6.1×10^{-10}

conditions was solid amorphous hydrous ThO_2 (am)(1) based on data from Felmy et al. (1991). The solid ThO_2 (am) was selected as a conservative solubility limit for thorium, because laboratory studies have shown that this solid precipitates in low-temperature aqueous solutions. On the other hand, crystalline ThO_2 (c) equilibrates very slowly in low-temperature aqueous systems. As will be noted below, the species $Th(OH)_4^\circ$ (aq) is a dominant thorium aqueous species at high pH

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(1) This compound will be referred to as ThO_2 (am) through the remainder of the report.

conditions. Therefore, selection of the appropriate stability constant for this species is important to predicting thorium solubility. The equilibrium constant reported for the species $Th(OH)_4^\circ$ (aq) by Ryan and Rai (1987) was used for the calculations described below.

Concentrations of dissolved thorium (second column from left in Table 4.8) were also calculated using the thermodynamic constants reported for thorium-carbonate complexes by Östhols et al. (1994). These calculations were also based on the average ground-water composition and assuming ThO_2 (am) as the solubility control. Constants for the thorium-carbonate complexes were derived for the MINTEQ database from the values of Östhols et al. (1994) by assuming that the solubility product reported by Felmy et al. (1991) for ThO_2 (am) was equivalent to that reported by Östhols et al. for ThO_2 (act).(1)

The three sets of concentration limits listed for dissolved thorium in Table 4.8 are significantly different. These differences can be explained by examining the distribution of dominant thorium aqueous species as a function of pH. The distribution, given as the percent of total mass of dissolved thorium, of the dominant thorium aqueous species for the three sets of modeling results are listed in Table 4.9 for several pH values. The thorium concentrations calculated for the average ground-water composition without and with the thorium-carbonate complexes differ by as much as two orders of magnitude at pH values from 7.5 to 11.5. The increase in concentrations of dissolved thorium are due to formation and dominance of the thorium-carbonate complex $Th(OH)_3CO_3^-$. The differences between the maximum concentrations calculated for dissolved thorium without the thorium-carbonate complexes using the average and maximum anion ground-water compositions are due to increase in concentrations of dissolved phosphate (0.1 to 2.2 ppm) and predicted formation of the $Th(HPO_4)_3^{2-}$ complex. For the maximum anion ground-water composition, the $Th(HPO_4)_3^{2-}$ complex dominates, as noted from the species distributions listed in Table 4.9, the speciation of dissolved thorium from pH values of 5.0 to 9.0. The accuracy of the available thermodynamic data for thorium-phosphate aqueous complexes has been questioned by others (for example, see Östhols [1995]). Additional experimental studies will be required to validate these solubility calculations, especially the importance of thorium-carbonate and thorium-phosphate species.

The concentrations of dissolved thorium in Table 4.8 calculated without and with the thorium-carbonate complexes for the average ground-water composition are plotted as a function of pH as thick solid and dashed lines, respectively, in Figure 4.7.

4.12.2 Published Solubility Data

Ewart et al. (1992) experimentally determined the concentrations of dissolved thorium resulting from the equilibration of cement-equilibrated waters that were oversaturated with dissolved thorium. Values estimated from data reported graphically by Ewart et al. (1992, Figure 1) are plotted as filled circles in Figure 4.7 for comparison to the values calculated in our study by computer modeling.

The experiments of Ewart et al. (1992) involved the addition of thorium chloride solutions to cement equilibrated waters in a controlled atmosphere chamber with low CO_2 contents. Sufficient thorium solution was added to obtain an initial concentration of 10^{-4} M dissolved thorium (thin dotted horizontal line in Figure 4.7). The pH of the resulting mixtures was adjusted with sodium hydroxide or hydrochloric acid. Aliquots of the equilibrated mixtures were taken and filtered. Thorium concentrations in the filtered solutions were determined by inductively coupled plasma mass spectrometry.

The thorium concentrations calculated in our study without the thorium-carbonate complexes using the average ground-water composition are in fair agreement with the experimental measurements made by Ewart et al. (1992). Our calculations of the solubility of ThO_2 (am) are approximately less than an order of magnitude lower than the data from Ewart et al.

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(1) The "act" descriptor refers to a microcrystalline solid.

Table 4.9 Distribution of thorium aqueous species for the NRC LLW PA test case

Thorium species	pH 4.0	5.8	7.5	9.0	12.5
	% mol/l				
	Average Ground-Water Composition Without Th-CO_3 Species				
Th^{4+}	14.1	<1.0	<1.0	<1.0	<1.0
$ThOH^{3+}$	11.8	<1.0	<1.0	<1.0	<1.0
$Th(OH)_2^{2+}$	45.4	2.1	<1.0	<1.0	<1.0
$Th(OH)_3^{+}$	8.4	24.5	2.2	11.8	<1.0
$Th(OH)_4^{\circ}$ (aq)	<1.0	<1.0	<1.0	88.1	99.9
$Th(HPO_4)_2^{\circ}$ (aq)	<1.0	35.3	<1.0	<1.0	<1.0
$Th(HPO_4)_3^{2-}$	<1.0	37.8	96.7	<1.0	<1.0
ThF^{3+}	3.7	<1.0	<1.0	<1.0	<1.0
$ThSO_4^{2+}$	14.2	<1.0	<1.0	<1.0	<1.0
$Th(SO_4)_2^{\circ}$ (aq)	1.8	<1.0	<1.0	<1.0	<1.0
	Average Ground-Water Composition With Th-CO_3 Species				
Th^{4+}	14.1	<1.0	<1.0	<1.0	<1.0
$ThOH^{3+}$	11.8	<1.0	<1.0	<1.0	<1.0
$Th(OH)_2^{2+}$	45.4	2.0	<1.0	<1.0	<1.0
$Th(OH)_3^{+}$	8.4	23.6	<1.0	<1.0	<1.0
$Th(OH)_4^{\circ}$ (aq)	<1.0	<1.0	<1.0	<1.0	13.0
$Th(HPO_4)_2^{\circ}$ (aq)	<1.0	34.1	<1.0	<1.0	<1.0
$Th(HPO_4)_3^{2-}$	<1.0	36.4	24.3	<1.0	<1.0
ThF^{3+}	3.7	<1.0	<1.0	<1.0	<1.0
$ThSO_4^{2+}$	14.2	<1.0	<1.0	<1.0	<1.0
$Th(SO_4)_2^{\circ}$ (aq)	1.8	<1.0	<1.0	<1.0	<1.0
$Th(OH)_3CO_3^{-}$	<1.0	3.5	74.9	99.9	86.9
	Maximum Anion Concentrations Without Th-CO_3 Species				
Th^{4+}	6.9	<1.0	<1.0	<1.0	<1.0
$ThOH^{3+}$	5.5	<1.0	<1.0	<1.0	<1.0
$Th(OH)_2^{2+}$	20.1	<1.0	<1.0	<1.0	<1.0
$Th(OH)_3^{+}$	3.6	1.6	<1.0	<1.0	<1.0
$Th(OH)_4^{\circ}$ (aq)	<1.0	<1.0	<1.0	6.2	99.9
$Th(HPO_4)_2^{\circ}$ (aq)	5.0	21.6	<1.0	<1.0	<1.0
$Th(HPO_4)_3^{2-}$	<1.0	75.9	99.8	92.9	<1.0
ThF^{3+}	8.6	<1.0	<1.0	<1.0	<1.0
$ThSO_4^{2+}$	31.2	<1.0	<1.0	<1.0	<1.0
$Th(SO_4)_2^{\circ}$ (aq)	18.9	<1.0	<1.0	<1.0	<1.0

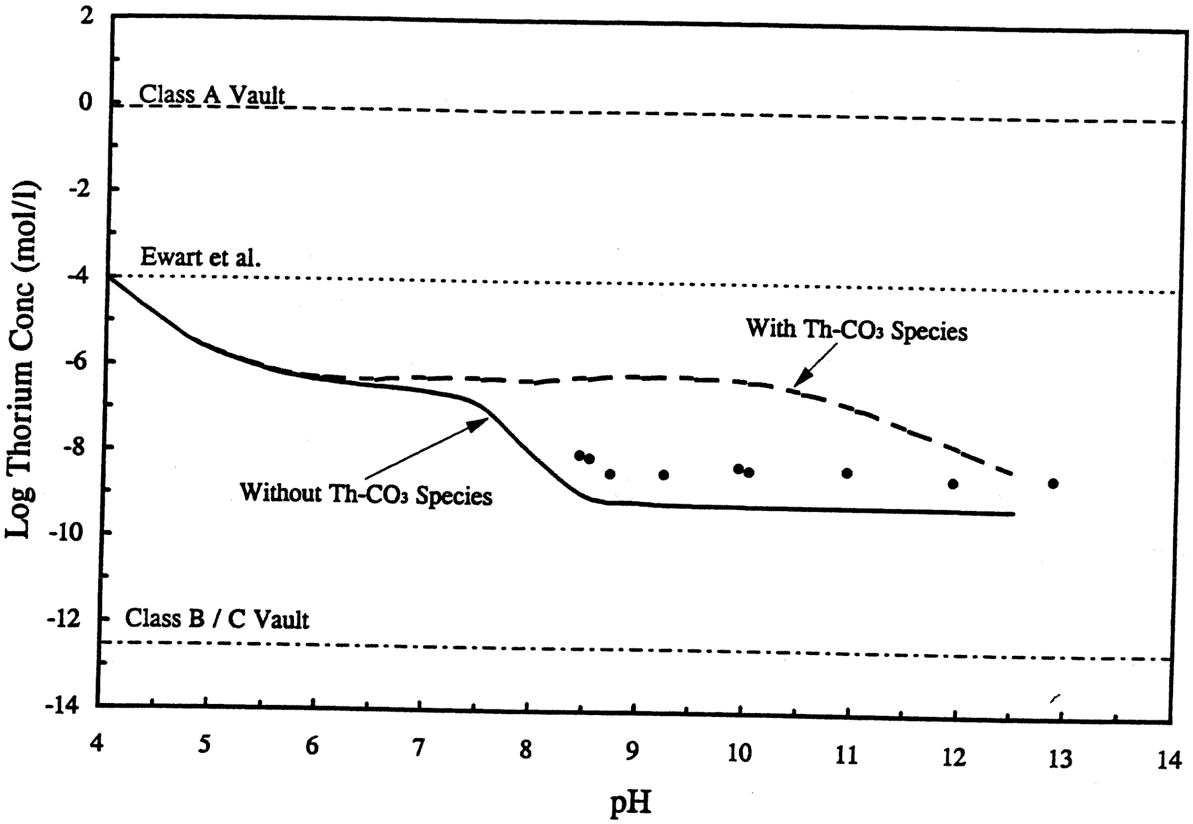

Figure 4.7 Concentration limits for dissolved thorium

[The thick solid and dashed curves represent the thorium concentrations calculated without and with thorium-carbonate complexes, respectively, using the average ground-water composition and ThO_2 (am) as the solubility control. Filled circles represent values estimated from data presented in Ewart et al. (1992). The thin dotted horizontal line shows the initial concentration of total dissolved thorium used in experiments by Ewart et al. The thin dashed and dashed-dotted horizontal lines show the thorium concentrations calculated by the NRC using the rinse release model and water volume fluxes of 1,000 ft^3/yr for ^{232}Th in Class A and 100 ft/yr for ^{228}Th in Class B/C vaults, respectively.]

Until additional laboratory studies are conducted to validate the predicted solubility limits for thorium, the thorium concentrations predicted using the thorium-carbonate complexes from Östhols et al. (1994) provide the more conservative set of concentration limits.

4.12.3 NRC LLW PA Test Case Rinse Release Model

The thorium concentrations (Table 4.1) calculated by the NRC using the rinse release model (prior to application of solubility limits or sorption coefficients) and water volume fluxes of 1,000 ft^3/yr for ^{232}Th in Class A and 100 ft^3/yr for ^{228}Th in Class B/C vaults are plotted in Figure 4.7 as thin dashed and dashed-dotted horizontal lines, respectively. These values were selected for plotting purposes, because they represented the highest radionuclide concentrations of the results provided to PNNL by the NRC. The thorium concentrations derived using the rinse release model for the Class A vault scenario are higher than those based on solubility considerations for the pH range 4.0 to 12.5. It is important to note that the high thorium concentration predicted by the rinse release model for a Class A vault cannot occur and is not observed. In the NRC LLW PA test case, the concentrations calculated with the rinse release model only apply to very mobile radionuclides such as ^{36}Cl or radionuclides for which there are no solubility or sorption coefficient data. For the Class B/C vault scenario, the solubility limits calculated for thorium are three orders of magnitude or more greater than the value determined with the rinse release model value.

4.13 Uranium

4.13.1 Calculated Solubilities

Concentration limits calculated for dissolved uranium for the range of pH/Eh conditions limited by the cement- and ground-water buffered systems are listed in Table 4.10. Two solubility controls were considered in calculating maximum concentration limits of dissolved uranium. These controls included the solids schoepite [$UO_2(OH)_2 \cdot H_2O$] (Table 4.10) and uranophane [$Ca(H_3O)_2(UO_2)_2(SiO_4)_2 \cdot 3H_2O$] (Table 4.10). Concentration limits based on schoepite are suspected to be highly conservative. Uranophane is known to exist in uranium-loaded C-S-H mixtures and thus may be a realistic solubility control for dissolved uranium. Calculation of its solubility, however, may be more susceptible to uncertainties in conceptual models and available thermodynamic data.

Schoepite is known to precipitate readily in low-temperature aqueous systems at laboratory time scales and result in high concentrations of dissolved uranium (Krupka et al. 1985). In natural low-temperature aqueous systems, the presence of alkali and/or alkaline earth ions at high pH conditions would result in the precipitation of alkali/alkaline earth uranium compounds that would control the solubility of uranium to concentrations lower than those resulting from equilibrium with schoepite.

Atkins et al. (1990, 1991) have investigated uranium interactions with $Ca(OH)_2$ and C-S-H using a range of uranium loadings and equilibration periods of 21 to 75 days. Solid phases in the resulting mixtures were characterized by x-ray diffraction and analytical electron microscopy. Three uranium-containing phases were identified in these mixtures. These phases, which included uranophane, a hydrated calcium uranyl oxide [$Ca_2UO_5 \cdot (1.2\text{-}1.5)H_2O$], and becquerelite [$CaU_6O_{19} \cdot H_2O$], could be possible solubility controls for uranium in cement-buffered systems. The solubility of uranophane was calculated using an equilibrium constant derived from the Gibbs free energy value published by Nguyen et al. (1992). Thermodynamic data have not been identified for the hydrated calcium uranyl oxide phase and becquerelite.

The modeling results indicated that dissolved uranium would exist in the +6 valence state and uranyl carbonate and hydroxyl species would dominate the aqueous speciation of dissolved uranium for the pH/Eh conditions considered for these calculations.

The distributions, given as the percent of total mass of dissolved uranium, of the dominant uranium aqueous species for the modeling results based on the average ground-water composition are listed below for several pH values:

Schoepite as solubility control

- pH = 5.8 $(UO_2)_2CO_3(OH)_3^-$ (43.7%), $UO_2CO_3^\circ$ (aq) (18.1%), $UO_2(OH)_2^\circ$ (aq) (17.7%), $UO_2HPO_4^\circ$ (aq) (5.2%), UO_2OH^+ (5.0%), $(UO_2)_3(OH)_5^+$ (4.3%), UO_2^{2+} (2.0%), $UO_2PO_4^-$ (1.3%), other uranium species (2.7%)
- pH = 12.5 $UO_2(OH)_3^-$ (88.5%), $UO_2(OH)_4^{2-}$ (7.1%), $(UO_2)_3(OH)_7^-$ (4.4%)

Table 4.10. **Maximum concentration limits calculated for dissolved uranium based on schoepite and uranophane as a solubility control for the NRC LLW PA test case**

pH	Eh (mV)	Solubility Control: Schoepite (mol/l)	Solubility Control: Uranophane (mol/l)
4.0	581	2.1×10^{-3}	1.3×10^{-3}
4.5	558	2.1×10^{-4}	2.9×10^{-4}
5.0	536	3.5×10^{-5}	5.5×10^{-5}
5.5	514	1.4×10^{-5}	8.5×10^{-6}
5.8	500	1.5×10^{-5}	3.9×10^{-6}
6.0	490	1.7×10^{-5}	2.5×10^{-6}
6.5	470	3.9×10^{-5}	7.7×10^{-7}
7.0	450	7.2×10^{-5}	2.3×10^{-7}
7.5	420	1.0×10^{-4}	7.5×10^{-8}
7.8	400	1.2×10^{-4}	2.9×10^{-8}
8.5	380	1.6×10^{-4}	1.9×10^{-8}
9.0	360	1.9×10^{-4}	1.7×10^{-8}
9.5	340	2.2×10^{-4}	1.7×10^{-8}
10.0	310	2.6×10^{-4}	1.7×10^{-8}
10.5	290	3.7×10^{-4}	1.5×10^{-8}
11.0	270	7.8×10^{-4}	7.9×10^{-8}
11.5	250	2.3×10^{-3}	2.8×10^{-7}
12.0	220	7.5×10^{-3}	1.4×10^{-6}
12.5	200	2.7×10^{-2}	1.0×10^{-5}

Uranophane as solubility control

- pH = 5.8 $UO_2CO_3^{\circ}$ (aq) (23.8%), $UO_2(OH)_2^{\circ}$ (aq) (23.4%), $(UO_2)_2CO_3(OH)_3^-$ (20.3%), $UO_2HPO_4^{\circ}$ (aq) (16.2%), UO_2OH^+ (6.6%), $UO_2PO_4^-$ (4.1%), UO_2^{2+} (2.7%), other uranium species (2.9%)
- pH = 12.5 $UO_2(OH)_3^-$ (93.4%) and $UO_2(OH)_4^{2-}$ (6.6%)

At pH values greater than 10, the model calculations indicate that hydrolytic species will dominate the aqueous speciation of dissolved U^{VI}.

The concentrations of dissolved uranium in Tables 4.10 for the average ground-water composition are plotted as a function of pH as thick dashed (schoepite as solubility control) and solid curves (uranophane as solubility control) in Figure 4.8. There are no significant differences between the maximum concentration limits calculated for dissolved uranium using the average and maximum anion ground-water compositions for either of the two identified potential solubility controls.

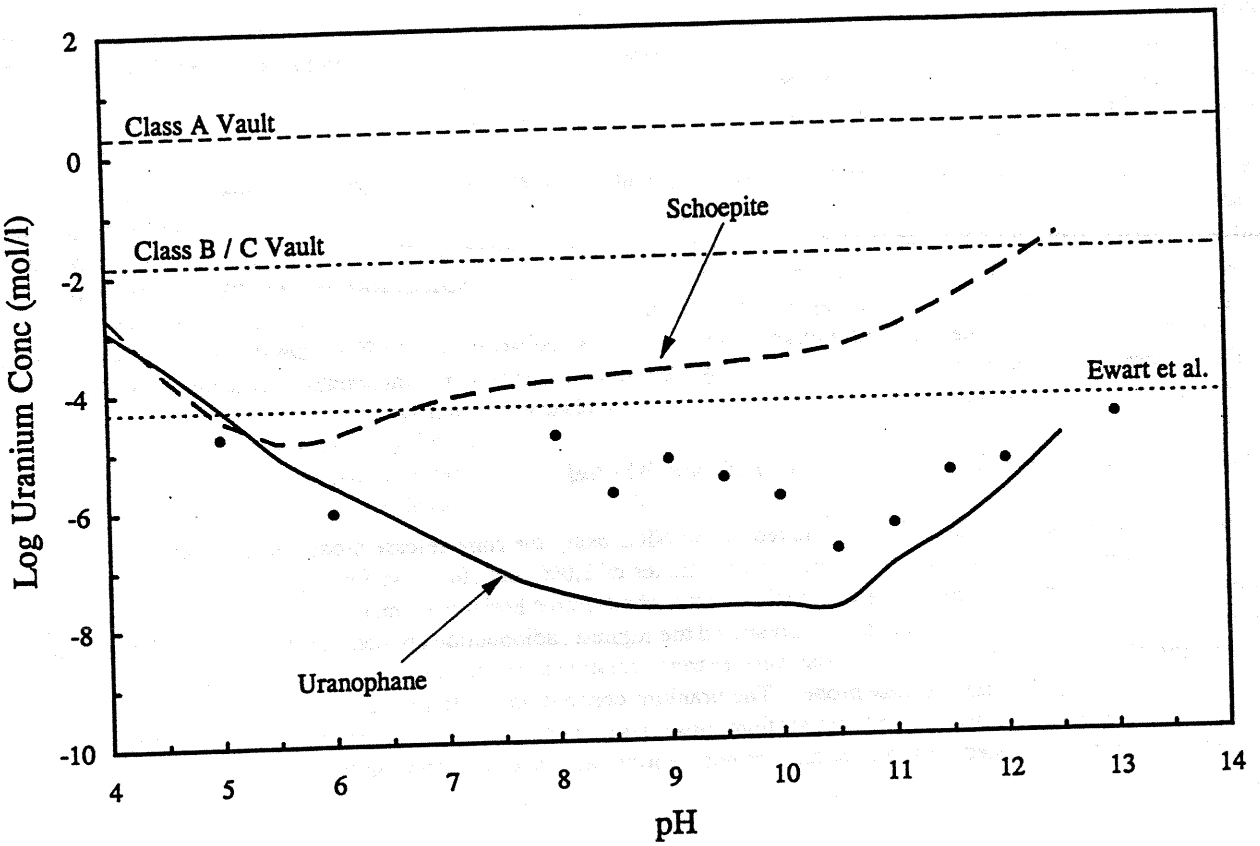

Figure 4.8 Concentration limits for dissolved uranium

[The thick dashed and solid lines represent values calculated in our study using schoepite and uranophane as solubility controls, respectively, for the average ground-water composition. Filled circles represent values estimated from data presented in Ewart et al. (1992). The thin dotted horizontal line shows the initial concentration of total dissolved uranium used in experiments by Ewart et al. The thin dashed and dashed-dotted horizontal lines show the uranium concentrations calculated by the NRC using the rinse release model and water volume fluxes of 1,000 and 100 ft^3/yr for ^{238}U in Class A and B/C vaults, respectively.]

In addition to pH and Eh, the calculation of solubility limited concentrations for dissolved uranium are sensitive to several other environmental parameters considered in the conceptual model. As noted from the dominant aqueous species listed above, carbonate complexation of U^{VI} has a major effect on the maximum solubility limits calculated for dissolved uranium. Moreover, given the composition of uranophane, the concentrations of dissolved calcium and silica are additional factors affecting the uranium concentrations based on equilibrium with uranophane.

4.13.2 Published Solubility Data

Ewart et al. (1992) experimentally determined the concentrations of dissolved uranium resulting from the equilibration of cement-equilibrated waters that were oversaturated with dissolved uranium. Values estimated from data reported graphically by Ewart et al. (1992, Figure 3) are plotted as filled circles in Figure 4.8 for comparison to the values calculated in our computer modeling study. The experiments described by Ewart et al. (1992) involved the addition of U^{VI} chloride solutions to cement equilibrated waters in a controlled atmosphere chamber with low CO_2 contents. Sufficient uranium solution was added to obtain an initial concentration of 5×10^{-5} M dissolved uranium (thin dotted horizontal line in Figure 4.8). The pH of the resulting mixtures was adjusted with sodium hydroxide or hydrochloric acid. Aliquots of the equilibrated mixtures were taken and filtered. Uranium concentrations in the filtered solutions were determined by alpha counting.

Results of our solubility calculations bracket the experimental data of Ewart et al. (1992). The uranium concentrations measured by Ewart et al. at pH values of 5 and 8 are approximately equal to the concentrations used to start their oversaturation experiments, and thus may not indicate solubility limited conditions. The uranium concentrations modeled using the solubility of schoepite are several orders of magnitude greater than the experimental values. The solubility of uranophane, on the other hand, is in good agreement with the experimental values for pH values greater than 10.5, and significantly underestimates the concentrations at lower pH values. Ewart et al. (1992) modeled the aqueous speciation and solubility controls for their experimental results. They also noted that uranium concentrations based on equilibrium with schoepite overestimated uranium concentrations relative to their observed values.

4.13.3 NRC LLW PA Test Case Rinse Release Model

The uranium concentrations (Table 4.1) calculated by the NRC using the rinse release model (prior to application of solubility limits or sorption coefficients) and water volume fluxes of 1,000 and 100 ft^3/yr for ^{238}U in Class A and B/C vaults, respectively, are plotted in Figure 4.7 as thin dashed and dashed-dotted horizontal lines, respectively. These values were selected for plotting purposes, because they represented the highest radionuclide concentrations of the results provided to PNNL by the NRC. These two values are also very extreme relative to the concentration release predicted for the other uranium isotopes using the rinse release model. The uranium concentrations derived using the rinse release model for the Class A and B/C vault scenarios are both higher than those based on solubility considerations for the pH range 4.0 to 12.5. The solubility limits calculated for uranium may provide a more accurate constraint on the upper concentration limits for uranium.

4.14 Conclusions

Conservative maximum concentration limits for dissolved americium, nickel, neptunium, plutonium, radium, strontium, thorium, and uranium were calculated using the MINTEQA2 geochemical code and associated thermodynamic database. The concentration limits were determined as a function of pH at oxidizing conditions for two ground-water environments associated with the NRC LLW PA test case. These environments include 1) a cement buffered system, wherein the leachate pH is controlled at values above 10 by the effective buffering capacity of the concrete; and 2) a ground-water buffered system, wherein the leachate pH and related solution parameters are dominated by the local ground-water system.

The solubility controls selected to constrain the maximum concentrations limits for these radionuclides are $AmOHCO_3$, $Am(OH)_3$ (am), $Ni(OH)_2$, $NpO_2(OH)$ (am), $PuO_2{\bullet}H_2O$ (am), $RaSO_4$, $SrCO_3$ (the mineral strontianite), ThO_2 (am), $UO_2(OH)_2{\bullet}H_2O$ (schoepite), and $Ca(H_3O)_2(UO_2)_2(SiO_4)_2{\bullet}3H_2O$ (uranophane). The maximum concentrations limits calculated for uranium for the pH range from 4 to 12.5 were lower than those calculated by NRC for Class A and Class B/C vaults using the rinse release model and inventory considered in the NRC LLW PA test case. Except for neptunium and thorium, the maximum concentrations limits calculated for the other radionuclides at pH values greater than 7 were lower than those calculated for Class B/C vaults using the rinse release model in the NRC test case. For Class A vaults in the NRC LLW PA test case, the maximum concentration limits calculated for the radionuclides, except for thorium and uranium, at pH values less than 10 were greater than those determined using the rinse release model.

Except for radium, the modeling results indicate that the maximum concentrations limits for the other radionuclides were increased as result of aqueous complexation with dissolved carbonate and/or phosphate. Given the potential importance of phosphate complexation of several radionuclides and questionable adequacy of thermodynamic values for these phosphate complexes, additional laboratory studies are needed to validate the importance of phosphate complexation of these contaminants.

The predicted solubility limits for dissolved neptunium, nickel, and strontium at pH values less than 6 are probably too high and not realistic. A different solid or another reaction process, such as sorption or coprecipitation, will likely constrain their solubilities at these pH values to concentrations lower than those predicted using the MINTEQA2 code. Moreover, the modeling calculations resulting in the high solubilities for these radionuclides are probably not valid given the lack of a charge balance constraint in the modeling calculations.

The maximum concentration limits for radionuclides will be constrained to different degrees by sorption processes. As noted in this chapter, sorption may have a greater impact than solubility reactions on the concentrations of some radionuclides. The sorption behavior of radionuclides may be significantly different than that observed for soils in ground-water buffered systems given the major differences in the composition and high pH conditions associated with cement-buffered systems. Therefore, a review was completed to assess the extent of sorption values, in the form of mass-related distribution coefficients (or K_d values), that are described in the literature. The results of this review are described in the next chapter.

5 Distribution Coefficient Data for Selected Radionuclides on Cementitious Materials

The available data for the sorption potential of selected radionuclides onto cement and concrete have been reviewed and critically analyzed. The cement may be present as a binder in solidified waste, construction and decontamination debris, or a concrete vault used for long-term storage and disposal of LLW. The supporting literature review was limited to a list of radionuclide elements that are of particular interest to the U.S. Nuclear Regulatory Commission (NRC). These radionuclides include americium, inorganic carbon, chlorine, iodine, lanthanide elements, niobium, nickel, neptunium, plutonium, radium, strontium, technetium, thorium, and uranium. Our review and analysis of sorption information focuses on the geochemical conditions associated with "fresh" cement/concrete where the expected pH of the cement pore waters will equal or exceed 10. Changes in sorption that may occur when cement is significantly weathered over thousands of years are also discussed. For these later conditions, the pH of the cement pore water will decrease to below 9 and the amorphous hydration products [calcium silicate hydrogel (C-S-H)] typical of cement will have remineralized to more crystalline and thermodynamically stable solid phases.

5.1 Review by Bradbury and Sarott (1995)

A recent critical review by Bradbury and Sarott (1995) discusses the potentially significant impact that materials in the disposed waste can have on the geochemical environment of pore water. The title of their review is "*Sorption Databases for Cementitious Near-Field of a L/ILW Repository for Performance Assessment.*" The review provides some expert opinion on factoring in the impacts of organic waste degradation, metallic iron corrosion, and the formation of radionuclide bearing colloids on the overall fate and transport of key radionuclides. Throughout the review of these issues, Bradbury and Sarott caution the reader that the actual experimental data under disposal relevant conditions is very sparse and the understanding of the controlling mechanisms for these processes is very limited.

Readers with performance assessment (PA) interests are encouraged to read and evaluate the important review by Bradbury and Sarott (1995). It presents interesting discussions on waste- and disposal material-induced processes that may perturb the expected environment geochemical conditions, including sorption potential, of the LLW disposal system.

As an aside, the most important perturbation that may enhance the potential of nuclide migration is the degradation of cellulosic material and formation of significant quantities of organic ligands. These processes can significantly increase the solubility of radionuclides and decrease the adsorption potential of radionuclides over unperturbed conditions. Bradbury and Sarott (1995) suggest that as little as 1 percent by weight loading of cellulose can show measurable effects on radionuclide migration and that 10 percent cellulose loading in a disposal facility may significantly enhance migration and thus warrants attention. The nuclides most influenced by the organic ligand degradation products are the actinide, lanthanide, and the transition metal (e.g., nickel) elements.

5.2 Background Information

Prior to discussing the adsorption potential of each radionuclide, the following general topics will be discussed:

- adequacy of the K_d approach to quantify adsorption
- relevancy of laboratory data using crushed samples of cement

- differences in cement types
- cement versus concrete
- long-term evolution of cement solid phases and pore water.

These discussions are important to understanding and evaluating the available information for the sorption potential of radionuclides in cementitious systems.

5.2.1 K_d Approach

The most common approach to quantifying adsorption is to use the distribution coefficient, K_d, which is also often referred to as the distribution ratio, R_d. This constant is defined as

$$K_d \text{ or } R_d = \frac{\text{concentration of radionuclide adsorbed on solid per mass}}{\text{concentration of radionuclide in solution per volume}} \tag{5.1}$$

Serne and Muller (1987) and Serne (1992) discuss the derivation and assumptions underlying the use of K_d in classical ion exchange literature and the use of the more generic distribution ratio, R_d, by the nuclear waste community. The proper use of the K_d construct requires the following conditions:

- adsorption of the contaminant of interest onto the adsorbent must be measured only when the system is known to be in equilibrium
- adsorption must be readily reversible
- contaminant must be present in trace amounts and not show differing adsorption tendencies as a function of its concentration.

Some or all these requirements are often not met or investigated in radionuclide sorption experiments. For this reason, the use of the R_d terminology has evolved to represent the less well-controlled and defined adsorption.

The K_d term will be used however throughout this document, because K_d is commonly used in the PA literature and cannot be easily confused with the retardation factor parameter, R, used in computerized hydrologic transport models. The reader is cautioned, however, that the sorption data discussed in subsequent sections may not meet the conditions described above for the more exact use of the K_d term.

Although K_d measurements are intended to be a quantification of adsorption, they are in most cases more properly a measure of total retardation, in that the investigators do not differentiate between the retardation processes of true surface adsorption and precipitation processes. Because K_d values are usually used in PA analyses to calculate retardation factors, which provides a measure of the speed at which the ground or pore water is moving versus the speed at which the contaminant is moving, it is important to not over estimate the distribution ratio by including precipitation processes. If the migration potential of a contaminant is predicted using an erroneously high K_d and R, then the actual migration will exceed the predicted and such predictions would be unacceptably non-conservative. Therefore the K_d values chosen should be scrutinized and, where possible, the primary citation should be critically analyzed to see if the experiments attempted to preclude precipitation reactions during their measurements. Experimenters can minimize precipitation-enhanced K_d values by using the following techniques:

- Blank container tests (i.e., without absorbent present) can be conducted to check for tracer stability in solution (i.e., changes in the tracer concentration, changes in the solution color, presence of turbidity, etc.).
- Empirical solubility tests can be conducted prior to performing the adsorption measurements to determine whether the tracer solution is prone to precipitation. The K_d measurements can then be completed at tracer concentrations lower than those where precipitation was observed.
- The preferred method for adding the contaminant spike involves pre-equilibrating the desired solution (free of radionuclide spike) with the adsorbent for sufficient time to reach steady state. After separating the absorbent from the pre-equilibrated water, the spike is then added to the water and the pH adjusted to the desired value. After several additional days of equilibration, the spiked water is filtered (0.45-µm and 18-Å filtrates if possible) and then reintroduced to the same adsorbent or a fresh adsorbent sample.

The most commonly used procedure that causes the greatest concern relative to precipitation is the direct spike of a known amount of tracer from its acid stock solution into a test vessel containing the adsorbent and aqueous solution (e.g., deionized and ground water) mixture that had pre-equilibrated for several days or weeks. This is often done without any heed to the fact that the acidity of the small volume of added tracer solution is very rapidly consumed by the excess $Ca(OH)_2$ present in the fresh cement. The pH of the tracer solution containing the radionuclide contaminant is thus rapidly changed from an acidic to a highly basic environment with pH values near 12 to 12.5 during which solubility-induced precipitation is quite likely.

In summary, fresh cement/concrete is a highly reactive and unstable assemblage of solids such that care must be taken when calculating the distribution ratio to avoid including copious precipitation of the nuclide because of wide swings in pH caused by the $Ca(OH)_2$ and C-S-H components of hydrated cement. It is likely that some coprecipitation loss of nuclide to the ever-evolving surfaces of the reactive cement phases will occur, but the radiotracer contacting solution should be adjusted to the appropriate pH prior to contacting the solution with the solid. Conversely, solubility experiments could be performed in cement equilibrated water prior to performing adsorption tests to be certain that the amount of radiotracer added to the adsorption experiment is appropriate.

5.2.2 Relevancy of Sorption Data for Crushed Cement Samples

Most of the available K_d values have been derived from tests using specimens of crushed cement. Because adsorption is generally considered to be quite sensitive to the available surface area of the adsorbent, K_d values measured for crushed cement might be biased too high. Bradbury and Sarott (1995) argue that hardened cement paste is a conglomeration of very fine-grained, microporous solids. The grain sizes of these materials may range from less than a few microns to tens of microns, and their porosity typically exceeds 20 percent. Thus, the disaggregation of a cementitious material should expose the same surfaces that would be available to contaminants released in the disposal facility. Further, Bradbury and Sarott state that the few literature citations that they found which address this issue explicitly show no significant effects between the K_d values measured on various sizes of cement particles. Primary references cited by Bradbury and Sarott include Atkinson and Nickerson (1988), Bayliss et al. (1991), and Atkinson et al. (1988).

On the other hand, several researchers (e.g., Jakubick et al. 1987 and Hietanen et al. 1985) point out the difficulty in applying the typical K_d measured on a specific weight of cement disaggregated to a selected particle size distribution to contaminant transport applications where the better normalizing parameter is arguably surface area. In fact, some researchers perform their adsorption experiments on small monolithic samples and report adsorption on a geometric, measured, or calculated reactive surface area. In these instances, it is important to consider the diffusion of contaminant from the solution into the interior of the porous monolith. That is, longer contact times than those normally afforded in batch adsorption testing of soils should be allowed in order to reach a true equilibrium state. Thus, if the adsorption measurements could be on monolithic samples carried out over the long time periods (months to years) that will exist for the performance of a disposal system, there would likely be little difference in the K_d values for monolithic or crushed samples calculated in the traditional units of weight of the adsorbent.

Therefore, K_d values on "crushed" cement likely represent accurate numbers for long-term PA calculations. K_d values based on short-term experiments (e.g., less than several months) involving sorption on small slabs or monolithic cylinders of cement/concrete may underestimate the true equilibrium values.

5.2.3 Sorption Versus Cement Types

There are many types of cement blends available that have different physical properties once hardened (see Lea 1988). In addition, cements contain minor impurities whose concentrations depend on the source of the starting materials. For cementitious waste forms, other additives, such as fly ash, furnace slags, clays and zeolites, are often added to tailor the solidification process to better sequester contaminants by adsorption or redox-mediated reactions.

Despite these potential differences, a literature review on the evolution of cement or grout pore waters reveals that their chemistry is generally remarkably similar. Highly reactive solids in the dry cement blends, often referred to as clinker, dominate the pore chemistry and its evolution. The pore-fluid chemistry is generally well-defined and the evolution of the solid phases towards more thermodynamically and crystalline forms is well documented. The reader is referred to the detailed discussions related to these processes in the appendices of this report and in Bradbury and Sarott (1995).

The one variable that can vary significantly in cement pore water and influence radionuclide adsorption potential is the solution redox potential, Eh. The major constituent that can influence the Eh of cement pore fluids is the sulfur contained in compounds found in slags that are often used in tailoring solidification of radioactive wastes. For details, the reader is referred to the discussions on this topic in Angus and Glasser (1985), Atkins and Glasser (1992), and references therein. The Eh conditions of the disposal facility may also be lowered by corrosion of iron containers (see Ewart et al. [1988]).

5.2.4 Sorption Potential of Cement Versus Concrete

For a few radionuclides (e.g., cesium), there appears to be a significant difference between the adsorption onto pure cement paste versus that onto concrete. Concrete is a mixture of cement (usually about one-fourth as much on a volume basis as found in cement-only pastes); sand-, pebble-, and cobble-sized aggregate material; and water. Most radionuclides appear to favor association with the very fine-grained cement and its hydration products. Thus K_ds for concrete are lower than those for cement on a weight basis. However, for cesium, many researchers have found that the aggregate in concrete "adsorbs" more cesium than cement paste, because of the high adsorption of cesium onto primary minerals, especially biotite and micaceous minerals, found in rocks used as aggregate material.

5.2.5 Adsorption Versus Long-Term Evolution of Cement Pore-Water Compositions and Solid Phases

The evolution of the cement pore water chemistry and the hydration solids versus time is discussed in Section 2.2 and Appendices A and B of this report. The reader is referred to the discussions and supporting references provided in the appendix of this report, as well as the discussions in Bradbury and Sarott (1995), Berner (1992), and references therein.

The convention of Bradbury and Sarott (1995) for the three types of physicochemical environments that all cements progress through will be used for our discussions and development of a preferred database of K_d values onto cement/concrete. These environments include the following:

- *Environment I*: This environment occurs immediately after the cement hardens and is wetted by infiltrating water. The cement pore water is characterized as having a high pH of >12.5, high ionic strength, and high concentrations of potassium and sodium resulting from the dissolution of alkali impurities in the clinker phases. The high concentration of sodium is sometimes augmented by the dissolution of inorganic salts that have been solidified and buried in the disposal facility. Some waste sources, such as those from some past commercial power reactors and the U.S. Department of Energy operations, also include other soluble constituents, such as NO_3^-, SO_4^{2-}, and $B(OH)_4^-$, that may readily dissolve during this period. Hydration is still continuing during Environment I with the formation of C-S-H and portlandite [$Ca(OH)_2$]. The composition of the cement pore fluid is at equilibrium with portlandite during this time. The duration of Environment I is relatively short when compared to the later "environments." Based on the modeling estimates discussed in Berner (1992), this environment may last for the first 100 to 10,000 years.

- *Environment II*: During this period, the soluble salts of the alkali metals are all dissolved. The pH of the cement pore water is controlled at a value of about 12.5 by the solubility of portlandite. The C-S-H and portlandite are the major solid phases present. Environment II may last for a long time. Its duration depends on how much water percolates through the system to dissolve all the slightly soluble portlandite. Using the estimates from Berner (1992), this environment may last from 100-10,000 yrs to 1,000-100,000 yrs.

- *Environment III*: The concentration of portlandite has been reduced to such an extent by this period that the solubility of C-S-H now controls the pH of the cement pore fluid. The C-S-H starts to dissolve incongruently with a continual decrease in pH. At the end of this evolution, Environment III can be conceptualized as leaving only silica (SiO_2) as the solubility control for the pore fluid pH. The ionic strength of the cement pore fluid during this period is low, and its pH is ~10 or less. For the sake of simplicity, the final end point of Environment III can be considered somewhat analogous to the geochemical conditions of the "normal" ambient soil environment. Of the three "environment" types, the duration of Environment II is thus the longest in which the pore fluid composition is influenced by the hydration and dissolution reactions of the cement components.

For the development of a preferred database of K_d values onto cement/concrete, the convention of Bradbury and Sarott (1995) was followed by assigning K_d values for most of the radionuclides present in an Environment III cementitious system at one-tenth of those K_d values selected for radionuclides associated with Environment II. This assumption is necessary because there are no laboratory data available on the sorption behavior of radionuclides on severely weathered cements. Bradbury and Sarott reason that most of the very high surface area C-S-H has been removed in severely weathered cement. The remaining solid phase, silica, has significantly less surface area and adsorption capacity for trace contaminants compared to the C-S-H.

5.2.6 Other Considerations

Many of the factors discussed above lead to significant variability in reported K_d values for the adsorption of radionuclides onto cement and concrete. Thus the proper selection of a K_d value for a specific application will require judicious selections from the available literature. The reader is also reminded that the focus of our review and following analysis is on the geochemical conditions associated with "fresh" cement/concrete (Environments I and II) where the expected pH of the cement pore waters will equal or exceed 12.

On a positive note, the adsorption measurements described in the literature are consistent on the qualitative adsorption (retardation) behavior of the radionuclides included in our review. That is, all sorption studies basically agree on which radionuclides are

- strongly retarded by cement paste (e.g., actinides, lanthanides, transition metals, inorganic carbon)
- moderately retarded by cement paste (e.g., radium, strontium, iodine, technetium)
- not significantly retarded by cement paste (e.g., chlorine and cesium).

K_d values for cementitious materials typically shows considerable scatter which could be misconstrued as inconsistency in sorption behavior. Experimentalists who have evaluated the precision of their adsorption (K_d) measurements have noted in some studies a factor of two difference in measured K_d values for identically treated, ostensibly duplicate samples. However, because cement is usually studied in its freshly cured state, unusually large variations in reported K_d values should be expected. At this point of the cement evolution, hydration reactions are continuing and alkali and OH^- ions are still leaching in significant quantities into the pore waters. Moreover, the resulting cement hydration minerals are not thermodynamically stable relative the geochemistry of most surface and ground waters. The confounding effects of precipitation/coprecipitation, especially in tests where higher concentrations of tracers are used to make K_d measurements easier, further adds to the variability of the results.

From the perspective of hydrologic transport or PA calculations, the fact that cement and concrete are very impermeable yet very porous media must be considered. The major transport pathway through cement or concrete may in fact be through fractures or other defects that are more amenable to advective flow of water and much more reactive to chemical weathering. The weathering products along these flow paths will exhibit different adsorption tendencies, or at least different reactive surface areas, compared to the bulk cement hydration gel minerals.

Bradbury and Sarott (1995), Dayal and Reardon (1992), and Serne (1990) discuss the potentially beneficial phenomenon of carbonate plugging or armoring. Carbonate precipitation might close up fractures that form in monolithic cement and concrete structures and thereby further retard the already slow diffusion of most radionuclides through the hardened cement paste. It would be useful to look for old cementitious structures and to see if water and/or contaminant migration are totally dominated by the harder-to-quantify fracture flow than the slow diffusion through the impermeable but porous cement matrix.

Atkinson(1) and colleagues have presented several papers (Atkinson 1983, Atkinson et al. 1986, and Atkinson and Nickerson 1988) that discuss a rather appealing conceptual model for the transport of contaminants through a porous, yet rather impermeable, material such as cement. The model recognizes the physical transport aspect (diffusion) and the chemical interactions (retardation) of radionuclide migration. The model requires that chemical interactions are reversible, such as surface adsorption reactions that have fast kinetics and exhibit a linear isotherm (i.e., K_d is independent of concentration and time). For these interactions, simple mathematical equations can be used to derive both apparent diffusion coefficients and K_ds from common laboratory experiments. These could include traditional techniques, such as batch adsorption, through-diffusion, in/out diffusion, and penetration profile measurements. Application of this model to data already in the literature could be important to several programmatic areas of interest to the NRC, including the disposal of LLW. Given that there are many more waste-form leach test reports in the literature than cement/concrete adsorption studies, it should be possible to use the Atkinson conceptual model to derive K_d values for many isotopes for which the adsorption literature offers no information. The model of Atkinson and Nickerson (1988) is briefly reviewed in Appendix E.

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5.3 K_d Database

A summary of preferred K_d values for the three environments that cement/concrete evolve to over thousands to tens of thousands of years is given in Table 5.1. The K_d values tabulated below represent equilibrium values where the contaminant has had adequate time to diffuse into all the available internal surfaces of the fine-grained hydration gel minerals and related reaction products, such as silica and carbonate phases, present at the alkaline conditions of Environments I-III.

Each cement/concrete environment was split into oxidizing and reducing sub-environments because some radionuclide elements may be present in very chemically different forms depending on their redox-influenced valence state. In general, an environment is considered reducing if metallic iron or ferrous iron (Fe^{II}) species predominate over ferric (Fe^{III}) species. However, we will use the terms "oxidizing" and "reducing" to refer to the valence states of the specific radionuclide contaminant of interest. For each redox-sensitive radionuclide, the distinction between these two redox conditions may require Eh values that are more reducing or oxidizing than those for the Fe^{II}/Fe^{III} redox couple.

The K_d values in Table 5.1 were selected from the information presented in the references reviewed in Sections 5.3.1 through 5.3.14. The reader is referred to these discussions for justification of selecting the preferred K_d values listed in Table 5.1.

5.3.1 Americium

In general, the adsorption potential of trivalent elements, such as americium, onto cement and concrete exceeds their adsorption potential onto sediments and soils, which is large. Therefore, very low migration potential should be expected for americium and other trivalent elements, such as curium and the lanthanides, in a cement-dominated near-field environment.

Ewart et al. (1988) determined K_d values of >10,000 ml/g for americium onto cements. Care was taken to maintain concentrations of dissolved americium to levels below those at which precipitation of americium-containing solids might inflate the apparent adsorption measurements and derived K_d values.

Bayliss et al. (1991) report a K_d value of ~12,000 ml/g for americium based on diffusion tests where a disc of cement was kept in contact with a solution of 2×10^{-11} M total dissolved americium for several months. Using the approach of Atkinson and Nickerson (1988) (see description in Appendix E), Bayliss et al. derived a K_d value for americium from the measured penetration profile of americium into the disk material.

Allard et al. (1984) and Hoglund et al. (1985) report on the adsorption of americium onto seven different concrete blends using several different simulated cement pore waters. The starting concentration of dissolved americium was 2.3×10^{-9} M and the final steady-state concentration was $\sim 1 \times 10^{-11}$ M. The K_d values calculated from the adsorption measurements ranged from 2500 to 35,000 ml/g. Interestingly the lowest K_d value for americium was determined in the test that used a sample of 74-year-old concrete removed from a hydroelectric dam inflow pipe. The concrete sample was contacted with "moderately fresh" pore water with medium high concentrations of dissolved sodium and potassium and low concentrations of dissolved calcium. Measurements for a 65-year-old concrete sample, on the other hand, resulted in K_d values of 10,000 ml/g using the same simulated cement pore fluid.

Kato and Yanase (1993) measured the adsorption of several elements onto cement powder (<0.35-mm particle size) using a cement equilibrated water (pH = 11) over a short contact time of 24 hours. The K_d measured for americium was 2,000 ml/g, which is approximately the same as the K_d of 2,400 ml/g determined for europium. The K_d value for cobalt was the highest measured value at 4,300 ml/g. The K_d values for other metals (calcium, strontium, cesium, and nickel) were lower.

Table 5.1 **Preferred distribution ratio (K_d) values (ml/g) for selected radionuclide elements for cement/concrete Environments I-III**

Radionuclide element	Environment I		Environment II		Environment III	
	Oxidizing conditions	Reducing conditions	Oxidizing conditions	Reducing conditions	Oxidizing conditions	Reducing conditions
	ml/g					
Am	5,000	5,000	5,000	5,000	500	500
C	500	500	100	100	10	10
Cl	5	5	1	1	0	0
I	10	10	5	5	1	1
Lanthanides	5,000	5,000	5,000	5,000	500	500
Ni	100	100	100	100	10	10
Nb	1,000	1,000	1,000	1,000	100	100
Np	2,000	5,000	2,000	5,000	200	500
Pu	5,000	5,000	5,000	5,000	500	500
Ra	100	100	100	100	100	100
Sr	1	1	3	3	3	3
Tc	0	1,000	0	1,000	0	100
Th	5,000	5,000	5,000	5,000	500	500
U	1,000	2,000	1,000	2,000	100	200

Jakubick et al. (1987) studied the adsorption of americium onto "pie wedges" and slabs of concrete that contained coarse aggregate (40 percent), fine aggregate (28.5 percent), cement (11 percent), water (14 percent), and voids (4.5 percent) by volume. The solution used for the measurements was a dilute nitric acid solution containing a trace concentration of dissolved americium. Over a contact time of 67 hours, the pH of the nitric acid leachate increased to 9.5 and the distribution ratio for americium was calculated to be 30,000 to 50,000 ml/g. Jakubick et al. prefer to use distribution ratios calculated on a surface area basis. Autoradiographical analysis of the specimens indicated that the sorbed americium showed a slight preference to associate with the cement paste versus that for the aggregates and carbonates formed during hydration. The reported K_d values may reflect some precipitation of americium, because the pH of original dilute nitric acid containing the unreported concentration of americium spike increased in the equilibrated system to 9.5 where americium is less soluble.

The available data indicate that americium and, by analogy, other trivalent elements, such as the lanthanides, will exhibit very high adsorption potentials onto fresh and moderately aged cement and concrete. For cement Environments I and II, a conservative K_d value of 5000 ml/g was selected for americium under both redox conditions. As an assumed value, a K_d value of 500 ml/g (one-tenth of 5000 ml/g) was chosen for americium for severely aged cement as represented by Environment III.

5.3.2 Inorganic Carbon (^{14}C)

For the purposes of this review, the discussion of the adsorption potential of carbon is limited to the inorganic forms of carbon, such as the aqueous species carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), and carbonic acid [$H_2CO_3^\circ$ (aq)], and the insoluble reduced forms of carbon (elemental C and carbides). These forms are the most common species found in the natural environment and typical wastes (e.g., spent ion exchange resins from reactor water demineralizers and reactor components) from power reactors. For details, the reader is referred to Dayal and Reardon (1992), Jefferies (1990), Gruhlke et al. (1986), Kunz (1985), Martin (1986), Cline et al. (1985), and Impell Corporation (1985). Research facility and pharmaceutical wastes may contain organic forms of ^{14}C, but it would be impossible to generalize on the adsorption potential of diverse organic molecules onto cement and concrete. The specific organic species would need to be identified and then studied in the laboratory.

Freshly hardened cement paste and concrete both remove large amounts of inorganic carbon from aqueous solutions. Serne et al. (1992), Allard et al. (1981), Dayal and Klein (1988), Hietanen et al. (1985), and Bayliss et al. (1988) show almost complete removal of ^{14}C added as bicarbonate or carbonate to waters contacting cementitious materials. The mechanism cited by all researchers is the precipitation of calcite ($CaCO_3$) within the pores of the cement or on the surfaces of the test specimens immersed in the water. The micro-environment near the cement surface and within the internal pores is very basic and saturated with calcium ions from the dissolution of portlandite [$Ca(OH)_2$]. At pH values above 12, calcite is more insoluble than portlandite and any carbonate molecules present in the solution will combine with the enriched calcium to form a carbonate precipitate. During cement Environments I and II, there is an excess of portlandite present in the hydrated cement that will readily dissolve and maintain high pH conditions and calcium concentrations. Under most low water flow conditions, it takes many hundreds to thousands of years before the portlandite solid is exhausted (all dissolved away) (Haworth et al. 1989, 1990). During this period, there is a net precipitation reaction occurring that will remove a significant mass of the inorganic carbon present as dissolved aqueous species. Dayal and Reardon (1992) also describe how the C-S-H and some of the other cement weathering products can also react with dissolved inorganic carbon species to form insoluble calcite.

The distribution ratio for inorganic ^{14}C is dependent upon how much activity is introduced into the test vessel used for the adsorption measurement. With essentially complete removal, the K_d can be quite large if the investigator starts with a convenient amount of radioactivity in hopes of making their analysis of ^{14}C by liquid scintillation counting easy. Typical K_d values reported in Allard et al.(1981), Bayliss et al. (1988), and Hietanen et al. (1985) are >100 to 10,000 ml/g.

Bradbury and Sarott (1995) present a conceptual model that produces an effective K_d that is the ratio of the total inactive carbonate in the cement divided by the amount of inactive carbonate in the pore water which is controlled by the solubility of calcite. The distribution of the radioactive carbon is thus exactly the same as the stable inorganic carbonate in the system regardless of the starting inventory of radioactive carbon. For convenience, preferred K_d values are listed in Table 5.1 because the necessary data on stable inorganic carbonate to generate the required ratio is seldom on hand. The values of 500 and 100 ml/g for cement/concrete Environments I and II were chosen as conservative estimates.

5.3.3 Chlorine (^{36}Cl)

Only two studies were identified that allow the calculation of a distribution ratio for the chloride ion (Cl^-). Sarott et al. (1992) performed diffusion experiments using cement discs and stable chloride solution concentrations between 3×10^{-5} and 3×10^{-7} M total dissolved chloride. Using the approach of Atkinson and Nickerson (1988) (see description in

Appendix E), Sarott et al. (1992) calculated a distribution ratio of 25 ml/g. It is not clear whether the chloride is sorbing or being incorporated into a weathering product via coprecipitation. The cement used for the measurements was a French sulfate-resistant cement similar to many Type III Portland cements used in the United States. If chloride concentration of the pore water is much lower or much higher than the concentrations studied, it is difficult to predict whether the measured K_d would be similar. Johnston and Wilmot (1992) also show that the diffusion of ^{36}Cl through cement and cement-silica fume grout disks (6 mm thick) is slower that ^{3}H. These data qualitatively show that ^{36}Cl may interact (adsorbs) with cements.

Kato and Yanase (1993) measured the adsorption of chloride onto cement powder (<0.35-mm particle size) using cement equilibrated water (pH = 11) over a short contact time of 24 hours. The K_d value measured for chloride was 0.8 ml/g.

Given the scarcity of measurements for the adsorption of chloride, it would seem prudent to use conservative K_d values for initial PA calculations for the given scenario with the ^{36}Cl inventory. These calculations may then be compared to a second iteration of performance calculations that could be based on K_d values for ^{36}Cl of 25 ml/g from Sarott et al. (1992) for cement Environments I and II and an assumed default value of 2.5 ml/g for Environment III.

More work is needed to determine whether chloride reacts with all cements in a fashion that can be represented by a distribution ratio. Several investigators have found that iodine in the iodide (I^-) form does interact with hardened cement paste (see next section). Thus it is reasonable to assume that chloride also may react.

5.3.4 Iodine (^{129}I)

There have been many studies on the incorporation of iodide (I^-) and iodate (IO_3^-) species into cement and adsorption studies of these species onto crushed cement and concrete. The results of all these studies are in agreement in that there is some interaction between the cement paste and the iodine. The iodine species, in fact, appears to associate with cement paste more strongly than the dissolved cesium ion (Cs^+).

Allard et al. (1984) and Hoglund et al. (1985) present batch adsorption data on iodine, as I^-, onto seven types of concretes. The concretes included two ordinary Portland cements (OPCs), blast furnace slag (BFS), sulfate resistant, high alumina, silica fume, and fly ash cements. All of the concretes used quartz sand ballast (0.1 to 0.3 mm). The typical mix was ~50 percent sand, ~32 percent cement, and ~18 percent water. The specimens were cured under CO_2-free water for over a year prior to being disaggregated to 0.09 to 0.125 mm and used in batch adsorption tests. The authors performed complete chemical analyses on the pore waters within the concretes prior to starting the adsorption tests. Simulated pore waters were prepared and each disaggregated concrete sample was pre-equilibrated with two batches of the pore water over a three-week period before small aliquots of radioiodide tracer (~2×10^{-9} M ^{125}I) were added. The batch adsorption tests lasted for up to six months with small aliquots of solution removed periodically for gamma energy analysis and pH measurement. The solid-to-solution ratio used in the tests was 0.9 g:45 ml. The phases were separated by centrifugation at 1700 rpm for 30 minutes prior to sampling the small aliquots of solution. The K_d value for iodide increased slowly for the first several months, and then remained steady for the remainder of the six-month test. The increase with time may reflect slow diffusion of the iodide species into the concrete particles. Iodide K_d values ranged from 25 to 130 ml/g with no obvious trend between tests that used "fresher" pore water with higher concentrations of alkali metals versus those that used "older" pore water with lower concentrations of alkali metals but higher concentrations of dissolved calcium. There was a slight increase in the K_d value for the standard OPC blends over blends that contained the other additives.

Atkins et al. (1988) and Atkins and Glasser (1990) generated various cement specimens that used either iodide (I^-)- or iodate (IO_3^-)-laden waters. After curing for up to 300 days, the pore fluid was squeezed out as a function of time and the amount of iodine measured. The iodine remained as the iodide species, and as much as 98 percent and 77 percent of the iodide was removed from solution for OPC and BFS cement, respectively. The removal of iodate was even greater for both cement blends. The authors of these studies believe that the iodate was reduced to iodide in the BFS cement which contains significant amounts of reduced sulfur species in its pore waters. They speculated that the iodine species may substitute for sulfate anions in cement reaction products, such as calcium aluminomonosulfate (Af_m) and ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$, ($AF_t$)]. Adsorption tests show that calcium aluminomonosulfate can adsorb more iodide than ettringite (~30 percent versus 8 percent). Neither solid, however, appears to adsorb the chloride anion.

Atkins et al. (1988) and Atkins and Glasser (1990) also performed adsorption tests on individual cement reaction products, such as portlandite [$Ca(OH)_2$], hydrotalcite [nominally $4CaO \cdot Al_2O_3 \cdot SO_3 \cdot 12H_2O$ ($M_{4\text{-}6}AH_{10\text{-}13}$)], and C-S-H. Small quantities of crushed solid (0.2 g) were contacted with 40 ml of solution containing 5 x 10^{-4} M iodide or iodate. Neither portlandite or hydrotalcite adsorbed much of the iodine. Hydrotalcite adsorbed less than 20 percent of the iodine at pH values between 10 and 13. There was a slight increase in adsorption of iodate versus that for iodide. The C-S-H adsorbed less than 5 percent of the dissolved iodide, but adsorbed 88 percent of the iodate. This would yield a K_d value of ~1500 ml/g for iodate. It thus appears that the C-S-H may have a high affinity for oxyanions, such as IO_3^-.

Atkinson and Nickerson (1988) found that the adsorption of iodide onto cement is very dependent upon iodide concentrations. At low concentrations (10^{-8} M), the K_d value can be as high as 1000 ml/g. At high iodide concentrations (10^{-2} M), the K_d value decreases to 1.4 ml/g. The observed adsorption appears to be reversible. Atkinson and Nickerson suggest that iodide is adsorbed by the cement paste (C-S-H) as opposed to the weathering product or ballast phases.

Hietanen et al. (1985) performed adsorption tests on crushed concrete that used sand ballast on small slabs 20 x 20 x 10 mm in size. The tests using crushed materials were conducted for a contact time of seven days at a solid-to-solution ratio of 10 g:100 ml. The phases were separated by centrifugation followed by filtration through 0.45-µm filters. The slabs were contacted for 30 days at a solid-to-solution ratio of 10 g:10 ml. Two simulated waters were used. One solution represented a "fresh" cement leachate with higher concentrations of dissolved sodium and potassium than that of calcium. The other solution represented a "more aged" cement pore fluid where the concentration of dissolved calcium was greater than those of sodium and potassium. All experiments were run at pH=12.5. The K_d values calculated from these tests were 2.5 ± 0.2 and 7.7 ± 0.1 ml/g for the fresh and aged pore waters, respectively. Hietanen et al. recommend that the K_d values should be converted to a surface area basis prior to being used in transport calculations. The contact times used for the tests by Hietanen et al. were shorter than many of those used in other published studies, which might account for the lower K_d values.

Barnes et al. (1982), Clark (1977), and Kalinin et al. (1983) present the results of studies where large concentrations of insoluble iodide-containing salts are solidified into cement and then leached. It may be possible to derive a K_d value using the approach of Atkinson and Nickerson (1988) described in Appendix E, but the high loadings (up to 50 percent by weight) and exotic forms, such as barium and lead iodates, would likely be affected by solubility processes that may make the data less relevant to the pursuit of adsorption values.

5.3.5 Lanthanides

Only one reference, Kato and Yanase (1993), was found that discusses the adsorption of lanthanide elements onto cement. Kato and Yanase (1993) measured the adsorption of europium onto cement powder (<0.35-mm particle size) using cement equilibrated water (pH = 11) over a short contact time of 24 hours. The K_d measured for europium was 2400 ml/g, while that determined for americium was 2000 ml/g.

Given the shortage of adsorption data for lanthanide elements and the similarity in the chemical behavior of lanthanides and trivalent actinides, the reader is referred to the discussion in Section 5.3.1 for the adsorption potential for americium. It is appropriate to consider the one citation for europium along with the data available for americium, another trivalent element, which should have adsorption properties analogous to the those of the lanthanide elements.

5.3.6 Nickel

Three studies (Hietanen et al. 1984, Kato and Yanase 1993, and Pilkington and Stone 1990) were found that include adsorption data for nickel onto cement and concrete specimens. The variation of adsorption potential indicated by these studies could be resolved from information on the cement type or composition of the cement pore fluid. The adsorption of nickel measured in all three studies is fairly high with the ranges of K_d values being 500 to 3000 ml/g [Hietanen et al. (1984)], 1500 ml/g [Kato and Yanase (1993)], and 500 to 3000 ml/g [Pilkington and Stone (1990)]. There is no clear distinction as to whether the C-S-H or the ballast materials are the preferred phases controlling the adsorption of nickel. At present, the values chosen by Bradbury and Sarott (1995), which are 100 ml/g for cement Environments I and II regardless of redox state and an assumed default value of 10 ml/g for Environment III, were selected for the database.

5.3.7 Niobium

Only one reference (Pilkington and Stone 1990) was identified, in which the adsorption of niobium onto cement was investigated. The experiments appear to be fraught with problems in keeping niobium stable in solution. The niobium adsorption measurements used crushed cement (0.25-mm to 1-mm particle size) that was made from a mix of 10 parts pulverized fuel ash and 1 part OPC. The water-to-solids mix ratio was 0.45:1. Niobium was introduced to the cement-equilibrated water by placing solid Nb_2O_5 into the cement-equilibrated water and allowing it to dissolve for 30 days. At this time, the slurry was centrifuged and filtered through a 0.45-µm membrane. The solution was diluted by an unspecified amount with additional cement equilibrated water, and aliquots of solution added to crushed cement at six different solution-to-solid ratios varying from 25:1 to 200:1. After contact times of one and two months in a controlled atmosphere chamber under anoxic conditions and devoid of CO_2, the mixtures were centrifuged and the separated solutions filtered through 25,000 molecular weight (MW) Amicon(1) membrane cones. The concentrations of niobium in the filtrates were measured by inductively coupled plasma emission spectroscopy. The initial composition given by Pilkington and Stone for the cement-equilibrated water is listed in Table 5.2.

Table 5.2 Composition of the cement-equilibrated water used by Pilkington and Stone (1990) for niobium adsorption measurements at pH 11.8

Constituent	Concentration
	—mg/l—
Al	9
Ca	37
K	120
Na	30
Si	7
Cl	8
SO_4	250
CO_3	24

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(1) Amicon Corporation, Lexington, Massachusetts. These membranes have an equivalent pore size of approximately 1.8 nm (18Å).

The starting concentration of 5.3 x 10^{-3} M niobium used by Pilkington and Stone (1990) seems rather high for a solution being used in adsorption measurements. Before filtration, the loss of niobium from solution in blank tubes containing no crushed cement was almost as much as the loss of niobium after one month in tubes with cement. Therefore, if a correction for niobium adsorption is applied by the container walls, the K_d value of niobium on crushed cement should be approximately zero. If no corrections are applied to the measurements, the K_d for unfiltered solution samples varies from 390 to 6,000 ml/g. After two months of contact time, the niobium concentrations for the unfiltered solutions from tubes containing cement appeared to be slightly less than those for the blank tubes. For the two-month samples, the K_d values varied from 350 to 3500 ml/g depending upon whether corrections were made for adsorption by the container walls.

The concentrations of niobium in the solution samples after filtration through 25,000 MW membranes were negligible. Based on the concentrations measured for the filtered solutions, the K_d values ranged from 11 to 69,000 ml/g with blank-container corrections and from 500 to 120,000 ml/g without blank-container corrections. It appears that niobium is very unstable in solution and was present as dispersed colloids or sols awaiting coagulation into precipitating agglomerates.

At present, we will defer to the values chosen by Bradbury and Sarott (1995) as 1000 ml/g for cement Environments I and II regardless of Eh conditions for niobium, and a value of 100 ml/g for Environment III.

5.3.8 Neptunium

Two references (Allard et al. 1984 and Hoglund et al. 1985) containing data on the adsorption of neptunium onto cement and concrete were identified. Both references report the same studies completed in Sweden in the mid 1980s. Batch adsorption tests were performed on seven types of concrete and a few specimens of ~70-year-old concrete using simulated cement pore waters. The concretes had ~50 percent quartz sand aggregate, ~32 percent cement and additives, and 18 percent by weight water. The laboratory specimens were cured in water for one year prior to being crushed (0.1 to 0.3 mm) and used in adsorption tests. A combination of ^{237}Np and ^{235}Np was used in simulated pore waters with pH values above 12.5. The starting concentration of dissolved neptunium was 1.9 x 10^{-7} M. Based on information presented in these reports, we infer that the neptunium tracer was in the pentavalent state (Np^{V}) at the start of the adsorption tests. The distribution ratio for neptunium was monitored from one day to up to one year. The K_d values reached steady state after 50-70 days depending on the compositions of concrete and pore water used in the tests.

The range in K_d values reported by Allard et al. (1984) and Hoglund et al. (1985) was 1500 to 9500 ml/g. There was no clear trend in the K_d values for neptunium as a function of type of cement or the composition of the simulated pore waters. The two highest K_d values were measured for the 70-year-old concrete samples contacting "aged" pore water having concentrations of dissolved sodium and potassium that are less than those in the "fresh" pore water. Aside from these two tests, the K_d values for neptunium were generally always lower than the K_d values for americium, similar to the K_d values for thorium, and higher than those for plutonium and uranium for the same concrete/pore water combinations.

There was no evidence that redox conditions were a key variable in the neptunium adsorption tests. Several of the test specimens contained BFS which is a reductant. Although no direct measurements of Eh were presented by the authors, other researchers who have monitored Eh generally find that systems with BFS yield highly reducing redox conditions. Given the known large decrease in neptunium solubility upon reducing Np^{V} to Np^{IV}, it is curious that there was no obvious change in the measured K_d values for concretes containing BFS.

Based on the limited available data, minimum K_d values of 2000 and 5000 ml/g were selected for neptunium under oxidizing and reducing conditions, respectively, for Environments I and II. This is in contrast to Bradbury and Sarott (1995) who chose 5000 ml/g for the K_d of neptunium under both redox states. Following the convention of Bradbury and Sarott (1995), K_d values for neptunium for Environment III were selected as one tenth of the values for Environments I and II.

5.3.9 Plutonium

Allard et al. (1984) and Hoglund et al. (1985) present adsorption data for plutonium onto seven different concretes. In almost all of the tests, plutonium adsorption was equal to or slightly less than neptunium adsorption and always less than americium adsorption. The authors do not specify which valence state of plutonium was used to spike the simulated pore waters or suggest which valence state of plutonium existed in solution once the tests were underway. The K_d values measured for concretes specimens that contained BFS were not greater than those for concretes that did not contain known reducing agents. The plutonium distribution ratio ranged from 1000 to 12,000 ml/g. The only trend in the variation was a weak correlation between decreasing K_d values with increasing pH in the equilibrating pore waters.

Jakubick et al. (1987) used "pie wedge" pieces (75 x 75 x 300 mm) and thin square slabs (40 x 40 x 2 mm) of four different types of concrete in contact with a dilute nitric acid solution that contained 1.3×10^{-5} M plutonium. After 66 hours of contact, the specimens were removed from the solutions and characterized by autoradiography in conjunction with mineralogical analysis. The solution was analyzed for pH and radionuclide content to calculate the distribution ratio. The K_d for plutonium varied from 390 to 17,000 ml/g and was correlated with the type of concrete. The low K_d value was measured in a test where the concrete contained silica fume and less Portland cement, while the high value was determined for a concrete that contained only Portland cement and aggregate. The autoradiographs show that plutonium associates much more preferentially with the C-S-H than with the carbonate and gneissic aggregate. The plutonium showed no association with the quartz aggregate. In high-density concrete that contained iron-oxide containing aggregates, plutonium showed more association with the magnetite (Fe_3O_4) aggregate than with other iron rich aggregates, such as hematite (Fe_2O_3) and specularite. Based on the high initial concentration of dissolved plutonium and the unrealistic nature of the solution (i.e., dilute nitric acid), it is likely that these K_d values for plutonium are not very representative of LLW disposal site conditions.

Some studies (e.g., Serne et al. 1992, Flambard et al. 1985, Nomine and Billon 1989) are available where the leaching of plutonium from cement waste forms has been measured. The results consistently show that plutonium leaches very slowly from the cement compared to many other radionuclides. Most researchers attribute the slow leaching to the low solubility of plutonium in high pH solutions.

From the above observations, we have elected to concur with the recommendations of Bradbury and Sarott (1995) and have assigned a K_d value of 5000 ml/g for plutonium in either oxidizing or reducing conditions for cement Environments I and II and, as assumed default, a value of 500 ml/g for the Environment III condition.

5.3.10 Radium

Bayliss et al. (1988, 1989) and Berry et al. (1991) are interrelated studies that address the adsorption of radium in cementitious environments. Two types of concrete, a sulfate resistant Portland cement (SRPC) blend and a BFS/OPC mix were used in the studies. The exact mix for the SRPC was 9:19:4.5 parts of sulfate resistant cement, fine limestone aggregate, and water, respectively. The BFS/OPC was 7.2:1.8:19:4.5 parts of slag, Portland cement, fine limestone aggregate, and water, respectively. The concretes were cured for 28 days and then crushed to a particle size between 250 and 500 μm. Each concrete was contacted with a simulated pore water that contained many of the major elements observed in actual pore water, such as dissolved sodium, calcium, aluminum, silica, carbonate, and hydroxide. The SRPC pore water had a higher pH (12.2-12.6 versus 11.8) and higher concentration of dissolved calcium (270 versus 90 ppm) than the BFS/OPC pore water. The BFS/OPC pore fluid had higher concentrations of dissolved sodium, aluminum, silica, and carbonate.

The radium adsorption measurements were performed in a controlled atmosphere chamber under nitrogen gas. A 40-ml volume of the appropriate simulated pore water was placed in a centrifuge tube and ^{226}Ra tracer in HCl solution was added at one of five concentrations between 10^{-11} and 10^{-7} M. After one day of equilibration, the pH and Eh were measured and

1 g of crushed concrete was then added. The tubes were then gently shaken and sampled at set intervals. A small aliquot (~0.5 ml) was removed and either analyzed directly for radium using gamma energy analysis or filtered through two different pore size membranes prior to analysis. Because the measured radium concentrations did not differ between the three techniques for separating the effluent solution from the solids, the authors concluded that there was no formation of colloidal-size particles of radium. After 20 days of contact, the radium activity reached steady values in the solutions. Blank tubes containing radium-spiked solution and no concrete indicated that there was no radium adsorption by the container walls. The steady state K_d values for the two concrete types at the five radium starting concentrations are shown in Table 5.3.

The results suggest that radium adsorbs onto concretes that contain BFS cement more strongly than onto concrete made with sulfate-resistant cement. There is also a trend in the measured K_d values to increase as the total amount of radium present in the test container is reduced. The authors suggest that the former trend may reflect the formation of very insoluble RaS, but no corroborating data are presented, such as measured Eh values. In our opinion, the trend more likely is caused by the very high surface area exhibited by BFS and/or differences in solution chemistry, such as lower calcium concentrations in BFS/OPC pore water. The reduction in K_d values as the initial radium concentrations increase suggests that non-linear adsorption processes could be the binding mechanism for radium removal from solution. Such an argument is presented by Berry et al. (1991).

We do not believe that radium concentrations greater than 10^{-9} M (2.2×10^5 pCi/l) will ever exist in leachates from LLW disposal units and thus we selected a K_d value for radium of 100 ml/g as applicable to all redox conditions for cement Environments I and II. For Environment III, where the assumed default value is equal to one-tenth of those values selected for Environments II, we have decided to not reduce the value and list a K_d of 100 ml/g for radium, given the high K_d values found for radium adsorption onto most geologic materials (see Ames and Rai 1978).

5.3.11 Strontium

Jakubick et al. (1987) developed strontium adsorption isotherms for slab- and pie-wedge shaped pieces of four types of concrete immersed in two types of Canadian ground waters representative of deep geologic repository environments. The four concretes were normal density, normal density with Class F fly ash, high density, and high density with silica fume. The composition details for these concretes are shown in Table 5.4. The two ground-water compositions represented the Standard Canadian Shield Saline Solution (SCSSS) and a more dilute solution (WN-1). Table 5.5 gives the initial

Table 5.3 Distribution ratios (K_ds) for radium onto concretes reported by Bayliss et al. (1988, 1989) and Berry et al. (1991)

Initial radium concentration (M)	Concrete types	
	SRPC	OPC/BFS
	ml/g	
10^{-11}	100±10	>1800
10^{-10}	530±110	1600±100
10^{-9}	100±15	860±140
10^{-8}	50±10	900±140
10^{-7}	55±7	1500±200

Table 5.4 Compositions of concretes used for adsorption measurements by Jakubick et al. (1987)

Concrete composition	Normal density	Normal density with fly ash	High density	High density with silica fume
	Volume %			
Coarse Aggregate	38.4	43.3	40.4	40.7
Fine Aggregate	30.5	30.0	27.3	27.5
Fly Ash	0.0	0.3	0.0	0.0
Silica Fume	0.0	0.0	0.0	3.7
Cement	12.1	8.6	12.9	10.4
Water	15.6	14.1	15.0	11.4
Voids	3.4	3.4	4.4	6.3

Table 5.5 Chemical composition of Canadian ground-water solutions used for adsorption measurements by Jakubick et al. (1987) (mg/l)

Constituent	Ground water SCSSS	Ground water WN-1
	mg/l	
Ca	14,700	2,125
Na	5,080	2,000
Mg	200	125
NO_3	48	28
Cl	33,800	6,380
SO_4	785	5,077

compositions of the ground waters prior to interaction with the concrete specimens. The concrete specimens were pre-equilibrated in one of these waters for three days. Fresh samples of the appropriate ground water spiked with a set amount of ^{85}Sr tracer were then added to the concrete samples in a plastic bag in a ratio of 90 to 170 g of concrete to 25 ml of spiked, simulated ground water. The initial concentrations of dissolved strontium ranged from 2 x 10^{-6} M to 1 x 10^{-2} M.

The rate of strontium adsorption was rapid over the first 24 hours and then decreased thereafter. The strontium adsorption isotherm was very linear for all four concretes and both water compositions. After 7 days of contact, the pH of the waters ranged from 9.8 to 10.4 for the SCSSS water and 9.3 to 11.3 for the WN-1 water. The lowest pH was always measured in the experiments that involved the concrete containing silica fume. The strontium K_d values measured for these systems were 0.8 and 1.6 for the high density and normal density concretes for the SCSSS water, respectively, and 1.3 to 1.9 and

~3 ml/g for the high density and normal density concretes for the WN-1 water, respectively. The slightly lower K_d for the SCSSS water likely reflects lower adsorption caused by the competing ions in this high ionic strength solution.

Hietanen et al. (1985) completed strontium adsorption tests on concrete and sand aggregate used in the concrete. They used two ground-water compositions. One water had approximately the same dissolved salts content as the WN-1 solution used by Jakubick et al. (1987), and the other was a very dilute sodium-calcium-bicarbonate-chloride-sulfate water representative of a water from a Finnish shallow aquifer (see Table 5.6 for details). The batch adsorption tests were performed by placing 10 g of crushed concrete into a tube and adding 100 ml of the appropriate ground-water solution that had been spiked with trace amounts of radionuclides. After 7 days, the solution was centrifuged and filtered through 0.45-μm filters, and the ^{85}Sr measured by gamma energy analysis. The K_d results are shown in Table 5.7. The results indicate that the adsorption of strontium is higher on the concrete than on the aggregate itself when contacted with cement-equilibrated waters. Adsorption is lower in Ground Water Composition A resulting from the higher concentrations of dissolved calcium and sodium that compete with the dissolved strontium for the available adsorption sites. For aggregate contacting "normal" ground waters that have not dissolved readily soluble alkali metals and calcium from cement, strontium adsorption can be significant as shown by the last value in Table 5.7.

Atkinson and Nickerson (1988) conducted a variety of tests on cement using dissolved strontium and strontium radiotracers. They used classical batch adsorption tests on crushed cement, which was sieved to get various ranges of particle sizes, with cement equilibrated waters (pH=12.5) for up to 147 days of contact time. Atkinson and Nickerson observed the K_d values for strontium to vary between 3 and 5 ml/g. Results of their studies indicate the following conclusions:

- Strontium interacts with cement more strongly than cesium.
- Sorption is independent of crushed cement particle size and to the liquid-to-solid ratio used in the tests.
- Over the range of concentrations of dissolved strontium of 10^{-7} to 10^{-2} M, the adsorption isotherm is linear and reversible (i.e., K_d desorption is equal to K_d adsorption).
- Strontium adsorption does show some time dependency in that the K_d increases slightly over long time periods (at least 150 days), which might reflect the slow substitution of strontium for calcium into the C-S-H.

Ewart et al. (1985) report some K_d values for strontium with cement and concrete as a function of the initial concentrations of dissolved strontium. Their measured K_d values for strontium ranged between 1 and 4 ml/g. Their results appeared to be independent of whether the sorbing solid was pure hardened cement paste or concrete. The final calculated K_ds also varied very little with respect to the initial concentrations of dissolved strontium used in the experiments.

Kato and Yanase (1993) measured the adsorption of several species onto cement powder (<0.35-mm particle size) using a cement equilibrated water (pH = 11) over a short contact time of 24 hours. The K_d value measured for strontium was 56 ml/g, which was the lowest value that they determined for any cation, including the K_d for calcium of 310 ml/g. Their value for the K_d of strontium is higher by about an order of magnitude than the other K_d values reported for strontium. We have elected to disregard this high value, because the information given in Kato and Yanase (1993) is insufficient to evaluate the starting concentration of dissolved strontium and the exact nature of the cement powder used in their measurements.

Results from all of the studies listed above, excepting those from Kato and Yanase (1993), are consistent and suggest that the strontium K_d for cement and concrete should range between 1 to 5 ml/g. The chemical composition of the water in contact with the cement or concrete seems to have a small effect. The presence of high total dissolved salts in contact with very fresh cement, which may compete with strontium for adsorption sites, may somewhat lower the K_d for strontium.

Table 5.6 Ground-water compositions used and measured by Hietanen et al. (1985)

Species	Ground water	Composition A	Ground water	Composition B
pH	7.3	12.5	7.0	12.5
		mg/l		
Na	2,200	1,810	31	78
K	21	141	3	78
Ca	600	100	13	460
Mg	260	<0.1	5	<0.1
Cl	5,200	NM(a)	58	NM
SO_4	570	NM	44	NM
HCO_3	83	NM	61	NM

(a) NM ≡ not measured.

Table 5.7 Strontium K_d values determined by Hietanen et al. (1985)

Ground water/solid phase matrix	K_d (ml/g)
Ground Water Composition A and Concrete	0.96 ± 0.06
Ground Water Composition A and Aggregate with Concrete	0.04 ± 0.03
Ground Water Composition A and Aggregate	0.72 ± 0.08
Ground Water Composition B and Concrete	4.1 ± 0.1
Ground Water Composition B and Aggregate with Concrete	0.6 ± 0.1
Ground Water Composition B and Aggregate	25 ± 2

Thus, K_d values of 1 and 3 ml/g have been selected for cement Environments I and II, respectively. For Environment III, where the cement has significantly weathered to leave behind silica-rich phases, a K_d value of 3 was selected as a conservative choice in case the ionic strength of the water contacting the cementitious material remains high.

5.3.12 Technetium

Bayliss et al. (1991) was the only study identified that involved the adsorption of technetium onto cement or concrete. The test system used for the adsorption experiments was set up in anoxic glove boxes and regulated using 0.05 M of sodium dithionite to assure highly reducing conditions. The cement was OPC with limestone flour used as an "aggregate." After hardening and curing, the cement material was crushed and sieved to yield 250-µm to 500-µm sized particles. Adsorption measurements were made using cement equilibrated and saline (1.5 M NaCl) cement equilibrated waters that were generated by contacting water with crushed cement for 28 days at a ratio of 50:1 (water to crushed cement). Chemical compositions of these waters are listed in Table 5.8.

Table 5.8 Composition of cement equilibrated waters used by Bayliss et al. (1991)

Species	Saline cement	Cement equilibrated
pH	12	12
	mg/l	
Ca	2,800	800
Na	34,500	20
Mg	36	<0.001
Cl	51,760	3
SO_4	3,840	1
CO_3	NM[(a)]	1.2

(a) NM = not measured.

Bayliss et al. (1991) used the special radiotracer ^{95m}Tc in these tests, because it emits a gamma ray whose energy can be conveniently measured. Very low amounts (10^{-11} to 10^{-10} M) of Tc^{IV} were added to the two waters that already contained 0.05 M sodium dithionite. Crushed cement (1 g) was added to the solutions after they had been equilibrated and filtered. The solid-to-solution ratio was not explicitly stated, but we believe it was 1 g:10 ml. The slurry was sampled weekly and a small amount of filtered solution analyzed by gamma energy analysis. During the first six weeks, there was continued decrease in the concentration of dissolved technetium. Some loss of dissolved technetium was observed in control experiments that did not contain any cement. The authors suggest that the technetium loss in the experiments involving no cement was due to adsorption of technetium on the container walls, and did not result from solubility driven precipitation. There was, however, no way to distinguish between these two processes. After seven weeks, the measured K_d values were 5000 ± 1200 ml/g for the cement equilibrated water and 2300 ± 1700 ml/g for the saline cement equilibrated water. The variability in the results was quite large. These data were obtained at measured Eh values of ~-230 to -260 mV and pH values between 12.6 and 13.1.

It is not certain if any of the commercial LLW disposal systems in the United States will result in highly reducing redox conditions comparable to those studied by Bayliss et al. (1991). The British are fairly certain that highly reducing conditions will exist in their deep repositories that are planned for the disposal of their intermediate and low-level radioactive waste. Therefore, the redox conditions used in investigations of radionuclide adsorption and solubility in the United Kingdom tend to be reducing. The behavior of technetium in ground-water systems is well known to be redox sensitive with the more oxidized form of technetium, Tc^{VI}, known to be much more soluble and mobile than Tc^{IV} in soil/water environments.

Several studies have been published on the leachability of technetium from cements having reducing and oxidizing characteristics. The leach rate of technetium was determined to be sensitive to whether reducing agents, such as BFS which contains reduced sulfur species, are present or not. The reader is referred to studies by Angus and Glasser (1985), Gilliam et al. (1989), Tallent et al. (1988), Brodda (1988), Serne (1990), and Serne et al. (1992). Studies also indicate that the leaching of Tc^{VI} from cement and grout waste forms, which are thought to contain no reducing agents, still appears to be slower than that of other anionic species, such as nitrate (Serne et al. 1992). Using the model of Atkinson and Nickerson (1988) to convert effective diffusion coefficient data to adsorption values, Tc^{VI} should therefore have a non-zero K_d value.

However, calculations based on the approach of Atkinson and Nickerson (1988) have not been attempted. Therefore, we will default to a K_d value of 0 for technetium for all three cement environments when oxidizing conditions are anticipated. This assumes Tc^{VI} is present under oxidizing conditions. For a cementitious system that is expected to be reducing and where technetium is present as Tc^{IV} or Tc^{III}, the K_d value selected for technetium for Environments I and II is 1000 ml/g and the value for Environment III is 100 ml/g following the arguments of Bradbury and Sarott (1995).

5.3.13 Thorium

Adsorption experiments for thorium onto cement and concrete have been conducted in Sweden and reported in Allard et al. (1984) and Hoglund et al. (1985). The thorium batch adsorption experiments used the same seven types of concretes listed above in the previous sections describing the results of adsorption studies for americium, neptunium, and plutonium. In addition, three samples of ~70-year-old concretes were also tested. Four simulated waters with pH values of~13, high concentrations of dissolved sodium and potassium, and moderate concentrations of dissolved calcium were used to represent pore fluids resulting from equilibration with different types of concretes. The waters were uniformly spiked with about 2×10^{-10} M natural thorium which included ^{232}Th and the addition of trace quantities of ^{234}Th. The ^{234}Th emits a gamma ray whose energy is readily measured which allows for cost-effective analysis.

Crushed samples of the concretes (0.09 to 0.125 mm in size) were contacted with the appropriate spiked cement pore water at a solid-to-solution ratio of 0.9 g:45 ml. At selected times, the equilibrated solutions were sampled and the resulting aliquots centrifuged. A small volume of each supernatant solution was then analyzed for ^{234}Th. The experiment was then continued by slowly shaking the containers in a CO_2-free controlled chamber. After several weeks, the measured K_d appeared to reach a steady-state value. The K_d values for thorium ranged from 2500 to 5500 ml/g depending on the type of concrete being studied. The thorium K_d values were consistently smaller than the K_d values for americium, essentially identical to those for neptunium and plutonium values for the same concrete types, and always significantly greater than the K_d values for uranium.

Given these results, a K_d value of 5000 ml/g was selected for thorium for Environments I and II under oxidizing and reducing conditions. This value is the same as those selected for lanthanides and plutonium under these cement physicochemical conditions. For Environment III, we use the assumed default convention (i.e., one-tenth of the value for Environment II) and selected a K_d of 500 ml/g for thorium.

5.3.14 Uranium

The Swedish studies by Allard et al. (1984) and Hoglund et al. (1985) also present the most data for the adsorption of uranium onto cements or concretes. Uranium was added as the oxidized form U^{VI} to the simulated cement pore waters. For the seven types of concretes and the weathered concretes, the K_d values for uranium ranged from 350 to 13,000 ml/g. The average K_d value was ~1000, and the median value was 1400 ml/g. Although the behavior of uranium in aqueous systems is known to be sensitive to redox conditions, there was no significant increase in the uranium K_d value measured in the experiments that used concrete containing BFS, an expected reductant.

Numerous investigators, such as Atkins et al. (1988), Atkins and Glasser (1992), Serne et al. (1989), and others, have studied the incorporation of U^{VI} into cementitious waste forms. Under these conditions, the release of uranium is reduced significantly over the release of many other potentially soluble contaminants. Atkins et al. (1988), Atkins and Glasser (1992), and Serne et al. (1989) describe plausible solubility- and adsorption-incorporation processes for U^{VI} into the C-S-H. As previously mentioned, it should be possible to use such leachate data to calculate K_d values using the approach of Atkinson and Nickerson (1988) (see discussion in Appendix E).

It should be adequate to consider the adsorption of uranium, in either of its +6 or +4 valence states, as being readily retarded within the pore waters of cements and concretes where high pH conditions, relatively high concentrations of dissolved calcium, and low concentrations of dissolved carbonate exist. For this reason, the K_d values selected for uranium on concrete and cement in Environments I and II are 1000 and 2000 ml/g for oxidizing and reducing conditions, respectively. For Environment III, assuming the one-tenth default convention, uranium K_d values of 100 and 200 ml/g are selected for oxidizing and reducing conditions, respectively.

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Appendix A

Approaches to Modeling Compositions of Cement Pore Fluids

Appendix A

Approaches to Modeling Compositions of Cement Pore Fluids

A literature review of modeling approaches and experimental studies pertaining to the composition and pH of pore water resulting from the dissolution of cement was completed as part of this study. This appendix describes the scope of the literature review and summarizes the literature pertaining to modeling methods used to calculate the compositions of cement pore fluids.

A.1 Scope of Literature Review

Titles of relevant published studies were identified from a computerized literature search completed by staff at the Hanford Technical Library located in Richland, Washington. The search included the Energy Science and Technology (U.S. Department of Energy), National Technical Information Service, INSPEC (Institution of Electrical Engineers), and Ei Compendex*Plus™ (EI, Inc.) databases available on the DIALOG® Information Retrieval Service (DIALOG Information Services, Inc. 1994). The search was constrained to journal articles and reports published in the ten years prior to January 1994. The search included the following string of criteria terms: (cement* or grout) and (aqueous or leach* or solution* or water* or groundwater* or model*) and (equilibri* or composition* or solubilit*), where the asterisk symbol signifies any additional characters. Abstracts listed in the output from the database search were reviewed and appropriate references identified for collection and detailed review.

Manual searches of relevant titles were also completed for several selected publications as part of the literature review. These sources typically contain a significant number of papers that pertain to the geochemistry of radioactive waste disposal or the chemistry of cement/water systems. These included searches of papers in following publications: Materials Research Society Symposium Proceedings for Scientific Basis for Nuclear Waste Management [Volume 1 (1978 meeting) through Volume XVI (1992 meeting)], *Cement and Concrete Research* (1981-1993), and *Radiochimica Acta* (1982-1993). Relevant papers were compiled from these sources and reviewed.

Information collected during the literature review pertaining to modeling approaches is summarized in the remaining sections of Appendix A. References dealing with experimental studies of cement/water interactions are summarized in Appendix B.

Three literature reviews published in the United Kingdom (UK), which conducts a substantial research and development program in the use of cementitious materials for radioactive waste disposal, are also particularly useful. These include reviews of studies published in the UK and the international community on speciation and solubility (Smith-Briggs 1992a,b,c), sorption (Berry 1992a,b,c), and colloid formation (Tipping and Higgo 1992a,b,c) relative to the release and transport of radionuclides in the near and far field. Each literature review was published as three reports, and each of the nine total reports contains a chapter on studies related to cement systems. The first report of each literature review summarizes studies funded by the UK Nirex and Department of the Environment (UK DoE) that pertain to the subject area. The second report contains an extensive bibliography, including reference citations and complete abstracts, of UK and international publications on the subject area. The third report compares the objectives and approaches used in studies funded by Nirex and UK DoE to those in related studies undertaken by the international community.

A.2 Studies by F. P. Glasser and Others at the University of Aberdeen

F. P. Glasser and co-investigators at the University of Aberdeen in Scotland are responsible for a significant amount of our knowledge on the chemistry and phase equilibria of the cement/water system. Their studies have included a wide range of experimental and modeling studies designed to increase our understanding of the chemical durability of hydrated cement and its constituent phases. Many of their laboratory studies are summarized in Appendix B and are the basis for their model development efforts. Their modeling studies include those by Glasser et al. (1987,1988), Atkins et al. (1992a,b; 1994), and Bennett et al. (1992).

Glasser et al. (1987) improved a previously developed, simplified chemical model for the solubility and compositional properties of calcium silicate hydrate gels in the system $CaO\text{-}SiO_2\text{-}H_2O$. The objective of the modeling approach was the prediction of the compositions of cement pore fluids. Their proposed compositional representation for the gel was given as

$$Ca_xH_{6-2x}Si_2O_7 \cdot zCa(OH)_2 \cdot nH_2O$$

where x and z represent the mole fractions of calcium in the "calcium silicate" and "calcium hydroxide" solid solution components, respectively. The range of applicability of the model was extended to the range 0.8 < (calcium/silicon) < 1.7. Revisions to the gel dissolution model included a more complete treatment of the effects of aqueous speciation of dissolved silica on the formation of the solid phase. The chemical equilibria controlling the compositions of pore fluids from 30-day calcium silicate hydrogel (C-S-H) were modeled. Because the solubility products and the free energies of formation for C-S-H both decrease with increasing solid calcium/silicon ratio, the modeling results suggested that C-S-H having high calcium/silicon ratios were more stable in aqueous solutions. The calcium hydroxide component was determined to control the chemistry of the equilibrium pore fluids as long as portlandite [$Ca(OH)_2$] is present to buffer the pore fluids. If portlandite is depleted via dissolution and/or reaction with blending agents, C-S-H will control the pH of the cement pore fluid.

Glasser et al. (1988) present a modeling approach for the prediction of phase equilibria in hydrated cement pastes and pore fluids for the ordinary Portland cement-blast furnace slag system. The approach uses the calculated phase distribution and associated solubility products to predict the aqueous chemistry of the system. As part of model development, phase relations in the system $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}MgO\text{-}H_2O$ were evaluated. The following phases were observed to occur in the composition range relevant to this cement-slag system: portlandite, gehlenite hydrate, a hydrotalcite-structured phase (nominally $6MgO \cdot Al_2O_3 \cdot (OH)_x \cdot yH_2O$), an AF_m-type$^{(1)}$ phase (nominally $4CaO \cdot Al_2O_3 \cdot SO_3 \cdot 12H_2O$), and a poorly crystallized C-S-H. Appropriate products were listed, including that for C-S-H from Glasser et al. (1987). The dissolution model used for C-S-H did not account for its incongruent dissolution behavior as did the approach developed by Berner (see Section A.4). The modeling approach of Glasser et al. (1988) required input of the chemical compositions of both the slag and cement and initial blending proportions to predict the equilibrium distribution between the five hydrates and calcium/silicon ratio of the C-S-H.

Atkins et al. (1992a,b)$^{(2)}$ and Bennett et al. (1992) developed a thermodynamic model to calculate the equilibrium phase distribution for Ordinary Portland Cement (OPC) and OPC-derived blends. The purpose of the model (a normative chemical model), as formulated as the computer code CEMCHEM, was to predict from an initial cement composition the compositions of the solid and aqueous phase in a mature cement paste at 25°C. The model considers cements as the simplified

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(1) When used in a cement formula "F" refers to the Fe_2 O_2 component in the cement phase. The iron content in some phases may be very low and thus be neglected in their chemical formula. The "m" subscript refers to mono-sulfate.

(2) Reference contains an extensive reference list (90 references).

CaO-Al_2O_3-SiO_2-SO_4-MgO-H_2O system. Using results from experimental studies of cement pastes and compatibility experiments conducted as part of this investigation and experiments reported by others in the literature, phase relations in the calcic portion of this system were determined for 25°C to complete the model. Six stable phase assemblages were identified in this study and encoded in CEMCHEM.

The code CEMCHEM (Atkins et al. 1992a,b; Bennett et al. 1992) may be used to model near field chemistry of cementitious systems after ground-water intrusion, and to serve as a precursor to computer codes such as MINTEQ, PHREEQE, EQ3/6, and MINEQL. The code CEMCHEM predicts the equilibrium phase distribution at 25°C, including mol% of each constituent hydrate phase, as a function of blending proportions based on the starting chemical composition for the OPC and blending agents. The range of applicability of CEMCHEM extends to 9:1 blast furnace slag-OPC and 2:3 fly ash-OPC blends. Atkins et al. (1992, Appendix 1) provides a description and FORTRAN source code listing of CEMCHEM. The code was validated by showing agreement between observed and predicted aqueous compositions for the compatibility experiments.

Additional objectives of the work of Atkins et al. (1992b) and Bennett et al. (1992) were to determine new equilibrium constants for cement relevant phases as upgrades to thermodynamic databases and to develop solubility models for cement phases that dissolve incongruently, such as the C-S-H. Atkins et al. measured the solubilities using the repeated dispersion/filtration technique of phases of interest synthesized in pure form. Solubility product (K_{sp}) values were determined for C_3AH_6 and AF_t.(1) A model for the congruent solubility of silica-containing hydrogarnets was developed using an ideal solid solution approach to represent the log K_{sp} values as a function of silicon content. Solubility data sets were used to assess K_{sp} values for the hydrotalcite and gehlenite hydrate (C_2ASH_8) which were assumed to dissolve congruently. A preliminary K_{sp} value was also calculated for tobermorite, whose solubility data sets indicated an approach to congruent dissolution. Atkins et al. (1992a,b) modified Berner's solubility model (see Section A.4) for C-S-H to better represent the strong incongruent dissolution behavior exhibited by these gels. Their results indicate that Berner's published C-S-H dissolution model may not work adequately for the complete range of expected alkali hydroxide concentrations. However, as noted by Atkins et al., this may not be a limitation if the system is essentially alkali free as a result of rapid leaching of the alkalies relative to calcium in the C-S-H.

Atkins et al. (1992a,b) and Bennett et al. (1992) used tabulated and derived solubility values to develop a thermodynamic database called CEMENT. The database is internally consistent with the CHEMVAL 4 speciation data set. CEMENT, which includes 17 solid phases, may be used for thermodynamic modeling of interactions of cement/ground-water systems with codes such as MINTEQ, PHREEQE, EQ3/6, and MINEQL. Atkins et al. also compared and contrasted prior thermodynamic databases for cement/ground-water related aqueous species and solids to the CHEMVAL, USGS, HATCHES, EQ3/6, and MINEQL/AU databases.

A.3 Studies by A. Haworth and Others at Harwell Laboratory

Investigators at Harwell Laboratory in Oxfordshire, England have also conducted an extensive research program on cement chemistry. These studies have included laboratory (see discussion in Appendix B of this report) and transport modeling efforts. Haworth et al. (1989, 1990) described the development of a model for simulating the degradation of cement in a repository for radioactive waste. The modeling was completed using the coupled chemistry/transport code CHEQMATE, which combines transport of dissolved species by diffusion and advection with chemical equilibria simulated with the geochemical code PHREEQE. To model the equilibria associated with cement/water interactions, a thermodynamic model

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(1) The subscript "t" when used in a cement formula refers to tri-sulfate.

for the solubility of the C-S-H phase based on that of Berner was implemented in CHEQMATE. The coupled chemistry/transport model was used to evaluate pH values of cement pore fluids as affected by different cement compositions and ground-water interactions.. The predicted trends were in broad agreement with results from accelerated leaching experiments. Results of both the modeling and experimental studies indicated that pulverized fuel ash/OPC may not be appropriate for maintaining high pH conditions in the near field of a radioactive waste repository.

A.4 Studies by U. R. Berner

The modeling studies by Berner (1987, 1988, 1990, 1992) have resulted in a model for simulation of the incongruent dissolution of the C-S-H. Berner (1987) described a calculational model that predicts the quantities of solid phases in hydrated cement. The model assumes complete hydration of the clinker minerals, and includes parameters describing the reactions between the cement and blending agents. The first step of the model is to calculate a mineralogical composition (i.e., clinker minerals) of the cement from an analysis of its initial oxide composition. This calculation was performed using the approach suggested by Bogue (1929). In the second step of the model, a set of hydration reactions is used to simulate the reaction of these clinker minerals with water. The suite of solids resulting from these calculated reactions represents the phase assemblage for the hydrated cement. Berner demonstrated the approach by calculating the phase assemblages for the hydration of six cement formulations. The model was tested by comparing the concentrations of dissolved calcium calculated from the predicted phase assemblages to concentrations measured in actual pore fluids.

Berner (1988) developed a model (Table A.1) for simulation of the incongruent dissolution of C-S-H, a major component of hydrated cement. The C-S-H dissolution is modeled as a mixture of two congruently soluble components. The model separates the dissolution of C-S-H into three calcium/silicon (*C/S*) composition regions.

Each component's activity in the solid state was obtained from published solubility data for C-S-H using the Gibbs-Duhem equation for nonideal mixtures. The solubilities of these components were represented as a function of *C/S* ratio of the C-S-H solid by a series of equations derived using this approach. The model components for C-S-H and associated solubility equations are listed in Table A.1 for each region of C-S-H composition.

The *C/S*-dependent log K_{sp} values for the C-S-H dissolution model components derived by Berner were included in the chemical equilibria code MINEQL/EIR. Berner demonstrated the application of his model by modeling the degradation of OPC in pure water and in carbonate-rich ground water.

Berner (1990, 1992) presented the model that he used to simulate the hydration of Portland cement. The discussions included details of his model as previously given in Berner (1987, 1988) for the model solids in the cement hydration model and the solubility model for the incongruent dissolution of the C-S-H, respectively. Berner's hydration model included the following model solids: C_3AH_6--C_3FH_6 (solid solution), $C_3A \cdot 3C\bar{S} \cdot 32H$ (ettringite), $C_3A \cdot 3C\bar{S} \cdot 12H$ (low sulfate, calciumaluminate-monosulfate), C_xSH_x ($x \leq 1.8$), CH (portlandite), and MH (brucite). The phases and their associated solubility equations used in Berner's incongruent dissolution model for C-S-H are given in Table A.1. Berner (1992) also described in detail the thermodynamic relationships, procedures, and compiled data from the literature that were used to derive the solubility equations in his C-S-H dissolution model. Results were presented for the application of this approach to modeling the degradation of two sulfate-resistant cements in pure water and a marl ground water.

A.5 Studies by A. R. Alcorn and Others

A. R. Alcorn and co-investigators (Alcorn et al. 1989, 1990, 1991; Alcorn and Christian-Frear 1992; Onofrei et al. 1992) have published a series of studies in which the geochemical reaction codes PHREEQE and EQ3NR/EQ6 were used to model cement/water reactions. Their conceptual model included the use of 14-Å tobermorite as a proxy for the C-S-H

Table A.1 Berner's model for the incongruent dissolution of C-S-H

Composition	Model components and associated solubility expressions	
$C/S = 0$	SiO_2	$\text{Log } K_{sp} = -2.70$
$0 < C/S \leq 1$	SiO_2	$\text{Log } K_{sp} = -2.04 + [0.792/(C/S - 1.2)]$
	CaH_2SiO_4	$\text{Log } K_{sp} = -8.16 - [(1 - C/S)/C/S] \times \{0.78 + [0.792/(C/S - 1.2)]\}$
$1 < C/S \leq 2.5$	$Ca(OH)_2$	$\text{Log } K_{sp} = -4.945 - [0.338/(C/S - 0.85)]$
	CaH_2SiO_4	$\text{Log } K_{sp} = -8.16$
$C/S > 2.5$	$Ca(OH)_2$	$\text{Log } K_{sp} = -5.15$
	CaH_2SiO_4	$\text{Log } K_{sp} = -8.16$

phase. Alcorn et al. (1989) used the codes PHREEQE and EQ3NR/EQ6 to investigate chemical alterations resulting from interactions of Canadian Shield ground water with cementitious grout that may be used in seals for a high-level radioactive waste (HLW) repository. The grout model was based on a simplified Type V Portland cement, consisting of the following components: CaO, SO_3, Al_2O_3, SiO_2, O_2, and H_2O. A normative calculation was performed to identify the assemblage of cement phases to be used for geochemical modeling. The assemblage included 14 Å-tobermorite ($Ca_5Si_6O_{17} \cdot 10.5H_2O$), hydrogarnet ($Ca_3Al_2O_6 \cdot 6H_2O$), and ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$]. The cement grout/ground-water reactions were modeled as chemically open and closed systems. The feasibility of using a computer code to calculate chemical equilibrium for this simplified grout model was initially tested using the PHREEQE code. Analysis of more detailed grout models was completed using the EQ3NR/EQ6 code. The modeling results indicated increases in porosity and permeability caused by the dissolution of cement phases and the precipitation of secondary minerals.

Alcorn and Christian-Frear (1992) and Alcorn et al. (1991) used the EQ3NR/EQ6 geochemical code to model chemical equilibria between Portland cement-based grout, ground water, and granitic host rock phases. The cement conceptual model used for the calculations assumed a bulk composition of an average Type V Portland cement as a starting point. The cement composition was modified by 1) neglecting certain less abundant components and recalculating the composition to 100%, and 2) assuming sufficient silica, as silica fume, was available to react with free CaO for enhanced longevity. The bulk cement composition was then apportioned into the following six phases associated with partially crystallized grout: 14-Å tobermorite (71.6 mol%) as a proxy for the C-S-H phase, hydrogarnet (12.5 mol%) as a proxy for the CAH phase, an Fe-bearing hydrogarnet (6.1 mol%), ettringite (1.6 mol%) as the sulfate phase, Fe-bearing ettringite (0.9 mol%), and portlandite (7.3 mol%). Rationale for these selections are provided in Alcorn and Christian-Frear (1992).

Two geochemical conceptual models were used for the EQ3NR/EQ6 modeling calculations. For initial scoping calculations, the modeling assumed an equal molar basis titration in which equal amounts of grout and rock phases were incrementally added to the ground water. The most abundant reaction products predicted using this conceptual model included zeolites, C-S-H (i.e., 14-Å tobermorite), CAH (i.e., hydrogarnet), iron oxide, and gypsum. Two identified zeolites, mesolite and gismondine, are calcium-aluminum zeolites. Minor secondary phases included clay (smectites) and carbonate minerals (mostly calcite). The second conceptual model was based on a relative rate basis titration in which known or assumed relative rates of reaction were applied to the dissolution reactions. The suite of reaction products predicted using this conceptual model was similar to results listed above for the equal molar basis titration model. Differences in the suite of secondary minerals included an absence of gypsum, CAH (i.e., hydrogarnet), and iron oxide; presence of quartz and microcline feldspar; and mesolite as the only zeolite phase. Alcorn and Christian-Frear indicated that the presence of fracture minerals in the starting mineral assemblage had only a small effect on the modeling results.

Alcorn and Christian-Frear (1992) and Alcorn et al. (1991) concluded from the modeling results that some grout and rock phases would dissolve and overall volume of the precipitated secondary phases would be larger than that of the material dissolved. The results indicated that chemical buffering of the fracture system in the grout seals by the granitic rock may be important in determining the long-term stability of grout seals and the resulting fracture mineral assemblage. The results also suggested that equilibrium would be approached with time based on the similarity between the predicted reaction products and those observed in naturally filled fractures. Although magnesium, ferrous iron, and alkali were neglected in the calculations as a simplification, their presence in the grout in minor or trace amounts may not necessarily be inconsequential. The presence of tobermorite in C-S-H and the implication of a low degree of disorder in C-S-H supported the investigators' selection of tobermorite as a proxy for C-S-H in the modeling analysis.

Because the degree of crystallinity of the C-S-H phase may be lower than that of the tobermorite proxy, Alcorn and Christian-Frear (1992) examined the effect of lowering the crystallinity of tobermorite by increasing its Gibbs free energy using thermodynamic data for the silica polymorph phases as an analog for lowering the degree of crystallinity. Based on a corresponding state approximation, the Gibbs free energy of tobermorite was increased by the percent difference in Gibbs free energy between the SiO_2 phases quartz and amorphous silica. This resulted in using a tobermorite phase with an effectively higher solubility for the modeling analysis to account for structural disorder in the C-S-H phase. Silica was considered a reasonable analog, because semi-amorphous SiO_2 probably exists in C-S-H, at least in the early stages of hydration, and the thermodynamic properties of SiO_2 polymorphic forms are well known. If Alcorn and Christian-Frear's estimate for Gibbs free energy for C-S-H was adjusted to a hydroxide standard state as used by Atkinson and coworkers rather than an oxide standard state, the investigator's Gibbs free energy value of 875 kJ would be comparable with Atkinson's estimate of 885 kJ.

The approach used by Alcorn et al. (1990) to estimate the longevity of Portland cement grout is similar to that described in Alcorn and Christian-Frear (1992). The conceptual model used a normative composition for the initial cement that contained only five phases: 14-Å tobermorite (77.7 mol%), hydrogarnet (13.3 mol%), Fe-bearing hydrogarnet (6.4 mol%), ettringite (1.7 mol%), and Fe-bearing ettringite (0.9 mol%).

Onofrei et al. (1992) summarized major findings from combined laboratory and modeling studies of the development and longevity of a specially developed high-performance cement-grout. Their paper included discussions of the development of reference high-performance grout, such as mix design; laboratory testing; field trials; and longevity studies, such as laboratory studies of superplasticizer sorption, leaching, hydraulic conductivity, and porosity, and numerical modeling. The brief modeling section was analogous to the modeling approach used and discussed by Alcorn and Christian-Frear (1992). Normative cement composition used for geochemical modeling by Onofrei et al. was identical to that listed in Alcorn et al. (1990).

A.6 Studies by E. J. Reardon

Reardon (1990) developed a chemical equilibria model to simulate reactions between water and hydrated cement compounds at 25°C. Ion activity coefficients were calculated using Pitzer's ion interaction model, which allows modeling at high solute concentrations. The model calculates the solubility of the C-S-H phase using a variable compositional model based on the treatment and solubility data of Gartner and Jennings (1987). Reardon also lists the interaction parameters, aqueous species, and solids, and associated thermochemical data used in the model. The quadratic equations representing the $(Ca/Si)_{C\text{-}S\text{-}H}$ ratio and log K_{sp} for C-S-H as a function of the $Ca^{2+}/H_4SiO_4^\circ$ (aq) activity ratio were also given. The capabilities of the model were demonstrated by simulating the effect of progressive additions of sulfuric acid to a cement paste.

Reardon (1992) presented a detailed discussion of issues associated with the prediction of the chemical composition of cement pore fluids. Problems and approaches to modeling sodium and potassium concentrations in cement pore fluids and C-S-H were the focus of most of the discussions. The importance of this issue results from the major influence sodium and potassium have on the hydroxide content, ionic strength, and pH of cement pore fluids, which in turn affect the solubility of cement phases. The lack of a thermodynamic model to describe the uptake of alkalis from pore fluid by C-S-H contributes to problems associated with simulation of alkali equilibria in cement-water systems. Approaches used to predict alkali behavior, such as that presented by Taylor (1987) are reviewed. Use of Taylor's approach in a chemical equilibrium model presented by Reardon (1990, 1992) resulted in compositions of cement pore fluids that were reasonable. The model developed by Reardon to predict equilibria in cement-water systems was described in detail in Reardon (1992) and previously in Reardon (1990). Equilibrium constants used in this model for aqueous speciation and solubility reactions were also given. As noted by Reardon (1992), the presence of alkalis is expected to be short lived in a ground-water environment, because their concentrations in pore fluids will be reduced due to advection and diffusion into the surrounding ground-water system.

Reardon (1990) also discussed limitations of his ion interaction model for simulating chemical equilibrium in the cement/water system. Many of these limitations are relevant to other approaches used to calculate cement/water equilibria. These limitations included the following:

- There was insufficient experimental data at that time to support application of this C-S-H solubility model at pH values greater than 12.5 due to NaOH and KOH in cement pore waters.
- The speciation used in the model for dissolved silica, which included $H_4SiO_4^\circ$ (aq), $H_3SiO_4^-$, and $H_2SiO_4^{2-}$, may not be adequate. Species $HSiO_4^{3-}$ and SiO_4^{4-} may also form at pH values greater than 13. Reardon did not include these latter aqueous species in the model due to controversy over their existence and the absence of ion interaction parameters.
- Simulation of dissolved potassium in high pH, cement pore fluids resulting from contact with high alkali cements was not possible because the adopted C-S-H solubility model did not allow for incorporation of potassium in gel structure and an absence of thermodynamic data for alkali silica reaction products.
- This model does not consider protonation reactions or ion sorption at the surfaces of the crystalline and amorphous phases of hydrated cement.
- Determination of chemical equilibria between pore water and all mineral phases is not possible for cementitious systems containing aggregate material of heterogeneous mineralogy.

A.7 Studies by Others

Bailey and Hampson (1982) investigated the chemistry of Portland cement pore fluid using a simple computer code to reinterpret available chemical analyses. The computer code was written in BASIC and used available data for complex ion formation and activity coefficients. Results were presented for the saturation state of a set of pore-fluid compositions as a function of time relative to the solubilities of gypsum, portlandite, and $Al(OH)_3$. The pore-fluid composition data were taken from the literature. The modeling results for pore-fluid compositions from equilibrations of approximately 0 to 40 min indicated that the pore fluids were slightly undersaturated to near equilibrium with respect to portlandite, and were highly to slightly oversaturated with respect to gypsum.

Moragues et al. (1988) modeled chemical equilibria associated with concrete pore solutions. These investigators found that calculated concentrations based on the equilibrium constants for $Ca(OH)_2$ and $CaSO_4$ did not match experimental results obtained from measurements of the concentrations of the dissolved ions. The inconsistency between the modeling and experimental values was attributed to elevated concentrations of the dissolved ions in the pore fluids. As an alternative modeling approach, the investigators used "apparent constants" calculated from measured solution concentrations instead of Debye-Huckel theory to correct for ionic strength. In addition, to achieve complete consistency between the modeling and experimental values, these investigators also had to include the $CaOH^+$ ion in their calculations.

Lundén and Andersson (1989) modeled the chemical equilibria resulting from the mixing of cement pore fluid and ground water in contact with cement solids and rock/fracture filling minerals. The equilibria were calculated using the PHREEQE computer code. The cement conceptual model was based on the two-component solid phase model of Berner. The model includes a solid phase mixture of $Ca(OH)_2$ and CaH_2SiO_4 in which the associated equilibrium solubility constants are separated into three regions depending on the CaO/SiO_2 ratio of the cement. The model used for the ground-water/rock system included the fissure-filling minerals, chlorite and laumontite. The chemical equilibria were calculated for cement pore fluid and ground water systems mixed in ratios of 0, 20, 40, 60, 80, and 100%. The investigators presented results for the degree of saturation of the resulting solutions relative to various mineral phases. The main mineral phases that were predicted to be oversaturated when the cement pore fluid initially mixed with ground water included calcite, hydroxyapatite, chlorite, and laumontite.

Criscenti and Serne (1990) used geochemical modeling to analyze the results from 150-day static leach tests of cylinders of Type III Portland cement in synthetic ground water. The modeling was completed using the MINTEQ computer code. The cement conceptual model was based on Berner's cement-hydration model which was used to calculate hydrated cement composition from dry cement composition. Berner's model indicated that ettringite, monosulfate, and hydrogarnet would coexist in the hydrated cement. Because monosulfate and hydrogarnet can combine to form ettringite, which the investigators considered a phase rule violation, the hydrated cement "equilibrium phase" assemblage was defined by removing hydrogarnet and redistributing the moles of calcium and aluminum between ettringite and monosulfate. The equilibrium phase assemblage consisted of, in decreasing number of moles, portlandite, $C_{1.5}$-S-$H_{1.5}$, monosulfate, brucite, C_3FH_6, NaOH, KOH, and ettringite. Because C-S-H has variable composition and dissolves incongruently, its thermodynamic properties cannot be readily represented by the reaction conventions used in the MINTEQ database. Criscenti and Serne therefore substituted afwillite [$Ca_3Si_2O_4(OH)_6$] for C-S-H in the phase assemblage representing the hydrated cement. Because the precipitation of calcite ($CaCO_3$) was observed in the leaching experiments, it was allowed to precipitate in MINTEQ calculations of the equilibria between the hydrated cement and synthetic ground water.

The modeling results by Criscenti and Serne (1990) indicated that the equilibrium was not reached in 150-day static leach tests. The calculated pH values and dissolved calcium concentrations were adequately predicted relative to those measured in the leachates. However, the concentrations of other major leachate constituents, such as dissolved aluminum, silica, and sulfate, were poorly predicted using this thermodynamic approach.

Gardiner et al. (1991) and Hinkebein and Gardiner (1990, 1991) modeled the geochemical stability of cement formulations for use as shaft liner and sealing components at the Yucca Mountain Site in Nevada, which is being characterized as a potential geologic repository for the disposal of HLW. The geochemical interactions of cementitious materials and water were modeled at 25°C using the EQ3NR/EQ6 computer code. The conceptual model used for the hydrated cement included 14-Å tobermorite, hydrogarnet, and ettringite as proxies for the C-S-H, CAH, and calcium sulfate phases, respectively. Three candidate cement formulations were modeled. The formulations included a high-silica ordinary Portland cement formulation (OPC-B), a low-silica ordinary Portland cement formulation (OPC-C), and a high-sulfate, high-silica expansive

Portland cement formulation (EPC-S). The water composition was that of ground water from Well J-13 at the Yucca Mountain Site. The starting hydrated cement phase assemblages and predicted reaction products for the three cement formulations are listed in Table A.2. The predicted pH values were 11.94, 12.46, and 12.12, respectively, for geochemical equilibria predicted from the OPC-B, OPC-C, and EPC-S cement formulations.

The modeling results indicated that changing the composition of the cementitious materials within the range used in this study affected both the predicted compositions of ground water and assemblages of secondary alteration phases. The study also suggested that only a small number of reactions were required to account for the majority of the predicted dissolution/ precipitation reactions. For example, the gross net effect of reacting EPC-S cement with Well J-13 water could be represented by the following two reactions:

$$\text{ettringite} \rightarrow \text{hydrogarnet} + 3\ \text{gypsum} + 20\ H_2O$$

and

$$5\ \text{hydrogarnet} + 22\ \text{cristobalite} + 11\ H_2O \rightarrow 5\ \text{gismondine} + 2\ \text{tobermorite}.$$

Höglund (1992) discussed the stability of ettringite in sulfate-containing systems. As part of this analysis, the PHREEQE and EQ3NR computer codes were used to assess the chemical equilibrium conditions for the formation of ettringite and monosulfate hydrate. Based on the available thermodynamic data, the modeling results indicate that the formation of ettringite is favored relative to monosulfate by higher sulfate conditions. At 25°C, ettringite was predicted to be stable at sulfate concentrations greater than 3 x 10^{-6} mol/l, whereas monosulfate was stable at sulfate concentrations of 2 x 10^{-8} to

Table A.2 Cement conceptual model used in studies by Gardiner and others

Starting Hydrated Cement Phase Assemblage		Predicted Reaction Products for Cement and Well J-13 Water at 25°C	
OPC-B Cement Formulation			
14-Å tobermorite		gypsum	zeolite (gismondine)
hydrogarnet		secondary CAH	clay (minor)
ettringite		secondary C-S-H	fluorite (minor)
		calcite	
OPC-C Cement Formulation			
14-Å tobermorite	NaOH	gypsum	fluorite (minor)
hydrogarnet	KOH	secondary CAH	portlandite (minor)
ettringite		secondary C-S-H	clay (minor)
portlandite		brucite (minor)	
EPC-S Cement Formulation			
14-Å tobermorite	NaOH	gypsum	zeolite (gismondine)
hydrogarnet	KOH	secondary CAH	fluorite (minor)
ettringite		secondary C-S-H	clay (minor)
silica		calcite	

3×10^{-6} mol/l. The stability limits for ettringite and monosulfate were also modeled as a function of sulfate concentrations for temperatures between 5 and 50°C. The minimum sulfate concentrations predicted for formation of ettringite at 5 and 50°C were 2×10^{-7} and 5×10^{-4} mol/l, respectively.

Schmidt and Rostásy (1993) presented a method for the calculation of the chemical composition of the concrete pore fluid. The method is based on a non-linear system of equations that included solubility products of $CaSO_4$, $Ca(OH)_2$, the ion product of water, and the equilibrium constant for the reaction between $CaOH^+$ and Ca^{2+} in water. The Stokes and Robinson equation was applied for ionic strength corrections, including an approximation algorithm for the activity coefficients of $CaSO_4$ and $Ca(OH)_2$. The calculation method was tested against analytical data published for the compositions of cement pore fluids. Schmidt and Rostásy proposed that the activity coefficients of electrolytes in concrete pore solutions may need to be determined by methods, such as the Pitzer ion-interaction model, for more precise calculations.

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Appendix B

Phase Equilibria Studies of the Cement/Water System

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Phase Equilibria Studies of the Cement/Water System

Solution chemistry and associated cement-mineral phase relations for pore fluids resulting from reaction of cement with water have been studied extensively. The results of these studies are the foundation of the modeling approaches (see Chapter 2 and Appendix A) developed to predict the composition of pore fluids. Those laboratory studies identified from the computerized literature and manual title searches are summarized below. We recommend that the reader also review the references cited by the following studies for a more complete understanding of phase equilibria studies conducted in the cement/water system.

B.1 Studies by F. P. Glasser and Others at University of Aberdeen

Macphee et al. (1989) studied the solubility and aging of calcium silicate hydrogel (C-S-H) in alkaline solutions at 25°C. The study investigated the effect of NaOH and KOH on the compositions of aqueous and solid phases for precipitates and tricalcium silicate (C_3S) hydration products. Data were presented for sodium-bearing C-S-H which were aged for up to 1 year. The experiments indicated differences in properties, especially for the compositions of the aqueous phases. The properties of precipitated gels and those resulting from C_3S hydration converged with time. After 182 days, the gel properties were essentially identical. The experiments indicated an increase in $Ca(OH)_2$ content of C_3S hydrates which resulted from the increased alkali concentrations. This increase of $Ca(OH)_2$ was important because of the potential for $Ca(OH)_2$ formation and related affects to the durability of cement pastes. The authors attributed the measured high and low concentrations of dissolved silica and calcium, respectively, that resulted with some precipitates in the sodium C-S-H system, to the associated alkali-silicate reactions. Increasing the alkali concentration also resulted in an expansive effect observed in C_3S hydration products.

Atkins et al. (1990) briefly review phase relations in the CaO-SiO_2-Al_2O_3-MgO-H_2O system based on studies conducted at their laboratory. The authors discuss their measurements of the solubilities of pure cement mineral phases at 25°C. They list solubility products (K_{sp}) for the phases $Ca_6Al_2(SO_4)_3(OH)_{12}$ (AF_t) and $Ca_3Al_2(OH)_{12}$ (hydrogarnet, C_3AH_6) as

$$Ca_6Al_2(SO_4)_3(OH)_{12} = 6\ Ca^{2+} + 2\ Al^{3+} + 3\ SO_4^{2-} + 12\ OH^-$$
$$K_{sp} = 4.75 \times 10^{-112}$$

$$Ca_3Al_2(OH)_{12} = 3\ Ca^{2+} + 2\ Al^{3+} + 12\ OH^-$$
$$K_{sp} = 1.56 \times 10^{-87}$$

The degradation of cementitious materials by CO_2 attack is also discussed.

Atkins et al. (1991b) completed solubility measurements of many of the more thermodynamically stable cement hydrate phases at 25°C in CO_2-free water. A large data set was generated, in the form of data sheets, from which solubility product values (i.e., K_{sp}) may be calculated. Solubility calculations were completed using the MINEQL code. The agreement with previously published K_{sp} values was generally good. Solubility data were included for the following phases: C_3AH_6 (hydrogarnet), $C_3AS_{0-1}H_{6-4}$ (siliceous hydrogarnet), C_4AH_{13}, AF_t or $C_6A\bar{S}_3H_{32}$ (ettringite), AF_m or C_4ASH_{12} (monosulfate), C_2ASH_8 (gehlenite hydrate), C-S-H, $C_5S_6H_5$ (tobermorite), and $M_{4-6}AH_{10-13}$ (hydrotalcite). The mean K_{sp} values listed by

Atkins et al. (1991b) for hydrogarnet and ettringite are identical to those listed in Atkins et al. (1991a,c). Values listed for tobermorite and hydrotalcite were considered preliminary. Additional investigations, especially for hydrotalcite, were recommended to further establish solubility relations for cement hydrate phases. The study indicated that monosulfate dissolved incongruently, due to precipitation of ($C_6A\bar{S}_3H_{32}$) (ettringite). The presence of impurities hindered solubility measurements for the calcium aluminum silicate hydrates.

Atkins et al. (1991c) report the results of solubility measurements for four hydrated cement phases. These are apparently the same solubility measurements (i.e., same K_{sp} values) briefly described in Atkins et al. (1990). By using a technique of repeated solution dispersion and filtration, the authors made the necessary measurements to derive the solubility products for ettringite ($C_6A\bar{S}_3H_{32}$) and hydrogarnet (C_3AH_6), which dissolve congruently. The authors' measurements of the solubilities of monosulfate ($C_4A\bar{S}H_{12}$) and tetra-calcium aluminate hydrate (C_4AH_{13}) indicate that these two phases dissolve incongruently and cannot therefore be described by a conventional solubility product. The log K_{sp} values for the ettringite and C_3AH_6 phases are

$$Ca_6Al_2(SO_4)_3(OH)_{12} = 6\ Ca^{2+} + 2\ Al^{3+} + 3\ SO_4^{2-} + 12\ OH^-$$
$$\log K_{sp} = -111.3 \qquad \Delta G^\circ_{f,298} = -5016.9\ \text{kJ/mol}$$

$$Ca_3Al_2(OH)_{12} = 3\ Ca^{2+} + 2\ Al^{3+} + 12\ OH^-$$
$$\log K_{sp} = -86.8 \qquad \Delta G^\circ_{f,298} = -9048.2\ \text{kJ/mol}$$

These values may be added to thermodynamic databases for use in modeling cement-water systems.

Atkins et al. (1991a) combined results from their experimental studies with data from the literature to develop a better understanding of phase relations in the CaO-SiO_2-Al_2O_3-MgO-SO_3-H_2O system. Their phase-equilibria studies consisted o more than 40 compatibility experiments conducted for 10 weeks using pure cement hydrate phases shaken continuously in CO_2-free water. Some problems were encountered with the interpretation of the experimental results because of precipitation of metastable phases. The MINEQL reaction code was used with the Organization for Economic Co-Operation and Development/Nuclear Energy Agency thermodynamic database to calculate saturation indices for the compositions of solutions sampled from the compatibility experiments.

Damidot and Glasser (1992) studied the thermodynamic relations of phases in the CaO-Al_2O_3-$CaSO_4$-H_2O system at 50 and 85°C. Equilibrium solubility phase diagrams were calculated for $Al(OH)_3$ (gibbsite, AH_3), $Ca_3Al_2(OH)_{12}$ (hydrogarnet, C_3AH_6), $Ca(OH)_2$ (portlandite, CH), $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$ (ettringite, $C_6A\bar{S}_3H_{32}$), monosulfoaluminate ($3CaO\cdot Al_2O_3\cdot CaSO_4\cdot 12H_2O$), and $CaSO_4$ (gypsum). Results of the thermodynamic analysis indicate that monosulfoaluminate is the stable phase at elevated temperature. Because ettringite also remains stable at 85°C, the calculations resulted in new invariant points, for which the authors calculated the compositions of the associated aqueous phases.

Phase relations in the CaO-Al_2O_3-$CaSO_4$-H_2O system were investigated by Damidot and Glasser (1993a) at 25°C. Calculations of phase diagrams involving the equilibrium solubilities of gibbsite (AH_3), hydrogarnet (C_3AH_6), portlandite (CH), ettringite ($C_6A\bar{S}_3H_{32}$), monosulfoaluminate ($C_4A\bar{S}H_{12}$), and gypsum were used to define the solid phases in equilibrium with aqueous solutions for a range of compositions. Phase diagrams were presented in two and three dimensions for this system Ettringite was calculated to be stable over a range of pH values and solution compositions. This study indicated that monosulfoaluminate was metastable with respect to hydrogarnet and ettringite. The equilibria in this system were also determined to be sensitive to the presence of other dissolved ions, such as sodium.

Damidot and Glasser (1993b) calculated the equilibrium phase diagram for the CaO-Al_2O_3-$CaSO_4$-K_2O-H_2O system at 25°C for several KOH concentrations relevant to compositions of cement pore fluids. The study showed that the potassium-containing system behaves differently to those having sodium, such as the need for inclusion of syngenite [$K_2Ca(SO_4)_2\cdot H_2O$] and K_2SO_4 in the phase calculations. The authors also discuss the general features of this system at temperatures to 100°C.

B.2 Studies by A. Atkinson and Others at Harwell Laboratory

A. Atkinson and co-investigators have studied the changes of pore fluid pH resulting from cement/water reactions as a function of time. These studies were published in three parts as Atkinson et al. (1989a,b) and Atkinson and Guppy (1989). Atkinson et al. (1989a) conducted accelerated laboratory experiments using sulfate-resisting Portland cement (SRPC) and demineralized water to validate predicted changes in pH as a function of time. The experiments consisted of leaching granules of hydrated SRPC paste for periods of one week with increasing volumes of demineralized water. The leachates were analyzed for pH and concentrations of dissolved calcium, silica, and aluminum. A simplified model of cement chemistry and published equilibrium data for the $CaO-SiO_2-H_2O$ system were used to predict changes of pH and concentrations of dissolved calcium and silica as a function of time resulting from reaction of SRPC with water. The model assumes that the pH of mature hydrated cements in open aqueous systems is controlled by the $CaO-SiO_2-H_2O$ system. The modeling results and experimental data were generally in reasonable agreement. Atkinson et al. attributed residual differences between the modeling and experimental results to the lack of complete equilibrium in the leaching studies.

Atkinson et al. (1989b) experimentally studied several reactions that could potentially reduce the pH values of pore fluids resulting from the reaction of cement with water. These reactions included 1) cement with pulverized fuel ash (PFA), 2) cement with blast furnace slag (BFS), 3) aqueous $Ca(OH)_2$ with siliceous aggregate, and 4) crystallization of amorphous hydration products. The effects of reactions between ordinary Portland cement (OPC) and cement modifiers (e.g., PFA and BFS) on pore fluid pH values were studied in water saturated systems using cements with high concentrations of modifier phase. Solution pH was measured periodically over the 221-day duration of these experiments. The results indicate that the BFS/OPC cements reached an apparent metastable equilibrium at which the pH value was between 11.8 and 12.15. Metastable equilibrium was not established for the PFA/OPC cement reactions because their kinetics were much slower. For this material, the authors expected the final pH could be in the range of 9 to 10 due to the high silica content of the PFA.

Experiments by Atkinson et al. (1989b) to investigate the reactions between dissolved $Ca(OH)_2$ and siliceous aggregate were conducted by exposing surfaces of either amorphous or crystalline SiO_2 to $Ca(OH)_2$ solution. The experiments were completed at 25 and 90°C for a duration of 41 days. Based on their 25°C results, the authors indicate that this reaction could be ignored because it is sufficiently slow.

To study reactions associated with the crystallization of amorphous hydration products, Atkinson et al. (1989b) measured pH values in leachates resulting from the equilibration of museum specimens of xonotlite, afwillite, foshagite, hillebrandite, truscottite, tobermorite (11.3 Å), and scarwtite with water. The authors considered these natural hydrated calcium silicate minerals as crystalline analogues of the amorphous gels which form during cement hydration. The measured pH values varied from 7.8 to 9.6, with the majority of pH values being between 8.5 and 9.5. These values are lower that those resulting from the solubility of the amorphous gels. Atkinson et al. did not know if these lower pH values resulted from the crystalline minerals having slower equilibration kinetics and/or being more stable than the gels.

Atkinson and Guppy (1989) conducted a series of experiments to determined how pH will change in leachates that have resulted from reactions of water with three types of cements that might be used in a repository for radioactive waste disposal. The experiments were conducted using demineralized water and a synthetic ground water with a composition typical for a clay environment. The cements included a SRPC, a slag modified cement containing 90 percent BFS and 10 percent OPC, and an ash-modified cement containing of 90 percent PFA and 10 percent OPC. The experiments consisted of leaching the cement samples for periods of one week with separate volumes of demineralized water. After each equilibration period, the volume of leachate was removed from the reaction vessel, and replaced with a new volume of leachant. The leachates were analyzed for pH and concentrations of dissolved calcium, silica, aluminum, potassium, sodium, sulfur, and magnesium. The leachate analyses indicated that the solutions were not in equilibrium with any of the solid phases. However, the change of pH measured in the leachates as a function of time was similar to that predicted from equilibrium considerations. The measured pH and buffering capacity of cement leached with synthetic ground water were lower than those observed in the leaching experiments using demineralized water. This was attributed to the precipitation of $CaCO_3$ as a result of dissolved carbonate in the ground-water leachant.

Atkinson et al. (1989c) conducted experimental studies of the leaching of cement in demineralized water and synthetic ground water to assess the importance of different processes affecting the pH of the cement leachate. Their studies indicate that pore fluids from Portland cements and BFS cements will have pH values above 10.5 for long periods of time. For the scenarios (i.e., flow conditions) considered by Atkinson et al. (1989), this period of high pH may extend for several hundre thousand years. In cases where extensive use is made of PFA, the long-term pH may be as low as 9 to 10. The authors present several plots of pH as a function of water volume per unit mass of anhydrous cement to support their conclusions.

Atkinson and Hearne (1990) conducted experiments to quantify the reactions that affect the degradation of concrete by sulfate. Reaction kinetics and endpoints between hydrated cements and dissolved sulfate and the resulting expansions were analyzed. The authors incorporated these data into a mechanistic model for sulfate degradation. The modeling results enable extrapolation of the sulfate degradation mechanisms to different concretes and ground-water compositions.

Atkinson et al. (1990, 1991b) studied the solubility of phases in the $CaO-Al_2O_3-SiO_2-H_2O$ system at 25°C. The sol-gel method, which involves co-hydrolysis of mixtures of alkoxides, was used to synthesize the solids used for the solubility studies. Solid assemblages of known overall element composition were equilibrated with water at 25°C. The leachates wer analyzed for pH and total concentrations of dissolved aluminum, calcium, and silica. The database of Gibbs free energy values used by Atkinson et al. was expanded to include values for aluminum-containing aqueous species and the solid phases gibbsite, hydrogarnet solid solution, kaolinite, pyrophyllite, and gehlenite hydrate. A thermodynamic model was used to evaluate the effects of aluminum concentrations on the chemistry of the system and to interpret the experimental solubility for the sol gel synthesized solids. The SOLGASMIX computer code was used to calculate the equilibrium state of the system by minimizing the total Gibbs free energy. Results of the modeling calculations account for most experimental data, except for systems with high aluminum/silica and low calcium/silica ratios. The predictions indicate that the main influence of aluminum was to promote formation of a hydrogarnet solid solution of general composition $C_3Al_{6-2x}S_x$.

Atkinson et al. (1991a) completed solubility studies at 80°C of gels for the $CaO-SiO_2-H_2O$ system to derive their thermodynamic properties. Detailed descriptions of the experimental methods, including synthesis of materials and phase characterization, were provided. A solid solution model was used to express the Gibbs free energies of the poorly crystalline gels that form in this system. As a result of the change in the dissociation constant for water and, to a lesser extent, lower calcium solubilities at the higher temperature, the main effect of the temperature increase from 25 to 80°C was a reduction of solution pH. Crystalline phases were observed to precipitate, but they were not considered to be in equilibrium with the aqueous phase.

B.3 Studies by Others

Rechenberg and Sprung (1983) studied the compositions of solutions resulting from the hydration of cement. Two types of investigations were conducted. One study included two series of tests where pure $Ca(OH)_2$ solutions were mixed with 1) sodium sulfate or potassium sulfate, and 2) sodium carbonate, sodium hydroxide, or potassium hydroxide. The second type of study, as a test against the $Ca(OH)_2$ experiments, included analysis of the compositions of solutions in contact with hydrated cement. Analyses of solutions from the $Ca(OH)_2$ experiment indicated that the solubility of $Ca(OH)_2$ decreased and the solution pH values increased with increasing alkali content. The magnitude of increase of solution pH was dependent on the types of dissolved cations, such that the solutions containing potassium sulfate or potassium hydroxide ha higher pH values than those with sodium sulfate or sodium hydroxide. The addition of dissolved sulfate resulted in higher concentrations of dissolved calcium. Similar results were attained for solutions that were in contact with Portland cement.

The precipitation of ettringite or monosulfate and subsequent solubility equilibrium with $Ca(OH)_2$ resulted in the concentrations of dissolved calcium decreasing in some solutions to the same extent as the concentrations of dissolved sulfate.

Andersson et al. (1989) analyzed the compositions of pore fluids that were pressure extracted from pastes of seven cement types. The cements included one Swedish and one French standard Portland cement, a sulfate-resistant cement, a BFS cement, a fly ash cement, a silica cement, and a high alumina cement. The elapsed time between the molding and subsequent pore-solution pressing of the cement pastes was not given. Analyses included measurements of solution pH and Eh and concentrations of dissolved sodium, potassium, calcium, magnesium, aluminum, iron, and silica. The pH values of the analyzed pore fluids ranged from 12.4 to 13.5. The Eh values of the pore solutions from all but two of the cement pastes, the BFS cement and French Portland cement, had positive redox potentials. Negative Eh values were, however, measured in the pore fluids from the BFS and French Portland cements. Sodium and potassium were the dominant cations in the solutions extracted from the standard Portland, sulfate-resistant, slag, silica, and fly ash cements. Dissolved calcium was also important in the sulfate-resistant cement pore solution. Sodium and aluminum were the main dissolved constituents in the solutions from the aluminate cement. The concentrations of dissolved silica and iron were low in all pore solutions. The ionic strength of the analyzed pore fluids ranged from 0.03 to 0.29 M.

Duerden et al. (1990) conducted a laboratory study of the durability of blended cements in contact with sulfate-bearing ground water. The investigation consisted of mineralogical analyses of leached cement resulting from the contact of OPC blended with PFA or ground BFS with sulfate-containing ground water under accelerated test conditions. Mineralogical analyses of leached cement included characterization by scanning electron microscopy and x-ray diffraction (XRD). The study indicated minimum reaction between the intact cement blocks and sulfate-containing ground water. Sulfate secondary minerals precipitated in voids in the cement blocks without adversely affecting the cement structure. However, crystallization of C-S-H and sulfate minerals along cracks in hardened cement specimens generated expansion of the fracture surfaces. This process could result in more accessible paths for ground-water flow and radionuclide migration. The experiments indicated that the use of powdered cement materials greatly accelerated the reactions. Under these conditions, the results suggested that ettringite $[Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O]$ and C-S-H may decompose as a result of carbonation to form calcite ($CaCO_3$) and quartz (SiO_2). The hydration of slag particles resulted in the formation of hydrotalcite $[Mg_6Al_2(CO_3)(OH)_{16}\cdot 4H_2O]$ as a durable phase.

Vieillard and Rassineux (1992) used laboratory experiments and thermodynamic modeling techniques to study the alteration mechanisms when a cement matrix is contacted by a dilute aqueous solution. The laboratory experiments included flow-through (i.e., open system) and static-mode (i.e., closed system) leach experiments completed at 40°C. Test materials included an OPC and a cement composed of mixing OPC slag with blast furnace slag fly ash (BFS-FA). Demineralized water with a pH of 5.6 was used as the leachate for both types of experiments. The flow-through experiments were completed at a flow rate of 20 l/day and a solution/solid volume ratio of 4. In these tests, the cement specimens were sampled at 0, 3, 6, 9, 12, 15, and 18 months. The leachates were sampled twice a month. The closed-system experiments were conducted at a solution/solid volume ratio of 6.8. The cement specimens and leachates were sampled at 0, 6, 12, and 18 months. Samples of the leached cement specimens were characterized by petrographic microscopy, XRD, scanning electron microscopy, and electron microprobe analysis.

Alteration processes observed by Vieillard and Rassineux (1992) included the maturing of the cement matrix, changes in the C-S-H phase, transformation of the calcium sulfate aluminates, and formation of hydrated gehlenite. In the flow-through experiments, the extent of the dissolution of the OPC material was apparently limited by carbonate formation. For the BFS-FA cement, however, where there was an absence of carbonate formation, the dissolution was intense and rapid. The results also indicated that equilibrium between the compositions of the cement constituents and leachates were approached in closed-system experiments with the solution/solid volume ratio of 6.8. The extent of this process was greater in the experiments involving the BFS-FA cement.

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Appendix C

Natural Analogues for Cementitious Systems

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Natural Analogues for Cementitious Systems

Scientists use natural analogue studies to assess and communicate the feasibility and risks of radioactive waste disposal. Natural analogue studies provide unique opportunities to study chemical and physical processes that occur slowly over historical or geologic time scales that are impossible or difficult to study in laboratory or field experiments. The scientific community can use the natural analogue information to test the applicability of computer models that are used to extrapolate to long-time periods in performance assessments (PAs) of radioactive waste disposal facilities. For example, see the PA-related papers presented in Kovach and Murphy (1995).

C.1 Definition of Natural Analogues

Natural analogue studies, as considered by the International Atomic Energy Agency (IAEA 1989), "involve the use of the analogy approach to investigate natural occurrences of materials, conditions and processes which are the same or similar to those known or predicted to occur in some part of a disposal system." Using a definition modified from that given by Cadelli et al. (1988, p. 264), a natural analogue may be defined as

> a natural geologic system in which one or more processes similar to those that may exist at a potential disposal facility and/or induced by the storage of radioactive wastes are thought to be operating over long time periods or spatial scales.

Both of the above definitions suggest that natural analogues are in fact long-term natural experiments involving natural or man-made materials in an environment uncontrolled by man.

Some researchers further distinguish between natural analogues and anthropogenic (or historical) analogues.(1) A typical study of a natural analogue, for example, might be the measurement and analysis of the subsurface dispersion of uranium and other trace elements associated with a uranium ore deposit. Studies of anthropogenic analogues, on the other hand, may include the evaluation of processes affecting the survival of archaeological artifacts, ancient metals, concretes, or clay barriers in natural settings. Anthropogenic analogues may also include sites where past waste-disposal practices and/or equipment-testing activities (e.g., detonation of nuclear explosive devices) have resulted in the release of radionuclides to the natural environment. Studies of these sites provide process information for the migration of trace elements, such as radionuclides, over long time periods and/or large spatial scales.

C.2 General Application of Natural Analogue Studies

During the past 20 years, the scientific community has conducted a broad spectrum of natural analogue studies. These have included studies of archaeological artifacts (e.g., bronze cannons and Roman nails), ancient tombs, ancient concretes, medieval glass, metallic meteorites, mineral alteration caused by radioactive decay, native metals, and volcanic and

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(1) Through the remainder of this document, natural analogue will refer to both natural and anthropogenic analogues.

meteoritic glasses. Results of these analogue studies provide a understanding of the long-term behavior of materials that may be used for waste forms, containers, engineered barriers, and construction materials for storing radioactive waste.

Analogue studies have also included investigations of radionuclide and trace metal migration in a diversity of geological environments, such as alkaline springs, clay deposits, deep sea sediments, geothermal fields, granitic and other igneous rocks, highly weathered soils, hydrothermal mineral deposits, nuclear testing sites, sedimentary basins, and uranium-ore deposits. Studying analogue sites supplies information on the physical and chemical processes that affect the migration of radionuclides in surface- and ground-water systems and their retardation in the geologic environment.

Given the diversity of natural analogues studied from the perspective of radioactive waste disposal issues, Chapman (1987) lists the following general applications for data from natural analogue studies:

- replication, as natural experiments, of a process, or a group of processes, being considered in a model
- determination of bounding values for specific parameters used in models
- identification of which phenomena can occur in the system being modelled by reference to a parallel natural system
- evaluation of the end result of many processes in an empirical sense, including demonstration of large-scale behavior of geochemical systems.

C.3 Published Reviews of Natural Analogue Studies

Several reviews of the utility of the natural analogue approach and applications of information from analogue studies have been published. Some of these reviews are discussed in this section.

C.3.1 Miller et al. (1994)

A book by Miller et al. (1994) is probably the most extensive review of natural analogue studies published to date. The book has two main purposes. One goal was to provide a comprehensive review of the state of development of natural analogue studies. Miller et al. emphasized those studies that are particularly relevant to disposal concepts being studied in Switzerland, Sweden, and the United Kingdom (UK) for storage of low-, intermediate-, and high-level radioactive wastes (HLWs). The focus of most natural analogue studies funded in the United States has been on disposal concepts and candidate sites that have been considered for geologic disposal of HLWs, such as spent fuel and glass waste forms. The second purpose of Miller et al. was to review the application of natural analogue studies with respect to communication to decision makers, scientific peers, and the general public of the risks associated with the geological disposal of radioactive wastes. Their review is concerned only with those physical-chemical processes that control the release of radionuclides from the near field and their subsequent migration in the geosphere. Processes related to climatic changes, radionuclide up-take by plants, and ingestion by animals are not covered by their review.

Miller et al. (1994) begin their review with discussions of the disposal concepts being studied in Switzerland, Sweden, and the UK for the disposal of low-, intermediate-, and high-level radioactive wastes. Performance assessment issues related to the disposal facility and far-field environment associated with each design are also considered. Guidelines are then suggested for selecting appropriate analogue studies based on considerations of the types of data needed by the end user. After providing detailed reviews of the types of natural analogues, the authors discuss how natural analogue studies have been used in PAs associated with these disposal programs and recommend how analogue data can be used for model construction, data acquisition, and model testing and validation.

Miller et al. divide their detailed descriptions of natural analogues into two groups: 1) analogues for repository materials, and 2) analogues for radionuclide release and transport processes. The repository material group includes discussions of natural analogues for waste glasses, spent fuel, metals, bentonite, concretes and cements, bitumen, cellulose, polymers, and resins. The radionuclide migration group includes descriptions of natural analogues with respect to radionuclide solubility and speciation, retardation processes, matrix diffusion, radiolysis, redox fronts, colloids, microbiological activity, and gas generation and migration. The review includes an extensive list of 560 supporting references. The authors end their book describing in detail some of the better known sites of natural analogue studies, including the following (in alphabetical order):

- Alligator Rivers Project - study of the Koongarra enriched secondary uranium deposit in the Northern Territory of Australia
- Broubster - study of uranium and thorium migration to, and retardation in, a peat bog in northern Scotland
- Cigar Lake - study of a Cigar Lake uranium deposit in northern Saskatchewan, Canada
- Inchtuthil- study of an ancient cache of buried nails found at the site of a Roman fortress of the Roman Empire at Inchtuthil in Scotland
- Kronan - study of a bronze cannon salvaged from a Swedish man-of-war that sank during a battle in 1676 in the Baltic Sea
- Maqarin - study of hyperalkaline springs of the Maqarin area of northern Jordan
- Loch Lomond - study of element migration in sediment samples from Loch Lomond in central Scotland
- Needle's Eye - study of a uranium deposit at Needle's Eye in southwestern Scotland
- Oklo - study of the Oklo uranium deposit in the Republic of Gabon
- Oman - study of the hyperalkaline ground waters in the Semail Opjiolite Nappe of northern Oman
- Palmottu - study of a uranium-thorium deposit located at Nummi-Pusula in southwestern Finland
- Poços de Caldas - study of rare earth elements and uranium-thorium series radionuclides at Morro do Ferro and the Osamu Utsumi mine on the Poços de Caldas plateau in the state of Minas Gerais in Brazil
- South Terra - study of a uranium deposit in Cornwall in southwestern England
- Tono - study of the Tono uranium deposit region located southwest of Tokyo in Japan.

The Maqarin and Oman studies will be described in greater detail below. The hyperalkaline waters studied in these two regions were considered possible analogues to the chemical evolution of pore waters resulting from the interaction of water with cementitious materials used in a waste disposal facility.

C.3.2 Côme and Chapman (1987)

Côme and Chapman (1987) compiled more than 40 technical papers presented at a symposium directed at the application of natural analogues to radioactive waste disposal issues. The symposium was organized by the Commission of the European Communities and held in Brussels in April 1987. The papers at this conference were organized into the following general categories:

- rationale for natural analogue studies
- major field sites of natural analogue studies
- analogue studies related to radioactive waste forms and engineered barriers (i.e., near-field environment)
- analogue studies related to processes affecting the migration of radionuclides in soil/rock/water systems (i.e., far-field environment).

The proceedings by Côme and Chapman (1987) are a valuable collection of papers representing some of the strategies, goals, and sites of analogue studies conducted during the past decade. These studies were the platforms for many analogue studies continued or initiated in the 1990's.

C.3.3 Pearcy and Murphy (1991)

Pearcy and Murphy (1991) published an extensive literature review of natural analogue studies that are relevant to radionuclide migration at the site being characterized at Yucca Mountain, Nevada, as a candidate repository for the geologic disposal of HLW. Descriptions are given for numerous natural analogue studies and potential analogue sites reported in the published literature. Pearcy and Murphy include an annotated bibliography (64 pages) that lists the titles and provides short summaries of pertinent information from all of the papers reviewed.

C.4 Application to Cementitious Materials and Associated Source-Term Environment

Natural analogue studies described in Miller et al. (1994) and other supporting references as relevant to cementitious materials and disposal systems fall into the following two categories:

- studies pertaining to the physical stability of cement hydration compounds
- studies related to the interactions between cement, rock, and ground water.

Data from these studies have been used to test conceptual and computerized models used for PAs of cement-containing disposal facilities for radioactive waste.

C.4.1 Overview

McKinley and Alexander (1992), who are also coauthors of Miller et al. (1994), discuss the use of the natural analogue approach for testing PA models of the near-field environment of a radioactive waste disposal facility containing cementitious materials. This paper is essentially a summary of similar discussions contained in Miller et al. (1994). Studies of archaeological samples of ancient concretes are considered as possible analogues to the physical degradation of cementitious materials, including cement hydration mineral phases. McKinley and Alexander consider these studies as having limited applicability, because of the differences in compositions and environments of ancient cements and mortars versus those of modern cementitious materials and the expected conditions of a waste disposal facility.

McKinley and Alexander (1992) describe possible approaches for using analogue studies for testing of models for waste-form leaching and radionuclide solubility and speciation. The focus of these discussions was the use of information from analogue studies of the hyperalkaline ground waters at the northern Oman site and hyperalkaline springs from the Maqarin area in northern Jordan (discussed below). One appropriate application identified by McKinley and Alexander for these data is the testing of geochemical codes used to predict solubility concentrations and aqueous speciation of trace constituents, such as radionuclide elements. Blind predictions of maximum trace element concentrations, calculated with the geochemical models, have been compared to measured concentrations of the same elements in the hyperalkaline waters. Analysis of the differences between the analytical determinations and computer simulations provides a test of the adequacy of the computerized model, the model's associated thermodynamic database, and the conceptual model used for the solubility calculations.

Several other applications of natural analogue information were proposed by McKinley and Alexander (1992). These include the effects of microbial growth, dissolved organic components, colloids, gas (produced from corrosion, biodegradation, and/or radiolysis), and composition changes at the interface between the engineered materials and the host geologic setting. Data from analogue studies relevant to these effects is, however, very limited, especially for the high pH conditions associated with cement pore fluids.

C.4.2 Physical Stability Studies

Numerous natural analogue studies related to the physical stability of cementitious materials have been reported in the literature. Although cement longevity is not a technical issue covered by the scope of our report, some of these studies are briefly reviewed here as useful starting points for more detailed examination by interested readers.

Miller et al. (1994) provide an extensive review of analogue studies related to the physical stability of calcium silicate hydrogel (C-S-H) phases in cementitious materials. As these authors note, Portland cement was first manufactured in 1824. It is therefore a rather modern industrial material when compared to archaeological artifacts and time frames of regulatory consequence to a radioactive waste disposal facility. Studies reviewed by Miller et al. (1994) of Portland cement-containing concretes suggest that C-S-H compounds can survive for up to 150 years in a variety of environments. Examples of such studies include the following:

- Steadman (1986) used electron probe microanalysis (EPMA) to examine samples of materials containing Portland cement taken from an 80-year-old concrete sea wall at a dockyard in Scotland and from hardened cement that was part of a consignment of cement paste found in barrels in a ship wreck from 1848 on the Thames estuary.

- Yusa et al. (1991) studied concrete components from tunnels and estuary walls with known ages. Techniques, such as EPMA, scanning electron microscopy (SEM), transmission electron microscopy, and x-ray diffraction (XRD) were used to characterize the phase alteration in these samples.

- Mallinson and Davies (1987, as cited by Miller et al. 1994) examined materials from Britain's first multi-story reinforced concrete framed building and first reinforced concrete marine structure.

The analogue studies described by Miller et al. (1994) of archaeological materials, such as ancient Roman mortars, indicate that C-S-H compounds may survive for several thousands of years. They caution the reader that these materials may be from environments dissimilar to those expected for a radioactive waste repository. Studies of archaeological samples of mortar and cement include those of Rassineux et al. (1989), Rayment and Pettifer (1987), and Steadman (1986). The studies by Rassineux et al. (1989) and Rayment and Pettifer (1987) are also reviewed in detail by Thomassin and Rassineux (1992).

Rassineux et al. (1989) examined samples of mortar and concrete collected from several Gallo-Roman thermal baths in western France. The samples were analyzed by optical microscopy, SEM, XRD, and EPMA. Their results demonstrated good stability of C-S-H-like phases over time spans of 1800 years and such compounds do not exhibit any noticeable recrystallization. Rassineux et al. credit the long-term persistence of these phases to confinement of cement matrix and to formation of a surface-protective carbonate crust.

Rayment and Pettifer (1987) studied samples of 1,700-year-old mortar from Hadrian's Wall(1) in northern England. The samples were analyzed by optical microscopy, EPMA, and SEM. Selected samples were also examined by differential scanning calorimetry, XRD, and wet chemical techniques. Their study reveals that considerable quantities of C-S-H phases were formed in the mortar and this has remained uncarbonated.

Steadman (1986) analyzed several samples of archaeological concrete and mortar for the presence of C-S-H phases. Some of the samples included the Roman concrete and mortar from Verulamium which is 30 km northwest of London, Hadrian's Wall, and various Roman structures in Italy, France, and Germany; cementitious material from a 2,500-year-old water tank in Kamiros, Rhodes; and concrete from a 800-year-old wall of the Reading Abbey in England. The samples were studied by optical microscopy, thermal analysis, XRD, and EPMA techniques. Analyses of these samples indicated that they were essentially fully carbonated and contained insufficient quantities of C-S-H to be detected by EPMA. Steadman (1986) also described later studies of a core sample from Hadrian's Wall. Chemical, thermal analysis, and XRD studies of this core material indicated that the mortar matrix is largely amorphous C-S-H with small quantities of calcium hydroxide and carbonate mineralization.

Several studies have been conducted by D. M. Roy(2) and coworkers of analogue materials related to the physical stability of cementitious materials. These investigations include the characterization studies of archaeological cementitious materials by Roy and Langton (1983, 1989), Langton and Roy (1984), and Jiang and Roy (1994). Roy and Langton (1983) and Langton and Roy (1984) investigated the long-term stability of cement in plasters, mortars, and/or concrete from the perspective of their use as borehole plugging and shaft sealing materials in a radioactive waste disposal facility. They examined approximately 100 samples of ancient materials dated from 1,400 to 3,000 years old from Italy, Greece, Crete, and Cyprus. Types of analyses included optical microscopy, SEM, XRD, differential thermal analysis (DTA), thermal gravimetric analysis (TGA), quantitative chemical analysis, and chemical structure determination by the trimethylsilylation (TMS) technique. These studies indicated that a significant amount of C-S-H in their samples was still x-ray amorphous after 3,000 years. This observation indicated to Roy and Langton that the kinetics for the crystallization and/or other changes of the gel structure are very slow under atmospheric or near surface burial above or below the water table. Chemical and mineralogical analysis of the phases in the cementitious binders in these materials was determined to be similar to those found in modern materials containing Portland cement. Roy and Langton concluded that the design and control of the chemical and physical properties of the composite materials and cementitious binder in particular were necessary to achieve a durable concrete.

Roy and Langton (1989) studied the durability of ancient cementitious materials to assess the resistance to weathering of concrete products for sealing a geologic repository for radioactive waste. The focus of this investigation was to extend their knowledge of the production methods used for these materials and examine their response to environmental conditions

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(1) Hadrian's Wall was a fortified frontier boundary built in Britain when the Romans were consolidating their empire in Europe.
(2) Materials Research Laboratory, Pennsylvania State University, University Park, Pennsylvania.

under consideration in the United States for storing HLWs in an underground geologic repository in tuff at Yucca Mountain in Nevada. Samples of ancient mortars, plaster, and concretes that were up to 2,000 years old were collected from sites in Rome, Ostia, and Cosa in Italy. The materials were characterized by optical microscopy, SEM, XRD, DTA, TGA, quantitative chemical analysis, and chemical structure determination with the TMS technique and gas chromatography/gel permeation chromatography. Their data suggest that modern sealing materials similar to ancient pozzolanic(1) cementitious materials will adjust slowly to the expected environmental conditions.

Jiang and Roy (1994) assess the potential stability of cementitious materials as waste forms for radioactive waste by combining information from selected data from studies of ancient building materials with their information on the behavior of modern Portland cement. They examined selected chemical composition and structural data for materials from France, Italy, China, and Egypt. These samples included mortar from the Great Pyramid, Giza, Egypt; lime-soil mix from the Great Wall, China (100-200 BC); mortar from Mole, Pozzuoli, Italy (100-200 BC); and cement from a Roman aqueduct, Lyon, France (200-300 AD). Their results confirm the longevity of these ancient cementitious materials.

C.4.3 Cement/Rock/Ground-Water Interaction Studies

Ground waters from two sites have been studied as natural analogues to the chemical evolution of pore waters resulting from cement/rock/ground-water interactions. These include studies of hyperalkaline waters at sites in northern Oman and northern Jordan. Because of their high pH values (≥11 at the Oman site and ≥12.5 at the Maqarin site) and presence of portlandite [$Ca(OH)_2$], these ground waters are considered possible analogues to cement pore waters. The emphasis of these studies has been on the determination of the solubility and speciation of radionuclides, and the verification testing of geochemical models and associated thermodynamic databases.

C.4.3.1 Semail Ophiolite Nappe of Northern Oman

The trace element chemistry and microbiology(2) of some hyperalkaline waters from springs in the Semail Ophiolite Nappe of northern Oman have been studied as an analogue to pore waters from aged cement. These studies have been described in numerous papers and reports, including Bath et al. (1987a,b), Chapman (1986), and McKinley et al. (1986, 1988). The springs in this area are highly alkaline with pH values of 10 to 12. The waters are often extremely reducing, containing significant quantities of free hydrogen gas. The Eh values vary from -165 to -630 mV. The spring waters are also somewhat saline. The alkaline composition of these waters is thought to result from the hydration (i.e., serpentinization) of calcium and magnesium silicate minerals in the ultramafic ophiolite rock. Deposits of portlandite and brucite [$Mg(OH)_2$] may be found at these springs. Carbonate precipitation also occurs when the hyperalkaline waters react with atmospheric CO_2 or bicarbonate-rich surface waters.

Water samples from five springs were analyzed for pH, Eh, alkalinity, anions, and major, minor, and trace cations. Measurements of uranium and thorium isotopes were also completed for water samples from two springs. Water samples were filtered sequentially through 1-µm, 0.45-µm, and 0.1-µm membrane filters before being submitted for chemical analysis. A 500-ml sample of water from each site was also reacted with a mixture of cation and anion exchange resins. The compositions of any natural precipitates, filter deposits, and resin-retained species were also characterized.

The analytical results were used in a validation test of geochemical models and associated thermodynamic databases being applied in PA calculations. Maximum concentration limits were calculated for the trace metals nickel, palladium, selenium,

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(1) Pozzolan is defined by IAEA (1993) as "a siliceous or siliceous and aluminous material that in itself possesses little or no cementitious value but, in finely divided form and in the presence of moisture, will chemically react with calcium hydroxide at room temperature to form compounds with cementitious properties."

(2) The reader should refer to Bath et al. (1987b) for details of the microbiological studies completed at the hyperalkaline springs in northern Oman.

tin, thorium, uranium, and zirconium using geochemical models and the major element compositions for a number of wate sampled in the Oman study. The predicted concentrations were then compared in a blind test to the trace metal concentrations measured analytically. The solubilities of thorium and uranium were calculated with the MINEQL model (Westall et al. 1976). The solubilities of nickel, palladium, selenium, tin, and zirconium were predicted with the PHREEQE model (Parkhurst et al. 1980). The thermodynamic databases originally supplied with both models had been extensively modified to include radionuclide elements of interest by the organizations conducting the modeling calculation

The low solubilities predicted for the trace metals by the geochemical models were considered to be generally consistent with their measured concentrations. However, comparison of the modeling results to measured concentrations was limited by the sensitivity of the analytical methods and variable quality and completeness of the models' thermodynamic database The predicted concentrations at these highly alkaline, reducing conditions were considerably lower than the detection limit for palladium and tin, and near the detection limits for nickel, thorium, and uranium for the analytical methods used in the studies. Except for uranium and zirconium, the observed trace metal concentrations for the other trace metals were mostly below detection limits. The results identified particular cases where the modeling results appeared to be lower than (under conservative) (e.g., nickel and palladium) or greater than (overconservative) (e.g., zirconium and uranium, particularly under oxidizing conditions) analytically-determined trace metal concentrations. The predicted solubilities for uranium in particular identified important differences in the databases. The researchers involved in the Oman study will use the result of this validation test to focus future review and development of the thermodynamic databases.

C.4.3.2 Maqarin Area in Northern Jordan

Another site being studied as a natural analogue to aged-cement pore waters is the hyperalkaline springs from the Maqarin area in northern Jordan at the Jordanian-Syrian border. The rock formations of interest include intercalated marls and bituminous limestones that have undergone high-temperature metamorphism. The highly alkaline pH conditions result fro the interaction of the ground waters with these rock formations. The alkaline pH values are controlled by the solubility of portlandite and formation of hydrated calcium sulfate minerals, such as ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$] and thaumasite [$Ca_3Si(OH)_6CO_3SO_4\cdot 12H_2O$]. Site information is given in Khoury et al. (1992).

Studies of this hyperalkaline environment include investigations of major and trace elements in the ground waters, organic complexation of dissolved trace elements, and the interaction of the hyperalkaline waters and host rocks. Water samples were analyzed for pH, Eh, alkalinity, anions, and major, minor, and trace cations. Results of geochemical modeling studie published to date primarily include predictions of trace metal solubilities in these hyperalkaline ground waters. Trace metals selected for modeling include those of interest to radioactive waste disposal. Analogue studies of Maqarin hyperalkaline springs are continuing.

The modeling studies are being conducted as a validation test of geochemical models used for PAs of radioactive disposal systems. The results are also used for a verification of the different codes and comparison of the different thermodynamic databases applied by the participating organizations. The geochemical models used for these studies include EQ3NR/EQ6 (Wolery and Daveler 1992), HARPHRQ (Brown et al. 1990), and PHREEQE (Parkhurst et al. 1980). The versions of thes codes and sources of their thermodynamic databases are identified in Linklater et al. (1994). The modeling studies generally show that solubilities predicted using simple solids, such as oxide and hydroxide phases, from current thermodynamic databases are conservative limits for trace metal concentrations. The predicted concentrations of dissolved trace metals were several orders of magnitude greater than those measured in water samples from the Maqarin site. Site studies indicate that coprecipitation of trace metals in secondary minerals controls the concentrations of these dissolved constituen (Linklater et al. 1994).

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Appendix D

MINTEQA2 Thermodynamic Database for Radionuclides

Appendix D

MINTEQA2 Thermodynamic Database for Radionuclides

D.1 Thermodynamic Equations

Thermodynamic data used by the MINTEQA2 geochemical model are stored in the form of equilibrium constants (log $K^\circ_{r,298}$) and enthalpies (heats) of reaction ($\Delta H^\circ_{r,298}$) for aqueous complexation, mineral, and gas solubility reactions. The reference temperature for the MINTEQA2 database, as with most geochemical models, is 298 K (25°C). Equilibrium constants (log $K^\circ_{r,T}$) may be based on values that have been experimentally determined or calculated from Gibbs free energies of reaction ($\Delta G^\circ_{r,T}$, cal/mol) according to the equation

$$\log K^\circ_{r,T} = \frac{-\Delta G^\circ_{r,T}}{2.303\ R\ T} \qquad \text{(D.1)}$$

where T is temperature in degrees Kelvin and R is the gas constant (1.9872 cal/mol·K). Values for $\Delta G^\circ_{r,T}$ are in turn calculated from published values for the Gibbs free energy of formation ($\Delta G^\circ_{f,298}$) for each product and reactant in the aqueous complexation or solubility reaction by the equation

$$\Delta G^\circ_{r,298} = \Sigma\ \Delta G^\circ_{f,298}\ \text{(products)} - \Sigma\ \Delta G^\circ_{f,298}\ \text{(reactants)} \qquad \text{(D.2)}$$

To calculate aqueous speciation and solubilities at temperatures other than 25°C, the equilibrium constants are recalculated by the MINTEQA2 code to the temperature T of interest using the van't Hoff relation (Lewis and Randall 1961)

$$\log K^\circ_{r,T} = \log K^\circ_{r,298} - \frac{\Delta H^\circ_{r,298}}{2.303\ R}\left(\frac{1}{T} - \frac{1}{298}\right) \qquad \text{(D.3)}$$

Values for enthalpies of reaction are calculated from published enthalpy of formation values ($\Delta H^\circ_{f,298}$) using the equation

$$\Delta H^\circ_{r,298} = \Sigma\ \Delta H^\circ_{f,298}\ \text{(products)} - \Sigma\ \Delta H^\circ_{f,298}\ \text{(reactants)} \qquad \text{(D.4)}$$

Values for $\Delta H^\circ_{r,298}$ cannot be calculated for some reactions, because $\Delta H^\circ_{f,298}$ values are undetermined for one or more reaction products and/or reactants.

In these cases, the MINTEQA2 code assumes that

$$\log K^\circ_{r,T} \approx \log K^\circ_{r,298} \qquad \text{(D.5)}$$

Because of the limitations in using the van't Hoff relation for extrapolations over a wide range of temperature, applications of the MINTEQA2 code are limited to temperatures less than 100°C.

The structures of the MINTEQA2 database files are described in detail in Appendix A in Allison et al. (1991).

D.2 MINTEQ Thermodynamic Database for Radionuclides

This section lists the aqueous species and solid compounds that are in the MINTEQA2 thermodynamic database for the radionuclides considered in this study. Tables D.1-D.8 list the formulas and reference sources of the thermodynamic data for the aqueous species and solid compounds of americium, neptunium, nickel, plutonium, radium, technetium, thorium, and uranium, respectively.

Table D.1 Formula and sources of thermodynamic data for americium aqueous species and solid compounds

Formula	Reference source	Formula	Reference source
		Aqueous Species	
Am^{3+}	Kerrisk (1984)	AmF^{2+}	Kerrisk (1984)
Am^{4+}	Kerrisk (1984)	AmF_2^+	Kerrisk (1984)
AmO_2^+	Kerrisk (1984)	AmF_3° (aq)	Kerrisk (1984)
AmO_2^{2+}	Kerrisk (1984)	$AmNO_3^{2+}$	Kerrisk (1984)
$AmOH^{2+}$	Kerrisk and Silva (1986)	$Am(NO_3)_2^+$	Kerrisk (1984)
$Am(OH)_2^+$	Kerrisk and Silva (1986)	$AmSO_4^+$	Kerrisk (1984)
$Am(OH)_3^\circ$ (aq)	Kerrisk and Silva (1986)	$Am(SO_4)_2^-$	Kerrisk (1984)
$AmCO_3^+$	Kerrisk and Silva (1986)	$AmH_2PO_4^{2+}$	Kerrisk (1984)
$Am(CO_3)_2^-$	Kerrisk and Silva (1986)	$Am(H_2PO_4)_2^+$	Kerrisk (1984)
$Am(CO_3)_3^{3-}$	Kerrisk and Silva (1986)	$Am(H_2PO_4)_3^\circ$ (aq)	Kerrisk (1984)
$AmCl^{2+}$	Kerrisk (1984)	$Am(H_2PO_4)_4^-$	Kerrisk (1984)
$AmCl_2^+$	Kerrisk (1984)	$AmO_2HCO_3^\circ$ (aq)	Kerrisk (1984)
		Solid Compounds	
Am	Oetting et al. (1976)	$Am(OH)_3$ (a)	Kerrisk and Silva (1986)
$Am(OH)_3$	Kerrisk and Silva (1986)	$AmOHCO_3$	Kerrisk and Silva (1986)

Table D.2 Formula and sources of thermodynamic data for neptunium aqueous species and solid compounds

Formula	Reference source	Formula	Reference source
		Aqueous Species	
Np^{3+}	Lemire (1984)	$NpSO_4^{2+}$	Lemire (1984)
Np^{4+}	Lemire (1984)	$Np(SO_4)_2^{\circ}$ (aq)	Lemire (1984)
NpO_2^+	Lemire (1984)	NpO_2Cl° (aq)	Lemire (1984)
NpO_2^{2+}	Lemire (1984)	NpO_2F° (aq)	Lemire (1984)
$NpOH^{2+}$	Lemire (1984)	NpO_2OH° (aq)	Lemire (1984)
$NpH_2PO_4^{2+}$	Lemire (1984)	$NpO_2CO_3^-$	Lemire (1984)
$Np(H_2PO_4)_2^+$	Lemire (1984)	$NpO_2(CO_3)_2^{3-}$	Lemire (1984)
$Np(H_2PO_4)_3^{\circ}$ (aq)	Lemire (1984)	$NpO_2(CO_3)_3^{5-}$	Lemire (1984)
$NpCl^{3+}$	Lemire (1984)	$NpO_2H_2PO_4^{\circ}$ (aq)	Lemire (1984)
$NpCl_2^{2+}$	Lemire (1984)	$NpO_2HPO_4^-$	Lemire (1984)
NpF^{3+}	Lemire (1984)	$NpO_2SO_4^-$	Lemire (1984)
NpF_2^{2+}	Lemire (1984)	NpO_2Cl^+	Lemire (1984)
$NpOH^{3+}$	Lemire (1984)	NpO_2F^+	Lemire (1984)
$Np(OH)_2^{2+}$	Lemire (1984)	$NpO_2F_2^{\circ}$ (aq)	Lemire (1984)
$Np(OH)_3^+$	Lemire (1984)	NpO_2OH^+	Lemire (1984)
$Np(OH)_4^{\circ}$ (aq)	Lemire (1984)	$(NpO_2)_2(OH)_2^{2+}$	Lemire (1984)
$Np(OH)_5^-$	Lemire (1984)	$(NpO_2)_3(OH)_5^+$	Lemire (1984)
$Np(CO_3)_5^{6-}$	Lemire (1984)	$NpO_2(CO_3)_2^{2-}$	Lemire (1984)
$NpHPO_4^{2+}$	Lemire (1984)	$NpO_2(CO_3)_3^{4-}$	Lemire (1984)
$Np(HPO_4)_2^{\circ}$ (aq)	Lemire (1984)	$NpO_2H_2PO_4^+$	Lemire (1984)
$Np(HPO_4)_3^{2-}$	Lemire (1984)	$NpO_2HPO_4^{\circ}$ (aq)	Lemire (1984)
$Np(HPO_4)_4^{4-}$	Lemire (1984)	$NpO_2SO_4^{\circ}$ (aq)	Lemire (1984)
$Np(HPO_4)_5^{6-}$	Lemire (1984)		
		Solid Compounds	
Np	Lemire (1984)	$Np(HPO_4)_2$	Lemire (1984)
$NaNpO_2CO_3 \cdot 3.5H_2O$	Lemire (1984)	$NpO_2(OH)$ (a)	Lemire (1984)
$Np(OH)_4$	Lemire (1984)	Np_2O_5	Lemire (1984)
NpO_2	Lemire (1984)	$NpO_2(OH)_2$	Lemire (1984)

Table D.3 Formula and sources of thermodynamic data for nickel aqueous species and solid compounds

Formula	Reference source	Formula	Reference source
		Aqueous Species	
Ni^{2+}	Ball et al. (1981)	$NiHCO_3^+$	Ball et al. (1981)
$NiBr^+$	Ball et al. (1981)	$NiCO_3^\circ$ (aq)	Ball et al. (1981)
$NiCl^+$	Ball et al. (1981)	$Ni(CO_3)_2^{2-}$	Ball et al. (1981)
$NiCl_2^\circ$ (aq)	Ball et al. (1981)	$NiSO_4^\circ$ (aq)	Ball et al. (1981)
NiF^+	Ball et al. (1981)	$Ni(SO_4)_2^{2-}$	Ball et al. (1981)
$NiOH^+$	Ball et al. (1981)	$NiSeO_4^\circ$ (aq)	Ball et al. (1981)
$Ni(OH)_2^\circ$ (aq)	Ball et al. (1981)		
$Ni(OH)_3^-$	Ball et al. (1981)		
		Solid Compounds	
$NiCO_3$	Ball et al. (1981)	Morenosite	Ball et al. (1981)
$Ni(OH)_2$	Ball et al. (1981)	Ni_2SiO_4	Ball et al. (1981)
$Ni_4(OH)_6SO_4$	Ball et al. (1981)	$Ni_3(AsO_4)_2 \cdot 8H_2O$	Ball et al. (1981)
Bunsenite	Ball et al. (1981)	NiSb	Sehmel (1989)
$Ni_3(PO_4)_2$	Ball et al. (1981)	NiSe	Deutsch and Krupka (1985)
Millerite	Ball et al. (1981)	Ahlfeldite	Deutsch and Krupka (1985)
Retgersite	Ball et al. (1981)		

Table D.4 Formula and sources of thermodynamic data for plutonium aqueous species and solid compounds

Formula	Reference source	Formula	Reference source
		Aqueous Species	
Pu^{3+}	Lemire and Tremaine (1980)	$Pu(HPO_4)_4^{4-}$	Lemire and Tremaine (1980)
Pu^{4+}	Lemire and Tremaine (1980)	$PuSO_4^{2+}$	Lemire and Tremaine (1980)
PuO_2^+	Lemire and Tremaine (1980)	$Pu(SO_4)_2^{\circ}$ (aq)	Lemire and Tremaine (1980)
PuO_2^{2+}	Lemire and Tremaine (1980)	$PuCO_3^{2+}$	Falck (1992)
$PuCl^{2+}$	Schwab and Felmy (1982)	$Pu(CO_3)_2^{\circ}$ (aq)	Falck (1992)
$PuOH^{2+}$	Lemire and Tremaine (1980)	$Pu(CO_3)_3^{2-}$	Falck (1992)
$PuH_2PO_4^{2+}$	Lemire and Tremaine (1980)	$Pu(CO_3)_4^{4-}$	Falck (1992)
$PuSO_4^+$	Lemire and Tremaine (1980)	$Pu(CO_3)_5^{6-}$	Falck (1992)
$Pu(SO_4)_2^-$	Read (1991)	$Pu(OH)_3CO_3^-$	Falck (1992)
$PuCl^{3+}$	Schwab and Felmy (1982)	PuO_2OH° (aq)	Lemire and Tremaine (1980)
PuF^{3+}	Nash and Cleveland (1984)	PuO_2Cl^+	Lemire and Tremaine (1980)
PuF_2^{2+}	Nash and Cleveland (1984)	PuO_2F^+	Lemire and Tremaine (1980)
PuF_3^+	Nash and Cleveland (1984)	$PuO_2F_2^{\circ}$ (aq)	Lemire and Tremaine (1980)
PuF_4° (aq)	Nash and Cleveland (1984)	$PuO_2F_3^-$	Lemire and Tremaine (1980)
$PuOH^{3+}$	Lemire and Tremaine (1980)	$PuO_2F_4^{2-}$	Lemire and Tremaine (1980)
$Pu(OH)_2^{2+}$	Lemire and Tremaine (1980)	PuO_2OH^+	Lemire and Tremaine (1980)
$Pu(OH)_3^+$	Lemire and Tremaine (1980)	$(PuO_2)_2(OH)_2^{2+}$	Lemire and Tremaine (1980)
$Pu(OH)_4^{\circ}$ (aq)	Lemire and Tremaine (1980)	$(PuO_2)_3(OH)_5^+$	Lemire and Tremaine (1980)
$Pu(OH)_5^-$	Lemire and Tremaine (1980)	$PuO_2(OH)_2^{\circ}$ (aq)	Lemire and Tremaine (1980)
$PuHPO_4^{2+}$	Lemire and Tremaine (1980)	$PuO_2(OH)_3^-$	Lemire and Tremaine (1980)
$Pu(HPO_4)_2^{\circ}$ (aq)	Lemire and Tremaine (1980)	$(PuO_2)_2OH^{3+}$	Lemire and Tremaine (1980)
$Pu(HPO_4)_3^{2-}$	Lemire and Tremaine (1980)	$PuO_2CO_3^{\circ}$ (aq)	Lemire and Tremaine (1980)
		$PuO_2(CO_3)_2^{2-}$	Lemire and Tremaine (1980)
		$PuO_2(CO_3)_3^{4-}$	Lemire and Tremaine (1980)
		$PuO_2H_2PO_4^+$	Lemire and Tremaine (1980)
		$PuO_2SO_4^{\circ}$ (aq)	Lemire and Tremaine (1980)
		Solid Compounds	
Pu	Morss (1986)	PuF_4	Lemire and Tremaine (1980)
$Pu(OH)_3$	Lemire and Tremaine (1980)	$Pu(HPO4)_2$	Lemire and Tremaine (1980)
β-Pu_2O_3	Lemire and Tremaine (1980)	$PuO_2(OH)$ (a)	Lemire and Tremaine (1980)
PuF_3	Lemire and Tremaine (1980)	$PuO_2(OH)_2$	Lemire and Tremaine (1980)
$Pu(OH)_4$	Lemire and Tremaine (1980)	PuO_2HPO_4	Lemire and Tremaine (1980)
PuO_2	Lemire and Tremaine (1980)		

Table D.5 Formula and sources of thermodynamic data for radium aqueous species and solid compounds

Formula	Reference source	Formula	Reference source
		Aqueous Species	
Ra^{2+}	Wagman et al. (1982)		
		Solid Compounds	
Ra	Wagman et al. (1982)	$RaCl_2 \cdot 2H_2O$	Wagman et al. (1982)
$Ra(NO_3)_2$	Wagman et al. (1982)	$RaSO_4$	Wagman et al. (1982)

Table D.6 Formula and sources of thermodynamic data for technetium aqueous species and solid compounds

Formula	Reference Source	Formula	Reference Source
		Aqueous Species	
Tc^{3+}	Rard (1983)	TcO_4^{2-}	Rard (1983)
TcO^{2+}	Rard (1983)	$HTcO_4^-$	Rard (1983)
$TcO(OH)^+$	Rard (1983)	$H_2TcO_4^{\circ}$ (aq)	Rard (1983)
$TcO(OH)_2^{\circ}$ (aq)	Rard (1983)	TcO_4^-	Rard (1983)
$[TcO(OH)_2]_2^{\circ}$ (aq)	Rard (1983)	$HTcO_4^{\circ}$ (aq)	Rard (1983)
TcO_4^{3-}	Rard (1983)		
		Solid Compounds	
Tc	Rard (1983)	TcOH	Rard (1983)
$KTcO_4$	Rard (1983)	$TcO_2 \cdot 2H_2O$ (am)	Rard (1983)
$NaTcO_4$	Rard (1983)	Tc_4O_7	Rard (1983)
$Tc(OH)_2$	Rard (1983)	TcS_3	Rard (1983)
$Tc(OH)_3$	Rard (1983)	TcO_3	Rard (1983)
Tc_3O_4	Rard (1983)	Tc_2S_7	Rard (1983)
TcS_2	Rard (1983)		

Table D.7 Formula and sources of thermodynamic data for thorium aqueous species and solid compounds

Formula	Reference source	Formula	Reference source
		Aqueous Species	
Th^{4+}	Langmuir and Herman (1980)	$ThCl_2^{2+}$	Langmuir and Herman (1980)
$ThOH^{3+}$	Wagman et al. (1982)	$ThCl_3^+$	Langmuir and Herman (1980)
$Th(OH)_2^{2+}$	Langmuir and Herman (1980)	$ThCl_4^\circ$ (aq)	Langmuir and Herman (1980)
$Th(OH)_3^+$	Langmuir and Herman (1980)	$ThSO_4^{2+}$	Langmuir and Herman (1980)
$Th(OH)_4^\circ$ (aq)	Baes and Mesmer (1976)	$Th(SO_4)_2^\circ$ (aq)	Langmuir and Herman (1980)
$Th_2(OH)_2^{6+}$	Langmuir and Herman (1980)	$Th(SO_4)_3^{2-}$	Langmuir and Herman (1980)
$Th_4(OH)_8^{8+}$	Langmuir and Herman (1980)	$Th(SO_4)_4^{4-}$	Langmuir and Herman (1980)
$Th_6(OH)_{15}^{9+}$	Langmuir and Herman (1980)	$ThH_3PO_4^{4+}$	Langmuir and Herman (1980)
ThF^{3+}	Langmuir and Herman (1980)	$ThH_2PO_4^{3+}$	Langmuir and Herman (1980)
ThF_2^{2+}	Langmuir and Herman (1980)	$Th(H_2PO_4)_2^{2+}$	Langmuir and Herman (1980)
ThF_3^+	Langmuir and Herman (1980)	$Th(HPO_4)_2^\circ$ (aq)	Langmuir and Herman (1980)
ThF_4° (aq)	Langmuir and Herman (1980)	$Th(HPO_4)_3^{2-}$	Langmuir and Herman (1980)
$ThCl^{3+}$	Langmuir and Herman (1980)	$Th(CO_3)_5^{6-}$	Östhols et al. (1994)
		$Th(OH)_3CO_3^-$	Östhols et al. (1994)
		Solid Compounds	
Th	Cox et al. (1989)	$ThCl_4$	Langmuir and Herman (1980)
Th_2S_3	Wagman et al. (1982)	ThF_4	Langmuir and Herman (1980)
Th_7S_{12}	Wagman et al. (1982)	$ThF_4 \cdot 2.5H_2O$	Wagman et al. (1982)
ThS_2	Wagman et al. (1982)	ThI_4	Wagman et al. (1982)
$Th(OH)_4$	Naumov et al. (1974)	$Th(NO_3)_4 \cdot 5H_2O$	Wagman et al. (1982)
ThO_2	Cox et al. (1989)	$Th(SO_4)_2$	Wagman et al. (1982)
$ThBr_4$	Wagman et al. (1982)	Th_2Se_3	Mills (1974)

Table D.8 Formula and sources of thermodynamic data for uranium aqueous species and solid compounds

Formula	Reference source	Formula	Reference source
		Aqueous Species	
U^{3+}	Grenthe et al. (1992)	UO_2Cl^+	Grenthe et al. (1992)
U^{4+}	Grenthe et al. (1992)	$UO_2Cl_2^\circ$ (aq)	Grenthe et al. (1992)
UO_2^+	Grenthe et al. (1992)	UBr^{3+}	Grenthe et al. (1992)
UO_2^{2+}	Grenthe et al. (1992)	UO_2Br^+	Grenthe et al. (1992)
UOH^{3+}	Grenthe et al. (1992)	UI^{3+}	Grenthe et al. (1992)
$U(OH)_2^{2+}$	Grenthe et al. (1990)	USO_4^{2+}	Grenthe et al. (1992)
$U(OH)_3^+$	Grenthe et al. (1990)	$UO_2SO_4^\circ$ (aq)	Grenthe et al. (1992)
$U(OH)_4^\circ$ (aq)	Grenthe et al. (1990)	$U(SO_4)_2^\circ$ (aq)	Grenthe et al. (1992)
$U(OH)_5^-$	Grenthe et al. (1990)	$UO_2(SO_4)_2^{2-}$	Grenthe et al. (1992)
UO_2OH^+	Grenthe et al. (1992)	UNO_3^{3+}	Grenthe et al. (1992)
$UO_2(OH)_2^\circ$ (aq)	Grenthe et al. (1992)	$U(NO_3)_2^{2+}$	Grenthe et al. (1992)
$UO_2(OH)_3^-$	Grenthe et al. (1992)	$UO_2NO_3^+$	Grenthe et al. (1992)
$UO_2(OH)_4^{2-}$	Grenthe et al. (1992)	$UO_2PO_4^-$	Grenthe et al. (1990)
$(UO_2)_2OH^{3+}$	Grenthe et al. (1992)	$UO_2HPO_4^\circ$ (aq)	Grenthe et al. (1990)
$(UO_2)_2(OH)_2^{2+}$	Grenthe et al. (1992)	$UO_2H_2PO_4^+$	Grenthe et al. (1990)
$(UO_2)_3(OH)_4^{2+}$	Grenthe et al. (1992)	$UO_2H_3PO_4^{2+}$	Grenthe et al. (1990)
$(UO_2)_3(OH)_5^+$	Grenthe et al. (1992)	$UO_2(H_2PO_4)_2^\circ$ (aq)	Grenthe et al. (1990)
$(UO_2)_3(OH)_7^-$	Grenthe et al. (1992)	$UO_2(H_2PO_4)(H_3PO_4)^+$	Grenthe et al. (1990)
$(UO_2)_4(OH)_7^+$	Grenthe et al. (1992)	$U(CO_3)_4^{4-}$	Grenthe et al. (1992)
$U_6(OH)_{15}^{9+}$	Grenthe et al. (1992)	$U(CO_3)_5^{6-}$	Grenthe et al. (1992)
UF^{3+}	Grenthe et al. (1992)	$UO_2CO_3^\circ$ (aq)	Grenthe et al. (1992)
UF_2^{2+}	Grenthe et al. (1992)	$UO_2(CO_3)_2^{2-}$	Grenthe et al. (1992)
UF_3^+	Grenthe et al. (1992)	$UO_2(CO_3)_3^{4-}$	Grenthe et al. (1992)
UF_4° (aq)	Grenthe et al. (1992)	$UO_2(CO_3)_3^{5-}$	Grenthe et al. (1992)
UF_5^-	Grenthe et al. (1992)	$(UO_2)_3(CO_3)_6^{6-}$	Grenthe et al. (1992)
UF_6^{2-}	Grenthe et al. (1992)	$UO_2OHCO_2^+$	Grenthe et al. (1990)
UO_2F^+	Grenthe et al. (1992)	$(UO_2)_{11}(CO_3)_6(OH)_{12}^{2-}$	Grenthe et al. (1990)
$UO_2F_2^\circ$ (aq)	Grenthe et al. (1992)	$(UO_2)_2CO_3(OH)_3^-$	Grenthe et al. (1990)
$UO_2F_3^-$	Grenthe et al. (1992)	$UO_2SiO(OH)_3^+$; same as $UO_2H_3SiO_4^+$	Grenthe et al. (1990)
$UO_2F_4^{2-}$	Grenthe et al. (1992)		
UCl^{3+}	Grenthe et al. (1992)		

Table D.8 continued

Formula	Reference source	Formula	Reference source
	Solid Compounds		
UBr_2Cl	Grenthe et al. (1990)	Na_3UO_4	Grenthe et al. (1990)
UBr_3	Grenthe et al. (1990)		
UCl_3	Grenthe et al. (1990)	UBr_5	Grenthe et al. (1990)
$UBrCl_2$	Grenthe et al. (1990)	$UOBr_3$	Grenthe et al. (1990)
$UOCl$	Grenthe et al. (1990)	UCl_5	Grenthe et al. (1990)
UF_3	Grenthe et al. (1990)	$UOCl_3$	Grenthe et al. (1990)
UI_3	Grenthe et al. (1990)	UO_2Cl	Grenthe et al. (1990)
UO_2 (am)	Grenthe et al. (1990)	$U_5O_{12}Cl$	Grenthe et al. (1990)
U_4O_9	Langmuir (1978)	α-UF_5	Grenthe et al. (1990)
U_3O_8	Grenthe et al. (1990)	β-UF_5	Grenthe et al. (1990)
UBr_4	Grenthe et al. (1990)	UPO_5	Grenthe et al. (1990)
$UOBr_2$	Grenthe et al. (1990)	β-$UO_2(OH)_2$	Grenthe et al. (1990)
UBr_3Cl	Grenthe et al. (1990)	Schoepite	Grenthe et al. (1990)
$UBrCL_3$	Grenthe et al. (1990)	Dehyrated Schoepite	O'Hare et al. (1988)
UCl_4	Grenthe et al. (1990)	Dehyrated Schoepite	O'Hare et al. (1988)
UBr_2Cl_2	Grenthe et al. (1990)	Dehyrated Schoepite	O'Hare et al. (1988)
$UOCl_2$	Grenthe et al. (1990)	Dehyrated Schoepite(.9)	Grenthe et al. (1990)
$U_2O_2Cl_5$	Grenthe et al. (1990)	Dehyrated Schoepite	O'Hare et al. (1988)
UF_4	Grenthe et al. (1990)	UO_2, Uraninite	Grenthe et al. (1990)
$UF_4 \cdot 2.5H_2O$	Grenthe et al. (1990)	α-UO_3	Grenthe et al. (1990)
U_2F_9	Grenthe et al. (1990)	β-UO_3	Grenthe et al. (1990)
U_4F_{17}	Grenthe et al. (1989)	γ-UO_3	Grenthe et al. (1990)
$UClF_3$	Grenthe et al. (1990)	Gummite	Langmuir (1978)
UCl_2F_2	Grenthe et al. (1990)	K_2UO_4	Grenthe et al. (1990)
UCl_3F	Grenthe et al. (1990)	Li_2UO_4	Grenthe et al. (1990)
UOF_2	Grenthe et al. (1990)	$Na_2U_2O_7$	Grenthe et al. (1990)
$UOF_2 \cdot H_2O$	Grenthe et al. (1990)	α-Na_2UO_4	Grenthe et al. (1990)
UOFOH	Grenthe et al. (1990)	$BaUO_4$	Grenthe et al. (1990)
UI_4	Grenthe et al. (1990)	$CaUO_4$	Grenthe et al. (1990)
$UClI_3$	Grenthe et al. (1990)	$MgUO_4$	Grenthe et al. (1990)
UCl_2I_2	Grenthe et al. (1990)	$NaUO_3$	Grenthe et al. (1990)
UCl_3I	Grenthe et al. (1990)	$NaUO_2(CO_3)_3$	Grenthe et al. (1990)
$U(CO_3)_2$	Grenthe et al. (1990)	Rb_2UO_4	Grenthe et al. (1990)
$U(OH)_2SO_4$	Grenthe et al. (1990)	α-$SrUO_4$	Grenthe et al. (1990)
$U(SO_4)_2$	Grenthe et al. (1990)	UO_2Br_2	Grenthe et al. (1990)
$U(SO_4)_2 \cdot 4H_2O$	Grenthe et al. (1990)	$UO_2Br_2 \cdot H_2O$	Grenthe et al. (1990)
$U(SO_4)_2 \cdot 8H_2O$	Grenthe et al. (1990)	$UO_2Br_2 \cdot 3H_2O$	Grenthe et al. (1990)
$U(HPO_4)_2 \cdot 4H_2O$	Grenthe et al. (1990)	$UO_2BrOH \cdot 2H_2O$	Grenthe et al. (1990)
Coffinite	Grenthe et al. (1990)	UCl_6	Grenthe et al. (1990)

Table D.8 continued

Formula	Reference source	Formula	Reference source
	Solid Compounds (continued)		
UO_2Cl_2	Grenthe et al. (1990)	UO_2HPO_4	Tripathi (1984)
$UO_2Cl_2 \cdot H_2O$	Grenthe et al. (1990)	$UO_2HPO_4 \cdot 4H_2O$	Grenthe et al. (1990)
$UO_2Cl_2 \cdot 3H_2O$	Grenthe et al. (1990)	$UP_2O_7 \cdot 20H_2O$	Grenthe et al. (1990)
$UO_2ClOH \cdot 2H_2O$	Grenthe et al. (1990)	$UO_2(AsO_3)_2$	Grenthe et al. (1990)
$(UO_2)_2Cl_3$	Grenthe et al. (1990)	$(UO_2)_2As_2O_7$	Grenthe et al. (1990)
UF_6	Grenthe et al. (1990)	$(UO_2)_3(AsO_4)_2$	Grenthe et al. (1990)
UO_2FOH	Grenthe et al. (1990)	$K(UO_2)AsO_4$	Wagman et al. (1982)
$UO_2FOH \cdot H_2O$	Grenthe et al. (1990)	Boltwoodite	Hemingway (1982)
$UO_2FOH \cdot 2H_2O$	Grenthe et al. (1990)	Haiweeite	Hemingway (1982)
UO_2F_2	Grenthe et al. (1990)	Kasolite	Hemingway (1982)
$UO_2F_2 \cdot 3H_2O$	Grenthe et al. (1990)	Sklodowskite	Hemingway (1982)
$U_2O_3F_6$	Grenthe et al. (1990)	Soddyite	Hemingway (1982)
$U_3O_5F_8$	Grenthe et al. (1990)	Weeksite	Hemingway (1982)
UOF_4	Grenthe et al. (1990)	Tyuyamunite	Langmuir (1978)
Rutherfordine	Grenthe et al. (1990)	Carnotite	Langmuir (1978)
$UO_2(NO_3)_2$	Grenthe et al. (1990)	Autunite	Sverjensky (1990)
$UO_2(NO_3)_2 \cdot H_2O$	Grenthe et al. (1990)	H-Autunite	Grenthe et al. (1990)
$UO_2(NO_3)_2 \cdot 2H_2O$	Grenthe et al. (1990)	K-Autunite	Sverjensky (1990)
$UO_2(NO_3)_2 \cdot 3H_2O$	Grenthe et al. (1990)	Na-Autunite	Sverjensky (1990)
$UO_2(NO_3)_2 \cdot 6H_2O$	Grenthe et al. (1990)	Sr-Autunite	Langmuir (1978)
UO_2SO_4	Grenthe et al. (1990)	USb_2	
$UO_2SO_4 \cdot H_2O$	Owens and Mayer (1964)	U_3Sb_4	
$UO_2SO_4 \cdot 2.5H_2O$	Owens and Mayer (1964)	Ningoyite	Langmuir (1978)
$UO_2SO_4 \cdot 3H_2O$	Owens and Mayer (1964)	Uramphite	Langmuir (1978)
$UO_2SO_4 \cdot 3.5H_2O$	Owens and Mayer (1964)	Saleeite	Sverjensky (1990)
$(UO_2)_3(PO_4)_2$	Grenthe et al. (1990)	Uranocirite	Langmuir (1978)
$(UO_2)_3(PO_4)_2 \cdot 4H_2O$	Grenthe et al. (1990)	Bassetite	Langmuir (1978)
$(UO_2)_2P_2O_7$	Grenthe et al. (1990)	Torbernite	Sverjensky (1990)
Parsonite	Rickard and Nriagu (1978)	Przhevalskite	Langmuir (1978)
$UO_2(PO_3)_2$	Grenthe et al. (1990)	Uranophane	Langmuir (1978)

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Appendix E

Extracting K_d Values From Diffusion and Leaching Data

Appendix E

Extracting K_d Values From Diffusion and Leaching Data

Atkinson (1983), Atkinson et al. (1986), and Atkinson and Nickerson (1988) present a useful conceptual model for describing the transport of contaminants through a porous media such as cement. The authors consider that the transport is a combination of both physical processes, such as diffusion, and chemical processes, such as precipitation/solubility and adsorption/desorption. The first two references discuss diffusion-controlled release (leaching) of a contaminant from cement, while the last reference describes how to evaluate the diffusion of a contaminant through a slab of cement or into a thick slab of cement.

E.1 Diffusion

Diffusion formalisms are used and based on the movement of a species caused by the concentration gradient, wherein species move from regions of high concentration to regions of lower concentration. In an infinitely dilute aqueous solution, the movement is quantified by the diffusion coefficient, D_f. For most simple aqueous species D_f is about 10^{-9} m^2/s or 10^{-5} cm^2/s.

In the constrained geometry of a porous media, such as cement, the D_f is reduced compared to the D_f in free aqueous solution. The D_f for a species within a porous media is defined as D_p and is equal to

$$D_p = D_f \, \delta/\tau^2 \tag{E.1}$$

where δ = constrictivity of the porous media and τ = tortuosity of the porous media.

For experimentalists, it is convenient to measure the average flux of a contaminant per unit area of the porous media in relation to the concentration gradient of the contaminant in the aqueous phase. The concentration gradient in the aqueous phase is influenced by the volume fraction of the void space in the porous media (the porosity, given the symbol ε). This leads to another equation that defines the "intrinsic" diffusion coefficient, D_i:

$$D_i = D_p \, \varepsilon = D_f \, \varepsilon \, \delta / \tau^2 \tag{E.2}$$

A key assumption herein is that all the porosity in the porous media is interconnected and thus can contribute to diffusion of the contaminant. All three parameters, porosity (ε), constrictivity (δ), and tortuosity (τ), characterize the physical contribution to diffusion through the porous media.

E.2 Chemical Contributions

The chemical contributions to diffusion can potentially be quite varied, such as ion exchange, specific adsorption, precipitation, and lattice substitution. If we assume a very simple chemical process, reversible surface adsorption having fast kinetics and a linear isotherm (adsorption is proportional to the concentration in solution via a fixed constant, K_d), then diffusion of a reactive contaminant can be characterized by an apparent diffusion coefficient, D_a:

$$D_a = D_i/\alpha = D_p\, \varepsilon / \alpha = (D_f\, \delta\, \varepsilon) / (\tau^2 \alpha) \tag{E.3}$$

where α is the capacity factor or ratio of the moles per unit volume of water-saturated solid, C_s, to the moles per unit volume of liquid, C_l. The capacity factor is related to the K_d by the equation

$$\alpha = \varepsilon + \rho\, K_d \tag{E.4}$$

where ρ is the dry bulk density of the porous media and K_d is the amount of contaminant adsorbed per unit mass of porous solid divided by the amount of contaminant per unit volume of liquid. Also note that α/ε is the familiar retardation factor used in transport modeling:

$$\alpha / \varepsilon = R = 1 + \rho\, K_d / \varepsilon \tag{E.5}$$

It should be noted that these simple relationships are strictly only valid for reversible, linear adsorption reactions with fast kinetics. Most often this is not the case for interactions between real cementitious porous media and contaminant-bearing waters of interest to low-level radioactive waste disposal. This point is often overlooked and should not be. Nevertheless, such simplifying assumptions allow for some interesting analysis of common laboratory data and experiments.

E.3 Analysis of Laboratory Leach Data

In Equation E.3, the term D_i contains all the physical aspects of diffusional transport and the term α contains all the chemical aspects of diffusional transport. Several experimental approaches can be used to measure these two parameters. Atkinson et al. (1986) and Atkinson and Nickerson (1988) have determined by observation which experimental techniques give the best results for various contaminants under various geochemical conditions.

Atkinson et al. (1986) suggest that classical leach tests that use the intermittent solution exchange method, such as International Standards Organization (ISO) and American Nuclear Society (ANS) tests (see ISO 1979; Mendel 1982; and ANS 1986), and the purely static leach test can be used in concert to calculate D_a and α, respectively. Using the combination of these two leach test methods, fairly accurate values can be obtained for the physical and chemical parameters of interest. The static leach test at long time periods allows a good estimate to be determined of the amount of contaminant that has migrated from the solid waste into solution. From knowledge of the starting inventory in the waste $A_s(t = 0)$, the final inventory left in the solid $A_s(t = \infty)$ can be determined. From knowledge of the volumes of solution and the volume of the solid present in the static test, α can be calculated from Equation E.6 as follows:

$$\alpha = [A_s(t{=}\infty)\, V_L] / [A_L(t{=}\infty)\, V_s] \tag{E.6}$$

where A_s = contaminant amount in solid per volume at end of test, A_L = contaminant amount in solution per volume at end of test, V_L = volume of liquid used in static test, and V_s = volume of solid used in static test.

After α has been calculated, the K_d value can then be estimated by using Equation E.4 and known solid characteristics of porosity and dry bulk density.

Likewise, the intermittent solution exchange leach tests previously mentioned provide a direct measurement of D_a (often called D_{eff} in the leaching literature). Given that the apparent diffusion coefficient or effective diffusion coefficient (D_a or D_{eff}) is related to the D_i of the porous media by Equation E.3, one can thus estimate D_i from knowledge of α from the static test for a given cement type.

Alternatively, one can estimate D_i and α for a contaminant solely from data obtained from intermittent leach tests using the following logic. If a constituent that does not interact with the cement chemically is assumed to exist, then intermittent leach data for this constituent can be used to measure the D_i directly, because α will be equal to the porosity since the K_d for a non-reacting constituent is zero (see Equation E.4). Some researchers have assumed that nitrate, tritium, chloride, sodium, or potassium are non-reactive constituents in leach tests. If the assumption concerning the behavior of these constituents is valid, then the measured D_a can be used to estimate the intrinsic diffusion coefficient for the particular cement by multiplying by the cement porosity (see Equations E.3 and E.4). The D_i is assumed to be a property solely of the cement and not the contaminants within the cement.

Once D_i is established, then the intermittent leach data for the other reactive constituents within the cement provide a measure of their unique D_a from which the individual values of α can be calculated. From the porosity and dry bulk density, a K_d value of each individual contaminant can be estimated. Atkinson et al. (1986) suggest that such an approach should provide an estimate of α that is within an order of magnitude for contaminants with large K_d values and much better for contaminants with small K_d values.

E.4 Analysis of Laboratory Diffusion Profile Data

Numerous through-diffusion and diffusion-penetration profile types of experiments have been performed by the nuclear waste community to evaluate migration potential of contaminants of interest. These data can also be used to estimate the two basic parameters in Atkinson and Nickerson's conceptual model, D_i and α, from which the K_d value can be obtained.

E.4.1 Through-Diffusion Experiments

Atkinson and Nickerson (1988) found by extensive analysis of experimental data that D_i is most accurately measured using the through-diffusion type of test where a thin slab of porous media is mounted between two reservoirs of liquid. In one reservoir the solution is devoid of the contaminant of interest. In the other reservoir, the solution has the same chemical composition excepting the contaminant is present. The solution reservoir containing the contaminant is connected to a large recirculating reservoir such that there is no drop in the contaminant concentration throughout the test. The build-up of the contaminant in the initially blank reservoir is monitored until it reaches a steady state.

Steady state is reached when a plot of the breakthrough curve C/C_o (y-axis) versus time (x-axis) is a straight line. The value of D_p is related to the slope of such a plot by the constant factor (V L / A), where

V = volume of solution in the initially "cold" reservoir (no contaminant present)
L = thickness of the porous slab or disk
A = geometric surface area of the porous slab or disk
C = concentration of the contaminant in the "cold" reservoir at time t
C_o = concentration in the "hot" reservoir at all times (must be kept constant).

If the experiment is performed correctly, the chemical term α can also be estimated from the equation

$$\alpha = (6\ D_i\ t_o) / (L^2) \qquad \text{(E.7)}$$

where t_o = the intercept point on the x-axis (time) at $C/C_o = 0$ for the extrapolation of the straight line segment of the breakthrough curve. In other words, t_o is the amount of time delay before contaminant starts to appear in the cold reservoir under steady-state conditions.

Atkinson and Nickerson (1988) suggest that the through-diffusion tests give an accurate measure of D_i. They believe that the estimate of α was not as accurate, because there appear to be two types of porosity in cement. This dual porosity observation causes the estimates of α to be lower than they really are. One type of porosity makes up a small percentage of the total porosity and is conceptualized as well-connected pores allowing fast transport and relatively lower chemical capacity (adsorption). The second type of porosity makes up the bulk of the total porosity and allows slow transport because of constrictions/tortuosity in the pores "connectiveness." Because this second type of porosity makes up most of the total porosity, it also can adsorb (chemically react) more than the first type of porosity and thus it exhibits a higher chemical capacity factor, α.

One drawback to the through-diffusion testing is that highly adsorbing contaminants take long time periods to show up in the reservoir initially free of the contaminant. For concretes with large aggregate, one must also make the slabs or disks thicker to prevent short circuits of the flow pattern around individual grain boundaries. The length of time required to obtain useful data increases as the thichness of the slag increases.

E.4.2 Penetration Profile Experiments

A second experimental approach generally referred to as the penetration profile test uses a slab of porous media that has all but one if its surfaces blocked off to solution penetration. The other surfaces may be isolated from the solution by being cast in an epoxy mold or embedded in hydrophobic plastic or wax. If the slab is assumed to be semi-infinitely thick, then, at any given time, the penetration profile of a contaminant that is in contact with the surface (x = 0) of the slab is related to the physical aspects of diffusion, D_i, and the chemical capacity factor, α, through the complementary error function as shown in Equation E.8.

$$C_s(x) / C_L = \alpha \text{ erfc } \{(\alpha x^2 / 4 D_i t)^{1/2}\} \tag{E.8}$$

where C_s = concentration of contaminant on solid at depth x and time t and C_L = concentration in liquid at time t.

Brown et al. (1964, 1969), Phillips and Brown (1964), and Relyea et al. (1986) describe a convenient data reduction scheme that transforms the contaminant penetration profile into the cement or other porous media as a probability distribution called probit. The breakthrough profile is first determined as the concentration of the contaminant in the cement at depth x at time t divided by the concentration of the contaminant in the face of the cement at x = 0 and at time = 0. After calculating this ratio (as a percentage), the equivalent probit value for all the data points between 5 percent and 95 percent can be looked up using the probit table in Finney (1971) or equivalent tables of mathematical functions. The probit values are then plotted as a function of the depth of penetration. Such plots should generate a straight line as opposed to the sigmoidal curve obtained from Equation E.8. Thus the probit transformation (y axis), when plotted as a function of penetration depth on the x-axis, results in a curve that is easier to interpret. The effective diffusion coefficient, D_a, is related to the slope of the line through the following equation:

$$D_a = 1 / (2 \text{ slope}^2 t) \tag{E.9}$$

By using several tracers or contaminants and having one that is considered a non-reacting constituent (e.g., nitrate, tritium, or chloride), K_d values can be estimated for the other reactive constituents using Equations E.3 and E.4. That is, the slope of the curves (probit values versus depth) for conservative tracers gives D_a and, by virtue of $K_d = 0$ and $\alpha = \varepsilon$ (a known quantity), an estimate of D_i. Because D_i is a property of the porous media, it is the same for all the tracers or contaminants moving through a given cement. When a particular contaminant is determined to be non-reacting, then its measured effective diffusion coefficient, D_a, is equivalent to D_i/ε or the D_i divided by the porosity of the cement because the K_d value for a non-reactive contaminant is zero. Once D_i is known, then α for each reactive contaminant can be calculated from its measured effective diffusion coefficient, D_a, and the measured value of the cement's D_i just determined from data for the non-reactive contaminant. When the value of α has been determined for each reactive contaminant, then the K_d value can be estimated from Equation E.3 and the known porosity and dry bulk density of the cement.

E.4 Summary

Application of these conceptual models and mathematical techniques to diffusion and leach data published in the literature could increase the available estimates of K_d values for important contaminants. The number of waste-form leach tests and diffusion tests for cement in the literature is greater than the number of well-implemented adsorption tests. We have not pursued this approach for this review as it is beyond our scope. Perhaps a preliminary effort should be attempted to see if the leach and diffusion data in the literature are in fact readily converted and whether the calculated α values seem plausible.

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11. ABSTRACT *(200 words or less)*

The U.S. Nuclear Regulatory Commission is developing a technical position document that provides guidance regarding the performance assessment of low-level radioactive waste disposal facilities. This guidance considers the effects that the chemistry of the vault disposal system may have on radionuclide release. The geochemistry of pore waters buffered by cementitious materials in the disposal system will be different from the local ground water. Therefore, the cement-buffered environment needs to be considered within the source term calculations if credit is taken for solubility limits and/or sorption of dissolved radionuclides within disposal units. A literature review was conducted on methods to model pore-water compositions resulting from reactions with cement, experimental studies of cement/water systems, natural analogue studies of cement and concrete, and radionuclide solubilities experimentally determined in cement pore waters. Based on this review, geochemical modeling was used to calculate maximum concentrations for americium, neptunium, nickel, plutonium, radium, strontium, thorium, and uranium for pore-water compositions buffered by cement and local ground-water. Another literature review was completed on radionuclide sorption behavior onto "fresh" cement/concrete where the pore water pH will be ≥10. Based on this review, a database was developed of preferred minimum distribution coefficient (K_d) values for these radionuclides in cement/concrete environments.

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