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Environmental Geochemistry of Radioactive Contamination

Malcolm D. Siegel and Charles R. Bryan

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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Malcolm D. Siegel and Charles R. Bryan

Sandia National Laboratories, Albuquerque, NM

Abstract

This report attempts to describe the geochemical foundations of the behavior of radionuclides in the environment. The information is obtained and applied in three interacting spheres of inquiry and analysis: 1) experimental studies and theoretical calculations, 2) field studies of contaminated and natural analog sites and 3) model predictions of radionuclide behavior in remediation and waste disposal. Analyses of the risks from radioactive contamination require estimation of the rates of release and dispersion of the radionuclides through potential exposure pathways. These processes are controlled by solubility, speciation, sorption, and colloidal transport, which are strong functions of the compositions of the groundwater and geomeia as well as the atomic structure of the radionuclides.

The chemistry of the fission products is relatively simple compared to the actinides. Because of their relatively short half-lives, fission products account for a large fraction of the radioactivity in nuclear waste for the first several hundred years but do not represent a long-term hazard in the environment. The chemistry of the longer-lived actinides is complex; however, some trends in their behavior can be described. Actinide elements of a given oxidation state have either similar or systematically varying chemical properties due to similarities in ionic size, coordination number, valence, and electron structure. In dilute aqueous systems at neutral to basic pH, the dominant actinide species are hydroxy- and carbonato-complexes, and the solubility-limiting solid phases are commonly oxides, hydroxides or carbonates. In general, actinide sorption will decrease in the presence of ligands that complex with the radionuclide; sorption of the (IV) species of actinides (Np, Pu, U) is generally greater than of the (V) species.

The geochemistry of key radionuclides in three different environments is described in this report. These include: 1) low ionic strength reducing waters from crystalline rocks at nuclear waste research

sites in Sweden; 2) oxic water from the J-13 well at Yucca Mountain, Nevada, the site of a proposed repository for high level nuclear waste (HLW) in tuffaceous rocks; and 3) reference brines associated with the Waste Isolation Pilot Plant (WIPP). The transport behaviors of radionuclides associated with the Chernobyl reactor accident and the Oklo Natural Reactor are described. These examples span wide temporal and spatial scales and include the rapid geochemical and physical processes important to nuclear reactor accidents or industrial discharges as well as the slower processes important to the geologic disposal of nuclear waste.

Application of geochemical information to remediating or assessing the risk posed by radioactive contamination is the final subject of this report. After radioactive source terms have been removed, large volumes of soil and water with low but potentially hazardous levels of contamination may remain. For poorly-sorbing radionuclides, capture of contaminated water and removal of radionuclides may be possible using permeable reactive barriers and bioremediation. For strongly sorbing radionuclides, contaminant plumes will move very slowly. Through a combination of monitoring, regulations and modeling, it may be possible to have confidence that they will not be a hazard to current or future populations. Abstraction of the hydrogeochemical properties of real systems into simple models is required for probabilistic risk assessment. Simplifications in solubility and sorption models used in performance assessment calculations for the WIPP and the proposed HLW repository at Yucca Mountain are briefly described.

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Contents

1. INTRODUCTION	9
1.1 Approach and Outline of Report.....	9
1.2 Previous Reviews and Report Scope	10
2. THE NATURE AND HAZARDS OF RADIOACTIVE ENVIRONMENTAL CONTAMINATION.....	11
2.1 Sources of Radioactivity	11
2.1.1 Radioactive Processes.....	11
2.1.2 Natural Sources of Radioactivity	14
2.1.3 Nuclear Waste.....	15
2.1.4 Sites of Radioactive Environmental Contamination.....	17
2.2 Exposure to Background and Anthropogenic Sources of Radioactivity	19
2.3 Health Effects and Radioactive Contamination.....	20
2.3.1 Biological Effects of Radiation Damage	20
2.3.2 Epidemiological Studies	21
2.3.3 Toxicity and Carcinogenicity.....	22
3. EXPERIMENTAL AND THEORETICAL STUDIES OF RADIONUCLIDE GEOCHEMISTRY	23
3.1 Principles and Methods.....	24
3.1.1 Experimental Methods.....	24
3.1.1.1 Solubility and Speciation.....	24
3.1.1.2 Sorption Studies.....	25
3.1.1.2.1 Batch Techniques.....	25
3.1.1.2.2 Other Techniques.....	27
3.1.1.2.3 Surface Analytical Techniques	28
3.1.2 Theoretical Geochemical Models and Calculations	29
3.1.2.1 Aqueous Speciation and Solubility.....	29
3.1.2.2 Sorption.....	30
3.1.2.2.1 Overview.....	30
3.1.2.2.2 Representation of Sorption of Radionuclides Under Natural Conditions	34
3.1.2.2.3 Sorptive Properties of Mineral Assemblages and Soils.....	37
3.2 Results of Radionuclide Solubility, Speciation and Sorption Studies	38
3.2.1 Fission Products.....	38
3.2.1.1 ⁹⁰ Sr	39
3.2.1.2 ¹³⁷ Cs	39
3.2.1.3 ⁹⁹ Tc.....	40
3.2.1.4 ¹²⁹ I.....	41
3.2.2 Uranium and Other Actinides [An(III), An(IV), An(V), An(VI)].....	42
3.2.2.1 General Trends in Solubility, Speciation, and Sorption	42
3.2.2.1.1 Oxidation State.....	42
3.2.2.1.2 Complexation and Solubility	43
3.2.2.1.3 Sorption.....	44

3.2.3 Site-Specific Geochemistry of the Actinides	45
3.2.3.1 Introduction: Actinide Solubilities in Reference Waters	45
3.2.3.1.1 Americium	47
3.2.3.1.2 Thorium.....	49
3.2.3.1.3 Uranium	50
3.2.3.1.4 Neptunium.....	53
3.2.3.1.5 Plutonium.....	56
3.3 Other Topics.....	58
3.3.1 Colloids.....	58
3.3.1.1 Introduction.....	58
3.3.1.2 Naturally Occurring Colloids.....	59
3.3.1.3 Experimental Studies	60
3.3.1.4 Microbial and Humic Colloids.....	61
3.3.1.5 Transport of Radionuclides by Colloids	62
3.3.2 Microbe-Actinide Interactions	64
4. FIELD STUDIES OF RADIONUCLIDE BEHAVIOR.....	65
4.1 Introduction.....	65
4.2 Short-term Behavior of Radionuclides in the Environment – Contamination from the Chernobyl Reactor Accident.....	66
4.3 Natural Analogs for the Long-term Behavior of Radionuclides in the Environment – the Oklo Natural Reactor	68
5. APPLICATIONS: DEALING WITH RADIONUCLIDE CONTAMINATION IN THE ENVIRONMENT	70
5.1 Remediation	70
5.1.1 Permeable Reactive Barriers.....	70
5.1.2 Bioremediation.....	71
5.1.3 Monitored Natural Attenuation.....	72
5.2 Geochemical Models in Risk Assessment	73
5.2.1 Overview.....	73
5.2.2 Solubility Calculations for the Waste Isolation Pilot Plant	73
5.2.3 Models for Radionuclide Sorption at Yucca Mountain	74
6. SUMMARY - CHALLENGES AND FUTURE RESEARCH NEEDS	75
REFERENCES	79
APPENDIX A: SYMBOLS AND DEFINITIONS.	113

Figures

Figure 1. The major decay path for ^{238}U	12
Figure 2. Ingestion toxicity for high-level waste as a function of decay time.....	16
Figure 3. Sorption and desorption edges for uranyl on goethite in 0.01 M NaNO_3 solution. 27	
Figure 4. Comparison of sorption models.....	31
Figure 5. Calculated theoretical K_d for sorption of uranyl onto a goethite substrate as a function of pH at fixed total carbon concentration in the presence of a sequestering agent (EDTA).....	36
Figure 6. Aqueous speciation of uranium(VI) and the solubility of crystalline schoepite ($\beta\text{-UO}_2(\text{OH})_2$) under atmospheric conditions ($p\text{CO}_2 = 10^{-3.5}$).....	51
Figure 7. Calculated Np solubilities as a function of pH and Eh in J-13 groundwater variants	55
Figure 8. Eh-pH diagram showing dominant plutonium solid phases and species for J-13 water variants at 25 $^\circ\text{C}$	57

Tables

Table 1. The Major Decay Paths for Several Important Actinides (isotope, half life, and decay mode).....	13
Table 2. Examples of Sources of Radioactivity in the Environment.....	15
Table 3. Environmentally Important Fission Products.	38
Table 4. Important Actinide Oxidation States in the Environment.	43
Table 5. Compositions of Low Ionic Strength Reference Waters Used in Speciation and Solubility Calculations.....	46
Table 6. Compositions of Brines Used in WIPP Speciation and Solubility Calculations.	47
Table 7. Solubility-Limiting Solids and Range of Solubility-Limited Concentrations (Concentration in M) for Low-Ionic Strength Geochemical Environments.....	48
Table 8. Calculated Actinide Solubilities in WIPP Brines	49

Acronyms

Bq	becquerel
CCA	Compliance Certification Application
CEC	cation exchange capacity
Ci	Curie
DLM	Double Layer or Diffuse Layer Model
DOE	Department of Energy
EPA	Environmental Protection Agency
EXAFS	Extended X-ray Absorption Fine Structure Spectroscopy
FSU	Former Soviet Union
Gy	Gray
HLW	high-level waste
LLW	low-level waste
MNA	monitored natural attenuation
N	neutron number
NEA	Nuclear Energy Agency
NRC	Nuclear Regulatory Commission
R	Roentgen
rad	radiation-absorbed-dose
rem	roentgen-equivalent-man
SCM	surface complexation model
SF	spent fuel
Sv	Sievert
TEDE	total effective dose equivalent
TLM	triple-layer model
TRU	transuranic
U.S.	United States
UMTRA	Uranium Mill Tailings Remedial Action (Project)
UMTRCA	Uranium Mill Tailings Radiation Control Act of 1978
WIPP	Waste Isolation Pilot Plant
Z	proton number

1. Introduction

Psychometric studies of public perception of risk have shown that dangers associated with radioactive contamination are considered the most dreaded and among the least understood hazards (Slovic, 1987). Fear of the risks associated with nuclear power and associated contamination has had important effects on policy and commercial decisions in the last few decades. In the United States (U.S.), no new nuclear power plants were ordered between 1978 and 2002, even though it has been suggested that the use of nuclear power has led to significantly reduced CO₂ emissions and may provide some relief from the potential climatic changes associated with fossil fuel use. The costs of the remediation of sites contaminated by radioactive materials and the projected costs of waste disposal of radioactive waste in the U.S. dwarf many other environmental programs. The cost of disposal of spent nuclear fuel at the proposed repository at Yucca Mountain will likely exceed \$10 billion. The estimated total life cycle cost for remediation of U.S. Department of Energy (DOE) weapons production sites ranged from \$203 – 247 billion dollars in constant 1999 dollars, making the cleanup the largest environmental project on the planet (U.S. DOE, 2001). Estimates for the cleanup of the Hanford site alone exceeded \$85 billion through 2046 in some of the remediation plans.

Policy decisions concerning radioactive contamination should be based on an understanding of the potential migration of radionuclides through the geosphere. In many cases, this potential may have been overestimated, leading to decisions to clean up contaminated sites unnecessarily and exposing workers to unnecessary risk. It is important for both the general public and the scientific community to be familiar with information that is well established, to identify the areas of uncertainty and to understand the significance of that uncertainty to the assessment of risk.

1.1 Approach and Outline of Report

This report provides an applications-oriented summary of current understanding of environmental radioactive contamination by addressing three major questions:

- 1) What are the major sources of radioactive contamination on the planet?
- 2) What controls the migration of radioactive contaminants in the environment?
- 3) How can an understanding of radionuclide geochemistry be used to facilitate environmental remediation or disposal of radioactive wastes, and how can we assess the associated risks?

The report starts with an overview of the nature of major sites of radioactive environmental contamination. A brief summary of the health effects associated with exposure to ionizing radiation and radioactive materials follows. The remainder of the report summarizes current knowledge of the properties of radionuclides as obtained and applied in three interacting spheres of inquiry and analysis: 1) experimental studies and theoretical calculations, 2) field studies and 3) predictions of radionuclide behavior for remediation and waste disposal. Recent studies of radionuclide speciation, solubility and sorption are reviewed, drawing upon the major U.S. and European nuclear waste and remediation programs. Examples are given of the application of that information to understanding the behavior of radionuclides as

observed at sites of natural and anthropogenic radioactive contamination. Finally, the uses of that information in remediation of radioactive contamination and in predicting the potential behavior of radionuclides released from proposed nuclear waste repositories are described.

1.2 Previous Reviews and Report Scope

Information describing the environmental geochemistry of radionuclides is being gathered at a rapid rate due to the high interest and pressing need to dispose of nuclear wastes and to remediate radioactively contaminated areas. Several important books have been written on the subject of actinide chemistry in the last few decades. Notable ones include Seaborg and Katz (1954), Katz, Seaborg and Morse (1986), Ivanovich (1992); and Choppin, Liljenzin and Rydberg (1995). This report updates similar reviews that have been published in the last few decades, such as those by Allard (1983), Krauskopf (1986), Choppin and Stout (1989), Hobart (1990), Fuger (1992), Kim (1993), Silva and Nitsche (1995) and chapters in Barney et al. (1984), Langmuir (1997a), and Zhang and Brady (2002). National symposia dealing with the disposal of nuclear waste and remediation of radioactive environmental contamination have been held annually by the Material Research Society (for example, see McGrail and Cragolino, 2002) and Waste Management Symposia, Inc. (for example, see WM Symposia, Inc., 2001) for the last two decades. Proceedings of these conferences should continue to be valuable sources of the results of current research and work carried out after the publication of this report.

This report focuses on the interactions of radionuclides with geomedia in near-surface low temperature environments. Due to the limitations on the report length, this review will not describe the mineralogy or economic geology of uranium deposits; the use of radionuclides as environmental tracers in studies of the atmosphere, hydrosphere or lithosphere, the nature of the nuclear fuel cycle or processes involved in nuclear weapons production. Likewise, radioactive contamination associated with the use of atomic weapons during World War II, the contamination of the atmosphere, hydrosphere or lithosphere related to nuclear weapons testing, and concerns over the contamination of the Arctic Ocean by the Soviet nuclear fleet are not discussed. The interested reader is advised to turn to other summaries of these topics and included references. The nuclear fuel cycle is summarized in publications of the U.S. Department of Energy (*The Legacy Story*, U.S. DOE, 1997b <http://legacystory.apps.em.doe.gov/index.asp>). Eisenbud (1987) provides a comprehensive overview of environmental radioactivity from natural, industrial and military sources. A recent publication of the Mineralogical Society of America included a series of review articles describing the mineralogy and paragenesis of uranium deposits and the environmental geochemistry of uranium and its decay products (Burns and Finch, 1999). Mahara and Kudo (1995) and Kudo et al. (1995) review the environmental behavior of plutonium released by the Nagasaki atomic bomb blast. A recent summary of the extent of contamination from atmospheric nuclear testing is found in Beck and Bennett (2002). Descriptions of radioactive contamination of the Arctic Ocean are found in Salbu et al. (1997), Aarkrog et al. (1999) and in publications of the Arctic Monitoring and Assessment Programme (AMAP, 2003; <http://www.amap.no/>).

2. The Nature and Hazards of Radioactive Environmental Contamination

The relationships between radioactive contamination and the risks to human health have scientific and regulatory dimensions. From the scientific perspective, the risks associated with radioactive contamination depend systematically on the magnitude of the source, the type of radiation, exposure routes and biological susceptibility to the effects of radiation damage. The effects of radiation on human health can be ascertained from the health status of people exposed to different levels of radiation in nuclear explosions or occupational settings. The most extreme exposures include those experienced by survivors of the atomic bomb blasts in Hiroshima and Nagasaki in World War II. Researchers have not observed an increase in cancer frequency for Japanese bomb survivors below an external dose of 0.2 Gy (20 rad), thus providing a lower limit for human biological susceptibility to the effects of radiation. In contrast, the regulatory perspective addresses estimates of an upper limit to biological susceptibility and involves a *di minimus* approach to exposure limits. Radiation protection standards are based on a “zero threshold” dose response relationship and exposure for the public is limited to 1 mSv yr⁻¹ (0.1 rem yr⁻¹). The following sections summarize basic information about the scientific and regulatory aspects of this issue. The different types of radioactivity are characterized, natural and anthropogenic sources of radioactivity are described, levels of exposure to these sources are estimated and compared to regulatory exposure limits, and the effects of radiation on human health are discussed.

2.1 Sources of Radioactivity

2.1.1 Radioactive Processes

Only certain combinations of protons and neutrons result in stable atomic nuclei. Figure 1 shows a section of the chart of the nuclides, on which nuclides are plotted as a function of their proton number (Z) and neutron number (N). The radioactive decay chain for ²³⁸U is indicated; only ²⁰⁶Pb has a stable combination of protons and neutrons. At low atomic numbers (below Z=20), isotopes with proton:neutron ratios of approximately one are stable, but a progressively higher proportion of neutrons is required to produce stability at higher atomic numbers. Unstable nuclei undergo radioactive decay—spontaneous transformations involving emission of particles and/or photons, resulting in changes in Z and N, and transformation of that atom into another element. Several types of radioactive decay may occur:

- β^- decay — a negatively charged beta particle (electron) is emitted from the nucleus of the atom, and one of the neutrons is transformed into a proton. Z increases by one and N decreases by one.
- β^+ decay — a positively charged beta particle (positron) is emitted from the nucleus and a proton is transformed into a neutron. Z decreases by one and N increases by one.
- Electron capture — an unstable nucleus may capture an extranuclear electron, commonly a K-shell electron, resulting in the transformation of a proton to a neutron.

This results in the same change in Z and N as β^+ decay; commonly, nuclides with a deficiency of neutrons can decay by either mechanism.

- α decay — nuclei of high atomic number (heavier than cerium), and a few light nuclides, may decay by emission of an α particle, a ${}^4\text{He}$ nucleus consisting of two protons and two neutrons. Z and N both decrease by two.

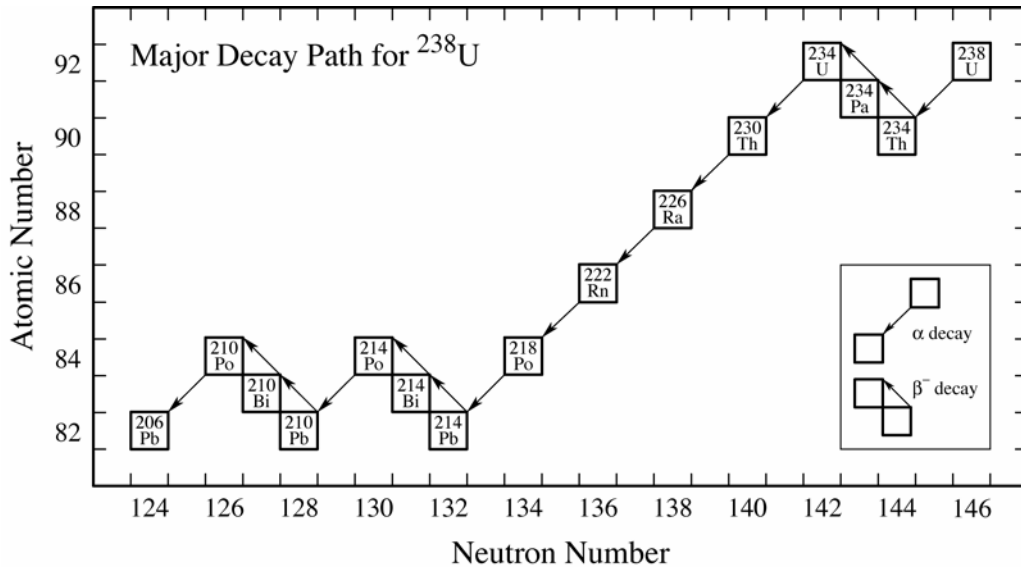


Figure 1. The major decay path for ${}^{238}\text{U}$.

A small fraction of decays will follow other possible decay paths—for example, decaying by β^- emission from ${}^{218}\text{Po}$ to ${}^{218}\text{At}$, and then by α emission to ${}^{214}\text{Bi}$ —but ${}^{206}\text{Pb}$ is the stable end product in all cases.

In each case, the daughter nucleus is commonly left in an excited state and decays to the ground state by emission of gamma rays. If there is a significant delay between the two processes, the γ emission is considered a separate event. Decay by γ emission, resulting in no change in Z or N , is called an isomeric transition (for example, decay of ${}^{99\text{m}}\text{Tc}$ to ${}^{99}\text{Tc}$).

Many radioactive elements decay to produce unstable daughters. The radioactivity of many forms of radioactive contamination is due primarily to daughter products with short half-lives. The longest such decay chains that occur naturally are those for ${}^{238}\text{U}$, ${}^{235}\text{U}$, and ${}^{232}\text{Th}$, which decay through a series of intermediate daughters to ${}^{206}\text{Pb}$, ${}^{207}\text{Pb}$, and ${}^{208}\text{Pb}$, respectively (see Table 1). The decay of ${}^{238}\text{U}$ to ${}^{206}\text{Pb}$ results in the production of eight alpha particles and six beta particles; that of ${}^{235}\text{U}$ to ${}^{207}\text{Pb}$, seven alpha and four beta particles; and that of ${}^{232}\text{Th}$ to ${}^{208}\text{Pb}$, six alpha and four beta particles. Thus, understanding the geochemistry of radioactive contamination requires consideration of the chemistries of both the abundant parents and of the transient daughters, which have much lower chemical concentrations. After several half-lives of the longest-lived intermediate daughter, a radioactive parent and its unstable daughters will reach secular equilibrium; the contribution of each nuclide to the total activity will be the same. Thus, a sample of ${}^{238}\text{U}$ will, after about a million and a half years, have a total α activity that is about eight times that of the uranium alone.

Table 1. The Major Decay Paths for Several Important Actinides (isotope, half life, and decay mode). From Parrington et al. (1996).

²³⁸ U decay series			²³⁵ U decay series			²²⁸ Th decay series			²³⁷ Np decay series		
²³⁸ U	4.47·10 ⁹ y	α	²³⁵ U	7.04·10 ⁸ y	α	²³² Th	1.40·10 ¹⁰ y	α	²³⁷ Np	2.14·10 ⁶ y	α
²³⁴ Th	24.1 d	β ⁻	²³¹ Th	1.06 d	β ⁻	²²⁸ Ra	5.76 y	β ⁻	²³³ Pa	27.0 d	β ⁻
²³⁴ Pa	1.17 m	β ⁻	²³¹ Pa	3.28·10 ⁴ y	α	²²⁸ Ac	6.15 h	β ⁻	²³³ U	1.59·10 ⁵ y	α
²³⁴ U	2.46·10 ⁵ y	α	²²⁷ Ac	21.8 y	β ⁻	²²⁸ Th	1.91 y	α	²²⁹ Th	7.30·10 ³ y	α
²³⁰ Th	7.54·10 ⁴ y	α	²²⁷ Th	18.7 d	α	²²⁴ Ra	3.66 d	α	²²⁵ Ra	14.9 d	β ⁻
²²⁶ Ra	1.6·10 ³ y	α	²²³ Ra	11.4 d	α	²²⁰ Rn	55.6 s	α	²²⁵ Ac	10.0 d	α
²²² Rn	3.82 d	α	²¹⁹ Rn	4.0 s	α	²¹⁶ Po	0.15 s	α	²²¹ Fr	4.8 m	α
²¹⁸ Po	3.10 m	α	²¹⁵ Po	1.78·10 ⁻³ s	α	²¹² Pb	10.6 h	β ⁻	²¹⁷ At	32 ms	α
²¹⁴ Pb	27.0 m	β ⁻	²¹¹ Pb	36.1 m	β ⁻	²¹² Bi	60.6 m	β ⁻	²¹³ Bi	45.6 m	β ⁻
²¹⁴ Bi	19.9 m	β ⁻	²¹¹ Bi	2.14 m	α	²¹² Po	45 s	α	²¹³ Po	4 μs	α
²¹⁴ Po	1.64·10 ⁻⁴ s	α	²⁰⁷ Tl	4.78 m	β ⁻	²⁰⁸ Pb	Stable		²⁰⁹ Pb	3.25 h	β ⁻
²¹⁰ Pb	22.6 y	β ⁻	²⁰⁷ Pb	Stable					²⁰⁹ Bi	Stable	
²¹⁰ Bi	5.01 d	β ⁻									
²¹⁰ Po	138 d	α									
²⁰⁶ Pb	Stable										
²³⁹ Pu decay series			²³⁸ Pu decay series			²⁴¹ Am decay series					
²³⁹ Pu	2.44·10 ⁴ y	α	²³⁸ Pu	87.7 y	α	²⁴¹ Am	433 y	α			
²³⁵ U	Follows ²³⁵ U series		²³⁴ U	As in ²³⁸ U series		²³⁷ Np	Follows ²³⁷ Np series				

Heavy nuclei can also decay by *fission*, by splitting into two parts. Although some nuclei can spontaneously fission, most require an input of energy. This is most commonly accomplished by absorption of neutrons, although alpha particles, gamma rays and even x-rays may also induce fission. Fission is usually asymmetric—two unequal nuclei, or *fission products*, are produced, with atomic weights ranging from 66 to 172. Fission product yields vary with the energy of the neutrons inducing fission; under reactor conditions, fission is highly asymmetric, with production maxima at masses of ~95 and ~135. High-energy neutrons result in more symmetric fission, with a less bimodal distribution of products.

Fission products generally contain an excess of neutrons and are radioactive, decaying by successive β⁻ emissions to stable nuclides. The high radioactivity of spent nuclear fuel and of the wastes generated by fuel reprocessing for nuclear weapons production is largely due to fission products, and decreases rapidly over the first few tens of years. In addition to the daughter nuclei, neutrons are released during fission (2.5-3 per fission event for thermal neutrons), creating the potential for a fission chain reaction—the basis for nuclear power and nuclear weapons.

The major decay paths for the naturally occurring isotopes of uranium and thorium are shown in Table 1. Other actinides of environmental importance include ²³⁷Np, ²³⁸Pu, ²³⁹Pu, and ²⁴¹Am. These have decay series similar to and overlapping those of uranium and thorium. ²³⁷Np (t_{1/2} = 2.14 × 10⁶ years, α) decays to ²⁰⁹Bi through a chain of intermediates, emitting seven α and four β⁻ particles. ²³⁸Pu (t_{1/2} = 86 y, α) decays into ²³⁴U, an intermediate daughter

on the ^{238}U decay series. ^{239}Pu ($t_{1/2} = 2.44 \times 10^4$ y, α) decays into ^{235}U . ^{241}Am ($t^{1/2} = 458$ y, α) decays into ^{237}Np .

The basic unit of measure for radioactivity is the number of atomic decays per unit time. In the SI system, this unit is the Becquerel (Bq), defined as one decay per second. An older, widely used measure of activity is the Curie (Ci). Originally defined as the activity of one gram of ^{226}Ra , one Ci is equal to 3.7×10^{10} Bq. The units used to describe the dose, or energy absorbed by a material exposed to radiation, are dependent upon the type of radiation and the material. X-ray or γ radiation absorbed by air is measured in Roentgens (R). The dose absorbed by any material, by any radiation, is measured in rads (radiation-absorbed-dose), where one rad corresponds to 100 ergs per gram of absorbed energy. The SI equivalent is the Gray (Gy), which is equal to 100 rads.

Different types of radiation affect biological materials in different ways, so a different unit is needed to describe the dose necessary to produce an equivalent biological damage. Historically, this unit is the rem (roentgen-equivalent-man). The dose in rem is equal to the dose in rad multiplied by a quality factor, which varies with the type of radiation. For β^- , γ and X-ray radiation, the quality factor is 1; for neutrons, it is 2–11, depending upon the energy of the particle; and for α particles, the quality factor is 20. The SI unit for equivalent dose is the Sievert (Sv), which is equivalent to 100 rem.

2.1.2 Natural Sources of Radioactivity

Radioactive materials have been present in the environment since the accretion of the earth. The decay of radionuclides provides an important source of heat that drives many large-scale planetary processes. The most abundant naturally occurring radionuclides are ^{40}K , ^{232}Th , and ^{238}U and ^{235}U . The bulk of the natural global inventory of actinide radioactivity in the upper 100 meters of the lithosphere (about 10^{22} Bq, or 2.7×10^{11} Ci) is due to activity of uranium and thorium isotopes (Santschi and Honeyman, 1989; Ewing, 1999). This is about equal to the total activity of ^{40}K in the world ocean. Average crustal concentrations of uranium (mostly 238) and thorium (mostly 232) are 2.7 and $9.6 \mu\text{g g}^{-1}$, respectively. Both elements are enriched in silica-rich igneous rocks (4.4 and $16 \mu\text{g g}^{-1}$ respectively in granites) and are highly enriched in zircons (2000 and $2500 \mu\text{g g}^{-1}$ respectively).

In groundwater, average uranium concentrations range from < 0.1 (reducing) to $100 \mu\text{g L}^{-1}$ (oxidizing) (Langmuir, 1997a). The average thorium concentration in groundwater is $< 1 \mu\text{g L}^{-1}$ and is not affected by solution redox conditions. Other naturally occurring radionuclides include actinium, technetium, neptunium and protactinium. Small amounts of actinides (^{237}Np and ^{239}Pu) are present from neutron capture reactions with ^{238}U . Natural ^{99}Tc is a product of ^{238}U spontaneous fission (Curtis et al., 1999). For comparison, Table 2 provides examples of large-scale sources of natural and anthropogenic radioactivity in the environment throughout the world.

Table 2. Examples of Sources of Radioactivity in the Environment.

Location	Source of radioactivity	Major radionuclides	Amount of radioactivity	Ref.
Global	Top 100 meters of lithosphere	$^{238,235}\text{U}$, ^{232}Th	1.0×10^{22} Bq	1,2
HLW geologic repository	70,000 metric tons spent fuel (proposed)	^{137}Cs , ^{90}Sr	1.0×10^{22} Bq	1, 2
Atmospheric testing	220 Megaton yield	^{131}I and ^3H $^{239,240}\text{Pu}$	2.0×10^{20} Bq 1.0×10^{17} Bq	1,2
Mayak, Russia	nuclear production	Various HLW ^{90}Sr , ^{137}Cs	3.6×10^{19} Bq 2.1×10^{19} Bq	4
US Weapons Complex	High Level Waste/ 100 million gallons (380,000 m ³)	Short-lived ($t_{1/2} < 50$ yr): ^{137}Cs , ^{90}Sr , ^{90}Y , $^{137\text{m}}\text{Ba}$, ^{241}Pu longer lived ($t_{1/2} = 50$ -500 yr): ^{238}Pu , ^{131}Sm , ^{241}Am long lived ($t_{1/2} = 500 - 50,000$ yr): ^{239}Pu , ^{240}Pu , ^{14}C longest lived ($t_{1/2} > 50,000$ yr): ^{99}Tc , ^{135}Cs , ^{233}U	3.3×10^{19} Bq 1.1×10^{17} Bq 3.3×10^{15} Bq 2.0×10^{15} Bq	5
Chernobyl	Reactor accident in 1986	^{131}I , $^{134,137}\text{Cs}$, $^{103,106}\text{Ru}$	1.2×10^{19} Bq	1,2
U.S.	U mining and milling	^{226}Ra	1.9×10^{15} Bq	1

References:

1. Ewing (1999)
2. Santschi and Honeyman (1989)
3. NRC (2001)
4. Cochran et al. (1993)
5. U.S. DOE (1997a)

2.1.3 Nuclear Waste

It is estimated that the inventory of nuclear reactor waste in the U.S. will reach 1.3×10^{21} Bq by 2020 (Ewing, 1999). Decay of the radionuclides from a reference inventory over 10^{10} years is shown in Figure 2. In this figure, the change of ingestion toxicity of radionuclides important for disposal of high level wastes is shown. Ingestion toxicity for a given radioisotope is defined as the isotopic quantity (in microcuries) divided by the maximum permissible concentration in water (in microcuries per cubic meters) for that isotope (Campbell et al., 1978). Plots of time-dependent thermal output from the radionuclides show similar trends. It can be seen that initially the bulk of the radioactivity is due to short-lived radionuclides ^{137}Cs and ^{90}Sr . After 1000 years, the bulk of the hazard is due to decay of ^{241}Am , ^{243}Am , $^{239,240}\text{Pu}$ and ^{237}Np , and during the longest time periods, a

mixture of the isotopes ^{99}Tc , ^{210}Pb and ^{226}Ra dominate the small amount of radioactivity that remains. U.S. DOE (1980) shows that the relative toxicity (hazard) index (toxicity associated with ingesting a given weight of material) of spent fuel is about the same as uranium ore (0.2% U ore) after 100,000 years.

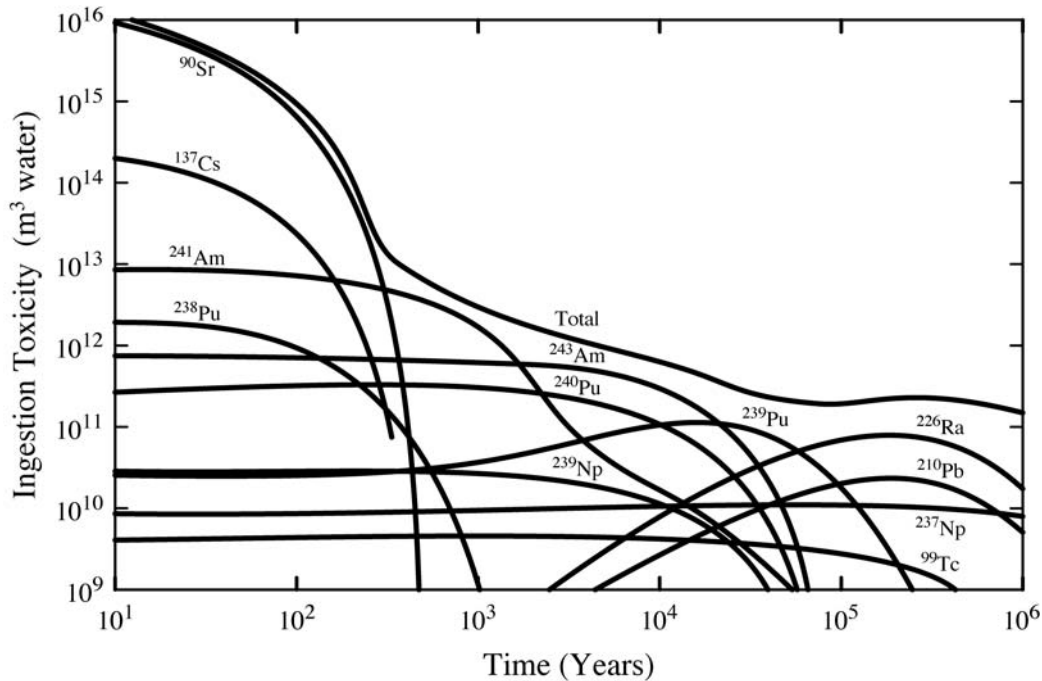


Figure 2. Ingestion toxicity for high-level waste as a function of decay time.

(Used by permission of Nuclear Regulatory Commission; modified from Campbell et al., 1978. *Risk Methodology for Geologic Disposal of Nuclear Waste: Interim Report*, p. 30).

Current regulations focus on the time period up to 10,000 and 100,000 years after emplacement when radioactivity is dominated by the decay of americium, neptunium and plutonium. Disposal of nuclear waste in the U.S. is regulated by the Environmental Protection Agency (EPA) and the Nuclear Regulatory Commission (NRC). There are several classes of nuclear waste; each type is regulated by specific environmental regulations and each has a preferred disposal option, as described below.

Spent fuel (SF) consists of irradiated fuel elements removed from commercial reactors or special fuels from test reactors. It is highly radioactive and generates a lot of heat; therefore, remote handling and heavy shielding are required. It is considered a form of high-level waste because of the uranium, fission products and transuranics that it contains. **High-level waste (HLW)** includes highly radioactive liquid, calcined or vitrified wastes generated by reprocessing of SF. Both SF and HLW from commercial reactors will be entombed in the geological repository at Yucca Mountain about 100 miles northwest of Las Vegas, Nevada. Disposal of spent nuclear fuel and HLW in the U.S. is regulated by 40 CFR Part 197 (U.S. EPA, 2001) and 10 CFR Part 60 (U.S. NRC, 2001). It is discussed in more detail in a later section of this report.

Transuranic waste (TRU) is defined as waste contaminated with alpha-emitting radionuclides of atomic number greater than 92 and half-life greater than 20 years in concentrations greater than 100 nanocuries g^{-1} ($3.7 \times 10^3 \text{ Bq g}^{-1}$). Transuranic waste is primarily a product of the reprocessing of spent fuel and the use of plutonium in the fabrication of nuclear weapons. In the U.S., the disposal of TRU at the Waste Isolation Pilot Plant in Southeastern New Mexico is regulated by 40 CFR Part 194 (U.S. EPA, 1996). It is also discussed in more detail in a later section of this report.

Uranium mill tailings are large volumes of radioactive residues that result from the processing of uranium ore. In the U.S., the DOE has the responsibility for remediating mill tailing surface sites and associated groundwater under the Uranium Mill Tailings Radiation Control Act (UMTRCA) of 1978 and its modification in 1988. **Low-Level wastes (LLW)** are radioactive wastes not classified as HLW, TRU, SF or uranium mill tailings. They are generated by institutions and facilities using radioactive materials and may include lab waste, towels, and lab coats contaminated during normal operations. Disposal of LLW is governed by agreements between states through state compacts at several facilities in the continental U.S. Geochemical data, conceptual models and performance assessment methodologies relevant to LLW are summarized in Serne et al. (1990).

2.1.4 Sites of Radioactive Environmental Contamination

In the U.S., radioactive contamination is of particular importance in the vicinity of U.S. nuclear weapons production sites, near proposed or existing nuclear waste disposal facilities and in areas where uranium mining was carried out. Contamination from mining was locally significant in areas within the Navajo Nation in the southwestern U.S. Abdelouas et al. (1999) and Jove-Colon et al. (2001) provide concise reviews of the environmental problems associated with uranium mill tailings. These large volume mining and milling residues contain about 85% of the radioactivity of the unprocessed uranium ore, primarily in the form of U radioisotopes, ^{230}Th , Ra (^{226}Ra and ^{222}Ra) and Rn isotopes. In the U.S., more than 230 million tons of tailings are stored at 24 inactive tailing sites; in Canada more than 300 million tons of tailings have accumulated (Abdelouas et al., 1999). By 1999, remediation of all 24 Title I UMTRA uranium mill tailings sites in the U.S. had been completed through either in-place stabilization or relocation to more favorable sites. Other UMTRA sites (Title II sites) still had their mill tailings in place as of 2002 and have relatively long plumes that could release uranium to nearby aquifers (Brady et al., 2002).

Both surface and subsurface processes are important for environmental contamination from uranium mill tailings. Surface soil/water contamination occurs by erosion and wind dispersion of contaminated soil; air pollution occurs by radon emission. Leaching and subsequent leaking of radioactive and hazardous metals (Cd, Cu, As, Mo, Pb, Zn) from mill tailings contaminate groundwater. Concentrations of uranium in mill tailings and tailings pore waters in deposits reviewed by Abdelouas et al. (1999) were as high as 1.4 g Kg^{-1} and 0.5 mg L^{-1} , respectively. Abdelouas et al. (1999) provide good examples of the relationships among environmental contamination, radiological hazards and remediation activities in their discussion of the tailings piles sites at Tuba City, Arizona, at Rayrock, Northwest Territories, Canada, and at the complex of solution mining sites, open pits and tailings piles managed by the WIZMUT company in the uranium mining districts of East Germany.

The U.S. DOE estimates that nuclear weapons production activities have led to radioactive contamination of approximately 63 million cubic meters of soil and 1310 million cubic meters of groundwater in the U.S. (U.S. DOE, 1997a, b). The contamination is located at 64 DOE environmental management sites in 25 states. The Hanford Reservation in Washington State provides a good example of the diverse sources of radioactive contamination associated with weapons production. At this site, nine plutonium production reactors were built in the 100 Area; high level wastes are stored in buried tanks in the 200 Area where spent fuel was processed; and nuclear fuel was fabricated in the 300 Area. A complex mixture of radioactive and hazardous wastes is either stored in ageing underground tanks or has been discharged to seeps or trenches and to the vadose zone in surface impoundments. The total inventory at the Hanford Site is estimated to be 1.33×10^{19} to 1.37×10^{19} Bq (360–370 MCi); between 8.1×10^{15} and 2.4×10^{17} Bq (0.22–6.5 MCi) has been released to the ground (National Research Council, 2001).

In Europe and the former Soviet Union (FSU), large areas have been contaminated by nuclear weapons production and uranium mining. The extent of contamination in the FSU is greater than in the U.S. because of fewer controls on the disposal of nuclear wastes and less strict mining regulations. Extensive contamination has occurred due to solution mining of uranium ore deposits. In solution mining, complexing agents (lixiviants) are added to groundwater and reinjected into a uranium ore body. In the U.S., nearly all of uranium solution mining was carried out using carbonated, oxidizing solutions to produce mobile uranyl carbonate complexes. These practices did not lead to significant contamination. In contrast, more aggressive acid leach techniques using large amounts of sulfuric and nitric acids were used in solution mining operations in the FSU. These operations created a legacy of widespread contamination comprised of large volumes of groundwater contaminated with acid and leached metals. In addition, a large number of open pit and underground mines, tailing ponds, waste rock and low grade ore piles are sources of potential radioactive contamination in Central and eastern European countries.

The Straz deposit in the Hamr District of the Czech Republic provides a good example of this problem (Slezak, 1997). Starting in 1968, more than 4 million tons of sulphuric acid, 300 thousand tons of nitric acid, and 120 thousand tons of ammonia were injected into the subsurface to mine uranium ore. Now, approximately 266 million cubic meters in the North Bohemian Cretaceous Cenomanian and Turonian aquifers are contaminated with uranium, radium, and manganese and other solutes. The contaminated area is more than 24 km² and threatens the watershed of the Plucnice River.

Large-scale contamination in regions of the Ural Mountains of Russia is severe due to weapons production at the Chelyabinsk-65 complex near the city of Kyshtym. Cochran et al. (1993) and Shutov et al. (2002) provide overviews of the extent of the contamination at the site, drawing upon a number of Russian source documents. The main weapons production facility, the Mayak Chemical Combine, produced over 5.5×10^{19} Bq of radioactive wastes from 1948 through 1992. Over 4.6×10^{18} Bq of long-lived radioactivity were discharged into open lake storage and other sites. During the period 1948–1951, approximately 9.3×10^{16} Bq of medium level β^- activity liquid waste was discharged directly into the nearby Techa River;

from March 1950 to November 1951, the discharge averaged 1.6×10^{14} Bq day⁻¹. During this period, about 124,000 people living downstream from the facility were exposed to elevated levels of radioactivity. In 1951, the medium level waste was discharged into nearby Lake Karachay. Through 1990, the lake had accumulated 4.4×10^{18} Bq of long-lived radionuclides (primarily ¹³⁷Cs [3.6×10^{18} Bq] and ⁹⁰Sr [7.4×10^{17} Bq]). By 1993, seepage of radionuclides from the lake had produced a radioactive groundwater plume that extended 2.5–3 miles from the lake. In 1993, the total volume of contaminated groundwater was estimated to be more than 4 million m³, containing at least 1.8×10^{14} Bq of long-lived (> 30 yr half-life) fission products.

Several large-scale nuclear disasters have occurred at the Chelyabinsk-65 complex. Two of these events led to the spread of radioactive contamination over large areas, exposure to large numbers of people and to relocation of entire communities. In 1957, during the so-called “Kyshtym Disaster,” an explosion of a HLW storage tank released 7.4×10^{17} Bq of radioactivity into the atmosphere (Medvedev, 1980; Trabalka et al., 1979). About 90% of the activity fell out in the immediate vicinity of the tank. Approximately 7.8×10^{16} Bq formed a kilometer-high radioactive cloud that contaminated an area greater than 23,000 km² to levels above 3.7×10^9 Bq km⁻² of ⁹⁰Sr. This area was home to about 270,000 people; many of the inhabitants were evacuated after being exposed to radioactive contamination for several years.

A second disaster at the site occurred in 1967, after water in Lake Karachay evaporated during a hot summer that followed a dry winter. Dust from the lakeshore sediments was blown over a large area, contaminating 1800-2700 km² with a total of 2.2×10^{13} Bq of ¹³⁷Cs and ⁹⁰Sr. Approximately 41,000 people lived in the area contaminated at levels of 3.7×10^9 Bq km⁻² of ⁹⁰Sr or higher. According to Botov (1992), releases of radioactive dust from the area continued through at least 1972. Since 1967, a number of measures have been taken to reduce the dispersion of radioactive contamination from Lake Karachay as described in Cochran et al. (1993) and source documents cited therein.

2.2 Exposure to Background and Anthropogenic Sources of Radioactivity

The amounts of radioactivity listed in Table 2 provide some idea of the maximum amount of radioactivity potentially available for exposure to the public. However, such inventories by themselves provide little information about the actual risk associated with the radioactive hazards. Although the exposure has been very high for those unfortunate few that have been involved in nuclear accidents, the exposure of the general public to ionizing radiation is relatively low. The 200,000 workers involved in the cleanup of Chernobyl nuclear power plant after the 1986 accident received average total body effective doses of 100 mSv (10 rem) (Ewing, 1999). Current U.S. regulations limit whole body dose exposures (internal + external exposures) of radiological workers to 50 mSv yr⁻¹ (5 rem yr⁻¹).

The calculated effective whole-body γ radiation doses on tailings piles at the Rayrock mill tailings site in Northwest Territories, Canada, ranged from 42-73 mSv yr⁻¹. This is about 24 times the annual dose from average natural radiation in Canada (Abdelouas et al., 1999). Exposure to natural sources of radon (produced in the decay chain of crustal ²³⁸U) averages 2

mSv yr⁻¹ while other natural sources account for 1 mSv yr⁻¹ (National Research Council, 1995). Total exposure to anthropogenic sources averages about 0.6 mSv yr⁻¹, with medical x-ray tests accounting for about 2/3 of the total. The average exposure related to the nuclear fuel cycle is estimated to be less than 0.01 mSv yr⁻¹ and is comparable to that associated with the release of naturally occurring radionuclides from the burning of coal in fossil-fuel plants (Ewing, 1999; McBride et al., 1978).

As shown previously, radioactive hazards associated with spent fuel and high level waste decrease exponentially over time (see Figure 2). After 10,000–100,000 years, the risk to the public of a nuclear waste disposal vault approaches that of a high grade uranium ore deposit and is less than the time invariant toxicity risk of ore deposits of mercury and lead (Langmuir, 1997a). The new EPA standard for nuclear waste repositories seeks to limit exposures from all exposure pathways for the reasonably maximally-exposed individual living 18 kilometers from a nuclear waste repository to 0.15 mSv yr⁻¹ (15mrem yr⁻¹) (U.S. EPA, 2001). For comparison, the radiation dose on the shores of Lake Karachay near the Chelyabinsk-65 complex is about 0.2 Sv hr⁻¹ (Cochran et al., 1993).

2.3 Health Effects and Radioactive Contamination

2.3.1 Biological Effects of Radiation Damage

A summary of the nature of radioactive contamination would be incomplete without some mention of the human health effects related to radioactivity and radioactive materials. Several excellent reviews at a variety of levels of detail have been written and should be consulted by the reader. (ATSDR, 1990a,b,c, 1999, 2001; Harley, 2001; Cember, 1996; BEIR V, 1988). The subject is extremely complex, with a number of important controversies that are beyond the scope of this report. Some general principles, however, are summarized below.

Ionizing radiation loses energy by producing ion pairs when passing through matter. These can damage biological material directly or produce reactive species (free radicals) that can subsequently react with biomolecules. External and internal exposure pathways are important for human health effects. External exposure occurs from radiation sources outside the body such as soil particles on the ground, surface water, and from particles dispersed in the air. It is most important for gamma radiation that has high penetrating potential; however, except for large doses, most of the radiation will pass through the body without causing significant damage. External exposure is less important for beta and alpha radiation, which are less penetrating and will deposit their energy primarily on the outer layer of the skin.

Internal exposures of alpha and beta particles are important for ingested and inhaled radionuclides. Dosimetry models are used to estimate the dose from internally deposited radioactive particles. The amount and mode of entry of radionuclides into the body, the movement and retention of radionuclides within various parts of the body, and the amount of energy absorbed by the tissues from radioactive decay are all factors in the computed dose (BEIR IV, 1988). The penetrating power of alpha radiation is low; therefore, most of the

energy from alpha decay is absorbed in a relatively small volume surrounding an ingested or inhaled particle in the gut or lungs. This means that the chance that damage to DNA or other cellular material will occur is greater and the associated human health risk is higher for radioactive contamination composed of alpha emitters than for the other forms of radioactive contamination. As mentioned above, weighting parameters that take into account the radiation type, the biological half-life and the tissue or organ at risk are used to convert the physically absorbed dose in units of gray (or rad) to the biologically significant committed equivalent dose and effective dose, measured in units of Sv (or rem).

There is considerable controversy over the shape of the dose-response curve at the chronic low dose levels important for environmental contamination. Proposed models include linear models, non-linear (quadratic) models and threshold models. Because risks at low dose must be extrapolated from available data at high doses, the shape of the dose-response curve has important implications for the environmental regulations used to protect the general public. Detailed description of dosimetry models can be found in Cember (1996), BEIR IV (1988), and Harley (2001).

The health effect of radiation damage depends on a combination of events on the cellular, tissue and systemic levels. Exposure to high doses of radiation (> 5 Gy) can lead to direct cell death before division due to interaction of free radicals with macromolecules such as lipids and proteins. At acute doses of 0.1–5 Gy, damage to organisms can occur on the cellular level through single strand and double strand DNA breaks. These lead to mutations and/or cellular reproductive death after one or more divisions of the irradiated parent cell. The dose level at which significant damage occurs depends on the cell type. Cells that reproduce rapidly, such as those found in bone marrow or the gastrointestinal tract, will be more sensitive to radiation than those that are longer lived, such as striated muscle or nerve cells. The effect of high radiation doses on an organ depends on the various cell types that it contains.

Cancer is the major effect of low radiation doses expected from exposure to radioactive contamination. Laboratory studies have shown that alpha, beta and gamma radiation can produce cancer in virtually every tissue type and organ in animals that have been studied (ATSDR, 2001). Cancers observed in humans after exposure to radioactive contamination or ionizing radiation include cancers of the lungs, female breast, bone, thyroid and skin. Different kinds of cancers have different latency periods; leukemia can appear within 2 years after exposure, while cancers of the breast, lungs, stomach and thyroid have latency periods greater than 20 years. Besides cancer, there is little evidence of other human health effects from low-level radiation exposure (ATSDR, 2001; Harley, 2001).

2.3.2 Epidemiological Studies

The five large epidemiological studies that provide the majority of the data on the effects of radiation on humans are reviewed by Harley (2001). These include radium exposures by radium dial painters, atom bomb survivors, patients irradiated with x-rays for ankylosing spondylitis and ringworm (tinea capitis), and uranium miners exposed to radon. The first four studies examine health effects due to external exposures of high doses of ionizing

radiation. The studies of uranium miners are more relevant to internal exposures. There have been eleven large follow-up studies of underground miners who were exposed to high concentrations of radon (^{222}Rn) and radon decay products. The carcinogens are actually the short-term decay products of ^{222}Rn (^{218}Po , ^{214}Po), which are deposited on the bronchial airways during inhalation and exhalation. Because of their short range, the alpha particles transfer most of their energy to the thin layer of bronchial epithelium cells. These cells are known to be involved in induction of cancer, and it is clear that even relatively short exposures to the high levels possible in mines lead to excess lung cancers.

The results of the studies on miners have been used as a basis for estimating the risks to the general public from exposures to radon in homes. There is considerable controversy over this topic. Although the health effects due to the high radon exposures experienced by the miners have been well established, the risks at the lower exposure levels in residences are difficult to establish due to uncertainties in the dose-response curve and the confounding effects of smoking and urbanization. The reader is referred to extensive documentation by the National Academy of Sciences (1998) and the National Institute of Health (1994) for more information.

Epidemiological studies of populations in the former Soviet Union exposed to fallout from the 1986 nuclear reactor explosion at Chernobyl and releases from the Chelyabinsk-65 complex demonstrate the health effects associated with exposure to radioactive iodine, strontium and cesium. A study of 28,100 individuals exposed along the Techa River, downstream from Chelyabinsk-65, revealed that a statistically significant increase in leukemia mortality arose between 5 and 20 years after the initial exposure (37 observed deaths vs. 14-23 expected deaths; see Cochran et al. 1993 and cited references and comments). There has been a significant increase of thyroid cancers among children in the areas contaminated by fallout from the Chernobyl explosion (Harley, 2001; UNSCEAR, 2000). The initial external exposures from Chernobyl were due to ^{131}I and short-lived isotopes. Subsequently, external exposures to ^{137}Cs and ^{134}Cs and internal exposures to radiocesium through consumption of contaminated foodstuffs were important.

2.3.3 Toxicity and Carcinogenicity

Toxicity and carcinogenicity of radioactive materials are derived from both the chemical properties of the radioelements and the effects of ionizing radiation. The relative importance of the radiological and chemical health effects are determined by the biological and radiological half-lives of the radionuclide and the mechanism of chemical toxicity of the radioelement. Ionizing radiation is the main source of carcinogenicity of the radionuclides. Many of the damaging effects of radiation can be repaired by the natural defenses of cells and the body. However, the longer a radionuclide is retained by the body or localized in a specific organ system, the greater the chances that the damage to DNA or proteins will not be repaired and a cancer will be initiated or promoted. The biological half-life of a radioelement, therefore, is an important determinant of the health risk posed by a radionuclide. This is determined by the chemical and physical form of the radioelement when it enters the body, the metabolic processes that it participates in and the routes of elimination from the body. For example, ^{90}Sr substitutes for calcium and accumulates on the

surfaces of bones. It has a long biological half-life (50 yr) because it is recycled within the skeletal system. In young children, it is incorporated into growing bone where it can irradiate both the bone cells and bone marrow. Consequently, high exposures to ^{90}Sr can lead to bone cancer and cancers of the blood such as leukemia.

In contrast, the chemical toxicity of uranium is more important than its radiological hazard. In body fluids, uranium is present as soluble U(VI) species and is rapidly eliminated from the body (60% within 24 hr; Goyer and Clarkson, 2001). It is rapidly absorbed from the gastrointestinal tract and moves quickly through the body. The uranyl carbonate complex in plasma is filtered out by the kidney glomerulus, the bicarbonate is reabsorbed by the proximal tubules, and the liberated uranyl ion is concentrated in the tubular cells. This produces systemic toxicity in the form of acute renal damage and renal failure.

Because there are few data on the results of human exposure to actinides, the health effects of these radioelements are more uncertain than those discussed above for ionizing radiation, radon and fission products. Americium accumulates in bones and will likely cause bone cancer due to its radioactive decay. Animal studies suggest that plutonium will cause effects in the blood, liver, bone, lung and immune systems. Other potential mechanisms of chemical toxicity and carcinogenicity of the actinides are similar to those of heavy metals and include 1) disruption of transport pathways for nutrients and ions, 2) displacement of essential metals such as Cu^{2+} , Zn^{2+} and Ni^{2+} from biomolecules, 3) modification of protein conformation, 4) disruption of membrane integrity of cells and cell organelles, and 5) DNA damage. More details can be found in the references cited at the beginning of this section.

3. Experimental and Theoretical Studies of Radionuclide Geochemistry

Analysis of the risk from radioactive contamination requires consideration of the rates of release and dispersion of the contaminants through potential exposure pathways. Prediction of the release and dispersion of radionuclides from nuclear waste sites and contaminated areas must consider a series of processes including: 1) contact of the waste with groundwater, degradation of the waste, and release of radioactive aqueous species and particulate matter, 2) transport of aqueous species and colloids through the saturated and vadose zone, and 3) uptake of radionuclides by exposed populations or ecosystems. The geochemistry of the radionuclides will control migration through the geosphere by determining solubility, speciation, sorption, and the extent of transport by colloids. These are strong functions of the compositions of the groundwater and geosol as well as the atomic structure of the radionuclides. These topics are the main focus of the sections that follow.

General predictions of radionuclide mobility are difficult to make; instead, site-specific measurements and thermodynamic calculations for the site-specific conditions are needed to make meaningful statements about radionuclide behavior. However, for the purposes of this report, some underlying themes are described. Trends in solubility and mobility are described from several perspectives: 1) by identity of the radionuclide and its dominant oxidation state under near-surface environmental conditions, 2) by composition of the groundwater or pore waters (i.e., Eh, pH and nature of complexing ligands and competing

solutes), and 3) by composition of the geomeedia in contact with the solutions (i.e., mineralogy, organic matter).

3.1 Principles and Methods

3.1.1 Experimental Methods

A wide variety of experimental techniques are used in radiochemical studies; a review of this subject is beyond the scope of this report. The interested reader should refer to the reviews and textbooks of actinide chemistry listed in the Section 1.2 above. Some general points, which should be considered in evaluating available data relevant to environmental radioactive contamination, are made below.

3.1.1.1 Solubility and Speciation

Minimum requirements for reliable thermodynamic solubility studies include: 1) solution equilibrium conditions, 2) effective and complete phase separation, 3) well-defined solid phases and 4) knowledge of the speciation/oxidation state of the soluble species at equilibrium. Ideally, radionuclide solubilities should be measured in both “oversaturation” experiments, in which radionuclides are added to a solution until a solid precipitates, and “undersaturation” experiments, in which a radionuclide solid is dissolved in aqueous media. Due to the difference in solubilities of crystalline versus amorphous solids and different kinetics of dissolution, precipitation, and recrystallization, the results of these two types of experiments rarely agree. In some experiments, the maximum concentration of the radionuclide source term in specific water is of interest, so the solid that is used may be spent fuel or nuclear waste glass rather than a pure radionuclide solid phase.

In addition, the maximum concentrations measured in laboratory experiments and the solubility-limiting solid phases identified are often not in agreement with the results of theoretical thermodynamics calculations. This discrepancy could be due to differences in the identity or the crystallinity of solubility-limiting solids assumed in the calculation or to errors in the thermodynamic property values used in the calculations. Thus, although theoretical thermodynamic calculations are useful in summarizing available information and in performing sensitivity analyses, it is important also to review the results of empirical experimental studies in site-specific solutions.

Good summaries of accepted experimental techniques can be found in the references that are cited for individual radionuclides in the sections below. Nitsche (1991) provides a useful general summary of the principles and techniques of solubility studies. A large number of techniques have been used to characterize the aqueous speciation of radionuclides. These include potentiometric, optical absorbance and vibrational spectroscopy. Silva and Nitsche (1995) summarize the use of conventional optical absorption and laser-based photothermal spectroscopy for detection and characterization of solution species and provide an extensive citation list. A recent review of the uses of Raman and infrared spectroscopy to distinguish various uranyl hydroxy complexes is given by Runde et al. (2002b).

Extraction techniques to separate oxidation states and complexes are often combined with radiometric measurements of various fractions. A series of papers by Choppin and coworkers provides good descriptions of these techniques (see for example Caceci and Choppin, 1983; Schramke et al., 1989). Cleveland and coworkers used a variety of extraction techniques to characterize the speciation of plutonium, neptunium, and americium in natural waters (Cleveland et al., 1983a,b; Cleveland and Rees, 1981).

A variety of methods have been used to characterize the solubility-limiting radionuclide solids and the nature of precipitated or sorbed species at the solid/water interface in experimental studies. Electron microscopy and standard x-ray diffraction techniques can be used to identify some of the solids from precipitation experiments. X-ray absorption spectroscopy (XAS) can be used to obtain structural information on solids and is particularly useful for investigating non-crystalline and polymeric actinide compounds that cannot be characterized by x-ray diffraction analysis (Silva and Nitsche, 1995). X-ray Absorption Near Edge Spectroscopy (XANES) can provide information about the oxidation state and local structure of actinides in solution, solids or at the solution/solid interface. For example, Bertsch et al. (1994) used this technique to investigate uranium speciation in soils and sediments at uranium processing facilities. Many of the surface spectroscopic techniques have been reviewed recently by Bertsch and Hunter (2001) and Brown et al. (1999). Specific recent applications of the spectroscopic techniques to radionuclides are described by Runde et al. (2002b). Rai and coworkers have carried out a number of experimental studies of the solubility and speciation of plutonium, neptunium, americium and uranium that illustrate combinations of various solution and spectroscopic techniques (Rai et al., 1980, 1997, 1998; Felmy et al., 1989, 1990; Xia et al., 2001).

3.1.1.2 Sorption Studies

Several different approaches have been used to measure the sorption of radionuclides by geomedia. These include: 1) the laboratory batch method, 2) the laboratory flow-through (column) method, and 3) the *in situ* field batch sorption method. Laboratory batch tests are the simplest experiments; they can be used to collect distribution coefficient (K_d ¹) values or other partitioning coefficients to parameterize sorption and ion exchange models. The different sorption models are summarized in Section 3.1.2.2.

3.1.1.2.1 Batch Techniques

Descriptions of the batch techniques for radionuclide sorption and descriptions of calculations used to calculate distribution coefficients can be found in ASTM (1987), Park et al. (1995), Siegel et al. (1995a) and U.S. EPA (1999a). The techniques typically involve the following steps: 1) contacting a solution with a known concentration of radionuclide with a

¹ The term *sorption* is often used to describe a number of surface processes including adsorption, ion exchange and coprecipitation that may be included in the calculation of a K_d . For this reason, some geochemists will use the term sorption ratio (R_d) instead of distribution coefficient (K_d) to describe the results of batch sorption experiments. In this report, both terms are used in order to be consistent with the terminology used in the original source of information summarized.

given mass of solid, 2) allowing the solution and solid to equilibrate, 3) separating the solution from the solid, and 4) measuring the concentration of radionuclide remaining in solution.

In batch systems, the distribution or sorption coefficient (K_d or R_d) describes the partitioning of a contaminant between the solid and liquid phases. The K_d is commonly measured under equilibrium or at least steady-state conditions, unless the goal of the experiment is to examine the kinetics of sorption. It is defined as follows:

$$K_d (ml/g) = \frac{C_s}{C_L} \quad (1)$$

where C_s is the concentration of the contaminant on the solid and C_L is the concentration in solution. In practice, the concentration of the contaminant on the solid is rarely measured. Rather, it is calculated from the initial and final solution concentrations, and the operative definition for the K_d becomes:

$$K_d (ml/g) = \frac{(C_i V_i - C_f V_f) / m}{C_f} \quad (2)$$

where C_i and C_f are the initial and final concentrations of contaminant in solution, respectively; V_i and V_f are the initial and final solution volumes; and m is the mass of the substrate added to the system.

Measured batch K_d values can be used to calculate a retardation factor (R), which describes the ratio of the groundwater velocity v_w to the velocity of radionuclide movement v_r :

$$R = v_w / v_r = 1 + \frac{K_d \rho}{\phi} \quad (3)$$

where ρ is the bulk density of the porous medium and ϕ is the porosity. This equation can be rearranged, and contaminant retardation values measured from column breakthrough curves can be used to calculate K_{ds} .

Many published data from batch sorption measurements are subject to a number of limitations as described by Siegel and Erickson (1984, 1986), Serne and Muller (1987) and by U.S. EPA (1999a). These include a solution:solid ratio that is much higher than that present in natural conditions, an inability to account for multiple sorbing species, an inability to measure different adsorption and desorption rates and affinities, and an inability to distinguish between adsorption and coprecipitation.

Batch methods are also used to collect data used to calculate equilibrium constants for the surface complexation models (SCMs), which are described in more detail in the next section. Commonly for these models, sorption is measured as function of pH and data are presented as pH-sorption edges similar to the one shown in Figure 3. Sorption is strongly affected by

the surface charge of the geomeadia. The proton is the surface potential determining ion (PDI) in metal oxyhydroxides and of the high-energy edge sites in aluminosilicates. At low ionic strengths and in the absence of significant sorption of metal ions (i.e. low surface loading or site occupancy), the surface charge is determined primarily by the difference between the surface concentrations of positively charged, protonated sites and negatively charged, deprotonated sites.

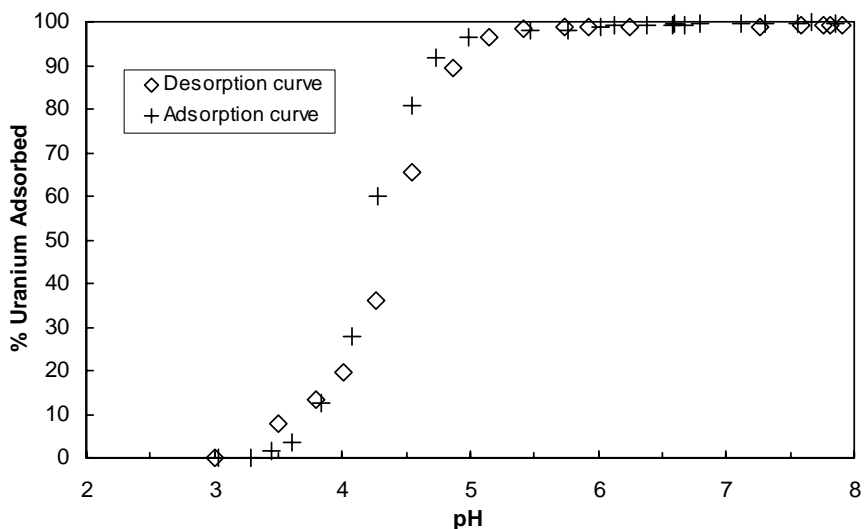


Figure 3. Sorption and desorption edges for uranyl on goethite in 0.01 M NaNO₃ solution. Each sample contained 60m²/L goethite, 100 µg/ml uranium. The sorption edge was measured two days after uranium addition; desorption samples were contacted with the uranyl solution at pH 7 for five days, the pH was adjusted to cover the range of interest, and the samples were re-equilibrated for two days prior to sampling. (see Bryan and Siegel, 1998).

Considerable data have been collected describing the influence of pH on actinide sorption. Sorption edges are most commonly (and usefully) measured for single oxidation states of the radionuclide. Figure 3 shows a plot of a sorption/desorption edge for uranium under oxidizing conditions and illustrates reversible sorption. The effect of competition between protons and the radionuclide is illustrated by the sorption edge. Appreciable sorption can occur at a relatively low pH for radionuclides that form strong bonds with the surface, resulting in a low pH₅₀ value (the pH at which 50% of the radionuclide is adsorbed). Radionuclides that form weaker surface complexes can only sorb appreciably when the concentration of competing protons is low (high pH) and therefore have high pH₅₀ values. Comparisons of sorption edges for different radionuclides on the same substrate or for a single radionuclide on several substrates can be made by referring to their pH₅₀ values. For example, Kohler et al. (1992) show that goethite strongly sorbs Np(V) from NaClO₄ solutions while quartz only weakly sorbs Np(V). The pH₅₀ sorption values for Np(V) increase in the order goethite<hematite<gibbsite<albite<quartz.

3.1.1.2.2 Other Techniques

Laboratory column tests are more difficult to perform but overcome some of the limitations of the batch tests. Proper design, descriptions of experimental procedures and methods of

data interpretation for column tests can be found in U.S. EPA (1999a); Relyea (1982), Van Genuchten and Wierenga (1986), Triay et al. (1992, 1996, 1997), Torstenfelt (1985a,b), Siegel et al. (1995b), Sims et al. (1996) and Gabriel et al. (1998). In these experiments, a solution containing a known concentration of radionuclide is introduced into a column of packed soil or rock at a specified flow rate. The concentration of the radionuclide in the column effluent is monitored to obtain a breakthrough curve; the shape of the curve provides information about sorption equilibrium and kinetics and other properties of the crushed rock or intact rock column. Limitations of this technique are: 1) complex, time-consuming and expensive experimental procedures are required; 2) symmetric breakthrough curves are rarely obtained and a number of *ad hoc* assumptions may be required to interpret them; and 3) the sorption parameters are dependent on the hydrodynamics of the specific experiment and are not applicable to other conditions.

***In situ* (field) batch sorption tests** use measurements of the radionuclide contents of samples of rock cores and consanguineous pore water obtained at a field site. The advantage of this approach is that the water and rock are likely to be in chemical equilibrium and that the concentrations of any cations or anions competing for sorption sites are appropriate for natural conditions. Disadvantages of this technique are associated with limitations in obtaining accurate measurements of the concentration of radionuclides on the rock surface in contact with the pore fluid. Applications of this technique are described in Jackson and Inch (1989), McKinley and Alexander (1993), Read et al. (1991), Ward et al. (1990), and Payne et al. (2001).

3.1.1.2.3 *Surface Analytical Techniques*

A variety of spectroscopic methods have been used to characterize the nature of adsorbed species at the solid/water interface in natural and experimental systems (Brown et al., 1999). Surface spectroscopy techniques such as Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) have been used to characterize complexes of fission products, thorium, uranium, plutonium, and uranium sorbed onto silicates, goethite, clays and microbes (Chisholm-Brause et al. 1992, 1994; Dent et al., 1992; Combes et al., 1992; Bargar et al., 2000; Brown and Sturchio, 2002). A recent overview of the theory and applications of synchrotron radiation to the analysis of the surfaces of soils, amorphous materials, rocks and organic matter in low temperature geochemistry and environmental science can be found in Fenter et al. (2002).

Before the application of these techniques became possible, the composition and predominance of adsorbed species was generally inferred from information about aqueous species. In some cases, these models for adsorbed species have been shown to be incorrect. For example, spectroscopic studies demonstrated that U(VI)-carbonato complexes were the predominant adsorbed species on hematite over a wide pH range (Bargar et al., 2000). This was contrary to expectations based on analogy to aqueous U(VI)-carbonato complexes, which are present in very low concentration at near-neutral and acidic pH. As discussed later, the use of different sorption models will produce alternate stoichiometries for surface species when data are fit to sorption edges. The information obtained from surface

spectroscopy helps to constrain the interpretation of the results of batch sorption tests by revealing the stoichiometry of the sorbed species. For example, Redden and Bencheikh-Latmar (2001) demonstrate how data from an EXAFS study helped to elucidate the interactions among UO_2^{2+} , citrate and goethite over the pH range 3.5 to 5.5. Previous studies of sorption equilibria (Redden et al. (1998) showed that whereas citric acid reduced the sorption of uranium by gibbsite and kaolinite, the presence of citrate led to enhanced uranyl sorption at high citrate: UO_2^{2+} ratios. The EXAFS spectra were consistent with the existence of two principal surface species: an inner-sphere uranyl-goethite complex and an adsorbed uranyl-citrate complex, which displaces the binary uranyl-goethite complex at high citrate: UO_2^{2+} ratios. Other examples of the use of these techniques to understand the nature of radionuclide sorption can be found in a recent review by Brown and Sturchio (2002).

3.1.2 Theoretical Geochemical Models and Calculations

3.1.2.1 Aqueous Speciation and Solubility

Several geochemical codes are commonly used for calculations of radionuclide speciation and solubilities. Recent reviews of the codes can be found in Serne et al. (1990), Mangold and Tsang (1991), NEA (1996), and U.S. EPA (1999a). Extensive databases of thermodynamic property values and kinetic rate constants are required for these codes. Several databases of thermodynamic properties of the actinides have been developed over the last three decades. Of historical importance are the compilations and reviews of Lemire and Tremaine (1980), Phillips et al. (1988), and Fuger et al. (1990). The most recent comprehensive and consistent databases have been based on compilations produced by the Nuclear Energy Agency (NEA) for plutonium and neptunium (Lemire et al., 2001), americium (Silva et al., 1995), uranium (Grenthe et al., 1992) and technetium (Rard et al., 1999). These books contain suggested values for ΔG , ΔH , C_p and $\log K_f$ for formation reactions of radionuclide species. More recent publications often use these compilations as reference and add more recent property values or correct errors. For example, Langmuir (1997a) updates the 1995 NEA database for uranium (Grenthe et al., 1995 in Silva et al., 1995) and provides results of solubility, speciation and sorption calculations using the MINTEQ2A code (Allison et al., 1991) as described later in this report.

The most recent compilations have been *internally self consistent*. The process of compiling an internally self consistent database consists of several steps: 1) compilation of process values such as equilibrium constants for reactions involving the element of interest, 2) extrapolation of equilibrium constants to reference conditions (usually zero ionic strength and 25°C), and 3) calculation of property values such as free energies of formation of the products through reaction networks (Wagman et al., 1982; Grenthe et al., 1992). Calculated thermodynamic constants from different experimental studies will be incompatible if different reference states or reaction networks are used. Caution must be exercised in combining constants from different compilations because they are dependent on the methods used for ionic strength correction and the values used for auxiliary species such as OH^- or SO_4^{2-} . Thus, strictly speaking, as new species are identified or suspect ones eliminated, and as constants of previously recognized species are revised, the entire reaction network must be used to rederive all of the constants in order to maintain internal consistency. Software is available to recalculate the reaction networks to ensure that internal consistency is

maintained with the NEA Thermochemical Data Base Project (<http://www.nea.fr/html/dbtdb/cgi-bin/tbdbocproc.cgi>). In practice, however, these recalculations are not commonly done, especially if only minor changes in values of equilibrium constants are expected.

For most solubility and speciation studies, calculations of the activity coefficients of aqueous species are required. For waters with relatively low ionic strength (0.01 to 0.1 molal), simple corrections such as the Debye-Hückel equation are used (Langmuir, 1997a, p. 127). This model accounts for the electrostatic, non-specific, long-range interactions between water and the solutes. At higher ionic strengths, short range, non-electrostatic interactions must be taken into account. The NEA has developed a database based on the Specific Interaction Theory (SIT) approach of Bronsted (1922), Scatchard (1936), and Guggenheim (1966). In this model, activity coefficients are calculated from a set of virial coefficients obtained from experimental data in simple solutions (Ciavatta, 1980). This method is assumed to be valid for ionic strengths up to 3.0 molal and had been used to extrapolate experimental data to zero ionic strength to obtain equilibrium constants and free energies for the NEA databases (Lemire et al., 2001; Silva et al., 1995; Grenthe et al., 1992; Rard et al., 1999).

The U.S. DOE has adopted the more complex Pitzer model (Pitzer, 1973, 1975, 1979) for calculations of radionuclide speciation and solubility in its Nuclear Waste Management Programs. This model includes concentration-dependent interaction terms and is valid up to ionic strengths greater than 10 molal. However, because it requires three parameters instead of the single interaction parameter of the SIT model, this method requires more extensive experimental data. Pitzer coefficients and coefficients from the Harvie-Möller-Weare model (Harvie et al., 1984) are used in several geochemical codes such as PHRQPITZ (Plummer et al., 1988), EQ3/6 (Wolery, 1992a) and REACT (Bethke, 1998). Considerably more experimental data is needed for the radionuclides, and the Pitzer coefficient database is currently being developed by the U.S. DOE. Data are available for some radionuclides (Felmy and Rai, 1999) and have been used in the Waste Isolation Pilot Plant (WIPP) program as described in a later section.

3.1.2.2 Sorption

3.1.2.2.1 Overview

Both empirical and mechanistic approaches have emerged in the last three decades to describe interactions between radionuclides and geomeia. These are based on “conditional” constants, which are valid for specific experimental conditions, or more robust “intrinsic” constants, which are valid over a wider range of conditions. The ‘empirical approach’ involves measurements of conditional radionuclide distribution or sorption coefficients (K_{ds} or R_{ds}) in site-specific water-rock systems using synthetic or natural ground waters and crushed rock samples. Mechanistic-based approaches produce intrinsic, thermodynamic surface-complexation constants for simple electrolyte solutions with pure mineral phases.

The different approaches to describing sorption can be discussed in order of increasing model complexity and the robustness of their associated constants:

1. Linear sorption (K_d or R_d)
2. Non-linear sorption (Freundlich and other isotherms)
3. Constant-charge (ion-exchange) model
4. Constant-capacitance model
5. Double Layer or Diffuse Layer Model (DLM)
6. Triple-layer model (TLM)

Figure 4 compares several of these models with respect to the nature of the constants that each uses. The simplest model (linear sorption or K_d) is the most empirical model and is widely used in contaminant transport models. K_d values are relatively easy to obtain using the batch methods described above. The K_d model requires a single distribution constant, but the K_d value is conditional with respect to a large number of variables. Thus, even if a batch K_d experiment is carefully carried out to avoid introduction of extraneous effects such as precipitation, the K_d value that is obtained is valid only for the particular conditions of the experiment. As Figure 4 shows, the radionuclide concentration, pH, major and minor element composition, rock mineralogy, particle size and solid-surface-area/solution volume ratio must be specified for each K_d value.

MODEL	Constants	Conditional for (or dependent on)
K_d	K_d	(Me), pH, I, (M), (L), mineral, particle size, (S)
Isotherm	K, n	pH, I, (M), (L), mineral, particle size, (S)
Constant Capacitance	K_+ , K_- , C, σ	I, (M), (L), surface site type, assumed N_s and S_a
Triple Layer	β^+ , β^- , β^{an} , β^{cat} , C_1 , C_2 , σ_o , σ_b	Surface site type, assumed N_s and S_a

Figure 4. Comparison of sorption models.

Several commonly used sorption models are compared with respect to the independent *constants* that they require. These *constants* are valid only under specific conditions, which must be specified in order to properly use them. In other words, the constants are *conditional* with respect to the *experimental* variables described in the third column of the figure. K_d is the radionuclide distribution constant; K and n are the Freundlich isotherm parameters; β^+ and β^- are surface complexation constants for protonation and deprotonation of surface sites; K_+ , K_- , β^{an} , β^{cat} are surface complexation constants for sorption of cations and anions in the constant capacitance model and TLM respectively; C, C_1 , and C_2 are capacitances for the electrical double layers; σ , σ_o , and σ_b are surface charges at different surface planes; (Me) and (S) are concentrations of the sorbing ions and the surface sites, (M), (L) are concentrations of other cations and ligands in solution, respectively; I is the ionic strength of the background electrolyte; N_s and S_a are the site density and specific surface of the substrate, respectively. The requirements of the DLM are similar to those of the constant capacitance model.

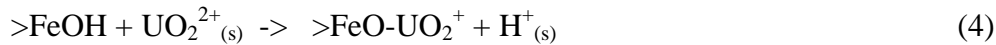
Ion exchange models are commonly used to describe radionuclide sorption onto the fixed-charged sites of materials like clays. Ion exchange will be strongly affected by competition

with monovalent and divalent ions such as Na^+ and Ca^{2+} , whereas it will be less dependent on pH over the compositional ranges common for natural waters. Many studies of strontium and cesium sorption by aluminosilicates (e.g., Wahlberg and Fishman, 1962; Tamura, 1972) have been carried out within the framework of ion exchange theory. Early mechanistic studies of uranium sorption were carried out within an ion exchange framework (e.g., Tsunashima et al., 1981); however, more recent studies relevant to environmental conditions have used surface complexation models (SCMs) (e.g., Davis, 2001).

The Triple-Layer Model (TLM) (Davis and Leckie, 1978) is the most complex model described in Figure 4. It is an example of a SCM. These models describe sorption within a framework similar to that used to describe reactions between metals and ligands in solutions (Kent et al., 1988; Davis and Kent, 1990; Stumm, 1992). Reactions involving surface sites and solution species are postulated based on experimental data and theoretical principles. Mass balance, charge balance and mass action laws are used to predict sorption as a function of solution chemistry. Different SCMs incorporate different assumptions about the nature of the solid-solution interface. These include the number of distinct surface planes where cations and anions can attach (double layer vs. triple layer) and the relations between surface charge, electrical capacitance and activity coefficients of surface species.

Aqueous radionuclide species and other solutes can sorb to mineral surfaces by forming chemical bonds directly with the amphoteric sites or may be separated from the surface by a layer of water molecules and be bound through longer-range electrostatic interactions. In the Triple Layer Model, complexes of the former type are often called “inner-sphere” complexes; those of the latter type are called “outer-sphere” complexes (Davis and Kent, 1990). The TLM includes an inner plane (o-plane), an outer plane (β -plane) and a diffuse layer that extends from the β -plane to the bulk solution. Sorption via formation of inner-sphere complexes is often referred to “chemisorption” or “specific sorption” to distinguish it from ion exchange at fixed charged sites or outer-sphere complexation that is dominantly electrostatic in nature.

The sorption of uranium to form the sorbed species ($>\text{FeOH}-\text{UO}_2^+$) at the o-plane of an iron oxyhydroxide surface (represented as $>\text{FeOH}$) can be represented by a surface reaction in a TLM as:



where $\text{UO}_2^{2+}{}_{(s)}$ and $\text{H}^+{}_{(s)}$ are the aqueous uranyl ion and proton at the surface, respectively. The mass action law (equilibrium constant) for the reaction using the TLM is:

$$\beta^{\text{UO}_2^+} = \frac{\{>\text{FeO}-\text{UO}_2^+\} \times a_{\text{H}^+} \times \exp[e\psi_o / kT]}{\{>\text{FeOH}\} \times a_{\text{UO}_2^{2+}}} \quad (5)$$

where $\beta^{\text{UO}_2^+}$ is the intrinsic surface complexation constant for the uranyl cation; $\{>\text{FeOH}\}$ and $\{>\text{FeO}-\text{UO}_2^+\}$ are the activities of the uncomplexed and complexed surface sites, respectively; a_{H^+} and $a_{\text{UO}_2^{2+}}$ are activities of the aqueous species in the bulk solution; ψ_o is

the electrical potential for the inner (o) surface plane; and k , T and e are the Boltzmann constant, absolute temperature and the fundamental charge, respectively. The exponential term describes the net change in electrostatic energy required to exchange the divalent uranyl ion for the proton at the mineral surface².

In natural waters, other surface reactions will be occurring simultaneously. These include protonation and deprotonation of the >FeOH site at the inner o-plane and complexation of other cations and anions to either the inner (o) or outer (β) surface planes. Expressions similar to Eq. 5 above can be written for each of these reactions. In most studies, the activity coefficients of surface species are assumed to be equal to unity; thus, the activities of the surface sites and surface species are equal to their concentrations. Different standard states for the activities of surface sites and species have been defined either explicitly or implicitly in different studies (Sverjensky, 2003). Sverjensky (2003) notes that the use of a hypothetical 1.0 Molar standard state or similar convention for the activities of surface sites and surface species leads to surface complexation constants that are directly dependent on the site density and surface area of the sorbent. He defines a standard state for surfaces sites and species that is based on site occupancy and produces equilibrium constants independent of these properties of the solids. For more details about the properties of the electrical double layer, methods to calculate surface speciation and alternative models for activity coefficients for surface sites, the reader should refer to the reference cited above and other works cited therein.

The TLM contains eight adjustable constants (identified in the caption of Figure 4) that are valid over the ranges of pH, ionic strength, solution composition, specific areas and site densities of the experiments used to extract the constants. The surface-complexation constants, however, must be determined for each type of surface site of interest and should not be extrapolated outside the original experimental conditions. Although the TLM constants are valid under a wider range of conditions than are K_{ds} , considerably more experimental data must be gathered to obtain the adjustable parameters. An important advantage of surface complexation constant models is that they provide a structured way to examine experimental data obtained in batch sorption studies. Application of such models may ensure that extraneous effects such as precipitation have not been introduced into the sorption experiment.

Between the simplicity of the K_d model and the complexity of the TLM, there are several other sorption models. These include various forms of isotherm equations (e.g., Langmuir and Freundlich isotherms) and models that include kinetic effects. The generalized two-layer model (Dzombak and Morel, 1990) (also referred to as the diffuse layer model, double-layer model or DLM) recently has been used to model radionuclide sorption by several research groups (Langmuir, 1997a; Jenne, 1998; Davis, 2001). Constants used in this model are dependent upon the concentration of background electrolytes and are thus less robust than

² The activities of the uranyl ion and proton at the surface differ from their activities in the bulk solution: $\{UO_2^{2+}_{(s)}\} = a_{UO_2^{2+}} \times \exp[-2e\psi_o/kT]$ and $\{H^+_{(s)}\} = a_{H^+} \times \exp[-e\psi_o/kT]$. Eq. 5 can be derived from the equilibrium constant for Eq. 4, $\beta^{UO_2^{2+}} = [\{>FeO-UO_2^+\}/\{>FeOH\}] \times [\{H^+_{(s)}\}/\{UO_2^{2+}_{(s)}\}]$, by substitution.

those of the TLM. Reviews by Turner (1991), Langmuir (1997b) and U.S. EPA (1999a) provide concise descriptions of many of these models.

Several researchers have illustrated the interdependence of the adjustable parameters and the non-unique nature of the SCM constants by fitting the same or similar sorption edges to a variety of alternate SCM models (Westall and Hohl, 1980; Turner, 1995; Turner and Sassman, 1996). Robertson and Leckie (1996) systematically examined the effects of SCM model choice on cation binding predictions when pH, ionic strength, cation loading and proposed surface complex stoichiometry were varied. They show that although different models can be used to obtain comparable fits to the same experimental data set, the stoichiometry of the proposed surface complex will vary considerably between the models. In the near future, it is possible that the actual stoichiometry of adsorbed species can be determined using combinations of the spectroscopic techniques discussed in a previous section and molecular modeling techniques similar to those described in Cygan (2002).

Currently, there is no set of reference surface complexation constants corresponding to the reference thermodynamic property values contained in the NEA thermodynamic database described in the previous section (Grenthe et al., 1992; Silva et al., 1995; Rard et al., 1999; Lemire et al., 2001). Recently, Wang et al. (2001a, 2001b) used the diffuse-layer model (DLM) with original experimental data to obtain a set of internally consistent surface complexation constants for Np(V), Pu(IV), Pu(V) and Am(III), I^- , IO_3^- and TcO_4^- sorption by a variety of synthetic oxides and geologic materials in low ionic strength waters (< 0.1 M). Turner and Sassman (1996) and Davis (2001) provide databases for uranium sorption also using the DLM. Langmuir (1997b) compiles surface complexation constants for actinides and fission products based on several different SCMs. Other compilations are based on the TLM; these include those of Hsi and Langmuir (1985), Tripathi (1983), McKinley et al. (1995), Turner et al. (1996), and Lenhart and Honeyman (1999) for uranium; Girvin et al. (1991) and Kohler et al. (1999) for neptunium; LaFlamme and Murray (1987), Quigley et al. (1996), and Murphy et al. (1999) for thorium and Sanchez et al. (1985) for plutonium. Langmuir (1997b), Davis (2001), Wang et al. (2001a, b), and Turner et al. (2002) provide references to a large number of other surface complexation studies of radionuclides.

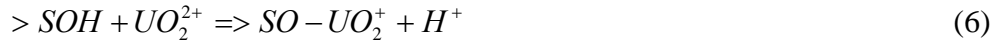
3.1.2.2.2 Representation of Sorption of Radionuclides Under Natural Conditions

Several approaches have been used to represent variability of sorption under natural conditions. These include: 1) sampling K_d values from a probability distribution function (pdf), 2) calculating a K_d using empirical relations based on measurements over a range of experimental conditions, solution compositions and mineral properties, and 3) calculating aqueous and surface speciation using a thermodynamically-based SCM. The first approach is used most commonly in risk assessment and remediation design calculations. Because of the diversity of solutions, minerals, and radionuclides that could be present at contaminated sites and potential waste disposal repository sites, a large body of empirical radionuclide sorption data has been generated. Databases of K_d values that can be used to estimate pdf's for various geologic media are summarized by Barney (1981a,b), Tien et al. (1985), Bayley et al. (1990), U.S. DOE (1988), McKinley and Scholtis (1992), Triay et al. (1997), the U.S. Environmental Protection Agency (1999a,b) and Krupka and Serne (2000). Methods used to specify pdf's for K_d s for use with sampling techniques such as Latin Hypercube Sampling

(Iman and Shortencarier, 1984; Helton and Davis, 2002) have been described by Siegel et al. (1983, 1989), Wilson et al. (1994) and Rechar (1996).

Serne and Muller (1987) describe attempts to find statistical empirical relations between experimental variables and the measured sorption ratios (R_{ds}). Mucciardi and Orr (1977) and Mucciardi (1978) used linear (polynomial regression of first-order independent variables) and nonlinear (multinomial quadratic functions of paired independent variables, termed the Adaptive Learning Network) techniques to examine effects of several variables on sorption coefficients. The dependent variables considered included cation exchange capacity (CEC) and surface area (SA) of the solid substrate, solution variables (Na, Ca, Cl, HCO_3^-), time, pH, and Eh. Techniques such as these allow modelers to construct a narrow probability density function for K_{ds} .

The dependence of a K_d on the composition of the groundwater can be also described in terms of more fundamental thermodynamic parameters. This can be illustrated by considering the sorption of uranyl (UO_2^{2+}) onto a generic surface site ($>\text{SOH}$) of a mineral:



with an equilibrium sorption binding constant β^{cat} defined for the reaction. The concentration of UO_2^{2+} available to complex with the surface site will be affected by complexation reactions with other ligands such as carbonate. The K_d in a system containing the uranyl ion and its hydroxo and carbonato complexes can be calculated as

$$K_d = \frac{\beta^{cat} \times \{\text{SOH}\} \times C}{\{\text{H}^+\} \times \left[1 + \sum_{ijk} K_{i,j,k} \{\text{UO}_2^{2+}\}^{i-1} \{\text{OH}\}^j \{\text{CO}_3^{2-}\}^k \right]} \quad (7)$$

For simplicity, in this equation, we have assumed that activities are equal to concentrations and brackets refer to activities. C is a units conversion constant = V_v/m , relating void volume V_v (mL) in the porous media and the mass m (g) of the aquifer material in contact with the volume V_v ; $K_{i,j,k}$ is the formation constant for an aqueous uranyl complex, and the superscripts i, j, k describe the stoichiometry of the complex. The form that the sorption binding constant β^{cat} takes is different for the different sorption models shown in Figure 4 (for example, see Eq. 5). Leckie (1994) derives similar expressions for more complex systems in which anionic and cationic metal species form polydentate surface complexes³.

³ Equation 7 can be derived from the following relationships for this system:

- K_d = total sorbed uranium/total uranium in solution.
- Total sorbed uranium = $\{>\text{SO}-\text{UO}_2^{2+}\} = \beta^{cat} \times \{>\text{SOH}\} \times \{\text{UO}_2^{2+}\} / \{\text{H}^+\}$
- Total uranium in solution = $\{\text{UO}_2^{2+}\} + \{\text{UO}_2\text{CO}_3\} + \dots$ other uranyl complexes
- $\{\text{UO}_2\text{CO}_3\} = K_{\text{UO}_2\text{CO}_3} \times \{\text{UO}_2^{2+}\} \times \{\text{CO}_3^{2-}\}$;
- similar expressions can be written for other uranyl species

Substituting Eq. e and d into Eq. c, and then substituting Eq. c and b into Eq. a, yields Eq. 7 after some manipulation. Note that activity coefficients of all species are assumed to be equal to 1.0.

Expressions like Eq. 7 can be solved using computer programs such as HYDRAQL. Using a spreadsheet program for post-processing of the results, K_d values can easily be calculated over ranges of solution compositions. Using this approach, the effects of relatively small changes in the composition of the groundwaters can be shown to result in order-of-magnitude changes in the K_d . Figure 5 shows that the calculated K_d of uranium in systems containing several competing ligands can be sensitive to the concentration of other cations such as Ca^{2+} . Leckie (1994) provides examples of this methodology and produces multi-dimensional K_d response surfaces. Approaches to using thermodynamic sorption models to predict, interpret or guide the collection of K_d data are summarized by the NEA (2001).

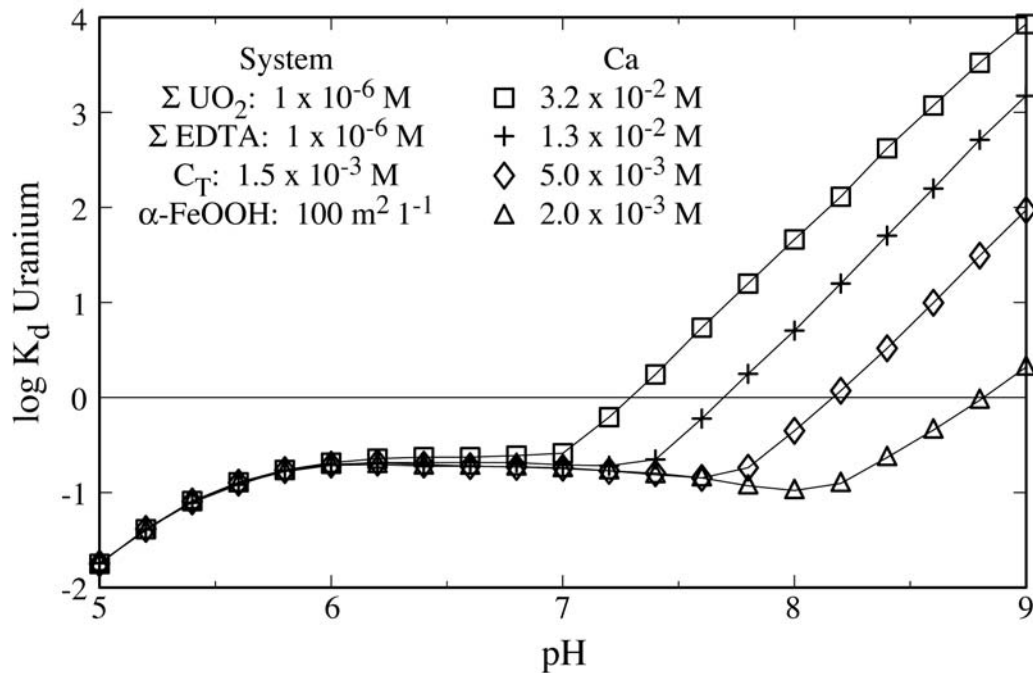


Figure 5. Calculated theoretical K_d for sorption of uranyl onto a goethite substrate as a function of pH at fixed total carbon concentration in the presence of a sequestering agent (EDTA). K_d s are shown for several levels of calcium concentration. Surface area of the substrate is $100 \text{ m}^2 \text{ L}^{-1}$; total carbon is fixed at $1.5 \times 10^{-3} \text{ M}$ and total uranium content is 10^{-6} M . Simulations were carried by J.O. Leckie (Stanford University).

K_{ds} , whether sampled from probability distribution functions or calculated by regression equations or SCMs, can be used in many contaminant transport models. Alternate forms of the retardation factor equation that use a K_d (Eq. 3) and are appropriate for porous media, fractured porous media or discrete fractures have been used to calculate contaminant velocity and discharge (e.g., Erickson, 1983; Neretnieks and Rasmuson, 1984). An alternative approach couples chemical speciation calculations to transport equations. Such models of *reactive transport* have been developed and demonstrated by a number of researchers including Parkhurst (1995), Lichtner (1996); Bethke (1997); Szecsody et al. (1998), Yeh et al. (1995, 2002), and others reviewed in Lichtner et al. (1996), Steefel and Van Cappellen (1998), and Browning and Murphy (2003). Uses of such models to simulate radionuclide transport of uranium in 1-D column experiments are illustrated by Sims et al. (1996) and

Kohler et al. (1996). Glynn (2003) models transport of redox sensitive elements Np and Pu in a 1-D domain with spatially variant sorption capacities. Simulations of 2-D reactive transport of neptunium and uranium are illustrated by Yeh et al. (2002) and Criscenti et al. (2002), respectively. Such calculations demonstrate that the results of reactive transport simulations differ markedly from those obtained in transport simulations using constant K_d , Langmuir or Freundlich sorption models. Routine use of the reactive transport codes in performance assessment calculations, however, is still limited by the substantial computer simulation time requirements.

3.1.2.2.3 Sorptive Properties of Mineral Assemblages and Soils

An important question for the prediction of radionuclide migration is whether sorption in the geomeedia can be predicted from the properties of the constituent minerals. Attempts by researchers to use sorption models based on weighted radionuclide K_d values of individual component minerals (“sorptive additivity”) have met with limited success (Meyer et al., 1984; Jacquier et al., 2001). Tripathi et al. (1993) used a “competitive-additivity” model based on surface complexation theory to model the pH-dependent sorption of lead by goethite/Ca-montmorillonite mixtures. They used complexation constants obtained from single sorbent systems and predicted the sorption behavior of mineral mixtures from the proportion of the two sorbents and their respective affinities for the metals. Davis et al. (1998) describe the component additivity model (CA), a similar approach in which the wetted surface of a complex mineral assemblage is assumed to be composed of a mixture of one or more reference minerals. The surface properties of the individual phases are obtained from independent studies in mono-mineralic model systems and then are applied to the mineral assemblage without further fitting, based on the contributions of the individual minerals to the total surface area of the mixture. Applications of this approach to radionuclides are described by McKinley et al. (1995), Waite et al. (2000), Prikryl et al. (2001), Arnold et al. (2001), Davis (2001), and Davis et al. (2002). Strongly sorbent minerals such as clays or goethite are produced by the alteration of host rocks and line the voids of porous geomeedia. In these cases, the sorption behavior of the mineral assemblage can be approximated by using the properties of one or two of minerals even though they constitute a small fraction of the rock mass (Davis and Kent, 1990; Ward et al., 1994; Barnett et al., 2002).

The generalized composite approach (GC) is an alternative approach in which surface complexation constants are obtained by fitting experimental data for the natural mineral assemblage directly (Koß, 1988; Davis et al., 1998). A simplified form of this approach fits the pH-dependent sorption of the radionuclide without representation of the electrostatic interaction terms found in other SCMs. The disadvantages of this approach are: 1) the constants obtained are site-specific, and 2) it is difficult to apply it to carbonate-rich mineral assemblages. However, it can be used to calibrate simpler sorption models that are used in performance assessment codes.

3.2 Results of Radionuclide Solubility, Speciation and Sorption Studies

In this section, results of studies of the geochemistry of fission products and actinides are summarized. The chemistry of the fission products are described as a group first because their behavior is relatively simple compared to the actinides. Next, general trends and then site-specific environmental chemistry of the actinides are summarized.

3.2.1 Fission Products

Fission products of uranium and other actinides are released to the environment during weapons production and testing, and by nuclear accidents. Because of their relatively short half-lives, they commonly account for a large fraction of the activity in radioactive waste for the first several hundred years. Important fission products are shown in Table 3. Many of these have very short half-lives and do not represent a long-term hazard in the environment, but they do constitute a significant fraction of the total released in a nuclear accident. Only radionuclides with half-lives of several years or longer represent a persistent environmental or disposal problem. Of primary interest are ^{90}Sr , ^{99}Tc , ^{129}I , and ^{137}Cs , and to a lesser degree, ^{79}Se and ^{93}Zr ; all are β^- emitters.

Table 3. Environmentally Important Fission Products.

Fission product	$t_{1/2}$, yrs
^{79}Se	6.5×10^5
^{90}Sr	28.1
^{93}Zr	1.5×10^6
^{99}Tc	2.12×10^5
^{103}Ru	0.11
^{106}Ru	0.56
$^{110\text{m}}\text{Ag}$	0.69
^{125}Sb	2.7
^{129}I	1.7×10^7
^{134}Cs	2.06
^{137}Cs	30.2
^{144}Ce	0.78

While fission product mobility is mostly a function of the chemical properties of the element, the initial physical form of the contamination can also be important. For radioactive contaminants released as particulates—“hot particles”—radionuclide transport is initially dominated by physical processes, namely, transport as aerosols (Wagenpfeil and Tschiersch, 2001) or as bedload/suspended load in river systems. At Chernobyl, the majority of fission products were released in fuel particles and condensed aerosols. Fission products were effectively sequestered—e.g., little downward transport in soil profiles and little biological uptake—until dissolution of the fuel particles occurred and the fission products were released (Petryaev et al., 1991; Konoplev et al., 1992; Baryakhtar, 1995; Konoplev and Bulgakov, 1999). Thus, fuel particle dissolution kinetics controlled the release of fission products to the

environment (Kruglov et al., 1994; Kashparov et al., 1999; Uchida et al., 1999; Sokolik et al., 2001; Kashparov et al., 2001).

3.2.1.1 ^{90}Sr

Strontium occurs in only one valence state, (II). It does not form strong organic or inorganic complexes and is commonly present in solution as Sr^{2+} . The concentration is rarely solubility-limited in soil or groundwater systems because the solubility of common strontium phases is relatively high (Lefevre et al., 1993; U.S. EPA, 1999b). The concentration of strontium in solution is commonly controlled by sorption and ion exchange reactions with soil minerals. Parameters affecting strontium transport are CEC, ionic strength and pH (Sr^{2+} sorption varies directly with pH, presumably, due to competition with H^+ for amphoteric sites). Clay minerals—illite, montmorillonite, kaolinite, and vermiculite—are responsible for most of the exchange capacity for strontium in soils (Goldsmith and Bolch, 1970; Sumrall and Middlebrooks, 1968). Zeolites (Ames and Rai, 1978) and Mn oxides/hydroxides also exchange or sorb strontium in soils. Because of the importance of ion exchange, strontium K_{ds} are strongly influenced by ionic strength of the solution, decreasing with increasing ionic strength (Mahoney and Langmuir, 1991; Nisbet et al., 1994); calcium and natural strontium are especially effective at competing with ^{90}Sr . Strontium in soils is largely exchangeably bound; it does not become fixed with time (Serne and Gore, 1996). However, coprecipitation with calcium sulfate or carbonate and soil phosphates may also contribute to strontium retardation and fixation in soils (Ames and Rai, 1978).

3.2.1.2 ^{137}Cs

Cesium, like strontium, occurs in only one valence state, (I). Cesium is a very weak Lewis acid and has a low tendency to interact with organic and inorganic ligands (Hughes and Poole, 1989; U.S. EPA, 1999b); thus, Cs^+ is the dominant form in groundwater. Inorganic cesium compounds are highly soluble, and precipitation/coprecipitation reactions play little role in limiting cesium mobility in the environment. Retention in soils and groundwaters is controlled by sorption/desorption and ion exchange reactions.

Cesium is sorbed by ion exchange into clay interlayer sites, and by surface complexation with hydroxy groups comprised of broken bonds on edge sites, and the planer surfaces of oxide and silicate minerals. CEC is the dominant factor in controlling cesium mobility. Clay minerals such as illite, smectites, and vermiculite are especially important because they exhibit a high selectivity for cesium (Douglas, 1989; Smith and Comans, 1996). The selectivity is a function of the low hydration energy of cesium; once it is sorbed into clay interlayers, it loses its hydration shell and the interlayer collapses. Ions, such as magnesium and calcium, are unable to shed their hydration shells and cannot compete for the interlayer sites. Potassium is able to enter the interlayer and competes strongly for exchange sites. Because it causes collapse of the interlayers, cesium does not readily desorb from vermiculite and smectite and may in fact be irreversibly sorbed (Douglas, 1989; Ohnuki and Kozai, 1994; Khan et al., 1994). Uptake by illitic clay minerals does not occur by ion exchange but rather by sorption onto frayed edge sites (Cremers et al., 1988; Comans et al., 1989; Smith et al., 1999), which are highly selective for cesium. Although illite has a higher selectivity for

cesium, it has a much lower capacity than smectites because cesium cannot enter the interlayer sites.

Cesium mobility increases with ionic strength because of competition for exchange sites (Lieser and Peschke, 1982). Potassium competes more effectively than calcium or magnesium. Since cesium is rapidly and strongly sorbed by soil and sediment particles, it does not migrate downward rapidly through soil profiles, especially forest soils (Bergman, 1994; Rühm et al., 1996; Panin et al., 2001). Estimated downward migration rates for cesium released by the Chernobyl accident are on the order of 0.2 to 2 cm yr⁻¹ in soils in Bohemia (Hölgye and Malý, 2000), Russia (Sokolik et al., 2001), and Sweden (Rosén et al., 1999; Isaksson et al., 2001).

3.2.1.3 ⁹⁹Tc

Technetium occurs in several valence states, ranging from -1 to +7. In groundwater systems, the most stable oxidation states are (IV) and (VII) (Lieser and Peschke, 1982). Under oxidizing conditions, Tc(VII) is stable as pertechnetate, TcO₄⁻. Pertechnetate compounds are highly soluble, and being anionic, pertechnetate is not sorbed onto common soil minerals and is not readily sequestered by ion exchange. Thus, under oxidizing conditions, technetium is highly mobile. Significant sorption of pertechnetate has been seen in organic-rich soils of low pH (Wildung et al., 1979), probably due to the positive charge on the organic fraction and amorphous iron and aluminum oxides, and possibly coupled with reduction to Tc(IV).

Under reducing conditions, Tc(IV) is the dominant oxidation state because of biotic and abiotic reduction processes. Tc(IV) is commonly considered to be essentially immobile because it readily precipitates as low-solubility hydrous oxides and forms strong surface complexes on iron and aluminum oxides and clays.

Tc(IV) behaves like other tetravalent heavy metals and occurs in solution as hydroxo and hydroxo-carbonato complexes. In carbonate-containing groundwaters, TcO(OH)_{2(aq)} is dominant at neutral pH; at higher pH values, Tc(OH)₃CO₃⁻ is more abundant (Erikson et al., 1992). However, the solubility of Tc(IV) is low and is limited by precipitation of the hydrous oxide, TcO₂ · nH₂O. The number of waters of hydration is traditionally given as n = 2 (Rard, 1983) but has more recently been measured as 1.63 ± 0.28 (Meyer et al., 1991). In systems containing H₂S or metal sulfides, the solubility-limiting phase for technetium may be Tc₂S₇ or TcS₂ (Rard, 1983).

Retention of pertechnetate in soil and groundwater systems usually involves reduction and precipitation as Tc(IV)-containing hydroxide or sulfide phases. Several mineral phases have been shown to fix pertechnetate through surface-mediated reduction/coprecipitation. These include magnetite (Haines et al., 1987; Byegård et al., 1992; Cui and Erikson, 1996) and a number of sulfides, including chalcocite, bournonite, pyrrhotite, tetrahedrite, and to a lesser extent, pyrite and galena (Strickert et al., 1980; Winkler et al., 1988; Lieser and Bauscher, 1988; Huie et al., 1988; Bock et al., 1989). Sulfides are most effective at reducing technetium if they contain a multivalent metal ion in the lower oxidation state (Strickert et al., 1980). Technetium sorption by iron oxides is minimal under near-neutral, oxidizing

conditions but is extensive under mildly reducing conditions, where Fe(III) remains stable. It is minimal on ferrous silicates (Vandergraaf et al., 1984).

In addition, technetium may be fixed by bacterially-mediated reduction and precipitation. Several types of Fe(III)- and sulfate-reducing bacteria have been shown to reduce technetium, either directly (enzymatically) or indirectly through reaction with microbially-produced Fe(II), native sulfur, or sulfide (Lyalikova and Khizhnyak, 1996; Lloyd and Macaskie, 1996; Lloyd et al., 2002).

3.2.1.4 ¹²⁹I

Iodine can exist in the oxidation states -1, 0, +1, +5, and +7. However, the +1 state is not stable in aqueous solutions and disproportionates into -1 and +5. In surface and ground waters at near-neutral pH, IO₃⁻ (iodate) is the dominant form in solution, while under acidic conditions, I₂ can form. Under anoxic conditions, iodine is present as I⁻ (iodide) (Allard et al., 1980; Liu and van Gunten, 1988).

Iodide forms low solubility compounds with copper, silver, lead, mercury, and bismuth, but all other metal iodides are quite soluble. As these metals are not common in natural environments, they have little effect on iodine mobility (Couture and Seitz, 1985). Retention by sorption and ion exchange appears to be minor (Lieser and Peschke, 1982). However, significant retention has been observed by the amorphous minerals imogolite and allophane (mixed Al/Si oxide-hydroxides, with SiO₂/Al₂O₃ ratios between 1 and 2). These minerals have high surface areas and positive surface charge at neutral pH and contribute significantly to the anion exchange capacity in soils (Gu and Schultz, 1991). At neutral pH, Al- and Fe-hydroxides are also positively charged and contribute to iodine retention, especially if iodine is present as iodate (Couture and Seitz, 1985). Sulfide minerals containing the metal ions which form insoluble metal iodides strongly sorb iodide, apparently through sorption and surface precipitation of the metal iodide. Iodate is also sorbed, possibly because it is reduced to iodide on the metal/sulfide surfaces (Allard et al., 1980; Strickert et al., 1980). Lead, copper, silver, silver chloride, and lead oxides/hydroxides and carbonates can also fix iodine through surface precipitation (Bird and Lopato, 1980; Allard et al., 1980). None of these minerals are likely to be important in natural soils but may be useful in immobilizing iodine for environmental remediation.

Organic iodo compounds are not soluble and form readily through reaction with I₂ and, to a lesser extent, I⁻ (Lieser and Peschke, 1982; Couture and Seitz, 1985); retention of iodine in soils is mostly associated with the organic matter (Wildung et al., 1974; Muramatsu, et al., 1990; Gu and Schultz, 1991; Yoshida et al., 1998; Kaplan et al., 2000). Several studies have suggested that fixation of iodine by organic soil compounds appears to be dependent upon microbiological activity, because sterilization by heating or radiation commonly results in much lower iodine retention (Bunzl and Schimmack, 1988; Koch et al., 1989; Muramatsu et al., 1990; Bors et al., 1991; Rädlinger and Heumann, 2000).

3.2.2 Uranium and Other Actinides [An(III), An(IV), An(V), An(VI)]

3.2.2.1 General Trends in Solubility, Speciation, and Sorption

Actinides are hard acid cations (i.e., comparatively rigid electron clouds with low polarizability) and form ionic species as opposed to covalent bonds (Silva and Nitsche, 1995; Langmuir, 1997a). Several general trends in their chemistry can be described (although there are exceptions). Due to similarities in ionic size, coordination number, valence, and electron structure, the actinide elements of a given oxidation state have either similar or systematically varying chemical properties (David, 1986; Choppin, 1999; Vallet et al., 1999). For a given oxidation state, the relative stability of actinide complexes with hard base ligands can be divided into three groups in the order: CO_3^{2-} , $\text{OH}^- > \text{F}^-$, HPO_4^{2-} , $\text{SO}_4^{2-} > \text{Cl}^-$, NO_3^- . Within those ligand groups, stability constants generally decrease in the order $\text{An}^{4+} > \text{An}^{3+} \approx \text{AnO}_2^{2+} > \text{AnO}_2^+$ (Lieser and Mohlenweg, 1988; Silva and Nitsche, 1995). In addition, the same order describes the decreasing stability (increasing solubility) of actinide solids formed with a given ligand (Langmuir, 1997a).

These trends have allowed the use of an oxidation state analogy modeling approach, in which data for the behavior of one actinide can be used as an analog for others in the same oxidation state. An oxidation state analogy was used for the WIPP to evaluate the solubility of some actinides and to develop a more complete set of modeling parameters for actinides included in the repository performance calculations. The results are assumed to be either similar to the actual case or can be shown to vary systematically (Fanghänel and Kim, 1998; Neck and Kim, 2001; Wall et al., 2002). The similarities in chemical behavior extend beyond the actinides to the lanthanides—Nd(III) is commonly used as a nonradioactive analog for the +III actinides. For instance, complexation and hydrolysis constants and Pitzer ion interaction parameters used in modeling Am(III) speciation and solubility for the WIPP were extracted from a suite of published experimental studies involving not only Am(III) but also Pu(III), Cm(III), and Nd(III) (U.S. DOE, 1996).

3.2.2.1.1 Oxidation State

Differences among the potentials of the redox couples of the actinides account for much of the differences in their speciation and environmental transport. Detailed information about the redox potentials for these couples can be found in numerous references (e.g., Hobart, 1990; Silva and Nitsche, 1995; Runde, 2002a). This information is not repeated here, but a few general points should be made. Important oxidation states for the actinides under environmental conditions are described in Table 4. Depending on the actinide, the potentials of the III/IV, IV/V, V/VI and/or IV/VI redox couples can be important under near-surface environmental conditions. When the redox potentials between oxidation states are sufficiently different, then one or two redox states will predominate; this is the case for uranium, neptunium and americium (Runde, 2002a). The behavior of uranium is controlled by the predominance of U(VI) species under oxidizing conditions and U(IV) under reducing conditions. In the intermediate Eh range and neutral pH possible under many settings, the solubility of neptunium is controlled primarily by the Eh of the aquifer and will vary between the levels set by $\text{Np}^{\text{IV}}(\text{OH})_{4(\text{s})}$ (10^{-8} M under reducing conditions) and $\text{Np}^{\text{V}}_2\text{O}_{5(\text{s})}$ (10^{-5} M under oxidizing conditions). Redox potentials of Pu in the III, IV, V and VI states are similar

(around 1.0 V), therefore, plutonium can coexist in up to four oxidation states in some solutions (Langmuir, 1997a; Runde, 2002a). However, Pu(IV) is most commonly observed in environmental conditions and sorption of plutonium is strongly influence by reduction of Pu(V) to Pu(IV) at the mineral-water interface. More discussions of these behaviors will be found in the individual sections for each actinide that follow.

Table 4. Important Actinide Oxidation States in the Environment.

Actinide Element	Oxidation States		
thorium	IV		
uranium	IV		VI
neptunium	IV	V	
plutonium	IV	V	VI
americium	III		
curium	III		

3.2.2.1.2 Complexation and Solubility

In dilute aqueous systems, the dominant actinide species at neutral to basic pH are hydroxy- and carbonato-complexes. Similarly, solubility-limiting solid phases are commonly oxides, hydroxides or carbonates. The same is generally true in high ionic strength brines, because common brine components— Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} —do not complex as strongly with actinides. However, weak mono-, bis-, and tris-chloro complexes with hexavalent actinides (U(VI) and Pu(VI)), can contribute significantly to the solubility of these actinides in chloride-rich brines. Runde et al. (1999) measured shifts in the apparent solubility product constants for uranyl and plutonyl carbonate of nearly one log unit as chloride concentrations increased to 0.5 M. Carbonate complexes are important for radionuclides; thorium, plutonium, neptunium and uranium all have strong carbonate complexes under environmental conditions. Carbonate complexation also leads to decreased sorption by forming strong anionic complexes that will not sorb to negatively-charged mineral surfaces. The potential importance of carbonate complexes with respect to increasing actinide solubility and decreasing sorption influenced a decision by the DOE to use MgO as the engineered barrier in the WIPP repository. MgO and its hydration products sequester CO_2 through formation of carbonates and hydroxycarbonates, as well as buffering the pH at neutral to moderately basic values, where actinide solubilities are at a minimum.

Dissolved organic carbon may be present as strong complexing ligands that increase the aqueous concentration limits of actinides (Olofsson and Allard, 1983). In environments with high organic matter from natural or anthropogenic sources, complexation of actinides with ligands such as EDTA and other organic ligands may decrease the extent of sorption onto rocks. Langmuir (1997a) suggests that to a first approximation, complexation of An^{4+} , AnO_2^+ , and AnO_2^{2+} with humic and fulvic acids can be ignored because the actinides form such strong hydroxyl and carbonato-complexes in natural waters. In contrast, however, although An^{3+} species form OH^- and or CO_3^{2-} complexes, important actinide/humic-fulvic

complexation does occur. Conditions under which actinide-humic interactions are important are discussed in more detail in Section 3.3.1.

3.2.2.1.3 Sorption

In general, actinide sorption will decrease in the presence of ligands that complex with the radionuclide (most commonly humic or fulvic acids, CO_3^{2-} , SO_4^{2-} , F^-) or cationic solutes that compete with the radionuclide for sorption sites (most commonly Ca^{2+} , Mg^{2+}). In general, sorption of the (IV) species of actinides (Np, Pu, U) is greater than of the (V) species.

As discussed previously (Section 3.1.1 – Sorption Studies), plots of pH sorption edges (see Fig. 3) are useful in summarizing the sorption of radionuclide by substrates that have amphoteric sites (i.e. SOH , SO^- , SOH_2^+). The pH sorption edges of actinides are similar for different aluminosilicates (quartz, α -alumina, clinoptilolite, montmorillonite, and kaolinite). For example, Np(V) and U(VI) exhibit similar pH-dependent sorption edges that are independent of specific aluminosilicate identity (Bertetti et al., 1998; Pabalan et al., 1998). Under similar solution conditions, the amount of radionuclide adsorbed is primarily a function of the surface area. This observation has led several workers to propose that the amount of actinide sorption onto natural materials can be predicted from the surface site density and surface area rather than the specific molecular structure of the surface (Davis and Kent, 1990; Turner and Pabalan, 1999).

Carroll et al. (1992), Stout and Carroll (1993), van Cappellen et al. (1993), Meece and Benninger (1993), Brady et al. (1999), and Reeder et al. (2001) summarize empirical data and theoretical models of actinide-carbonate mineral interactions. The surface potential determining ion on carbonate minerals may be Ca^{2+} or Mg^{2+} . Increased solution concentration of Ca^{2+} will lead to decreased actinide sorption, which then leads to complex sorption behavior if the carbonate concentration and pH of the solution are varied. Carroll et al. (1992) studied the uptake of Nd(III), U(VI) and Th(VI) by pure calcite in dilute NaHCO_3 solutions using a combination of surface analysis techniques. They found that U(VI) uptake was limited to monolayer sorption and uranium-calcium solid solution was minimal even in solutions supersaturated with rutherfordine (UO_2CO_3). In contrast, they found that surface precipitation and carbonate solid solution was extensive for thorium and neodymium. Similarly, irreversible sorption and surface precipitation of americium onto carbonates were observed by Shanbhag and Morse (1982) and Higgo and Rees (1986).

Attempts to propose representative K_d values for actinides have met with controversy. For example, Silva and Nitsche (1995) suggested average K_d values for actinides in the order $\text{An}^{4+} > \text{An}^{3+} > \text{AnO}_2^{2+} > \text{AnO}_2^+$, as 500, 50, 5 and 1, respectively. This order corresponds to the order of the pH_{50} values of sorption edges for Th(IV), Am(III), Np(V), and Pu(V) in studies of sorption by γ - Al_2O_3 (Bidoglio et al., 1989); and of Pu(IV), U(VI), and Np(V) in studies of sorption by α - FeOOH (Turner, 1995). Calculated or measured element-specific K_{ds} for natural soils and geomeia for many environmental sites, however, are quite different from these values. For example, a recent compilation listed the following suggested general ranges for soil/mineral K_{ds} , in ml g^{-1} : Pu: 11–300,000; U: 10.5–4400; Am: 1–47,230 (Krumhansl et al., 2002). These wide ranges exist because sorption of radionuclides is very

dependent on the radionuclide oxidation state, groundwater composition and nature of rock surface, all of which may be variable and/or poorly characterized along the flow path. The databases of K_d values described previously (Section 3.1.2 – Sorption) should be used to obtain K_{ds} for site-specific conditions instead of using broad “generic” ranges whenever possible.

3.2.3 Site-Specific Geochemistry of the Actinides

3.2.3.1 Introduction: Actinide Solubilities in Reference Waters

In this section, the environmental chemistry of the actinides is examined in more detail by considering three different geochemical environments. Compositions of groundwater from these environments are described in Tables 5 and 6. These include 1) low ionic strength reducing waters from crystalline rocks at nuclear waste research sites in Sweden; 2) oxic water from the J-13 well at Yucca Mountain, Nevada, the site of a proposed repository for high level nuclear waste in tuffaceous rocks; and 3) reference brines associated with the Waste Isolation Pilot Plant, a repository for transuranic waste in the Permian Salt beds of SE New Mexico. These last brines are model solutions produced by the reaction of the Permian formation waters with the components of the engineered barrier at the WIPP as discussed below.

The Swedish repository science program has investigated crystalline rock as a host rock for the disposal of radioactive waste and has measured the composition of granitic groundwaters (Andersson, 1990). Much of this was done at the Stripa site, an abandoned iron mine located in a granitic intrusion in south-central Sweden. At Stripa, shallow groundwaters are dilute, carbonate-rich, pH neutral, oxidizing waters of meteoric origin; naturally occurring uranium is present in concentrations of 10-90 p.p.b. Once below this zone, the waters are slightly more saline (up to 1.3 g L^{-1} total dissolved solids), more basic (up to pH 10.1) and the Eh is lower—groundwater uranium concentrations are less than one p.p.b. (Andrews et al., 1989; Nordstrom et al., 1989). The trace amounts of sulfide and ferrous iron in the groundwater have little capacity for maintaining reducing conditions, and groundwater interactions with radioactive waste, waste containers, or repository backfill materials are likely to govern the redox conditions in a real repository (Nordstrom et al., 1989). The dilute, near-neutral, mildly reducing groundwater composition given in Table 5 is a composite of analyses from several Swedish sites and is a suggested reference composition (Andersson, 1990) for deep granitic groundwaters.

The proposed nuclear waste repository at Yucca Mountain, Nevada, would be located in a thick sequence of Tertiary volcanic tuffs. The range of groundwater compositions sampled at the site is discussed by Perfect et al. (1995). Numerous geochemical studies have been carried out in high-Eh waters from the alluvium and tuffaceous rocks (e.g., UZ-TP-7) from the unsaturated zone, high-Eh waters from the saturated zone (e.g., J-13) within tuffaceous rocks, and in lower Eh-waters from a deeper Paleozoic carbonate aquifer (e.g., UE252p-1) (Tien et al., 1985; Triay et al., 1997). Table 5 describes the composition of water from the J-13 well, which has been used as a reference water in systematic studies of sorption, transport, and solubility (Nitsche et al., 1992). Its composition is controlled by a number of

processes including dissolution of vitric and devitrified tuff, precipitation of secondary minerals, and ion exchange (Tien et al., 1985; Triay et al., 1997).

Table 5. Compositions of Low Ionic Strength Reference Waters Used in Speciation and Solubility Calculations.

Component	SKI-90 Stripa (mM) ^a	J-13 YM (mM) ^b
Na ⁺	1.39	1.96
K ⁺	0.0256	0.14
Ca ²⁺	0.5	0.29
Mg ²⁺	0.0823	0.07
Fe (total)	0.00179	–
SiO ₂	0.0682	1.07
Cl ⁻	0.423	0.18
SO ₄ ²⁻	0.417	0.19
F ⁻	0.142	0.11
PO ₄ ³⁻	3.75·10 ⁻⁵	–
HCO ₃ ⁻	2.0	2.81
pH*	8.2	6.9
Eh(mV)	-0.3	0.34 – 0.7*

^a SKI (1991)

^b Ogard and Kerrisk (1984)

* - range of Eh used in different works

Table 7 contains the results of actinide solubility and speciation calculations for the J-13 and SKI-90 reference waters carried out using the MINTEQ2A code (Allison et al., 1991) as described by Langmuir (1997a). The MINTEQ2A thermodynamic database of Turner et al. (1993) was used with revised data for americium (Silva et al., 1995) and modifications for uranium described in Langmuir (1997a). Langmuir (1997a) used formation constants that effectively eliminated the influence of Np(OH)₅⁻ and Pu(OH)₅⁻ complexes and assumed that the most soluble amorphous hydroxides and mixed carbonato-hydroxide phases controlled the solubility. These concentrations should be considered maximum soluble concentrations that might be important for short-term behavior of the radionuclides. Over longer time periods, the solubilities are likely controlled by more crystalline phases at levels that are several orders of magnitude lower than those listed in Table 7. These calculations should be considered as a set of baseline calculations for low-ionic strength solutions; they illustrate the effect of redox potential on speciation and solubility.

The WIPP is an underground repository for the permanent disposal of defense-related TRU wastes (NAS, 1996). The facility is located in the U.S. in southeastern New Mexico in a thick, bedded salt, the Salado Formation, at a depth of 655 meters. The Castile Formation is an evaporite sequence below the Salado that may serve as a brine source if the repository is breached by human activities in the future. Brines from both formations are a mixture of Na⁺, Mg²⁺, K⁺, Ca²⁺, Cl⁻, and SO₄²⁻ (see Table 6) and are saturated with respect to halite

(NaCl) and anhydrite (CaSO₄). For the discussion below, the pH, P_{CO₂} and radionuclide solubilities and speciation were calculated assuming that the brines were in equilibrium with halite, anhydrite and minerals produced by hydration and carbonation of the MgO engineered barrier (brucite and hydromagnesite). The Eh of the reference brines was assumed to be controlled by the metallic iron in the waste and waste packages. Calculated solubilities in the two brines are grossly similar. The dominant aqueous species and solubility-limiting phases contain hydroxide and/or carbonate, and solubility differences in the two brines are largely due to differences in the pH (8.7 for the Salado, and 9.2 for the Castile) and CO₃²⁻ activities (3.81 x 10⁻⁷ M and 4.82 x 10⁻⁶ M, for the Salado and Castile brines, respectively).

Table 6. Compositions of Brines Used in WIPP Speciation and Solubility Calculations
(U.S. DOE, 1996).

Component	Salado brine (mM)	Castile brine (mM)
Na ⁺	1,830	4,870
K ⁺	770	97
Ca ²⁺	20	12
Mg ²⁺	1,440	19
Fe (total)	—	—
SiO ₂	—	—
Cl ⁻	5,350	4,800
SO ₄ ²⁻	40	170
F ⁻	—	—
PO ₄ ³⁻	—	—
Br ⁻	10	11
B ₄ O ₇ ²⁻	5	16
pH*	8.7	9.2
pC _{H⁺} *†	9.4	9.9
P _{CO₂} , atm.*	10 ^{-5.5}	10 ^{-5.5}
Eh	—	—
Total dissolved solids	306,000	330,000
Ionic strength	6990	5320

* in equilibrium with brucite and hydromagnesite

† pC_{H⁺} = negative log of the molar concentration of H⁺.

Because of the high ionic strength of the brines, the calculations were carried out using a Pitzer ion interaction model (U.S. DOE, 1996) for the activity coefficients of the aqueous species (Pitzer, 1987, 2000). Pitzer parameters for the dominant nonradioactive species present in WIPP brines are summarized in Harvie and Weare, (1980), Harvie et al. (1984), Felmy and Weare (1986), and Pitzer (1987, 2000). For the actinide species, the Pitzer parameters that were used are summarized in the WIPP Compliance Certification Application (CCA) (U.S. DOE, 1996). Actinide interactions with the inorganic ions H⁺, Na⁺, K⁺, Mg²⁺, Cl⁻, and HCO₃⁻/CO₃²⁻ were considered.

3.2.3.1.1 Americium

The low solubilities and high sorption affinity of thorium and americium severely limit their mobility under environmental conditions. However, because each exists in a single oxidation state—Th(IV) and Am(III)—under environmentally-relevant conditions, they are relatively

easy to study. In addition, their chemical behaviors provide valuable information about the thermodynamic properties of trivalent and tetravalent species of uranium, neptunium and plutonium.

Silva et al. (1995) provide a detailed summary of experimental and theoretical studies of americium chemistry as well as a comprehensive, self-consistent database of reference thermodynamic property values. Solubility and speciation experiments with Am(III) indicate that the mixed hydroxycarbonate $\text{AmOHCO}_3(\text{cr})$ is the solubility-limiting solid phase under most surface and subsurface conditions. At neutral pH, AmOH^{2+} or AmCO_3^+ can be the dominant solution species depending on the carbonate concentration. Langmuir (1997a) calculated a solubility of 5.6×10^{-8} M for J-13 water with the MINTQA2 code using a revised formation constant $\log K_{\text{sp}} = 7.2$ for AmOHCO_3 (compared to NEA $\log K_{\text{sp}} = 8.605$ of Silva et al. (1995)); see Table 7. This is similar to the value of 1.2×10^{-9} M measured by Nitsche et al. (1993) in solubility experiments in J-13 water. The americium solubility calculated by Langmuir (1997a) for reducing water from crystalline rock in Table 7 ($\leq 1.4 \times 10^{-7}$ M) is similar to the range calculated by Bruno et al. (2000) using the EQ3NR (Wolery, 1992b) code for slightly basic, reducing groundwaters in granite at Äspö and Gideå, Sweden.

Table 7. Solubility-Limiting Solids and Range of Solubility-Limited Concentrations (Concentration in M) for Low-Ionic Strength Geochemical Environments.¹

Element	Environment	
	YMP ²	Stripa ³
Tc	none	$\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ $\leq 3.3 \cdot 10^{-8}$
Th	$\text{Th}(\text{OH})_{4(\text{am})}$ $\leq 6.0 \times 10^{-7}$	$\text{Th}(\text{OH})_{4(\text{am})}$ $\leq 5.7 \times 10^{-7}$
U	$\text{Ca}(\text{H}_3\text{O})_2(\text{UO}_2)_2(\text{SiO}_4)_2 \cdot 3\text{H}_2\text{O}(\text{cr})$ 5.4×10^{-9}	$\text{UO}_2(\text{am})$ $\leq 1.4 \times 10^{-8}$
Np	$\text{NaNpO}_2\text{CO}_3 \cdot 3.5\text{H}_2\text{O}(\text{cr})$ 8.9×10^{-4}	$\text{Np}(\text{OH})_{4(\text{am})}$ $\leq 1.6 \times 10^{-9}$
Pu	$\text{Pu}(\text{OH})_{4(\text{am})}$ $\leq 6.6 \times 10^{-8}$	$\text{Pu}(\text{OH})_{4(\text{am})}$ $\leq 1.7 \times 10^{-9}$
Am	$\text{AmOH}(\text{CO}_3)(\text{cr})$ 5.6×10^{-8}	$\text{AmOH}(\text{CO}_3)(\text{cr})$ $\leq 1.4 \times 10^{-7}$

¹ based on Langmuir (1997a, Table 13.11)

² J-13 reference water (Ogard and Kerrisk, 1984)

³ SKI-90 reference water (SKI, 1991).

Fanghänel and Kim (1998) evaluated the solubility of trivalent actinides in brines, using Cm(III) as a representative analog, and found that An(III) hydroxy and carbonate complexes are the most stable aqueous complexes. Multiple-ligand complexes with a high negative charge are more stable in brines than in dilute solutions, apparently because of the high cation concentrations. Chloride and sulfate complexes, although very weak, may be important aqueous species in some brines, especially at low pH.

In the WIPP speciation and solubility calculations, the solubility controlling solid phase for Am, and by analogy, for all +III actinides under WIPP conditions, was $\text{Am}(\text{OH})\text{CO}_3(\text{cr})$ (Novak, 1997; U.S. EPA, 1998a-d; Wall et al., 2002). $\text{Am}(\text{OH})_2^+$ was the most abundant

aqueous species, and estimated americium solubilities in the reference Salado and Castile brines (Table 8) were 9.3×10^{-8} M and 1.3×10^{-8} M, respectively (Novak, 1997; U.S. EPA, 1998d).

Table 8. Calculated Actinide Solubilities in WIPP Brines, (data from U.S. EPA, 1998d).

Actinide	Solubility, M		Solubility-limiting phase	Dominant aqueous phases
	Salado	Castile		
An(VI)*	8.7×10^{-6}	8.8×10^{-6}	—	—
An(V)	1.2×10^{-7}	4.8×10^{-7}	$\text{KNpO}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}_{(s)}$	$\text{NpO}_2\text{CO}_3^-$
An(IV)	1.2×10^{-8}	4.1×10^{-8}	$\text{ThO}_{2(\text{am})}$	$\text{Th}(\text{OH})_3\text{CO}_3^-$
An(III)	9.3×10^{-8}	1.3×10^{-8}	$\text{Am}(\text{OH})\text{CO}_{3(\text{cr})}$	$\text{Am}(\text{OH})_2^+$

* estimated from literature data (values as listed in U.S. DOE, 1996)

Americium is strongly sorbed by tuffaceous rocks from Yucca Mountain in waters of low ionic strength (Triay et al., 1997). In a compilation by Tien et al. (1985), americium K_{ds} obtained with tuff in J-13 water ranged from 130–13,000 ml g^{-1} . Average values for devitrified, vitric and zeolitized tuff were 2975, 1430 and 1513 ml g^{-1} , respectively. Turin et al. (2002) recently measured K_{ds} ranging from 410 to 510 ml g^{-1} using similar waters and tuffaceous rocks from Busted Butte on the Nevada Test Site. They also provide Freundlich isotherm parameters from the sorption measurements. A K_d range of 500 – 50,000 ml g^{-1} is reported for crystalline rocks by McKinley and Scholtis (1992); a value of 5000 ml g^{-1} is recommended for performance assessment.

Data are sparse for Am sorption in high ionic strength solutions. In experimental studies with near-surface sediments from the Gorleben site, Lieser et al. (1991) showed that americium sorption did not vary ($K_d \sim 1,000 \text{ ml g}^{-1}$) over a range of NaCl concentrations of 0 to 2 M, at a pH of 7.5. They concluded that americium sorption was not sensitive to ionic strength because at this pH, americium is nearly completely hydrolyzed. Thus, ion exchange reactions did not contribute to americium sorption, and competing ion concentrations had little effect on sorption K_{ds} . *In situ* studies of radionuclide transport through brackish bay sediments in Sweden (~seawater solution compositions) measured K_{ds} of 1,000–10,000 ml g^{-1} (Andersson et al. 1992).

3.2.3.1.2 Thorium

Experimental and theoretical studies of thorium speciation, solubility and sorption in low ionic strength waters are described by Langmuir and Herman (1980), LaFlamme and Murray (1987), Östhols et al. (1994), Östhols (1995) and Quigley et al. (1996). Langmuir and Herman (1980) provide a critically evaluated thermodynamic database for natural waters at low temperature that is widely used. However, it does not contain information about important thorium carbonate complexes, and the stability of phosphate complexes may be overestimated (U.S. EPA, 1999b).

In both low-ionic strength groundwaters and in the WIPP brines, the solubility limiting phase is $\text{ThO}_{2(\text{am})}$. In seawater, waters from Yucca Mountain, and reducing waters in crystalline rocks, the dominant aqueous species are $\text{Th}(\text{OH})_{4(\text{aq})}$ and mixed hydroxy-carbonate complexes. In alkaline lakes and other environments with high carbonate concentrations, thorium carbonate complexes are dominant (LaFlamme and Murray, 1987; Öthols et al., 1994). In organic-rich stream waters, swamps, soil horizons and sediments, organic thorium complexes may predominate (Langmuir and Herman, 1980). Calculated thorium solubilities in waters from Yucca Mountain and crystalline rocks in Table 7 are similar (about 6.0×10^{-7} M) but are much higher than those calculated by Bruno et al. (2000) for waters from Äspö and Gideå using EQ3NR (about 2×10^{-10} M).

The solubility of $\text{ThO}_{2(\text{am})}$ increases with increasing ionic strength; above pH 7 in 3.0 M NaCl solutions, the solubility is approximately three orders of magnitude higher than that measured in 0.1 M NaClO_4 solution (Felmy et al., 1991). Rai et al. (1997) describe solubility studies and a thermodynamic model for Th(IV) speciation and solubility in concentrated NaCl and MgCl_2 solutions. A Pitzer ion-interaction model was used to obtain a solubility product of $\log K_{\text{sp}} = -45.5$ for $\text{ThO}_{2(\text{am})}$. In the speciation and solubility calculations for the WIPP performance assessment (Table 8), the only important aqueous species was $\text{Th}(\text{OH})_3(\text{CO}_3)^-$; the corresponding estimated Th(IV) solubilities were 1.2×10^{-8} M in the Salado brine and 4.1×10^{-8} M in the Castile brine (Novak, 1997; U.S. EPA 1998d).

Thorium sorbs strongly to iron oxyhydroxides and humic matter (Nash and Choppin, 1980; Hunter et al., 1988; Murphy et al., 1999) and weakly to silica at neutral to basic pH (Öthols, 1995). Thorium sorption is sensitive to carbonate alkalinity due to the formation of negatively charged aqueous mixed hydroxy-carbonate complexes (LaFlamme and Murray, 1987); at alkalinities of 100 meq/L, thorium sorption by goethite decreases markedly. However, at the relatively low alkalinities measured at Yucca Mountain, this effect is not important for the proposed repository site (Triay et al., 1997). Measured thorium sorption ratios in J-13 water from Yucca Mountain for devitrified, vitric and zeolitized tuff ranged from 140 ml g^{-1} to $23,800 \text{ ml g}^{-1}$ (Tien et al., 1985; Thomas, 1987). Other compilations contain representative K_d values for thorium in crystalline rock that range from 100 to 5000 ml g^{-1} (McKinley and Scholtis, 1992) and from 20–300,000 ml g^{-1} for low temperature geochemical environments (U.S. EPA, 1999b).

Thorium sorption at high ionic strength was examined using uranium series disequilibrium techniques by Laul (1992). Laul measured thorium retardation in saline ground waters from the Palo Duro Basin, Texas, and determined sorption K_{ds} of around 2100 ml g^{-1} . Because tetravalent actinides are strongly sorbed by mineral colloids and have a strong tendency to form intrinsic colloids, increases in ionic strength may have more effect on An(IV) transport through destabilization and flocculation of colloidal particles (Lieser and Hill, 1992), rather than through changes in the degree of sorption.

3.2.3.1.3 Uranium

Uranium, neptunium and plutonium are probably the most important actinides in assessment of the environmental risks posed by radioactive contamination. Uranium contamination is

present at numerous sites contaminated by uranium mining, milling and solution mining as described in previous sections. It is highly mobile and soluble under near-surface oxidizing conditions and thus presents an exposure hazard to humans and ecosystems.

Under oxidizing near-surface conditions, U(VI) is the stable oxidation state. Figure 6 shows the aqueous speciation of U(VI) and the solubility of crystalline schoepite ($\beta\text{-UO}_2(\text{OH})_2$) under atmospheric conditions ($P_{\text{CO}_2} = 10^{-3.5}$) over the pH range 4–9. The calculations were carried out with the HYDRAQL code (Papelis et al., 1988) using a thermodynamic database described by Davis et al. (2001), which is based primarily on the compilation of Grenthe et al. (1992). The figure shows that over the pH range 6–8, the mixed hydroxy-carbonato binuclear complex ($(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$) is predicted to predominate; that at lower pH, the uranyl ion (UO_2^{2+}) is most important; and that at higher pH, the polycarbonate $\text{UO}_2(\text{CO}_3)_3^{4-}$ has the highest concentration. In Figure 6, the total concentration of uranium is limited by the solubility of schoepite; therefore, it varies as a function of pH and can exceed 10^{-3} M. The relative importance of the multinuclear uranyl complexes is different from those shown in Figure 6 at different fixed total uranium concentrations. For example, if the total uranium concentration is limited to $< 10^{-8}$ M (e.g. by slow leaching of uranium from a nuclear waste form), then the species $\text{UO}_2(\text{OH})_{2(\text{aq})}$ predominates at pH 6–7. At higher total uranium concentrations (e.g., 10^{-4} M), the multinuclear uranyl hydroxy complex $(\text{UO}_2)_3(\text{OH})_5^+$ predominates at pH 5–6.5 (Davis et al., 2001).

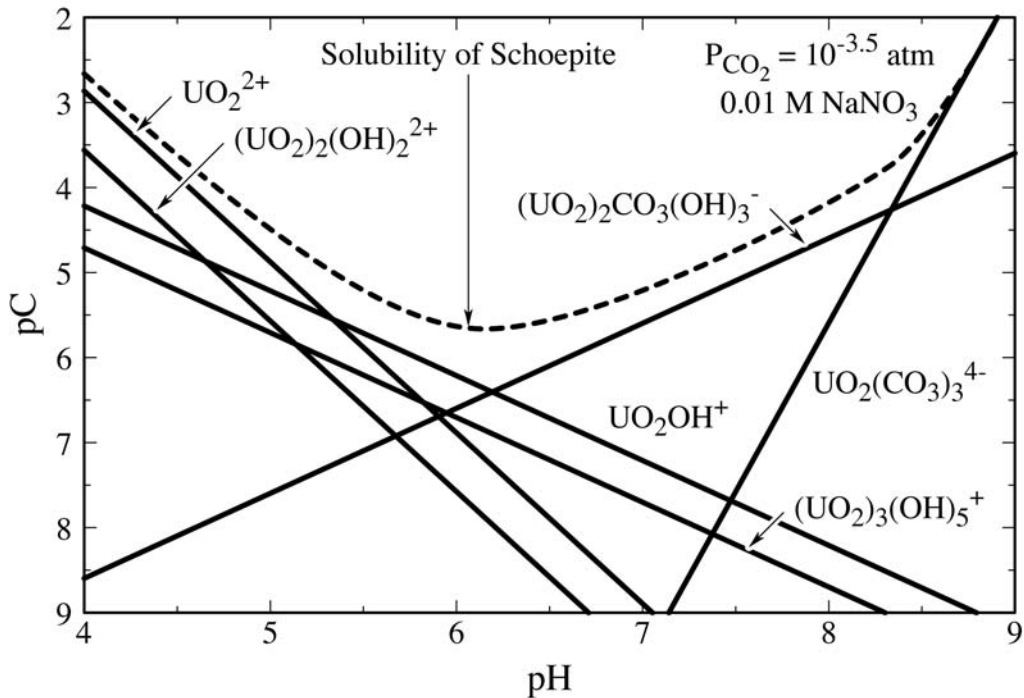


Figure 6. Aqueous speciation of uranium(VI) and the solubility of crystalline schoepite ($\beta\text{-UO}_2(\text{OH})_2$) under atmospheric conditions ($p\text{CO}_2 = 10^{-3.5}$).

(Used by permission of Nuclear Regulatory Commission; modified from Davis, 2001. *Surface Complexation Modeling of Uranium(VI) Adsorption on Natural Mineral Assemblages*, p. 12).

Uncertainties in the identity and solubility product of the solubility-limiting uranium solid in laboratory studies lead to considerable uncertainty in estimates of the solubility under natural conditions. If amorphous $\text{UO}_2(\text{OH})_2$ is assumed to limit the solubility in solutions open to the atmosphere, then the value of the minimum solubility and the pH at which it occurs change. If crystalline schoepite ($\beta\text{-UO}_2(\text{OH})_2$) controls the solubility, then the minimum solubility of 2×10^{-6} M occurs at about pH 6.5. If amorphous $\text{UO}_2(\text{OH})_2$ controls the solubility, the solubility minimum of 4×10^{-5} M occurs closer to pH 7.0 if the solubility product of Tripathi (1983) is assumed (Davis et al., 2001).

In water of low Eh, such as crystalline rock environments studied in the European nuclear waste programs, uranium solubility is controlled by saturation with UO_2 and coffinite (USiO_4) (Langmuir, 1997a). Langmuir (1997a, pp. 501-502) describes some of the controversy surrounding estimation of the solubility of UO_2 . Estimates for the $\log K_{\text{sp}}$ of UO_2 range from -51.9 to -61.0, corresponding to soluble concentrations (as $\text{U}(\text{OH})_{4(\text{aq})}$) ranging from 10^{-8} M (measured by Rai et al., 1990) to $10^{-17.1}$ M (computed by Grenthe et al., 1992). The reason for the wide range lies in the potential contamination of the experimental systems by O_2 and CO_2 and the varying crystallinity of the solid phase. Contamination and the presence of amorphous rather than crystalline UO_2 would lead to higher measured solubilities.

In the WIPP performance assessment calculations, it was assumed that redox conditions would be controlled by the presence of metallic iron and that U(VI) would be reduced to U(IV). An upper bound for the solubility of U(IV) was estimated from that of Th(IV), using the oxidation state analogy. Calculations by Wall et al. (2002) suggest that this is a conservative assumption—that the solubility of U(IV) is much lower than that of Th(IV). This is because the solubility product constant of $\text{ThO}_{2(\text{am})}$, the solubility limiting phase in the An(IV) model, is several orders of magnitude greater than that of $\text{UO}_{2(\text{am})}$.

Reed et al. (1996) examined An(VI) stability in WIPP brines under anoxic conditions (one atm H_2 gas) and found that U(VI) was stable as a carbonate complex in Castile brine at pH 8–10. Xia et al. (2001) also observed that U(VI) may be stable under some WIPP-relevant conditions, finding that while U(VI) was rapidly reduced to U(IV) by Fe^0 in water and 0.1 M NaCl, it was not reduced in the Castile brine, at pC_{H^+} 8–13, over the course of a 55-day experiment. The possible occurrence of U(VI) was considered in WIPP performance assessment calculations—solubility-limited concentrations for U(VI) in the Salado and Castile brines were estimated from literature values to be 8.7×10^{-6} M and 8.8×10^{-6} M, respectively (U.S. DOE, 1996).

In areas affected by uranium solution mining using sulfuric acid, $\text{UO}_2\text{SO}_{4(\text{aq})}$ will be important. In alkaline waters, carbonate complexes will dominate. Bernhard et al. (1998) studied uranium speciation in water from uranium mining districts in Germany (Saxony) using laser spectroscopy, and found that $\text{Ca}_2\text{UO}_2(\text{CO}_3)_{3(\text{aq})}$ was the dominant species in neutral pH carbonate- and Ca-rich mine waters; $\text{UO}_2(\text{CO}_3)_3^{4-}$ was the dominant aqueous species in basic (pH = 9.8), carbonate-rich, Ca-poor mine waters; and $\text{UO}_2\text{SO}_{4(\text{aq})}$ dominated in acidic (pH = 2.6), sulfate-rich mine waters.

A large number of studies of uranium sorption have been carried out in support of the nuclear waste disposal programs and the uranium mill tailings program (UMTRA). Park et al. (1992) and Prasad et al. (1997) describe studies of sorption of uranyl ion by corrensite, the clay mineral lining many fractures in the fractured Culebra Dolomite member of the Rustler Formation above the WIPP in SE New Mexico. The studies were carried out in dilute and concentrated NaCl (0.1 to 3 M) solutions in the presence of Ca^{2+} , Mg^{2+} , carbonate and citrate. Binding constants for the triple layer model were fit to the sorption edges. They found that the adsorption edges were typical of cation adsorption on mineral surfaces; the uranium was nearly completely bound to the surface at neutral and near-neutral pH values. Neither the background electrolyte (NaCl) nor Ca^{2+} or Mg^{2+} ions (at 0.05 M) influenced the adsorption, suggesting that uranyl binds at pH-dependent edge sites on the corrensite surface as an inner-sphere complex. Both carbonate and citrate reduced the adsorption of uranyl on corrensite in near-neutral solutions. Redden et al. (1998) carried out similar studies of uranium sorption by goethite, kaolinite and gibbsite in the presence of citric acid. Davis (2001) and Jenne (1998) provide good summaries of studies of uranium sorption by synthetic and natural aluminosilicates and iron oxyhydroxides. Qualitative features of the sorption edges for these minerals are similar: U(VI) sorption at higher pH is typically low and likely is controlled by the predominance of the negatively charged uranyl-carbonate solution species. By analogy, sorption of U(VI) by aluminosilicates is predicted to be low in waters sampled at Yucca Mountain (Turner et al., 1998; Turner and Pabalan, 1999).

Luckscheiter and Kienzler (2001) examined uranyl sorption onto corroded HLW glass simulant in deionized water, 5.5 M NaCl and 5.0 M MgCl_2 , and found that sorption was greatly inhibited by the Mg-rich brine while the NaCl brine had little effect. Uranyl sorption at high ionic strength was also studied by Vodrias and Means (1993), who examined uranyl sorption onto crushed impure halite and limestone from the Palo Duro Basin, Texas, in a synthetic Na-K-Mg-Ca-Cl brine ($I = 10.7$ M). They measured K_{ds} of 1.3 ml g^{-1} on the halite and $4\text{--}7 \text{ ml g}^{-1}$ on the limestone. This is in contrast to a K_d of 2100 ml g^{-1} determined from uranium series disequilibrium measurements on formation brines from the same region (Laul, 1992). The isotopic ratios suggest that naturally-occurring uranium was more strongly sorbed because it was present as U(IV).

3.2.3.1.4 *Neptunium*

Neptunium and plutonium are the radioelements of primary concern for the disposal of nuclear waste at the proposed repository at Yucca Mountain. This is due to their long half-lives, radiotoxicity and transport properties. Neptunium is considered to be the most highly mobile actinide because of its high solubility and low potential for sorption by geomedia. Its valence state (primarily Np(V) or Np(IV)) is the primary control of its environmental geochemistry. Oxide, hydroxide and carbonate compounds are the most important solubility-limiting phases in natural waters. In low ionic strength, carbonate-free systems, $\text{NpO}_2(\text{OH})$ and Np_2O_5 are stable Np(V) solids, while in brines, Np(V) alkaline carbonate solids are stable. Under reducing conditions, $\text{Np}(\text{OH})_4$ am and NpO_2 are the stable Np(IV) solids. Under most near-surface environmental conditions, the dominant complexes of neptunium are those of the pentavalent neptunyl species (NpO_2^+). Np(IV) aqueous species may be

important under reducing conditions possible at some underground nuclear waste research facilities such as the WIPP and Stripa.

Kaszuba and Runde (1999) compiled thermodynamic data for neptunium relevant to Yucca Mountain. They updated the database of Lemire (1984) with recent experimental data and used the Specific Interaction Theory (S.I.T.) to calculate ion activity coefficients. Their report has an extensive reference list and list of interaction parameters. Kaszuba and Runde (1999) used the EQ3NR (Wolery, 1992b) and the Geochemist's Workbench (Bethke, 1998) codes to calculate solubility and speciation in the J-13 and UE25p#1 well waters that span the expected geochemical conditions for the proposed HLW repository at Yucca Mountain. They predicted that $\text{Np}(\text{OH})_{4(\text{aq})}$ is the dominant aqueous complex in neutral solutions at $E_h < 0$ mV, while under oxidizing conditions, NpO_2^+ and $\text{NpO}_2\text{CO}_3^-$ are predominant at $\text{pH} < 8$ and pH 8-13, respectively.

Although the calculations of Kaszuba and Runde (1999) indicate that $\text{NpO}_{2(\text{s})}$ is the thermodynamically stable solid for most E_h - pH conditions of environmental interest, that phase has never been observed to precipitate in solubility experiments in natural waters; instead $\text{Np}_2\text{O}_{5(\text{s})}$ and amorphous $\text{Np}(\text{OH})_{4(\text{s})}$ precipitate. Figure 7 shows that if $\text{Np}_2\text{O}_{5(\text{s})}$ controls the solubility under oxidizing conditions ($E_h > 0.25$ V), then the calculated solubility of neptunium decreases from $\sim 10^{-3.5}$ M at $\text{pH} = 6$, to 10^{-5} M at $\text{pH} = 8$. If amorphous $\text{Np}(\text{OH})_{4(\text{s})}$ controls the solubility under reducing conditions ($E_h < -0.10$ V), the solubility is approximately 10^{-8} M over the same pH range. In the intermediate E_h range and neutral pH conditions possible under many environmental settings, the solubility of neptunium is controlled primarily by the E_h of the aquifer and will vary between the levels set by the solubilities of $\text{Np}(\text{OH})_{4(\text{s})}$ and $\text{Np}_2\text{O}_{5(\text{s})}$ (Figure 7). The inset in the figure illustrates that at $\text{pH} = 6.8$, at $E_h = -0.10$ V, the concentration of neptunium in solution is approximately equal to that of the $\text{Np}(\text{IV})$ species and is controlled by the solubility of $\text{Np}(\text{OH})_{4(\text{s})}$. As the redox potential increases, $\text{Np}(\text{IV})$ in solution is oxidized to $\text{Np}(\text{V})$ and the aqueous concentration of neptunium increases. Phase transformation of $\text{Np}(\text{OH})_{4(\text{s})}$ to $\text{Np}_2\text{O}_{5(\text{s})}$ occurs at about $E_h = 0.25$ V and then the solubility of the $\text{Np}(\text{V})$ oxide controls the aqueous neptunium concentration at higher E_h values.

Neptunium is expected to be present in the WIPP in either the IV or V oxidation state. For the WIPP CCA speciation and solubility calculations, an upper bound for the solubility of $\text{Np}(\text{IV})$ was estimated from that of $\text{Th}(\text{IV})$, using the oxidation state analogy. As with $\text{U}(\text{IV})$, calculations suggest that this assumption is conservative (Wall et al., 2002). Modeling for the WIPP project suggested that $\text{Np}(\text{V})$ solubility in the reference Salado and Castile brines is limited by $\text{KNpO}_2\text{CO}_3 \times 2\text{H}_2\text{O}_{(\text{s})}$ and is 1.2×10^{-7} M and 4.8×10^{-7} M, respectively (Novak, 1997; U.S. EPA, 1998d). The most abundant aqueous species in both brines is $\text{NpO}_2(\text{CO}_3)^-$. Experimental measurements of the solubility of $\text{Np}(\text{V})$ in laboratory solutions representing unaltered Salado brine yielded a value of 2.4×10^{-7} M, after allowing the brine systems to equilibrate for up to two years (Novak et al., 1996). The solubility-limiting phase was identified as $\text{KNpO}_2\text{CO}_3 \times n\text{H}_2\text{O}_{(\text{s})}$, in agreement with the results of the WIPP performance assessment modeling.

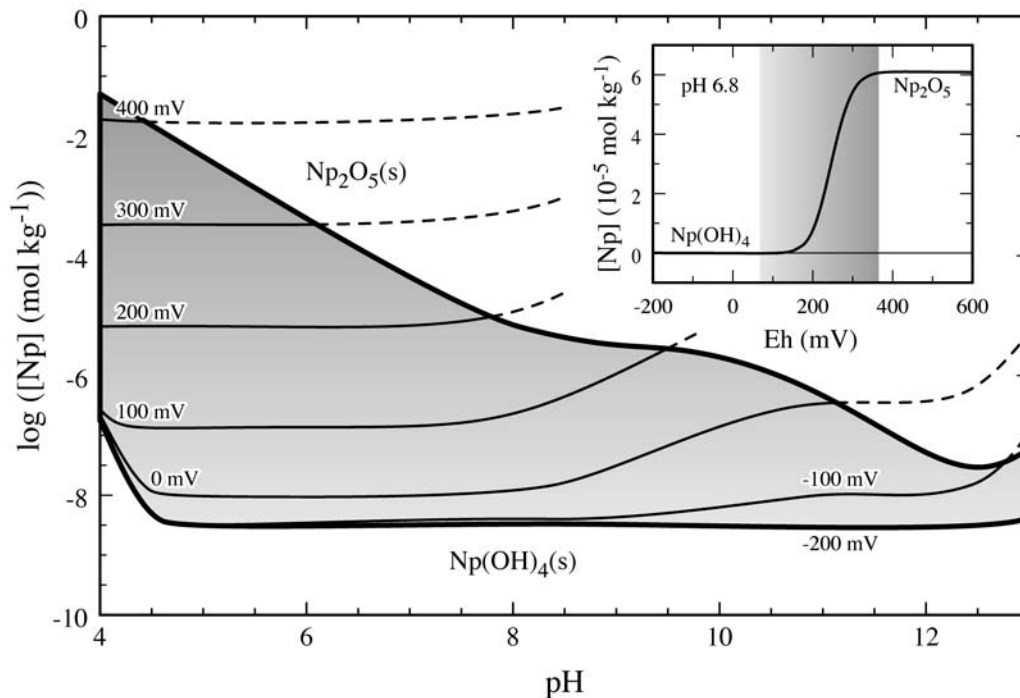


Figure 7. Calculated Np solubilities as a function of pH and Eh in J-13 groundwater variants (Table 5). $\text{Np}_2\text{O}_5(\text{s})$ and $\text{Np}(\text{OH})_4(\text{s})$ were assumed to be the solubility-limiting phases. Inset shows regions of solubility control versus redox control (shaded area). Reprinted with permission from *Environmental Science and Technology* 33, 4433. Copyright (1999) American Chemical Society.

Aqueous neptunium species including bishydroxo and mixed hydroxy-carbonato species may be important, though not dominant, at higher pH and carbonate concentrations. Such conditions may exist at the Hanford Waste tanks, where $\text{MNpO}_2\text{CO}_3 \cdot n\text{H}_2\text{O}$ and $\text{M}_3\text{NpO}_2(\text{CO}_3)_2$ ($\text{M} = \text{Na}^+, \text{K}^+$) are predicted to be stable phases. The solubilities are 2-3 orders of magnitude higher than in waters in which Np_2O_5 is stable. Under conditions expected in the near field of high-level waste geologic repositories in saline groundwater environments such as the salt domes and the bedded salts in Europe, Np(VI) species like $\text{NpO}_2(\text{CO}_3)_3^{4-}$ might be important due to radiolysis.

In general, sorption of Np(V) by aluminosilicates is expected to be low in waters at Yucca Mountain (Turner and Pabalan, 1999; Turner et al., 1998). K_{ds} for sorption of neptunium by zeolites and tuff particles were typically less than 10 ml g^{-1} in waters from that site (Tien et al., 1985; Runde, 2002b). The low neptunium sorption is due to the relative dominance of the poorly-sorbed hydrolyzed species $\text{NpO}_2(\text{OH})_{(\text{aq})}$ and the anionic $\text{NpO}_2\text{CO}_3^-$ species in solution. In contrast, the average K_{ds} for Np(V) uptake by colloidal hematite, montmorillonite and silica were 880, 150 and 550 ml g^{-1} , respectively in Yucca Mountain J-13 water (Efurd et al. (1998), probably due to the high surface area of the particles.

Similarly, McCubbin and Leonard (1997) reported neptunium K_{ds} of 1,000–10,000 ml g^{-1} for particulates in seawater, but the oxidation state was uncertain. Like other tetravalent actinides, Np(IV) has a strong tendency to polymerize and form colloids and is strongly sorbed. Np(IV) migration is likely to occur as intrinsic colloids or sorbed species on pseudocolloids, and changes in ionic strength are likely to impact mobility mostly through

destabilization of colloidal particles. Np(V) intrinsic colloids are not expected at neutral pH (Tanaka et al., 1992) and uptake by carrier colloids occurs by ion exchange and surface complexation. Competition for sorption sites between Np(V) species and other ions, especially Ca^{2+} and Mg^{2+} , could be significant (Tanaka and Muraoka, 1999; McCubbin and Leonard, 1997).

3.2.3.1.5 Plutonium

Plutonium chemistry is complicated by the fact that it can exist in 4 oxidation states over an Eh range of -0.6 to 1.2 V and a pH range of 0–14. In the system Pu-O₂-H₂O, 4 triple points exist (Eh-pH where 3 oxidation states may coexist) and thus disproportionation reactions can occur in response to radiolysis or changes in Eh, pH or the concentrations of other chemical species (Langmuir, 1997a). The most important of these reactions are disproportionation of PuO_2^+ to PuO_2^{2+} and Pu^{4+} or disproportionation of plutonium facilitated by humic acid (Guillaumont and Adloff, 1992) and radiolysis (Nitsche et al., 1995).

Langmuir's Eh-pH calculations (1997a) show that in systems containing only Pu, H₂O and carbonate/bicarbonate (10^{-2} M), the stability field for the species Pu^{4+} is nearly nonexistent (limited to high Eh and very low pH) but the field for $\text{Pu}(\text{OH})_{4(\text{aq})}$ is extensive at pH > 5 and Eh < 0.5. Carbonato-complexes of Pu(VI) and Pu(V) are important at pH > 5 and higher Eh. Plutonium solubilities are generally low over most environmental conditions (< 10^{-8} M); the solubility fields for $\text{PuO}_2(\text{cr})$ and $\text{Pu}(\text{OH})_{4(\text{am})}$ cover the Eh-pH field over the pH > 5 at all Eh and substantial portions of the Eh-pH field at lower pH where Eh > 0.5 V. As discussed below, the system is different when other ligands, cations and higher concentrations of carbonate are present.

Runde et al. (2002a) compiled an internally consistent database to calculate solubility and speciation of plutonium in more complex low ionic strength waters. A specific interaction model (Grenthe et al., 1992) was used for ionic strength corrections. The reader is referred to that work for details of the data sources and methods used for extrapolation and interpolation. Where reliable data for plutonium species were unavailable, thermodynamic constants were estimated from data for analogous americium, curium, uranium, and neptunium species. The most important solution species of plutonium are the aqueous ions, hydroxides, carbonates and fluoride complexes. Important solids include oxides and hydroxides ($\text{Pu}(\text{OH})_3$, PuO_2 , $\text{PuO}_2 \times n\text{H}_2\text{O}$ [or $\text{Pu}(\text{OH})_4$], PuO_2OH , $\text{PuO}_2(\text{OH})_2$) and the carbonate PuO_2CO_3 . The dominant solid phases and species are shown in an Eh-pH diagram for J-13 water variants in Figure 8. Note that in this system, the only triple point occurs at a pH of 2.4 where species in the IV, V, and VI oxidation states are calculated to be in equilibrium. In reference J-13 water (pH= 7, Eh = 0.43 V), $\text{Pu}(\text{OH})_{4(\text{aq})}$ dominates solution speciation, and $\text{Pu}(\text{OH})_{4(\text{s})}$ is the solubility-limiting phase. Under certain environments affected by interactions of groundwater and nuclear waste forms, Pu(V) or Pu(VI) could be produced by radiolysis or Pu(III) species could be produced by reduction.

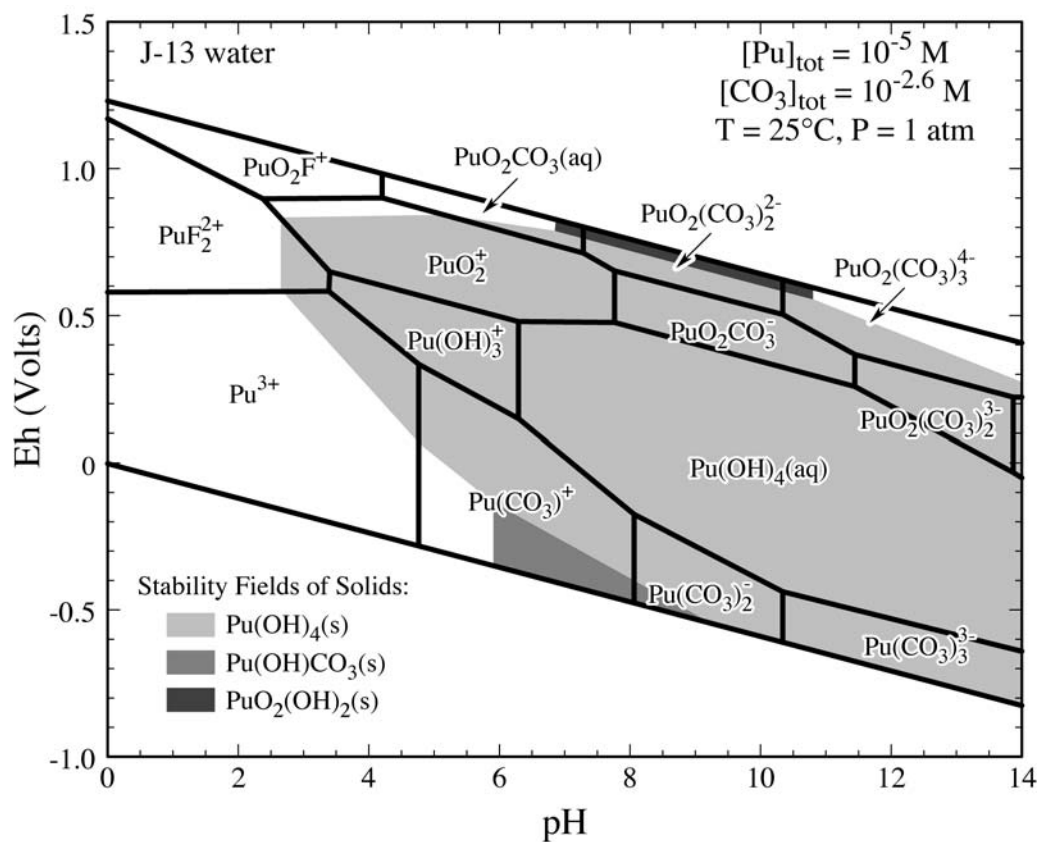


Figure 8. Eh-pH diagram showing dominant plutonium solid phases and species for J-13 water variants at 25 C° as calculated by Runde et al. (2002a). Solid lines indicate dominant solution species; shaded areas indicate solids supersaturated in 10^{-5} M Pu solutions. Precipitation of PuO_2 was suppressed in the calculations; see Runde et al. (2002a) for details. Reprinted from *Applied Geochemistry*, Vol. 17, "Solubility and sorption of redox-sensitive radionuclides (Np, Pu) in J-13 water from Yucca Mountain site: comparison between experiment and theory" page 844, Copyright (2002), with permission from Elsevier.

Runde et al. (2002a) demonstrates that significant changes in plutonium solubility can occur due to the formation of Pu(V) and Pu(VI) species at $\text{pH} > 6$ or due to the formation of Pu(III) species at $\text{pH} < 6$. Using either $\text{Pu(OH)}_4(\text{s})$ or the more crystalline $\text{PuO}_{2(\text{s})}$ as the solubility controlling solids, Runde et al. (2002a) calculated plutonium solubilities over ranges of pH (3–10), Eh (0–0.6 V) and total carbonate concentration (0.1–2.8 mmol). For conditions typical of groundwater environments, (pH range 6–9 and Eh range 0.05–0.45 V), $\text{Pu(OH)}_4(\text{aq})$ is the dominant aqueous species. Under alkaline conditions, solubility increases with Eh due to formation of Pu(V) and Pu(VI) solution species. At $\text{pH} > 8$ and Eh > 0.4 V, carbonate species are dominant. At pH values below 7, the solubility increases with decreasing Eh due to the stability of Pu(OH)_3^+ . The calculated solubilities and speciation are sensitive to changes in both Eh and pH . For systems in which $\text{Pu(OH)}_4(\text{s})$ is the stable solid, they ranged from $> 10^{-2}$ M at $\text{pH} = 4$ and Eh = 0 V to 10^{-11} M at $\text{pH} > 5$ and Eh < 0.4 V. Calculated solubilities were about 4 orders of magnitude lower when $\text{PuO}_{2(\text{s})}$ was the stable solid.

Experimentally measured solubilities over this range of solution compositions are typically two orders of magnitude higher than calculated values (Runde et al., 2002a), presumably due to the presence of Pu(IV) colloids (Capdevila and Vitorge, 1998; Efurud et al., 1998; Knopp et al., 1999). In experimental studies in J-13 water, at ambient temperature, plutonium solubility decreased from 5×10^{-8} M at pH = 6, to 9×10^{-9} M at pH = 9 (Efurud et al., 1998).

Because of the presence of Fe⁰ and Fe(II), Pu(VI) is not expected to be stable under WIPP repository conditions. Pu(IV) is expected to be the dominant oxidation state, although Pu(III) was also considered to be a possibility in the WIPP CCA. In the WIPP performance assessment speciation and solubility calculations, Th(IV) was used as an analog for Pu(IV) (U.S. DOE, 1996). Wall et al. (2002) evaluated the appropriateness of the analogy and found that this assumption was highly conservative and that predicted solubilities for Pu(IV) in Salado and Castile brines were ten-to-eleven orders of magnitude lower than those for Th(IV). Similarly, Am(III) was used to estimate the solubility of Pu(III).

Studies of the sorption of plutonium are complicated by the high redox reactivity of Pu. Sorption of Pu(V) by pure aluminosilicates and oxyhydroxide phases is usually characterized by initial rapid uptake followed by slow irreversible sorption and may represent a reductive uptake mechanism catalyzed by the electrical double layer of the mineral surface (Turner et al., 1998; Runde et al., 2002a). In Yucca Mountain waters, the K_d ranges for Pu(V) uptake by hematite, montmorillonite and silica colloids were 4.9×10^3 to 1.8×10^5 ml g⁻¹; 5.8×10^3 ml g⁻¹ and 8.1×10^3 ml g⁻¹, respectively. These are much higher than those observed for Np(V) in the same waters as described previously. High surface redox reactivity for plutonium and possible disproportionation of Pu(V) to Pu(VI) and Pu(IV) were observed in sorption studies using goethite by Keeney-Kennicutt and Morse (1985) and Sanchez et al. (1985). Desorption by plutonium was typically less from hematite than from aluminosilicates in studies with J-13 water described by Runde et al. (2002a).

3.3 Other Topics

3.3.1 Colloids

3.3.1.1 Introduction

Colloidal suspensions are defined as suspensions of particles with a mean diameter less than 0.45 microns, or a size range from 1 nm to 1 μ m. They represent potentially important transport vectors for highly insoluble or strongly sorbing radionuclides in the environment. Colloids are important in both experimental systems and natural settings. In the former, unrecognized presence of colloids may lead to overestimation of the solubility and underestimation of the sorption of radionuclides if they are included in the estimation of the concentration of radionuclide solution species. In natural systems, they may provide an important transport mechanism for radionuclides if they are not filtered out by the host rock. In fractured rock, local transport of radionuclides by colloids may be important. Useful reviews of the behavior of colloids in natural systems and their potential role in transporting contaminants include those of Moulin and Ouzounian (1992), Ryan and Elimelech (1996), Kretzschmar et al. (1999), and Honeyman and Ranville (2002).

Two types of colloids are recognized in the literature. Intrinsic colloids (also called "true" colloids, type I colloids, precipitation colloids, or "Eigencolloids") consist of radioelements with very low solubility limits. Carrier colloids (also known as "pseudocolloids", type II colloids or "Fremdkolloides") consist of mineral or organic phases (in natural waters primarily organic complexes, silicates and oxides) to which radionuclides are sorbed. Both sparingly soluble and very soluble radionuclides can be associated with this type of colloid. In addition, radionuclides can be associated with microbial cells and be transported as biocolloids.

Natural carrier colloids exist in most groundwaters; they include mineral particles, alteration products of mineral coatings, humic substances and bacteria. In nuclear waste repositories, carrier colloids will be produced by degradation of engineered barrier materials and waste components: Fe-based waste package materials can produce iron oxyhydroxide colloids, degradation of bentonite backfills can produce clay colloids, and alteration of HLW glass can produce a variety of silicate particulates. Intrinsic colloids potentially could be produced by direct degradation of the nuclear waste or by remobilization of precipitated actinide compounds (Avogadro and de Marsily, 1984; Bates et al., 1992; Kim, 1994).

Two different processes could be important for the initiation of radionuclide transport by carrier colloids: 1) reversible sorption of radionuclides from solution onto pre-existing colloids and 2) detachment of colloids from the host rock with high concentrations of previously sorbed irreversibly-bound colloids. In both cases, radionuclides that sorb strongly to the rock matrix and would normally migrate very slowly will travel at a rapid rate while they are bound to colloids.

3.3.1.2 Naturally Occurring Colloids

Degueldre et al. (2000) and Honeyman and Ranville (2002) summarize modern techniques used to sample colloids from groundwater and to characterize particle concentration and size distributions. Naturally occurring colloids and radionuclide-colloid associations have been characterized at several natural analog sites for nuclear waste repositories. These include the Cigar Lake Uranium deposit in altered sandstone (Vilks et al., 1993); the altered schist at the Koongarra Uranium deposit (Payne et al., 1992); altered volcanic rock sites in Pocos de Caldas, Brazil (Miekeley et al., 1991); shallow freshwater aquifers above the salt-hosted Gorleben repository test site in Germany (Dearlove et al., 1991); the Grimsel test site in the Swiss Alps (Degueldre et al., 1989); the Whiteshell Research area in fractured granite in Canada (Vilks et al., 1991); the El Borrocal site in weathered fractured granite near Madrid, Spain (Gomez et al., 1992); and 24 springs and wells near or within the Nevada Test Site (Kingston and Whitbeck, 1991). Major international studies of the occurrence of natural colloids and their potential importance to the European nuclear waste disposal program were carried out by the MIRAGE 2 (Migration of Radionuclides in the Geosphere) project and the Complex Colloid Group of the Commission of European Communities; these are reviewed in Moulin and Ouzounian (1992).

Although locally and globally there are wide variations in colloid concentration and size distribution, several general trends can be observed. Many of the observed particle

concentrations fall within the range 0.01 to 5 mg L⁻¹; however, concentrations of > 200 mg L⁻¹ have been observed. There is an inverse correlation between particle concentration and particle size. Degueldre (1997) summarized the occurrence of colloids in groundwater from 17 different sites. In a marl aquifer near a proposed Swiss repository site for low-level nuclear waste, the concentration was found to be independent of flow rate, and colloid generation was caused only by resuspension/detachment of the rock clay fraction. Degueldre et al. (2000) expanded the scope of that study and found that colloid stability can be parsimoniously described as a function of groundwater chemistry while colloid composition is a function of rock composition. They found that at certain ionic strengths, the concentration of colloids was inversely correlated to the concentration of alkali metals and alkaline earth elements (below about 10⁻⁴ M and 10⁻² M, respectively). Large concentrations of organics and the process of water mixing enhance colloid stability and concentration.

3.3.1.3 Experimental Studies

Sorption of radionuclides by colloids is affected by the same solution composition parameters discussed in the previous section on sorption processes. The important parameters include pH, redox conditions, the concentrations of competing cations such as Mg²⁺ and K⁺, and the concentrations of organic ligands and carbonate. The high surface area of colloids leads to relatively high uptake of radionuclides compared to the rock matrix. This means that a substantial fraction of mobile radionuclides could be associated with carrier colloids in some systems. The association of radionuclides with naturally occurring colloids and studies of radionuclide uptake by colloids in laboratory systems give some indication of the potential importance of colloid-facilitated radionuclide transport in the environment as discussed below.

For example, Kim (1994) summarizes evidence for strong sorption of americium by silica and alumina colloids in simple NaClO₄ solutions ($K_d > 10^4$ at pH = 8 and is independent of ionic strength, temperature and concentrations of both americium and colloids). He also reports that significant sorption of Np(V) by alumina colloids occurs at pH > 7 at high colloid concentrations (> 100 p.p.m.) under the same conditions. Lieser et al. (1990) studied partitioning of strontium, cesium, thorium and actinium between molecular (< 0.002 μm) and particle-bound (0.002 to > 0.45 μm) fractions in batch systems at low concentrations (several orders of magnitude below estimated solubility limits). Sediment-water systems comprised of several particle-size fractions and natural waters of different salinities from the aquifers above the Gorleben salt dome were examined. In the groundwaters, colloids consisted primarily of clays, amorphous silica, and iron hydroxide. Appreciable fractions of the total concentrations of the cations in the groundwaters was associated with the large (> 0.45 μm) and fine (0.002 to 0.45 μm) particles (in the order Ac = Th > Cs > Sr). When the groundwaters were passed through columns filled with sediments associated with the groundwaters, most of the cesium (99%) was retained (presumably by ion exchange) and the eluted cesium was primarily associated with fine-grained pseudocolloids. About 99% of the actinium and thorium were retained in the columns (presumably by chemisorption) and the colloidal fraction of the radionuclides dominated the effluent. In contrast, retention of strontium in the columns was less effective due to its lower potential for ion exchange.

Runde et al. (2002a) characterized plutonium precipitates and examined neptunium and plutonium uptake by inorganic colloidal particulates in J-13 water from the Yucca Mountain site. Plutonium solubilities determined experimentally at pH values of 6, 7, and 8.5 were about two orders of magnitude higher than those calculated using the existing thermodynamic database, indicating the influence of colloidal Pu(IV) species. Solid phase characterization using X-ray diffraction revealed primarily Pu(IV) in all precipitates formed at pH 6, 7, and 8.5. As discussed previously, hematite, montmorillonite, and silica colloids were used for uptake experiments with $^{239}\text{Pu(V)}$ and $^{237}\text{Np(V)}$. The capacity of hematite to sorb plutonium significantly exceeded that of montmorillonite and silica. A low desorption rate was indicative of highly stable Pu-hematite colloids, which may facilitate plutonium transport to the accessible environment. Pu(V) uptake on all mineral phases was far greater than Np(V) uptake, suggesting that a potential Pu(V)-Pu(IV) reductive sorption process was involved.

3.3.1.4 Microbial and Humic Colloids

The transport of radionuclides and metals adsorbed to microbes has been considered by a number of researchers including McCarthy and Zachara (1989), Han and Lee (1997), and Gillow et al. (2000). Because of their small size (< 10 microns diameter), these colloids can be transported rapidly through fractured media and either filtered out or be transported through porous media. Microbes can sorb to geologic media, thereby retarding transport. Alternatively, under conditions of low nutrient concentrations, the microbes can reduce their size and adhesion capabilities and become more easily transported. Studies performed in support of WIPP compliance certification indicated that, under relevant redox conditions, microbially-bound actinides contributed significantly to the concentration of mobile actinides in WIPP brines (Strietelmeyer et al., 1999; Gillow et al., 2000). For performance assessment calculations, the concentration of each actinide sorbed onto microbial colloids was estimated to be 3.1, 0.0021, 12.0, 0.3, and 3.6 times the dissolved concentration for thorium, uranium, neptunium, plutonium, and americium, respectively (U.S. DOE, 1996).

Evidence for strong sorption of actinides and fission products by humic substances, both in dilute and high ionic strength media, is provided by experimental studies and thermodynamic calculations. Humic colloids are stable and occur in concentrations up to 0.4 g L^{-1} in dilute, shallow groundwaters overlying the Gorleben test site in Germany (Buckau et al., 2000). Humic substances have experimentally been shown to strongly complex the trivalent actinides (Czerwinski et al., 1996; Artinger et al., 1998; Morgenstern et al., 2000); Th(IV) (Nash and Choppin, 1980); U(VI) and probably U(IV) (Czerwinski et al., 1994; Zeh et al., 1997); and Np(V) (Kim and Sekine, 1991; Rao and Choppin, 1995; Marquardt et al., 1996; Marquardt and Kim, 1998) at mildly acidic to neutral pH. Under basic conditions, actinide-humic substance complexation is strongly a function of the carbonate concentration, because carbonate competes effectively with the humic acid as a ligand (Zeh et al., 1997; Unsworth et al., 2002). Little data are available for tetravalent actinides, but Tipping (1993) suggests, based on thermodynamic modeling, that these should be even more strongly complexed by humic substances than other oxidation states.

Several studies have shown that actinide-humic acid complexes are thermodynamically stable in high ionic strength solutions (Czerwinski et al., 1996; Marquardt et al., 1996;

Labonne-Wall et al., 1999). However, destabilization of humic colloids at high ionic strength (Buckau et al., 2000) and competition for humic acid sites by divalent metal cations (Tipping, 1993; Marquardt et al., 1996) may limit the importance of colloidal transport of actinides in brines. In the WIPP performance assessment, the estimated contribution of actinide sorbed onto humic substances to the total mobile concentration was >0.01 times the dissolved fraction for An(V), 0.1 to 1.4 times the dissolved fraction for An(III) and An(VI), and 6.3 times the dissolved fraction for An(IV) (U.S. DOE, 1996).

3.3.1.5 Transport of Radionuclides by Colloids

Several numerical models have been developed to assess the potential magnitude of colloidal-facilitated transport of radionuclides compared to the transport of dissolved species. Vilks et al. (1998) proposed a simple modification to the standard equation for the retardation factor. The equation applies to the ideal case where colloids are not trapped by the rock matrix and the composition of the colloids and the rock matrix are the same:

$$R_{F,eff} = 1 + \frac{(1-\phi)\rho K_d}{\phi(1+CFK_d)} \quad (8)$$

where $R_{F,eff}$ is the effective retardation factor for radionuclides including the effect of reversible sorption onto and transport by colloids. In the equation, ρ is the bulk density of the porous medium, ϕ is the porosity, K_d is the distribution coefficient for both the colloid and the rock matrix (ml g^{-1}), and C is the colloid concentration (mg L^{-1}). F is defined as:

$$F = (A'_{colloid} / A'_{IP}) \quad (9)$$

where $A'_{colloid}$ and A'_{IP} are the specific surface areas of the colloid and rock matrix, respectively.

When the above conditions are not met, more complex models that account for colloid generation, irreversible sorption, differences between the sorptive capacity of colloids and rock matrix (i.e. different K_{ds}), and colloid filtration should be used. Avogadro and de Marsily (1984) developed a simple model involving colloid filtration under field conditions. Nuttall et al. (1991) developed a 2-D population-balance model for radiocolloid transport that includes production and filtration of colloids under saturated and unsaturated conditions. Van der Lee et al. (1992) and Smith and Degueldre (1993) developed numerical models for colloid-facilitated transport through fractured media that incorporate a finite number of sorption sites, Langmuir isotherms, and irreversible sorption. Finally, the incorporation of colloid transport in systems with slow desorption, contrasts between the sorptive capacity of colloids and the rock matrix, and variable K_{ds} as functions of solution composition are simulated by the LEHGC reactive transport model as described by Yeh et al. (1995) and Honeyman and Ranville (2002).

There is considerable debate concerning the potential importance of colloid-facilitated transport of radionuclides for the design and performance assessment of nuclear waste repositories and for risk assessments of radioactively contaminated sites. Honeyman and

Ranville (2002) develop a framework to determine the conditions under which colloid-facilitated contaminant transport will be important compared to the transport of solution species. They conclude that such conditions will be relatively rare in the environment. In contrast, Penrose et al. (1990) and Nuttall et al. (1991) suggest that colloidal transport of radionuclides in the unsaturated zone can be important. They describe field evidence, laboratory results and computer simulations that suggest that colloidal transport of strongly sorbing actinides such as plutonium and americium is potentially significant in the unsaturated zone and in shallow aquifers near Los Alamos, New Mexico. Similarly, Kersting et al. (1999) provide evidence that measurable amounts of Pu and perhaps Co, Eu and Cs produced by nuclear weapons tests (1956 – 1992) at the Nevada Test site have been transported at least 1.3 km from the blast sites by colloids. They argue that models that do not include colloid-facilitated transport may significantly underestimate the extent of radionuclide migration. In contrast, Vilks (1994) proposes that colloids do not have to be considered in the safety assessment for the Canadian repository in granite. He argues that the clay-based buffer to be used in the repository will filter out any colloids produced by degradation of the waste package. In addition, the concentration of naturally occurring colloids is too low to provide a substantial transport vector for radionuclides that escape to the far field of the repository.

Four types of colloids were considered in the WIPP program: intrinsic actinide colloids, mineral colloids, microbes, and humic acid colloids (U.S. DOE, 1996). Intrinsic actinide colloids, consisting of polymerized hydrated actinide hydroxides, are not stable in the neutral to moderately basic pH conditions expected in the WIPP, and were assumed not to contribute to the total actinide concentrations in solution. Mineral colloids are destabilized and tend to flocculate in the high ionic strength WIPP brines (Kelly et al. 1999). In the performance assessment calculations for the WIPP, a highly conservative value of 2.6×10^{-8} moles actinide per liter, for each actinide, was assumed to be bound to mineral colloids and to contribute to the mobile fraction. Actinides sorbed onto microbes and humic acids were estimated to contribute significantly to the concentration of mobile actinides in WIPP brines as discussed above (Section 3.2.2).

Contardi et al. (2001) used a surface complexation model (SCM) to examine the potential effect of colloidal transport on the effective retardation factors for americium, thorium, uranium, neptunium and plutonium in waters from the proposed repository site at Yucca Mountain. They found that colloidal transport reduced the effective retardation of strongly sorbed radionuclides such americium and thorium by several orders of magnitude compared to simulations in which such transport was ignored. Uranium, Np, and Pu(V) are less strongly sorbed by colloids and therefore were relative unaffected by colloidal transport. They also described performance assessment calculations of the effect of colloid-facilitated radionuclide transport on the peak mean annual total effective dose equivalent (TEDE) from the proposed nuclear waste repository. The colloid transport simulations showed no increase in the TEDE within a compliance period of 10,000 years; however, at longer simulation times, as the waste container failures increased, the TEDE from the colloid models are up to 60 times that of the base (non-colloid) case. Such simulations are strongly dependent on scenario assumptions and can be used to provide conservative estimates of the potential

importance of colloids for radionuclide transport. They are also useful in demonstrating the relative importance of processes included in the performance assessment models.

3.3.2 Microbe-Actinide Interactions

In addition to possible transport of radionuclides by microbial colloids, microbe-actinide chemical interactions are important for the genesis of uranium ore bodies, dissolution of radioactive waste and remediation of contaminated sites. Chapelle (1993) provides a recent comprehensive treatment of microbial growth, metabolism and ecology for geoscience applications. Suzuki and Banfield (1999) and Abdelouas et al. (1999) provide well-documented overviews of geomicrobiology of uranium with discussion of applications to environmental transport and remediation of sites contaminated with uranium and actinides. Microbial-uranium interactions have been studied for technological applications such as bioleaching, which is an important method for uranium extraction (Berthelot et al., 1997). *In-situ* stabilization of uranium plumes by microbial reduction is an important method for remediation (Barton et al., 1996). Microbial ecology in high uranium environments has been studied in uranium mill tail wastes, and the effects of microbes on the stability of radioactive wastes buried in geological repositories is discussed by Francis (1994) and Pedersen (1996).

Microbes can control the local geochemical environment of actinides and affect their solubility and transport. Francis et al. (1991) report that oxidation is the predominant mechanism of dissolution of UO_2 from uranium ores. The dominant oxidant is not molecular oxygen but Fe(III) produced by oxidation of Fe(II) in pyrite in the ore by the bacteria *Thiobacillus ferrooxidans*. The Fe(III) oxidizes the UO_2 to UO_2^{2+} . The rate of bacterial catalysis is a function of a number of environmental parameters including temperature, pH, TDS, f_{O_2} and other factors important to microbial ecology. The oxidation rate of pyrite may be increased by 5-6 orders of magnitude due to the catalytic activity of microbes such as *Thiobacillus ferrooxidans* (Abdelouas et al. 1999).

Suzuki and Banfield (1999) classify methods of microbial uranium accumulation as either *metabolism-dependent* or *metabolism-independent*. The former consists of precipitation or complexation with metabolically produced ligands, processes induced by active cellular pumping of metals, or enzyme-mediated changes in redox state. Examples include precipitation of uranyl phosphates due the activity of enzymes such as phosphatases, formation of chelating agents in response to metal stress, and precipitation of uraninite through enzymatic uranium reduction.

Metabolism-independent processes involve physicochemical interactions between ionic actinide species and charged sites in microorganisms; these can occur with whole living cells or cell fragments. Uranium can be accumulated in the cells by passive transport mechanisms across the cell membrane or by biosorption, a term that includes non-directed processes such as adsorption, absorption, ion exchange or precipitation. Suzuki and Banfield (1999) describe the effects of pH and concentrations of other cations and anions on uranium uptake by a variety of organisms. Uptake of uranium by microbes can be described using the techniques and formalisms used to analyze the sorption of metals by metal hydroxide

surfaces such as the Freundlich, Langmuir, and surface-complexation sorption models (Fein et al., 1997; Fowle and Fein, 2000).

A large number of species of bacteria, algae, lichen and fungi have been shown to accumulate high levels of uranium through these processes. Suzuki and Banfield provide examples of organisms whose uranium uptake capacities range from approximately 50 to 500 mg U per gram dry cell weight. Maximum uptake occurs from pH 4–5. Microorganisms can develop resistance to the chemical and radioactive effects of actinides through genetic adaptation. In contaminated environments such as uranium mill tailings and mines, uranium accumulation levels exceed those observed in laboratory experiments with normal strains of bacteria. Suzuki and Banfield (1999) describe several mechanisms used by microbes to detoxify uranium.

Suzuki and Banfield (1999) discuss the similarities between the uranium-microbe interactions and transuranic-microbe interactions. Macaskie (1991) notes that it is possible to extrapolate the data for microbial uranium accumulation to other actinides. Hodge et al. (1973) observes that the biological behavior of uranium, thorium and plutonium resemble that of ferric iron. Microbes can also affect the speciation and transport of multivalent fission products. For example, Fe^{3+} -reducing bacteria and sulfate-reducing bacteria can reduce soluble pertechnetate to insoluble Tc(IV), as discussed by Lloyd et al. (1997). For additional information about these topics, the reader is referred to the references cited above. Applications of these principles are described in the section on bioremediation later in this report.

4. Field Studies of Radionuclide Behavior

4.1 Introduction

Studies of field sites establish the link between theoretical calculations, laboratory studies and the behavior of radionuclides in the environment. The field observations may complement or in some cases conflict with information obtained in laboratory studies. Important field sites include the areas of anthropogenic radioactive contamination described in previous sections, such as the areas surrounding the Chernobyl reactor, the Hanford reservation, the Chelyabinsk-65 complex, the Hamr uranium mining district of the Czech Republic, the Nevada test site, releases from the Nagasaki atomic bomb detonation and the Konegstein mine in Germany. Important sites of natural radioactivity (natural analogs) include the Pena Blanca deposit, the Alligator River Region, Cigar Lake and the Oklo natural reactor. The Pena Blanca deposit in northern Mexico is an analog for the proposed HLW repository in the unsaturated tuffs at Yucca Mountain (Pearcy et al., 1994; Murphy, 2000). The Koongarra uranium deposit in the Alligator Rivers Region, Australia, has been widely studied in a coordinated international program (Payne et al., 1992; van Maravic and Smellie, 1992; Davis, 2001). The Cigar Lake uranium deposit in altered sandstone in Saskatchewan, Canada, is another analog for nuclear waste repositories located below the groundwater table (Vilks et al., 1993; Bruno et al., 1997; Curtis, 1999). Natural analog studies have also been carried out in the uranium, thorium and rare earth element ore bodies in altered volcanic rock

at Pocos de Caldas, Brazil (Miekeley et al., 1991) and in a uranium-bearing quartz dike/breccia complex in weathered fractured granite at the El Borrocal site near Madrid, Spain (Gomez et al., 1992). The interested reader is referred to the sources cited above for detailed descriptions of how the geochemical and hydrologic characteristics of those sites are used to validate or calibrate hydrogeochemical models for radionuclide behavior.

The following section provides detailed information concerning the transport of radionuclides associated with two very different field analogs: the Chernobyl reactor accident and the Oklo Natural Reactor. These examples span wide temporal and spatial scales and include the rapid geochemical and physical processes important to nuclear reactor accidents or industrial discharges as well as the slower processes important to the geologic disposal of nuclear waste.

4.2 Short-term Behavior of Radionuclides in the Environment – Contamination from the Chernobyl Reactor Accident

On April 26, 1986, an explosion at the Chernobyl Nuclear Power Plant, and the subsequent fire in the graphite reactor core, released about 3% (6–8 metric tons) of the total fuel inventory of the reactor core. During the initial explosion, most radionuclide release occurred as fragments of unoxidized uranium dioxide fuel, which were deposited mostly in a plume extending 100 km to the west of the plant. The core fire lasted 10 days and releases were again dominated by fuel particles. However, because the core was exposed, these particles were partially or completely oxidized. For the first four days, high temperatures in the reactor resulted in the release of volatile elements (Xe, Kr, I, Te, and Cs), much of which was deposited as condensed particles in plumes to the northwest, west, and northeast of the plant, extending as far as Scandinavia. Over the next six days, temperatures in the reactor decreased, and the release of volatile fission products decreased. The lower temperatures (600–1200°K) favored oxidation of the nuclear fuel, therefore, fuel particles released during this phase were more heavily oxidized. Radionuclides released during this phase were deposited mostly in a southern plume, extending as far south as Greece.

A major part of the radionuclides released at Chernobyl were deposited as “hot particles,” either fuel particles with an average median diameter of 2–3 μm or condensed particles. Within the exclusion zone, extending 30 km from the plant, more than 90% of the radioactive contamination was in the form of fuel particles (Kashparov et al., 1999). This included about 80% of the ^{90}Sr and about 50–75% of the ^{137}Cs contamination. Particle size decreased with distance from the Chernobyl plant, and the proportion of condensed particles relative to the fuel particles increased. Other radionuclides released include the fission products ^{134}Cs , ^{144}Ce , ^{125}Sb , ^{106}Ru , ^{103}Ru , and ^{95}Zr , and the neutron activation products $^{110\text{m}}\text{Ag}$ and ^{54}Mn (Petropoulos et al., 2001).

Considerable attention has been given to fuel particle behavior in the environment because of their importance to the total radionuclide release from Chernobyl. The transport properties of the radionuclides present in the fuel particles and type of hazard that they represented changed as the particles weathered. Initially, particle (and radionuclide) transport was governed by physical processes. Particles were transported both as aerosols in the

atmosphere and as suspended load in runoff and rivers. The primary hazards represented by the particles were inhalation and dermal exposure. Particle alpha activities were similar to that of the original nuclear fuel (2.5×10^8 Bq cm⁻³; Boulyga et al., 1999), while beta and gamma activities were somewhat lower due to loss of volatile fission products. The median fuel particle size released at Chernobyl (2–3 μm) falls within the respirable fraction of aerosols (defined as < 7 μm), and such particles are easily re-suspended by anthropogenic or natural processes that disturb the soil. Fuel particles are not readily transported downward through the soil column, and soil sampling in the exclusion zone, carried out ten years after the accident, showed that the particles were still concentrated in the upper 5 cm (Kashparov et al., 1999). Thirteen years after the accident, agricultural activities in the exclusion zone resulted in local airborne concentrations of hot particles of 50–200 particles per cubic meter (Boulyga et al., 1999).

Radionuclides sequestered in the fuel particles are not immediately available to the biosphere because the particles generally have a low solubility in water, simulated lung fluids, and HCl solutions (Chamberlain and Dunster, 1958; Oughton et al., 1993; Salbu et al., 1994). Release of biologically important radionuclides such as ⁹⁰Sr and ¹³⁷Cs into the biosphere requires weathering and dissolution of the fuel particles. Particle weathering rates vary with several source-related particle characteristics (particle size, oxidation state, and structure) and depend on environmental parameters such as soil pH and redox conditions. Field studies have shown that the fraction of exchangeable ⁹⁰Sr in soil increases as fuel particles dissolve (Petryaev et al., 1991; Konoplev et al., 1992; Baryakhtar, 1995; Konoplev and Bulgakov, 1999). Kashparov et al. (1999) and Konoplev and Bulgakov (1999) used these observations to estimate the fraction of undissolved fuel particles present in soils in the Chernobyl 30 km exclusion zone. They found that the unoxidized fuel particles, deposited from the initial explosion in a plume to the west of Chernobyl, are more resistant to leaching and dissolution than the oxidized fuel particles released during the subsequent fire and deposited to the north, northeast, and south of the plant. Dissolution rates for the unoxidized fuel particles were about one-third those of oxidized particles, with 27–79% remaining undissolved in 1995, while only 2–30% of the oxidized fuel remained. Fuel particle dissolution rates also increased with increasing soil acidity and with decreasing particle size (Kashparov et al., 1999; Konoplev and Bulgakov, 1999).

These results are consistent with laboratory measurements of the effects of pH and oxidation state on the leachability of nuclear fuel particles (Kashparov et al., 2000). The increased leachability of the oxidized fuel particles may be due to 1) an increased solubility because of the change in oxidation state; 2) the higher surface area of the highly fractured oxidized particles; or 3) the diffusion of radionuclides (strontium, cesium) to grain boundaries and particle surfaces during the heating and oxidation process.

Once released from the fuel particles, strontium and cesium are available to the biosphere and can be taken up by plants or can be transferred down the soil profile. At present, the relative rates of each process are not well enough constrained to predict future levels of ⁹⁰Sr and ¹³⁷Cs in vegetation in the exclusion zone (Kashparov et al., 1999).

In more distal areas, cesium and strontium concentrations in soils, lakes, and rivers were initially high from direct fallout but have progressively dropped as these elements move downward into the soil profile and are flushed or sedimented out of bodies of water. The estimated ecological half-life for ^{137}Cs in German forest soils is 2.8 ± 0.5 yrs for the L horizon and 7.7 ± 4.9 yrs for the Ah horizon (Rühm et al., 1996). ^{90}Sr concentrations in the Black Sea had dropped to pre-Chernobyl levels by 1994, and ^{137}Cs is predicted to reach pre-accident levels by 2025–2030 (Kanivets et al., 1999). The main causes of the decreases are radioactive decay and loss through the Bosphorus Strait. However, the relative proportion of ^{90}Sr entering the Black Sea as river input is increasing as fuel particles in the major watersheds weather and release sequestered radionuclides. Smith et al. (1999, 2000) have shown that cesium removal from lakes and rivers is dominantly by lake outflow and by sedimentation. Cesium is strongly sorbed onto the frayed edge sites of illitic clay minerals, and cesium removal rates from lakes correlate with aqueous K^+ concentrations.

4.3 Natural Analogs for the Long-term Behavior of Radionuclides in the Environment – the Oklo Natural Reactor

Naturally-occurring uranium deposits have been an important source of information on the long-term behavior of actinides and fission products in the environment. Of special interest are the Oklo and Bangombe deposits of Gabon, which hosted natural fission reactors about two billion years ago (Pourcelot and Gauthier-Lafaye, 1999; Jensen and Ewing, 2001). The Gabon deposits occur in the Francevillian series, a 2.1 Ga sedimentary series consisting of sandstones, conglomerates, black shales, and volcanoclastic sediments. All uranium mineralization occurs in the basal sandstone formation near the upper contact with overlying black shales. The ore deposits have been interpreted as classic uranium roll-front deposits, which formed in oil traps where uranium-rich oxidizing fluids met reducing conditions in the hydrocarbon accumulations. The uranium is present primarily as uraninite, and uranium concentrations in the normal ore vary from 0.1 wt% to 10 wt%. In the reactor zones, the sandstone was highly fractured, and the mineralized stockwork ore initially contained up to 20 wt% uranium.

As redox conditions continued to concentrate uranium in the ore zone, the conditions required to initiate and sustain criticality were achieved. With initiation of criticality, hydrothermal circulation cells formed in the sandstone, resulting in migration of silica and other components out of the reactor. Uraninite was concentrated in the core; uranium grades as high as 80 wt% have been reported. In some reactors, the volume lost from the core was sufficient to cause slumping and collapse of the overlying beds. The reactor cores are generally 10-50 cm thick and are commonly overlain by a clay-rich hydrothermal gangue, consisting of Mg-chlorite and illite, known as the “reactor clays” or “argile de pile.” During criticality and cooling, Al-rich chlorites formed in the reactor core (Pourcelot and Gauthier-Lafaye, 1999).

During operation, the reactor cores reached temperatures of 200-450°C (Brookins, 1990; Pourcelot and Gauthier Lafaye, 1999), perhaps as high as 1000°C (Holliger and Devillers, 1981). The reactors operated for 100,000 to 800,000 years (Gauthier-Lefaye et al., 1996) and in the largest, consumed up to 1800 kg of ^{235}U . Because of this, uranium from the reactor

cores is depleted in ^{235}U , with this isotope constituting as little as 0.29% of the total (in “normal” ore, it would be 0.72%).

Analysis of the isotopic concentrations of U, Th, fission products, and their daughters gives information on element mobility during and after criticality. There is evidence for some actinide and fission product migration during criticality, during dolerite dike intrusion, and due to recent supergene weathering. Element retentivity in the Oklo natural reactors has application to nuclear waste disposal because the uranium oxide reactor core and the reactor clays have been described as analogous to spent nuclear fuel that is embedded in a clay-rich backfill (Menet et al., 1992).

A summary of actinide and fission product behaviors at Oklo is given by Gauthier-Lafaye et al. (1996). In general, the core of the reactor consists mainly of uraninite with varying amounts of clay. Grains of metal/metal-oxide/sulfide are present in the uraninite, similar to metal/metal oxide grains found in depleted uranium fuel. As the reactors have seen little oxidation, actinides and fission products that are compatible with the uraninite structure have largely been retained by the core. Evidence that uranium and plutonium did not migrate during criticality is given by the presence of large amounts of ^{232}Th in the reactor cores. ^{232}Th is formed by decay of ^{236}U and ^{240}Pu , both of which were produced by neutron capture processes during criticality. Thorium is of low abundance in the surrounding rocks, and its presence in the reactor zones is taken to indicate that uranium and plutonium were mostly retained in the reactor core. Plutonium was also retained by clays in the *argile de pile*, as is evidenced by enrichments of ^{235}U , the long-lived daughter of ^{239}Pu , in some reactor clay samples (Pourcelot and Gauthier-Lafaye, 1999). Concentrations of ^{209}Bi , the stable daughter of ^{237}Np , suggest that neptunium was also mostly retained by the reactor core.

Many environmentally important fission products have short half-lives; hence their behavior in the reactors is determined by proxy, by examining the distribution of stable daughters. Such parent/daughter pairs include $^{90}\text{Sr}/^{90}\text{Zr}$, $^{137}\text{Cs}/^{137}\text{Ba}$, $^{135}\text{Cs}/^{135}\text{Ba}$, $^{129}\text{I}/^{129}\text{Xe}$, and $^{99}\text{Tc}/^{99}\text{Ru}$. The daughters commonly have a significantly different chemistry than the parents and may have migrated during criticality, the 800 Ma dike intrusion, or during supergene weathering. Despite this uncertainty, comparisons between measured concentrations and theoretical fission yields have provided valuable information on fission product mobility (Hidaka et al., 1992). These studies suggest that retention of fission products by the reactors was variable. Gaseous and volatile fission products — Xe, Kr, I, Cd, Cs — were largely lost from the reactor. Highly mobile alkali metals and alkali earths — Rb, Sr, and Ba — were also lost. Fission products that are compatible with the uraninite crystal structure — the REE, Y, Nd, and Zr — were largely retained in the uraninite core, the reactor clays, minor phosphate phases, and uranium and zirconium silicate phases (Gauthier-Lafaye, et al., 1996). Lighter REE—La, Ce, and Pr—were partially lost from the reactor. Finally, Mo, Tc, Ru, Rh, and other metallic elements were retained in the metal/metal oxide inclusions and arsenide/sulfide inclusions in the core, and in the reactor clays (Hidaka et al., 1993; Jensen and Ewing, 2001).

5. Applications: Dealing with Radionuclide Contamination in the Environment

The previous sections of this report have briefly described the nature and locations of the most serious radioactive environmental contamination on the planet and have established the geochemical foundations for understanding the behavior of radionuclides in the environment. Applications of this information to remediating or assessing the risk posed by the contamination is the subject of this section of the review.

5.1 Remediation

In many current remediation programs, simple excavation of contaminated soil and removal of contaminated groundwater by pumping are the preferred techniques. These techniques may be practical for removal of relatively small volumes of contaminated soils and water; however, after these source terms have been removed, large volumes of soil and water with low but potentially hazardous levels of contamination may remain. For poorly-sorbing radionuclides, capture of contaminated water and removal of radionuclides may be possible using permeable reactive barriers and bioremediation. Alternatively, radionuclides could be immobilized in place by injecting agents that lead to reductive precipitation or irreversible sorption.

For strongly sorbing radionuclides, contaminant plumes will move very slowly and likely pose no potential hazards to current populations (Brady et al., 2002). However, regulations may require cleanup of sites to protect present and future populations under a variety of future-use scenarios. In these cases, it may be necessary to use soil-flushing techniques to mobilize the radionuclides and then to collect them. Alternatively, it may be possible to demonstrate that contaminant plumes will not reach populations and that monitoring networks and contingency remedial plans are in place to protect populations if the plume moves more rapidly than predicted. This approach is called Monitored Natural Attenuation (MNA) and is described in a later section.

5.1.1 Permeable Reactive Barriers

Permeable reactive barriers include reactive filter beds containing materials such as zero-valent iron (Fe^0), phosphate rock (apatite), silica sand, organic materials or combinations of these materials (U.S. EPA, 1999c). The barriers can be installed by digging a trench in the flow path of a contaminated groundwater plume and backfilling with reactive material or by injecting either a suspension of colloidal material or a solution containing a strong reductant (Cantrell et al., 1995; Cantrell et al., 1997; Abdelouas et al., 1999). The reactive filter material is used to reduce and precipitate the contaminant from solution while allowing the treated water to flow through the reactive bed. In some installations, the drain-field can be designed to have removable cells should replacement and disposal of the reactive material be required. A classical funnel and gate arrangement can be used for this purpose. In this system, impermeable subsurface walls are used to direct the flow of the plume through a narrow opening where the reactive material is emplaced. A number of techniques applicable for remediation of radionuclide plumes are described in a collection of articles edited by

Looney and Falta (2000) and in publications of the Federal Remediation Technologies Roundtable (e.g. U.S. EPA, 2000).

The use of Fe^0 to reduce and precipitate uranium out of solution has been shown to be effective by Gu et al. (1998) and Fiedor et al. (1998). The technique has been deployed in permeable reactive barriers at the Rocky Flats site in Colorado (Abdelouas et al., 1999), the Y-12 Plant near Oak Ridge National Laboratories (Watson et al., 1999), and other DOE sites. In this method, the Fe^0 reduces the U(VI) species to U(IV) aqueous species, which then precipitates as U(IV) solids (Gu et al., 1998; Fiedor et al., 1998). Reduction of U(VI) to U(IV) usually results in the precipitation of poorly crystalline U(IV) (e.g., uraninite, compositions ranging from UO_2 to $\text{UO}_{2.25}$) or mixed U(IV)/U(VI) solids (e.g., U_4O_9).

U(VI) readily precipitates in the presence of phosphate to form a number of sparingly-soluble U-phosphate phases (U phases, such as saleeite, meta-autunite, and autunite) and also is removed by sorption and coprecipitation in apatite. Several studies have shown that hydroxyapatite is extremely effective at removing heavy metals, uranium and other radionuclides from solution (Gauglitz, et al., 1992; Arey and Seaman, 1999). Apatite was shown to be effective at removing a number of metals including uranium at Fry Canyon, Utah (U.S. EPA, 2000). Krumhansl (2002) reviews the sorptive properties of a number of other materials for backfills around nuclear waste repositories and permeable reactive barriers.

Injection of a reductant such as sodium dithionite creates a reducing zone that may be effective in immobilizing uranium and other redox-active radionuclides. The technique is known as *in situ* redox manipulation (ISRM). It has been shown to be moderately effective for chromium and is proposed for use at the Hanford site for remediation of a uranium groundwater plume (Fruchter et al., 1996).

5.1.2 Bioremediation

A number of remediation techniques based on biological processes are in use at contaminated sites. Examples include use of microbes to sequester uranium (as discussed in Section 3.3.2) and phytoremediation of a number of metals. The former method involves reductive reactions by bacteria, particularly those of sulfate reduction (Lovely and Phillips, 1992a) and direct reduction (Lovely and Phillips, 1992b; Truex et al., 1997). Several techniques have been employed to generate high organic loading by growth of plant and algal biomass. Injection of nutrients into the subsurface and subsequent microbial bloom leads to the low redox conditions favorable for reductive reactions, a significant decrease in the solubility and consequently, removal of the metal onto the geomeedia.

Abdelouas et al. (1999) provide a good review of remediation techniques for uranium mill tailings and groundwater plumes. Biological processes used in bioremediation include biosorption, bio-accumulation and bio-reduction. Biosorption includes uptake of uranium by ion exchange or surface complexation by living microbes or the cell membranes of dead organisms. In bio-accumulation, the radionuclides are precipitated with enzymatic reactions (Macaskie et al., 1996; Abdelouas et al., 1999; and cited references). Bio-reduction includes both direct reduction of radionuclides by organisms and indirect reduction. The latter

involves creation of reducing conditions by the activity of sulfate and iron reducing microbes and the subsequent reduction of the radionuclides by produced reductants such as H₂ and H₂S. Abdelouas et al. (1999) provide an excellent review of laboratory and field studies of microbes such as various *Desulfovibrio* species that have been shown to be effective in reducing hexavalent uranium by both of these processes.

Phytoremediation has been used to remove uranium and strontium from groundwaters and surface waters. Studies have been conducted on the uptake of heavy metals, uranium and other radionuclides (Cornish et al., 1995; Abdelouas et al., (1999); both the uptake rates and the phytoconcentration of the radionuclides are high. The plants can be harvested and the volume of the residuals minimized by combusting the plant material.

5.1.3 Monitored Natural Attenuation

Natural attenuation encompasses processes that lead to reduction of the mass, toxicity, mobility or volume of contaminants without human intervention. The U.S. EPA has recently published guidelines for the use of monitored natural attenuation (MNA) for a variety of contaminated sites (U.S. EPA, 1997). For inorganic constituents, the most potentially important processes include dispersion and immobilization (reversible and irreversible sorption, coprecipitation, and precipitation) (Brady et al., 1998). Studies of remediation options at UMTRA sites (Jove-Colon et al., 2001) and the Hanford Site (Kelley et al., 2002) have addressed the viability of adopting a MNA approach for uranium and strontium, respectively. As discussed below, different approaches are required to establish the viability of MNA for these radioelements.

Laboratory experiments, transport modeling, field data and engineering cost analysis provide complementary information to be used in an assessment of the viability of a MNA approach for a site. Information from kinetic sorption/desorption experiments, selective extraction experiments, reactive transport modeling and historical case analyses of plumes at several UMTRA sites can be used to establish a framework for evaluation of MNA for uranium contamination (Brady et al., 1998; Bryan and Siegel, 1998; Jove-Colon et al., 2001; Brady et al; 2002). The results of a recent project conducted at the Hanford 100-N site provided information for evaluation of MNA for a ⁹⁰Sr plume that has reached the Columbia River (Kelley et al., 2002). The study included strontium sorption-desorption studies, Sr transport and hydrologic modeling of the near-river system, and evaluation of the comparative costs and predicted effectiveness of alternative remediation strategies.

It is likely that it will be easier to gain acceptance for an MNA approach for radionuclides like ⁹⁰Sr compared to ^{235/238}U. This is because ⁹⁰Sr has a short half-life and uniformly strong sorption, whereas uranium isotopes have very long half-lives and complex sorption behavior. Strontium transport merely needs to be slowed enough to allow radioactive decay to remove the strontium, whereas demonstrating sorption irreversibility might be a key component of a MNA remedy for uranium. MNA may be acceptable for uranium only if it can be shown that an appreciable fraction of the uranium is irreversibly sequestered on mineral sorption sites or physically occluded and cannot be leached out in the foreseeable future. Institutional

controls are also important for MNA. Monitoring programs and contingency remediation plans are required as part of an overall MNA strategy (U.S. EPA, 1997; Brady et al., 1998)

5.2 Geochemical Models in Risk Assessment

5.2.1 Overview

In performance assessment models, simplified process models and sampling techniques are linked to provide a description of the release of radionuclides from idealized source terms, transport through engineered barriers and surrounding geomeia, and finally uptake by potentially exposed populations. The resulting doses are compared to environmental and health regulatory standards to estimate the risk posed by the releases. A basic overview of the process of risk assessment is presented by Fjeld and Compton (1999). Probabilistic performance assessment methods have been developed to provide a basis for evaluation of the risk associated with nuclear waste disposal in geological repositories (Cranwell et al., 1987; Rechard, 1996, 2002; Wilson et al., 2002). Similar approaches are used for LLW disposal and uranium mill tailings (Serne et al., 1990). Development of risk assessment models by the European community is summarized in NEA (1991). The current status of risk assessment programs in several countries was reviewed in a session devoted to performance assessment at the 2001 Materials Research Society Symposium on the Scientific Basis for Nuclear Waste Management (McGrail and Cragolino, 2002).

Abstraction of the hydrogeochemical properties of real systems into simple models is required for risk assessment. Heterogeneities in geochemical properties along potential flow paths, uncertainties in or lack of thermodynamic and kinetic parameter values, and the lack of understanding of geochemical processes all necessitate the use of a probabilistic approach to risk assessment. System complexity and limitations in computer technology preclude precise representation of geochemical processes in risk assessment calculations. Uncertainties in properties of the engineered and natural barriers are incorporated into the risk assessment by using ranges and probability distributions for the parameter values (K_{ds} and maximum aqueous radionuclide concentrations) in Monte Carlo simulations, by regression equations to calculate sorption and solubility limits from sampled geochemical parameter ranges, and by the use of alternative conceptual models. Representation of the probabilistic aspects of geochemical processes in risk assessment is discussed in Siegel et al. (1983, 1992), Chen et al. (2002) and Turner et al. (2002). Simplifications in solubility and sorption models used in performance assessment calculations for the WIPP and the proposed HLW repository at Yucca Mountain, respectively are described below.

5.2.2 Solubility Calculations for the Waste Isolation Pilot Plant

Performance assessment calculations of actinide speciation and solubility, and of the potential releases that could result if the repository is breached, were carried out as part of the CCA (Compliance Certification Application) for the WIPP (U.S. DOE, 1996; U.S. EPA, 1998a-d). The calculations modeled actinide behavior in a reference Salado brine and a less magnesium-rich brine from the Castile Formation as described previously (see Tables 6

and 8). The performance assessment calculations will be periodically repeated with updated parameter sets as part of site recertification.

Predicted repository conditions placed several constraints on the WIPP actinide speciation and solubility model. These conditions include 1) high ionic strength, requiring the use of a Pitzer ion interaction model for calculating activity coefficients; 2) the presence of magnesium oxide backfill, which will buffer P_{CO_2} and pH in the repository; and 3) the presence of large amounts of iron and organics in the waste, establishing reducing conditions in the repository and constraining the actinides to their lower oxidation states.

The predicted waste inventory for the repository indicates that potentially significant quantities of the organic ligands acetate, citrate, oxalate, and EDTA will be present (U.S. DOE, 1996). Actinide interactions with these compounds were not considered in the speciation and solubility modeling, as calculations suggested that they would be mostly complexed by transition metal ions (Fe^{2+} , Ni^{2+} , Cr^{2+} , V^{2+} , and Mn^{2+}) released by corrosion of the steel waste containers and waste components. A thermodynamic model of actinide-ligand interactions appropriate to brines will be included in solubility calculations for WIPP recertification.

Under many experimental conditions, it is difficult to maintain plutonium and some other actinides in a single oxidation state (Choppin, 1999; Neck and Kim, 2001). Depending on pH and solution composition, as many as four plutonium oxidation states may coexist, not necessarily in equilibrium. This leads to uncertainty in the oxidation state(s) present in experimental solutions. For this reason, there is little reliable speciation and solubility data available for Pu(III) and Pu(IV). WIPP solubility models were only developed for Am(III), Th(IV), and Np(V). Results of Am(III) calculations were used, through an oxidation state analogy, to predict the speciation of Pu(III) and to place an upper bound on its solubility. Similarly, results of the Th(IV) calculations were used to predict and bound the speciation and solubilities of Pu(IV), Np(IV), and U(IV). Recently, Wall et al. (2002) evaluated the appropriateness of the analogy and found that the predicted behavior of Am(III) was reasonably similar to that of Pu(III), while predicted solubilities for Th(IV) in Salado and Castile brines were ten-to-eleven orders of magnitude higher than those for Pu(IV). Thus, Th(IV) is a highly conservative analog for Pu(IV).

The An(V) model was developed using Np(V) but was not used for other actinides because none are expected to be present in the +V oxidation state. Although U(VI) may be present, there were insufficient experimental data to develop an An(VI) model for the WIPP, and solubilities for this oxidation state were estimated from literature data rather than using a Pitzer model.

5.2.3 Models for Radionuclide Sorption at Yucca Mountain

For the last three decades, the U.S. DOE has evaluated the suitability of Yucca Mountain, Nevada, as a potential site for a geologic repository for high-level nuclear waste. The proposed site is approximately 170 km northwest of Las Vegas, Nevada, and occupies a portion of the Nevada Test Site where nuclear weapons testing has been carried out since

approximately 1945. The geochemical setting of the proposed repository site was described in Section 3.2.2 above. The results of performance assessment calculations for the proposed repository at Yucca Mountain suggest that the most significant contributors to risk are radionuclides that are highly soluble or poorly sorbing (^{99}Tc , ^{129}I and ^{237}Np) in the oxidizing, Na-bicarbonate-rich waters at the site. In addition, other radionuclides such as ^{239}Pu , ^{241}Am , ^{238}U and ^{230}Th may be important due to colloidal transport or high dose-conversion factors.

Sorption of a radionuclide may vary drastically over postulated flow paths and over time at Yucca Mountain. Changes in mineralogy and transient concentrations of competing and complexing ligands may cause the sorption at any point along the flow path to change. One approach to represent this variability in performance assessment calculations is to sample K_{ds} for transport equations from a probability distribution based on experimental measurements as discussed above (Siegel et al., 1983; Wilson et al., 2002). Another approach is to calculate a range of K_{ds} from thermodynamic data for a range of groundwater compositions. Turner and Pabalan (1999) and Turner et al. (2002) outline two methods by which SCMs can be used to obtain reasonable bounds on K_{ds} for stochastic performance assessment calculations for nuclear waste repositories. The authors represented the mineral surfaces of rocks at Yucca Mountain as two different types of sorption sites ($>\text{SiOH}$ and $>\text{AlOH}$). They used a Double Layer Model (DLM) in the MINTEQA code (Allison et al., 1991) to calculate ranges and distributions of K_{ds} for Am(III), Th(IV), Np(V), Pu(V) and U(VI) in a suite of groundwater compositions sampled at the site. The contours in calculated K_{ds} due to spatial variations in hydrochemistry were presented on maps of Yucca Mountain. In an alternate approach, Turner et al. (2002) used a simplified SCM to calculate neptunium sorption behavior over a wide range of pH and P_{CO_2} . K_{ds} can be sampled from multi-dimensional graphs of such calculations for use in simple transport codes in Monte Carlo simulations for performance assessment.

6. Summary - Challenges and Future Research Needs

Disposal of nuclear waste in geological repositories remains a topic of bitter controversy 30 years after the nuclear waste program was initiated. Public opposition to geologic disposal occurs in all countries with active waste disposal programs. Many people have not accepted geologic disposal of nuclear waste and many environmental groups and some scientists call for monitored retrievable storage until additional information is gathered. The ability of the public to accept the risks associated with disposal and clean up of nuclear contamination depends in part on our ability to predict the behavior of radionuclides in the environment. Although much data collection and model development has occurred in the last three decades, active research in a number of areas could potentially enhance our ability to predict nuclide migration accurately. These include 1) better characterization of the chemical interactions between radionuclides and geomedial media, 2) better characterization of the sorptive media along potential flow paths between radionuclide sources and exposed populations, and 3) cost-effective monitoring of potential radionuclide releases from waste sites. These areas are currently being pursued by advances in 1) spectroscopic techniques and molecular simulation models, 2) geostatistical models and computer simulations of radionuclide transport, 3) improved geophysical and drilling techniques for characterizing the properties

of geomechanics, and 4) improved monitoring technologies for potential radionuclide releases and exposures.

A large body of empirical sorption (K_d) data has been generated during the last three decades. One of the accomplishments of the last decade has been the widespread awareness of the limitations of much of the data as discussed previously. It has been recognized that many of these data do not describe reversible equilibrium sorption. When precipitation or other mass transfer processes influence measurements of sorption, the resulting K_d will not provide accurate estimates of radionuclide velocities when used in transport equations. In addition, even when the K_d values represent only reversible sorption, they are valid only for the specific conditions of their experiment. Critically evaluated data sets that are useful for performance assessment of waste repositories have been assembled by several workers. It is hoped that when used with sampling schemes in Monte Carlo calculations, the data can be used to provide order-of-magnitude estimates and reasonable confidence intervals for radionuclide migration velocities that reflect uncertainties in radionuclide sorptive properties along flow paths.

Some workers argue that a more fundamental approach to sorption and solubility will lead to more accurate estimates of radionuclide transport behavior. During the last three decades, much sorption data have been collected within the framework of SCMs. These data can be critically evaluated to determine if processes other than adsorption or ion exchange have occurred. They can also be applied over much wider ranges of solution compositions than empirical K_d measurements. Most of the available surface complexation data have been collected in simple electrolyte solutions for single mineral phases. Application of SCMs to natural mineral assemblages is difficult due to the existence of multiple sorption sites. New experimental and theoretical methods for determination of the surface complexation constants would improve our ability to apply the SCMs to natural systems. The resulting capacity to predict radionuclide sorption on natural materials based on fundamental properties could increase confidence in risk assessment and in the design of remediation of contaminated sites.

Cooperative international efforts like those carried out by the NEA/OECD Thermodynamic Database Project allow sharing of the results of basic research, standardization of techniques for experiments and establishment of reference values for thermodynamic and kinetic calculations. A comparable effort would be useful for sorption data modeling. A number of alternative SCMs are used in the literature. They are all based on conditional constants that are obtained by fitting equations or curves to experimental data obtained in solutions. The surface complexation constants from different models cannot be combined. This is because the constants are dependent on the assumed stoichiometry of the surface species, the identity and properties of species present in solution, and properties of the electrical double layer. Recent advances in surface spectroscopy can remove some of the conditional nature of the sorption constants by providing direct information about the stoichiometry of the sorbing species. Molecular modeling could also be used to constrain the likely stoichiometry of surface species. These techniques would allow establishment of a set of reference surface species. High quality existing sorption data sets could then be reinterpreted in light of the

reference surface species and the chosen SCM. This effort would result in a much larger internally-consistent set of thermodynamic data than currently exists.

Prediction of radionuclide transport in the environment is complicated by the heterogeneity of rocks along radionuclide migration paths. Estimates of expected values or ranges of radionuclide discharges at exposed populations can benefit from improvements in computer technology and applications of geostatistical methods to the geochemical properties of the flow field. Surface complexation constants have been used to calculate sorption ratios for a suite of groundwater compositions and plotted on a map of the Yucca Mountain site. This method provides a framework to assess the range of sorption behavior at the proposed waste site. The approach could be combined with geostatistical simulation of the sorptive properties of the site (site density, surface areas, identity of sorbing sites) based on samples from boreholes. When used as input parameters to reactive transport codes, geostatistical simulation of the compositions of coexisting water and rock could be used to produce multiple realizations of radionuclide transport at a site. These multiple simulations of radionuclide transport will lead to greater confidence that reasonable upper limits for the release of radionuclides to the environment have been calculated.

Improved monitoring techniques that are cheaper and more robust with respect to the environment will allow networks of monitoring wells to be placed between sources of radionuclides such as repositories or disposal sites and potentially exposed populations. This will improve the acceptance of Monitored Natural Attenuation. With improved modeling and monitoring capabilities and better understanding of radionuclide interactions, public confidence in predictions of the risks associated with radioactive waste management will increase.

This overview of the geochemistry of radioactive contamination in the environment has included an overview of the current hazards, a summary of available data and conceptual models, descriptions of experimental and computational methods, and examples of applications of the information to address environmental problems. Historical improvements in our ability to predict the migration of radionuclides in the environment and the hazards they pose to humans and ecosystems have benefited from advances in the field of geochemistry in general. Geochemical conceptual models have progressed from early thermodynamic models through kinetic models, *ab initio* molecular models and models incorporating the molecular biology of microbes. Future advances in these areas will lead to an improved understanding of radionuclide geochemistry and an improved ability to manage radioactive contamination in the environment.

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Appendix A: Symbols and Definitions.

Symbol	Definition
$A'_{colloid}$	Specific surface area of the colloid, in a colloid/rock system
A'_{IP}	Specific surface area of the rock matrix, in a colloid/rock system
a_{H^+}	Activity of the hydrogen ion in solution
$a_{UO_2^{2+}}$	Activity of uranyl in solution
β^{cat}	Intrinsic surface complexation constant for a cationic species
C	Colloid concentration in solution
C_i	Initial concentration of contaminant in solution
C_f	Final concentration of contaminant in solution
C_L	Concentration of a contaminant in solution
C_S	Concentration of a contaminant sorbed onto solid
e	Fundamental electrical charge of a surface complex
F	The ratio of the specific surface areas of the colloid and the rock matrix, in a colloid/rock system.
k	Boltzmann's constant
$K_{i,j,k}$	Intrinsic formation constant for an aqueous species (i,j,k describe stoichiometry)
K_d	Distribution coefficient for a contaminant in a water/rock system
m	Mass of substrate present in a batch system
ϕ	Bulk porosity of a porous medium
ρ	Bulk density of a porous medium
ψ_o	Electrical potential of the inner (o) surface plane
R	Retardation factor for a contaminant
$R_{F,eff}$	Effective retardation factor (including the effects of transport on colloids)
R_d	Sorption coefficient for a contaminant in a water/rock system
T	Absolute temperature, in °K
V_i	Initial solution volume in a batch system
V_f	Final solution volume in a batch system

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