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Review of the Transport of Selected Radionuclides in the Interim Risk Assessment for the Radioactive Waste Management Complex, Waste Area Group 7 Operable Unit 7-13/14, Idaho National Engineering and Environmental Laboratory, Idaho

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Review of the Transport of Selected Radionuclides in the Interim Risk Assessment for the Radioactive Waste Management Complex, Waste Area Group 7 Operable Unit 7-13/14, Idaho National Engineering and Environmental Laboratory, Idaho

Volume 1

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Table of Contents

| | |
|--|------|
| Abstract | ES-1 |
| Executive Summary | ES-2 |
| <i>J.P. Rousseau</i> | |
| 1.0 Introduction | 1-1 |
| <i>J.P. Rousseau</i> | |
| 1.1 Purpose | 1-1 |
| 1.2 Scope | 1-1 |
| 1.2.1 Task 1: Review of radionuclide sampling data at the Radioactive Waste Management Complex | 1-1 |
| 1.2.2 Task 2: Radionuclide transport processes | 1-2 |
| 1.2.3 Task 3: Distribution coefficients (K_d s) and their application to transport analysis | 1-2 |
| 1.2.4 Task 4: Transport model analysis | 1-2 |
| 1.2.5 Task 5: Further work | 1-2 |
| 1.3 Acknowledgments | 1-2 |
| 1.4 Report Organization | 1-3 |
| 2.0 Conceptual model of aqueous-phase fluid flow and contaminant transport | 2-1 |
| <i>J.R Nimmo, S.R. Anderson, R.C. Bartholomay, J.P. Rousseau, L.L. Knobel</i> | |
| 2.1 Regional setting | 2-1 |
| 2.2 Conceptual models | 2-1 |
| 2.3 Geologic framework | 2-1 |
| 2.3.1 Geologic data | 2-2 |
| 2.3.2 Stratigraphy | 2-2 |
| 2.3.3 Basalt flows | 2-2 |
| 2.3.3.1 Typical basalt-flow characteristics | 2-3 |
| 2.3.3.2 Typical basalt-flow geochemistry | 2-3 |
| 2.3.3.3 Fractures | 2-3 |
| 2.3.4 Surficial sediment and sedimentary interbeds | 2-4 |
| 2.3.4.1 Depositional environments | 2-4 |
| 2.3.4.2 Lithologic variations | 2-5 |
| 2.3.4.3 Physical characteristics and mineralogy | 2-5 |
| 2.3.4.4 Pedogenesis | 2-6 |
| 2.3.4.5 Thickness and areal extent | 2-6 |
| 2.3.4.6 Hydraulic conductivity | 2-6 |
| 2.3.5 Hydrologic pathways | 2-7 |
| 2.4 Hydrologic framework | 2-8 |
| 2.4.1 Meteorology | 2-8 |
| 2.4.2 Surface water and local runoff | 2-8 |
| 2.4.2.1 Areal infiltration | 2-8 |
| 2.4.2.2 Stream infiltration | 2-8 |
| 2.4.3 Unsaturated-zone flow | 2-9 |
| 2.4.3.1 Flow in a homogeneous medium | 2-9 |
| 2.4.3.2 Flow and perching in stratified unsaturated zones | 2-10 |
| 2.4.3.3 Preferential flow | 2-10 |
| 2.4.3.3.1 Macropore flow—heterogeneity of the porous medium | 2-11 |
| 2.4.3.3.2 Funneled flow—heterogeneity of the porous medium | 2-11 |
| 2.4.3.3.3 Unstable flow—heterogeneities in the condition of the medium | 2-12 |
| 2.4.3.4 Quantitative treatment of preferential flow | 2-12 |
| 2.4.3.4.1 Effective properties | 2-12 |
| 2.4.3.4.2 Dual-modality and multi-modality | 2-13 |

iv Review of the transport of selected radionuclides in the Interim Risk Assessment

| | |
|---|------|
| 2.4.3.4.3 Additional considerations in the quantification of unstable flow | 2-13 |
| 2.4.3.5 Contentions and ambiguities concerning preferential flow | 2-13 |
| 2.4.3.6 Flow in the unsaturated zone at and near the Subsurface Disposal Area | 2-14 |
| 2.4.3.6.1 Surficial sediments | 2-14 |
| 2.4.3.6.2 Basalts | 2-14 |
| 2.4.3.6.3 Sedimentary interbeds | 2-14 |
| 2.4.3.7 Current qualitative understanding of flow in the unsaturated zone at the Idaho National Engineering and Environmental Laboratory | 2-15 |
| 2.4.3.7.1 Vertical flow of local origin | 2-15 |
| 2.4.3.7.2 Combined vertical and lateral flow | 2-15 |
| 2.4.3.8 Summary of unsaturated-zone flow | 2-16 |
| 2.4.4 Flow in the saturated zone | 2-16 |
| 2.5 Contaminant transport | 2-17 |
| 2.5.1 Source-term description | 2-17 |
| 2.5.1.1 Point sources | 2-17 |
| 2.5.1.2 Nonpoint sources | 2-18 |
| 2.5.2 Summary of geochemical processes at the Subsurface Disposal Area | 2-18 |
| 2.5.2.1 Lithology and mineralogy | 2-18 |
| 2.5.2.2 Water chemistry | 2-19 |
| 2.5.3 Description of contaminant transport processes | 2-20 |
| 2.5.3.1 Solute transport | 2-20 |
| 2.5.3.2 Colloid transport | 2-20 |
| 2.6 Summary | 2-21 |
| 3.0 Task 1: Review of radionuclide sampling program and available data at the Subsurface Disposal Area | 3-1 |
| <i>L.D. Cecil, L.L. Knobel, E.R. Landa</i> | |
| 3.1 Introduction | 3-1 |
| 3.1.1 Background | 3-1 |
| 3.1.2 Purpose and scope | 3-1 |
| 3.2 Detection limits, statistical screening criteria, and reporting of data | 3-1 |
| 3.3 Sampling methodology | 3-3 |
| 3.3.1 Sampling location, frequency, and media | 3-3 |
| 3.3.2 Sample identification | 3-4 |
| 3.3.3 Sampling equipment and procedures | 3-4 |
| 3.3.4 Sample handling, packaging, and shipping | 3-4 |
| 3.3.5 Documentation | 3-5 |
| 3.3.6 Handling and disposition of investigation-derived waste | 3-5 |
| 3.4 Analytical methods and laboratory techniques | 3-5 |
| 3.5 Quality assurance and quality control protocols | 3-5 |
| 3.6 Reported detections in sediments and water | 3-7 |
| 3.6.1 Surficial sediments and sedimentary interbed data | 3-7 |
| 3.6.2 Perched-water and ground-water data | 3-10 |
| 3.6.3 Significance of reported detections | 3-12 |
| 3.7 Summary | 3-12 |
| 4.0 Task 2: Actinide transport processes | 4-1 |
| <i>G.P. Curtis, P.D. Glynn, K.G. Stollenwerk, R.C. Bartholomay</i> | |
| 4.1 Introduction | 4-1 |
| 4.2 Summary of geochemical characteristics at the Subsurface Disposal Area | 4-1 |
| 4.3 Potential effects of speciation on actinide transport | 4-1 |
| 4.3.1 Am, U, Np, and Pu chemistry and speciation | 4-3 |
| 4.3.1.1 Am | 4-3 |

| | |
|--|------|
| 4.3.1.2 U | 4-3 |
| 4.3.1.3 Np | 4-5 |
| 4.3.1.4 Pu | 4-7 |
| 4.3.2 Speciation calculations for aqueous Am, U, Np, and Pu in INEEL waters | 4-8 |
| 4.3.2.1 Speciation calculations for aqueous Am | 4-8 |
| 4.3.2.2 Speciation calculations for aqueous U | 4-8 |
| 4.3.2.3 Speciation calculations for aqueous Np and Pu | 4-9 |
| 4.3.2.4 Additional speciation calculations for Np and Pu | 4-16 |
| 4.3.3 Summary | 4-17 |
| 4.4 Applicability of the local equilibrium concept to actinide transport | 4-19 |
| 4.4.1 Chemically-mediated kinetics | 4-19 |
| 4.4.2 Transport-controlled kinetics | 4-20 |
| 4.5. Colloid-facilitated transport of actinides | 4-21 |
| 4.5.1 Colloid definition and mobility | 4-21 |
| 4.5.2 Previous studies of actinide colloid formation and transport | 4-21 |
| 4.5.2.1 Batch experiments | 4-21 |
| 4.5.2.2 Column experiments | 4-22 |
| 4.5.2.3 Field studies | 4-22 |
| 4.5.3 Evidence for colloid-facilitated transport of actinides at the Idaho National Engineering and Environmental Laboratory | 4-23 |
| 4.5.3.1 Field evidence | 4-23 |
| 4.5.3.2 Laboratory column experiments | 4-23 |
| 4.5.4 Summary of colloid-facilitated transport of actinides | 4-25 |
| 4.6 Summary | 4-25 |
| 5.0 Task 3: Distribution coefficients (K_d s) and their application to transport analysis | 5-1 |
| <i>E.R. Landa, P.D. Glynn, K.G. Stollenwerk, G.P. Curtis</i> | |
| 5.1 Introduction | 5-1 |
| 5.2 Literature review | 5-1 |
| 5.2.1 K_d basics | 5-1 |
| 5.2.2 Sorption processes | 5-3 |
| 5.2.2.1 Alternatives to single K_d values | 5-4 |
| 5.2.2.2 Importance of secondary minerals | 5-4 |
| 5.2.2.3 Role of Fe^{2+} -bearing minerals | 5-5 |
| 5.2.2.4 Influence of organic compounds on subsurface migration of actinides | 5-6 |
| 5.3 Evaluation of the K_d s for Am, U, and Pu used in the Interim Risk Assessment model— experimental data | 5-7 |
| 5.3.1 Materials and methods | 5-8 |
| 5.3.1.1 Solid phases | 5-8 |
| 5.3.1.1.1 Interbed sediments | 5-8 |
| 5.3.1.1.2 Basalt | 5-8 |
| 5.3.1.2 Aqueous phase | 5-8 |
| 5.3.1.3 Column experiments | 5-8 |
| 5.3.1.3.1 Crushed basalt and interbed sediments—saturated | 5-8 |
| 5.3.1.3.2 Intact basalt—saturated | 5-8 |
| 5.3.1.3.3 Crushed basalt—unsaturated | 5-11 |
| 5.3.1.4 Batch experiments | 5-11 |
| 5.3.2 Results and discussion | 5-11 |
| 5.3.2.1 Batch experiments | 5-11 |
| 5.3.2.1.1 Am | 5-11 |
| 5.3.2.1.2 U | 5-11 |
| 5.3.2.1.3 PU | 5-11 |

| | |
|--|------|
| 5.3.2.2 Risk assessment K_{ds} for Am, U, and Pu | 5-12 |
| 5.3.2.3 Column experiments | 5-12 |
| 5.3.2.3.1 Interbed sediment columns | 5-12 |
| 5.3.2.3.2 Crushed-basalt columns | 5-13 |
| 5.3.2.3.3 Enhanced mobility fraction | 5-13 |
| 5.3.2.4 Additional experiments | 5-14 |
| 5.3.2.4.1 pH and ionic-strength variability | 5-14 |
| 5.3.2.4.2 Reproducibility of K_{ds} | 5-14 |
| 5.3.2.4.3 Solid:liquid ratio | 5-14 |
| 5.3.2.4.4 Crushed basalt versus intact basalt | 5-14 |
| 5.3.2.4.5 Unsaturated column experiments | 5-14 |
| 5.3.3 Summary of the evaluation of K_{ds} for Am, U, Np, and Pu used in the Interim Risk Assessment | 5-14 |
| 5.4 Evaluation of the K_{ds} for Np used in the Interim Risk Assessment model—literature review | 5-15 |
| 5.4.1 Studies of potential relevance to the Idaho National Engineering and Environmental Laboratory | 5-18 |
| 5.4.2 Summary of K_{ds} for Np used in the Interim Risk Assessment model | 5-19 |
| 5.5 Use and limitations of the K_d concept as applied to actinide transport at the Idaho National Engineering and Environmental Laboratory | 5-9 |
| 5.5.1 Advantages and limitations of the K_d approach in modeling contaminant retardation | 5-19 |
| 5.5.1.1 Advantages of the K_d approach | 5-20 |
| 5.5.1.2 Limitations of the K_d approach | 5-20 |
| 5.5.1.3 Applicability of the K_d approach to ground-water systems in chemical steady state | 5-21 |
| 5.5.2 Advantages and limitations of speciation-based approaches in modeling sorption reactions | 5-21 |
| 5.5.3 Uncertainties at the Idaho National Engineering and Environmental Laboratory site and their potential effects on simulation of radionuclide sorption and retardation | 5-22 |
| 5.5.4 One-dimensional transport simulations for U and Np | 5-23 |
| 5.5.4.1 U(VI) transport calculations | 5-23 |
| 5.5.4.1.1 Calibration of the reactive-transport model | 5-23 |
| 5.5.4.1.2 Application of the surface complexation model to ground water at the Idaho National Engineering and Environmental Laboratory | 5-24 |
| 5.5.4.1.3 Comparison of one-dimensional transport simulations and calculated K_{fs} | 5-24 |
| 5.5.4.2 Np transport calculations | 5-25 |
| 5.5.4.2.1 Description of the Np transport simulations | 5-27 |
| 5.5.4.2.2 Np infiltration results | 5-27 |
| 5.5.4.2.3 Np cleanup results | 5-28 |
| 5.5.4.2.4 Np sorption isotherms for the PHREEQC surface complexation models | 5-29 |
| 5.5.6 Evaluation of the uncertainties associated with selected K_{ds} | 5-29 |
| 5.5.7 Summary | 5-30 |
| 6.0 Task 4: Transport model analysis | 6-1 |
| <i>J.R. Nimmo, E.M. Kwicklis, J.P. Rousseau, S.R. Anderson, C.R. Bossong, G.P. Curtis</i> | |
| 6.1 Introduction | 6-1 |
| 6.2 Review of significant Interim Risk Assessment assumptions and simplifications | 6-1 |
| 6.2.1 Hydrogeologic framework—geometrical aspects | 6-1 |
| 6.2.1.1 Definition and description of the model domain | 6-1 |
| 6.2.1.2 Geostatistical applications | 6-2 |
| 6.2.1.2.1 Variogram construction | 6-3 |
| 6.2.1.2.2 Kriging results | 6-5 |
| 6.2.2 Nature of materials | 6-5 |

| | |
|--|-------|
| 6.2.2.1 Means used to determine hydraulic properties | 6-8 |
| 6.2.2.2 Fractured basalts in the unsaturated zone | 6-8 |
| 6.2.2.3 Surficial sediments | 6-11 |
| 6.2.2.4 Sedimentary interbeds | 6-11 |
| 6.2.2.5 Aquifer properties | 6-12 |
| 6.2.2.6 Heterogeneity and anisotropy of hydraulic properties | 6-13 |
| 6.2.3 Unsaturated-zone flow | 6-14 |
| 6.2.3.1 Infiltration | 6-14 |
| 6.2.3.2 Percolation | 6-14 |
| 6.2.3.3 Lateral flow | 6-15 |
| 6.2.4 Contaminant input and transport | 6-17 |
| 6.2.4.1 Source term | 6-17 |
| 6.2.4.2 Solute transport | 6-17 |
| 6.2.4.3 Colloid transport | 6-17 |
| 6.2.5 Saturated-zone flow | 6-17 |
| 6.3 Review of the numerical simulator | 6-18 |
| 6.3.1 Description of the numerical simulator | 6-18 |
| 6.3.1.1 Discretization and grid refinement | 6-19 |
| 6.3.2 Model calibration | 6-19 |
| 6.3.2.1. Calibration for unsaturated-zone hydraulics | 6-21 |
| 6.3.2.1.1 Perched water | 6-21 |
| 6.3.2.1.2 Travel time | 6-22 |
| 6.3.2.2. Calibration for saturated-zone hydraulics | 6-23 |
| 6.3.2.3 Calibration for contaminant transport | 6-23 |
| 6.3.2.3.1 Nitrate | 6-23 |
| 6.3.2.3.2 Carbon tetrachloride | 6-24 |
| 6.3.2.3.3 Detected contaminants of potential concern | 6-25 |
| 6.4 Model utilization | 6-26 |
| 6.4.1 Sensitivity analyses | 6-26 |
| 6.4.2 Predictions | 6-26 |
| 6.5 Summary | 6-27 |
| 7.0 Summary and conclusions | 7-1 |
| <i>J.P. Rousseau</i> | |
| References Cited | Ref-1 |
| Appendix: Task 5 | App-1 |
| <i>J.P. Rousseau, B.R. Orr</i> | |

Figures (Located in Volume II)

Figure 1-1. Location of the Radioactive Waste Management Complex, Idaho National Engineering and Environmental Laboratory, Idaho

Figure 2-1. Geologic section A-A' at the Radioactive Waste Management Complex, Idaho National Engineering and Environmental Laboratory, Idaho

Figure 2-2. Location of sampling sites for the Waste Area Group 7 ground-water monitoring wells, perched-water wells, and lysimeters at and near the Radioactive Waste Management Complex and vicinity, Idaho National Engineering and Environmental Laboratory, Idaho

Figure 2-3. Location of selected wells, Idaho National Engineering and Environmental Laboratory and vicinity, Idaho

Figure 4-1. Reaction scheme illustrating the competition between the formation of dissolved species (UO_2^{2+} and $\text{UO}_2\text{L}_3^{2-3n}$) and surface species (SOUO_2OH)

Figure 4-2. Dependence of K_{rs} on (a) total UO_2^{2+} concentration, (b) pH, and (c) ligand concentration

viii Review of the transport of selected radionuclides in the Interim Risk Assessment

- Figure 4-3. Aqueous speciation of Am(III) in the presence of CO₂ for (a) 10⁻⁷ M Am(III) and 10^{-3.5} atm CO₂(g), (b) 10⁻⁵ M Am(III) and 10^{-3.5} atm CO₂(g), and (c) 10⁻⁷ M Am(III) and 0-2.5 atm CO₂(g)
- Figure 4-4. Computed surface-area-referenced distribution coefficient (K_r) values for adsorption of Am(III) by quartz, α-alumina, and γ-alumina at (a) 10^{-3.5} atm CO₂(g), and (b) 10^{-2.5} atm CO₂(g)
- Figure 4-5. Aqueous speciation of U(VI) in the presence of CO₂ for (a) 10⁻⁷ M U(VI) and 10^{-3.5} atm CO₂(g), (b) 10⁻⁵ M U(VI) and 10^{-3.5} atm CO₂(g), and (c) 10⁻⁷ M U(VI) and 10^{-2.5} atm CO₂(g)
- Figure 4-6. Computed surface-area-referenced distribution coefficient (K_r) values for adsorption of U(VI) by ferrihydrite at different partial pressures of CO₂ (g) and total adsorption site density (S_T)
- Figure 4-7. Computed surface-area-referenced distribution coefficient (K_r) values for adsorption of U(VI) by quartz, montmorillonite, goethite, and ferrihydrite at (a) 10^{-3.5} atm CO₂(g), and (b) 10^{-2.5} atm CO₂(g)
- Figure 4-8. Size range of waterborne particles and filter pores
- Figure 5-1. The appearance of a typical adsorption isotherm.
- Figure 5-2. The effect of surface area and normalization on Np⁵⁺ sorption
- Figure 5-3. Behavior of ²³⁷Np (initially NpO₂⁺) in rock-water systems
- Figure 5-4. Distribution ratio (R_d, equivalent to K_d) for Np sorption onto Pomona Basalt from synthetic ground water in the presence of various concentrations of humic acid
- Figure 5-5. Breakthrough of ³H from interbed packed column
- Figure 5-6. Breakthrough of ²⁴¹Am from interbed packed column
- Figure 5-7. Breakthrough of ²³⁹Pu from interbed packed column
- Figure 5-8. Breakthrough of ²³³U from interbed packed column
- Figure 5-9. Breakthrough of ³H from crushed-basalt packed column
- Figure 5-10. Breakthrough of ²⁴¹Am from crushed-basalt packed column
- Figure 5-11. Breakthrough of ²³⁹Pu from crushed-basalt packed column
- Figure 5-12. Breakthrough of ²³³U from crushed-basalt packed column
- Figure 5-13. Variation of calcite saturation indices (SI_{calcite}) and ⁹⁰Sr partitioning (K_d) between the solution and an ion-exchange phase in a one-dimensional column at chemical steady state
- Figure 5-14. Temporal and spatial changes in ⁹⁰Sr partitioning (K_d) between the solution and an ion-exchange phase in a dynamically evolving system
- Figure 5-15. Fitted reactive transport simulations and experimental breakthrough curves for U(VI) in columns packed with sedimentary interbed materials
- Figure 5-16. Simulated breakthrough curves for the transport of one pore volume of 10⁻⁷ M U(VI) in 12 INEEL surface- and ground-water samples for (a) a total site density assuming a constant pH of 8, and (b) a total site density assuming a constant pH of 8.48
- Figure 5-17. Np aqueous concentrations as a function of distance according to PHREEQC simulations of one-dimensional advective-dispersive transport with a surface and aqueous complexation model. Simulations used Np aqueous thermodynamic data from the ANSTO data base
- Figure 5-18. Np aqueous concentrations as a function of distance according to PHREEQC simulations of one-dimensional advective-dispersive transport with a surface and aqueous complexation model. Simulations used Np aqueous thermodynamic data from the EQ3/6 data base
- Figure 5-19. Np aqueous concentrations as a function of timestep
- Figure 5-20. Np aqueous concentrations as a function of distance according to PHREEQC reactive transport simulations. Np thermodynamic data were taken from the ANSTO data base
- Figure 5-21. Np aqueous concentrations as a function of distance according to PHREEQC reactive transport simulations. Np thermodynamic data were taken from the EQ3/6 data base
- Figure 5-22. Np aqueous concentrations as a function of distance according to PHREEQC reactive transport simulations. Np thermodynamic data were taken from the ANSTO data base
- Figure 5-23. Np aqueous concentrations as a function of distance according to PHREEQC reactive transport simulations. Np thermodynamic data were taken from the EQ3/6 data base
- Figure 5-24. Np aqueous concentrations as a function of timestep as simulated by PHREEQC for mid-column and end-of-column sampling points

- Figure 5-25. Np sorption isotherms calculated from PHREEQC simulations according to various geochemical conditions (specification or lack thereof of calcite equilibrium; presence or absence of water from well USGS 92)
- Figure 5-26. Np sorption isotherms calculated from PHREEQC simulations according to various geochemical conditions and to the source of Np aqueous thermodynamic data (ANSTO or EQ3/6 data base)
- Figure 6-1. Model domain and grid of the Waste Area Group 7 numerical simulator, Radioactive Waste Management Complex and vicinity, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-2. Variograms for the top elevation (a) and thickness (b) of surficial sediments in the model domain of the Waste Area Group 7 numerical simulator, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-3. Variograms for the top elevation (a) and thickness (b) of the A-B interbed in the model domain of the Waste Area Group 7 numerical simulator, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-4. Variograms for the top elevation (a) and thickness (b) of the B-C interbed in the model domain of the Waste Area Group 7 numerical simulator, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-5. Variograms for the top elevation (a) and thickness (b) of the C-D interbed in the model domain of the Waste Area Group 7 numerical simulator, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-6. Discretization, measured points, and relative confidence in kriged estimates for the top elevation of the surficial sediments in the vicinity of the Radioactive Waste Management Complex, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-7. Discretization, measured points, and relative confidence in kriged estimates for the top elevation of the surficial sediments in the Waste Area Group 7 model domain, Radioactive Waste Management Complex, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-8. Discretization, measured points, and relative confidence in kriged estimates for the thickness of the surficial sediments in vicinity of the Radioactive Waste Management Complex, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-9. Discretization, measured points, and relative confidence in kriged estimates for the thickness of the surficial sediments in the Waste Area Group 7 model domain, Radioactive Waste Management Complex, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-10. Discretization, measured points, and relative confidence in kriged estimates for the top elevation of the A-B sedimentary interbed in the vicinity of the Radioactive Waste Management Complex, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-11. Discretization, measured points, and relative confidence in kriged estimates for the top elevation of the A-B sedimentary interbed in the Waste Area Group 7 model domain, Radioactive Waste Management Complex, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-12. Discretization, measured points, and relative confidence in kriged estimates for the thickness of the A-B sedimentary interbed in the vicinity of the Radioactive Waste Management Complex, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-13. Discretization, measured points, and relative confidence in kriged estimates for the thickness of the A-B sedimentary interbed in the Waste Area Group 7 model domain, Radioactive Waste Management Complex, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-14. Discretization, measured points, and relative confidence in kriged estimates for the top elevation of the B-C sedimentary interbed in the vicinity of the Radioactive Waste Management Complex, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-15. Discretization, measured points, and relative confidence in kriged estimates for the top elevation of the B-C sedimentary interbed in the Waste Area Group 7 model domain, Radioactive Waste Management Complex, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-16. Discretization, measured points, and relative confidence in kriged estimates for the thickness of the B-C sedimentary interbed in the vicinity of the Radioactive Waste Management Complex, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-17. Discretization, measured points, and relative confidence in kriged estimates for the thickness of the B-C sedimentary interbed in the Waste Area Group 7 model domain, Radioactive Waste Management Complex, Idaho National Engineering and Environmental Laboratory, Idaho

- Figure 6-18. Discretization, measured points, and relative confidence in kriged estimates for the top elevation of the C-D sedimentary interbed in the vicinity of the Radioactive Waste Management Complex, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-19. Discretization, measured points, and relative confidence in kriged estimates for the top elevation of the C-D sedimentary interbed in the Waste Area Group 7 model domain, Radioactive Waste Management Complex, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-20. Discretization, measured points, and relative confidence in kriged estimates for the thickness of the C-D sedimentary interbed in the vicinity of the Radioactive Waste Management Complex, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-21. Discretization, measured points, and relative confidence in kriged estimates for the thickness of the C-D sedimentary interbed in the Waste Area Group 7 model domain, Radioactive Waste Management Complex, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-22. Location of spreading areas, Radioactive Waste Management Complex, and selected boreholes used in the 1999 tracer monitoring program, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-23. Flow diversions to the spreading areas from January 1965 to January 2000, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-24. Southwestern portion of the Idaho National Engineering and Environmental Laboratory showing contours on the water table of the Snake River Plain aquifer and inferred directions of ground-water movement, March 1972
- Figure 6-25. Generalized net increase of the regional water table July 1981 to July 1985 (from Pittman and others, 1988, fig. 10), Snake River Plain aquifer, Idaho National Engineering and Environmental Laboratory, Idaho
- Figure 6-26. Water levels in borehole USGS 88 from January 1975 to July 1998, Idaho National Engineering and Environmental Laboratory, Idaho

Tables

Table 3-1. Concentrations of selected radionuclides in sediment samples collected in 1972 from wells at and near the Subsurface Disposal Area 3-14

Table 3-2. Concentrations of selected radionuclides in sediment samples collected in 1975 from wells USGS 93 and USGS 96. 3-15

Table 3-3. Concentrations of selected radionuclides in sediment samples collected in 1976 from wells 76-1, 76-2, and 76-3. 3-16

Table 3-4. Concentrations of selected radionuclides in sediment samples collected in 1976 from wells 76-4, 76-4A, 76-5, 76-6, and 77-2. 3-17

Table 3-5. Concentrations of radionuclides ²³⁸Pu, ^{239,240}Pu, ²⁴¹Am, ⁹⁰Sr, and ¹³⁷Cs in split samples reanalyzed on the basis of initially statistically positive results listed in tables 3-3 and 3-4 3-18

Table 3-6. Concentrations of radionuclides ²³⁸Pu, ^{239,240}Pu, ²⁴¹Am, ⁹⁰Sr, ¹⁴⁴Ce, ¹³⁷Cs, and ⁶⁰Co in sediment samples collected in 1978 from wells 78-2, 78-3, and 78-5. 3-19

Table 3-7. Concentrations of radionuclides ²³⁸Pu, ^{239,240}Pu, ²⁴¹Am, ⁹⁰Sr, ¹⁴⁴Ce, ¹³⁷Cs, and ⁶⁰Co in new samples taken from cores collected during 1976-77 3-21

Table 3-8. Concentrations of radionuclides ²³⁸Pu, ^{239,240}Pu, ²⁴¹Am, ⁹⁰Sr, and ¹³⁷Cs in sediment samples collected in 1987 from wells D-O2, D-O6A, and TW-1. 3-23

Table 3-9. Comparison of results obtained by EG&G (table 3-8) with results obtained by the Radiological and Environmental Sciences Laboratory for radionuclides ²³⁸Pu, ^{239,240}Pu, and ²⁴¹Am in samples from well TW-1, B-C interbed. 3-25

Table 3-10. Summary of statistically significant (>3 s) concentrations for waste radionuclides in samples from selected depth intervals and wells 3-26

Table 3-10A. Interval 1 (10 to 75 feet (3 to 23 meters) below land surface) 3-27

Table 3-10B. Interval 2 (82 to 142 feet (25 to 43 meters) below land surface) 3-28

Table 3-10C. Interval 3 (217 to 265 feet (66 to 81 meters) below land surface). 3-36

Table 3-10D. Background sites. 3-39

| | |
|---|------|
| Table 3-11. Comparison of actinide data (^{238}Pu , $^{239,240}\text{Pu}$, and ^{241}Am from tables 3-1 through 3-9 of this report) for the B-C and C-D interbeds. | 3-40 |
| Table 3-12. Actinide detections (^{241}Am , ^{238}Pu , and $^{239,240}\text{Pu}$) reported in tables 3-1 through 3-9 of this report from the B-C interbed | 3-41 |
| Table 3-13. Actinide detections (^{241}Am , ^{238}Pu , and $^{239,240}\text{Pu}$) reported in tables 3-1 through 3-9 of this report from the C-D interbed. | 3-42 |
| Table 3-14. Number of radionuclide detections in water samples from the perched water zone at the Radioactive Waste Management Complex using the site contractor's criterion of detection, 2s and greater | 3-11 |
| Table 4-1. Surface complexation models for describing the adsorption of U(VI) by selected mineral surfaces | 4-6 |
| Table 4-2. Computed Am K_r values of five surface complexation models for water samples from the Idaho National Engineering and Environmental Laboratory | 4-8 |
| Table 4-3. Computed U K_r values of five surface complexation models for water samples from the Idaho National Engineering and Environmental Laboratory | 4-9 |
| Table 4-4. Chemical compositions of water speciated with the PHREEQC model. | 4-11 |
| Table 4-5. Calculated partial pressures of CO_2 and O_2 and redox state distributions of aqueous Np and Pu in water samples from sites at or near the Subsurface Disposal Area | 4-12 |
| Table 4-6. Measured pH values and calculated aqueous speciation of Np and Pu in water samples from sites at or near the Subsurface Disposal Area | 4-13 |
| Table 4-7. Calculated distribution of Np and Pu surface complexes on goethite and molar ratios of total sorbed to total aqueous concentrations for Np (K_r Np) and Pu (K_r Pu) for water samples from sites at or near the Subsurface Disposal Area | 4-14 |
| Table 4-8. Calculated aqueous Np and Pu redox-state distributions at equilibrium for selected water samples from the Idaho National Engineering and Environmental Laboratory determined using either the ANSTO or the EQ3/6 data bases | 4-16 |
| Table 4-9. Concentrations and redox states of the three dominant species of Np and Pu in water samples from the Idaho National Engineering and Environmental Laboratory calculated on the basis of the ANSTO and EQ3/6 data bases | 4-18 |
| Table 4-10. K_r values of Np and Pu surface complexes on goethite for water samples from the Idaho National Engineering and Environmental Laboratory, calculated on the basis of data from the ANSTO and EQ3/6 data bases | 4-17 |
| Table 5-1. Important (*) and usually unimportant (**) oxidation states of some actinides in natural rock-water systems (from Langmuir, 1997). | 5-1 |
| Table 5-2. Summary of K_d s obtained using batch and column tests reported by Dicke (1997) | 5-9 |
| Table 5-3. Particle-size distribution for five interbed sediments and their composite, and for crushed basalt used in K_d experiments at the Idaho National Engineering and Environmental Laboratory | 5-10 |
| Table 5-4. Composition of synthetic ground water, water from the Snake River Plain aquifer, and perched and soil-zone water. | 5-10 |
| Table 5-5. Np K_d s from references considered applicable to the Idaho National Engineering and Environmental Laboratory. | 5-16 |
| Table 5-6. Np K_d references not considered applicable to the Idaho National Engineering and Environmental Laboratory. | 5-16 |
| Table 5-7. Summary of U(VI) K_r s calculated for four surface complexation models calibrated to U(VI) breakthrough in column experiments at pH 8.48 | 5-26 |
| Table 5-8. Effect of cation exchange capacity on K_d s | 5-31 |
| Table 6-1. Variogram models, parameters, and cross-validation statistics for thickness and top elevation variables for surficial sediments and interbeds A-B, B-C, and C-D. | 6-4 |
| Table 6-2. Relative confidence in kriging estimates. | 6-6 |
| Table 6-3. Summary of hydrologic characterizations used in the Interim Risk Assessment (IRA) model | 6-7 |

xii Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 6-4. Estimated permeability of fractured basalts at the Subsurface Disposal Area (SDA) considered for use in the Interim Risk Assessment model 6-10

Table 6-5. Characteristics of TETRAD discretization 6-19

Table 6-6. Summary and review of IRA model calibration steps, target data, and estimated properties used by Magnuson and Sondrup 6-20

Conversion Factors

| Multiply | By | To obtain |
|--------------------------------------|------------|---|
| Length | | |
| centimeter (cm) | 0.3937 | inch (in.) |
| millimeter (mm) | 0.03937 | inch (in.) |
| meter (m) | 3.281 | foot (ft) |
| kilometer (km) | 0.6214 | mile (mi) |
| micron (µm) | 0.00003937 | inch (in.) |
| Area | | |
| square meter (m ²) | 0.0002471 | acre |
| square kilometer (km ²) | 247.1 | acre |
| square centimeter (cm ²) | 0.001076 | square foot (ft ²) |
| square meter (m ²) | 10.76 | square foot (ft ²) |
| square centimeter (cm ²) | 0.1550 | square inch (in ²) |
| square kilometer (km ²) | 0.3861 | square mile (mi ²) |
| Volume | | |
| cubic centimeter (cm ³) | 0.06102 | cubic inch (in ³) |
| liter (L) | 61.02 | cubic inch (in ³) |
| cubic meter (m ³) | 35.31 | cubic foot (ft ³) |
| cubic kilometer (km ³) | 0.2399 | cubic mile (mi ³) |
| Flow rate | | |
| meter per day (m/d) | 3.281 | foot per day (ft/d) |
| meter per year (m/yr) | 3.281 | foot per year (ft/yr) |
| millimeter per year (mm/yr) | 0.03937 | inch per year (in/yr) |
| Mass | | |
| gram (g) | 0.03527 | ounce, avoirdupois (oz) |
| kilogram (kg) | 2.205 | pound avoirdupois (lb) |
| Pressure | | |
| kilopascal (kPa) | 0.009869 | atmosphere, standard (atm) |
| kilopascal (kPa) | 20.88 | pound per square foot (lb/ft ²) |
| kilopascal (kPa) | 0.1450 | pound per square inch (lb/in ²) |

| | | |
|--|---------|--|
| Density | | |
| kilogram per cubic meter (kg/m ³) | 0.06242 | pound per cubic foot (lb/ft ³) |
| gram per cubic centimeter (g/cm ³) | 62.4220 | pound per cubic foot (lb/ft ³) |
| Radioactivity | | |
| becquerel per liter (Bq/L) | 27.027 | picocurie per liter (pCi/L) |
| Specific capacity | | |
| liter per second per meter [(L/s)/m] | 4.831 | gallon per minute per foot [(gal/min)/ft] |
| Hydraulic conductivity | | |
| meter per day (m/d) | 3.281 | foot per day (ft/d) |
| Hydraulic gradient | | |
| meter per kilometer (m/km) | 5.27983 | foot per mile (ft/mi) |
| Transmissivity* | | |
| meter squared per day (m ² /d) | 10.76 | foot squared per day (ft ² /d) |

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows: °F=(1.8×°C)+32

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows: °C=(°F-32)/1.8

Vertical coordinate information is referenced to the “North American Vertical Datum of 1988 (NAVD 88)”

Horizontal coordinate information is referenced to the “Idaho State Plane Coordinate System East Zone Datum of 1927 (NAD27)”

Altitude, as used in this report, refers to distance above the vertical datum.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25°C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Acronyms

| <u>Acronym</u> | <u>Definition</u> |
|-----------------------|--|
| ANSI | American National Standards Institute |
| ANSTO | Australian Nuclear Science and Technology Organization |
| ASTM | American Society for Testing Materials |
| BLR | Big Lost River |
| BWIP | Basalt Waste Isolation Program |
| CEC | cation exchange capacity |
| COC | contaminant of concern |
| COPC | contaminant of potential concern |
| DO | dissolved oxygen |
| DOC | dissolved organic carbon |
| DOE | Department of Energy |
| DOT | Department of Transportation |
| DQO | data quality objective |
| EDS | electron microscopy/energy dispersive X-ray spectroscopy |
| EG&G | former site contractor |
| EPA | Environmental Protection Agency |
| EQ3/6 | thermodynamic database |
| ERDA | Energy Research and Development Administration |

| | |
|---------|---|
| FSMs | field sampling methods |
| FSP | field sampling plan |
| FY | fiscal year |
| HATCHES | thermodynamic database |
| ICPP | Idaho Chemical Processing Plant |
| INEEL | Idaho National Engineering and Environmental Laboratory |
| INTEC | Idaho Nuclear Technology and Engineering Center |
| IRA | Interim Risk Assessment |
| IUPAC | International Union of Pure and Applied Chemistry |
| LEA | local equilibrium assumption |
| LMITCO | Lockheed Martin Idaho Technologies, Inc. |
| LSD | land surface datum |
| LSIT | Large Scale Infiltration Test |
| MCL | maximum concentration limit |
| MDL | minimum detection level |
| NEA | Nuclear Energy Agency |
| NIST | National Institute of Standards and Technology |
| OECD | Organization for Economic Cooperation and Development |
| PHREEQC | computer program (pH redox equilibrium equations in the C programming language) |
| PNNL | Pacific Northwest National Laboratory |
| QAP | quality assurance plan |
| QAPjP | quality assurance project plan |
| QC | quality control |
| RATEQ | biogeochemical reactive-transport model |
| RESL | Radiological and Environmental Sciences Laboratory |
| RI/FS | remedial investigation/feasibility study |
| ROD | record of decision |
| RWMC | Radioactive Waste Management Complex |
| SAP | sampling analysis plan |
| SCM | surface complexation model |
| SDA | Subsurface Disposal Area |
| SI | saturation indices |
| SMO | Sample Management Office |
| SOW | statement of work |
| SRP | Snake River Plain |
| TETRAD | multiphase flow and solute transport computer code |
| TDS | total dissolved solids |
| TOC | total organic carbon |
| TRA | Test Reactor Area |
| TSA | Transuranic Storage Area |
| USGS | United States Geological Survey |
| VOC | volatile organic compound |
| WAG-3 | Waste Area Group 3 |
| WAG-7 | Waste Area Group 7 |
| WRIT | Waste/Rock Interaction Technology |
| XRD | X-ray diffraction |

Chemical Symbols

| | |
|-----------------------------------|---|
| Al | aluminum |
| Am | americium |
| AN-65 | labradorite |
| Ba | barium |
| Br | bromide |
| Ca | calcium |
| CaCO ₃ | calcium carbonate |
| CaCl ₂ | calcium chloride |
| Ca(NO ₃) ₂ | calcium nitrate |
| Ce | cerium |
| Cl | chloride |
| Cm | curium |
| Co | cobalt |
| CO ₂ | carbon dioxide |
| CO ₃ | carbonate |
| Cs | cesium |
| DTPA | diethylenetriaminepentacetic acid |
| EDTA | ethylenediaminetetraacetic acid |
| Eh | redox potential |
| F | fluoride |
| fo-50/10-90 | olivine |
| Fe | iron |
| HEDTA | N-hydroxyethylene-diaminetriacetic acid |
| H | hydrogen |
| H ₂ O | water |
| HCl | hydrochloric acid |
| HCO ₃ | bicarbonate |
| HClO ₄ | perchloric acid |
| HNO ₃ | nitric acid |
| K | potassium |
| N | nitrogen |
| Na | sodium |
| NaNO ₃ | sodium nitrate |
| NH ₄ | ammonium |
| NO ₂ | nitrite |
| NO ₃ | nitrate |
| Np | neptunium |
| NTA | nitriolotriacetic acid |
| Mg | magnesium |
| Mn | manganese |
| O ₂ | oxygen |
| OH | hydroxide |
| P | phosphorus |

| | |
|------------|--|
| P_{CO_2} | partial pressure of carbon dioxide |
| PO_4 | phosphate |
| Pu | plutonium |
| Ru | ruthenium |
| Sb | antimony |
| SiO_2 | silica |
| SO_4 | sulfate |
| Sr | strontium |
| Th | thorium |
| U | uranium |
| pH | hydrogen ion activity |
| XO | metal oxide |
| Zn | zinc |
| 2H | hydrogen isotope |
| ^{18}O | oxygen isotope |
| δ | delta notation for oxygen and hydrogen stable isotope ratios |

Symbols

q = flux density

K_{sat} = saturated hydraulic conductivity

ψ = water pressure

ρ = density of water

g = gravitational acceleration

θ = water content

z = vertical distance

K = hydraulic conductivity

∂ = differential operator

C = differential water capacity

K_d = distribution coefficient (volume per mass)

C_s = mass of solute adsorbed per mass of adsorbent

C_{Aq} = mass of solute dissolved per volume of water

R_F = retardation factor

P_b = bulk density (mass per volume)

K_r = distribution coefficient (mass per mass per unit volume or unit mass)

S_T = surface site density

M = molar concentration

m = molal concentration

K_a = distribution coefficient (defined on basis of surface area)

S_A = specific surface area

k = permeability

k_v = vertical permeability

k_h = horizontal permeability

n_f = fracture porosity

V_L = longitudinal dispersivity

P_c = capillary pressure

h = capillary rise

σ = interfacial surface tension

Θ = contact angle

b_f = fracture aperture

k_{fc} = fracture continuum permeability

V_T = transverse dispersivity

I_g = gas-phase tortuosity

n_m = effective matrix porosity

$^\circ$ = degrees

∇ = gradient

\propto = proportionality

Abstract

The U.S. Department of Energy (DOE) requested that the U.S. Geological Survey conduct an independent technical review of the Interim Risk Assessment (IRA) and Contaminant Screening for the Waste Area Group 7 (WAG-7) Remedial Investigation, the draft Addendum to the Work Plan for Operable Unit 7-13/14 WAG-7 comprehensive Remedial Investigation and Feasibility Study (RI/FS), and supporting documents that were prepared by Lockheed Martin Idaho Technologies, Inc.

The purpose of the technical review was to assess the data and geotechnical approaches that were used to estimate future risks associated with the release of the actinides americium, uranium, neptunium, and plutonium to the Snake River Plain aquifer from wastes buried in pits and trenches at the Subsurface Disposal Area (SDA). The SDA is located at the Radioactive Waste Management Complex in southeastern Idaho within the boundaries of the Idaho National Engineering and Environmental Laboratory. Radionuclides have been buried in pits and trenches at the SDA since 1957 and 1952, respectively. Burial of transuranic wastes was discontinued in 1982.

The five specific tasks associated with this review were defined in a "Proposed Scope of Work" prepared by the DOE, and a follow-up workshop held in June 1998. The specific tasks were (1) to review the radionuclide sampling data to determine how reliable and significant are the reported radionuclide detections and how reliable is the ongoing sampling program, (2) to assess the physical and chemical processes that logically can be invoked to explain true detections, (3) to determine if distribution coefficients that were used in the IRA are reliable and if they have been applied properly, (4) to determine if transport model predictions are technically sound, and (5) to identify issues needing resolution to determine technical adequacy of the risk assessment analysis, and what additional work is required to resolve those issues.

Executive Summary

This review of the Interim Risk Assessment (IRA) for Waste Area Group 7 (WAG-7) 13/14 Operable Units focuses on the fate and transport of selected actinides—americium (Am), uranium (U), neptunium (Np), and plutonium (Pu)—in mixed transuranic wastes buried in the shallow subsurface at the Subsurface Disposal Area (SDA), Radioactive Waste Management Complex (RWMC), Idaho National Engineering and Environmental Laboratory. The purpose of the IRA is to quantify the risk to human health and safety associated with the potential release of toxic and hazardous waste buried in shallow pits and trenches in the SDA.

The review team believes that the principal investigators for the IRA have done a commendable job of integrating the available information, justifying the different approaches used, documenting their assumptions, and acknowledging data limitations that they view as critical to the conclusions reached in the assessment. The latter is especially noteworthy and appreciated by the review team because of the complex issues involved in this review. The review team also acknowledges the excellent cooperation of the principal investigators of the IRA study in responding to requests for clarification, additional information, and supporting documentation.

The review team shares many of the concerns about data limitations that were expressed by the principal investigators of the IRA and other supporting studies. It is premature to conclude that these data limitations invalidate the conclusions reached in the IRA; however, they do raise doubt about the overall rigor of the study.

The contaminant transport analysis that was used in support of the IRA is based on (1) a source-term release-rate model that assumes the entire inventory of buried actinides will be mobilized at different rates over an extended period of time, (2) laboratory- or literature-derived distribution coefficients (K_{ds}) that define the capacity of the media to remove contaminants that are presumed to be in solution or behave like they are in solution, and (3) a flow model that tracks the migration of waterborne contaminants in time and space. As pointed out in the IRA, the release-rate model has not been calibrated and remains a major deficiency that needs to be resolved before completion of the Comprehensive Remedial Investigation/Feasibility Study (RI/FS). Many of the factors that affect the fate and transport of contaminants in the subsurface apply as well to the release-rate model.

The review team did not address issues that involved definition of the source term and modeling of contaminant release rates, both of which add additional uncertainty to an already complex problem. It is clear that definition of the source term and release rates are at least as important as other issues related to the formulation of the computational scheme to predict actinide transport. The solubility of the actinides depends on their chemical form and on the chemistry of the water that comes into contact with the actinides. Water chemistry is affected by the degradation and dissolution of other wastes that are buried with or near the actinide-bearing wastes. The implications of local water chemistry on actinide solubility, release rates, and contaminant transport are uncertain.

With a few exceptions, predictions of future actinide concentrations (Am, U, Np, and Pu) in the Snake River Plain aquifer that are presented in the IRA are less than, and in many cases significantly less than, maximum contaminant levels established by the U.S. Environmental Protection Agency. Notable exceptions are U and Np. Predicted concentrations, however, are based on limited and incomplete data that, in the opinion of the review team, are not adequate to demonstrate adherence to the guiding philosophy for model development presented in the IRA.

The guiding philosophy in developing the numerical simulator (Magnuson and Sondrup, 1998) was to use technically defensible estimates for the K_{ds} and conservative estimates of model parameters wherever “realistic” estimates were not available. The intent of the IRA was to present a conservative (but not overly conservative or unrealistic) scenario. It was not the intent of the IRA to present a “worst-case scenario”. However, the distinction between what is conservative or technically defensible and what is realistic is oftentimes blurred.

The review team examined many supporting documents for the IRA in arriving at the conclusion that model results are not shown to be conservative because of incomplete and inadequate knowledge of subsurface flow conditions and transport processes. For example, the K_{ds} that were used for Am, U, and Pu transport were derived from a limited number of batch tests of a single composite sedimentary interbed sample. This sample was prepared from a mixture of five samples from different depths and stratigraphic units and sieved to represent only the fine fraction of an otherwise heterogeneous suite of samples with different physical and chemical properties. Forty percent of the bulk sample (the coarse fraction) was eliminated from the batch tests, possibly biasing the results toward higher K_{ds} because of the greater surface

area represented by the finer size fraction. Furthermore, the batch tests were conducted using synthetic water with concentrations of major cations and anions that were generally lower than those measured for ground water and perched water near the SDA. The lower ionic strength of the solution reduces competition for available sorbing sites leading to higher K_d estimates. The synthetic water also was undersaturated with respect to calcite, even though calcite is a common mineral phase in the sedimentary interbeds. This is a potentially serious departure from actual field conditions because aqueous stability and mobility of the actinides may be enhanced by the formation of weakly sorbing carbonate complexes.

The importance of carbonate complexation is demonstrated in the thermodynamic modeling that was conducted as part of this review. Formation of carbonate complexes was also suggested, along with colloidal transport, as possible explanations for the early elution of a “fast fraction” that was observed in the column experiments for Am and Pu referenced in this review. Although the K_d s selected for use in the numerical simulator were selected from the lower end of the range of these laboratory-derived measurements, it is not obvious that the limited data and experimental protocols provide adequate opportunity to demonstrate that these K_d s are reasonably conservative or technically defensible.

The K_d issue is further complicated by the manner in which K_d s are dealt with in the numerical simulator. The numerical simulator treats individual K_d s as constant and independent of the effects that other contaminants, both actinide and nonactinide, have on competition for sorbing sites. This approach assumes that the availability of sorbing sites is infinite. Additionally, model simulations of flow indicate that the downward flux of waterborne contaminants in the subsurface is not uniformly distributed. This is a realistic portrayal of infiltration and percolation in the unsaturated zone that places higher stresses locally on the sorption capacity of the media.

The review team is of the opinion that more, and presumably better, data are needed to justify predictions of actinide transport presented in the numerical simulator that forms the basis of the IRA. In the absence of “reliable field calibration opportunities” for the actinides, the reviewers believe that several of the simplifying assumptions and model parameters selected for use in the numerical simulator warrant much greater scrutiny than might otherwise be the case if it were possible to evaluate model performance on the basis of direct comparisons to field observations.

Calibration of the numerical simulator is based on matching short-term observations of perched water in the unsaturated zone (flow component) and short-term measurements of nitrate concentrations in the saturated zone (transport component). These calibration controls are only indirectly suggestive of the model’s ability to predict long-term movement of the actinides. No attempt was made, and the review team believes rightly so, to calibrate the model to actinide detections in the field. For several reasons, calibration of actinide transport to actual field observations is not realistic. The limited number of detections, their sporadic and seemingly random nature, and uncertainty over whether or not these detections represent dissolved-phase transport, preclude their use for this purpose, and in that sense, we agree with the approach presented in the IRA. However, the validity of using the nondetects as general indicators of model performance is questionable and may even be misleading. The only valid conclusion that can be reached from the simulated results is that the model predicts actinide concentrations that are below the minimum detection level. Nothing can be said about whether the model overpredicts or underpredicts actinide concentrations because there is no way to objectively confirm or refute the claim.

Although the apparent lack of widespread contamination is good news, because it probably means that there is no wholesale release of the actinides at concentrations above the minimum detection level, it does present a dilemma. One of the best defenses of a model’s ability to predict future outcomes is its ability to match the historic record. The longer the historic record, the higher the confidence in the predictions. To help mitigate the uncertainty that this dilemma presents, the review team feels that more rigorous definition of the hydrologic properties of the sedimentary interbeds and the actinide distribution coefficients associated with these geologic units are needed.

The numerical simulator for the IRA places considerable emphasis on the role of the sedimentary interbeds to arrest the movement of the actinides. The review team feels that this emphasis is appropriate. However, because the sedimentary interbeds figure so prominently in the modeling of flow and transport, thorough characterization of their hydrologic and geochemical properties should be a very high priority.

Characterization of the interbeds should include definition of the vertical and lateral variability of their physical, hydrological, and chemical properties. The validity of simplifying assumptions, that are needed to

ES-4 Review of the transport of selected radionuclides in the Interim Risk Assessment

represent these geologic units in a numerical simulator, cannot be established without data that can show how these basic properties vary in space.

Similarly, K_d s for the sedimentary interbeds should be determined using samples that are truly representative of the different lithologic units and subunits present in the sedimentary interbeds. Homogenization of these samples, for purposes of expediting analysis or determining average properties, should be avoided. Batch and column K_d experiments should be conducted with solutions that more closely replicate both the natural- and contaminated-water chemistry in the vicinity of the RWMC. These tests should also include an assessment of the impact that other contaminants in solution have on measured K_d s. The validity of using a constant K_d , for individual actinide species, needs to be evaluated in the context of a dynamically evolving chemical system. The evolution of this system is affected by temporal and spatial variations in water chemistry, actinide and nonactinide contaminant concentrations in the ground water, release rates of other contaminants that are buried at the SDA, and the affinity of these other contaminants to occupy sorption sites.

Finally, there is considerable uncertainty over how the exclusion of lateral flow of water from outside the SDA affects actinide predictions. Until recently (1999), there was very little evidence to demonstrate that water, diverted from the Big Lost River (BLR) into the spreading areas located west of the SDA, can migrate laterally in the unsaturated zone beneath the SDA. The conceptual model of flow in the unsaturated zone beneath the SDA assumes that essentially all flow is derived from precipitation and surface runoff that occurs within the immediate vicinity of the SDA. Exclusion of lateral flow from outside the SDA (BLR and/or spreading areas) may represent a significant departure from real world conditions. If so, then interpretations of field data that were used to calibrate the flow and transport component of the numerical simulator may be seriously compromised. Until the effects of lateral flow are better defined, then the reliability of the numerical simulator to predict the fate and transport of waterborne contaminants in the subsurface will remain controversial. Thus, the intent to present a “technically defensible” approach that would lead to a conservative (but not overly conservative or unrealistic) scenario has not been demonstrated.

1.0 Introduction

The Interim Risk Assessment (IRA) and Contaminant Screening for the Waste Area Group 7 (WAG-7) Remedial Investigation (Becker and others, 1998) was prepared for the U.S. Department of Energy (DOE) by Lockheed Martin Idaho Technologies, Inc. (LMITCO) as a formal record of work completed for the Waste Area Group Comprehensive Remedial Investigation and Feasibility Study (RI/FS). The draft Addendum to the Work Plan for Operable Unit 7-13/14 WAG-7 RI/FS (DOE, 1998) defined revised strategies and additional requirements for conducting the WAG-7 RI/FS. These two reports and supporting documents will be used to complete the draft Record of Decision (ROD) for remediation of WAG-7 by December 2002. The DOE, in order to prepare for ROD negotiations with the U.S. Environmental Protection Agency and the State of Idaho, requested that the USGS conduct an independent technical review of the Interim Risk Assessment, the Addendum, and associated documents.

The current version of the IRA represents a preliminary analysis of the potential risks to human health and safety associated with the release of buried mixed-chemical, low-level, and high-level wastes at the Radioactive Waste Management Complex (RWMC) Subsurface Disposal Area (SDA) (fig 1-1). The current IRA is a comprehensive evaluation of risks associated with all contaminants of potential concern (COPC's). This review of the IRA is concerned only with the analysis of predicted releases of long-lived actinides (Am, U, Np, and Pu) to the accessible environment. It is further limited to a review of the radionuclide data and geotechnical methodologies that were used in the numerical model to predict actinide migration in the subsurface. Evaluation of the contaminant source term and the model that was used to predict the rate and timing of releases of the actinides from buried waste containers are not included in this review. For purposes of this review, the accessible environment is defined as the Snake River Plain (SRP) aquifer.

The SDA comprises an area 975 m long from east to west and 520 m wide along its eastern boundary. Radioactive wastes have been buried within its boundaries in trenches since 1952 and in pits since 1957. The pits and trenches range from 15 to 91 m wide, 76 to 335 m long, and 1.4 to 4.6 m deep. Burial of transuranic wastes at the SDA ceased in 1982.

The potential for future releases of the actinides to the SRP aquifer and the risks associated with those releases depend on the source term (quantity and types of other contaminants present, their chemical form, and their

release rates) and the mobility of the actinides themselves. Actinide mobility presumably is enhanced by the presence of water because water moves and is constantly replenished, which sustains downward movement of the contaminant. The form of the contaminant determines how mobile it will be as an aqueous species, whether in true solution or in suspension. Its movement from beneath present burial sites to the accessible environment is controlled by water and rock interactions that are determined by the geology and chemistry of the environment that it comes into contact with. These complex physical and chemical processes can be expected to vary in both time and space.

1.1 Purpose

The purpose of this technical review was to evaluate the data and the geotechnical approaches that were used by LMITCO to estimate future risks associated with the release of four actinides (Am, U, Np, and Pu) to the accessible environment (SRP aquifer) from wastes buried in pits and trenches at the SDA.

1.2 Scope

The scope of this review and the organization of this report are defined by a series of five tasks, each framed as a question. These questions were developed from discussions with DOE based on a preliminary "Proposed Scope of Work" prepared by DOE and a follow-up workshop in June 1998 that was attended by review-team members, DOE, and LMITCO personnel. The workshop included summary presentations by the principal investigators from LMITCO who were involved in the development of the IRA and supporting studies, and a visit to the RWMC that was hosted by the DOE and LMITCO personnel involved in site monitoring activities.

The scope and objectives of the individual tasks identified in the review proposal are summarized as follows:

1.2.1 Task 1: Review of radionuclide sampling data at the Radioactive Waste Management Complex

Question: How reliable and significant are the reported radionuclide detections, and how reliable is the ongoing sampling program?

The objective of Task 1 was to evaluate the reliability and significance of the reported detections of actinide radionuclides at the RWMC and to assess the reliability of the ongoing sampling program. The radionuclide species to be considered were Am, U, Np, and Pu. Data to be con-

1-2 Review of the transport of selected radionuclides in the Interim Risk Assessment

sidered were data presented in the IRA, data published by the USGS, and any additional data provided by LMITCO and DOE.

Multiple criteria were to be considered in evaluating the available data: (1) statistical significance, (2) isotopic association, (3) consistency of detections with the historical data record, (4) the possibility of cross contamination, and (5) the adequacy of the sampling program.

1.2.2 Task 2: Radionuclide transport processes

Question: What physical and chemical processes can logically be invoked to explain (true) detections?

The objective of Task 2 was to provide reasonable explanations to account for the observed transport of the actinide radionuclides at the SDA, as interpreted from data evaluated in Task 1. Both geochemical and hydrologic factors were to be considered in explaining true detections that were summarized in Task 1. The scope of this task involved (1) speciation calculations to evaluate what conditions at the SDA are consistent with enhanced mobility of Am, U, Np, and Pu, (2) an assessment of the role of colloid-facilitated transport on actinide movement in the subsurface, and (3) an evaluation of the possible role of preferential flow on actinide migration.

1.2.3 Task 3: Distribution coefficients (K_{ds}) and their application to transport analysis

Question: Are K_{ds} that were used in the IRA reliable and have they been applied appropriately?

The objective of Task 3 was to evaluate the reliability and appropriateness of K_{ds} that were used in the fate-and-transport modeling of the actinides as described in the IRA. The scope of this task involved (1) a review of the literature on K_{ds} that may be considered applicable to the RWMC and K_{ds} reported for similar subsurface sediments, (2) an evaluation of K_{ds} used in the IRA in terms of the existing subsurface mineralogy and aqueous geochemical conditions, (3) an evaluation of the experimental protocols used to determine K_{ds} , (4) determination of the extent to which the K_d concept may be applicable to the site, and (5) an assessment of the uncertainty associated with the K_{ds} used for fate-and-transport modeling.

1.2.4 Task 4: Transport model analysis

Question: Are model predictions defensible?

The objective of Task 4 was to evaluate whether or not the 3D model predictions of actinide transport made in support of the IRA are defensible. The scope of this task

includes (1) an evaluation of the conceptual model, (2) and assessment of the numerical model's representation of the stratigraphic framework of the fractured basalts and the role of the sedimentary interbeds, (3) an evaluation of the adequacy of the data sets selected for model calibration, and (4) an assessment of the predictive capabilities of the model.

1.2.5 Task 5: Further work

Question: What are the most significant issues that need to be resolved to support and defend the risk assessment analysis?

Question: What additional work is required to resolve those issues?

The objective of Task 5 was to provide timely interim guidance to several questions. First, what are the most significant issues that need to be resolved to support and defend the risk assessment analysis? Second, what additional work is immediately required to resolve those issues? This interim guidance was offered to provide sufficient lead time to resolve those issues within the time frame of the draft ROD (2002).

The scope of Task 5 included preliminary reviews of the Interim risk Assessment (Becker and others, 1998), results of the Large-Scale Infiltration Test (Wood and Norrell, 1996), Distribution Coefficients and Contaminant solubilities for the Waste Area Group 7 Baseline Risk Assessment (Dicke, 1997), and the flow and transport model (Magnuson and Sondrup, 1998). Additionally, planned work items were evaluated that were identified in the Addendum to the Work Plan (DOE/ID, March 1998). The intent of this task was to focus primarily on data needs rather than analytical approaches.

1.3 Acknowledgments

Preparing a report of this magnitude requires the support of many people. The authors acknowledge the contributions of the following USGS personnel: Elizabeth Jones compiled solid-phase data contained in chapter 3, and the solid-phase data tables were verified against the original data tables by Betty J. Tucker. The authors appreciate the technical reviews of the report that were conducted by LMITCO employees Laurence C. Hull, A. Jeffrey Sondrup, Swen O. Magnuson, Carol Craiglow, and Bruce H. Becker.

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1.4 Report Organization

This report is organized into 7 chapters—Introduction, Conceptual Model, and Tasks 1 through 5. Each chapter with the exception of the introduction contains its own summary.

1-4 Review of the transport of selected radionuclides in the Interim Risk Assessment

2.0 Conceptual model of aqueous-phase fluid flow and contaminant transport

2.1 Regional setting

The Subsurface Disposal Area (SDA) (fig. 1-1) is on the eastern Snake River Plain (SRP), and the ground water immediately below it is part of the large and heavily used SRP aquifer. The climate is semiarid; average annual precipitation is about 22 cm. Subsurface water movement is affected by a variety of topographic and hydrogeologic features, both natural and artificial. The unsaturated zone at the SDA is unusually thick—about 200 m. It also is complex, comprising granular media and consolidated, fractured rock, both of which affect the subsurface hydrology in many ways. These media are highly stratified. The contrasts in properties of adjacent layers may impede downward flow but also may lead to various types of fast, or preferential flow. Near the SDA, surface-water features, notably the Big Lost River (BLR) and spreading areas, sometimes are major sources of infiltration.

Key issues related to subsurface contaminant transport include (1) travel times to and within the aquifer, both average or typical values and the range of values to be expected, and (2) modes of contaminant transport, especially adsorption processes. Some of the complicating factors are the effectiveness of natural and artificial barriers; the direction (horizontal, vertical, or other) of flowpaths; the diffuse or preferential nature of flow; the chemical nature of the contaminants and subsurface media; and sources of water now in the subsurface, such as local precipitation, runoff, and lateral flow from spreading areas or elsewhere.

2.2 Conceptual models

In hydrologic contexts, the term “conceptual model” is used in at least two different ways: (1) An ideal sort of conceptual model was defined by Hoxie (1989) with a quote from Russell (1948) that considers a conceptual model of a natural system to be a “hypothesis which fits the (available) data, which are as simple as compatible with this requirement, and which make it possible to draw inferences subsequently confirmed by observation,” and (2) An applied conceptual model was defined by Anderson and Woessner (1992) as “a pictorial representation of the ground water flow system, frequently in the form of a block diagram or a cross section. The nature of the conceptual model will determine the dimensions of the numerical model and the design of the grid.” In both

usages, the conceptual model relates a physical system to a mathematical model, though definition 1 emphasizes the validity of the connection to the physical system, requiring it to produce “inferences subsequently confirmed by observations,” whereas definition 2 is less rigorous, emphasizing the practical connection to the mathematical model, but not implying that the predictions will necessarily be realistic. In USGS research at Yucca Mountain in Nevada, there has been a continual effort, presented in a series of publications (Montazer and Wilson, 1984; Wittwer and others, 1992; Hoxie, 1989), to create and develop a conceptual model that is intended, with each refinement, to more closely approximate an ideal conceptual model. Research at the INEEL SDA relies heavily on a practical conceptual model that has not been explicitly presented in the INEEL reports but is implied by the assumptions and other details of numerical modeling (Becker and others, 1998; Magnuson and Sondrup, 1998). In this chapter, we describe our best approximation of an ideal conceptual model of transport processes at the SDA. In chapter 6, we explicitly evaluate the practical conceptual model used in the most advanced numerical modeling of actinide transport at this site.

The construction of an ideal conceptual model necessitates choice among competing hypotheses, and recognition of uncertainties of individual components of the model. One example of competing hypotheses is whether sedimentary interbeds are a major retarding influence on vertical contaminant transport or an expediting influence because of preferential flowpaths within them. Another is whether the perched water commonly observed within and above interbeds comes from local infiltration whose downward flow is impeded or from lateral flow from areas that sometimes are sources of substantial infiltration (for example, the spreading areas west of the SDA).

2.3 Geologic framework

The geologic framework of the SDA consists of interbedded basalts and sediments of Quaternary age. Basalt flows erupted from numerous fissures and small shield volcanoes located on and near the Arco-Big Southern Butte volcanic rift zone (Kuntz and others, 1992). Sediment consists of alluvial and eolian deposits derived from the ancestral channel and floodplain of the BLR (Rightmire and Lewis, 1987b; Hughes, 1993). These deposits make up a thick unsaturated zone and the SRP aquifer at the SDA.

2-2 Review of the transport of selected radionuclides in the Interim Risk Assessment

2.3.1 Geologic data

The geologic framework of the SDA and adjacent areas has been characterized on the basis of data from 94 wells (Magnuson and Sondrup, 1998). About half of these wells are at and near the SDA (figs. 2-1 and 2-2). Continuous cores ranging in length from less than 30 m to 550 m were obtained from 34 of the 94 wells (Davis and others, 1997); however, only three of these cores are longer than 90 m. Most basalt cores represent nearly complete recovery. Past recoveries of sediment cores ranged from 0 to 100 percent, but commonly were less than 50 percent (Hughes, 1993; Burgess and others, 1994). Common borehole geophysical logs, such as caliper, neutron, natural-gamma, and density logs, were obtained from most wells (Bartholomay, 1990a). These wells include 20 U.S. Geological Survey wells that are labeled as USGS 9, 87, 88, 89, 90, 91, 92, 93, 93A, 94, 95, 96, 96A, 96B, 105, 109, 117, 118, 119, and 120 in figures 2-1 and 2-2.

Numerous studies have been conducted to characterize the geohydrologic properties of basalt and sediment at the SDA. Kuntz and others (1980) described the geologic ages, petrographic characteristics, and paleomagnetic properties of basalt cores from wells 77-1, 76-6, USGS 93A, USGS 94, and USGS 95, located at and near the SDA (fig. 2-2), that form the foundation of stratigraphic interpretations at the SDA; basalt cores from three additional wells, C1A, WWW 1, and USGS 118, were evaluated for paleomagnetic properties at a later time. Stratigraphic relations were refined by Anderson and Lewis (1989) and Anderson and others (1996) using a combination of these core data and natural-gamma logs from 72 wells at and near the SDA. Rightmire (1984) and Rightmire and Lewis (1987b) described the grain-size distributions, bulk mineralogy, clay mineralogy, carbonate contents, and cation exchange capacities of surficial sediment and sedimentary interbeds on the basis of samples from 18 coreholes and selected waste pits at and near the SDA. Hughes (1993) described the mean grain sizes, sorting, skewness, kurtosis, general lithologies, and interpreted depositional environments and sedimentary structures of interbeds on the basis of samples obtained from 17 shallow cores at the SDA. Hydraulic characteristics of the basalt and sediment have been evaluated on the basis of numerous aquifer tests (Ackerman, 1991; Wylie and others, 1995), *in situ* and laboratory measurements of geologic materials (Bishop, 1991; Bishop, 1996; Welhan and Wylie, 1997), and simulations of data obtained from the Large-Scale Infiltration Test (LSIT), which was conducted about 1.5 km south of the SDA (Magnuson, 1995). Despite these and other studies, currently not enough is known about the characteristics and distribution of the

fine-scale features of basalt and sediment that are most likely to affect the potential for downward and lateral movement of water and wastes at the SDA. This is because these features throughout the SDA have not been characterized in a systematic and comprehensive way.

2.3.2 Stratigraphy

At least 11 basalt-flow groups, 10 sedimentary interbeds, and a veneer of surficial sediment are present between the land surface and the uppermost 60 m of the aquifer at the SDA (fig. 2-1) (Anderson and Lewis, 1989; Anderson and Bartholomay, 1995; Anderson and others, 1996). Basalt-flow groups informally are referred to as A through I. Sedimentary interbeds are referred to as A-B through H-I; interbeds A-B, B-C, and C-D are the thickest and most widespread interbeds. They also have been referred to in previous studies as the 30-ft (9-m), 110-ft (34-m), and 240-ft (73-m) interbeds, respectively. In this report, the letter designation will be used to identify these interbeds. Each flow group consists of from one to five separate basalt flows (Kuntz and others, 1980). Sedimentary interbeds and the surficial sediment consist of well sorted to poorly sorted deposits of clay, silt, sand, and gravel (Rightmire and Lewis, 1987a, b; Hughes, 1993). Basalt makes up about 90 percent of the volume of this stratigraphic section. Geologic ages of basalt flows in the section range from about 100 thousand years for those of flow group A to about 640 thousand years for those of flow group I. Ages of sedimentary interbeds A-B, B-C, and C-D range from about 100 thousand to 230 thousand years. The surficial sediment has been deposited during the past 100 thousand years following the eruption of basalt-flow group A. Because of their young ages and shallow depths, the surficial sediment and sedimentary interbeds A-B, B-C, and C-D are mostly unconsolidated.

2.3.3 Basalt flows

Source vents for most basalt flows at and near the INEEL, including those at the SDA, are concentrated in volcanic rift zones that trend perpendicular to the axis of the eastern SRP and parallel to the adjacent mountain ranges (Kuntz and others, 1992; Kuntz and others, 1994). Volcanic rift zones are characterized by eruptive and non-eruptive fissures, dikes, monoclines, faults, graben, and volcanoes having elongated slot-shaped vents (Rodgers and others, 1990; Kuntz, 1992; Kuntz and others, 1992; Smith and others, 1996). The distribution of fissures, dikes, and volcanoes is of hydrologic importance at and near the SDA because these features probably are numer-

ous and may greatly affect the range and distribution of hydraulic conductivity and the movement of ground water and wastes (Anderson and others, 1999). Areas proximal to volcanic vents are composed of highly permeable basalt flows and other volcanic deposits that may provide localized, preferential pathways for ground-water flow and movement of wastes. Dikes are thin, dense, vertical sheets of intrusive rock that locally may impede the movement of ground water and wastes. Noneruptive fissures that parallel dikes locally may provide additional highly permeable conduits for ground-water flow and movement of wastes. The SDA lies within a suspected vent corridor, one of many narrow, northwest-trending extensional features within and near the Arco-Big Southern Butte volcanic rift zone where there is a high probability for concealed volcanic vents, feeder dikes, and open fissures (Anderson and Liszewski, 1997; Anderson and others, 1999). The heterogeneity of volcanic rocks within this and other nearby vent corridors may impart complex anisotropy to the hydrologic system at and near the SDA.

2.3.3.1 Typical basalt-flow characteristics

A basalt-flow group, such as A through I at the SDA (fig. 2-1), consists of one or more distinct basalt flows deposited during a single, brief, eruptive event (Kuntz and others, 1980). All basalt flows of a group erupted from the same vent or several nearby vents, represent the accumulation of one or more lava fields from the same magma, and have similar geologic ages, paleomagnetic properties, and chemical compositions (Anderson and Bartholomay, 1995). The basalt flows mostly were deposited as tube-fed pahoehoe flows in the medial to distal parts of their respective lava fields. Individual flows generally range from 3 to 15 m thick and locally are interbedded with scoria and thin layers of sediment. Tube-fed pahoehoe flows, which are the most common type of flows in the eastern SRP, are characterized by dense interiors and rubbly, vesicular tops and bottoms cut by horizontal and vertical cooling fractures. Fractures and vesicles commonly are coated with fine-grained sediment infill and sometimes with secondary minerals consisting of calcite, clays, and zeolites (Rightmire and Lewis, 1987b; Morse and McCurry, 1997). Fractures within and contacts between individual basalt flows provide a complex network of potential vertical and horizontal pathways for the movement of water and wastes within the unsaturated zone and the aquifer.

2.3.3.2 Typical basalt-flow geochemistry

Most basalt flows at the INEEL have the chemical characteristics of both tholeiitic and alkali olivine basalts.

The small silica and large iron contents indicate that liquid temperatures were approximately 1,050 °C (Stout and Nichols, 1977). These basalts generally are medium to dark gray and range from vesicular, having elongated vesicles up to 4 cm in length, to dense. Typical basalt samples consist mainly of plagioclase feldspar (averaging An₆₅, the composition of labradorite), pyroxene (tentatively identified as augite), and olivine (Fo₅₀ to Fo₉₀); and contain lesser amounts of ilmenite, magnetite, hematite, and accessory apatite (Kuntz and others, 1980; Rightmire and Lewis, 1987b; Knobel and others, 1997). Chemical compositions of selected basalt samples at the INEEL were presented in reports by Kuntz and Dalrymple (1979), Knobel and others (1995), Reed and others (1997), and Collelo and others (1998). Stout and Nichols (1977) state that the augite contains 18.8 percent CaO and that opaque minerals constitute between 7 and 21 percent of the rock. With the exception of some basalt flows at Craters of the Moon (about 2 to 18 thousand years old) and basalt flows associated with Cedar Butte (about 420 thousand years old), there are no significant differences in chemical or mineralogical composition related to age or geographic location among basalt flows of the eastern SRP.

2.3.3.3 Fractures

Basalt flows on the eastern Snake River Plain and underlying the SDA contain abundant horizontal and vertical cooling fractures. Many of these fractures are interconnected and provide potential pathways for the movement of water, suspended sediment, and wastes in the subsurface. In general, the number of and aperture widths of fractures are much greater near the top and bottom of a basalt flow and are greatest along the top surface. Knutson and others (1992) describe a range of typical aperture widths measured from outcrops at the INEEL of from 0.0005 to 0.0025 m; however, aperture widths may range from several micrometers to several meters (Rightmire and Lewis, 1987b). Some of the widest, longest, and deepest fractures occur along the edges of sinuous lobes of inflated pahoehoe flows.

Rightmire and Lewis (1987a) describe fractures in basalt core samples from the SDA that range from those having fresh surfaces to those containing abundant sediment infill. Fractures having fresh surfaces most likely are dead-end fractures that transmit little, if any, water (Wood and Norrell, 1996; Magnuson and Sondrup, 1998). Fractures containing sediment infill or coatings probably are interconnected fractures that periodically transmit large quantities of water. Sediment in these fractures ranges from clay- to sand-sized and was transported by water and wind mainly during the deposition of overlying sedimen-

2-4 Review of the transport of selected radionuclides in the Interim Risk Assessment

tary interbeds. Sediment relations indicate multiple episodes of fracture filling during the geologic past. Post-depositional fracture filling probably continues as infiltrating water transports sediment. Sediment coloration indicates a wide range of minerals and depositional environments and includes hues of tan, brown, red, gray, orange, yellow, and green. Many of the deposits are calcareous. Additional fracture coatings consist of amorphous silica, precipitates consisting of calcite and mixed-layer illite/smectite clays, and possibly zeolites (Rightmire and Lewis, 1987a).

2.3.4 Surficial sediment and sedimentary interbeds

The geologic framework of the SDA has been affected by periodic eruptions of basalt followed by long periods of basin subsidence and sediment accumulation. The surficial sediment and sediment from the A-B, B-C, and C-D interbeds most likely represent deposition from meltwater discharge and periodic floods along the ancestral channel and floodplain of the BLR during past glacial declines (Hughes, 1993; Rathburn, 1993). The presence of gravel in the surficial sediment and the aforementioned interbeds indicates that a watercourse with flow capable of moving gravel at least occasionally traversed the area of the SDA during the past few hundred thousand years. Loess, windblown sediment having grain sizes ranging from fine silt to very fine sand, is a major part of the surficial sediment and sedimentary interbed A-B and, although not documented, probably also is present in sedimentary interbeds B-C and C-D.

The SDA is located near the southern end of the Big Lost trough (Gianniny and others, 1997), an area of past sediment accumulation along the channel and floodplain of the BLR and between the BLR sinks and Mud Lake (fig. 1-1). Sediment within this trough generally grades from a predominance of sand and gravel near the SDA to mainly clay and silt near Mud Lake. Barraclough and others (1976) hypothesized that the SDA was in the floodplain of the BLR prior to the Quaking Aspen Butte eruption and deposition of basalt-flow group A about 100 thousand years ago (Kuntz and others, 1994). Similar migrations of the BLR channel and floodplain, into and away from the SDA, probably occurred many times during the geologic past in response to the eruptions of basalt-flow groups B through I. During periods of volcanic quiescence, sediment accumulated in the topographic depressions of underlying basalt flows. Eolian material derived from the finer fraction of alluvial deposits probably accumulated in these and other areas, including along the flanks of volcanoes. Sedimentary units having large

amounts of clay-sized material probably were deposited in small lakes, some of which were formed by lava dams. Clay- to sand-sized sediment also was transported by water and wind into the fractures of underlying basalt flows. The thicknesses and areal extents of interbeds A-B, B-C, and C-D suggest that these units, like the surficial sediment, accumulated for long enough periods of time to fill and overtop most local topographic depressions. Sediment did not accumulate on some local basalt ridges, and sediment accumulation of interbed A-B was restricted in areal extent by the northward-sloping surface of basalt-flow group B, which erupted from a vent south of the SDA, near Big Southern Butte (fig. 1-1). These kinds of gaps in interbeds may provide local pathways for rapid infiltration of water and wastes through basalt fractures in the unsaturated zone.

2.3.4.1 Depositional environments

Although the surficial sediment at the SDA contains a few minor sand-and-gravel lenses it consists predominantly of clay- and silt-sized material deposited as loess (Rightmire and Lewis, 1987a, b). Two periods of loess accumulation in this surficial sediment have been identified: one from about 80 to 60 thousand years ago, and one from about 40 to 10 thousand years ago (Forman and others, 1993). Two different interpretations have been made regarding the depositional environment of sedimentary interbed A-B. According to McElroy and others (1989), the primary source of this sediment is the accumulation of loess. According to Hughes (1993), the sediment of interbed A-B consists mainly of very fine sand and silt and represents deposition in a floodplain environment. At least one period of loess accumulation in interbed A-B has been identified (Forman and others, 1993); the age of this loess is not precisely known, but it probably accumulated from about 150 to 140 thousand years ago. The sediment of interbed B-C consists mainly of sand and gravel that is interpreted to have been deposited in a braidplain setting in channel systems as wide as 300 m between topographic highs in the basalt (Hughes, 1993). The sediment of interbed C-D consists mainly of sand and silt that is interpreted to have been deposited in low-energy channels and floodplains (Hughes, 1993). The continuous nature of this interbed indicates deposition in a broad, shallow braidplain setting that aggraded to above most of the topographic highs in the basalt (Hughes, 1993). Although current (1999) interpretations of depositional environments are useful for evaluating overall sediment relations, they are still too generalized to be useful for evaluating the potential for movement of water and wastes.

2.3.4.2 Lithologic variations

Significant lithologic variations occur within the surficial sediment and sedimentary interbeds A-B, B-C, and C-D owing to differences in depositional environments through time (Rightmire and Lewis, 1987a, b; Hughes, 1993). The lithology of interbed F-G and other deep interbeds has not been characterized. Fine-scale (centimeter) vertical and horizontal lithologic variations within the surficial sediment and sedimentary interbeds A-B, B-C, and C-D beneath the SDA generally are poorly defined. This is because too few sediment cores have been described in sufficient detail to quantify these variations. The most detailed descriptions of vertical lithologic variations were reported by Rightmire and Lewis (1987a) for coreholes 76-1, 76-2, 76-3, 76-4, 76-4A, 76-5, 76-6, and 77-2 (fig. 2-2). Samples from these coreholes include many thin, discrete layers or lenses of plastic clay, especially within the C-D interbed. The most detailed descriptions of horizontal lithologic variations were reported by Hughes (1993), but these descriptions are somewhat generalized. Both Rightmire and Lewis (1987a) and Hughes (1993) examined the sedimentary materials from coreholes 76-1, 76-2, 76-3, 76-4, 76-4A, 76-5, and 76-6, but there are many discrepancies between lithologic descriptions in these independent studies. For example, Rightmire and Lewis (1987a) described abundant plastic clay in the lower part of the C-D interbed from corehole 76-5, whereas Hughes (1993) described this same interval as sandy silt and slightly silty, fine to coarse sand. These discrepancies and the paucity of detailed descriptions of sediment cores make it difficult to quantify the role of these sedimentary materials in unsaturated-zone processes.

2.3.4.3 Physical characteristics and mineralogy

Other factors, such as sedimentary structures, grain-size distributions, bulk mineralogy, clay mineralogy, and ion exchange capacity may retard or enhance the movement of wastes through the surficial sediment and sedimentary interbeds A-B, B-C, and C-D. However, like lithology, these features have not been characterized in a systematic and comprehensive way across the SDA. Sedimentary structures include paleosols, cracks formed by hydrocompaction and dessication, freeze-thaw features, burrow and rootlet holes, caliche development, horizontal laminations, ripple cross-stratification, planar cross-stratification, lenticular bedding, flaser bedding, rip-up clasts, load casts, and varves (Rightmire and Lewis, 1987b; Hughes, 1993). Many sedimentary materials are dark reddish-brown which may result from dehydration and oxidation of iron-rich minerals by heat from the overlying lava flows. This coloration also may result from oxidation

of the ferrous iron to ferric iron in a historical oxygenated soil atmosphere where ferrous iron is released during the weathering of olivine and augite (Rightmire and Lewis, 1987b). Grain-size distributions, determined on the basis of sieve analyses of at least 236 samples from the surficial sediment and sedimentary interbeds A-B, B-C, and C-D, range from clay to pebble sized (Barraclough and others, 1976; Rightmire and Lewis, 1987b; Hughes, 1993). The median size of the grains in 46 samples analyzed by Barraclough and others (1976) was 0.066 mm, but the grain size probably was somewhat biased because of difficulty in recovering coarse sand and gravel lenses from interbeds while drilling. Fracture- and vesicle-infill sediments generally are finer grained than interbed sediments. This is expected because infiltrating water preferentially deposits finer grained particles in the vesicles and fractures (Rightmire, 1984).

Analyses of bulk mineralogy of sediments show the presence of quartz, plagioclase feldspar, potassium feldspar, pyroxene, olivine, calcite, and total clay minerals. Bartholomay (1990c, table 3, p. 11) statistically summarized the previously published bulk mineralogy data by interbed depth. Additional data on two cores from the SDA were published in a report by Reed and Bartholomay (1994). In general, quartz and plagioclase feldspar are the most abundant minerals in the sediment. Pyroxene and total clay minerals also are present in most of the sediment samples from the SDA. Abundance of clay minerals in interbed samples from the SDA ranges from 0 to 60 percent and averages about 20 percent (Bartholomay, 1990b). Olivine is present in some samples in trace amounts. Calcite also was identified in some samples. The calcite generally is attributed to the formation of caliche in the interbeds (Rightmire and Lewis, 1987b). Rightmire and Lewis (1987b, p. 35–36) reported trace amounts of iron oxyhydroxides, hematite, siderite, and dolomite in some samples. C.T. Rightmire and B.D. Lewis (USGS, written commun., 1995) reported one tentative identification of the zeolite mineral chabazite. This lack of zeolite in the system probably precludes zeolite exchange with radionuclides in solution as a major factor in preventing the migration of radionuclides to the aquifer.

Analyses of the clay minerals indicate that illite is predominate (ranging from 10–100 percent of the clay minerals identified), and that lesser amounts of smectite, mixed-layer illite/smectite, kaolinite, and possibly chlorite are present. Illite generally is considered detrital; but fluctuations in the amounts of smectite and mixed-layer clays, the presence of altered potassium feldspars, and the possibility of thermal alteration, suggest that some illite and also smectite is forming (Rightmire and Lewis,

2-6 Review of the transport of selected radionuclides in the Interim Risk Assessment

1987b). The water chemistry also is favorable for the precipitation of these minerals. The clay minerals that are present in the system provide sites for sorption and/or ion exchange with any water containing radionuclides moving in the system. These processes would prevent migration of radionuclides to the aquifer. Conditions that need to be present to prevent sorption or exchange of radionuclides with clay minerals will be discussed in more detail in chapters 4 and 5.

2.3.4.4 Pedogenesis

Weakly-developed to well-developed paleosols have been identified in the surficial sediment and sedimentary interbed A-B and, although not documented, probably also occur in interbeds B-C and C-D. Forman and others (1993) identified paleosols associated with young loess units in two excavations at the SDA; one of these paleosols is thought to represent a prolonged period of pedogenesis, possibly exceeding 20 thousand years. These units contain A, B, and C soil horizons, carbonized zones, and abundant clay cutans having a maximum clay concentration of from 24 to 36 percent. Carbonized zones represent vegetation that was inundated and baked by lava flows during the geologic past. The distribution and characteristics of these zones have not been described on the basis of sediment cores from the SDA. Carbonate content of these paleosols generally is smaller than 10 percent but is as large as about 20 to 25 percent in some zones. Mineralogical analyses of the sediments indicate that most of the carbonate in the system is in the form of calcite, but some dolomite also was identified (Bartholomay and others, 1989). Mineralogical analyses of core samples of the surficial sediment and sedimentary interbeds A-B, B-C, and C-D reported by Barraclough and others (1976) show carbonate in the form of calcite. Calcite contents range from absent for most of the samples to 54 percent for others. Calcite content larger than 10 percent was reported for interbed C-D in wells USGS 88, 89, 90, and 96; for surficial sediment in wells USGS 92 and 95; and from a vesicle at about 9 m in well USGS 9 (figs. 2-2 and 2-3). Subsequent analyses by Rightmire and Lewis (1987b) showed carbonate contents as large as about 12 percent in interbed B-C, as large as about 29 percent in interbed C-D in well USGS 93A, and as large as about 2 percent in interbeds B-C and C-D in well USGS 96B (Rightmire, 1984). The largest carbonate content in interbed B-C in well USGS 93A is at the base of the interbed.

2.3.4.5 Thickness and areal extent

Elevations of the tops and thicknesses of the surficial sediment and at least 10 sedimentary interbeds in 94 wells

at and near the SDA were described by Anderson and Lewis (1989), Anderson and others (1996), and Magnuson and Sondrup (1998). Of these sedimentary units, only the surficial sediment and sedimentary interbeds A-B, B-C, C-D, and F-G are substantially thick and areally extensive. Surficial sediment is present in all 94 wells, has a top elevation that ranges from 1,514 to 1,544 m above sea level, and is up to 8 m thick. Sedimentary interbed A-B is present in 44 wells, has a top elevation that ranges from 1,511 to 1,528 m above sea level, and ranges in thickness from 0 to 6 m. Sedimentary interbed B-C is present in 91 wells, has a top elevation that ranges from 1,474 to 1,504 m above sea level, and ranges in thickness from 0 to 10 m. Interbed C-D is present in 76 wells, has a top elevation that ranges from 1,443 to 1,469 m above sea level, and ranges in thickness from 0 to 11 m. Sedimentary interbed F-G is near the base of the unsaturated zone and is about 90 m deeper than interbed C-D. Interbed F-G is present in 12 of 15 deep wells near the SDA, has a top elevation that ranges from 1,347 to 1,373 m above sea level, and ranges in thickness from 0 to 6 m. The surficial sediment and all sedimentary interbeds contain known gaps that are related to the irregular surfaces of underlying basalt flows. Interbeds B-C and C-D have the fewest known gaps and dip gently southeastward across the SDA. Surface reliefs of interbeds B-C and C-D, between well NA-89-1, near spreading area A located approximately 1.5 km west of the SDA (fig. 1-1), and well USGS 90, near the eastern side of the SDA, are 8 and 18 m, respectively. Perched ground water in wells at the SDA is present above and within interbeds A-B, B-C, and C-D (Rightmire and Lewis, 1987b; Magnuson and Sondrup, 1998) and may be related partly to the lateral movement of infiltrating water from the spreading areas to the SDA (Rightmire and Lewis, 1987b).

2.3.4.6 Hydraulic conductivity

Hydraulic conductivity, an indirect measure of sediment lithology, varies more than four orders of magnitude in the surficial sediment, more than three orders of magnitude in interbed A-B, more than six orders of magnitude in interbed B-C, and more than seven orders of magnitude in interbed C-D (Barraclough and others, 1976; McCarthy and McElroy, 1995). Barraclough and others (1976, p. 50) reported a range of vertical hydraulic conductivity for these sedimentary units in 10 wells, USGS 87, 88, 89, 90, 91, 92, 93, 94, 95, and 96 (figs. 2-2 and 2-3), of from 1.6×10^{-7} to 3.0 m/d. The smallest vertical hydraulic conductivity reported for interbed C-D in each of these wells ranges from 8.0×10^{-7} m/d in well USGS 88 to 2.6×10^{-1} m/d in well USGS 91. The largest

vertical hydraulic conductivity reported for interbed C-D in each of these wells ranges from 6.1×10^{-5} m/d in well USGS 89 to 9.3×10^{-1} m/d in well USGS 95. The largest range of vertical hydraulic conductivity reported for interbed C-D was for well USGS 88, 8.0×10^{-7} to 1.3×10^{-1} m/d (Barracough and others, 1976). These ranges of hydraulic conductivity probably reflect centimeter-scale changes in lithology, from clay- to gravel-sized clasts, within the surficial sediment and sedimentary interbeds A-B, B-C, and C-D.

2.3.5 Hydrologic pathways

Sedimentary interbeds at the SDA are characterized by abrupt changes in thickness related to the topography of underlying basalt flows (Anderson and Lewis, 1989). Most of these flows are pahoehoe flows, which commonly contain inflation and deflation features, including ridges and closed depressions, and vary in relief a few meters within distances of a few tens of meters. Anderson and Lewis (1989, p. 38 and 47) described one such structure on the top of basalt-flow group C in the western part of the SDA, where the thickness of sedimentary interbed B-C changes abruptly from zero on a basalt ridge to more than 6 m in an adjacent depression. Rightmire and Lewis (1987a) suggested, on the basis of carbonate encapsulating clay pellets covered with desiccation cracks present in interbed B-C, that sediment and water collected in a topographic depression at the present-day location of wells 76-4 and 76-4A during the deposition of interbed B-C. Infiltrating water may migrate towards such depressions at some sediment-basalt interfaces, possibly resulting in areas of localized perched water and/or preferential flow. Some basalt ridges, such as those on the top of basalt-flow group C in the western part of the SDA, that are penetrated by wells 76-1, 76-2, and 78-3 (Anderson and Lewis, 1989, p. 38 and 47), also may be areas of preferential flow. This is because these ridges were not covered by sediment and probably are inflated lobes of pahoehoe basalt cut by large cooling fractures.

Vertical water movement through the basalt-sedimentary sequence is largely controlled by the hydraulic conductivity of fractures in the basalt flows and by the smaller hydraulic conductivity of some of the finer sediments in the interbeds. An additional and even greater constraint occurs at the base of each sedimentary layer, at the sediment-basalt interface. "This is caused by the discontinuity of pore spaces from the sediment to the basalt, due both to the lower porosity of the basalt and to the relatively great distances between its fractures. In other words, at the interface, perhaps only 10 percent of the

basalt surface is composed of permeable openings, and these are partially filled by sediment. The other 90 percent is virtually impermeable. This, in effect, provides a thin skin that is estimated to have one-tenth or less of the permeability of the sediments alone" (Barracough and others, 1976).

Horizontal water movement through the basalt-sediment sequence is largely controlled by the large hydraulic conductivity associated with basalt fractures, rubble, and scoria, a term synonymous with cinders. In the saturated zone, these features provide the main conduits for groundwater flow. In the unsaturated zone, fractures, rubble, and scoria have the potential to channel perched water over large distances within short periods of time. Estimates of ratios of horizontal to vertical basalt permeabilities at the INEEL range from about 3:1 to 300:1 (Barracough and others, 1976; Magnuson, 1995; Magnuson and Sondrup, 1998).

The presence, absence, or transient nature of perched water in wells at the SDA may be the result of several geologic factors. Cecil and others (1991) suggested four possible mechanisms to explain zones of perched water. These include: (1) contrasts in vertical hydraulic conductivity between basalt flows and sedimentary interbeds, (2) decreased hydraulic conductivity in interflow baked zones, (3) decreased vertical hydraulic conductivity in dense, unfractured basalt, and (4) decreased vertical hydraulic conductivity from sedimentary and chemical filling of fractures in basalt. Cecil and others (1991, p. 23) demonstrated that perching can take place within sedimentary interbeds and basalt flows.

The recurring presence of a ground-water mound beneath the spreading areas indicates that most of the water from this source moves vertically to the water table (Rightmire and Lewis, 1987b). However, the lateral continuity of some of the interbeds, particularly the C-D interbed, suggests that water recharged from the spreading areas also could move to the east the approximately 1.5 km necessary for it to be present in the unsaturated zone beneath the western edge of the SDA. Rightmire and Lewis (1987b) reported the presence of water coinciding with the A-B, B-C, and C-D interbeds on the northwest side of the SDA, and it is conceivable that this water moved laterally from the spreading areas in a stepwise depth progression from the shallowest to deepest interbeds. If so, there is possibly significant lateral movement of water from beneath the spreading areas. Thus, it is possible that the perched water beneath the SDA is derived largely from the spreading areas and (or) the BLR and receives only a minor contribution of moisture from ver-

2-8 Review of the transport of selected radionuclides in the Interim Risk Assessment

tical water movement derived from atmospheric precipitation.

Basalt fractures, rubble, and scoria are present in the subsurface at the SDA, but their locations and orientations are poorly known. Simple cooling fractures likely are present in all basalt flows, but large fractures, such as those along the edges of inflated pahoehoe flows, probably are very localized. These fractures, which can be as much as a few meters wide and tens of meters long, are oriented in the direction that each lobe of pahoehoe lava traveled during its emplacement, inflation, and cooling. These directions are only approximately known for basalt-flow groups A and B. Basalt rubble in some wells has been described but has not been systematically characterized. Magnuson and Sondrup (1998) described a rubble zone across the SDA at a depth of about 60 m that could affect the distribution of carbon tetrachloride. The potential for scoria, a near-vent deposit, is greatest in basalt-flow group C. This is because its vent is thought to be in the subsurface near the SDA (Anderson and Liszewski, 1997, p. 10). Rightmire and Lewis (1987a, p. 64) reported the presence of grout cement in well 76-3, which likely was carried by water through a cinder (scoria) zone beneath interbed B-C from well USGS 93 to well 76-3, a distance of 168 m. Basalt fractures, rubble, and scoria probably affect the potential for perched water in complex ways.

2.4 Hydrologic framework

2.4.1 Meteorology

The INEEL receives an average of about 22 cm of precipitation each year. On average, May and June are the wettest months and July is the driest month (Robertson and others, 1974, p. 8). Normal annual snowfall is about 66 cm and accounts for about 30 percent of the annual precipitation.

2.4.2 Surface water and local runoff

2.4.2.1 Areal infiltration

Areal recharge on the eastern SRP from rainfall and snowmelt infiltration generally is considered to be small. Cecil and others (1992, p. 709) calculated net areal infiltration rates at the SDA to range from 0.36 to 1.10 cm/yr, or 2 to 5 percent of the long-term annual precipitation. However, topographic features locally may focus areal recharge in lower areas. The SDA is located in a topographic depression. Barraclough and others (1976, p. 8)

reported that the SDA has been flooded at least twice (1962 and 1969) by local runoff from rapid spring thaws. Heavy rainfall and melting snow within the SDA have also introduced water into trenches and pits.

Areal recharge may be affected by changes in soil properties introduced by construction of waste trenches in surficial sediments at the SDA. Shakofsky (1995, p. 24) determined that the hydraulic conductivity of disturbed soils overlying trenches in the vicinity of the SDA and corresponding recharge from areal precipitation, generally are larger than the hydraulic conductivity of and recharge through nearby undisturbed soils.

2.4.2.2 Stream infiltration

It has long been recognized that the BLR is an important component of the hydrologic system that controls the fate and transport of waste constituents in the subsurface at the INEEL. Robertson (1974, p. 26) noted that recharge from the BLR is the "biggest hydrologic variable" in determining the future behavior of waste constituents in the aquifer.

Since 1965, a large proportion of flow in the BLR has been diverted to the INEEL spreading areas for flood control. During 1982–85, approximately two-thirds of the flow that entered the INEEL was diverted to the spreading areas (Pittman and others, 1988, p. 18). Rapid infiltration of these diverted flows locally affects water levels in the SRP aquifer. Pittman and others (1988, p. 18) observed that the water table in the vicinity of the SDA rose as much as 4.9 m during 1982–85 in response to recharge from surface water diverted to the spreading areas.

Some evidence exists that rapid infiltration also may produce significant lateral flow in the unsaturated zone. Barraclough and others (1976, p. 51) noted the presence of perched water in several boreholes within the SDA. They observed that an extensive zone of saturated to nearly saturated basalt existed beneath the burial ground. The source of water was not known, but they believed that thin perched-water zones could represent long-term local accumulation of percolating precipitation or more rapid recharge from the 1969 flood at the SDA. They suggested that isotopic analyses might reveal the source and history of the perched water.

Rightmire and Lewis (1987, p. 83) noted that an anomalously light isotopic content in water samples from perched water samples at the SDA may be attributed to a water source at an altitude higher than the surface of the SRP. They stated (1987, p. 1) that "...stable isotope and chemical data suggest that the perched water observed beneath the SDA is not due to vertical infiltration through the ground surface at the SDA, but is due to lateral flow of

water that infiltrated through the diversion ponds." They hypothesized at that time that water accumulates as a perched mound on a thick, continuous sedimentary interbed at a depth of 73 m and then moves laterally to the SDA 1.5 km to the northeast.

Rightmire (1984, p. 32) observed that "...sedimentary lining and filling of fractures is the result of water-borne sedimentation. Layers of oriented clay particles overlain by disoriented coarser material suggest a series of minor recharge events followed by a major recharge event to fill the fractures." Rightmire also noted that the presence of cement grout in fractures penetrated in a test hole demonstrates that open fractures occur at depths of at least 54 m. These fractures would permit transport of sediments and fluids through the unsaturated zone.

Anderson and Lewis (1989, p. 20) noted that basalt flows contain numerous fractures that may provide unrestricted avenues for vertical and horizontal flow of contaminated water. They suggested that sediment layers may control vertical flow depending on grain size and sorting characteristics. They noted that lateral flow and perching of water may take place along some clay and silt layers, and that discontinuous layers may divert flow toward underlying or adjacent basalt flows. They also stated that the potential for lateral flow away from the SDA along the east-sloping surface of the C-D interbed is large. Anderson and Lewis stated that additional evaluation of rock and sediment characteristics, including the distribution and characterization of flow contacts, fractures, and vesicles, and the lithology of major sedimentary interbeds, is needed to determine the potential for contaminant migration to the Snake River Plain aquifer.

2.4.3 Unsaturated-zone flow

The unsaturated zone is defined as the portion of the subsurface between the land surface and the lowest water table. The 200 m thick unsaturated zone at the SDA includes both saturated conditions (where perching occurs; discussed in section 2.4.3.2) and unsaturated conditions.

2.4.3.1 Flow in a homogeneous medium

For water driven by gravity and pressure gradients when the medium is saturated, as from ponded infiltration or perching, Darcy's law can quantify the flow as:

$$q = -K_{sat} [\nabla \psi + \rho g] \quad (2.1)$$

where:

q = flux density, in volume rate of flow per unit area;

K_{sat} = saturated hydraulic conductivity, in length per time;

ψ = water pressure in length;

ρ = density of water, in mass per volume; and

g = gravitational acceleration, in length per time squared.

For simplicity, this equation frequently is applied with ρg , the weight of water per unit volume, set equal to dimensionless unity. Then ψ has dimensions of length (m), and K of length per time (m/s).

If the medium is unsaturated and the flow is diffuse, an unsaturated form of Darcy's law can quantify the flow at a point in space and time.

In one-dimension:

$$q = -K(\theta) \left[\frac{d\psi}{dz} + \rho g \right] \quad (2.2)$$

where:

θ = water content, in volume of water per total volume;

z = vertical distance, in length;

K = hydraulic conductivity, in length per time.

K depends strongly and nonlinearly on θ . The matric pressure (ψ) is of particular interest because it often determines the chief transport processes in an unsaturated medium. It arises from the interaction of water with a rigid matrix. Matric pressure, defined very precisely by Bolt and others (1976), may be thought of as the pressure of the water in a pore of the medium relative to the pressure of the air. When a medium is unsaturated, the water generally is at lower pressure than the air, so the matric pressure is negative. Darcy's law applies directly in field situations where flow is steady, though steadiness in actuality is often temporary or approximate. In steady conditions equation 2.2 with a single $K(\theta)$ function can describe the flow within any homogeneous portion of the medium.

When unsaturated flow is transient (nonsteady), as it generally is, the flow itself causes the water content to change throughout the medium, which leads to continuously changing hydraulic conductivity and driving forces. These effects can be accommodated mathematically by combining the equation of continuity with Darcy's law (2.2) to get Richards' (1931) equation, which for one-dimensional vertical flow can be written:

$$C(\psi) \frac{\partial \psi}{\partial t} = \frac{\partial}{\partial z} \left(K \frac{\partial \psi}{\partial z} \right) + \rho g \frac{\partial K}{\partial z} \quad (2.3)$$

where:

C = differential water capacity, a property of the medium defined as $d\theta/d\psi$.

With certain implicit assumptions, such as homogeneity of the medium, Richards' equation keeps track of the whole dynamic, unsteady flow process. In practice, most mathematical models of unsaturated flow assume equa-

2-10 Review of the transport of selected radionuclides in the Interim Risk Assessment

tion 2.3 applies, whether appropriately or not. The equation is nonlinear and can be solved numerically in the general case (Lappala and others, 1987; Healy, 1990) or analytically (Salvucci, 1996) with simplifying assumptions that may be suitable in some, but perhaps not most, applications.

2.4.3.2 Flow and perching in stratified unsaturated zones

Contacts between layers that contrast in hydraulic properties commonly impede vertical flow. Such impediments occur most obviously when water moves down from a coarse to a fine layer, as from coarse sand to silt. If both layers are near saturation, the fine layer has smaller hydraulic conductivity; therefore, flow slows when it reaches the fine layer. If the coarse layer is nearly saturated but the fine layer is initially fairly dry, it is possible for flow to be initially dominated by the sorptive nature of the fine medium, which tends to suck water out of the coarse material. In the latter case flow is not impeded by the fine layer until more uniformly saturated conditions occur.

Where a fine layer overlies a coarse layer, water moving downward is impeded under many conditions. When coarse material is dry, it has an extremely small hydraulic conductivity; thus it tends not to admit water into the pores and exhibits a somewhat self-perpetuating resistance to flow. Water breaks into the coarse layer if the pressure at the layer interface builds to the point that the water-entry pressure (the minimum water pressure needed to fill an empty pore) of some of the large pores is exceeded. This can generate instabilities, as discussed in section 2.4.3.3. Stable or not, water flowing into the pores of the coarse medium increases its hydraulic conductivity drastically. Then the wetter coarse medium will conduct more easily, and will progress toward steady-state flow. The effective hydraulic conductivities of the two layers will then be essentially equal. In the approach to steady flow, the water content in each layer adjusts to accommodate this equalizing of conductivities. The water content of the coarse medium, however, does not increase enough to make the effective hydraulic conductivity as large as it would be for a single-layered system composed of fine material only. Thus, typical flow through layers where fine overlies coarse is slower than it would be if both layers had the properties of the fine medium. Miller and Gardner (1962) demonstrated this effect experimentally.

A thin layer of small hydraulic conductivity can limit downward flow to the point of being the dominant influence on flow through the sequence. Stothoff (1997) considered a granular medium above a fractured bedrock (similar to much of the INEEL unsaturated zone). The

bedrock admits water only under nearly saturated conditions. Stothoff's interpretation assumes the fractures are of greater-than-microscopic width and the rock is otherwise impermeable. The thickness of the granular layer strongly influences the fraction of average precipitation that flows into the bedrock (and presumably further, to the aquifer); thus, a thin alluvial layer more easily becomes saturated to the layer interface and hence more frequently permits deep percolation.

Perching, an accumulation of water in a region of the unsaturated zone such that it becomes locally saturated even though there is unsaturated material below, is not unusual in the unsaturated zone at the INEEL. The artificial infiltration of wastewater has created perched zones that have persisted for several years (Orr, USGS written commun., 1999). Perching usually results from a large flux of water that encounters a severely impeding layer. It may be a temporary or permanent feature, depending on the nature of the medium, the prevailing hydrologic conditions, and the effect of artificial modifications. Perching complicates a contamination problem in several ways. The high water content of a perched zone causes greater hydraulic conductivity and potentially faster transport through the three-dimensional system. The main effect is not a direct increase in vertical flux because the increase in effective vertical hydraulic conductivity is offset by a diminished vertical hydraulic gradient within the perched water. (Vertical flux within and below the perched water cannot be faster than the vertical flux above the perched water or the perched water would have drained). Horizontally, however, there may be greatly increased flow. This enhanced horizontal flow may in turn bring much water to points where the vertical conductivity is locally large (for example, where there is a vertical fracture), or to where perching occurs at a sloping interface along which the enhanced flow has a substantial vertical component. Perched zones commonly are large in horizontal extent, so these effects related to horizontal flow can become more important than vertical flow for contaminant transport. New and different processes may significantly affect contaminant transport in a perched zone. Reduced aeration, for example, may affect biochemical processes. At the scale of the entire stratified unsaturated zone, perching may significantly increase anisotropy.

2.4.3.3 Preferential flow

In an unsaturated medium, flowpaths that permit faster transport than other paths are common. Flow through these preferential paths is called preferential flow. Such a path may be a single pore, a connected series of pores, or a group of adjacent pores acting in parallel. A

path may be preferential because of either the permanent character (for instance pore size) or the present state (for instance water content) of its pores. The path may be a single pore, a connected series of pores, or a group of adjacent pores acting in parallel.

Preferential flow, although difficult to observe or sample, can convectively transport contaminants to the aquifer far sooner than might be predicted on the basis of ordinary analysis of bulk medium properties and Richards' equation (2.3). Additionally, if the flow is entirely or primarily through preferential paths, the interaction of contaminants with solid material is effectively limited to a fraction of the subsurface medium. This limits adsorption and other attenuating processes. Thus, preferential flow decreases both the time and the space available for contaminant attenuation, chemical or radioactive decay.

Various mechanisms cause preferential flow (Steenhuis and others, 1995; Or, 1996). Three kinds of preferential flow and the contributing mechanisms are: (1) macropore (or short-circuiting) flow, caused by flow-enhancing features of the medium, (2) funneled (or deflected or focused) flow, caused by flow-impeding features of the medium, and (3) unstable (or fingered) flow, caused by flow-enhancing conditions of parts of the medium at the time of interest. This categorization is similar to several others in widespread use and includes, directly or indirectly, essentially every known process that might be considered preferential-flow phenomenon. As for other subjects for which theory is in the early stages of development, the terminology classifying preferential flow often is imprecise or ambiguous. For example, focused flow might refer to funneled flow or to flow in certain types of macropores. Sometimes distinctions between flow types blur. Often several mechanisms are acting within the same medium.

2.4.3.3.1 Macropore flow—heterogeneity of the porous medium

Macropores, which are distinguishable from other pores by their larger size, greater continuity, or other attributes, conduct preferential flow under some conditions (Luxmoore, 1981), such as extreme wetness. Common macropores include wormholes, rootholes, and fractures. These may be visible by eye, or difficult to detect without special techniques. Where macropore flow occurs, flow through the remainder of the medium may be called matrix flow. Macropore flow may be interpreted to include preferential flow arising not only from individual large pores but also from the areal heterogeneity of bulk properties. Hydraulic conductivity, wetability, and other flow-affecting properties generally vary from place to

place, so that flow rates are greater in some locations than others.

The speed and behavior of macropore flow vary. When macropores are filled, flow is generally fast. When macropores are empty, they constitute a barrier to matrix flow and there may be essentially no flow through the macropores themselves (Montazer and Wilson, 1984). In some conditions, however, there may be significant film flow along fracture walls (Tokunaga and Wan, 1997). In macropores that are partly filled, there are many possibilities for the configuration and flow behavior of water (Su and others, 1999; Nicholl and others, 1994; Pruess, 1998; Nitao and Buschek, 1991; Persoff and Pruess, 1995). These possibilities and their effect on water and contaminant transport are not yet well understood. Recent research of Faybishenko (1999) suggests that there may be chaotic fluctuations in this type of flow, which in turn suggests the possibility of new mathematical treatments.

2.4.3.3.2 Funneled flow—heterogeneity of the porous medium

Layers or lenses of material that, to some degree, impede vertical flow because of textural contrasts or other reasons can cause horizontal flow. Often such layers are tilted so that gravity causes flow to move in a particular lateral direction. Whether or not tilting is a factor, both the lateral flow and the vertical flow that moves through or around the impeding feature normally follow preferential paths.

Several studies have investigated the effects of these impeding features in generating preferential flow. Some of the first rigorous research was by Kung (1990a, 1990b). In field experiments at a site with sandy soil, Kung found that the flow became more preferential with depth. At about 6-m depth, the flow was moving through less than 1 percent of the whole soil matrix. Although this medium had no significant observable macropores, preferential flowpaths were shown to be the dominant flow pattern. The main feature causing this preferential flow was "...an interbedded soil structure with textural discontinuities and inclined bedding planes." Striegl and others (1996) hypothesized that funneled flow could have transported tritium and carbon-14 contaminants over large horizontal distances in the unsaturated zone at a waste-disposal site near Beatty, Nevada. Considering the work of Kung and other researchers, Pruess (1998) noted that because funneling can produce very rapid flow and results from horizontal impediments "...we have the remarkable situation that unsaturated seepage can actually proceed faster in a medium with lower average permeability."

2-12 Review of the transport of selected radionuclides in the Interim Risk Assessment

2.4.3.3.3 Unstable flow—heterogeneities in the condition of the medium

An unstable variation in flow and water content can increase hydraulic conductivity in some parts of the medium even if the fundamental hydraulic properties of the medium are uniform. Usually, texturally contrasting layers contribute to this unstable flow. The classic case is a layer of fine material above coarse material. In this case infiltrating water does not immediately cross the interface into the coarse material. When water pressure builds up significantly at the interface, water may break through into the coarse medium at only a few points, as discussed in section 2.4.3.2. The material near individual points of breakthrough becomes wetter and hence much more conductive. For some time thereafter, additional flow into the coarse material moves in the few “fingers” that are already wet. Between fingers, the medium remains relatively dry for some time. In addition to textural contrasts, hydrophobicity or water repellency of the medium may contribute to unstable flow (Dekker and Ritsema, 1994; Ritsema and Dekker, 1994; de Rooij, 1995; Ritsema and others, 1998). Unstable flow may also be associated with air trapping (Wang and others, 1998a). Several researchers (Glass and others, 1988; Baker and Hillel, 1990; Yao and Hendrickx, 1996) have explored the general types of behavior expected in unstable flow.

Preferential flowpaths may be interrupted by layer boundaries. Numerical experiments by Russo and others (1998) suggest that the spatial variability of soil properties and the temporal variability of infiltration and redistribution both may act to homogenize transport phenomena. Shakofsky and Nimmo (1996) found that flow through undisturbed surficial soil at the INEEL appeared to be fast and highly preferential near the land surface, but was drastically slowed at about a 2-m depth, apparently because of a layer at this depth that differed in hydraulic properties. In nearby soil that had been disturbed and homogenized much like the soil at the SDA landfill, the flow was less preferential and there was no evidence of sudden slowing at a particular depth. It is possible for processes to be operative that homogenize preferential flow. How common these processes are, however, is currently a matter of speculation among unsaturated-zone hydrologists.

2.4.3.4 Quantitative treatment of preferential flow

2.4.3.4.1 Effective properties

A widely used approach to mathematical modeling when some or all of the flow is preferential is to assume that the effective hydraulic properties of a large volume of the medium are equivalent to the average properties of a

homogeneous granular porous medium. The effective hydraulic properties then can be applied directly in numerical simulators developed for diffuse flow in granular media based on Darcy’s law and Richards’ equation. This technique is often called the “equivalent-porous-medium” approach. In this report it is called the “equivalent-granular-medium” approach to prevent confusion with the fact that the basalts at the INEEL intrinsically are porous media themselves.

The equivalent-granular-medium approach is valid only if certain conditions are met. For example, the portion of the unsaturated zone under consideration must be divisible into finite volumes within each of which the net flow, including all preferential flow, is representative of the medium as a whole. Volumes taken too small will invalidate the approach because they have different amounts of preferential flow within them and therefore are not representative of the whole medium. On the other hand, if these finite volumes are so large that only a small fraction of the assumed volume is participating in the flow, the actual transport velocities can be much greater than the modeled velocities. In practice, an adjustment of the “effective porosity” of the equivalent granular medium is commonly done to compensate for such effects, though this adjustment will not produce accurate predictions if, as expected, the degree of preferential flow depends strongly on the degree of saturation. Bear (1978, p. 28–31) gives a detailed explanation of volume and homogeneity considerations for continuum approaches in general. Pruess (1998) describes in detail some of the possible large-scale transport-accelerating mechanisms associated with preferential flow. In many applications, the equivalent-granular-medium approach is the only one that is practical and has a significant history of prior use. Other approaches may be less subject to fundamental limitations but are not sufficiently developed or tested to make predictions with a high level of confidence.

The main advantage of the equivalent-granular-medium approach is that many existing theories, models, and familiar techniques can be immediately applied. A recent example is that of Reitsma and Kueper (1994), who found that the Brooks-Corey model (Brooks and Corey, 1996) of soil water retention, which was formulated to apply to ordinary soil materials, well represented measured retention properties of a rough-walled rock fracture. The equivalent-granular-medium approach has additional drawbacks, mostly because the flow theory and models involved were developed for wet, homogeneous granular, porous media. Preferential flow may be too irregular to be described accurately by a model in which averaged values of hydraulic properties have been applied. For example

Ma and Selim (1996) noted that averaging the flow rate and using the average to quantify solute transport is not an adequate method; using the actual distribution of flow rates is more suitable. The equivalent-granular-medium approach also is inadequate wherever it is essential to have knowledge of the specific flowpaths that may act as conduits for most of the contaminant transport.

2.4.3.4.2 Dual-modality and multi-modality

A family of approaches that rely on a conceptual partitioning of water or pore space into portions with different flow rates and behaviors and given names such as “dual-porosity” and “dual-modality”, may represent more realistically flow that includes preferential paths than do traditional unsaturated-flow models (Reedy and others, 1996). Magnuson and Sondrup (1998, p. 4-48) used a model of this type in calibrating for volatile organic contaminants (VOCs). The concept of mobility, that is, how easily moved certain system components (in particular, contaminants) are in different parts of the medium, is frequently used in defining and characterizing these approaches.

Some of these models are used more commonly for solute transport than for water flow in preferential paths. The simplest ones assume matrix flow to be negligible, so that all flow is preferential flow. Given the nonlinear nature of unsaturated flow, the difference in conductance between, say, a wormhole and an intraaggregate pore between clay particles may be several orders of magnitude and, for practical purposes, may constitute a mobile-immobile distinction (van Genuchten and Wierenga, 1976). Other models assume the matrix to be permeable but with different properties and possibly different modes of flow than the portion of the medium that has preferential flow. In extensive field experiments, Ghodrati and Jury (1992, fig. 2) showed effects of preferential contaminant transport and noted that existing transport models for nonhomogeneous soils were inapplicable. They concluded that “...new approaches will have to be developed to address preferential flow when the soil matrix is also permeable enough to permit transport of water and chemicals through it.”

The degrees of possible mobility cover a continuum, and truly immobile water is unlikely. Some models postulate as many as three degrees of effective mobility; a few models postulate more. For example mesopores in addition to micropores and macropores, may be considered (Luxmoore, 1981). A closer approach to a continuum of mobility is that of Griffioen and others (1998), who worked toward a parameterization of mobility.

Other recent models were described by Jaynes and others (1995), and Casey and others (1997). It is also possible to combine mobile-immobile models with other models, especially for reactive solute transport (Ma and Selim, 1997).

2.4.3.4.3 Additional considerations in the quantification of unstable flow

Quantification of unstable flow is complicated by two factors that do not apply to macropore or funneled flow: (1) unstable flow is not tied to particular permanent features of the medium, and (2) the preferentiality of unstable flow changes dynamically (for instance, flowpaths commonly would grow wider as flow progresses through them). Theories of unstable flow in terms of scaling (Miller and Miller, 1956) and other concepts, have been developed in studies by Glass and others (1989a, 1989b), Raats (1973), Philip and Forrester (1975), Parlange and Hillel (1976), Diment and others (1982), Hillel and Baker (1988), and Selker and others (1992a, 1992b).

2.4.3.5 Contentions and ambiguities concerning preferential flow

At present (1999) there is disagreement in the scientific community concerning the prevalence of preferential flow. Statements in many recent publications suggest that preferential flow is uncommon: “Pulses of infiltration are... naturally damped in a diffusion-like process” (Stephens, 1996, p. 97); “Field studies that demonstrate preferential flow are restricted mostly to fractured rock and root zones in arid regions” (Scanlon and others, 1997); “Fractures are unlikely to provide rapid, open channels for flow” (Soll and Birdsell, 1998); “It seems likely that the strong lateral potential gradients that result from preferential flow into the dry subsoil rapidly damp out irregular wetting fronts” (Phillips, 1994); “Soil hydraulic properties, initial soil water content, and infiltration rate exert an important control on instability” (Hendrickx and Yao, 1998).

Other statements argue for the prevalence of preferential flow: “The occurrence of preferential flow is the rule rather than the exception” (Flury and others, 1994); “Preferential flow is a dominant feature of structured soils, particularly those with pronounced layering” (Jury and Wang, 1999); “A most effective condition for fast preferential flow is the presence of sub-horizontal barriers of significant length” (Pruess, 1998); “It is now apparent that fingered flow should be expected in any sandy soil with unsaturated flow” (Selker and others, 1991); “While once believed to occur exclusively in structured soils, preferential flow is now recognized as prevalent under a wide range of conditions in permeable, structureless (for

2-14 Review of the transport of selected radionuclides in the Interim Risk Assessment

example, devoid of macropore structure) soils” (Jury and Wang, 1999).

In virtually every unsaturated-zone transport problem, it is essential to assess the prevalence of preferential flow and the flow mechanisms that might be active. One approach is to evaluate the features of a particular site that might cause macropore, funneled, or unstable flow. For example, for unstable flow, Wang and others (1998a, 1998b) analyzed the likelihood of a variety of mechanisms that might cause unstable flow. Another approach is to collect and evaluate evidence from observed water or solute distributions that cannot easily be explained without hypothesizing preferential flow.

2.4.3.6 Flow in the unsaturated zone at and near the Subsurface Disposal Area

2.4.3.6.1 Surficial sediments

The unsaturated hydraulic conductivity and water retention of the surficial sediments in the unsaturated zone at the INEEL are fairly typical of a medium in which structural features such as aggregation and macropores have evolved over time (Shakofsky, 1995; Nimmo and others, 1999). At the INEEL, much of the surficial sediment is in the silt loam textural class. At many locations, for example at the SDA, the hydraulic properties have been substantially altered by mechanical disturbances. The main known effects of these disturbances are less macropore flow and less stratification. Like other surface soils with developed structural features, the hydraulic conductivity of these sediments, disturbed or not, may exhibit substantial local anisotropy.

Available evidence suggests that flow in the unsaturated zone is highly preferential where the soil is undisturbed and preferential to some degree elsewhere. Especially under wet conditions during or shortly after infiltration, the flow may be dominated by macropores. Natural layers within these sediments, where they are undisturbed, and the interface with the basalt in all locations may significantly slow downward flow. This retarding influence may be especially important at shallow depths, where its effect is to retain more water high in the root zone where it is more likely to be removed by evapotranspiration.

2.4.3.6.2 Basalts

The hydraulic properties of the fractured basalts have been represented by the effective properties approach (Magnuson and Sondrup, 1998). The effective hydraulic conductivity has not been determined by direct measurements but rather through inverse modeling, as discussed

in chapter 6. There is likely to be substantial anisotropy in these basalts, large and small, though it is difficult to estimate its nature and degree.

Flow within the basalts is dominated by macropore flow through fractures. The basalt matrix is sometimes assumed impermeable, which for many purposes may be an adequate approximation. A large body of evidence, including that of the Large-Scale Infiltration Test (LSIT) (Dunnivant and others, 1998), indicates that when the basalt fractures are filled, they can conduct rapidly, perhaps meters per day or faster. Some fractures become filled from wetting events that might occur as often as several times per year. There is also evidence that some fractures, especially ones with dead ends, do not conduct significant flow, or at least do not allow significant downward flow (Dunnivant and others, 1998). Little is known about the processes or rates of flow in parts of basalt in which all fractures are unsaturated. A common assumption, possibly valid for some purposes, is that such flow is negligible compared with episodic flow through filled macropores.

2.4.3.6.3 Sedimentary interbeds

The sedimentary interbeds closely resemble the surficial sediments in some ways, but they differ significantly, for example in having greater density and more uniform structure. They probably have no significant wormholes or rootholes and may be less aggregated than the surficial sediments. The sedimentary interbeds are highly stratified; internal layers and lenses differ substantially from each other in texture and structure in terms of such features as baked zones. The hydraulic properties of interbeds would tend to be like those of the surficial sediments except for systematic differences such as smaller hydraulic conductivity resulting from greater bulk density. Another difference from surficial sediments is that interbed sediments are likely to retain more water after episodes of drainage. Because the sediments are granular, the interbeds may be less anisotropic within internal layers than other parts of the unsaturated zone. At scales of a few meters or greater, basalt-interbed interfaces lead to great effective anisotropy.

Flow behavior in sedimentary interbeds probably varies widely both seasonally and sporadically as water content and hydraulic conductivity vary. At least to some degree, sedimentary interbeds are likely to impede vertical flow and to cause preferential flow from basalt fractures to become more diffuse. The interbeds probably have less macropore flow within them than the surficial sediments or basalts, but their layered structure may be conducive to funneled or unstable flow. Thus it is likely

that, to some degree, they cause vertical and horizontal preferential flow.

Saturated hydraulic conductivity, an indirect measure of sediment lithology, ranges more than four orders of magnitude in the surficial sediment, more than three orders of magnitude in interbed A-B, more than six orders of magnitude in interbed B-C, and more than seven orders of magnitude in interbed C-D (Barraclough and others, 1976; McCarthy and McElroy, 1995). Barraclough and others (1976, p. 50) report a range of vertical hydraulic conductivity for these sedimentary units in ten wells, USGS 87, 88, 89, 90, 91, 92, 93, 94, 95, and 96 (figs. 2-2 and 2-3), of from 1.6×10^{-7} to 3.0 m/d. The smallest values of vertical hydraulic conductivity reported for interbed C-D in each of these wells ranges from 8.0×10^{-7} m/d in well USGS 88 to 2.6×10^{-1} m/d in well USGS 91. The largest values of vertical hydraulic conductivity reported for interbed C-D in each of these wells ranges from 6.1×10^{-5} m/d in well USGS 89 to 9.3×10^{-1} m/d in well USGS 95. The greatest range of vertical hydraulic conductivity reported for interbed C-D in any well, 8.0×10^{-7} to 1.3×10^{-1} m/d, occurs in well USGS 88 (Barraclough and others, 1976). These ranges of hydraulic conductivity probably reflect centimeter-scale changes in lithology, from clay- to gravel-sized clasts, within the surficial sediment and sedimentary interbeds A-B, B-C, and C-D.

2.4.3.7 Current qualitative understanding of flow in the unsaturated zone at the Idaho National Engineering and Environmental Laboratory

2.4.3.7.1 Vertical flow of local origin

Local infiltration from rainfall, snowmelt, and runoff initially moves downward. If the infiltration is uniform over a large enough area, it can be treated as one-dimensional vertical flow. At many locations, including the SDA, most of the infiltration eventually exits at the soil surface because of evapotranspiration or other mechanisms. Some fraction of infiltration becomes deep percolation that can continue downward until it reaches the aquifer (Cecil and others, 1992; Nimmo and others, 1999). The depth that water must reach for this to happen is described by some as the maximum depth at which plant roots are active. At most locations on the INEEL, this depth is probably a few meters. In the disturbed area of the SDA, where grasses are the dominant vegetation, the depth of active roots is about 2 m and this is within the surficial sediments.

In the surficial layers, infiltrating water can move quickly down to some depth, perhaps a few centimeters or meters, depending on macropores and soil layers, and

then move more slowly from that level onward (Shakofsky and Nimmo, 1996). The travel time for movement from the land surface to the top of the first basalt layer may range from a few days to a few years.

At the interface of the basalt, water accumulates until the sediment is wet enough to allow breakthrough into one or more fractures, or until the wetted portion of the interface broadens enough to include the entrance to a fracture that forms an effective downward conduit. Sometimes this causes perching just above the basalt interface (Bishop, 1996).

Through fractures in the basalt, water can move faster than it typically moves through the sediments, though only if the fractures are adequately filled. When much water is available to fill the fractures, the travel time through an effectively saturated basalt layer tens of meters thick could be from days to weeks (Dunnivant and others, 1998). Flow through unsaturated fractures is likely to be much slower (Tokunaga and Wan, 1997; Su and others, 1999).

When downward flow through basalt fractures reaches a sedimentary interbed, the flow can move in various ways that are poorly understood at present (1999). This flow, like flow through the surficial layers, can be a combination of diffuse and preferential flow. It is probably slower than flow through fractured basalt. Because interbed characteristics are different from those of the surficial sediment and because evapotranspiration at a basalt-interbed interface is insignificant, the flow at these interfaces is in some ways very different from flow through the surficial sediment. Evidence of perching of water in and near interbeds suggests that, in at least some circumstances, the interbeds conduct downward flow markedly more slowly than the basalts. Whether the interbeds on the whole act more as barriers to downward flow or as zones of substantial preferential flow is not yet clearly known.

2.4.3.7.2 Combined vertical and lateral flow

Large amounts of infiltration episodically occur in features near the SDA such as the BLR, spreading areas, and runoff-collecting depressions. Downward flow is likely to be fast and voluminous compared with flow generated only from local precipitation. Thus, travel times to the aquifer below these features are probably much shorter than where infiltration occurs in smaller amounts. The downward flow rate below these features is controlled by the hydraulic conductivity of some layer, most likely in the surficial sediments. Where adjacent layers within the unsaturated zone differ in conductivity, especially at the interfaces between basalt and sediments, lat-

2-16 Review of the transport of selected radionuclides in the Interim Risk Assessment

eral flow and possibly perching occurs; therefore, a two- or three-dimensional model rather than a one-dimensional model is necessary. Some of the perching that occurs near the SDA could result from water that has moved laterally from a wetter area. This additional water could then reduce the vertical travel times to less than it would be for only locally generated flow. Another possibly relevant process is that lateral preferential flow in perched layers could entrain contaminants in the subsurface and move them horizontally to places where vertical travel times are less than those at the SDA.

2.4.3.8 Summary of unsaturated-zone flow

Flow behavior in the unsaturated-zone basalts and sedimentary interbeds and the interfaces between them is not well enough understood to quantitatively predict on the basis of widely accepted theory its effect on the spread of contamination. Flow processes routinely occurring at the INEEL in the unsaturated zone cause both vertical and horizontal flow, and create flow impediments as well as preferential pathways. It is known that some types of behavior of great importance to contaminant transport (perching) are known to occur, and others (significant upward flow from interbeds) are unlikely or impossible. Whether many other types of flow behavior, such as unstable fingered flow in interbeds, occur is unknown.

2.4.4 Flow in the saturated zone

The SRP aquifer is composed of interbedded basalt and sediment of Quaternary age. Water in the aquifer generally moves from the northeast to the southwest, principally through interflow zones in the basalt. Depth to water at the SDA is about 180 m. Saturated thickness of the aquifer is unknown at this location, but estimates based on differing geohydrologic criteria range from about 75 to 340 m (Robertson, 1974; Morse and McCurry, 1997; Anderson and Liszewski, 1997). Water-level gradients in the vicinity of the SDA area were about 0.6 m/km in 1995 (Bartholomay and others, 1997). Water levels in this area are affected by periodic infiltration of streamflow from the BLR and spreading areas. Barraclough and others (1976) suggested that local reversals in water-level gradients may occur at the SDA during periods of high infiltration.

The number and ages of basalt flows in the aquifer at the SDA are uncertain because few basalt cores have been obtained from this area. Correlations made by Anderson and others (1996) between corehole C1A and well OW-2 (fig. 2-2), located northeast and southwest of the SDA, respectively, suggest that the aquifer is made up of at least

10 basalt-flow groups, each composed of one or more basalt flows that range in age from about 600 thousand to 1.8 million years.

Porosity and hydraulic conductivity of the basalts range from very small in dense portions of basalt flows to extremely large in the fractures, rubble, and scoria between their contacts. Vertical hydraulic conductivity of individual basalt flows, even in the dense basalts, is greatly enhanced by the presence of vertical fractures that penetrate the flows. Vesicular zones occur near the tops and bottoms of basalt flows. The vesicles commonly are not interconnected and, although the porosity of these units can be large, the hydraulic conductivity can be small.

Ackerman (1995, p. 9 and 10) reported a range of probable values for effective porosity of the aquifer of from 0.10 to 0.25. This range is based on numerous studies, including measurements of more than 1,500 core and outcrop samples (Bishop, 1991; Knutson and others, 1990, 1992). Porosity of individual basalt flows generally is least in dense basalt and greatest in vesicular basalt. Although difficult to measure, the largest porosity occurs in fractures, rubble, and scoria between individual basalt flows. Collectively these porosities are referred to as effective porosity. For analysis of steady-state flow and advective transport in the eastern SRP (Ackerman, 1995), the calibration value for effective porosity was 0.21.

The SDA lies within an inferred vent corridor near the Arco-Big Southern Butte volcanic rift zone. Measurements from 32 closely spaced wells that penetrate similar inferred vent corridors at the Idaho Nuclear Technology and Engineering Center (INTEC) (fig. 1-1), indicate that saturated hydraulic conductivity in such areas can vary three to five orders of magnitude within distances of 150 to 300 m (Anderson and others, 1999). The effective hydraulic conductivity of basalt flows in the SRP aquifer at the INEEL ranges from about 0.003 to 9,800 m/d (Anderson and others, 1999). At the SDA, measured hydraulic conductivity ranges from about 0.003 to 700 m/d. Hydraulic conductivity of less than about 30 m/d generally is attributed to the effects of feeder dikes, thick tube-fed pahoehoe flows, and altered basalt. Hydraulic conductivity of more than about 30 m/d generally is attributed to the effects of thin, tube-fed pahoehoe flows; shelly- and slab-pahoehoe flows; and scoria, spatter, and ash. Hydraulic conductivity from eight wells that trend northwestward along the southern boundary of the SDA ranges from about 0.003 to 0.3 m/d, among the smallest measured hydraulic conductivities at the INEEL. These values probably reflect the presence of concealed dikes associated with at least four inferred volcanic vents

in the unsaturated zone at this location (Anderson and Liszewski, 1997, p. 10). If dikes are present in this area—a speculation also reported by Burgess and others (1994)—they likely extend vertically from beneath the base of the aquifer to the top of interbed C-D. If the small hydraulic conductivity in wells along the southern boundary of the SDA is related to concealed dikes, water and wastes in this area must go around or through the zone of dikes. Although regions of similar hydraulic conductivity in the aquifer at the SDA can be delineated using existing data (Magnuson and Sondrup, 1998), these data may not be sufficient to describe the many significant local variations that are thought to occur within vent corridors (Anderson and others, 1999).

Magnuson and Sondrup (1998) assumed an aquifer thickness of about 75 m for simulations of saturated flow at and near the SDA. They reported that this estimate was originally developed from Robertson (1974) and has been used extensively since that time. Many different methods have been used to estimate the thickness of the aquifer at specific sites at the INEEL since the study by Robertson (1974). These methods include geophysical surveys, studies of basalt cores, and measurement of permeability, porosity, and water temperature (Mann, 1986; Whitehead, 1992; Anderson and Liszewski, 1997; Morse and McCurry, 1997). Estimates based on these methods range from about 120 to more than 360 m. Morse and McCurry (1997) estimated an aquifer thickness of about 137 m in well C1A, about 0.5 km northeast of the SDA. This estimate, which may be the best estimate for the SDA, is based on the depth to the top of altered basalt, and a corresponding decrease in permeability and porosity, and a change from convective to conductive heat flow.

According to Barraclough and others (1976), local ground-water altitude, gradients, and associated rates and directions of flow are affected by four composite recharge sources: (1) regional flow from the northeast, (2) infiltration from local precipitation, (3) infiltration from the BLR, about 3 km northwest of the SDA, and (4) infiltration from the INEEL spreading areas, about 1.5 km southwest of the SDA, which periodically contain overflow from the river. According to Barraclough and others (1976), the predominant influence appears to be the spreading areas. During years of larger discharge and associated diversions to the spreading areas, such as 1965, 1969, 1983, and 1984 (Bartholomay and others, 1997), local gradients at the SDA may be northeastward (Barraclough and others, 1976). During years of small or no discharge and diversions, such as 1988 to 1994, local gradients may be southwestward. Ground-water velocities in the southern part of the INEEL range from about 2

to 7 m/d and average about 3 m/d (Ackerman, 1995, p. 11; L.D. Cecil, USGS, oral commun., 1999). Ground-water velocities at the SDA probably are within this range.

2.5 Contaminant transport

2.5.1 Source-term description

Transport of radioactive contaminants of potential concern (COPC's) at the SDA is directly related to the type of contaminant source, the chemical form of the contaminants, and the chemical environment where the contaminants reside. The exact chemical form of transuranic waste originally disposed of at the SDA is unknown and it is possible that the chemical environment in the subsurface has changed since emplacement of the waste. The contaminant sources at the SDA and surrounding area include both point sources and nonpoint sources.

2.5.1.1 Point sources

Radioactive waste has been buried at the SDA since 1952. From 1952 to 1970, low-level and transuranic radioactive wastes were buried in pits and trenches excavated into the surficial sediment. Wastes sometimes were dumped randomly into the pits and compacted, which could have damaged containers. Since 1970, burial of low-level radioactive waste has continued and transuranic waste has been stored on above-ground asphalt pads in retrievable containers. Between 1952 and 1986, more than 170 thousand m³ of low-level and transuranic waste containing about 9.5 million Ci of radioactivity was buried at the SDA (Davis and Pittman, 1990, p. 2). Of this 9.5 million Ci, about 0.5 million Ci was transuranic radioactive waste (Roland Felt, DOE, oral commun., 1999). An inventory of annual amounts of 38 radioactive contaminants that were buried was provided by Becker and others (1998, table 4-1).

The chemical form of the buried transuranic waste is unclear; however Navratil (written commun., 1996) indicated that the major plutonium residue processes at Rocky Flats, Colorado consisted of dissolution, ion exchange, precipitation, fluorination, and reduction. Plutonium tetrafluoride (PuF₄), a finely divided powder, was handled in the last two processes. Because the powdered PuF₄ easily contaminates items such as plastics, paper, gloves, and filters, it is reasonable to conclude that waste buried at the SDA contained plutonium in the form PuF₄. Other forms of plutonium also may be buried at the SDA. The transuranic waste buried at the SDA is in a variety of different physical forms that include containerized sludge, assorted

2-18 Review of the transport of selected radionuclides in the Interim Risk Assessment

solid wastes, empty contaminated drums in cardboard boxes, sewage sludge, nitrate salts, depleted uranium waste, and secondary sources such as contaminated asphalt and soil (Becker and others, 1998, p. 3-38 to 3-42). Oxygen in the unsaturated zone at the SDA may react with organic material buried in the pits and trenches, which may create localized reducing conditions and environments where some forms of plutonium are more mobile than others. Stability and movement of various plutonium species are discussed in chapter 4 of this document.

The waste at the SDA is packaged in a variety of containers, such as steel boxes, concrete casks, steel drums, plywood boxes, and other containers (Becker and others, 1998, p. 6-2). Breaching of these containers or diffusion of contaminants through the container walls allows contaminant release that can be called point-source contamination. Although this definition does not precisely follow the definition of point source contamination, the nonsystematic release of contaminants in a small area and the release by historic waste disposal methods combine to produce many individual point sources of contamination in close proximity. These point sources can be very diversified in actual contaminant composition. Once released from their containers, the contaminants can be transported away from the release sites in a variety of ways, which are discussed in other parts of this document.

2.5.1.2 Nonpoint sources

Concentrations of selected radionuclides that are slightly larger than background concentrations have been detected in surficial sediments near the SDA (Markham, 1978; Beasley and others, 1998, p. i). For example, the range of $^{239,240}\text{Pu}$ concentrations near the SDA is from about 50 pCi/m² to greater than 600 pCi/m²; however, concentrations in 11 of 19 samples ranged from 270 to 650 pCi/m² (Beasley and others, 1998, fig. 15). These radionuclides in the shallow subsurface are a potential source of contamination to the unsaturated zone and, ultimately, to the eastern Snake River Plain aquifer. The concentrations of these radionuclides at the SDA are sufficiently large to be measured with conventional methods, but at distances of more than about 2 km from the SDA, mass spectrometry would be required to detect the concentrations (L.D. Cecil, U.S. Geological Survey, oral commun., 1999). In the layered unsaturated zone beneath the SDA, these contaminants potentially could be transported by a variety of natural preferential-flow processes that include, but are not limited to, macropore flow, funneled flow, or unstable flow. Chemical, biological, or physical means of mobilizing or retarding contaminants could affect contaminant migration. The specific means

of mobilizing or retarding contaminants and the types of flow that could transport the contaminants are discussed in other parts of this document. One implication of the widespread distribution of slightly larger than background concentrations of radionuclides in surficial sediments is that extreme care should be exercised during drilling operations to avoid dragging contaminants into the deeper subsurface.

2.5.2 Summary of geochemical processes at the Subsurface Disposal Area

Several studies of geochemical processes at the SDA have been done. Olmstead (1962) and Robertson and others (1974) described the chemical and physical properties of ground water beneath the INEEL, which included analyses of ground water near the SDA. Knobel and others (1997) delineated the geochemical reactions in the SRP aquifer at the SDA and other locations at the INEEL. Rightmire and Lewis (1987b) examined the geochemistry of the unsaturated zone at the SDA. C.T. Rightmire and B.D. Lewis (USGS written commun., 1995) examined the effect of the geochemical environment on radionuclide migration in the unsaturated zone at the SDA. Rawson and Hubbell (1989) and Rawson and others (1991) studied the geochemical controls on the composition of soil pore water in the unsaturated zone beneath a mixed-waste disposal site at the SDA to determine the extent of radionuclide migration from the disposal site. Cleveland and Mullin (1993) studied the speciation of Pu at various oxidation states and Am in ground water at the SDA and found that the solubility of Am was generally low in all cases. Their results also indicated that low-oxidation-state Pu was generally insoluble in water from the SRP aquifer, was more soluble in the perched water, and could be leached from waste and ultimately reach the aquifer. Dicke (1997) examined the distribution coefficients and contaminant solubilities for the WAG-7 Baseline Risk Assessment. A generalized overview of information from these and other reports is given in the following section.

2.5.2.1 Lithology and mineralogy

Understanding the lithology and mineralogy of sediment and rock below the SDA is important in characterizing the materials present that may inhibit radionuclide migration. Several studies have examined the lithology and mineralogy of surficial sediment, sedimentary interbeds, and vesicle- and fracture-infill material at the SDA. Core sample descriptions, thin-section observations, and observations made using scanning electron microscopy for selected cores were presented by Rightmire (1984)

and Rightmire and Lewis (1987a). Voegeli and Deutsch (1953) and Nace and others (1956) presented the cation exchange capacity (CEC) and mineralogy of surficial sediment. Additional data on surficial sediment at and near the SDA were presented as follows: Barraclough and others (1976)—CEC, mineralogy, and grain-size distribution data; Rightmire and Lewis (1987b)—CEC, mineralogy, and grain-size distribution data; Bartholomay and others (1989)—mineralogy and grain-size distribution data; Liszewski and others (1997)—mineralogy and grain-size distribution data; and Liszewski and others (1999)—chemical composition data. Grain-size distribution and CEC data from samples from sedimentary interbeds and vesicle- and fracture-infill material were presented by Barraclough and others (1976) and Rightmire (1984). Mineralogy of sedimentary interbeds and/or vesicle- and fracture-infill material was presented by Barraclough and others (1976), Rightmire (1984), Rightmire and Lewis (1987b), Bartholomay and others (1989), Burgess and others (1994), and Reed and Bartholomay (1994).

Typical basalt geochemistry, sediment grain lithology, and mineralogy were discussed earlier in this chapter. Analyses of distribution coefficients for several radionuclides for basalts indicate little exchange between basalts and water; thus, basalt probably is not much of a factor in preventing radionuclide migration (Dicke, 1997; Collelo and others, 1998). Pace and others (1999) found that vesicle and fracture infill material produced the largest strontium distribution coefficients of any material at the INEEL and were the most likely sites for sorption or exchange with radionuclides in solution. A more detailed discussion on the use of distribution coefficients for predicting contaminant transport is given in chapter 5.

2.5.2.2 Water chemistry

Several water properties can affect the solubility of radionuclides; these properties will be discussed in more detail in chapter 4. To evaluate water properties, water chemistry needs to be known. Water-chemistry data from the BLR at Arco, Idaho, upstream from the SDA, were given by Rightmire and Lewis (1987b) and Bartholomay (1990b). The surface water is a calcium bicarbonate type that includes small amounts of magnesium and sulfate. Water-chemistry data for perched ground water above the C-D interbed were presented by Barraclough and others (1976), Rightmire and Lewis (1987b), Hubbell (1990), Knobel and others (1992a), Tucker and Orr (1998), and Bartholomay (1998). Water chemistry data for several suction lysimeters at the SDA were presented by Laney and others (1988) and L.C. Hull, BBWI (unpub. data, 2000). The results of a search for data on quality of

perched water at the SDA along with a list of references for the data was presented by Becker and others (1998, table 4-7). Rawson and others (1991) determined major ion concentrations of soil pore water samples. Piper plots indicate that water in the shallow boreholes was either a sodium chloride or sodium bicarbonate type and water in the deeper boreholes was a sodium chloride type (Rawson and Hubbell, 1989, p. 245). C.T. Rightmire and B.D. Lewis (USGS written commun., 1995) described possible chemical reactions that could take place if infiltrating water reacts with the available minerals.

Saturation indices (SI) calculated from the analyses of perched-water at the SDA indicate that many of the mineral phases with which these water samples were oversaturated were those with large exchange capacities: zeolite minerals (laumontite, phillipsite, wairakite) and clay minerals (calcium smectite and illite) (Rightmire and Lewis, 1987b). As discussed previously, illite was the main exchange mineral present. Saturation indices of soil pore water samples show oversaturation with respect to quartz, chalcedony, cristobalite, calcite, talc, tremolite, iron oxides, hydroxides, oxyhydroxides, and a wide variety of aluminous phyllosilicates and tectosilicates (Rawson and Hubbell, 1989, p. 245-246).

Water-chemistry data for water from eight wells completed in the SRP aquifer at and near the SDA were presented by Mann and Knobel (1988), Knobel and others (1992a), and Liszewski and Mann (1993). Water chemistry data for water from six other wells at the SDA were presented by Burgess and others (1994). Concentrations of selected radionuclides in ground water at the SDA were reported by Barraclough and others (1976), Knobel and Mann (1988), and Knobel and others (1992a). The results of a search for data on ground water at the SDA were presented by Becker and others (1998, tables 4-11 through 4-13). The water samples from the aquifer at the SDA generally are a calcium magnesium bicarbonate type (Knobel and others, 1997), which is typical of most water in the SRP aquifer. Water samples from three wells at the SDA were slightly enriched with sodium plus potassium, and water from two wells were slightly enriched with chloride (Knobel and others, 1997, p. 20).

Median SI values for the carbonate minerals calcite, and dolomite indicate that the SRP aquifer water samples from the SDA are supersaturated with respect to these minerals; therefore, precipitation of the minerals is the only thermodynamic possibility. The median SI values with respect to fluorite; the sulfate minerals celestite and gypsum; and the silicate minerals diopside, clinoenstatite, and olivine indicate undersaturation and, hence, dissolution of these minerals, if present in the aquifer. Median SI

2-20 Review of the transport of selected radionuclides in the Interim Risk Assessment

values with respect to crystalline quartz and cryptocrystalline chalcedony indicate that they are stable in the solid phase; silica glass is unstable, but near equilibrium (Knobel and others, 1997, p. 20–24).

In a mineral stability diagram for the potassium system, all water chemistry data for samples from wells at the SDA plotted in the kaolinite stability field, which indicates that microcline, muscovite, and gibbsite are unstable solid phases and would react with water to form kaolinite. In similar diagrams for the plagioclase system, data for water associated with anorthite plotted in the calcium montmorillonite field, and data for water associated with albite plotted in the sodium montmorillonite field (Knobel and others, 1997, p. 24–33).

2.5.3 Description of contaminant transport processes

2.5.3.1 Solute transport

Solute transport is described further in chapters 4 and 5 of this report. In addition to hydrologic processes such as advection, dispersion and diffusion, chemical processes will strongly affect the transport of most radionuclides by controlling or limiting their aqueous concentrations. Redox-sensitive aqueous-phase constituents and adjoining redox-sensitive minerals (such as Fe(II)-rich biotite or organic carbon) may affect the solubility of radionuclides such as U, Pu and Np by controlling their oxidation state. Generally, the nuclides under higher oxidation states, such as U(VI), Pu(VI), Pu(V), and Np(V) will be more soluble than the equivalent nuclides under lower oxidation states (for example U(IV), Pu(IV), and Np(IV)). The major ion composition of the waters may also affect the solubility/mobility of the nuclides by providing radionuclide complexing agents (such as carbonate, sulfate, and phosphate ions). The effect of pH on the hydrolysis of the radionuclides will also be an important control on their solubility/mobility. Similarly, the mineralogy and composition of the solids contacting the contaminated waters will also be important, not only through their controlling effects on the redox state, complexing ion concentrations and pH of the waters, but also by providing surfaces on which the radionuclides may sorb. Minerals such as Fe-oxyhydroxides (of which goethite will be the most predominant), calcite, clays, solid-organic matter can be expected to be strong sorbents for various radionuclides depending on the aqueous speciation of the nuclides and on the speciation of the sorbing surfaces, which will often be pH dependent. The presence or formation of radionuclide minerals may also control their aqueous concentrations, particularly in the source areas.

A deterministic model of radionuclide transport requires a large amount of information on (1) the chemistry, mineralogy and amounts of solids and solid surfaces, (2) the chemistry of the various contacting waters, and (3) the thermodynamics and kinetics of the various chemical processes of importance. Because of the difficulty of characterizing, to a sufficient level of detail, all the relevant information, solute transport models often adopt a more empirical approach; they commonly assume that the retardation of a contaminant of interest relative to the movement of the water can simply be described as constant and uniform throughout the simulation domain. In other words they use the K_d approach.

2.5.3.2 Colloid transport

Transport of radionuclides beneath WAG-7 could be enhanced by association with colloids and larger particles capable of being transported by water. Colloids can be rock and mineral fragments, mineral precipitates and weathering products, macromolecular components of dissolved organic carbon such as humic substances, biocolloids such as micro-organisms, and microemulsions of nonaqueous phase liquids.

Actinides can form colloids by hydrolysis and precipitation. These reactions are affected by pH, the concentration of complexing agents, actinide concentration, and oxidation state. For example, Am solubility is at a minimum at pH 8. Both Np(IV) and Pu(IV) are much less soluble than other oxidation states of either element. Colloid as used in this section includes any non-aqueous phase state.

The mobility of colloids in the subsurface is controlled by the stability of the colloids in ground water, chemical interactions between colloids and immobile matrix surfaces, and hydrological and physical factors. Particles can be removed through mechanical filtration by smaller pore spaces. Changes in aqueous chemistry can cause aggregation of colloidal particles, or if electrostatic and London-van der Waals forces are present, attachment of particles to immobile surfaces. Colloids can be destabilized by increases in ionic strength, which result in compression of the double layer surrounding particles, or by pH-induced changes in surface charge.

There is evidence for transport of actinides as colloids during batch and column experiments (for example, Ramsay, 1988; Champ and others, 1982). Actinides are associated with a wide range of particle sizes, from 500 molecular weight to clay sized and larger. In the batch and column experiments, actinides often eluted from columns at much faster rates than would have been predicted from equilibrium sorption of aqueous species. Generally, the

form of the actinide eluting from the columns was not determined, so whether the fast elution was facilitated by transport as a colloid or transport as an aqueous complex is undetermined. However, in some experiments there was enough secondary evidence to implicate transport as a colloid.

Colloid facilitated transport of actinides in the field also has been documented. Pu and Am were found beneath and downgradient from waste-disposal beds at Los Alamos, NM at distances that indicate colloid facilitated transport (Nuttall and others, 1991). Arguments, although controversial, suggest that there also is evidence for migration of Pu as a colloid at the Nevada Test Site (Kersting and others, 1999). Isotopic ratios show that the Pu, measured in ground water came from a particular underground explosion 1.3 km away from the blast site. The 30-year travel time is consistent with the travel time for ground water in the area. U associated with colloidal kaolinite and silica has been detected in ground water from Australia (Payne and others, 1992).

Colloids are present in the basalt fractures at the INEEL and also have been measured in ground water. The tighter packed interbed sediments beneath the SDA could inhibit transport of colloids by filtration; however, colloid transport through the coarser fractures is a possibility. Detections of Pu and Am in the interbeds at the INEEL may indicate colloid-facilitated transport.

2.6 Summary

Diverse hydraulic processes control contaminant transport through the 200-m-thick unsaturated zone in the southwestern portion of the INEEL. The interbedded basalts and sediments that comprise this unsaturated zone are structurally complex in terms of both preferential-flow paths and layers that contrast in properties such as thickness, permeability, and porosity. The permeability of the fractured basalts is generally much larger than that of dense basalts and sediments.

The unsaturated zone at the INEEL site is complex in ways that have not been much investigated in other settings. The unsaturated zone near the SDA is about 200 m thick, and comprises granular media as well as fractured rock. Its uncommon features, relative to the most widely studied earth sites, include great thickness, severe contrasts between layers in the form of fractured igneous rock alternating with unconsolidated sediments, intense stratification of the media, and large nonuniform inputs of water over the land surface.

Vertical water movement through the basalt-sedimentary sequence is largely controlled by the hydraulic

conductivity of fractures in the basalt flows and by the lower hydraulic conductivity of some of the interbeds. The interfaces between sediments and basalt may have significant additional effects, both from the commonly expected phenomena of flow through contrasting layers in the unsaturated zone, and also from mechanisms peculiar to the combination of sediments and fractured rock.

The basalts and sedimentary layers and the interfaces between them are not well enough understood with respect to their unsaturated-zone flow behavior to predict on a theoretical basis the effect of unsaturated-zone flow on the spread of contamination. Various processes routinely operate in the unsaturated zone in this area to cause vertical and horizontal flow. Some relevant types of behavior (for example perching) are known to occur, and others (for example significant upward flow from interbeds) are unlikely or impossible, but there are many that may or may not occur (for example unstable fingered flow in interbeds) with an unknown net effect on contaminant transport.

Seasonal streamflow, local runoff, and snowmelts routinely generate large quantities of infiltrating water for periods of days or weeks. Particular concerns arise regarding seasonal diversion of water from the BLR to spreading areas located as close as 1 km to the SDA. Short-term, large-volume infiltration may cause rapid, long-range transport phenomena.

Vertical flow occurs mainly through highly conductive fractures. As a result of substantial surface inputs of water, some of the water perches in or on the interbeds, or on basalt flows of lesser effective vertical conductivity. The perched zones may persist for a few months or longer, until horizontal and vertical flow spreads them out enough to leave the porous materials unsaturated. The behavior and composition of perched water observed since the 1970's suggest that this water may sometimes move within the unsaturated zone at unusually high flow rates and volumes. These effects can severely affect contamination in various ways, including fast horizontal transport.

Certain features of basalt flows, volcanic rift zones, and sedimentary interbeds may constitute hydraulic pathways for the preferential movement of water in the unsaturated zone and in the aquifer (Anderson and others, 1999). Preferential-flow paths associated with subsurface features can transport water and contaminants horizontally to adjacent regions or vertically to the aquifer far sooner than might be predicted based on bulk medium properties and Richards equation. An important secondary feature of preferential flow is that the interaction with contaminants is effectively limited to a fraction of the subsurface medium, limiting adsorption and other attenuating

2-22 Review of the transport of selected radionuclides in the Interim Risk Assessment

processes. The equivalent-granular-medium approach is essentially the only fully practical means of treating preferential flow over large scales that has been widely applied, though it has significant limitations.

Rubble and fracture zones provide the main conduits for flow in the saturated zone. The effective hydraulic conductivity ranges from about 3×10^{-8} to 8.4×10^{-2} m/s. The aquifer is assumed to be anisotropic, with estimated ratios of horizontal to vertical basalt permeabilities ranging from about 3:1 to 300:1 (Barraclough and others, 1976; Magnuson, 1995; Magnuson and Sondrup, 1998).

Key issues related to subsurface contaminant transport include (1) travel times to and within the aquifer, both average or typical values and the range of values to be expected, and (2) modes of contaminant transport, especially adsorption processes. Some features promote transport of radionuclides, for example preferential flow, irregularity of layer interfaces, flooding, and perched water. Some features inhibit transport of radionuclides, for example layer contrasts, fineness of grains in interbeds, thickness of the unsaturated zone, relatively low average precipitation, and low porosity of many of the media, such as basalt between fractures.

3.0 Task 1: Review of radionuclide sampling program and available data at the Subsurface Disposal Area

3.1 Introduction

This chapter is divided into five parts. The first part is a review of the methods used by the site contractor to monitor for and report detections of selected radionuclides in the environment near the Subsurface Disposal Area (SDA) (section 3.2). The second part is a review of the site contractor's sampling methodology (section 3.3), analytical methods (section 3.4), and quality assurance and quality control protocols (section 3.5). The third part is a review of data from Lockheed Martin Idaho Technologies, Inc. (LMITCO) for reported detections of radionuclides in the unsaturated and saturated zones at and near the SDA (section 3.6). The fourth part is a brief discussion on the significance of the reported detections (section 3.6.3) and the fifth part is a list of specific recommendations to improve sample collection and analyses, data generation and reporting, and overall quality assurance and quality control for generating data in support of the Waste Area Group 7 (WAG-7) Comprehensive Remedial Investigation and Feasibility Study (RI/FS) (section 3.7). Multiple criteria were considered in evaluating the data. These criteria were (1) statistical significance, (2) isotopic association, (3) consistency of detections with the historical data record, (4) possibility of cross contamination, and (5) adequacy of the sampling program.

Tables referenced in this chapter are located at the end of section 3.7.

3.1.1 Background

Radionuclide data collected in support of the WAG-7 Comprehensive RI/FS will be used to determine the possible release of radioactive contaminants from the SDA and to aid in understanding the fate and transport of radionuclides (Barrie and Haney, 1997). The specific data quality objectives (DQOs) for radionuclide sampling of six perimeter ground-water monitoring wells near the SDA are to (1) detect contaminated ground water moving away from the SDA, (2) determine the lateral and vertical extent of contamination, (3) obtain samples representative of water quality, and (4) determine the ground-water flow direction and velocity. The specific DQOs for four ground-water monitoring wells upgradient in the far field are provided by the DOE (1998, table 4-3). They are to (1) identify contaminant concentrations in the aquifer to

determine whether the contaminants are derived from the SDA or from an upgradient source, (2) delineate the areal extent of the carbon tetrachloride (CCl_4) plume in the unsaturated zone upgradient of the SDA, (3) identify well (M14S, fig. 2.3) to determine background concentrations for long-term monitoring, (4) calibrate fate and transport models that predict plume dimensions and concentrations, and (5) track and discriminate the Test Reactor Area (TRA) and the Idaho Chemical Processing Plant (ICPP) (currently called the Idaho Nuclear Technology and Engineering Center (INTEC)) plumes and evaluate risk from SDA contaminants.

3.1.2 Purpose and scope

The purpose of this review is to determine whether the Department of Energy (DOE) site contractor at the INEEL is using scientifically defensible methods to quantify and monitor selected radionuclides in the environment near the SDA. This review includes the complete measurement process: reporting of data, sample collection and analysis, and quality control of selected radionuclide data. Therefore, each of these areas will be reviewed as they pertain to the criteria outlined in section 3.1. The scope is confined to WAG-7 and includes an evaluation of the methods used by the site contractor to monitor for and report detections of ^{241}Am , $^{232,234}\text{U}$ undivided, ^{234}U , ^{235}U , ^{238}U , ^{238}Pu , $^{239,240}\text{Pu}$ undivided, and ^{230}Th .

3.2 Detection limits, statistical screening criteria, and reporting of data

The detection limit currently used by the site contractor for ^{241}Am , $^{232,234}\text{U}$ undivided, ^{234}U , ^{235}U , ^{238}U , ^{238}Pu , $^{239,240}\text{Pu}$ undivided, or ^{230}Th in water is 0.05 picocuries per liter (pCi/L) (Dave Burgess, LMITCO, written commun., 1998). For these selected radionuclides in soils and other solid matrices, the detection limit is 0.003 pCi/g. As discussed in section 3.4, "Analytical Methods," these detection limits are adequate unless questions are raised about reported detections that are at these limits. Improvements in precision for detections at and near the quoted limits can be gained by using isotope dilution mass spectrometry, thermal ionization mass spectrometry, or accelerator mass spectrometry.

Data-reporting criteria outlined by Becker and others (1996) call for reporting detections to the DOE and State of Idaho if an analytical result is equal to or larger than two sample standard deviations ($2s$)¹. Becker and others (1996) further noted that when the above criterion is met, there is a 95-percent confidence that the target analyte has

3-2 Review of the transport of selected radionuclides in the Interim Risk Assessment

been detected. However, the correct application of the statistics of detection (hypothesis testing) according to Currie (1984) and the American Society for Testing and Materials (ASTM) (1996) leads to the conclusion that at $2s$, there is a 95-percent confidence that the true concentration is only within a range of plus or minus the associated uncertainty. For example, for the result 5 ± 2 , there is a 95 percent confidence that the true concentration is somewhere between 9 and 1. This does not address the question of detection or nondetection. During an interview of LMITCO personnel, the question of the origin of the $2s$ criterion was addressed and the consensus was that the $2s$ criterion was based solely on historical precedence (Kirk Dooley, LMITCO, oral commun., 1998).

Discussion with personnel from LMITCO, DOE, and the State of Idaho indicated that, among these groups, $2s$ is the agreed-upon reporting criterion for detections; however, hypothesis testing is the most defensible method for determining statistical detection of a target analyte. The following illustration of the application of hypothesis testing to the question of detection for any radionuclide is based on a method outlined by Currie (1984) and Cecil (1989), and is the method recommended by ASTM (1996) for reporting low-level radionuclide data.

In the analysis for radionuclides, laboratory measurements are made on a target sample and a prepared blank. In this discussion, it is assumed that the blank is a so-called well-known blank (Currie, 1984). Instrument signals for the sample and the blank vary randomly. Therefore, it is essential to distinguish between two key aspects of the problem of detection: (1) the instrument signal for the sample must be larger than the signal for the blank before the decision can be made that radionuclides were detected, and (2) an estimation must be made of the minimum radionuclide concentration that will yield a sufficiently large signal before the correct decision can be made for detection or nondetection of the radionuclide. The first aspect of the problem is a qualitative decision based on an observed signal and a definite criterion for detection. The second aspect is an estimation of the detection capabilities of a given measurement process.

In the laboratory, instrument signals must exceed a critical level before a qualitative decision can be made as to whether the radionuclide was detected. As a guide, radionuclide concentrations that are equal to 1.6 times their associated sample standard deviation meet this criterion. At $1.6s$, there is about a 95-percent probability that the correct decision, not detected, will be made. The mul-

tiplier on the sample standard deviation, 1.6, varies with background counts and is based on a measurement process that includes data for a well-known blank. Given a large number of samples, as many as 5 percent of the samples with measured concentrations larger than or equal to $1.6s$, which were concluded as being detected, might not contain radionuclides. These results are referred to as false positives and are errors of the first kind in hypothesis testing. Hypothesis testing may be applied to individual analytical results to determine detection versus nondetection.

Once the critical level of $1.6s$ has been defined in reporting data, the minimum detectable concentration may be estimated. Radionuclide concentrations that equal $3s$ represent a measurement at the minimum detectable concentration. Again, the multiplier on the sample standard deviation, 3, varies with background counts and is based on a measurement process that includes data for a well-known blank. For true radionuclide concentrations of $3s$ or larger, there is about a 95-percent probability that the radionuclide was detected in the sample. In a large number of samples, the conclusion "not detected" will be made in about 5 percent of the samples that contain true concentrations at the minimum detectable concentration of $3s$. These results are referred to as false negatives and are errors of the second kind in hypothesis testing.

True radionuclide concentrations between $1.6s$ and $3s$ have larger errors of the second kind. That is, the probability of false negative results for samples with true concentrations between $1.6s$ and $3s$ is larger than 5 percent. However, between $1.6s$ and $3s$ there may be true radionuclide concentrations in the sample. By equating $1.6s$ and $3s$ without discussing the possibilities of a true concentration between $1.6s$ and $3s$, the probability of false negatives is about 50 percent. In other words, if only the $3s$ minimum detectable concentration is used as a guide, at least 50 percent of the time, true concentrations between $1.6s$ and $3s$ will be missed.

LMITCO uses $2s$ as the criterion for detection versus nondetection and reports the results at $2s$ and larger as being 95-percent probable for detection. This is not an application of hypothesis testing and not a correct application of detection statistics. By not explaining the associated uncertainties of detection in terms of hypothesis testing, the end user of the data is being misled into thinking that at $2s$ there is a 95-percent probability that radionuclides have been detected in the sample. Using a one-tailed statistical test that is not based on hypothesis testing only gives a 95-percent probability that the result is within a range that is plus or minus $2s$ about the analyt-

¹ In this report, "s" represents the sample standard deviation and "σ" the population variance. These two terms are often used interchangeably and thus incorrectly in the references cited.

ical result. This does not answer the question of detection versus nondetection.

The hypothesis testing method of reporting low-level radionuclide data is recommended by the National Institute of Science and Technology, ASTM, the International Union of Applied and Pure Chemistry (IUPAC), and is used by the USGS. Personnel at DOE and LMITCO who are responsible for reporting radionuclide data generally do not use hypothesis testing to determine detection of radionuclides. It is recommended that all personnel at DOE, LMITCO, and the State of Idaho address this issue in reporting detections of radionuclides. If using 2s as the screening criterion for detection is to be continued, then it should be documented in the Quality Assurance Plan (QAP) or Sampling and Analysis Plan (SAP) as an arbitrary DQO that is not based on hypothesis testing.

In reviewing the reporting of detections for radionuclide data, two related problems concerning data validation were discovered. The first involved reporting detections that were apparently orders of magnitude larger than the analytical method detection limits with associated uncertainties as large as 30 percent. The following documentation is offered for illustration. On February 3, 1998, the USGS brought to the attention of DOE inconsistencies in reported detections of ^{241}Am and ^{54}Mn . The ^{241}Am concentration was reported as 1.03 ± 0.27 pCi/L. This concentration is almost two orders of magnitude larger than the method detection limit and the associated uncertainty is almost 30 percent of the concentration. LMITCO personnel were notified, and they subsequently learned that the laboratory had omitted a calibration correction. When the error was corrected, the associated uncertainty was reduced to 0.03 pCi/L. According to personnel from the LMITCO's Sample Management Office (SMO) (Cliff Watkins and Don Koeppen, LMITCO, oral commun., 1998) the calibration correction was missed initially because a Level C instead of a Level B validation had been performed.

The second problem concerning data validation involved reporting detections of isotopes that are highly unlikely to be in environmental samples collected in the aquifer near the SDA. An example is ^{54}Mn , which was reported as a detection in a water sample collected in October 1997 from a well completed in the regional aquifer. Because this isotope has a 320-day half-life, it should not have been reported as a detection until a complete data validation had been performed. A screen for exotic isotopes such as ^{54}Mn in the computer program used to construct the data base for WAG-7 could prevent this type of problem. LMITCO personnel were advised of the reported detection of ^{54}Mn , and they subsequently per-

formed a complete Level A validation and found that ^{54}Mn should not have been reported as a detection. In the documentation for reporting data generated in monitoring at the SDA, it is stated that for radionuclides, a Level B validation will be performed. In our interview of LMITCO employees, it was discovered that because of budget considerations, a Level C instead of a level B validation had been performed for both of the reported detections cited above. However, a Level A validation was performed when the analyses were called into question (Kathy Falconer, written commun., 1998). The level of data validation should be consistent for all radionuclides.

3.3 Sampling methodology

The sampling methodology used for routine monitoring in support of the WAG-7 Comprehensive RI/FS was described by Barrie and Haney (1997). The specific sections by Barrie and Haney (1997) dealing with sampling methodology are section 3, "Sampling Location, Frequency, and Media," section 4, "Sample Identification," section 5, "Sampling Equipment and Procedures," section 6, "Sample Handling, Packaging, and Shipping," section 7, "Documentation," and section 8, "Handling and Disposition of Investigation Derived Waste".

3.3.1 Sampling location, frequency, and media

Barrie and Haney (1997, fig. 1-1) designated six wells as water-quality monitoring sites. These wells are completed in the Snake River Plain (SRP) aquifer and are designated as M1SA, M3S, M4D, M6S, M7S, and M10S (fig. 2-2). The M in the site identifier indicates monitoring well, the S indicates shallow, approximately 190 m below land surface datum (LSD), and the D indicates deep, approximately 250 m below LSD. All of these sites are in the near field—situated close to the SDA. M3S and M7S are upgradient of the SDA; M6S is slightly southeast of the SDA; and the rest are downgradient. These six perimeter wells were installed in 1992 and were first sampled in October 1992. Four additional wells completed in the SRP aquifer were installed in 1998 and are upgradient of the SDA in the far field—situated at a distance from the SDA (Barrie and Haney, 1997, fig. 1.1). These wells, designated as M11S, M12S, M13S, and M14S (fig. 2-3) were first sampled in July 1998. An additional well (USGS 127, fig. 2-3) was completed in 1999 and will be incorporated into the monitoring program. This well also is upgradient from the SDA in the far field.

Perched-water bodies also are monitored at the SDA and water samples from several perched-water wells and

3-4 Review of the transport of selected radionuclides in the Interim Risk Assessment

lysimeters have been analyzed for water quality. In April 1997, a long-term, perched-water-quality program that consists of quarterly sampling was established at the SDA. It is not clear which wells and lysimeters are included in this sampling program; however, radionuclide concentrations in water from several sites have been reported since, on, or before April 1997. These sites include 77-2, 78-1, 88-02D, 89-01D, D-06, D-15, PA-01, PA-02, PA-03, TW-1, USGS 92, W-04, W-06, W-08, W-23, and W-25.

Generally, the locations of the wells in the ground-water monitoring program near the SDA (if well USGS 127 is incorporated) are adequate to meet the DQOs identified by Barrie and Haney (1997, section 2, p. 2-1) and by the DOE (1998, table 4-3, p. 4-22). Sampling the perched-water bodies and the unsaturated-zone water is more difficult because less water is available (sometimes no water is available) for determining the presence of radioactive contaminants. Because of this shortage of sample water, some components of the monitoring program need to be more rigorously defined in the SAP according to the prioritization scheme given by the DOE (1998, table 4-2, p. 4-16). The sample medium for the ground-water monitoring program is "ground water" and the frequency of sample collection is specified in the SAP Table for Chemical and Radiological Analysis (Barrie and Haney, 1997, appendix B, p. B1-B31). The frequency specified in the SAP for the original 6 perimeter ground-water monitoring wells is quarterly for 19 sampling rounds, and annually or semiannually for 6 lysimeters (PA-01, PA-02, PA-03, PA-04, D-06, and TW-1) (fig. 2-2) for 3 sampling rounds. The time period specified in this table is from the third quarter of fiscal year 1993 through the third quarter of fiscal year 1999. The table is very well planned and provides detailed information on what to sample for and the types of analyses to request; however, the table needs to be updated to include information on sampling rounds that follow the third quarter of fiscal year 1999. The table also needs to be expanded to include schedules for the four wells installed in 1998 that were added to the monitoring program (as indicated in DOE, 1998, p. 4-22), the ground-water monitoring well constructed in 1999 (USGS 127), and the perched-water wells and lysimeters (through fiscal year 2004 as indicated in DOE, 1998, p. 4-16).

3.3.2 Sample identification

Barrie and Haney (1997) specified that all samples collected be uniquely identified by a 10-character sample identification code. Barrie and Haney (1997, appendix B)

list the first six characters of this code under the heading Sampling Activity. When field guidance forms and sample labels are generated for the individual sample rounds, the final four characters are established and printed on the forms and labels along with the other six characters. The entire 10-character code is assigned by LMITCO's SMO and a data management system is used to ensure the uniqueness of the sample identification codes. This procedure appears to be adequate for the unique identification of samples. When appendix B is updated to incorporate the additional sampling rounds, wells, and lysimeters, the sampling activity field also should be updated.

3.3.3 Sampling equipment and procedures

Barrie and Haney (1997, section 5 and appendix A) gave detailed instructions for radionuclide ground water sample collection. Section 5 describes site preparation, field measurements, well purging, and well sampling. Appendix A describes field-sampling methods (FSMs) and standard operating procedures as follows: FSM #1, "Well Purging and Sampling with a Submersible Pump", FSM #2, "Decontamination", FSM #3, "Water level measurements with an electronic recorder", FSM #4, "Water level measurement with a steel measuring tape", and FSM #5, "Hydrolab operation". In general, the sampling procedures and equipment are adequate; however, the introduction to section 5 indicates that these procedures apply only to the six perimeter ground-water monitoring wells. The section should specify that these procedures also apply to the other ground-water, perched-water, and lysimeter sites. Appendix A also contains a copy of correspondence providing guidance on the calculation of the amounts of acid or base that can be added to ground-water samples of assorted sizes so that they are in compliance with the Department of Transportation (DOT) shipping regulations. Table 6 of Section 5 also gives guidance on the amount of acid or base to add to ground-water samples; however, David Sill (DOE, oral commun., 1999) indicated that samples for radionuclide analysis submitted to DOE's Radiological and Environmental Laboratory (RESL) have not been acidified sufficiently. To minimize the loss of radionuclides from solution to the container walls, steps should be taken to ensure adequate sample preservation in the field and the laboratory.

3.3.4 Sample handling, packaging, and shipping

Barrie and Haney (1997, section 6, p. 6-1 to 6-3) provided instructions for sample handling, packaging, and shipping. Procedures for these comply with the applicable

Federal regulations specified by Barrie and Haney (1997, p. 6-1) and are adequate to meet program requirements.

3.3.5 Documentation

Barrie and Haney (1997, section 7) provided general guidance on documentation procedures, including the controls and disposition of documents and instructions for data entry and corrections. They also identified and described necessary field documents: sample labels, sample tags, chain-of-custody forms, sample logbooks, shipping logbooks, calibration logbooks, field-team leader logbooks, quality assurance plan, field sampling plan and attachments, and the health and safety plan. These procedures and documents generally are adequate to meet the needs of the data acquisition program; however, a few minor deviations from recommended methods were noted and will be discussed in section 3.5 of this report, on quality assurance (QA) and quality control (QC) protocols.

3.3.6 Handling and disposition of investigation-derived waste

Barrie and Haney (1997, section 8) defined the various types of waste that could be generated by the sampling program and the storage and disposition of the wastes. The procedures for storage and disposition of the wastes were carefully considered and are adequate for the needs of the program. One potential type of waste, purge water, is addressed in their table 7. On the basis of previous analyses of samples from the perimeter wells M1SA, M3S, M4D, M6S, M7S, and M10S (fig. 2-2), it was determined that concentrations of various constituents (including radiochemical constituents) were within their release limits (either maximum concentration limits (MCLs) or proposed MCLs) and, therefore, need not be containerized. This is a well-designed table, but it should be updated to include the recently added and planned ground-water monitoring wells, the perched-water monitoring wells, and the lysimeters.

3.4 Analytical methods and laboratory techniques

The analytical methods used for routine monitoring samples collected in support of the WAG-7 Comprehensive RI/FS were summarized by Baumer and others (1997). The approved analytical method categories listed by Baumer and others (1997) in section 4.1, are to be used unless changes are documented in the site-specific field sampling plan (FSP) (Barrie and Haney, 1997, appendix C, p. C-1 to C-2). No exceptions are noted in appendix C

of the FSP. The approved method categories listed by Baumer and others (1997) are (1) Environmental Protection Agency (EPA) approved methods, (2) American National Standards Institute (ANSI) standard methods, (3) ASTM standards, (4) industry-accepted methods, and (5) methods described in the laboratory statement of work (SOW) prepared by the SMO. These analytical methods are adequate to meet the requirements of the program if the analyzing laboratory is in conformance with the SOW. However, because some reported detections at the method detection limit have been questioned, it would be useful to list the specific analytical method for each constituent in the SAP Table for Chemical and Radiological Analysis (Barrie and Haney, 1997, appendix B). Whenever possible, technical standards adopted by voluntary consensus standards bodies (such as ASTM) should be used for measuring concentrations of radioactive constituents in water and soils (Turner, 1999). Congress, in the National Technology Transfer and Advancement Act (Public Law 104-113) and its Amendments (Collins, 1999; Turner, 1999), has mandated the use of voluntary consensus standards by all Federal agencies.

3.5 Quality assurance and quality control protocols

“Each office or laboratory generating data has the responsibility to implement minimum procedures which assure that precision, accuracy, completeness, and representativeness of its data are known and documented. In addition, an organization should specify the quality levels which data must meet in order to be acceptable” (U.S. EPA, 1980, section 1). To ensure that these responsibilities are met, EPA requires that each data-producing organization must have a written QA project plan covering each monitoring or measurement activity within its purview. U.S. EPA (1980) provides (1) guidelines and specifications that describe the 16 essential elements of a QA project plan, (2) recommendations on the format to be followed, and (3) specifications on how plans will be reviewed and approved. The QA and QC protocols employed for WAG-7 are presented in the quality assurance project plan (QAPjP) (Baumer and others, 1997), and by Barrie and Haney (1997, appendix C). Additional documents relating to the contents and preparation of the QAPjP and the SAP are itemized in U.S. DOE (1998, section 4, p. 4–9). The EPA guidance document (U.S. EPA, 1980), particularly the 16 elements that must be *considered* in the preparation of a QAPjP, was used for evaluating the QA and QC protocols established for the data acquisition program. Following is a list of the 16 elements

3-6 Review of the transport of selected radionuclides in the Interim Risk Assessment

and our evaluation of how completely these elements are addressed in the QAPjP:

Title page.—The signatures required in section 5.1.A are satisfactory.

Table of Contents.—The most important recommended items are included in the table of contents, which is adequate for the needs of the monitoring program.

Program Description.—The recommendations for this section are adequately addressed in the QAPjP; however, Appendix B of the SAP (Barrie and Haney, 1997) needs to be updated to incorporate the additional sampling rounds, wells, and lysimeters to be in compliance with the last paragraph of Section 1.2 of the QAPjP (Baumer and others, 1997).

Program Organization and Responsibility.—The U.S. EPA (1980) implies that responsible individuals be identified. Although the QAPjP (Baumer and others, 1997) does not identify these individuals, it does identify the organizational positions that are responsible for the execution of the QAPjP (Baumer and others, 1997). This should be adequate to meet the requirements associated with program organization and responsibility.

QA Objectives for Precision, Accuracy, Completeness, Representativeness, and Comparability of Measurement Data.—The requirements of this section are met in section 2, tables 2-1 through 2-12, and section 9 of the QAPjP (Baumer and others, 1997) and are adequate for the needs of the program.

Sampling Procedures.—The specific requirements of this section are addressed in the QAPjP (Baumer and others, 1997, section 3, and tables 3-1 and 3-2) and in the SAP (Barrie and Haney, 1997). The sampling procedures specified in these documents are adequate for the needs of the program; however, the sample collection schedules (Barrie and Haney, 1997, appendix B) and sampling locations (Barrie and Haney, 1997, fig. A-1) should be updated to include the additional sampling rounds, wells, and lysimeters.

Sample Custody.—The specific requirements of this section are addressed in the QAPjP (Baumer and others, 1997, section 3.4) and in the SAP (Barrie and Haney, 1997, Section 7.1). The chain-of-custody record and the sample label are very well designed; however, it would be desirable to have an exact location (such as latitude and longitude) on the sample label. The other aspects of sample custody are adequate for the needs of the program.

Calibration Procedures and Frequency.—The requirements of this section are addressed in the QAPjP (Baumer and others, 1997, section 4.2) and the SAP (Barrie and Haney, 1997, appendix A). The provisions for cal-

ibration and documentation of calibration are adequate for the needs of the program.

Analytical Procedures.—Analytical procedures are addressed in the QAPjP (Baumer and others, 1997, section 4.1). Adequacy of the analytical procedures was previously discussed in this document in section 3.4, “Analytical methods (laboratory techniques).”

Data Reduction, Validation and Reporting.—The requirements of this section are addressed in the QAPjP (Baumer and others, 1997, sections 6 and 8). The data-reduction and validation methods, including the levels of data validation, are adequately identified in these sections. If the methods are rigorously followed, they should be adequate for the needs of the program. However, as noted in section 3.2, “Detection limits, statistical screening criteria, and reporting of data,” there have been inconsistencies in applying data validation levels in the review process.

Internal Quality Control Checks.—The requirements of this section are addressed in the QAPjP (Baumer and others, 1997, section 7 and table 2-12), and the SAP (Barrie and Haney, 1997, section 3 and appendix B). The QC identification and definition of QC sample types in the QAPjP (Baumer and others, 1997) are very good. Consideration should be given to the possibility of adding spiked samples to this list. The specific identification of QA/QC samples in the SAP tables (Barrie and Haney, 1997, appendix B) is also very well thought out and is adequate for program needs; however, the tables should be updated to include the additional sampling rounds, wells, and lysimeters.

Performance and System Audits.—The requirements of this section are addressed in the QAPjP (Baumer and others, 1997, section 8). As written, the procedures are adequate to meet the needs of the program; however, some concerns regarding laboratory selection and performance were identified in the Task 5 report submitted to DOE earlier in this investigation (U.S. Geological Survey, 1998).

Preventive Maintenance.—The requirements of this section are addressed in the QAPjP (Baumer and others, 1997, section 5) and the SAP (Barrie and Haney, 1997, appendix A). The procedures are adequate to meet program needs.

Specific Routine Procedures Used to Assess Data Precision, Accuracy, and Completeness.—The requirements of this section are addressed in the QAPjP (Baumer and others, 1997, section 2, tables 2-1 through 2-12, section 9) and are adequate to meet program needs.

Corrective Action.—The requirements of this section are addressed in the QAPjP (Baumer and others, 1997,

section 10) and are adequate for the needs of the program if properly implemented. Some reporting of data as identified in U.S. Geological Survey (1998) (see discussion in this section titled “Data reduction, validation and reporting”) indicate that implementation of corrective actions may not be complete. This situation needs to be remedied.

Quality Assurance Reports to Management.—The requirements of this section are addressed in the QAPjP (Baumer and others, 1997, section 11) and are adequate for the needs of the program.

The QAPjP (Baumer and others, 1997) meets the EPA requirement of having a written and approved QA plan (U.S. EPA, 1980, section 2.3), and, when combined with the SAP (Barrie and Haney, 1997), provides a framework for producing data of known and documented quality that meet the needs of the program. The few exceptions are noted in the above 16 elements.

3.6 Reported detections in sediments and water

Data on surficial sediment and sedimentary interbeds will be discussed first because this media is in close proximity to the buried waste at WAG-7. Any radioactive waste that is mobilized from the pits, trenches, or surface soils may move through the unsaturated zone and contact the sedimentary interbeds before reaching the aquifer. Data for ground water from the regional aquifer and from perched zones at WAG-7 will be discussed last.

3.6.1 Surficial sediments and sedimentary interbed data

Sampling of sediments for radionuclide analysis as part of the environmental monitoring program at the SDA began in the 1970's. The results of these studies (numbered 1-6) are summarized below.

(1) 1971–72 drilling program—During 1971–72, six observation wells, called “interior wells,” (USGS 91 to USGS 96) were drilled within the SDA to depths of 72 to 92 m below land surface (Barraclough and others, 1976). Well locations were selected (fig. 2-2) to provide representative coverage of the burial ground and to avoid drilling into or through any of the buried waste. Four additional wells, called “exterior wells,” (USGS 87 to USGS 90) were drilled at locations surrounding the SDA (fig. 2-2) to depths of 191 to 197 m below land surface. Most of the sampling and analyses of drill cuttings and core material were of the surficial sediments (below 0.5 m) and sedimentary interbeds B-C and C-D at depths of about 34 m and 73 m. A total of 58 sediment samples were analyzed; in 27 of these samples concentrations of one or more of the anthropogenic radionuclides ^{60}Co ,

^{90}Sr , ^{137}Cs , $^{140}\text{Ba/La}$, ^{238}Pu , $^{239,240}\text{Pu}$, and ^{241}Am were statistically positive (defined by Barraclough and others, 1976, as exceeding the 2s counting error). Analyses from the samples containing statistically positive concentrations are shown in table 3-1 (Barraclough and others, 1976, table II). The largest concentrations of actinides in subsurface samples from the interior wells were from the B-C interbed at the 31- to 34-m sample interval from wells USGS 93 and USGS 96:

$^{238}\text{Pu} 14 \pm 3 \text{ pCi/kg}$

$^{239,240}\text{Pu} 540 \pm 12 \text{ pCi/kg}$

$^{241}\text{Am} 230 \pm 20 \text{ pCi/kg}$

The report by Barraclough and others (1976, p. 74–83) contains an extensive discussion of potential artificial contamination of the samples during drilling and sample handling. The authors concluded that the potential for artificial contamination was greatest for the four exterior wells, which were drilled by using the cable-tool method and water as the drilling fluid. Therefore, although some statistically positive analytical results (determined by using the 2s criteria) were obtained for water from wells USGS 87, USGS 89, and USGS 90 (Barraclough and others, 1976, table IV), these results may be artifacts of sampling; radioactive contamination (from global fallout or INEEL operations) in the surficial sediment could have been carried downhole and artificially contaminated the subsurface samples. Concentrations of radionuclides in surface soil in and around the Radioactive Waste Management Complex (RWMC) are given in table V of the report by Barraclough and others (1976); an extensive 1973 sampling (done by Aerojet Nuclear Company) of surface soils from within the RWMC showed an average $^{239,240}\text{Pu}$ concentration of 2,300 pCi/kg. The six interior wells were drilled primarily by using dry-air, wire-line rotary techniques, and special precautions were taken to avoid contamination. Barraclough and others (1976, p. 87) concluded that there was evidence of migration of anthropogenic radionuclides, including isotopes of Am and Pu, to the B-C and perhaps the C-D interbeds at the SDA.

(2) 1975 core drilling program—In response to the USGS findings above, Aerojet Nuclear Company and U.S. Energy Research and Development Administration (ERDA)/Idaho Operations initiated a new drilling program in 1975 (Burgus and Maestas, 1976). Three wells, USGS 96A, 96B, and 93A (fig. 2-2), were drilled with air, and continuous cores from the top of the first basalt layer to the bottom of the C-D interbed were recovered. These wells were drilled 3 to 15 m from wells USGS 96 and 93, respectively, the wells noted by Barraclough and others (1976) to have the greatest percentage of detections and

3-8 Review of the transport of selected radionuclides in the Interim Risk Assessment

the largest concentrations of most anthropogenic radionuclides measured. The wells are in the oldest part of the burial ground. Contamination-control measures included installation of ground-surface protection (clean gravel) around each well, the use of an asphalt cover, a wooden working platform, and other clean protocols to avoid contact with the ground or dust.

Core samples for analysis were selected from the sediment depths (within the B-C and C-D interbeds) at which radionuclides had been detected during 1971–72 and from a shallow sediment zone overlying the basalt at depths of about 10 to 12 m below land surface. Radionuclide analyses were performed at the same ERDA laboratory—INEEL Health Services Laboratory, Idaho Falls—now the RESL, using the same error propagation techniques that were used previously. The method of calculation of uncertainty in radiochemical analyses was consistent through the 1987 sampling reviewed below (Dames and Moore, 1992, p. 32). Navratil (written commun., 1996) noted that analytical procedures (presumably at RESL) were changed in 1985 to decrease the possibility of interferences in Pu analyses (whether this improved procedure was restricted to reanalyses of initially positive samples is not clear). These new analytical procedures are presumed to be those of Sill (1987) and Sill and Sill (1989) and are described in appendix B of Dames and Moore (1992). Data is shown in table 3-2 (Burgus and Maestas, 1976, table 4). At the 2s uncertainty level, none of the results are statistically positive. Burgus and Maestas (1976) suggested that sample contamination may have been a factor in radionuclide concentrations in samples analyzed by Barraclough and others (1976).

The contamination-control measures developed for this drilling program were used in the 1976–77 (Humphrey and Tingey, 1978, p. 18), 1978 (Humphrey, 1980, p. 5) and subsequent drilling programs (through at least 1987) (Dames and Moore, 1992, p. 35) aimed at assessing contaminants in the interbed sediments. Arguments can be made as to the amount of surficial sediment that would have to be added to a sample to yield a measured concentration in a subsurface sample (Barraclough and others, 1976, p. 79; Dames and Moore, 1992, p. 33). Such arguments may make contamination seem unlikely as the major factor in a measured concentration. However, as the Dames and Moore (1992, p. 35) report aptly notes, the potential for artificial contamination in the field or in the lab is “an irresolvable issue.” However, the potential for its occurrence in the drilling programs conducted at and near the SDA since 1972 has been minimized by the contamination-control measures discussed in this section.

(3) 1976–77 core drilling program—In this EG&G study, the work of Burgus and Maestas (1976) was continued by the drilling of six additional wells in the SDA and one well in the Transuranic Storage Area (TSA) of the RWMC during 1976–77 (Humphrey and Tingey, 1978). The coring techniques and anticontamination measures used by Burgus and Maestas (1976) were used again here. Samples were collected for radiochemical analysis from the A-B, B-C, and C-D interbeds; in addition, samples were collected at irregular intervals from silt and clay material filling fractures in the basalt and from the basalt itself. Samples were analyzed either by the Allied Chemical Corporation laboratory at INEEL (wells 76-1, 76-2, 76-3, fig. 2-2) or by DOE RESL (wells 76-4, 76-4A, 76-5, 76-6, 77-2 (fig. 2-2), and all reanalyses). Initial analyses are shown in tables 3-3 and 3-4 (Humphrey and Tingey, 1978, tables 1, 2). Reanalyses of splits from 13 samples (from the 15 samples showing the presence of one or more radionuclides (at 2s level) upon initial analyses) are shown in table 3-5 (from Humphrey and Tingey, 1978; table 5); the top number is the concentration measured initially, and the numbers below are the concentrations measured during reanalysis. Upon reanalyses, only one statistically positive result was obtained—that for ^{90}Sr from the top of the CnD interbed at well 76-1. Samples had been ground, sieved, and blended prior to the initial analyses, and splits (10 g) for reanalyses had been removed from the same container. The analytical differences between the first and second analyses may reflect sample heterogeneity problems. This seems unlikely, however, given the 10-g aliquot size, unless contamination was caused by (1) “hot particles”—discrete particles of high specific radioactivity in an otherwise uncontaminated matrix, (2) contamination introduced (despite stringent laboratory protocols) into the first-round samples in the laboratory, or (3) unaccounted-for uncertainty terms, the cumulative effect of which is significant at these extremely low radioactivity levels.

Reanalyzing separate aliquots from a given core sample and looking for repeated statistically positive results qualitatively helps to rule out false positives. When the first result is statistically positive and the second is not, the discrepancy could be caused by an initial false positive, laboratory contamination during the initial analysis, an inhomogeneity problem, or a false negative during the second analysis; the situation here remains ambiguous. On the other hand, if the statistically positive analysis is repeatable, confidence in its accuracy is improved. The strategy is to reanalyze only initially positive samples to rule out false positives; the selective reanalysis approach

may be justified for actinides because of the cost and effort required for such measurements.

(4) 1978 core-drilling program—In 1978, three new wells were drilled in the SDA, and core samples were collected for analysis at RESL (table 3-6) (from Humphrey, 1980; table 1). Split samples from each selected depth were analyzed. In addition, new samples from the cores collected during 1976–77 (Humphrey and Tingey, 1978) were analyzed for ^{238}Pu , $^{239,240}\text{Pu}$, ^{241}Am , ^{90}Sr , ^{144}Ce , ^{137}Cs , and ^{60}Co (table 3-7) (Humphrey, 1980, table 2).

For the 1978 samples, there was only one case (^{238}Pu) in a silt and gravel sample from near the top of the B-C interbed of well 78-5) where there were statistically positive radionuclide concentrations in both of the split samples (3.1 ± 1.0 ; 1.7 ± 0.8 pCi/kg). None of the radionuclide concentrations in the new 1976–77 samples were statistically positive.

(5) 1979 core-drilling program—Results of this study were presented in an unpublished report (Waste Management Programs Division, Collection and radiochemical analyses of sedimentary interbed samples from the Radioactive Waste Management Complex, Idaho National Engineering Laboratory: 1979, EG&G-2083, February 1984). We were unable to locate a copy of the report, but the findings were summarized and the data tabulated by Dames and Moore (1992). In four samples from the B-C interbed at two wells drilled in the SDA, concentrations of one or more of the radionuclides ^{241}Am , ^{238}Pu , $^{239,240}\text{Pu}$, and ^{60}Co in both splits were statistically positive at the 2s level.

(6) 1986–87 core-drilling program—In fiscal year 1986, borehole D-02 (fig. 2-2) was drilled to the C-D interbed. Radiochemical analyses by EG&G showed positive results (at the 3s level) for concentrations of ^{238}Pu in four splits from about 70 m (table 3-8) (from Laney and others, 1988; table 20). Neither these results, nor a single positive result for $^{239,240}\text{Pu}$ in a sample from the same interval could be confirmed by RESL. It is not apparent if samples were collected from the B-C interbed (Laney and others, 1988).

In fiscal year 1987, borehole TW-1 (fig. 2-2) was drilled to the bottom of the C-D interbed within 4.5 m of borehole D-02. EG&G radiochemical analyses of samples from 31-m interval showed consistent (in multiple splits) statistically positive concentrations of ^{238}Pu , $^{239,240}\text{Pu}$, and ^{241}Am (table 3-8) (from Laney and others, 1988; table 20). Reanalysis of available splits by RESL confirmed these positive results (table 3-9) (Laney and others, 1988; table 21). The largest actinide concentrations reported by the RESL were 170 ± 13 pCi/kg for $^{239,240}\text{Pu}$, and 908 ± 7.5 pCi/kg for ^{241}Am . EG&G radiochemical analy-

ses of samples from the 69- to 69.5-m interval of the C-D interbed at TW-1 showed no positive results (table 3-8) (from Laney and others, 1988; table 20). Laney and others (1988) concluded that isotopes of Am and Pu had migrated to the B-C interbed; results from the C-D interbed were deemed, as in earlier cases, inconclusive.

(7) Discussion of 1971–87 sampling—The shift in the 1986–87 studies to a 3s decision criterion decreased the chances for false positive results. At 2s, the chance of a false positive is about 2.5 percent (or 1 in 40 samples). At 3s, it is about 0.13 percent (or 1 in 769 samples). Table 3-10 A, B, C, and D (modified from Dames and Moore, 1992, tables 5-5 to 5-8), show all results (from both interior wells and background wells (wells USGS 86–90, and wells 76-6 and 79-1) surrounding the SDA) from 1971 to 1987 that were judged to be positive at the 3s confidence level. It is difficult to explain the fact that in Interval 1, 3 to 23 m below land surface (Dames and Moore, 1992), which includes the A-B interbed and the fracture-filling-material sample, there are no repeatable, statistically positive results. This is puzzling because the subsurface zone closest to the buried waste would be expected to have the largest radionuclide concentrations; indeed, there are larger concentrations of ^{238}Pu , $^{239,240}\text{Pu}$, and ^{241}Am in the surface soils in areas around the SDA due to global and regional fallout (for example, Nevada Test Site, local emissions, and fugitive dust) than in the subsurface of the SDA (Dames and Moore, 1992, p. 72–73). Perhaps this is a reflection of the fewer number of samples in Interval 1 (27 samples) than in Interval 2 (which includes the B-C interbed; 105 samples) and Interval 3 (which includes the C-D interbed; 128 samples).

Table 3-10 lists samples from intervals between 3 and 80 m below land surface within and surrounding the SDA in which statistically positive (at 3s level) radionuclide concentrations were measured. Many discrepancies between the data in the original reports and in subsequent tabulations were found and are noted herein. Tables 3-11, 3-12, and 3-13 focus on the actinides ^{238}Pu , $^{239,240}\text{Pu}$, and ^{241}Am in the B-C and C-D interbeds. The occurrence of samples with statistically-significant (3s) detections, with or without verification upon reanalysis, are tabulated (tables 3-11, 3-12, and 3-13) and compared with similar information in tables by Navratil (written commun., 1996). Findings from this study are in general agreement with those of Navratil (written commun., 1996); differences largely reflect wells considered in the sampling pool. More statistically-significant (3s), repeatable detections occur in samples from the B-C interbed than from the C-D interbed. Although there are statistically significant concentrations of actinides in samples from the C-D

3-10 Review of the transport of selected radionuclides in the Interim Risk Assessment

interbed, and the evidence for ^{238}Pu at this depth in well D-02 is strong (table 3-13), the evidence for actinide transport to the B-C interbed is more compelling than that to C-D interbed.

(8) Other approaches in the Dames and Moore (1992) report—The purpose in each of the studies discussed above was primarily to identify statistically positive detections in samples from the subsurface at the SDA. Dames and Moore (1992) compiled and analyzed this data. In this 1992 study, statistical methods were used to determine whether the concentrations in samples from wells within the SDA boundaries were different from the concentrations in samples from background wells outside the boundaries of the SDA. Because the SDA data generally were not normally distributed, nonparametric statistical testing was used. A detailed analysis of the statistical methodologies they used is beyond the scope of this review. In summary, the entire 1971–87 data set without associated uncertainties was tested primarily by using the Wilcoxon Rank Sum test. Results show that in samples from SDA interior wells:

- ^{144}Ce was present in Interval 1 at concentrations statistically larger than background (note: the maximum concentration was not considered statistically positive at the 3s level),
- ^{60}Co , ^{241}Am , ^{238}Pu , and $^{239,240}\text{Pu}$ were present in Interval 2 at concentrations statistically larger than background, and
- anthropogenic radionuclide concentrations in Interval 3 were not statistically larger than those in background wells.

Another approach, described only briefly by Dames and Moore (1992, p. 74) provides additional, qualitative evidence of migration of radionuclides at the SDA. “The evidence supporting the conclusion of contaminant transport from the SDA was investigated qualitatively by conducting a between-interval comparison for the radionuclides identified above. The approach was similar to the qualitative assessment of repeatability between intervals, but was applied vertically. If a positive result for a specific radionuclide is observed between intervals at a specific location, this was considered supporting evidence of contaminant migration. Thus, the results from this evaluation provide qualitative evidence that radionuclides have been transported from the buried waste at the SDA. The following radionuclides can be correlated vertically at the SDA for the locations indicated: (a) ^{241}Am was detected at well USGS 93 in Intervals 1 and 2; (b) ^{241}Am was detected in well D-02 in Interval 1 and in Interval 2 at both wells 79-2 and TW-1 (note: wells D-02, 79-1, and TW-1 were grouped for comparison because of their close proximity

to each other); (c) $^{239,240}\text{Pu}$ was observed in well D-02 in Interval 1 and wells 79-2 and TW-1 in Interval 2; (d) $^{239,240}\text{Pu}$ was observed in well D-02 in Interval 3; and (e) ^{238}Pu was observed in Interval 1 at well D-02, in Interval 2 at well TW-1, and in Interval 3 at well D-02.”

It should be noted here that the criterion used for these detections (at 3s level) is less rigorous than the repeatable, statistically positive (3s) criterion used earlier in the Dames and Moore (1992, p. 66) report. For example, although the results listed above invoke Interval 1 data, there were no repeatable, statistically positive results in this interval.

(9) Additional investigations—Late in our review process, we learned of additional data. Becker and others (1996, p. 4–78) noted a 1993 study (Loehr and others, 1993) of archived cores collected from the SDA during 1971–89. Time did not permit detailed reanalysis of the data from that study. These data, originally were analyzed by a contract laboratory (Barringer Laboratories, Denver, Colorado), but were not included in the 1992–94 Dames and Moore compilation. Fifty-four samples from 21 wells were analyzed for radionuclides, including ^{238}Pu , $^{239,240}\text{Pu}$ and ^{241}Am . Samples came from massive, unfractured basalts, basalt rubble zones, sediment-filled fractured basalt, and sedimentary interbed material from the A-B, B-C, and C-D interbeds. The data do not contain counting error statistics; these apparently were not provided by the laboratory. In 4 to 25 percent of the samples from the fractured basalts, rubble zones, and sedimentary interbeds, the concentrations of ^{241}Am exceeded the stated detection limit (0.12 pCi/g). These were the only anthropogenic actinide detections (uranium isotopes excluded), and their statistical significance cannot be evaluated because of the omission of counting error data.

3.6.2 Perched-water and ground-water data

Perched water has been predominately located and sampled in 6 of the 45 wells completed within the RWMC (Scott Barrie, written commun., 1998). These perched water zones are primarily above the C-D interbed, and five wells routinely yield sufficient volumes of water for analyses; these wells are USGS 92, 88-02D, D-10, 78-1 and 77-2 (figs. 2-2 and 2-3). In addition to these wells, about 25 lysimeters are located within the SDA and are sampled for radionuclides. All but one of the lysimeters that yield water are within the perimeter of the SDA and are completed to depths of from about 2 to 7 m. The one lysimeter not within the SDA that yields water is about 30 m outside the perimeter. Since 1972, the site contractor at the INEEL has sampled water from these perched wells

and lysimeters at the RWMC. In that time, a total of 14 different radionuclides, including transuranics, have been detected at least once. These detections were based on the use of the 2s detection criteria as outlined in section 3.2 titled “Detection limits, statistical screening criteria, and reporting of data.” Reported detections of selected radionuclides since 1972 are summarized in table 3-14.

Table 3-14. Number of radionuclide detections in water samples from the perched water zone at the Radioactive Waste Management Complex using the site contractor’s criterion of detection, 2s and greater (Scott Barrie, written commun., 1998)

| Radionuclide | Total number of samples | Number of detections |
|-----------------------|-------------------------|----------------------|
| ^{241}Am | 75 | 5 |
| $^{233,234}\text{U}$ | 16 | 7 |
| ^{235}U | 46 | 7 |
| ^{238}U | 19 | 7 |
| ^{238}Pu | 43 | 8 |
| $^{239,240}\text{Pu}$ | 40 | 8 |
| ^{230}Th | 8 | 3 |

These data were provided by LMITCO and were reviewed first with the criteria of detection used by them (2s) and then using the method recommended by the National Institute of Standards Technology (NIST), ASTM, and IUPAC (3s and greater after reviewing all data between 1.6s and 3s). With so few detections reported for a given radionuclide, a rigorous statistical analysis was not possible, but some general observations can be made.

Three of the five (table 3-14) reported detections for ^{241}Am were in water or sediments from well USGS 92 (fig. 2-3). This well is completed to a depth of 65.5 m and is within the SDA. The reported detections in water from USGS 92 were 0.00041 ± 0.00012 pCi/L in 1976 and 0.07 ± 0.03 pCi/L in 1981; the reported detection in sediment was 0.0312 ± 0.0129 pCi/kg in 1998. There is a transcription problem with the 1976 value, which was correctly reported by the USGS as 0.041 ± 0.012 pCi/L. It is not correct to compare this value to the method detection limit used by LMITCO (0.05 pCi/L). By hypothesis testing this value may be a detection. Additionally, in 1997, there was a reported detection from well W-25 of 0.629 ± 0.233 pCi/L. The remaining detection of ^{241}Am reported for water from the perched zone at the SDA was from lysimeter PA-03; the completion depth of this lysim-

eter is 3 m. The ^{241}Am concentration in water from PA-03 in 1998 was 4.16 ± 0.656 pCi/L. This concentration is a valid detection by the application of hypothesis testing.

Six of the seven reported detections of $^{233,234}\text{U}$ were also in water from well D-06 and lysimeter PA-03. The concentrations of $^{233,234}\text{U}$ in the six water samples collected from D-06 and PA-03 in 1997–98 ranged from 8.45 ± 1.27 to 84.4 ± 6.23 pCi/L. The remaining reported detection of $^{233,234}\text{U}$ (90 ± 7.29 pCi/L) was in water collected from well TW-1 at a depth of 102 ft in February 1998.

Seven detections of ^{235}U were reported. The reported detections for ^{235}U were in water samples from two perched-water wells (D-06 and TW-1) and two lysimeters (PA-03 and W-08). The ^{235}U concentrations ranged from 1.61 ± 0.377 pCi/L in water from lysimeter PA-03 to 62.2 ± 25.5 pCi/L in water from lysimeter W-08. Seven detections of ^{238}U were also reported for water collected from the same two wells (D-06 and TW-1) and the two lysimeters (PA-03 and W-08) as the ^{235}U detections. The ^{238}U concentrations ranged from 7.2 ± 1.15 to 49.4 ± 3.75 pCi/L.

Eight detections of ^{238}Pu were reported. Because the reported inventories of ^{238}Pu at the SDA are about two orders of magnitude smaller than inventories reported for $^{239,240}\text{Pu}$ (Becker and others, 1998, table 4-1), any detection of ^{238}Pu in environmental samples at the SDA is questionable, especially in samples without detections of $^{239,240}\text{Pu}$. The reported detections for ^{238}Pu were in seven water samples and one sediment sample from one lysimeter (PA-03) and three wells (USGS 92, D-06, and D-15; the completion depth for D-06 is 26.8 m, and for D-15 is 29.9 m). The ^{238}Pu concentrations ranged from 0.0063 ± 0.0006 pCi/L in 1977 in water from USGS 92 to 24 ± 2.05 pCi/L in water from PA-03 in 1997. The concentration of ^{238}Pu in the sediment sample was reported as 1.39 ± 0.285 pCi/kg.

There were also eight reported detections of $^{239,240}\text{Pu}$ in water from wells and lysimeters in the perched-water zone at the SDA. Three of the detections were in sediment samples and three were in water samples collected from USGS 92. The remaining two detections were in water samples from lysimeter PA-03 and well D-15. The concentrations ranged from 0.023 ± 0.008 pCi/L to 1.06 ± 0.351 pCi/L. Because the stated method detection limit was 0.05 pCi/L, three of the reported detections for $^{239,240}\text{Pu}$ probably were not true detections. Concentrations in all three of the water samples collected at USGS 92 were smaller than the method detection limit and, therefore, should be viewed as nondetections. Information on recovery and counting times for analysis of these samples was

3-12 Review of the transport of selected radionuclides in the Interim Risk Assessment

unavailable. For these reasons these three results must be considered as nondetections.

The three detections reported for ^{230}Th were in water collected from one perched-water well (D-06) and one lysimeter (PA-03). In August 1997, water collected from the well had a ^{230}Th concentration of 1.18 ± 0.477 pCi/L. Water collected from lysimeter PA-03 in August 1997 had a ^{230}Th concentration of 0.857 ± 0.367 pCi/L; additionally, water collected from PA-03 in February 1998 had a concentration of 0.943 ± 0.394 pCi/L.

These same data were reviewed using the recommended method outlined previously. The number of detections reported by the site contractor for ^{241}Am and ^{238}Pu in water and sediment samples from the unsaturated zone remained the same. The number of detections for $^{239,240}\text{Pu}$ decreased to three and the largest concentration was then 0.7 pCi/L. Regardless of the detection criteria applied to these data, too few results were reported to definitively and statistically confirm the occurrence of radionuclides in water and sediments from wells and lysimeters at the SDA. However, it is not prudent or scientifically defensible to ignore true statistical detections. It is recommended that samples be collected during episodic recharge events and that sampling frequency be increased in areas where detections periodically have been reported. All of the reported $^{233,234}\text{U}$, all but two of the reported ^{235}U , and all of the reported ^{238}U concentrations were still detections. None of the reported ^{230}Th concentrations were detections.

In 1992, the site contractor completed six groundwater monitoring wells in the Snake River Plain aquifer at the SDA. Between October 1992 and March 1998 two detections for $^{239,240}\text{Pu}$ and five detections for ^{241}Am were reported. The detections for $^{239,240}\text{Pu}$ were 1.3 ± 0.3 and 4.3 ± 0.5 pCi/L. The concentration of 1.3 ± 0.3 pCi/L is questionable because the associated uncertainty is almost 30 percent of the result, and the result is about 1.5 orders of magnitude larger than the method detection limit. The associated uncertainty should not be this large. The same concentration was repeated with an ^{241}Am result that was discussed in section 3.2 titled "Detection limits, statistical screening criteria, and reporting of data." The ^{241}Am concentrations ranged from 0.045 ± 0.013 to 1.13 ± 0.3 pCi/L. The smallest concentration, 0.045 ± 0.013 pCi/L, is questionable because such precision is not possible for a concentration that is less than the method detection limit. For apparent statistical detections at and below the method detection limit, more QA/QC information should be provided for a defensible review.

3.6.3 Significance of reported detections

Regardless of the criteria used to report detections, there have been positive occurrences of radionuclides in the environment at the SDA. The source of the radionuclides is difficult to establish because of the small number of statistically positive results. Possible sources include cross contamination during sampling, radionuclides carried to the subsurface during well completion, laboratory contamination, global fallout from weapons tests of the 1950–60's, true radionuclide migration from buried waste at the SDA, and wastes injected into the aquifer upgradient from the SDA at the TRA or INTEC. One way to help delineate the source(s) of detected radionuclides would be to determine isotopic ratios of plutonium and americium in the environment. To better understand these apparent detections in the subsurface at the SDA, increased sampling, lower method detection limits, and increased cooperation between researchers is needed.

3.7 Summary

The following recommendations are offered in an attempt to improve sample collection and analyses, data generation and reporting, and overall quality assurance and quality control for the program that has been charged with generating data in support of the WAG-7 Comprehensive RI/FS.

(1) The decision as to whether to use a 2s or 3s detection (with consideration of concentrations between 1.6 and 3s) criterion has apparently yet to be resolved at the INEEL (see Becker and others (1996; p. 4-76 to 4-77)). To meet the requirements of the National Technology Transfer and Advancement Act (Public Law 104-113), the method recommended by ASTM should be considered and applied to radionuclide data sets as a minimum screening criteria (see section 3.4 of this report). Additionally, warning flags for exotic radionuclide isotopes should be included in the computer data base and in reports to the DOE and the State of Idaho.

(2) Data archiving problems were identified. Compilations of data, which tend to supplant original data, need greater QA. Additionally, all data generated in support of this program should be made available to the INEEL Earth-science community for review at the earliest time possible after completion and a thorough QA/QC check.

(3) ^{237}Np was highlighted in the SOW as a radionuclide of concern. This concern presumably stems from the long half life (2.1×10^6 years), high radiotoxicity, significant inventory in wastes, and the solubility and mobility of Np^{5+} species in natural waters (Langmuir, 1997;

Bertetti and others, 1998); however, no data for ^{237}Np , in either ground water or interbed sediments at the SDA was presented for review. If monitoring for ^{237}Np is not currently a part of this monitoring program, then it should be added.

(4) Thermal ionization mass spectrometry and (or) accelerator mass spectrometry for the determination of Pu isotopes in ground water and sediment samples may allow for lower detection limits than those achievable with α -spectroscopy. Lower detection limits could be of value in future sampling of the water and sediments at WAG-7. Use of Pu isotope ratios may help to resolve source issues (such as waste versus global fallout) at sites like well

USGS 87, which are upgradient and outside the SDA perimeter.

(5) A consistent method of data validation needs to be implemented. To date, all levels of validation from A through C have been applied to radionuclide data.

(6) The reporting of more precision in the uncertainty of an analytical result than is reported for the analytical result should be avoided. For example, a $^{239,240}\text{Pu}$ concentration of 1.06 ± 0.351 pCi/L was reported for perched water at the RWMC. It would be more appropriate to report the uncertainty of the measurement as 0.35 or 0.4 pCi/L.

3-14 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 3-1. Concentrations of selected radionuclides in sediment samples collected in 1972 from wells at and near the Subsurface Disposal Area (from Barraclough and others, 1976; table 2)

[Analyses performed at the Radiological and Environmental Sciences Laboratory. Sample depth intervals are in feet (ft) and inches (in.); concentrations are in microcuries per gram times 10^{-9} . Symbols: <, less than; \pm , plus or minus; [a] = rerun on different aliquot; [b] = ND, not detected; [c] = NA, not analyzed; and [d] = statistically positive at the 95 percent confidence level]

| Well | Sample depth interval | ⁶⁰ Co | ⁹⁰ Sr | ¹³⁷ Cs | ¹⁴⁰ Ba/La | ²³⁸ Pu | ^{239,240} Pu | ²⁴¹ Am |
|---------|----------------------------|------------------|---------------------|-------------------|----------------------|--------------------|-----------------------|----------------------|
| USGS 87 | 231 ft 2 in.-233 ft | <50 | 460 \pm 50 [d] | <50 | [b] | <4.0 | 29.0 \pm 4.5 [d] | <2.0 |
| USGS 88 | 521 ft-522 ft | [b] | 400 \pm 90 [d] | [b] | [b] | 15.0 \pm 3.0 [d] | 22.0 \pm 3.0 [d] | 5.0 \pm 3.0 |
| USGS 89 | 241 ft 7 in.-243 ft 2 in. | <3 | 640 \pm 70 [d] | 40 \pm 10 [d] | [b] | [c] | <1 | 2.0 \pm 3.0 |
| | 540 ft-545 ft | [b] | 300 \pm 90 [d] | [b] | [b] | [b] | [b] | [b] |
| USGS 91 | 7 ft 10 in.-8 ft 11 in. | [b] | <4,200 | [b] | [b] | [c] | 26.0 \pm 4.5 [d] | [c] |
| | 233 ft 9 in.-236 ft 3 in. | <30 | 1,200 \pm 100 [d] | <30 | [b] | 3.0 \pm 1.5 | 0.5 \pm 1.0 | 12.0 \pm 4.5 [d] |
| | 236 ft 6 in.-237 ft | [b] | <3,300 | [b] | [b] | [c] | 140.0 \pm 7.0 [d] | [c] |
| | 243 ft 2 in.-245 ft 1 in. | <90 | 500 \pm 90 [d] | <200 | [b] | 9.0 \pm 7.0 | 2.0 \pm 3.0 | 5.0 \pm 3.0 |
| USGS 92 | 5 ft-7 ft 6 in. | [b] | 240 \pm 70 [d] | [b] | [b] | [c] | <1.0 | [c] |
| | 88 ft 6 in.-90 ft | <20 | 300 \pm 90 [d] | <20 | [b] | 6.0 \pm 3.0 | 0.5 \pm 1.5 | 1.0 \pm 1.5 |
| | 223 ft-225 ft 6 in. | 230 \pm 20 [d] | 300 \pm 90 [d] | 130 \pm 30 [d] | [b] | 3.0 \pm 3.0 | 7.0 \pm 3.0 [d] | 2.0 \pm 1.5 |
| USGS 93 | 13 ft 10 in.-14 ft | <60 | 400 \pm 90 [d] | <40 | 48 \pm 12 [d] | 0.2 \pm 0.3 | 1.0 \pm 1.5 | 12.0 \pm 4.5 [d] |
| | 98 ft-101 ft | 62 \pm 12 [d] | <300 | 100 \pm 20 [d] | [b] | 8.0 \pm 1.5 [d] | 110.0 \pm 7.0 [d] | [c] |
| | 101 ft-103 ft | <30 | 690 \pm 110 [d] | <50 | [b] | 9.0 \pm 3.0 [d] | 230.0 \pm 11.0 [d] | 63.0 \pm 12.0 [d] |
| | 101 ft-103 ft [a] | [b] | <200 | [b] | [b] | 14.0 \pm 3.0 [d] | 540.0 \pm 12.0 [d] | 150.0 \pm 22.0 [d] |
| | 103 ft-105 ft | <310 | 400 \pm 100 [d] | <900 | [b] | [c] | 81.0 \pm 11.0 [d] | 45.0 \pm 6.0 [d] |
| USGS 94 | 98 ft 4 in.-98 ft 5 in. | [b] | 150 \pm 50 [d] | [b] | [b] | [b] | [b] | [b] |
| | 262 ft 3 in.-264 ft 7 in. | 250 \pm 30 [d] | <200 | 180 \pm 30 [d] | [b] | 4.0 \pm 3.0 | 3.0 \pm 1.5 | 1.0 \pm 1.5 |
| USGS 95 | 20 ft-22 ft | <50 | 200 \pm 90 [d] | <40 | [b] | 5.0 \pm 3.0 | 3.0 \pm 1.5 | 2.0 \pm 3.0 |
| | 112 ft-113 ft 4 in. | <30 | <200 | 220 \pm 10 [d] | [b] | 0.5 \pm 1.0 | 0.5 \pm 1.0 | 3.0 \pm 4.5 |
| | 226 ft 9 in.-229 ft 3 in. | 240 \pm 30 [d] | <200 | 230 \pm 30 [d] | [b] | 9.0 \pm 7.0 | 9.0 \pm 7.0 | 3.0 \pm 3.0 |
| USGS 96 | 100 ft 6 in.-101 ft | <20 | <200 | <40 | [b] | 6.0 \pm 1.5 [d] | 45.0 \pm 2.0 [d] | 10.0 \pm 7.0 |
| | 110 ft-112 ft 11 in. | <20 | <200 | <30 | [b] | 3.0 \pm 1.5 | 3.0 \pm 1.5 | 230.0 \pm 20.0 [d] |
| | 110 ft-110 ft 6 in. | <70 | --- | <40 | [b] | 9.0 \pm 7.0 | 0.5 \pm 1.0 | 30.0 \pm 6.0 [d] |
| | 122 ft 9 in.-123 ft 10 in. | <70 | 200 \pm 100 | 550 \pm 40 [d] | [b] | 2.0 \pm 1.5 | 2.0 \pm 1.5 | 5.0 \pm 3.0 |
| | 124 ft-124 ft 3 in. | <90 | 200 \pm 90 [d] | <90 | [b] | [c] | <0.5 | 3.0 \pm 4.5 |
| | 221 ft 7 in.-224 ft 1 in. | <30 | 200 \pm 100 | <40 | [b] | 1.0 \pm 3.0 | 4.0 \pm 1.5 [d] | 6.0 \pm 3.0 |

Table 3-2. Concentrations of selected radionuclides in sediment samples collected in 1975 from wells USGS 93 and USGS 96 (from Burgus and Maestas, 1976; table 4)

[Analyses performed at the Radiological and Environmental Sciences Laboratory. Sample depths are in feet. Concentrations are in microcuries per gram times 10^{-9} (10^{-9} $\mu\text{Ci/g}$) for ^{238}Pu , $^{239,240}\text{Pu}$, and ^{241}Am and in microcuries per gram times 10^{-8} (10^{-8} $\mu\text{Ci/g}$) for ^{90}Sr , ^{144}Ce , ^{137}Cs , and ^{60}Co]

| Sample no. | Well | Sample depth | ^{238}Pu | $^{239,240}\text{Pu}$ | ^{241}Am | ^{90}Sr | ^{144}Ce | ^{137}Cs | ^{60}Co |
|------------|------|--------------|-------------------|-----------------------|-------------------|------------------|-------------------|-------------------|------------------|
| 1 | 96A | 34.8-35.1 | 0.6±1.1 | 0.1±0.6 | -0.6±1.8 | -10±4 | 16±11 | -5±3 | 2±2 |
| 2 | 96B | 35-40 | 0.5±1.1 | 0.2±0.6 | -0.9±1.6 | 0±5 | 0±7 | 0±1 | -0.3±1.0 |
| 3 | 96B | 36.0 | -0.5±1.0 | 0.1±0.6 | -1.5±1.4 | -6±5 | 0±10 | -1±3 | -3±2 |
| 4 | 96B | 101.6-102.0 | 0.0±1.1 | 0.5±0.6 | -1.2±1.5 | -8±5 | 10±10 | -2±3 | -3±2 |
| 5 | 96B | 106.4-106.8 | 0.7±1.1 | 0.1±0.6 | -0.7±1.6 | -6±5 | 20±10 | 1±2 | 2±2 |
| 6 | 96B | 220.9-221.2 | 0.4±1.4 | 0.1±0.6 | 0.6±1.5 | -2±5 | 10±10 | 1±2 | 2±2 |
| 7 | 96B | 223.6-223.9 | 0.6±1.1 | 0.7±0.7 | 1.5±1.8 | 3±5 | 6±9 | 2±2 | 2±2 |
| 8 | 93A | 80.2-80.6 | 0.5±1.5 | -0.3±0.5 | 0.4±1.6 | -2±5 | 10±10 | 4±2 | 2±2 |
| 9 | 93A | 82.8-83.6 | 0.2±1.0 | 1.0±0.8 | -0.3±1.6 | -2±5 | 20±10 | 2±2 | 1±3 |
| 10 | 93A | 89.0-89.5 | -0.4±1.0 | -0.3±0.5 | -0.8±1.6 | 7±5 | 4±13 | -1±2 | 2±2 |
| 11 | 93A | 97.9-98.0 | 2.0±1.6 | 0.0±0.6 | 0.5±1.7 | 2±4 | 10±10 | 1±2 | 5±3 |
| 12 | 93A | 100.6-100.9 | 2.0±1.5 | 0.0±0.6 | -0.8±1.6 | 2±8 | 10±10 | -1±2 | 1±2 |
| 13 | 93A | 102.4-102.8 | 0.8±1.2 | 0.4±0.6 | -1.6±1.6 | 6±4 | 10±10 | -2±2 | 1±2 |
| 14 | 93A | 221.5-223.5 | -0.4±1.0 | 0.1±0.5 | -0.6±1.6 | 5±5 | -10±10 | 2±2 | 2±2 |
| 15 | 93A | 226.5-226.9 | -0.3±1.0 | 0.3±0.5 | 0.1±1.6 | 7±4 | -10±10 | -2±3 | -5±2 |

3-16 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 3-3. Concentrations of selected radionuclides in sediment samples collected in 1976 from wells 76-1, 76-2, and 76-3 (from Humphrey and Tingey, 1978; Table 1)

[Analyzed by Allied Chemical Corporation. Sample depths are in feet. Concentrations are in microcuries per gram times 10^{-9} (10^{-9} $\mu\text{Ci/g}$) for ^{238}Pu , $^{239,240}\text{Pu}$, and ^{241}Am and in microcuries per gram times 10^{-8} (10^{-8} $\mu\text{Ci/g}$) for ^{90}Sr , ^{144}Ce , ^{137}Cs , and ^{60}Co . Symbols: [a] = sample not analyzed; [b] = statistically positive at the 95 percent confidence level; [c] = sample material not available for rerun; and [d] = sample reanalyzed (see table 3-5)]

| Sample no. | Sample depth | ^{238}Pu | $^{239,240}\text{Pu}$ | ^{241}Am | ^{90}Sr | ^{144}Ce | ^{137}Cs | ^{60}Co |
|------------|--------------|-------------------|-----------------------|-------------------|------------------|-------------------|-------------------|------------------|
| 76-1-1 | 35.1 | 0.3±15.8 | -10.8±20.1 | [a] | 5±4 | 5±15 | 10±6 | 2±4 |
| 76-1-2 | 29.2 | -2.4±15.6 | -29.2±19.9 | [a] | -2±3 | -1±13 | 7±8 | -0.1±3 |
| 76-1-3 | 84.7-86.3 | 2.3±4.8 | 6.8±5.3 | [a] | -6±5 | 60±111 | 0±4 | 0±7 |
| 76-1-4 | 92.3-93.7 | 1.7±5.5 | 2.2±5.9 | [a] | -3±5 | 0±20 | -7±3 | 2±4 |
| 76-1-5 | 92.3 | 2.07±16.4 | 13.2±6.1 [b,c] | [a] | [a] | 0±50 | 0±9 | 11±11 |
| 76-1-6 | 103.0-104.5 | 9.9±7.1 | 4.5±6.6 | [a] | -10±5 | 0±20 | -1±5 | 4±4 |
| 76-1-7 | 217.2 | 10.7±4.2 [b,d] | -4.8±4.0 | [a] | -5±3 | 10±20 | 0±4 | 0±2 |
| 76-1-8 | 221.0 | 6.3±16.4 | 14.4±21 | [a] | 49±6 [b,d] | 0±10 | 1±2 | -2±2 |
| 76-1-9 | 228.3 | 3.3±15.4 | -1.7±20 | 2±1.6 | 7±8 | 2±11 | -5±4 | 4±3 |
| 76-1-10 | 70.0-75.0 | 13.0±15.8 | -21.6±20 | [a] | [a] | 0±7 | -3±2 | 0±3 |
| 76-2-1 | 16.0 | 5.7±5.6 | -7.1±5.7 | [a] | -7±5 | 3±12 | -3±3 | -2±3 |
| 76-2-2 | 24.0 | 7.3±6.9 | -10.7±6.3 | [a] | -4±5 | 20±20 | 5±4 | 0±4 |
| 76-2-3 | 24.3 | 33.0±16.6 | 1.1±5.4 | [a] | 1±4 | -6±14 | -4±2 | -1±2 |
| 76-2-4 | 60.0 | 12.7±4.6 [b,d] | -2.9±4.3 | [a] | [a] | -5±12 | 8±3 [b,d] | 2±4 |
| 76-2-5 | 82.5-83.5 | 5.7±4.0 | 11.5±4.4 [b,d] | [a] | -4±4 | 11±15 | -7±3 | 0±4 |
| 76-2-6 | 223.0 | 5.9±15.6 | 1.7±20.1 | [a] | 3±4 | 0±10 | 5±3 | 1±2 |
| 76-2-7 | 235.0 | 1.8±15.7 | 0.7±20.1 | [a] | 8±6 | -0.3±14 | -5±5 | -3±4 |
| 76-2-8 | 243.9 | -0.6±15.5 | 6.6±19.9 | [a] | -2±6 | -7±16 | 2±6 | 6±4 |
| 76-2-9 | 245.8 | 13.2±15.7 | 23.5±20.1 | [a] | -7±6 | -9±9 | -2±3 | 2±2 |
| 76-3-1 | 24.0-24.7 | 0.0±1.1 | -0.6±1.0 | 0.0±1.2 | 0.4±4 | -5±11 | -7±4 | 1±3 |
| 76-3-2 | 25.8-26.8 | -0.1±1.2 | 0.2±1.0 | 1±2 | 5±4 | 18±12 | -8±5 | 6±3 |
| 76-3-3 | 96.5-96.8 | -0.1±1.2 | -0.7±1.1 | 0.3±1.4 | 9±4 [b,d] | 0±10 | -5±3 | 0±3 |
| 76-3-4 | 97.5-97.8 | 8.7±4.4 | 16.8±5.0 [b,d] | 8.4±1.4 [b,d] | 7±4 | 0±10 | 6±3 | 0±2 |
| 76-3-5 | 110.5-111.0 | 1.0±1.2 | -0.4±1.1 | 2.7±1.2 [b,c] | 4±3 | 23±13 | 1±5 | 2±3 |
| 76-3-6 | 119.5-119.7 | 26.3±17 | 2.0±20.9 | [a] | -7±4 | 2±3 | 4±4 | 6±4 |
| 76-3-7 | 222.5 | 23.7±15.8 | -8.4±20 | [a] | 20±8 [b,d] | 16±14 | 3±3 | 3±3 |
| 76-3-8 | 228.5 | 19.3±15.7 | -7.4±19.9 | [a] | 5±4 | 40±20 | 1±3 | 2±3 |
| 76-3-9 | 240.4 | 1.3±4.5 | 10.7±5.6 | [a] | 7±4 | 3±10 | 2±3 | 9±5 |

Table 3-4. Concentrations of selected radionuclides in sediment samples collected in 1976 from wells 76-4, 76-4A, 76-5, 76-6, and 77-2 (from Humphrey and Tingey, 1978; table 2)

[Analysis performed at the Radiological and Environmental Sciences Laboratory. Sample depths are in feet. Concentrations are in microcuries per gram times 10^{-9} (10^{-9} $\mu\text{Ci/g}$) for ^{238}Pu , $^{239,240}\text{Pu}$, and ^{241}Am and in microcuries per gram times 10^{-8} (10^{-8} $\mu\text{Ci/g}$) for ^{90}Sr , ^{144}Ce , ^{137}Cs , and ^{60}Co . Symbols: [a] = sample not analyzed, and [b] = statistically positive at the 95 percent confidence level (see table 3-5 for reanalysis)]

| Sample no. | Sample depth | ^{238}Pu | $^{239,240}\text{Pu}$ | ^{241}Am | ^{90}Sr | ^{144}Ce | ^{137}Cs | ^{60}Co |
|------------|--------------|-------------------|-----------------------|-------------------|------------------|-------------------|-------------------|------------------|
| 76-4-1 | 12.0 | 0.1±0.9 | 1.3±0.9 | 0.0±1.0 | 1±3 | -100±100 | 1±2 | 2±2 |
| 76-4-2 | 20.0 | 0.0±0.8 | 0.4±0.6 | -0.2±0.9 | 2±3 | 5±9 | 1±2 | 1±2 |
| 76-4-3 | 99.5 | 0.5±0.9 | 3.1±1.3 [b] | 0.5±0.8 | 1±3 | 10±20 | 4±2 | 2±2 |
| 76-4A-1 | 23.5 | 0.0±0.7 | 1.0±1.0 | 21±3 [b] | -4±3 | -1±2 | -2±10 | 0±2 |
| 76-4A-2 | 97.8 | 1.3±1.0 | 0.5±0.5 | 6.4±1.7 [b] | -4±3 | 20±20 | 8±4 | 0±2 |
| 76-4A-3 | 223.5 | 0.7±0.9 | 1.2±0.8 | 0.0±1.0 | 0±3 | -14±10 | 0±3 | 1±2 |
| 76-4A-4 | 226.0 | 1.0±1.0 | -0.2±0.5 | 23±3 [b] | 1±3 | 40±30 | 2±3 | 2±2 |
| 76-5-1 | 25.4-26.0 | 2.5±1.5 | 0.0±1.0 | 0.6±1.0 | 0±3 | 30±20 | 2±2 | 2±2 |
| 76-5-2 | 75.1 | 2.0±2.0 | 2.0±3.0 | -1.0±1.0 | 0±3 | -10±20 | 2±2 | 2±2 |
| 76-5-3 | 95.9 | 2.0±2.0 | 0.0±1.0 | 1.0±1.0 | 2±3 | 2±9 | 1±2 | 2±2 |
| 76-5-4 | 223.7 | 0.8±0.7 | -0.7±0.5 | -1.0±1.0 | -2±6 | 8±10 | 2±2 | 2±2 |
| 76-5-5 | 114.3-114.8 | 0.6±0.9 | 0.8±0.7 | 0.0±1.0 | 3±3 | 4±9 | -1±2 | 1±2 |
| 76-6-1 | 17.1 | 0.0±1.0 | 0.1±0.6 | -0.9±0.7 | 4±4 | -15±9 | 1±2 | 3±2 |
| 76-6-2 | 102.1 | 3.0±2.0 | 1.4±1.1 | -1.4±1.5 | 9±5 | -10±20 | 3±2 | -2±2 |
| 76-6-3 | 232.2-233.2 | 2.9±1.4 [b] | 0.9±0.9 | 0.0±2.0 | -3±5 | -25±13 | -2±3 | 4±3 |
| 76-6-4 | 236.3 | -0.2±0.8 | 0.5±0.7 | 0.0±2.0 | 2±3 | 10±10 | 1±2 | 1±2 |
| 77-2-1 | 19.2 | 3.0±2.0 | 0.0±2.0 | 2.0±2.0 | [a] | 60±30 | 2±6 | 4±4 |
| 77-2-2 | 27.7 | -0.4±0.7 | 0.9±0.8 | 1.9±1.3 | 8±4 | 10±10 | 1±2 | 2±2 |
| 77-2-3 | 25.8-27.7 | 0.6±0.9 | 1.5±0.9 | -0.7±0.7 | 5±4 | -9±14 | 7±3 [b] | 0±2 |

3-18 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 3-5. Concentrations of radionuclides ^{238}Pu , $^{239,240}\text{Pu}$, ^{241}Am , ^{90}Sr , and ^{137}Cs in split samples reanalyzed on the basis of initially statistically positive results listed in tables 3-3 and 3-4 (from Humphrey and Tingey, 1978; table 5)

[Analysis performed at the Radiological and Environmental Sciences Laboratory. Sample depth is in feet. Concentrations are in microcuries per gram times 10^{-9} (10^{-9} $\mu\text{Ci/g}$) for ^{238}Pu , $^{239,240}\text{Pu}$, and ^{241}Am and in microcuries per gram times 10^{-8} (10^{-8} $\mu\text{Ci/g}$) for ^{90}Sr and ^{137}Cs . Abbreviations: [a] = statistically positive at 95% confidence level but not at the 99% confidence level, and [b] = statistically positive at the 99% confidence level]

| Sample no. | Sample depth | ^{238}Pu | $^{239,240}\text{Pu}$ | ^{241}Am | ^{90}Sr | ^{137}Cs |
|------------|--------------|---------------------------|-------------------------|------------------------------------|----------------------|-------------------|
| 76-1-7 | 217.3 | 10.7±4.2 [a] 0.0 ± 1.0 | | | | |
| 76-1-8 | 221.2 | | | | 49±6 [b] 42±5 [b] | |
| 76-2-4 | 60.0 | 12.7±4.6 [b] 0.0±2.0 | | | | 8±3 [a] 10±10 |
| 76-2-5 | 82.5-83.5 | | 11.5±4.4 [a] 0.0±1.0 | | | |
| 76-3-3 | 96.5-96.8 | | | | 9±4 [a] 1±3 | |
| 76-3-4 | 97.5-97.8 | | 16.8±5.0 [b] 0.0±1.0 | 8.4±1.4 [b] -1.0±1.0 | | |
| 76-3-7 | 222.5 | | | | 20±8 [a] 2±4 | |
| 76-4-3 | 99.5 | | 3.1±1.3 [a] -0.7±0.9 | | | |
| 76-4A-1 | 23.5 | | | 21±3 [b] 0.0±1.0 -1.0±1.0 | | |
| 76-4A-2 | 97.8 | | | 6.4±1.7 [b] -0.0±1.0 0.0±1.0 | | |
| 76-4A-4 | 226.0 | | | 23±3 [b] 2.3±1.5 -1.0±1.0 | | |
| 76-6-3 | 232.2-233.2 | 2.9±1.4 [a] 0.0±1.0 | | | | |
| 77-2-3 | | | | | | 7±3 [a] -5±3 |

Table 3-6. Concentrations of radionuclides ²³⁸Pu, ^{239,240}Pu, ²⁴¹Am, ⁹⁰Sr, ¹⁴⁴Ce, ¹³⁷Cs, and ⁶⁰Co in sediment samples collected in 1978 from wells 78-2, 78-3, and 78-5 (from Humphrey, 1980; Table 1)

[Analysis performed at the Radiological and Environmental Sciences Laboratory. Sample depths are in meters. Concentrations are in microcuries per gram times 10⁻⁸ (10⁻⁸ μCi/g) for ⁹⁰Sr, ¹⁴⁴Ce, ¹³⁷Cs, and ⁶⁰Co and in microcuries per gram times 10⁻⁹ (10⁻⁹ μCi/g) for ²³⁸Pu, ^{239,240}Pu, and ²⁴¹Am. Abbreviation: [a] = statistically positive at the 95 percent confidence level; (A,B) = splits of the original sample]

| Sample no. | Sample depth | ²³⁸ Pu | ^{239,240} Pu | ²⁴¹ Am | ⁹⁰ Sr | ¹⁴⁴ Ce | ¹³⁷ Cs | ⁶⁰ Co |
|------------|--------------|-------------------|-----------------------|-------------------|------------------|-------------------|-------------------|------------------|
| 78-2-1 (A) | 29.99 | -0.4±0.4 | 0.2±0.7 | -1.0±1.0 | -4±4 | -4±4 | 2.5±1.3 | 2±1 |
| 78-2-1 (B) | 29.99 | -0.9±0.7 | 1.2±0.7 | -0.57±1.2 | 3±4 | -9±6 | 3±3 | -4±2 |
| 78-2-2 (A) | 30.33 | 0.2±0.5 | 0.3±0.5 | -1.0±1.0 | 2±5 | -13±6 | -2±3 | -2±3 |
| 78-2-2 (B) | 30.33 | 0.1±0.5 | 0.9±0.8 | 1.0±5.0 | 1±3 | -10±6 | 2±3 | -5±3 |
| 78-2-3 (A) | 30.54 | 0.1±0.5 | 0.2±0.5 | -0.3±0.9 | 3±4 | -5±6 | -1±2 | -3±2 |
| 78-2-3 (B) | 30.54 | 0.2±0.5 | 0.9±0.9 | 0.1±0.1 | 4±3 | -4±6 | -5±2 | -4±2 |
| 78-2-4 (A) | 31.58 | -0.6±0.3 | 0.6±0.4 | 0.0043±0.8 | 0±3 | -3±6 | -3±2 | -2±2 |
| 78-2-4 (B) | 31.58 | 0.7±0.8 | 2.0±1.0 | 1.0±0.9 | 2±3 | -17±6 | -2±2 | -4±2 |
| 78-2-5 (A) | 70.65 | -0.9±0.8 | 0.5±0.6 | -1.0±1.0 | 4±4 | 10±10 | 4±2 | -3±2 |
| 78-2-5 (B) | 70.65 | -0.034±0.57 | -0.4±0.7 | -0.26±1.3 | 0±5 | -10±10 | 1±2 | -7±2 |
| 78-2-6 (A) | 71.84 | 2.0±2.0 | -0.1±0.3 | 33±3.0 [a] | 2±3 | 8±14 | -1±2 | -1±2 |
| 78-2-6 (B) | 71.84 | 0.4±0.7 | 0.3±0.9 | -0.31±1.3 | -7±4 | -5±6 | 2±2 | -3±2 |
| 78-2-7 (A) | 72.66 | -0.013±0.48 | -0.026±0.49 | 0.4±0.7 | 3±4 | -6±6 | -6±3 | -3±2 |
| 78-2-7 (B) | 72.66 | 0.2±0.8 | -0.7±0.5 | 0.7±0.9 | 4±4 | -2±8 | -10±4 | -2±3 |
| 78-2-8 (A) | 74.10 | -0.8±0.4 | -0.2±0.4 | 10.0±10.0 | 3±4 | -10±10 | 3±2 | -6±3 |
| 78-2-8 (B) | 74.10 | 0.6±0.7 | 0.1±0.7 | 0.9±10.0 | -3±5 | 0±9 | -13±4 | -3±3 |
| 78-3-1 (A) | 28.10 | -0.4±0.5 | 1.8±0.7 [a] | 0.2±1.3 | -2±4 | -7±6 | -3±2 | -3±2 |
| 78-3-1 (B) | 28.10 | -0.6±0.4 | 0.4±0.4 | -1.0±1.0 | 1±4 | -12±7 | 1±2 | -5±2 |
| 78-3-2 (A) | 68.21 | 0.6±0.6 | 0.5±0.4 | -1.0±1.0 | 2±4 | -1±10 | 2±2 | -3±2 |
| 78-3-2 (B) | 68.21 | -0.8±0.6 | 0.9±0.7 | 0.94±1.2 | 4±3 | 20±20 | 0±2 | -3±3 |
| 78-3-3 (A) | 69.16 | -0.07±0.32 | 0.002±0.48 | -0.34±1.3 | 0±3 | 10±10 | 0±3 | 0±3 |
| 78-3-3 (B) | 69.16 | -1.0±0.5 | -0.1±0.5 | 0.48±1.0 | -1±4 | -5±7 | 7±2 [a] | -6±3 |
| 78-3-4 (A) | 70.20 | 0.9±0.7 | 0.2±0.2 | 0.2±0.9 | 2±3 | 9±15 | 4±3 | 1±3 |
| 78-3-4 (B) | 70.20 | 1.2±0.8 | -0.059±0.51 | -0.53±1.0 | 4±4 | 3±7 | 1±3 | -9±3 |
| 78-3-5 (A) | 71.81 | 2.0±1.0 | 0.4±0.6 | -0.65±1.3 | 2±3 | -15±8 | 1±2 | 2±2 |
| 78-3-5 (B) | 71.81 | 2.0±3.0 | 0.15±1.4 | -0.23±1.4 | -4±4 | 4±8 | -12±4 | -2±3 |
| 78-3-6 (A) | 72.76 | -0.022±0.95 | 0.2±0.5 | 0.6±0.7 | 8±5 | -6±7 | -1±3 | -5±2 |
| 78-3-6 (B) | 72.76 | 1.0±1.0 | 1.3±0.9 | 0.2±0.8 | 0±4 | -16±7 | -0.4±3 | -1±3 |
| 78-3-7 (A) | 73.88 | -0.021±0.46 | -0.042±0.49 | 0.9±0.9 | 2±4 | 4±8 | 2±3 | -1±3 |
| 78-3-7 (B) | 73.88 | -0.7±0.6 | -0.5±0.6 | 2.0±1.0 | 12±4 [a] | -8±7 | 3±3 | -3±3 |
| 78-5-1 (A) | 31.00 | 3.1±1.0 [a] | 0.9±0.9 | 2.0±1.0 | -5±3 | 3±6 | 4±2 | -2±2 |
| 78-5-1 (B) | 31.00 | 1.7±0.8 [a] | 0.025±0.77 | -1.0±0.7 | -5±4 | -8±7 | 3±2 | -5±2 |
| 78-5-2 (A) | 32.37 | 0.3±0.5 | 0.4±0.5 | 0.6±0.9 | 6±4 | -19±7 | -1±3 | -3±3 |

3-20 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 3-6. Concentrations of radionuclides ^{238}Pu , $^{239,240}\text{Pu}$, ^{241}Am , ^{90}Sr , ^{144}Ce , ^{137}Cs , and ^{60}Co in sediment samples collected in 1978 from wells 78-2, 78-3, and 78-5 (from Humphrey, 1980; Table 1)—Continued

| Sample no. | | Sample depth | ^{238}Pu | $^{239,240}\text{Pu}$ | ^{241}Am | ^{90}Sr | ^{144}Ce | ^{137}Cs | ^{60}Co |
|------------|-----|--------------|-------------------|-----------------------|-------------------|------------------|-------------------|-------------------|------------------|
| 78-5-2 | (B) | 32.37 | 0.2±0.9 | -0.041±0.75 | 0.5±0.9 | -4±4 | -3±7 | -2±3 | -3±3 |
| 78-5-3 | (A) | 33.59 | 0.13±0.65 | 0.4±0.3 | 7.0±4.0 | -2±3 | -4±14 | 4±2 | 4±3 |
| 78-5-3 | (B) | 33.59 | 0.2±0.5 | 1.3±0.9 | 1.0±1.0 | 5±3 | -4±8 | -10±4 | -3±3 |
| 78-5-4 | (A) | 34.26 | -0.2±0.5 | 0.9±0.5 | 0.3±0.9 | 2±3 | -6±8 | 1±2 | -4±2 |
| 78-5-4 | (B) | 34.26 | -0.059±0.45 | 1.9±0.9 [a] | 0.84±1.1 | 5±3 | -12±6 | -1±2 | 0±2 |
| 78-5-5 | (A) | 69.04 | 0.048±0.18 | 1.4±0.9 | 0.53±2.4 | 7±4 | 5±7 | 0±3 | -2±2 |
| 78-5-5 | (B) | 69.04 | 0.8±0.9 | -0.071±0.45 | 2.0±3.0 | 2±3 | 1±11 | 5±3 | -4±3 |
| 78-5-6 | (A) | 70.13 | -0.9±0.9 | 0.7±0.8 | -0.91±1.2 | -6±4 | -26±8 | -4±3 | 1±2 |
| 78-5-6 | (B) | 70.13 | 0.7±0.7 | -0.9±0.6 | 2.0±1.0 | 1±4 | -20±20 | 1±2 | -5±2 |
| 78-5-7 | (A) | 70.99 | -0.9±0.7 | 0.074±0.5 | -0.75±1.5 | -1±4 | -3±8 | 5±2 [a] | -3±2 |
| 78-5-7 | (B) | 70.99 | -0.049±0.83 | -0.7±0.6 | 0.82±2.2 | 2±4 | 1±8 | 1±2 | 3±2 |
| 78-5-8 | (A) | 73.24 | -0.9±0.7 | 0.3±0.5 | 0.44±1.1 | 8±5 | 1±6 | -3±3 | 4±3 |
| 78-5-8 | (B) | 73.24 | 3.0±1.0 [a] | 13±2.0 [a] | 3.0±4.0 | -1±4 | 10±20 | 4±3 | 3±3 |

3.0 Task 1: Review of radionuclide sampling program and available data at the Subsurface Disposal Area 3-21

Table 3-7. Concentrations of radionuclides ²³⁸Pu, ^{239,240}Pu, ²⁴¹Am, ⁹⁰Sr, ¹⁴⁴Ce, ¹³⁷Cs, and ⁶⁰Co in new samples taken from cores collected during 1976-77 (from Humphrey, 1980; table 2)

[Analysis performed at the Radiological and Environmental Sciences Laboratory. Sample depth is in meters. Concentrations are in microcuries per gram times 10⁻⁹ (10⁻⁹ μCi/g) for ²³⁸Pu, ^{239,240}Pu, and ²⁴¹Am and in microcuries per gram times 10⁻⁸ (10⁻⁸ μCi/g) for ⁹⁰Sr, ¹⁴⁴Ce, ¹³⁷Cs, and ⁶⁰Co]

| Sample no. | Sample depth | ²³⁸ Pu | ^{239,240} Pu | ²⁴¹ Am | ⁹⁰ Sr | ¹⁴⁴ Ce | ¹³⁷ Cs | ⁶⁰ Co |
|------------|--------------|-------------------|-----------------------|-------------------|------------------|-------------------|-------------------|------------------|
| 76-1-1A | 9.54 | 0.2±0.8 | -0.043±0.45 | -0.025±0.86 | -1±4 | -13±5 | -2±2 | 0±2 |
| 76-1-2A | 68.34 | -0.023±1.2 | -0.7±0.6 | -0.34±1.2 | -6±4 | 30±20 | -2±5 | -3±5 |
| 76-1-3A | 69.01 | -0.005±0.72 | 1.3±0.8 | -0.3±1.3 | -1±3 | 9±14 | -3±4 | -2±3 |
| 76-1-4A | 69.43 | 0.6±0.7 | 0.031±0.53 | 0.38±1.1 | 4±4 | -9±8 | -4±4 | -5±3 |
| 76-1-5A | 69.59 | -0.1±0.9 | -0.4±0.5 | 0.37±1.0 | 7±4 | 14±9 | 1±2 | 0.9±2 |
| 76-2-1A | 68.70 | -0.009±0.63 | 0.6±0.8 | -0.57±1.9 | -3±3 | -9±8 | 0±1.4 | -3±3 |
| 76-2-2A | 69.19 | -0.8±0.7 | 0.2±0.6 | 0.074±0.94 | 1±3 | -10±6 | 3±2 | 0.4±2 |
| 76-2-3A | 71.14 | -0.6±0.7 | 0.1±0.5 | 1.3±1.0 | -5±3 | 10±10 | -1±2 | 0.6±2 |
| 76-2-4A | 71.69 | 0.3±0.5 | -0.5±0.6 | 0.9±1.0 | 3±3 | -9±8 | -1±2 | 3±2 |
| 76-2-5A | 72.97 | -0.3±0.6 | -0.5±0.5 | -0.001±0.69 | 4±3 | -2±7 | -5±3 | 0±2 |
| 76-2-6A | 73.97 | 2.0±1.0 | 0.5±0.6 | -0.0±0.1 | 1±3 | -20±7 | -3±3 | 3±3 |
| 76-3-1A | 30.27 | -0.036±0.77 | -0.04±0.02 | 0.55±1.0 | 2±4 | -3±8 | 2±2 | 1±2 |
| 76-3-2A | 31.85 | -0.03±0.78 | -0.7±0.6 | 0.6±0.9 | 1±3 | 13±13 | 7±4 | -2±3 |
| 76-3-3A | 32.40 | 0.1±0.4 | 0.1±0.4 | 0.2±0.7 | 4±4 | -6±8 | -1±1 | 0±2 |
| 76-3-4A | 34.75 | -0.6±0.5 | 0.2±0.1 | 0.1±1.0 | 5±3 | -8±6 | 1±2 | 3±2 |
| 76-3-5A | 35.36 | -0.024±0.45 | -0.7±0.5 | -0.2±0.1 | -1±3 | -7±8 | 2±4 | -1±2 |
| 76-3-6A | 68.88 | 1.5±0.9 | 0.6±0.7 | -1.4±0.9 | -5±3 | 10±10 | 0±2 | 0±2 |
| 76-3-7A | 70.81 | -0.4±0.6 | -0.4±0.5 | 10±10 | 2±3 | -4±8 | 2±3 | -4±3 |
| 76-3-8A | 71.60 | -0.45±0.45 | -0.45±0.45 | 0.36±1.2 | 0±3 | -2±8 | 0.5±2 | 1±1 |
| 76-3-9A | 73.12 | 0.005±0.53 | 0.005±0.45 | -0.3±0.6 | -2±3 | -1±6 | -4±2 | -5±2 |
| 76-4-1A | 7.01 | -0.4±0.5 | -0.4±0.5 | 3.0±2.0 | 4±3 | 3±13 | 0.4±2 | -2±2 |
| 76-4-2A | 30.33 | -0.6±0.9 | 0.003±0.33 | 0.4±1.0 | -5±4 | 0.7±8 | 2±2 | -2±2 |
| 76-4A-1A | 69.49 | 0.1±1.0 | 0.007±0.52 | 0.033±0.93 | 5±3 | -2±9 | -5±4 | -5±3 |
| 76-4A-2A | 70.29 | -0.9±0.6 | -0.1±0.6 | 1.0±1.0 | 6±3 | 2±9 | 2±2 | -8±4 |
| 76-4A-3A | 71.14 | 0.2±0.7 | 0.2±0.5 | 0.018±0.94 | 2±3 | -9±6 | -2±2 | 0±2 |
| 76-4A-4A | 72.05 | 1.1±0.7 | -0.5±0.6 | 0.58±1.2 | 1±3 | 4±6 | -1±2 | 0±2 |
| 76-4A-5A | 73.03 | 0.2±0.8 | -0.006±0.66 | 1.2±0.9 | -3±3 | 7±14 | 1±3 | -7±4 |
| 76-4A-6A | 73.82 | 0.2±0.7 | -0.029±0.45 | 0.4±0.8 | 4±3 | -8±8 | -2±4 | -1±3 |
| 76-4A-7A | 74.19 | 0.8±0.8 | 0.083±0.58 | -0.1±0.7 | -2±4 | 0±8 | 1±2 | 0±2 |

3-22 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 3-7. Concentrations of radionuclides ^{238}Pu , $^{239,240}\text{Pu}$, ^{241}Am , ^{90}Sr , ^{144}Ce , ^{137}Cs , and ^{60}Co in new samples taken from cores collected during 1976-77 (from Humphrey, 1980; table 2)—Continued

| Sample no. | Sample depth | ^{238}Pu | $^{239,240}\text{Pu}$ | ^{241}Am | ^{90}Sr | ^{144}Ce | ^{137}Cs | ^{60}Co |
|------------|--------------|-------------------|-----------------------|-------------------|------------------|-------------------|-------------------|------------------|
| 76-5-1A | 30.60 | -0.016±0.72 | -0.02±0.02 | 1.0±1.0 | 4±3 | -7±8 | 2±2 | 3±2 |
| 76-5-2A | 30.97 | 0.065±0.9 | 0.4±1.0 | 0.47±1.0 | 1±4 | -11±8 | -4±3 | -4±2 |
| 76-5-3A | 32.49 | -0.005±0.4 | 0.3±0.4 | 0.4±0.8 | -2±4 | -10±20 | 3±2 | -1±2 |
| 76-5-4A | 33.07 | 0.01±0.61 | 0.009±0.53 | 0.5±0.8 | 5±3 | -13±6 | -5±2 | 2±2 |
| 76-5-5A | 34.99 | 0.2±0.7 | -0.7±0.6 | -0.88±1.2 | 7±4 | 14±13 | 4±2 | -4±3 |
| 76-5-6A | 68.64 | 0.027±0.45 | -0.6±0.6 | 0.1±0.8 | -6±4 | 25±13 | -1±2 | -2±2 |
| 76-5-7A | 70.20 | -0.4±0.5 | -0.4±0.5 | 1.1±1.0 | -1±4 | -1±7 | 1±2 | 0.4±2 |
| 76-5-8A | 71.41 | 0.3±0.6 | 0.2±0.6 | 1.4±1.0 | 2±3 | -2±6 | 4±2 | -1±2 |
| 76-5-9A | 73.82 | -0.7±0.6 | -0.5±0.6 | -0.8±0.8 | 5±3 | -7±8 | -2±2 | 4±2 |
| 76-6-1A | 71.54 | -0.3±0.9 | 0.2±0.5 | -0.003±0.92 | 1±4 | 0±20 | -1±3 | -8±3 |
| 76-6-2A | 72.02 | 0.2±0.5 | -0.5±0.5 | 0.5±0.9 | -3±4 | 6±12 | 2±2 | -1±3 |

Table 3-8. Concentrations of radionuclides ²³⁸Pu, ^{239,240}Pu, ²⁴¹Am, ⁹⁰Sr, and ¹³⁷Cs in sediment samples collected in 1987 from wells D-02, D-06A, and TW-1 (from Laney and others, 1988; table 20)

[Analysis by EG&G Idaho, Incorporated. Sample depth is in feet-inches. Concentrations are in microcuries per gram (μCi/g). Symbol: * = sample result positive, >3σ]

| Sample | Sample depth interval | ²³⁸ Pu | | ^{239,240} Pu | | ²⁴¹ Am | | ⁹⁰ Sr | | ¹³⁷ Cs | | |
|--------------------------------------|-----------------------|-------------------|----------|-----------------------|----------|-------------------|----------|------------------|----------|-------------------|----------|--|
| | | Result | Exponent | Result | Exponent | Result | Exponent | Result | Exponent | Result | Exponent | |
| Deep Hole D-02 | | | | | | | | | | | | |
| D-13 | 1-2 to 1-8 | 2.6±0.2 | E-07* | 1.13±0.05 | E-06* | 1.52±0.06 | E-06* | 1.9±0.3 | E-07* | 7.2±1.0 | E-08* | |
| D-17 | 9-2 to 9-8 | 6±9 | E-10 | 0.6±1.1 | E-09 | 0.3±1.2 | E-09 | -2±3 | E-08 | 1±8 | E-09 | |
| D-20 | 15-6 to 16-0 | 1.49±0.18 | E-08* | 2.55±0.09 | E-07* | 5.0±0.5 | E-08* | 1.3±0.3 | E-07* | 10±7 | E-09 | |
| D-30 | 233-10 to 224-4 | 1.3±1.3 | E-09 | 8±9 | E-10 | -0.1±1.0 | E-09 | -2±4 | E-08 | -2±8 | E-09 | |
| D-31 | 224-4 to 226-4 | 2.6±1.1 | E-09 | 7±8 | E-10 | 0.0±1.2 | E-09 | 2±3 | E-08 | 4±7 | E-09 | |
| D-34 (field split) | 230-0 to 230-4 | 6.5±1.9 | E-09* | 0.8±1.0 | E-09 | 0.3±1.3 | E-09 | 4±3.0 | | -0±7 | E-09 | |
| D-34 (lab split) | 230-0 to 230-4 | 3.22±0.17 | E-08* | 5.8±0.2 | E-08* | | | | | | | |
| D-34 (lab split 4,000-min. count) | 230-0 to 230-4 | 1.5±0.4 | E-09* | 2±3 | E-10 | | | | | | | |
| D-34 (lab split 4,000-min. count) | 230-0 to 230-4 | 3.3±0.6 | E-09* | 3±4 | E-10 | | | | | | | |
| D-34A (field split 4,000-min. count) | 229-8 to 230-0 | 2.4±0.7 | E-09* | 3±6 | E-10 | | | | | | | |
| D-34A (lab split) | 229-8 to 230-0 | 1.3±1.1 | E-09 | -3±7 | E-10 | | | | | | | |
| D-34A (lab split) | 229-8 to 230-0 | 1.4±1.1 | E-09 | 4±6 | E-10 | | | | | | | |
| D-35 | 232-3 to 232-7 | 1.6±1.7 | E-09 | 1.1±1.0 | E-09 | -0.2±1.2 | E-09 | 2±3 | E-08 | 7±7 | E-09 | |
| D-36 | 233-9 to 234-2 | 1.8±1.5 | E-09 | 1.1±1.4 | E-09 | -0.3±1.2 | E-09 | 2±4 | E-08 | 0±6 | E-09 | |
| D-37 | 234-9 to 235-2 | 1.4±1.1 | E-09 | 1.0±0.9 | E-09 | 0.2±1.4 | E-09 | -3±4 | E-08 | 1.3±0.7 | E-08 | |

Table 3-8. Concentrations of radionuclides ^{238}Pu , $^{239,240}\text{Pu}$, ^{241}Am , ^{90}Sr , and ^{137}Cs in sediment samples collected in 1987 from wells D-02, D-06A, and TW-1 (from Laney and others, 1988; table 20)—Continued

| Sample | Sample depth interval | ^{238}Pu | | $^{239,240}\text{Pu}$ | | ^{241}Am | | ^{90}Sr | | ^{137}Cs | |
|-----------------------|-----------------------|-------------------|----------|-----------------------|----------|-------------------|----------|------------------|----------|-------------------|----------|
| | | Result | Exponent | Result | Exponent | Result | Exponent | Result | Exponent | Result | Exponent |
| Deep Hole D-06A | | | | | | | | | | | |
| D-29 | 47-0 to 49-0 | 1.5±1.2 | E-09 | 7±7 | E-10 | -2±9 | E-10 | 4±3 | E-08 | 5±2 | E-08 |
| Deep Hole TW-1 | | | | | | | | | | | |
| D-42 (field split) | 101-0 to 101-2 | 1.7±0.2 | E-08* | 7.4±0.4 | E-07* | 4.4±0.2 | E-07* | 5±4 | E-08 | | |
| D-42 (lab subsplit) | 101-0 to 101-2 | 1.18±0.17 | E-08* | 6.1±0.3 | E-07* | 4.7±0.2 | E-07* | | | | |
| D-43A (field split) | 101-2 to 101-7 | 4.6±1.4 | E-09* | 1.97±0.13 | E-07* | 1.03±0.08 | E-07* | 4±3 | E-08 | | |
| D-43 (field subsplit) | 101-2 to 101-7 | 6.3±1.7 | E-09* | 1.9±0.13 | E-07* | 1.06±0.09 | E-07* | | | | |
| D-43A (lab subsplit) | 101-2 to 101-7 | 6.5±1.6 | E-09* | 2.00±0.13 | E-07* | 1.37±0.11 | E-07* | | | | |
| D-47 | 225-9 to 225-11 | -4±6 | E-10 | 8±7 | E-10 | 2±9 | E-10 | 6±3 | E-08 | | |
| D-47 (lab subsplit) | 225-9 to 225-11 | 7±7 | E-10 | 2±6 | E-10 | 0.5±1.0 | E-09 | | | | |
| D-48 | 226-10 to 227-7 | 0.8±1.1 | E-09 | 3±6 | E-10 | 1.2±1.4 | E-09 | 3±3 | E-08 | 3±1.6 | E-08 |
| D-48 (lab subsplit) | 226-10 to 227-7 | 5±9 | E-10 | 2±7 | E-10 | 0.7±1.1 | E-09 | | | | |
| D-48 (lab subsplit) | 226-10 to 227-7 | 6±7 | E-10 | 7±7 | E-10 | 0.6±1.2 | E-09 | | | | |

Table 3-9. Comparison of results obtained by EG&G (table 3-8) with results obtained by the Radiological and Environmental Sciences Laboratory for radionuclides ^{238}Pu , $^{239,240}\text{Pu}$, and ^{241}Am in samples from well TW-1, B-C interbed (modified from Laney and others, 1988; table 21)

[Sample depths are in feet-inches. Concentrations are in microcuries per gram ($\mu\text{Ci/g}$). Abbreviations: EGG = EG&G; RESL = Radiological and Environmental Sciences Laboratory; Symbol: * = sample result statistically positive $>3\sigma$; ND = presumably not detected]

| Sample no. | Depth | EGG | | | | | | RESL | | | | | |
|----------------------|-------|-------------------|-------|-----------------------|-------|-------------------|---------|-------------------|-------|-----------------------|-------|-------------------|-------|
| | | ^{238}Pu | | $^{239,240}\text{Pu}$ | | ^{241}Am | | ^{238}Pu | | $^{239,240}\text{Pu}$ | | ^{241}Am | |
| D-43A | 101-2 | 4.6±1.4 | E-09* | 1.97±0.13 | E-07* | 1.3±0.08 | E-08**‡ | 10±3 | E-09* | 1.78±0.13 | E-07* | 8.47±0.95 | E-08* |
| D-43A (lab subsplit) | 101-2 | 6.3±1.7 | E-09* | 1.90±0.13 | E-07* | 1.06±0.09 | E-07* | ND | | 1.68±0.09 | E-07* | 9.08±0.075 | E-07* |
| D-43A (lab subsplit) | 101-2 | 6.5±1.6 | E-09* | 2.00±0.13 | E-07* | 1.37±0.11 | E-07* | 3.9±1.3 | E-09 | 1.7±0.09 | E-07* | 1.07±0.09 | E-07* |

‡ Value here does not match that given for D43A (field subsplit) in Laney and others, 1988, table 20 [$1.03 \pm 0.08 \text{ E-07}$]

3-26 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 3-10. Summary of statistically significant ($>3\sigma$) concentrations for waste radionuclides in samples from selected depth intervals and wells

- A: Interval 1, 10 to 75 ft (3 to 23 m) below land surface.
- B: Interval 2, 82 to 142 ft (25 to 43 m) below land surface.
- C: Interval 3, 217 to 265 ft (66 to 81 m) below land surface.
- D. Background sites

Summary of statistically positive results

Table 3-10A, B, C, and D is a modification of a summary table by Dames and Moore (1992, table 5-5, -6, -7, and -8, hereafter called D/M SUM) which presents data for statistically positive results determined by using the 3s criteria. The 1992 report was revised in 1994 (Dames and Moore, 1994); however only appendix A of the 1994 report (APX-94) was available for the preparation of this report. The picocurie units in appendix A of the 1992 report (APX-92) were changed to nanocurie units to correct a major (3 orders of magnitude) conversion error. Other than the change in units, the statistically positive results in APX-94 are the same (with two exceptions) as in APX-92, which was used to prepare the D/M SUM. Data presented in this table (table 3-10) reflect the corrections made in APX-94. In addition to the conversion error, other discrepancies were found among the data from the D/M SUM, APX-92 and APX-94 (D/M APX), and tables in several reports in which results for the selected samples were first presented (tables 3-1 to 3-9 of this report). Samples for which there are discrepancies are listed in boldface type, and results from each of the three data sources (D/M SUM, D/M APX, and the original tables) are listed. The type of discrepancy is documented in the "Discrepancy" column (see below for explanation of discrepancies). Where there are differences among the tables, the original reports are assumed to be correct.

Statistically positive results listed in the D/M APX from above 10 feet (3 meters) and below 500 feet (152 meters) below land surface are not in the D/M SUM and are not included in table 3-10. Some information that is not in the D/M SUM was added to table 3-10 (year, depth interval, analytical laboratory, and replication). Data from D/M SUM were reordered so that samples are listed by year in table 3-10. Samples that have statistically positive results are grouped by well and also by depth interval. Dashed lines (---) indicate that data for the well interval are not presented in table 3-10. Where the depth listed in the D/M SUM is different from that listed in the original report, the depth from the original report is listed in parentheses. Statistically positive results for replicate samples are listed consecutively and indicated by a letter (A, B, etc.) in the Replicates column. Statistically negative results for replicate samples are indicated by a number in the Replicates representing the number of negative analyses. Below this number, the statistically negative values are listed. "No" in the Replicates column indicates that no replicates were analyzed. In some cases, the replicates were analyzed in a different laboratory. The analyzing laboratories are abbreviated in the Lab column as follows: RESL, Radiological and Environmental Sciences Laboratory (formerly Idaho National Engineering Laboratory Health Service Laboratory); ACC, Allied Chemical Corporation; and EGG, EG&G.

Types of errors found:

- 0 Data verified against data in appendix A and the original report, except for probable rounding errors.
- 1 Data on Dames and Moore summary table does not agree with appendix A: uncertainty incorrect.
- 2 Data on Dames and Moore summary table does not agree with appendix A: exponent(s) incorrect; 2a both the value and uncertainty incorrect; 2b either value or uncertainty incorrect.
- 3 Error corrected in Dames and Moore, rev. 3 appendix A.
- 4 Dames and Moore summary table does not agree with appendix A: well listed incorrectly.
- 5 Statistically positive value not listed in Dames and Moore summary table.
- 6 Data listed in appendix A does not agree with data in original report.
- 7 The original report (Laney and others, 1988) states that EGG values from Table 20 have been used to prepare Table 21, however Am-241 value (nCi/g) $1.3\pm 0.08 \text{ E-5}$ in Table 21 does not agree with $1.03\pm 0.08 \text{ E-4}$ in Table 20. The former value appears in App. A (1992) and has been changed to the latter value in App A, Rev. 3. Pu-238 value is (nCi/g) $1.18\pm 0.17 \text{ E-5}$ in Table 20 and $1.18\pm 0.17 \text{ E-4}$ in Table 21.
- 8 Not statistically positive
- * Verification not possible because 1979 original report is unavailable.

Table 3-10A. Interval 1 (10 to 75 feet (3 to 23 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-5), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision) and data from the original reports, tables 3-1 through 3-9 (this report)

[Concentrations are in nanocuries per gram (nCi/g). Abbreviations: D/M SUM = Dames and Moore (1992, table 5-5); D/M APX = Dames and Moore (1992 and 1994 revision) Appendix A; ORIGINAL = Data from original reports, tables 3-1 through 3-9 (this report)]

| Year | Well | Depth (feet) | Radionuclide | Source | Concentration | Uncertainty | Anal. lab | Replicates | Error |
|------|---------|--------------|-----------------------|----------|---------------|-------------|-----------|------------|-------|
| 1972 | USGS 93 | 13.83-14.00 | ⁹⁰ Sr | D/M SUM | 4.00E-04 | 9.00E-05 | RESL | NO | 0 |
| 1972 | USGS 93 | 13.83-14.00 | ²⁴¹ Am | D/M SUM | 1.20E-05 | 3.00E-06 | RESL | NO | 1, 8 |
| | | | | D/M APX | 1.20E-05 | 3.00E-06 | | | |
| | | | | ORIGINAL | 1.20E-05 | 4.50E-06 | | | |
| 1987 | D-O2 | 15.50-16.00 | ²⁴¹ Am | D/M SUM | 5.00E-05 | 5.00E-06 | EGG | NO | 0 |
| 1987 | D-O2 | 15.50-16.00 | ²³⁸ Pu | D/M SUM | 1.49E-04 | 1.80E-05 | EGG | NO | 2a |
| | | | | D/M APX | 1.49E-05 | 1.80E-06 | | | |
| | | | | ORIGINAL | 1.49E-05 | 1.80E-06 | | | |
| 1987 | D-O2 | 15.50-16.00 | ^{239,240} Pu | D/M SUM | 2.55E-04 | 9.00E-06 | EGG | NO | 0 |
| 1987 | D-O2 | 15.50-16.00 | ⁹⁰ Sr | D/M SUM | 1.30E-04 | 2.00E-05 | EGG | NO | 1 |
| | | | | D/M APX | 1.30E-04 | 3.00E-05 | | | |
| | | | | ORIGINAL | 1.30E-04 | 3.00E-05 | | | |

Table 3-10B. Interval 2 (82 to 142 feet (25 to 43 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-6), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)

[Concentrations are in nanocuries per gram (nCi/g)]

| Year | Well | Depth (feet) | Radionuclide | Source | Concentration | Uncertainty | Anal. lab | Replicates | Error |
|------|---------|---------------|-----------------------|----------|---------------|-------------|-----------|------------|-------|
| 1971 | USGS 88 | 111.00-112.5 | ^{239,240} Pu | D/M SUM | 1.00E-05 | 0.00E+00 | RESL | NO | 8 |
| | | | | D/M APX | 1.00E-05 | --- | | | |
| | | | | ORIGINAL | --- | --- | | | |
| 1972 | USGS 93 | 98.00-101.00 | ⁶⁰ Co | D/M SUM | 6.20E-05 | 1.20E-05 | RESL | NO | 0 |
| 1972 | USGS 93 | 98.00-101.00 | ^{239,240} Pu | D/M SUM | 1.10E-04 | 7.00E-06 | RESL | NO | 0 |
| 1972 | USGS 93 | 98.00-101.00 | ²³⁸ Pu | D/M SUM | --- | --- | | | 5 |
| | | | | D/M APX | 7.60E-06 | 1.50E-06 | | | |
| | | | | ORIGINAL | 8.00E-06 | 1.50E-06 | | | |
| 1972 | USGS 93 | 98.00-101.00 | ¹³⁷ Cs | D/M SUM | 1.00E-04 | 2.00E-05 | RESL | NO | 0 |
| 1972 | USGS 93 | 101.00-103.00 | ²⁴¹ Am | D/M SUM | 6.30E-05 | 1.00E-05 | RESL | A | 0 |
| 1972 | USGS 93 | 101.00-103.00 | ²⁴¹ Am | D/M SUM | 1.50E-04 | 2.00E-05 | RESL | B | 0 |
| 1972 | USGS 93 | 101.00-103.00 | ^{239,240} Pu | D/M SUM | 5.40E-04 | 1.20E-05 | RESL | A | 0 |
| 1972 | USGS 93 | 101.00-103.00 | ^{239,240} Pu | D/M SUM | 2.30E-04 | 1.10E-05 | RESL | B | 0 |
| 1972 | USGS 93 | 101.00-103.00 | ²³⁸ Pu | D/M SUM | --- | --- | RESL | A | 5 |
| | | | | D/M APX | 1.40E-05 | 3.00E-06 | | | |
| | | | | ORIGINAL | 1.40E-05 | 3.00E-06 | | | |

Table 3-10B. Interval 2 (82 to 142 feet (25 to 43 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-6), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)—Continued

| Year | Well | Depth (feet) | Radionuclide | Source | Concentration | Uncertainty | Anal. lab | Replicates | Error |
|------|---------|---------------|-----------------------|----------|---------------|-------------|-----------|------------|-------|
| 1972 | USGS 93 | 101.00-103.00 | ²³⁸ Pu | D/M SUM | --- | --- | RESL | B | 5 |
| | | | | D/M APX | 8.60E-06 | 3.00E-06 | | | |
| | | | | ORIGINAL | 9.00E-06 | 3.00E-06 | | | |
| 1972 | USGS 93 | 101.00-103.00 | ⁹⁰ Sr | D/M SUM | 6.90E-04 | 1.10E-04 | RESL | NO | 0 |
| 1972 | USGS 93 | 103.00-105.00 | ⁹⁰ Sr | D/M SUM | 4.00E-04 | 1.10E-04 | RESL | NO | 0 |
| 1972 | USGS 93 | 103.00-105.00 | ²⁴¹ Am | D/M SUM | 4.50E-05 | 4.00E-06 | RESL | NO | 1 |
| | | | | D/M APX | 4.50E-05 | 6.00E-06 | | | |
| | | | | ORIGINAL | 4.50E-05 | 6.00E-06 | | | |
| 1972 | USGS 93 | 103.00-105.00 | ^{239,240} Pu | D/M SUM | 8.10E-05 | 1.10E-06 | RESL | NO | 2b |
| | | | | D/M APX | 8.10E-05 | 1.10E-05 | | | |
| | | | | ORIGINAL | 8.10E-05 | 1.10E-05 | | | |
| 1972 | USGS 92 | 88.5-90 | ⁹⁰ Sr | D/M SUM | 3.00E-04 | 9.00E-05 | RESL | NO | 0 |
| 1972 | USGS 94 | 95.92-102 | ⁹⁰ Sr | D/M SUM | 1.50E-04 | 5.00E-05 | RESL | NO | 0 |
| 1972 | USGS 96 | 100.50-101 | ^{239,240} Pu | D/M SUM | 4.50E-05 | 2.00E-07 | RESL | NO | 2b |
| | | | | D/M APX | 4.50E-05 | 2.00E-06 | | | |
| | | | | ORIGINAL | 4.50E-05 | 2.00E-06 | | | |

Table 3-10B. Interval 2 (82 to 142 feet (25 to 43 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-6), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)—Continued

| Year | Well | Depth (feet) | Radionuclide | Source | Concentration | Uncertainty | Anal. lab | Replicates | Error |
|------|---------|----------------------------------|-------------------|----------|---------------|-------------|-----------|-----------------------------------|-------|
| 1972 | USGS 96 | 100.50-101 | ²³⁸ Pu | D/M SUM | --- | --- | RESL | NO | 5 |
| | | | | D/M APX | 5.90E-06 | 1.50E-06 | | | |
| | | | | ORIGINAL | 6.00E-06 | 1.50E-06 | | | |
| | USGS 96 | 110.00-112.92 | ²⁴¹ Am | D/M SUM | --- | --- | RESL | A | 5, 6 |
| | | | | D/M APX | 2.30E-05 | 2.00E-05 | | | |
| | | | | ORIGINAL | 2.30E-04 | 2.00E-05 | | | |
| 1972 | USGS 96 | 110.00-112.92 (110.00-110.50) | ²⁴¹ Am | D/M SUM | 3.00E-05 | 6.00E-06 | RESL | B | 0 |
| 1972 | USGS 96 | 122.75-124.75 | ¹³⁷ Cs | D/M SUM | --- | --- | RESL | NO | 5 |
| | | | | D/M APX | 5.50E-04 | 4.00E-05 | | | |
| | | | | ORIGINAL | 5.50E-04 | 4.00E-05 | | | |
| 1972 | USGS 95 | 112.00-113.33 | ¹³⁷ Cs | D/M SUM | 2.20E-04 | 1.00E-05 | RESL | NO | 0 |
| 1976 | 76-4A | 97.8 | ²⁴¹ Am | D/M SUM | 6.40E-06 | 1.70E-06 | RESL | 2 (0.0±1.0E-6) (0.0±1.0E-6) | 0 |
| 1976 | 76-3 | 97.50-97.80 | ²⁴¹ Am | D/M SUM | 8.40E-06 | 1.40E-06 | ACC | 1 (-1.0±1.0E-6) | 0 |

Table 3-10B. Interval 2 (82 to 142 feet (25 to 43 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-6), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)—Continued

| Year | Well | Depth (feet) | Radionuclide | Source | Concentration | Uncertainty | Anal. lab | Replicates | Error |
|------|------|---------------------|-----------------------|----------|---------------|-------------|-----------|--------------|-------|
| 1976 | 76-3 | 97.50-97.80 | ^{239,240} Pu | D/M SUM | --- | --- | RESL | 1 | 5 |
| | | | | D/M APX | 1.68E-05 | 5.00E-06 | | (0.0±1.0E-6) | |
| | | | | ORIGINAL | 1.68E-05 | 5.00E-06 | | | |
| 1978 | 78-5 | 101.71 (31.00 m) | ²³⁸ Pu | D/M SUM | --- | --- | RESL | 1 | 5 |
| | | | | D/M APX | 3.10E-06 | 1.00E-06 | | (1.7±0.8E-6) | |
| | | | | ORIGINAL | 3.10E-06 | 1.00E-06 | | | |
| 1979 | 79-2 | 99.11-99.90 | ²⁴¹ Am | D/M SUM | 2.20E-05 | 2.00E-06 | * | A | * |
| 1979 | 79-2 | 99.11-99.90 | ²⁴¹ Am | D/M SUM | 3.10E-05 | 3.00E-06 | * | B | * |
| 1979 | 79-2 | 99.11-99.90 | ^{239,240} Pu | D/M SUM | --- | --- | * | A | 5, * |
| | | | | D/M APX | 6.10E-05 | 4.00E-06 | | | |
| | | | | ORIGINAL | * | * | | | |
| 1979 | 79-2 | 99.11-99.90 | ^{239,240} Pu | D/M SUM | --- | --- | * | B | 5, * |
| | | | | D/M APX | 5.60E-05 | 4.00E-06 | | | |
| | | | | ORIGINAL | * | * | | | |
| 1979 | 79-2 | 99.90-101.71 | ²⁴¹ Am | D/M SUM | 1.30E-05 | 3.00E-06 | * | A | * |
| 1979 | 79-2 | 99.90-101.71 | ²⁴¹ Am | D/M SUM | 1.80E-05 | 2.00E-06 | * | B | * |
| 1979 | 79-2 | 99.90-101.71 | ^{239,240} Pu | D/M SUM | --- | --- | * | A | 5, * |
| | | | | D/M APX | 3.40E-05 | 3.00E-06 | | | |
| | | | | ORIGINAL | * | * | | | |

Table 3-10B. Interval 2 (82 to 142 feet (25 to 43 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-6), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)—Continued

| Year | Well | Depth (feet) | Radionuclide | Source | Concentration | Uncertainty | Anal. lab | Replicates | Error |
|------|------|---------------|-----------------------|----------|---------------|-------------|-----------|------------|-------|
| 1979 | 79-2 | 99.90-101.71 | ^{239,240} Pu | D/M SUM | --- | --- | * | B | 5, * |
| | | | | D/M APX | 3.70E-05 | 3.00E-06 | | | |
| | | | | ORIGINAL | * | * | | | |
| 1979 | 79-2 | 101.71-102.99 | ^{239,240} Pu | D/M SUM | --- | --- | * | A | 5, * |
| | | | | D/M APX | 3.80E-05 | 3.00E-06 | | | |
| | | | | ORIGINAL | * | * | | | |
| 1979 | 79-2 | 101.71-102.99 | ^{239,240} Pu | D/M SUM | --- | --- | * | B | 5, * |
| | | | | D/M APX | 3.60E-05 | 3.00E-06 | | | |
| | | | | ORIGINAL | | | | | |
| 1979 | 79-2 | 101.71-102.99 | ²⁴¹ Am | D/M SUM | 2.40E-05 | 3.00E-06 | * | A | * |
| 1979 | 79-2 | 101.71-102.99 | ²⁴¹ Am | D/M SUM | 2.00E-05 | 3.00E-06 | * | B | * |
| 1979 | 79-2 | 101.71-102.99 | ⁶⁰ Co | D/M SUM | 5.20E-05 | 1.70E-05 | * | 3 | * |
| | | | | | | | | (2±2E-5) | |
| | | | | | | | | (-1±2E-5) | |
| | | | | | | | | (-1±2E-5) | |
| 1979 | 79-3 | 100.69-106.2 | ⁶⁰ Co | D/M SUM | 2.50E-04 | 2.00E-05 | * | A | * |
| 1979 | 79-3 | 100.69-106.2 | ⁶⁰ Co | D/M SUM | 2.80E-04 | 2.00E-05 | * | B | * |

Table 3-10B. Interval 2 (82 to 142 feet (25 to 43 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-6), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)—Continued

| Year | Well | Depth (feet) | Radionuclide | Source | Concentration | Uncertainty | Anal. lab | Replicates | Error |
|------|------|---------------|-----------------------|-------------------|---------------|-------------|-----------|------------|-------|
| 1987 | TW-1 | 101.00-101.17 | ^{239,240} Pu | D/M SUM | --- | --- | EGG | A | 5 |
| | | | | D/M APX | 7.40E-04 | 4.00E-05 | | | |
| | | | | ORIGINAL | 7.40E-04 | 4.00E-05 | | | |
| 1987 | TW-1 | 101.00-101.17 | ^{239,240} Pu | D/M SUM | --- | --- | EGG | B | 5 |
| | | | | D/M APX | 6.10E-04 | 3.00E-05 | | | |
| | | | | ORIGINAL | 6.10E-04 | 3.00E-05 | | | |
| 1987 | TW-1 | 101.00-101.17 | ²⁴¹ Am | D/M SUM | 4.70E-04 | 2.00E-05 | EGG | A | 0 |
| 1987 | TW-1 | 101.00-101.17 | ²⁴¹ Am | D/M SUM | 4.40E-04 | 2.00E-05 | EGG | B | 0 |
| 1987 | TW-1 | 101.00-101.17 | ²³⁸ Pu | D/M SUM | --- | --- | EGG | A | 5 |
| | | | | D/M APX | 1.70E-05 | 2.00E-06 | | | |
| | | | | (101) ORIGINAL | 1.70E-05 | 2.00E-06 | | | |
| 1987 | TW-1 | 101.00-101.17 | ²³⁸ Pu | D/M SUM | --- | --- | EGG | B | 5, 7 |
| | | | | D/M APX | 1.18E-05 | 1.70E-06 | | | |
| | | | | (101) ORIGINAL | 1.18E-05 | 1.70E-06 | | | |
| 1987 | TW-1 | 101.17 | ²³⁸ Pu | D/M SUM | --- | --- | EGG | A | 5 |
| | | | | D/M APX | 4.60E-06 | 1.40E-06 | | | |
| | | | | ORIGINAL | 4.60E-06 | 1.40E-06 | | | |

Table 3-10B. Interval 2 (82 to 142 feet (25 to 43 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-6), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)—Continued

| Year | Well | Depth (feet) | Radionuclide | Source | Concentration | Uncertainty | Anal. lab | Replicates | Error |
|------|------|-----------------|-----------------------|----------|---------------|-------------|-----------|------------|-------|
| 1987 | TW-1 | 101.17 | ²³⁸ Pu | D/M SUM | --- | --- | RESL | B | 5 |
| | | | | D/M APX | 1.00E-05 | 3.00E-06 | | | |
| | | | | ORIGINAL | 1.00E-05 | 3.00E-06 | | | |
| 1987 | TW-1 | 101.17 | ²³⁸ Pu | D/M SUM | --- | --- | EGG | C | 5 |
| | | | | D/M APX | 6.30E-06 | 1.70E-06 | | | |
| | | | | ORIGINAL | 6.30E-06 | 1.70E-06 | | | |
| 1987 | TW-1 | 101.17 | ^{239,240} Pu | D/M SUM | --- | --- | EGG | A | 5 |
| | | (101.17-101.58) | | D/M APX | 1.97E-04 | 1.30E-05 | | | |
| | | | | ORIGINAL | 1.97E-04 | 1.30E-05 | | | |
| 1987 | TW-1 | 101.17 | ^{239,240} Pu | D/M SUM | --- | --- | RESL | B | 5 |
| | | (101.17-101.58) | | D/M APX | 1.78E-04 | 1.30E-05 | | | |
| | | | | ORIGINAL | 1.78E-04 | 1.30E-05 | | | |
| 1987 | TW-1 | 101.17 | ^{239,240} Pu | D/M SUM | --- | --- | EGG | C | 5, 3 |
| | | (101.17-101.58) | | D/M APX | 1.97E-04 | 1.30E-05 | | | |
| | | | | ORIGINAL | 1.90E-04 | 1.30E-05 | | | |
| 1987 | TW-1 | 101.17 | ^{239,240} Pu | D/M SUM | --- | --- | RESL | D | 5 |
| | | (101.17-101.58) | | D/M APX | 1.68E-04 | 9.00E-06 | | | |
| | | | | ORIGINAL | 1.68E-04 | 9.00E-06 | | | |

Table 3-10B. Interval 2 (82 to 142 feet (25 to 43 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-6), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)—Continued

| Year | Well | Depth (feet) | Radionuclide | Source | Concentration | Uncertainty | Anal. lab | Replicates | Error |
|------|------|-----------------|-----------------------|----------|---------------|-------------|-----------|------------|-------|
| 1987 | TW-1 | 101.17 | ^{239,240} Pu | D/M SUM | --- | --- | EGG | E | 5 |
| | | | | D/M APX | 2.00E-04 | 1.30E-05 | | | |
| | | (101.17-101.58) | | ORIGINAL | 2.00E-04 | 1.30E-05 | | | |
| 1987 | TW-1 | 101.17 | ^{239,240} Pu | D/M SUM | --- | --- | RESL | F | 5 |
| | | | | D/M APX | 1.70E-04 | 9.00E-06 | | | |
| | | (101.17-101.58) | | ORIGINAL | 1.70E-04 | 9.00E-06 | | | |
| 1987 | TW-1 | 101.17 | ²⁴¹ Am | D/M SUM | 1.37E-04 | 1.10E-05 | EGG | A | 0 |
| 1987 | TW-1 | 101.17 | ²⁴¹ Am | D/M SUM | 1.00E-04 | 9.00E-06 | RESL | B | 0 |
| 1987 | TW-1 | 101.17 | ²⁴¹ Am | D/M SUM | 1.30E-05 | 8.00E-06 | EGG | C | 1, 7 |
| | | | | D/M APX | 1.30E-05 | 8.00E-07 | | | |
| | | | | ORIGINAL | 1.30E-05 | 8.00E-07 | | | |
| | | | | ORIGINAL | 1.03E-04 | 8.00E-06 | | | |
| 1987 | TW-1 | 101.17 | ²⁴¹ Am | D/M SUM | 8.47E-05 | 9.50E-06 | RESL | D | 0 |
| 1987 | TW-1 | 101.17 | ²⁴¹ Am | D/M SUM | 1.06E-04 | 9.00E-06 | EGG | E | 0 |
| 1987 | TW-1 | 101.17 | ²⁴¹ Am | D/M SUM | 9.08E-04 | 7.00E-06 | RESL | F | 0 |

Table 3-10C. Interval 3 (217 to 265 feet (66 to 81 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-7), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)

[Concentrations are in nanocuries per gram (nCi/g)]

| Year | Well | Depth (feet) | Radionuclide | Source | Concentration | Uncertainty | Anal. lab | Replicates | Error |
|------|---------|---------------|-------------------|----------|---------------|-------------|-----------|------------|-------|
| 1972 | USGS 95 | 226.75-229.25 | ⁶⁰ Co | D/M SUM | 2.40E-04 | 3.00E-05 | RESL | NO | 0 |
| 1972 | USGS 95 | 226.75-229.25 | ¹³⁷ Cs | D/M SUM | 2.30E-04 | 3.00E-05 | RESL | NO | 0 |
| 1972 | USGS 94 | 262.25-264.58 | ⁶⁰ Co | D/M SUM | 2.50E-04 | 3.00E-05 | RESL | NO | 0 |
| 1972 | USGS 94 | 262.25-264.58 | ¹³⁷ Cs | D/M SUM | 1.80E-04 | 3.00E-05 | RESL | NO | 0 |
| 1972 | USGS 92 | 223.00-225.50 | ⁶⁰ Co | D/M SUM | 2.30E-04 | 2.00E-05 | RESL | NO | 0 |
| 1972 | USGS 92 | 223.00-225.50 | ¹³⁷ Cs | D/M SUM | 1.30E-04 | 3.00E-05 | RESL | NO | 6 |
| | | | | D/M APX | 1.30E-04 | 3.00E-06 | | | |
| | | | | ORIGINAL | 1.30E-04 | 3.00E-05 | | | |
| 1972 | USGS 92 | 223.00-225.50 | ⁹⁰ Sr | D/M SUM | 3.00E-03 | 9.00E-04 | RESL | NO | 2a |
| | | | | D/M APX | 3.00E-04 | 9.00E-05 | | | |
| | | | | ORIGINAL | 3.00E-04 | 9.00E-05 | | | |
| 1972 | USGS 91 | 233.75-236.25 | ⁹⁰ Sr | D/M SUM | 1.20E-04 | 1.00E-04 | RESL | NO | 2b |
| | | | | D/M APX | 1.20E-03 | 1.00E-04 | | | |
| | | | | ORIGINAL | 1.20E-03 | 1.00E-04 | | | |

Table 3-10C. Interval 3 (217 to 265 feet (66 to 81 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-7), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)—Continued

| Year | Well | Depth (feet) | Radionuclide | Source | Concentration | Uncertainty | Anal. lab | Replicates | Error |
|------|---------|--------------------|-----------------------|----------|---------------|-------------|-----------|-----------------------------------|-------|
| 1972 | USGS 91 | 236.50-237.00 | ^{239,240} Pu | D/M SUM | 1.40E-04 | 7.00E-05 | RESL | NO | 2b |
| | | | | D/M APX | 1.40E-04 | 7.00E-06 | | | |
| | | | | ORIGINAL | 1.40E-04 | 7.00E-06 | | | |
| 1976 | 76-4A | 226 | ²⁴¹ Am | D/M SUM | 2.30E-05 | 3.00E-06 | RESL | 2 (2.3±1.5E-6 (-1.0±1.0E-6) | 0 |
| 1976 | 76-4 | 221 | ⁹⁰ Sr | D/M SUM | 4.90E-04 | 6.00E-05 | RESL | A | 4 |
| | 76-1 | | | D/M APX | 4.90E-04 | 6.00E-05 | | | |
| | 76-1 | | | ORIGINAL | 4.90E-04 | 6.00E-05 | | | |
| 1976 | 76-1 | 221.2 | ⁹⁰ Sr | D/M SUM | 4.20E-04 | 5.00E-05 | RESL | B | 0 |
| 1978 | 78-2 | 235.7 (71.84m) | ²⁴¹ Am | D/M SUM | 3.30E-05 | 3.00E-06 | RESL | 1 (-0.31±1.3E-6) | 0 |
| 1978 | 78-3 | 226.9 (69.16m) | ¹³⁷ Cs | D/M SUM | 7.00E-04 | 2.00E-05 | RESL | 1 (0±3E-5) | 2b |
| | | | | D/M APX | 7.00E-05 | 2.00E-05 | | | |
| | | | | ORIGINAL | 7.00E-05 | 2.00E-05 | | | |
| 1978 | 78-6 | 242.39 (73.88m) | ⁹⁰ Sr | D/M SUM | 1.20E-04 | 4.00E-05 | RESL | 1 (2±4E-5) | 4 |
| | 78-3 | | | D/M APX | 1.20E-04 | 4.00E-05 | | | |
| | 78-3 | | | ORIGINAL | 1.20E-04 | 4.00E-05 | | | |

Table 3-10C. Interval 3 (217 to 265 feet (66 to 81 meters) below land surface). Modified from Dames and Moore (1992, summary table 5-7), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)—Continued

| Year | Well | Depth (feet) | Radionuclide | Source | Concentration | Uncertainty | Anal. lab | Replicates | Error |
|------|------|--------------------|-----------------------|----------|---------------|-------------|-----------|--|-------|
| 1978 | 78-5 | 240.29 (73.24m) | ^{239,240} Pu | D/M SUM | 1.30E-05 | 2.00E-06 | RESL | 1 (0.3±0.5E-6) | 0 |
| 1978 | 78-5 | 240.29 (73.24m) | ²³⁸ Pu | D/M SUM | 3.00E-06 | 1.00E-07 | RESL | 1 | 2b |
| | | | | D/M APX | 3.00E-06 | 1.00E-06 | | (-0.9±0.7E-6) | |
| | | | | ORIGINAL | 3.00E-06 | 1.00E-06 | | | |
| 1987 | D-O2 | 229.67-230.00 | ²³⁸ Pu | D/M SUM | 2.40E-06 | 7.00E-07 | EGG | 2 (1.3±1.1E-6) (1.4±1.1E-6) | 0 |
| 1987 | D-O2 | 230.00-230.33 | ²³⁸ Pu | D/M SUM | 1.50E-06 | 4.00E-07 | EGG | A | 0 |
| 1987 | D-O2 | 230.00-230.33 | ²³⁸ Pu | D/M SUM | 6.50E-06 | 1.90E-07 | EGG | B | 2b |
| | | | | D/M APX | 6.50E-06 | 1.90E-06 | | | |
| | | | | ORIGINAL | 6.50E-06 | 1.90E-06 | | | |
| 1987 | D-O2 | 230.00-230.33 | ²³⁸ Pu | D/M SUM | 3.22E-05 | 1.70E-06 | EGG | C | 0 |
| 1987 | D-O2 | 230.00-230.33 | ²³⁸ Pu | D/M SUM | 3.30E-06 | 6.00E-08 | EGG | D | 2b |
| | | | | D/M APX | 3.30E-06 | 6.00E-07 | | | |
| | | | | ORIGINAL | 3.30E-06 | 6.00E-07 | | | |
| 1987 | D-O2 | 230.00-230.33 | ^{239,240} Pu | D/M SUM | 5.80E-05 | 2.00E-06 | EGG | 3 (0.8±1E-6) (2± 3E-7) (3±4E-7) | 0 |

Table 3-10D. Background sites. Modified from Dames and Moore (1992, summary table 5-8), and (for comparison when errors are noted) data from Dames and Moore appendix A (1992 and 1994 revision), and data from the original reports, tables 3-1 through 3-9 (this report)

[Concentrations are in nanocuries per gram (nCi/g)]

| Year | Well | Depth (feet) | Radionuclide | Source | Concentration | Uncertainty | Anal. lab | Replicates | Error |
|------|---------|---------------|-----------------------|----------|---------------|-------------|-----------|-------------------|-------|
| 1971 | USGS 87 | 231.17-233.00 | ⁹⁰ Sr | D/M SUM | 4.60E-04 | 5.00E-05 | RESL | NO | 0 |
| 1971 | USGS 87 | 231.17-233.00 | ^{239,240} Pu | D/M SUM | 4.60E-05 | 4.00E-06 | RESL | NO | 6 |
| | | | | D/M APX | 4.60E-05 | 4.00E-06 | | | |
| | | | | ORIGINAL | 2.90E-05 | 4.50E-06 | | | |
| 1971 | USGS 89 | 241.58-243.17 | ¹³⁷ Cs | D/M SUM | 4.00E-05 | 1.00E-05 | RESL | NO | 0 |
| 1971 | USGS 89 | 241.58-243.17 | ⁹⁰ Sr | D/M SUM | 6.40E-04 | 7.00E-05 | RESL | NO | 0 |
| 1979 | 79-1 | 114.8-121.19 | ¹³⁷ Cs | D/M SUM | 8.00E-05 | 2.00E-05 | * | 1 (0.2±1.5E-5) | * |
| 1979 | 79-1 | 121.59-123.39 | ¹³⁷ Cs | D/M SUM | 8.00E-05 | 2.00E-05 | * | 1 (3±4E-5) | * |
| 1979 | 79-1 | 139.70-141.70 | ¹³⁷ Cs | D/M SUM | 6.00E-05 | 2.00E-05 | * | 1 (-3±3E-5) | * |

3-40 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 3-11. Comparison of actinide data (^{238}Pu , $^{239,240}\text{Pu}$, and ^{241}Am from tables 3-1 through 3-9 of this report) for the B-C and C-D interbeds (modified from format of Navratil, 1996, table 4)

| Description of Data | B-C interbed | | C-D interbed | |
|---|----------------|-----------------|----------------|-----------------|
| | This study | Navratil 1996 | This study | Navratil 1996 |
| Number of wells showing statistically significant actinide (^{241}Am , $^{239,240}\text{Pu}$ and/or ^{238}Pu) detection at 99-percent confidence level: | 7 ^a | 8 ^{aa} | 5 ^b | 9 ^{bb} |
| Number of wells showing statistically significant actinide ($^{239,240}\text{Pu}$ and/or ^{238}Pu) detection at 99-percent confidence level: | 6 ^c | 7 ^{cc} | 3 ^d | 6 ^{dd} |
| Number of post-1972 wells showing statistically significant actinide (^{241}Am , $^{239,240}\text{Pu}$ and/or ^{238}Pu) detection at 99-percent confidence level: | 5 ^e | 6 ^{ee} | 4 ^f | 5 ^{ff} |
| Number of post-1972 wells showing statistically significant actinide ($^{239,240}\text{Pu}$ and/or ^{238}Pu) detection at 99-percent confidence level: | 4 ^g | 5 ^{gg} | 2 ^h | 2 ^{hh} |

This report

^a 1972: wells USGS 93 and USGS 96
 1976: wells 76-4A and 76-3
 1978: well 78-5
 1979: well 79-2
 1987: well TW-1

^g 1976: well 76-3
 1978: well 78-5
 1979: well 79-2
 1987: well TW-1

^{dd} 1971: wells USGS 87 and USGS 88
 1972: wells USGS 91 and USGS 96
 1978: well 78-5
 1987: well D-O2

^b 1972: well USGS 91
 1976: well 76-4A
 1978: wells 78-2 and 78-5
 1987: well D-O2

^h 1978: well 78-5
 1987: well D-O2

^{ee} 1976: wells 76-4A, and 76-3
 1978: well 78-5
 1979: well 79-2
 1987: well TW-1
 1988: well 88-01D

Navratil, 1996

^c 1972: wells USGS 93 and USGS 96
 1976: well 76-3
 1978: well 78-5
 1979: well 79-2
 1987: well TW-1

^{aa} 1972: wells USGS 93 and USGS 96
 1976: wells 76-4A and 76-3
 1978: well 78-5
 1979: well 79-2
 1987: well TW-1
 1988: well 88-01D

^{ff} 1976: well 76-4A
 1978: wells 78-2 and 78-5
 1987: well D-O2
 1989: well 89-01

^d 1972: well USGS 91
 1978: well 78-5
 1987: well D-O2

^{bb} 1971: wells USGS 87 and USGS 88
 1972: wells USGS 91 and USGS 96
 1976: well 76-4A
 1978: wells 78-2 and 78-5
 1987: well D-O2
 1989: well 89-01

^{gg} 1976: well 76-3
 1978: well 78-5
 1979: well 79-2

^e 1976: wells 76-4A and 76-3,
 1978: well 78-5
 1979: well 79-2
 1987: well TW-1

^{cc} 1972: wells USGS 93 and USGS 96
 1976: well 76-3
 1978: well 78-5
 1979: well 79-2

1987: well TW-1
 1988: well 88-01D

^f 1976: well 76-4A
 1978: wells 78-2 and 78-5
 1987: well D-O2

1987: well TW-1
 1988: well 88-01D

^{hh} 1978: well 78-5
 1987: well D-O2

Table 3-12. Actinide detections (²⁴¹Am, ²³⁸Pu, and ^{239,240}Pu) reported in tables 3-1 through 3-9 of this report from the B-C interbed (modified from format of Navratil,1996, table 2)

[Concentrations are in nanocuries per gram (nCi/g). Values shown are from original tables. Symbols: * = one result at the 99-percent confidence level and one non-detect duplicate; ** = one result at the 99-percent confidence level; *** = multiple results at the 99-percent confidence level]

| Well | ²⁴¹ Am | | ²³⁸ Pu | | ^{239,240} Pu | |
|----------------|-------------------|-------------------------------|-------------------|-------------------------------|-----------------------|-------------------------------|
| | Results | Concentration (with exponent) | Results | Concentration (with exponent) | Results | Concentration (with exponent) |
| USGS 93 (1972) | *** | 6.3±1.0 E-5 | *** | 8±1.5 E-6 | *** | 1.1± 0.07 E-4 |
| | | 1.5±0.2 E-4 | | 1.4±0.3 E-5 | | 8.1±1.1 E-5 |
| | | 4.5±0.6 E-5 | | 9±3 E-6 | | 5.4±0.12 E-4 |
| | | | | | | 2.3±0.11 E-4 |
| USGS 96 (1972) | * | 3±0.6 E-5 | ** | 6±1.5 E-6 | ** | 4.5±0.2 E-5 |
| 76-3 (1976) | * | 8.4±1.4 E-6 | | | * | 1.68±0.5 E-5 |
| 76-4A (1976) | * | 6.4±1.7 E-6 | | | | |
| 78-5 (1978) | | | * | 3.1±1 E-6 | | |
| 79-2 (1979) | *** | 2.2±0.2 E-5 | | | *** | 6.1±0.4 E-5 |
| | | 3.1±0.3 E-5 | | | | 5.6±0.4 E-5 |
| | | 1.3±0.3 E-5 | | | | 3.4±0.3 E-5 |
| | | 1.8±0.2 E-5 | | | | 3.7±0.3 E-5 |
| | | 2.4±0.3 E-5 | | | | 3.8±0.3 E-5 |
| | | 2±0.3 E-5 | | | | 3.6±0.3 E-5 |
| TW-1 | *** | 4.7±0.2 E-4 | *** | 1.7±0.2 E-5 | *** | 7.4±0.4 E-4 |
| | | 4.4±0.2 E-4 | | 1.18±0.17 E-5 | | 6.1±0.3 E-4 |
| | | 1.37±0.11 E-4 | | 4.6±1.4 E-6 | | 1.97±0.13 E-4 |
| | | 1.07±0.09 E-4 | | 10±3E-6 | | 1.78±0.13 E-4 |
| | | 1.3±0.08 E-5 | | 6.3±1.7 E-6 | | 1.9±0.13 E-4 |
| | | 8.47±0.95 E-5 | | 6.5±1.6 E-6 | | 1.68±0.09 E-4 |
| | | 1.06±0.09 E-4 | | 3.9±1.3 E-6 | | 2±0.13 E-4 |
| | | 9.08±0.08 E-4 | | | | 1.7±0.09 E-4 |
| | 1.03±0.08 E-4 | | | | | |

3-42 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 3-13. Actinide detections (²⁴¹Am, ²³⁸Pu, and ^{239,240}Pu) reported in tables 3-1 through 3-9 of this report from the C-D interbed(modified from format of Navratil,1996, table 3)

[Values shown are from the original reports. Concentrations are shown in nanocuries per gram (nCi/g). Symbols: * = one result at the 99–percent confidence level and one non-detect duplicate; ** = one result at the 99–percent confidence level; and *** = multiple results at the 99–percent confidence level]

| Well | ²⁴¹ Am | | ²³⁸ Pu | | ^{239,240} Pu | |
|----------------|-------------------|-------------------------------|-------------------|---|-----------------------|-------------------------------|
| | Results | Concentration (with exponent) | Results | Concentration (with exponent) | Results | Concentration (with exponent) |
| USGS 91 (1972) | | | | | ** | 1.4±0.07 E-4 |
| 76-4A (1976) | * | 2.3±0.3 E-5 | | | | |
| 78-2 (1978) | * | 3.3±0.3 E-5 | | | | |
| 78-5 (1978) | | | * | 3±1 E-6 | * | 1.3±0.2 E-5 |
| D-O2 (1987) | | | *** | 2.4±0.7 E-6 1.5±0.4 E-6 6.5±1.9 E-6 3.22±0.17 E-5 3.3±0.6 E-6 | * | 5.8±0.2 E-5 |

4.0 Task 2: Actinide transport processes

4.1 Introduction

The purpose of this chapter is to propose explanations for the reported detections of actinides in the subsurface at the Subsurface Disposal Area (SDA). The contractor provided selected historically reported detections of actinides in the subsurface at the SDA which are summarized in chapter 3. In that discussion, it was noted that the question of whether the reported detections were the result of cross contamination related to borehole drilling or the result of migration in ground-water flow was unresolvable. The possibility of cross contamination will not be discussed further in this chapter. Flow in the fractured rocks and sedimentary interbeds below the SDA was discussed in chapter 2. Chapter 2 notes that there are several kinds of preferential flow at the SDA: (1) macropore flow, (2) funneled flow, and (3) unstable flow. These different kinds of preferential flow could enhance migration of water and dissolved solutes. Transport of actinides in all cases is affected to some degree by the reactions between the actinides and solid surfaces and colloids. This chapter considers explanations of reported detections that involve reactive transport of actinides with the movement of water as the result of infiltration and recharge and includes geochemical effects such as adsorption, colloidal transport, and nonequilibrium effects.

4.2 Summary of geochemical characteristics at the Subsurface Disposal Area

The geochemical and lithological settings at the SDA are discussed in chapter 2. Geochemical characteristics at the site can have a large effect on some or all of the actinides considered. Specifically, water from perched zones below the SDA and from the Snake River Plain (SRP) aquifer have the following characteristics that can significantly affect actinide transport: (1) a pH that ranges from 7.8 to 8.4, (2) dissolved oxygen concentrations that are nearly saturated to slightly supersaturated with respect to air, (3) saturation indices that indicate the water is typically nearly saturated with respect to calcite, and (4) dissolved organic carbon (DOC) concentrations that are generally smaller than 1 mg/L (Knobel and others 1992a) or about 1 mg/L (Busenberg, USGS written commun., 1999). Generally, larger DOC concentrations are in water from wells that are contaminated by drilling-fluid surfactants or show evidence of other anthropogenic organic contamination (Busenberg, verbal commun.,

1999). In a previous study (Leenheer and Bagby, 1982) significantly larger DOC concentrations were measured in INEEL ground waters; concentrations ranged from 1.6 to 18 mg/L.

Investigations of cores collected at the site indicate that (1) calcite commonly occurs both in fractures and in the sedimentary interbeds, (2) iron oxyhydroxides, which can adsorb actinides strongly in certain conditions, are commonly observed on fracture surfaces and in the interbed sediments, and (3) clay minerals, most commonly identified as illite, account for an average of 20 percent of the interbed sediments analyzed (Bartholomay, 1990c). Both smectite and mixed-layer smectite clays were also observed in some interbed samples. These characteristics define an environment that controls the geochemical processes that affect actinide mobility. For example, the presence of oxygen and carbon impact the oxidation/reduction characteristics of the system. The oxidation/reduction conditions control the redox state of most actinides which affects the affinity of the chemical species for the aqueous or solid phase. The mineralogy, size, consolidation, and fracture pattern of the solid-phase matrix and the chemical composition of the aqueous solution will impact the rate and amount of sorption and subsequent solute transport. Section 4.3.1 discusses the speciation characteristics of Am, U, Np, and Pu and the effect on mobility of each in SDA ground water. First, however, the potential effects of speciation on transport are discussed by considering a simplified example (section 4.3). Section 4.4 discusses the effects of chemically mediated and transport controlled kinetics on sorption and desorption reactions, and section 4.5 discusses colloid facilitated transport of actinides.

4.3 Potential effects of speciation on actinide transport

A simple approach for describing adsorption of an actinide to subsurface solids is to use a distribution coefficient, or K_d value. K_d is the ratio of the concentration of adsorbed solute to the concentration of dissolved solute:

$$K_d = \frac{C_s}{C_{Aq}} \quad (4.1)$$

where:

K_d = distribution coefficient, in volume per mass;

C_s = mass of solute adsorbed per mass of adsorbent; and

C_{Aq} = mass of solute dissolved per volume of water.

The commonly used retardation factor (R_F) is defined by the equation

4-2 Review of the transport of selected radionuclides in the Interim Risk Assessment

$$R_F = 1 + \frac{P_b}{\theta} K_d \quad (4.2)$$

where:

P_b = bulk density of the porous medium, in mass per volume;

θ = water filled porosity, in volume water per volume pore space; and

R_F = ratio of the velocity of a linearly sorbing chemical to the velocity of a conservatively transported solute.

The term $\frac{P_b}{\theta}$ can be thought of as a conversion factor necessary so that the concentrations of the sorbed solute are expressed in the same units as those for concentration of the dissolved solute. In other words, the concentrations of sorbed solutes are expressed as mass sorbed per volume (or mass) of water. It is convenient to define a new distribution coefficient as:

$$K_r = \frac{C_s \text{ (mol sorbed/L (or Kg) water)}}{C_{Aq} \text{ (mol dissolved/L (or Kg) water)}} \quad (4.3)$$

where:

K_r = distribution coefficient that describes concentrations of both the dissolved and adsorbed solutes relative to a unit volume or mass of water.

The retardation factor then is defined by the equation

$$R_F = 1 + K_r \quad (4.4)$$

Using K_r as defined in equation 4.3, and R_F as defined in equation 4.4 has at least two advantages. First, most geochemical speciation codes express concentrations of adsorbed solutes in the same units as those used for dissolved solutes and therefore the simulation results can easily be used to define a K_r or R_F value. Second, it is very simple to convert between K_r values and the corresponding R_F values.

As discussed in chapter 2, a significant limitation of the K_d approach is that it does not account for the possible variable chemical conditions in the subsurface or for the possibly limited number of sorption sites. The surface complexation model (SCM) is one approach that can account for these effects. In this approach, the adsorbing surface is considered to possess surface functional groups that can form surface complexes analogous to the formation of aqueous complexes with ligands in solution (Stumm and Morgan, 1996). The adsorption interaction is written as a balanced chemical reaction and is described by a mass action expression (equilibrium equation) that is sometimes corrected for electrical double-layer effects (Stumm and Morgan, 1981; Dzombak and Morel, 1990). Figure 4.1 illustrates a simplified SCM for the adsorption

of U(VI) (UO_2^{+2}). In this model, UO_2^{+2} can react with surface sites to form a surface complex (SOUO_2OH) or UO_2^{+2} can react with a ligand (L^{-n}) to form an aqueous complex ($\text{UO}_2\text{L}_3^{2-3n}$). If electrostatic effects and activity corrections are ignored, the equilibrium equation for the formation of the surface complex is:

$$K_S = \frac{(>\text{SOU}_2\text{OH})(\text{H}^+)^2}{(>\text{SOH})(\text{UO}_2^{+2})} \quad (4.5)$$

where the quantities in parentheses are concentrations of dissolved or adsorbed solutes in units of mol/L (or kg) of water and the activity of water is assumed to equal 1.

K_r for the simplified SCM illustrated in figure 4-1 can be defined by assuming that (1) the surface site density (S_T) is constant and equal to the sum of $>\text{SOH}$ and $>\text{SOUO}_2\text{OH}$, (2) the concentration of the ligand is constant (a good approximation for the complexation of trace concentrations of an actinide by carbonate in the presence of calcite), and (3) the concentration of the aqueous complex $\text{UO}_2\text{L}_3^{2-3n}$ equals $K_L(\text{UO}_2^{+2})(\text{L})^3$. With these assumptions, K_r can be defined by:

$$K_r = \frac{K_S S_T}{[K_S(\text{UO}_2^{+2})^2 + (\text{H}^+)^2] + [1 + K_L(\text{L})^3]} \quad (4.6)$$

Although equation 4.6 does not replace the need to model speciation by using a general-purpose geochemical simulator, it can be used to illustrate the effects of speciation on K_r in certain simplified cases. Equation 4.6 shows that K_r is a nonlinear function of K_S , UO_2^{+2} , H^+ , and L^{-n} and a linear function of S_T . The bracketed term on the left side of the denominator illustrates the competition between UO_2^{+2} and H^+ for the limited number of surface sites. The bracketed term on the right side of the denominator accounts for the distribution of U(VI) between the free (UO_2^{+2}) and the complexed species ($\text{UO}_2\text{L}_3^{2-3n}$).

Figure 4-2 illustrates the dependence of K_r on total UO_2^{+2} concentration, pH, and the L concentration for three pairs of K_S and S_T values. These pairs of values were selected to represent adsorption on a solid having a few strongly adsorbing sites, a solid having many weakly adsorbing sites, and an intermediate case. The solution conditions, except as modified for each plot, are pH = 7, total uranium ($(\text{UO}_2^{+2})_T$) = 10^{-7} , $\text{L} = 10^{-6}$, and $K_L = 10^{18}$. Figure 4-2a illustrates that at small UO_2^{+2} concentrations, K_r is independent of UO_2^{+2} and that K_r decreases with increasing $(\text{UO}_2^{+2})_T$ concentration. This change results because at small $(\text{UO}_2^{+2})_T$ concentrations, $K_S(\text{UO}_2^{+2})$ is much greater than $(\text{H}^+)^2$ and at large UO_2^{+2} concentrations, $K_S(\text{UO}_2^{+2})$ is much greater than $(\text{H}^+)^2$. At larger UO_2^{+2} concentrations, the $K_S(\text{UO}_2^{+2})$ term domi-

nates and K_r is inversely proportional to UO_2^{+2} . Figure 4-2b illustrates that $\log K_r$ increases in proportion to the pH until a plateau is reached that is dependent on the values of K_S and S_T . Again, this change results from the relative importance of the term $K_S(\text{UO}_2^{+2})$ versus $(\text{H}^+)^2$ in the denominator of equation 4.6. Finally, figure 4-2c illustrates that K_r decreases rapidly when the concentration of ligand is larger than approximately 10^{-6} mol. At this concentration, and when the selected value of $\log K_L$ equals 18, the value of $K_L L^3$ starts to exceed unity and K_r decreases as the ligands in solution out-compete the surface for the UO_2^{+2} .

These effects on K_r of UO_2^{+2} concentration, pH, and ligand concentration recently have been demonstrated in a study of UO_2^{+2} transport in columns packed with quartz (Kohler and others, 1996). In that study, the retardation factor changed by a factor of 3 in response to (1) a pH change of 0.3 pH units, (2) a change in UO_2^{+2} concentration by a factor of 50, or (3) the addition of 0.1 mM of fluoride, a moderately strong complexing ligand for UO_2^{+2} .

In the following sections, the results of speciation calculations for Am, U, Np, and Pu are presented to illustrate the potential variability in adsorption properties of ground waters at the INEEL.

4.3.1 Am, U, Np, and Pu chemistry and speciation

4.3.1.1 Am

In ground water, Am exists only as the trivalent Am^{+3} ion. Am^{+3} hydrolyzes to form AmOH^{+2} , $\text{Am}(\text{OH})_2^+$, and $\text{Am}(\text{OH})_3$; in the presence of CO_3^{-2} , the species AmCO_3^+ , $\text{Am}(\text{CO}_3)_2^-$ and $\text{Am}(\text{CO}_3)_3^{-3}$ also form. Silva and others (1995) evaluated thermodynamic data for the formation of these species, and complexes of Am(III) with F^- , SO_4^{-2} , and PO_4^{-3} . These thermodynamic data were used in the calculations listed below. Although the existence of Am(III)- HCO_3 complexes have been suggested in the literature, Silva and others (1995) discounted their existence.

Figure 4-3 shows the computed distribution of aqueous Am(III) species for variable Am(III) concentrations and p_{CO_2} at different pH values. As in the speciation of other actinides, the hydrolysis species are more important at lower pH and p_{CO_2} values. The extent of hydrolysis increases with increasing pH, and at pH values above 7, Am- CO_3 complexes are the dominant aqueous species as shown in figure 4-3a for 10^{-7} M Am and $10^{-3.5}$ atm CO_2 . At a larger Am(III) concentration (10^{-5} M) and $10^{-3.5}$ atm CO_2 , the distribution of species is almost identical to that for 10^{-7} M Am(III) because no polynuclear Am(III) species are formed at the larger Am(III) concentration. Am-

CO_3 species are still dominant at pH values above 7. At $10^{-2.5}$ atm CO_2 and pH values above 6.5, the Am- CO_3 complexes become the dominant species.

Data from two studies (Righetto and others, 1988; Moulin and others, 1992) of the adsorption of Am^{+3} by single mineral phases were fitted to a diffuse double layer SCM by Turner (1995). The phases were quartz, α -alumina, and γ -alumina. K_r values were calculated using the SCM parameters reported by Turner (1995) for a pH range from 4 to 10 and p_{CO_2} equal to $10^{-3.5}$ and $10^{-2.5}$ atm. The results of these calculations are shown in figure 4-4. The K_r values are smallest at low and high pH values, and largest at almost neutral pH values. The range of K_r values for the sorption of Am is very large. For the two different forms of aluminum oxide, the K_r values differ by three orders of magnitude. This difference is probably the result of the limited amount of adsorption data available (only one Am(III) concentration and one sorbent concentration were available for each solid) and the differences in solid properties. The K_r for sorption by quartz is smaller than that for γ -alumina by another three orders of magnitude.

4.3.1.2 U

In subsurface environments, U exists primarily in either the +4 oxidation state, U(IV), or the +6 oxidation state, U(VI). Because minerals containing U(IV) are generally insoluble, most studies of U mobility in the subsurface consider only the U(VI) form. The U(VI) cation is coordinated axially by two oxygen atoms. This arrangement creates a linear species with a nominal charge of +2, typically called UO_2^{+2} , which reacts to form many different aqueous species in natural water. Because U(VI) mobility is dependent on the competition between aqueous ligands and surface ligands, it is worthwhile to consider the types and predominance of the different aqueous species. Grenthe and others (1992) summarized thermodynamic data for U(VI) speciation reactions with many ions including OH^- , CO_3^{-2} , Cl^- , SO_4^{-2} , F^- , PO_4^{3-} . Although the data in Grenthe and others (1992) were critically evaluated by an international committee assembled by the Nuclear Energy Agency (NEA) of the Organization for Economic Cooperation and Development (OECD), use of the data could be limited because of the lack of data for some species. For example, Grenthe and others (1992) acknowledged that there are no thermodynamic data for the formation of U orthosilicate ($\text{UO}_2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, soddyite), even though x-Ray diffraction studies previously had demonstrated that this solid exists. A second example of the limitations of the data base in Grenthe and others (1992) is that, although synthetic organic chelating agents such as ethylenediaminetetraacetic acid (EDTA) and nat-

4-4 Review of the transport of selected radionuclides in the Interim Risk Assessment

ural organic matter are known to form strong to moderately strong complexes with U(VI) (Choppin and Allard, 1985), neither of these nor any other organic species are included. In spite of these limitations and others (for example, slow kinetics), it is instructive to use the available data to consider the aqueous complexes that could form.

In natural water, U(VI) hydrolyzes to form multiple hydrolysis species that can be either mononuclear (for example UO_2OH^+ , UO_2OH_2^0 , etc.) or, at large concentrations, polynuclear (for example $(\text{UO}_2)_3(\text{OH})_5^+$, $(\text{UO}_2)_3(\text{OH})_4^{+2}$, etc.). U(VI) also reacts with carbonate ions in solution to form the U carbonate complexes UO_2CO_3 , $\text{UO}_2(\text{CO}_3)_2^{-2}$, and $\text{UO}_2(\text{CO}_3)_3^{-4}$. In addition to these complexes, several U hydroxy-carbonate species also can form. The formation of hydroxy and carbonate complexes of U(VI) in natural water indicates that both the pH and the P_{CO_2} are variables that control U(VI) speciation in ground water. Figure 4-5 illustrates the results of speciation calculations for variable U(VI) concentrations and P_{CO_2} at different pH values. At 10^{-7} M U(VI) and atmospheric P_{CO_2} , the mononuclear species are the dominant forms of U(VI) in the system, although the number of coordinating ligands increases as pH increases. As pH increases, the dominant form of U(VI) changes to UO_2OH^+ at a pH of 5.5 and to $\text{UO}_2(\text{OH})_2^0$ at a pH of 6.3 (fig. 4-5a). When pH is higher than 7.2, U(VI) – CO_3^{-2} complexes are the dominant species. At larger U(VI) concentration (10^{-5} M) and at atmospheric P_{CO_2} , polynuclear species are more important. In these conditions, when pH ranges from 5.8 to 8.5, the polynuclear species $(\text{UO}_2)_3(\text{OH})_5^+$ and $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ are the dominant species and above pH 8.5 the $\text{UO}_2(\text{CO}_3)_3^{-4}$ complex is the dominant species. Finally, when P_{CO_2} is equal to $10^{-2.5}$ atm, a value more representative of soil P_{CO_2} values and approximately equal to the upper limit of P_{CO_2} values at the SDA, the UO_2CO_3 complexes are the dominant species above pH 6 starting first with the monocarbonate complex followed by the dicarbonate and tricarbonate complexes (fig. 4-5c).

There have been several studies on the sorption of U(VI) in well-defined systems. These include studies of U(VI) adsorption on goethite (Tripathi, 1983), ferrihydrite (Hsi and Langmuir, 1985; Waite and others, 1994), montmorillonite (McKinley and others, 1995; Pabalan and others, 1997), quartz (Kohler and others, 1996), clinoptilolite (Pabalan and others, 1998), and alumina (Pabalan and others, 1998). At low pH values, U(VI) adsorption increases over a narrow pH range of approximately 1 to 2 pH units resulting in what is commonly called an adsorption edge. The pH of the adsorption edge

varies with the adsorbing mineral and the amount of available surface area but is generally between 4 and 5. In the absence of CO_2 and at pH values up to approximately 9, U(VI) is essentially completely adsorbed by goethite (Hsi and Langmuir, 1985; Tripathi 1983).

In the presence of CO_2 , the adsorption is more complex. The formation of $\text{UO}_2(\text{CO}_3)_2^{-2}$ and $\text{UO}_2(\text{CO}_3)_3^{-4}$ results in decreased adsorption at high pH values. The pH value at which sorption decreases varies as P_{CO_2} values and surface properties change. In the presence of atmospheric CO_2 and when pH is higher than 8, practically no U(VI) is adsorbed by goethite (Hsi and Langmuir, 1985; Tripathi 1983) or ferrihydrite (Waite and others, 1994). Modeling studies have shown that the adsorbing species also may change in the presence of CO_2 . It has been postulated (Hsi and Langmuir, 1985; Tripathi, 1983; Waite and others, 1994) that, in the presence of CO_2 , ternary complexes involving a surface site, U(VI) and CO_3^{-2} may be significant, if not the most dominant surface species. These postulated surface species eventually were confirmed by spectroscopy (Waite and others, 1994). Thus, in the ferrihydrite and goethite systems, and perhaps in other systems, CO_3^{-2} complexation forms a stronger surface species than species formed in the absence of CO_3^{-2} , but the strength of this species is still insufficient to overcome the aqueous carbonate complexes, particularly $\text{UO}_2(\text{CO}_3)_3^{-4}$.

The surface complexation approach has been used in at least five studies to model U(VI) sorption by different mineral surfaces. Most of the data reported in these studies were fitted to the Diffuse Double Layer model (Dzombak and Morel, 1990) or the Triple Layer model (Davis and others, 1978). For this report, only results from the Diffuse Double Layer model were considered. In many instances the composition of the sorbed species is not directly known from spectroscopy which often leads to a trial-and-error approach to formulating the reactions in a surface complexation model. Zachara and others (1995) and McKinley and others (1995) inferred the surface species from aqueous speciation calculations and suggested that the surface species at the edge sites of clay minerals ($>\text{XO}^-$) were $>\text{XO-UO}_2^{2+}$ and $>\text{XO-(UO}_2)_3(\text{OH})_5$. This latter species contributes to the formation of a multinuclear species involving 3 UO_2^{+2} ions. As in the case of solution speciation, the formation of this complex should depend on the total U(VI) concentration; however, multiple total U(VI) concentrations were not considered. Waite and others (1994) considered a range of U(VI) concentrations of four orders of magnitude and found that the U(VI) adsorption could be modeled by assuming that only mononuclear complexes adsorbed on ferrihydrite and that

two types of sites having different binding energies existed.

The reactions and the logarithms of the equilibrium constants ($\log K$) for the five different SCM's are summarized in table 4-1.

The differences in the SCM's in table 4-1 illustrate several different approaches that have been used to model the sorption reactions. These differences are often the result of assuming that the sorbed species is related to the dominant aqueous species. Although this has worked well for modeling the sorption of transition metals by ferrihydrite (Dzombak and Morel, 1990), the greater complexity of the aqueous speciation of U(VI) solutions has led to these different modeling approaches. Waite and others (1994) used spectroscopic studies to evaluate the structure of the adsorbed U(VI) species. This independent surface information was used as a basis for writing the SCM reactions. The variety of approaches illustrated in table 4-1 indicates that surface complexation modeling of U(VI) is still an evolving process and that the optimal approach has not been determined.

Although application of SCM's is still an evolving process, it is useful to examine the K_r values for different chemical conditions. Figure 4-6 shows the K_r value for the SCM by Waite and others (1994) for a pH range from 4 to 10 and variable P_{CO_2} and sorption site density. For a system with a total adsorption site density of 1 millimole per liter of solution (1 mM) and at atmospheric P_{CO_2} , the K_r values range from less than 1 at pH values near 4 and above pH 8.6 to more than 1,000 at pH 7. If the P_{CO_2} is increased by a factor of ten to $10^{-2.5}$ atm (which is still in the range of subsurface conditions at the SDA), the K_r values are significantly smaller at pH values above 7. Figure 4-6 also illustrates K_r values for a system with a P_{CO_2} of $10^{-2.5}$ atm and total adsorption site density of 10 mM. For this system, sorption is increased relative to the system of 1 mM sites and atmospheric P_{CO_2} below pH 7.5 but sorption is smaller above this pH. Although the total sorption site density at the SDA is not well known, values in the range from 1 mM to 10 mM may be reasonable based on similar SCM studies at research sites near Bemidji, Minn. and Cape Cod, Mass. as discussed in section 4.3.2.

Figure 4-7 illustrates K_r values for four of the SCM's listed in table 4-1 for both atmospheric P_{CO_2} and $10^{-2.5}$

atm CO_2 . The four different SCM's illustrate generally similar behavior of K_r values in that the K_r values are small at both low and high pH values and are largest at almost neutral pH values; however, the range of K_r values for the different mineral surfaces is significant. The K_r values for quartz and montmorillonite are generally 1 to 2 orders of magnitude smaller than those for the iron-containing solids goethite and ferrihydrite. This discrepancy is greater at large P_{CO_2} values because the goethite and ferrihydrite SCM's account for the formation of the ternary $UO_2^{+2}-CO_3^{-2}$ surface complex, which counteracts, to a limited extent, the tendency to form aqueous species $UO_2(CO_3)_3^{-4}$. In the system with $10^{-2.5}$ atm CO_2 , the K_r values are smaller than 30 at pH 8, which indicates that U(VI) may be mobile in these conditions which are present in some parts the subsurface at the SDA.

4.3.1.3 Np

In most ground-water environments, the dominant oxidation states of Np are Np(IV) and Np(V). The aqueous stability field of Np(V) is particularly large. In oxidizing environments, such as those at the INEEL, Np(V) is the dominant oxidation state and NpO_2^+ probably is the dominant aqueous species.

Sorption behavior of Np(V) on quartz, clinoptilolite, montmorillonite and α -alumina generally is similar (Bertetti and others, 1998). Sorption of Np(V) increases with increasing pH up to a pH of 8 to 8.5, at which point sorption may decrease. If the CO_2 concentration in ground waters is in equilibrium with atmospheric CO_2 , the increased formation of aqueous Np(V) carbonate complexes inhibits the sorption of Np(V). The dependence of Np(V) sorption on pH results in a change of about one order of magnitude in the effective K_d values for a change of 1 to 2 pH units in a given experiment.

Surface complexation data for conditions in which P_{CO_2} values are larger than atmospheric are sparse. Generally, soil P_{CO_2} values can be expected to exceed atmospheric P_{CO_2} values by about 2 orders of magnitude. When P_{CO_2} values are large, Np hydroxy-carbonate surface complexes could possibly be important, given that such complexes have been found important U(VI) sorption on ferrihydrite (Waite and others, 1994).

4-6 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 4-1. Surface complexation models for describing the adsorption of U(VI) by selected mineral surfaces

[Log K, logarithm of the equilibrium constant; References: A = Pabalan and others, 1998; B = Payne and others, 1992; C = Pabalan and Turner, 1996; D = Turner, 1995; E = Waite and others, 1994]

| Mineral surface | Reaction | Log K | Reference |
|-----------------|---|--------|-----------|
| Quartz | $\text{SiOH} = \text{SiO}^- + \text{H}^+$ | -7.20 | A |
| | $\text{SiOH} + \text{UO}_2^{+2} = \text{SiOUO}_2^{+2} + \text{H}^+$ | 0.3 | |
| | $\text{SiOH} + \text{UO}_2^{+2} + \text{H}_2\text{O} = \text{SiOUO}_2\text{OH} + 2\text{H}^+$ | -5.65 | |
| | $\text{SiOH} + 3\text{UO}_2^{+2} + 5\text{H}_2\text{O} = \text{SiO}(\text{UO}_2)_3(\text{OH})_5 + 6\text{H}^+$ | -16.75 | |
| Kaolinite | $\text{SiOH} = \text{SiO}^- + \text{H}^+$ | -7.2 | B |
| | $\text{SiOH} + \text{UO}_2^{+2} = \text{SiOUO}_2^+ + \text{H}^+$ | 0.96 | |
| | $\text{SiOH} + \text{UO}_2^{+2} = \text{SiOUO}_2^{+2}$ | 5.73 | |
| | $\text{SiOH} + \text{UO}_2^{+2} + \text{H}_2\text{O} = \text{SiUO}_2\text{OH} + 2\text{H}^+$ | -5.84 | |
| | $\text{AlOH} + \text{H}^+ = \text{AlOH}_2^+$ | 8.33 | |
| | $\text{AlOH} = \text{AlO}^- + \text{H}^+$ | -9.73 | |
| | $\text{AlOH} + \text{UO}_2^{+2} = \text{AlOUO}_2^+ + \text{H}^+$ | 2.18 | |
| | $\text{AlOH} + \text{UO}_2^{+2} = \text{AlOHUO}_2^{+2} + \text{H}^+$ | 9.20 | |
| | $\text{AlOH} + \text{UO}_2^{+2} + \text{H}_2\text{O} = \text{AlUO}_2\text{OH} + 2\text{H}^+$ | -4.74 | |
| Montmorillonite | $\text{SiOH} = \text{SiO}^- + \text{H}^+$ | -7.20 | C |
| | $\text{SiOH} + \text{UO}_2^{+2} = \text{SiOUO}_2^{+2} + \text{H}^+$ | 2.6 | |
| | $\text{SiOH} + 3\text{UO}_2^{+2} + 5\text{H}_2\text{O} = \text{SiO}(\text{UO}_2)_3(\text{OH})_5 + 6\text{H}^+$ | -15.29 | |
| | $\text{AlOH} + \text{H}^+ = \text{AlOH}_2^+$ | 8.33 | |
| | $\text{AlOH} = \text{AlO}^- + \text{H}^+$ | -9.73 | |
| | $\text{AlOH} + \text{UO}_2^{+2} = \text{AlOUO}_2 + \text{H}^+$ | 2.7 | |
| | $\text{AlOH} + 3\text{UO}_2^{+2} + 5\text{H}_2\text{O} = \text{Al}(\text{UO}_2)_3(\text{OH})_5 + 6\text{H}^+$ | 14.95 | |
| Goethite | $\text{FeOH} + \text{H}^+ = \text{FeOH}_2^+$ | 6.47 | D |
| | $\text{FeOH} = \text{FeO}^- + \text{H}^+$ | -9.03 | |
| | $\text{FeOH} + \text{UO}_2^{+2} + \text{CO}_3^{-2} + \text{H}^+ = \text{FeOHUO}_2\text{CO}_3\text{H}^+$ | 17.43 | |
| Ferrihydrite | $\text{FeOH} + \text{H}^+ = \text{FeOH}_2^+$ | 6.51 | E |
| | $\text{FeOH} = \text{FeO}^- + \text{H}^+$ | -9.13 | |
| | $\text{FeOH} + \text{H}_2\text{CO}_3 = \text{FeCO}_3\text{H} + \text{H}_2\text{O}$ | 2.90 | |
| | $\text{FeOH} + \text{H}_2\text{CO}_3 = \text{FeCO}_3^- + \text{H}_2\text{O} + \text{H}^+$ | -5.09 | |
| | $(\text{Fe}_s(\text{OH})_2) + \text{UO}_2^{+2} = (\text{Fe}_s\text{O}_2)\text{UO}_2 + 2\text{H}^+$ | -2.57 | |
| | $(\text{Fe}_w(\text{OH})_2) + \text{UO}_2^{+2} = (\text{Fe}_w\text{O}_2)\text{UO}_2 + 2\text{H}^+$ | -6.28 | |
| | $(\text{Fe}_s(\text{OH})_2) + \text{UO}_2^{+2} + \text{CO}_3^{-2} = (\text{Fe}_s\text{O}_2)\text{UO}_2\text{CO}_3^{-2} + 2\text{H}^+$ | 3.67 | |
| | $(\text{Fe}_w(\text{OH})_2) + \text{UO}_2^{+2} + \text{CO}_3^{-2} = (\text{Fe}_w\text{O}_2)\text{UO}_2\text{CO}_3^{-2} + 2\text{H}^+$ | -0.42 | |

4.3.1.4 Pu

Cleveland (1979) and Carnall and Choppin (1983) discussed the chemical behavior of Pu in natural environments and in laboratory experiments. The results presented in these references, particularly in Cleveland's compilation of Pu data (Cleveland, 1979), indicate that there are many uncertainties in attempting to predict, or even to describe, the chemical behavior of Pu in ground-water environments. Although a large amount of thermodynamic data for Pu have been collected, and several thermodynamic data bases are currently available (the HATCHES and EQ3/6 data bases), there are many uncertainties regarding the accuracy and consistency of these data. For example, most Pu speciation constants have been determined by using acidic solutions of HCl, HClO₄, or HNO₃. Use of acidic solution raises some troubling questions: How valid are these speciation constants? How valid is the Pu aqueous thermodynamic model when higher pH values are used, such as those between 8 and 8.5 that are generally found in ground water at the INEEL? Have all the relevant speciation and complexation reactions that are likely to predominate when pH values are high been documented and appropriately determined? The problems posed by Pu(IV) hydrolysis and Pu(OH)_x polymerization as pH values are increased indicate why most complexation and speciation reactions, especially for Pu(IV) species for conditions in which pH values are low, have been studied. The formation of Pu(IV) hydroxide polymers is well documented in the literature, and yet the conditions that cause the polymers to be in colloidal form or to precipitate out of solution and the conditions that cause depolymerization are not well known. The polymerization reaction is not accounted for in either the EQ3/6 (Wolery, 1992a, 1992b; Wolery and Daveler, 1992) or HATCHES (Cross and Ewart, 1991) thermodynamic data bases. Even if thermodynamic data were available, their usefulness could be limited by the relatively slow kinetics of polymerization, especially depolymerization. The question of colloid stability also would arise.

Although the complexation behavior of Pu with commonly used laboratory chelates such as EDTA is relatively well understood, the complexation behavior of Pu in contact with natural organic matter in both dissolved and solid forms is not well understood. Preliminary indications are that, in waters from granitic or sedimentary formations, organic complexes probably dominate the speciation of trivalent actinides (such as Am³⁺) and that inorganic complexes (such as hydroxide or carbonate species) probably dominate the speciation of pentavalent and hexavalent actinides (Np, U, Pu) (Moulin and others,

1992). Of course, in ground water having large concentrations of organic carbon (dissolved or solid), high oxidation states of actinides eventually may be reduced to trivalent or tetravalent oxidation states by oxidation of the organic carbon.

The oxidation state of actinide ions strongly determines their chemical interactions. In general, actinides in trivalent, tetravalent and hexavalent states are strongly complexed by carbonate, humate, and hydroxide ligands, moderately complexed by SO₄ and F, and weakly complexed by Cl (Jensen and others, 1996). Actinides in the pentavalent state, such as Np and Pu, however, show considerable aqueous stability even in the absence of complexing anions such as carbonate (Jensen and others, 1996).

Although Pu K_ds, that is, the distribution of gross Pu between aqueous and solid phases (generally crushed in the case of hard rocks or consolidated materials), have been measured during numerous experiments, relatively few specific surface complexation and ion exchange constants from these experiments have been determined. Although K_ds can be useful practical indicators of radionuclide sorptive affinity, the K_d measurements themselves often are made with little attention to the chemical processes responsible for the distribution. The results are generally applicable only to the specific conditions under which the experiments were carried out and, consequently, may be difficult to use in the prediction of radionuclide transport (see section 5.2.1).

Finally, it must be acknowledged that, although a high-quality thermodynamic data base capable of fully describing the aqueous speciation of Pu and its potential sorption and precipitation/dissolution reactions would be useful, such a data base still would not necessarily be able to predict the behavior of Pu in the ground-water environment. Indeed, many reactions may be limited kinetically and, therefore, a thermodynamic description would be of limited use. Predicting the transport behavior of Pu is also difficult because of the complexity and chemical and physical heterogeneity of natural ground water. The variability of the redox environment and the redox sensitivity of Pu make accurate transport predictions particularly difficult.

In most ground water, Pu exists in more than one oxidation state. In reducing environments, Pu(III) and Pu(IV) are the dominant oxidation states. In oxidizing environments, such as those at the INEEL, Pu(IV), Pu(V), and possibly Pu(VI) are the dominant oxidation states. Unless F, P, and SO₄ concentrations are very large, oxide, hydroxide, and carbonate complexes of Pu can be expected to be the dominant species.

4-8 Review of the transport of selected radionuclides in the Interim Risk Assessment

Pu(V) and Pu(IV) sorption on γ -alumina and goethite generally increases as a function of pH (Turner, 1995); however, Pu(IV) sorption on goethite occurs at pH values between 2 and 6, whereas Pu(V) sorption on goethite occurs at pH values between 4 and 8. Pu(V) sorption on γ -alumina also occurs at pH values between 6 and 10. In contrast, Pu sorption on amorphous silica or on quartz is expected to occur at much lower pH values because of the much lower pH_{ZPC} (the pH point of zero charge), near 2, of these materials compared with that of the iron and aluminum oxyhydroxides, which generally occurs between 7 and 9.

Because U(VI)-carbonate complexes, which are similar to Pu-carbonate complexes, generally sorb and form surface complexes, Pu carbonate complexes also may sorb and form surface complexes; however, there is no current (1999) information on the possible formation of these complexes.

4.3.2 Speciation calculations for aqueous Am, U, Np, and Pu in INEEL waters

4.3.2.1 Speciation calculations for aqueous Am

In spite of the large range of K_r s calculated for the reported SCM's for Am(III) (see section 4.3.1.1), speciation of Am(III) in each of the water samples listed in table

4-4 (see discussion under speciation calculation for aqueous Np and Pu, section 4.3.2.3) was calculated. The results are shown in table 4-2. The K_r s of the different sorbing phases in water samples from each sampling site varied by more than 4 orders of magnitude. The K_r values of quartz and γ -alumina in all ground-water samples varied by approximately a factor of 6; the K_r s of α -alumina were almost invariant.

For the case of Am, the SCM's derived from laboratory studies illustrate the large uncertainty in assessing the potential for mobility below the SDA because of the wide variability in the computed K_r s.

4.3.2.2 Speciation calculations for aqueous U

The speciation of U(VI) in each of the water samples listed in table 4-3 was calculated and K_r values were computed. The calculations included adsorption by quartz, montmorillonite, goethite, and ferrihydrite and assumed a surface site concentration of 1 mM. In addition, one set of calculations for sorption by ferrihydrite assumed a surface site concentrations equal to 10 mM. The results, summarized in table 4-3, indicate that small K_r s were expected if quartz and montmorillonite were the sorbing phases at surface site concentrations of 1 mM. The K_r values calculated for the ground-water samples ranged from 7 to 211 for goethite and from 2 to 41 for ferrihydrite. Generally, the K_r values decreased as pH and P_{CO_2} values

Table 4-2. Computed Am K_r values of five surface complexation models for water samples from the Idaho National Engineering and Environmental Laboratory

[mM, millimoles per liter]

| Sampling site | pH | P_{CO_2} | Quartz | γ -Alumina | α -Alumina |
|--------------------------------------|-----|------------|------------|-------------------|-------------------|
| | | | 1 mM sites | 1mM sites | 1mM sites |
| Big Lost River below INEEL diversion | 6.4 | -1.08 | 3E+01 | 2E+05 | 7E+07 |
| USGS 92 | 8.4 | -3.03 | 2E+03 | 3E+06 | 9E+07 |
| EBR 1 | 8.2 | -3.1 | 3E+03 | 5E+06 | 9E+07 |
| NPR Test | 8.0 | -2.76 | 2E+03 | 3E+06 | 9E+07 |
| P&W 2 | 8.0 | -2.86 | 2E+03 | 4E+06 | 9E+07 |
| USGS 8 | 8.1 | -2.92 | 2E+03 | 3E+06 | 9E+07 |
| USGS 19 | 7.8 | -2.53 | 9E+02 | 2E+06 | 8E+07 |
| USGS 112 | 7.8 | -2.74 | 2E+03 | 3E+06 | 9E+07 |
| RWMC Production | 8.1 | -2.93 | 2E+03 | 4E+06 | 9E+07 |
| USGS 87 | 8.1 | -3.05 | 3E+03 | 5E+06 | 9E+07 |
| USGS 89 | 8.3 | -3.38 | 6E+03 | 8E+06 | 9E+07 |
| USGS 90 | 8.1 | -3.02 | 3E+03 | 5E+06 | 9E+07 |

Table 4-3. Computed K_f values of five surface complexation models for water samples from the Idaho National Engineering and Environmental Laboratory

[mM, millimoles per liter]

| Sampling site | pH | P_{CO_2} | Quartz | Montmorillonite | Goethite | Ferrihydrite | Ferrihydrite |
|--|------|------------|------------|-----------------|------------|--------------|--------------|
| | | | 1 mM sites | 1 mM sites | 1 mM sites | 1 mM sites | 10 mM sites |
| Big Lost River below INEEL diversion | 6.4 | -1.08 | 5 | 1.2 | 6,119 | 128 | 1402 |
| USGS 92 | 8.39 | -3.03 | 0.1 | 0.03 | 7 | 2 | 19 |
| EBR 1 | 8.2 | -3.1 | 1 | 0.3 | 41 | 10 | 110 |
| NPR Test | 8.0 | -2.76 | 0.7 | 0.2 | 55 | 11 | 121 |
| P&W 2 | 8.0 | -2.86 | 1.5 | 0.8 | 93 | 20 | 216 |
| USGS8 | 8.1 | -2.92 | 0.6 | 0.2 | 40 | 9 | 96 |
| USGS 19 | 7.8 | -2.53 | 0.7 | 0.2 | 98 | 18 | 190 |
| USGS 112 | 7.8 | -2.74 | 2.6 | 0.8 | 211 | 41 | 442 |
| RWMC Production | 8.1 | -2.93 | 0.9 | 0.3 | 52 | 12 | 127 |
| USGS 87 | 8.1 | -3.05 | 1.8 | 0.6 | 80 | 19 | 206 |
| USGS 89 | 8.3 | -3.38 | 2.9 | 1 | 62 | 19 | 210 |
| USGS 90 | 8.1 | -3.02 | 1.6 | 0.5 | 72 | 17 | 183 |

increased. K_f values generally increased in proportion to the number of adsorbing sites when ferrihydrite was the sorbing phase and the surface site concentration was 10 mM. The K_f s of each sorbing phase in the SCM's varied by a factor of 20 to 30 for ground-water samples. The dominant U(VI) species in all of the surface- and ground-water samples were the carbonate complexes $UO_2(CO_3)_3^{-4}$ and $UO_2(CO_3)_2^{-2}$; complexes with other anions (OH^- , SO_4^{2-} , F^- , NO_3^- and PO_4^{-3}) were insignificant because of small anion concentrations or small formation constants. While it may be difficult to extrapolate the results shown in table 4-3, they indicate that U(VI) may be mobile because of the formation of soluble U(VI) carbonate complexes and the values of pH and P_{CO_2} and the nature of the sorbing site that are important in controlling the mobility of U(VI). The potential mobility of U(VI) is particularly notable for the perched water from well USGS 92.

4.3.2.3 Speciation calculations for aqueous Np and Pu

Thermodynamic data for aqueous Np and Pu were obtained from the ANSTO thermodynamic data base (Marianne Guerin, written commun., 1998), which was derived from the HATCHES data base (Cross and Ewart,

1991)². Because the database contains enthalpy data only for the major Pu species, the temperature dependence of Np and Pu speciation at temperatures other than 25°C could not be properly modeled. Surface complexation constants fitted to the Diffuse Double Layer SCM (Dzombak and Morel, 1990) were obtained from Turner (1995) for Pu(IV), Pu(V), and Np(V) sorption by goethite. Some surface complexation data for sorption of Np(V) (mainly) and Pu(V) (occasionally) on other phases, such as γ -alumina, α -alumina, boehmite (γ -AlOOH), lepidocrocite (γ -FeOOH), ferrihydrite, amorphous-silica, montmorillonite and kaolinite (Turner, 1995; Turner and others, 1998) were also available, but these data were not used in the initial examples presented here. The Np and Pu aqueous complexation and surface complexation constants were added to the default data base in the USGS geochemical computer code PHREEQC version 2 (Parkhurst and Appelo, 1999). Ideally, all thermodynamic data within a

²The Np and Pu data in the ANSTO (Australian Nuclear Science and Technology Organization) data base were checked and found to be identical to Np and Pu data in the HATCHES data base. Np and Pu data in both data bases were converted to PHREEQC format by Pierre Glynn and Robert Greene of the USGS.

4-10 Review of the transport of selected radionuclides in the Interim Risk Assessment

data base is internally consistent. This usually is not the case even for well-established data bases and certainly is not the case for the composite data base that was assembled for these calculations. Consequently, the calculations presented for Np and Pu in surface and ground water at the INEEL should be considered only generally illustrative of Np and Pu behavior in aqueous environments.

The geochemical speciation of Np and Pu in water samples from within or near the INEEL having a wide range of chemical compositions was simulated by using the PHREEQC code and the ANSTO thermodynamic data base amended with the SCM's from Turner (1995). For all simulations, 10^{-8} mol/kg of water of Np and Pu also were assumed to be present. All water samples were oxygenated and primarily CaHCO₃ types, although Ca:Na ratios, pH values, alkalinities, and DO concentrations varied significantly. All samples, except those from the Big Lost River (BLR) below the INEEL diversion (fig. 2-3), were ground-water samples. Water from well USGS 112 (fig. 2-3) was rich in Cl and represents water from the SRP aquifer taken from contamination plumes down gradient from the Idaho Nuclear Technology and Engineering Center (INTEC, formerly the Idaho Chemical Processing Plant). Well EBR-1, which is directly up gradient from the SDA (figure 2-2), represents deeper Snake River Plain (SRP) aquifer water. Well NPR Test, which is up gradient from the SDA, represents water from outside areas of known contaminant plumes. Water from well P&W2 (figure 2-3) represents underflow from the Birch Creek drainage. Water from well USGS 8 (figure 2-3) represents underflow from the BLR drainage. Water from well USGS 19 (figure 2-3) represents underflow from the Little Lost River drainage. Water from well USGS 92 (figure 2-3) represents perched water above the C-D interbed at the SDA. Water from wells RWMC Production, USGS 87, USGS 89, and USGS 90 (figure 2-3) represent water from the SDA area. Chemical compositions of water speciated with the PHREEQC model are shown in table 4-4.

PHREEQC was used to calculate the aqueous speciation of Np and Pu in the water samples listed above, and to calculate the speciation of goethite surfaces in equilibrium with the specified aqueous compositions. The goethite surface was assumed to contain 5×10^{-6} mol of surface sites per kg of H₂O and to have a surface area of 54 m²/kg of water. Only surface complexes of Np(V), Pu(IV), and

Pu(V), and protonated, deprotonated and neutral surface hydroxyl sites were considered in the calculations. Surface complexation of Np(VI) and Pu(VI) and of major ions, such as Ca, Mg, SO₄, and CO₃, were not considered because of a lack of data about their surface complexation with goethite. Redox equilibrium with the DO concentrations measured in the water samples was assumed and the redox state of the solutions and the corresponding distribution of heterovalent Pu and Np species were determined. The surface complexation reactions, the Np aqueous complexation reactions, and most of the Pu aqueous complexation reactions (except notably that of the PuO₂(CO₃)₂⁻² species) were assumed to be temperature independent, because of a lack of enthalpy data for these reactions. Temperature dependence was accounted for, however, in the speciation of major constituents.

Significant results of the PHREEQC speciation calculations are given in tables 4-5, 4-6, and 4-7. Although not shown in the tables, most of the water samples were almost saturated, or slightly supersaturated with respect to calcite. The calculated equilibrium partial pressures of CO₂ and O₂ show that most of the water samples were slightly supersaturated with respect to atmospheric oxygen and supersaturated with respect to atmospheric CO₂ by approximately a factor of 3. In addition to giving the most significant surface complex species for Np and Pu and their concentrations, table 4-5 also gives K_f values, that is the calculated molar ratios of total sorbed Np (or Pu) to total aqueous Np (or Pu).

The PHREEQC speciation calculations show that Np(V) was the dominant redox state for aqueous Np speciation in the INEEL water samples. The Np(VI) concentrations are also significant, and are the dominant redox state in the perched-water sample. Np(IV) and Np(III) concentrations were insignificant. The neptunyl ion, NpO₂⁺, is generally the dominant aqueous species, but Np(V) and Np(VI) neptunyl carbonate species, NpO₂CO₃⁻, NpO₂(CO₃)₂⁻², and NpO₂(CO₃)₃⁻⁴ were also important.

The calculations also show that Pu(V) was the dominant redox state for the INEEL water samples and PuO₂CO₃⁻ was the overwhelmingly dominant aqueous Pu species. Pu(IV) and Pu(VI) species concentrations were relatively small, except in the water sample from the BLR, which had a much lower pH.

Table 4-4. Chemical compositions of water speciated with the PHREEQC model

[Temperature, in degrees Celsius. Concentrations are in milligrams per liter. Abbreviations: DO = dissolved oxygen. Alk = alkalinity. *the water assumed to be at equilibrium with atmospheric O₂. Alkalinities expressed as CaCO₃, except for the Big Lost River sample, **, which is expressed as HCO₃]

| Sampling site | Temperature | pH | DO | Ca | Mg | Na | K | SiO ₂ | Alk. | Cl | SO ₄ | F | NO ₃ as N | P |
|--------------------------------------|-------------|------|-------|----|----|-----|-----|------------------|-------|-----|-----------------|-----|----------------------|------|
| Big Lost River below INEEL diversion | 10 | 6.4 | 8.24* | 61 | 18 | 11 | 1.7 | 15 | 260** | 8.2 | 23 | 0.3 | NA | |
| Perched water USGS 92 | 13.5 | 8.39 | 7.91* | 29 | 17 | 120 | 12 | 22 | 238 | 81 | 64 | .4 | NA | 0.18 |
| EBR 1 | 19.5 | 8.2 | 6.7 | 24 | 16 | 9.0 | 3.4 | 34 | 116 | 7.4 | 13 | .2 | .39 | |
| NPR Test | 14.5 | 8.0 | 9.2 | 59 | 15 | 8.4 | 2.5 | 22 | 173 | 20 | 26 | .2 | 1.1 | |
| P&W 2 | 10.5 | 8.0 | 9.7 | 40 | 14 | 7.9 | 1.2 | 14 | 139 | 11 | 21 | .3 | .38 | |
| USGS 8 | 12 | 8.1 | 8.0 | 46 | 15 | 6.7 | 1.8 | 20 | 154 | 10 | 22 | .3 | .86 | |
| USGS 19 | 17.5 | 7.8 | 6.9 | 48 | 18 | 13 | 1.6 | 16 | 177 | 14 | 24 | .3 | 1.1 | |
| USGS 112 | 14 | 7.8 | 6.6 | 70 | 18 | 47 | 4.5 | 23 | 116 | 120 | 34 | .3 | 3.8 | |
| RWMC Production | 13 | 8.1 | 8.2 | 45 | 15 | 9.0 | 2.8 | 28 | 148 | 13 | 27 | .2 | .67 | .03 |
| USGS 87 | 14 | 8.1 | 10.2 | 40 | 14 | 12 | 3.0 | 28 | 111 | 13 | 26 | .2 | .68 | |
| USGS 89 | 14 | 8.3 | 11.6 | 26 | 16 | 20 | 3.9 | 30 | 82 | 38 | 36 | .3 | 1.8 | |
| USGS 90 | 13.5 | 8.1 | 9.6 | 44 | 15 | 9.4 | 2.7 | 27 | 120 | 13 | 27 | .2 | .69 | |

4-12 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 4-5. Calculated partial pressures of CO₂ and O₂ and redox state distributions of aqueous Np and Pu in water samples from sites at or near the Subsurface Disposal Area

[Location of sampling sites shown in figs. 2-2 and 2-3; redox state distributions in percent; * water assumed to be at equilibrium with atmospheric O₂]

| Sampling site | log <i>P</i> _{CO₂} | log <i>P</i> _{O₂} | % Np (V) | % Np (VI) | % Pu(IV) | % Pu (V) | % Pu(VI) |
|---|---|--|----------|-----------|----------|----------|----------|
| Big Lost River below INEEL diversion | -1.08 | -0.7* | 93.8 | 6.23 | 10.5 | 88.6 | 0.878 |
| USGS 92 (perched water) | -3.03 | -0.7* | 33.0 | 67.0 | 0.137 | 99.8 | 0.114 |
| EBR 1 | -3.1 | -0.74 | 88.2 | 11.8 | 0.0437 | 99.9 | 0.0509 |
| NPR Test | -2.76 | -0.63 | 66.9 | 33.1 | 0.167 | 99.8 | 0.0934 |
| P&W 2 | -2.86 | -0.63 | 61.2 | 38.8 | 0.117 | 99.8 | 0.0902 |
| USGS 8 | -2.92 | -0.7 | 59.8 | 40.3 | 0.115 | 99.8 | 0.0840 |
| USGS 19 | -2.53 | -0.74 | 82.6 | 17.4 | 0.278 | 99.7 | 0.0896 |
| USGS 112 | -2.74 | -0.78 | 85.2 | 14.9 | 0.133 | 99.8 | 0.0764 |
| RWMC Production | -2.93 | -0.69 | 65.0 | 35.0 | 0.103 | 99.8 | 0.0800 |
| USGS 87 | -3.05 | -0.59 | 77.6 | 22.5 | 0.0530 | 99.9 | 0.0671 |
| USGS 89 | -3.38 | -0.53 | 80.4 | 19.7 | 0.0174 | 100. | 0.0526 |
| USGS 90 | -3.02 | -0.62 | 73.8 | 26.3 | 0.0638 | 99.9 | 0.0707 |

Table 4-6. Measured pH values and calculated aqueous speciation of Np and Pu in water samples from sites at or near the Subsurface Disposal Area. The three dominant aqueous species of Np and Pu are reported along with their molar concentrations and redox state

Locations of sampling sites shown in figs. 2-2 and 2-3; Abbreviations: aq., aqueous; conc., concentration; st., state]

| Sampling site | pH | 1 st Np aq. conc. redox st. | 2 nd Np aq. conc. redox st. | 3 ^d Np aq. conc. redox st. | 1 st Pu aq. conc. redox st. | 2 nd Pu aq. conc. redox st. | 3 ^d Pu aq. conc. redox st. |
|--------------------------------------|------|---|--|--|---|--|--|
| Big Lost River below INEEL diversion | 6.4 | NpO_2^+ 9.15E-9 (V) | $\text{NpO}_2(\text{CO}_3)_2^{-2}$ 5.04E-10 (VI) | $\text{NpO}_2\text{CO}_3^-$ 2.29E-10 (V) | $\text{PuO}_2\text{CO}_3^-$ 8.86E-9 (V) | $\text{Pu}(\text{CO}_3)_3^{-2}$ 1.05E-9 (IV) | PuO_2CO_3 7.62E-11 (VI) |
| USGS 92 (perched water) | 8.39 | $\text{NpO}_2(\text{CO}_3)_3^{-4}$ 3.65E-9 (VI) | $\text{NpO}_2(\text{CO}_3)_2^{-2}$ 3.05E-9 (VI) | $\text{NpO}_2\text{CO}_3^-$ 2.41E-9 (V) | $\text{PuO}_2\text{CO}_3^-$ 9.98E-9 (V) | $\text{Pu}(\text{CO}_3)_3^{-2}$ 1.29E-11 (IV) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 7.62E-11 (VI) |
| EBR 1 | 8.2 | $\text{NpO}_2\text{CO}_3^-$ 4.58E-9 (V) | NpO_2^+ 4.22E-9 (V) | $\text{NpO}_2(\text{CO}_3)_2^{-2}$ 8.94E-10 (VI) | $\text{PuO}_2\text{CO}_3^-$ 9.99E-9 (V) | $\text{Pu}(\text{CO}_3)_3^{-2}$ 4.30E-12 (IV) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 4.08E-12 (VI) |
| NPR Test | 8.0 | NpO_2^+ 3.52E-9 (V) | $\text{NpO}_2\text{CO}_3^-$ 3.16E-9 (V) | $\text{NpO}_2(\text{CO}_3)_2^{-2}$ 2.51E-9 (VI) | $\text{PuO}_2\text{CO}_3^-$ 9.98E-9 (V) | $\text{Pu}(\text{CO}_3)_3^{-2}$ 1.64E-11 (IV) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 7.26E-12 (VI) |
| P&W 2 | 8.0 | NpO_2^+ 3.69E-9 (V) | $\text{NpO}_2(\text{CO}_3)_2^{-2}$ 3.19E-9 (VI) | $\text{NpO}_2\text{CO}_3^-$ 2.43E-9 (V) | $\text{PuO}_2\text{CO}_3^-$ 9.98E-9 (V) | $\text{Pu}(\text{CO}_3)_3^{-2}$ 1.16E-11 (IV) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 6.10E-12 (VI) |
| USGS 8 | 8.1 | NpO_2^+ 3.06E-9 (V) | $\text{NpO}_2\text{CO}_3^-$ 2.90E-9 (V) | $\text{NpO}_2(\text{CO}_3)_2^{-2}$ 3.06E-9 (VI) | $\text{PuO}_2\text{CO}_3^-$ 9.98E-9 (V) | $\text{Pu}(\text{CO}_3)_3^{-2}$ 1.13E-11 (IV) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 6.34E-12 (VI) |
| USGS 19 | 7.8 | NpO_2^+ 5.06E-9 (V) | $\text{NpO}_2\text{CO}_3^-$ 3.19E-9 (V) | $\text{NpO}_2(\text{CO}_3)_2^{-2}$ 1.42E-9 (VI) | $\text{PuO}_2\text{CO}_3^-$ 9.97E-9 (V) | $\text{Pu}(\text{CO}_3)_3^{-2}$ 2.76E-11 (IV) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 6.71E-12 (VI) |
| USGS 112 | 7.8 | NpO_2^+ 6.20E-9 (V) | $\text{NpO}_2\text{CO}_3^-$ 2.30E-9 (V) | $\text{NpO}_2(\text{CO}_3)_2^{-2}$ 1.27E-9 (VI) | $\text{PuO}_2\text{CO}_3^-$ 9.98E-9 (V) | $\text{Pu}(\text{CO}_3)_3^{-2}$ 1.32E-11 (IV) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 4.66E-12 (VI) |
| RWMC Production | 8.1 | NpO_2^+ 3.360E-9 (V) | $\text{NpO}_2\text{CO}_3^-$ 3.13E-9 (V) | $\text{NpO}_2(\text{CO}_3)_2^{-2}$ 2.67E-9 (VI) | $\text{PuO}_2\text{CO}_3^-$ 9.98E-9 (V) | $\text{Pu}(\text{CO}_3)_3^{-2}$ 1.01E-11 (IV) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 6.07E-12 (VI) |
| USGS 87 | 8.1 | NpO_2^+ 4.50E-9 (V) | $\text{NpO}_2\text{CO}_3^-$ 3.24E-9 (V) | $\text{NpO}_2(\text{CO}_3)_2^{-2}$ 1.82E-9 (VI) | $\text{PuO}_2\text{CO}_3^-$ 9.99E-9 (V) | $\text{Pu}(\text{CO}_3)_3^{-2}$ 5.24E-12 (IV) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 4.72E-12 (VI) |
| USGS 89 | 8.3 | NpO_2^+ 4.37E-9 (V) | $\text{NpO}_2\text{CO}_3^-$ 3.65E-9 (V) | $\text{NpO}_2(\text{CO}_3)_2^{-2}$ 1.54E-9 (VI) | $\text{PuO}_2\text{CO}_3^-$ 1.00E-8 (V) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 3.56E-12 (VI) | $\text{Pu}(\text{CO}_3)_3^{-2}$ 1.71E-12 (IV) |
| USGS 90 | 8.1 | NpO_2^+ 4.17E-9 (V) | $\text{NpO}_2\text{CO}_3^-$ 3.20E-9 (V) | $\text{NpO}_2(\text{CO}_3)_2^{-2}$ 2.09E-9 (VI) | $\text{PuO}_2\text{CO}_3^-$ 9.99E-8 (V) | $\text{Pu}(\text{CO}_3)_3^{-2}$ 6.30E-12 (IV) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 5.07E-12 (VI) |

4-14 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 4-7. Calculated distribution of Np and Pu surface complexes on goethite and molar ratios of total sorbed to total aqueous concentrations for Np (K_r Np) and Pu (K_r Pu) for water samples from sites at or near the Subsurface Disposal Area. The three dominant surface complexes of Np and Pu are reported along with their molar concentrations and redox state. Goethite adsorption site concentration was 5×10^{-6} mole per kg of water.

[Locations of sampling sites shown in figs. 2-2 and 2-3. Abbreviations: s.c., surface complexes; conc., concentration; st., state]

| Sampling site | K_r Np | K_r Pu | 1 st Np s.c. conc. redox st. | 2 nd Np s.c. conc. redox st. | 3 ^d Np s.c. conc. redox st. | 1 st Pu s.c. conc. redox st. | 2 nd Pu s.c. conc. redox st. | 3 ^d Pu s.c. conc. redox st. |
|---|----------|----------|---|---|--|---|---|--|
| Big Lost River near the INEEL diversion | 3.69 | 8.1E-4 | $(>O)_2NpO_2^-$ 3.58E-8 (V) | $>OHNpO_2^+$ 5.44E-10 (V) | $>OH_2NpO_2OH^+$ 5.44E-10 (V) | $>OPuO_2OH^-$ 5.63E-12 (V) | $>OPuO_2$ 1.24E-12 (V) | $>OHPuO_2OH$ 1.24E-12 (V) |
| USGS 92 (perched water) | 198 | 5.5E-3 | $(>O)_2NpO_2^-$ 1.98E-6 (V) | $>ONpO_2OH^-$ 8.82E-10 (V) | $>ONpO_2$ 4.57E-10 (V) | $>OPuO_2OH^-$ 5.39E-11 (V) | $>OPuO_2$ 7.35E-13 (V) | $>OHPuO_2OH$ 7.34E-13 (V) |
| EBR 1 | 204 | 3.9E-3 | $(>O)_2NpO_2^-$ 2.04E-6 (V) | $>ONpO_2$ 1.20E-9 (V) | $>OHNpO_2OH$ 1.20E-9 (V) | $>OPuO_2OH^-$ 3.68E-11 (V) | $>OPuO_2$ 1.02E-12 (V) | $>OHPuO_2OH$ 1.02E-12 (V) |
| NPR Test | 182 | 3.6E-3 | $(>O)_2NpO_2^-$ 1.82E-6 (V) | $>ONpO_2$ 8.83E-10 (V) | $>OHNpO_2OH$ 8.83E-10 (V) | $>OPuO_2OH^-$ 3.34E-11 (V) | $>OPuO_2$ 1.09E-12 (V) | $>OHPuO_2OH$ 1.09E-12 (V) |
| P&W 2 | 181 | 4.6E-3 | $(>O)_2NpO_2^-$ 1.81E-6 (V) | $>OHNpO_2^+$ 9.77E-10 (V) | $>OH_2NpO_2OH^+$ 9.77E-10 (V) | $>OPuO_2OH^-$ 4.32E-11 (V) | $>OPuO_2$ 1.50E-12 (V) | $>OHPuO_2OH$ 1.50E-12 (V) |
| USGS 8 | 190 | 4.4E-3 | $(>O)_2NpO_2^-$ 1.90E-6 (V) | $>ONpO_2$ 8.90E-10 (V) | $>OHNpO_2OH$ 8.90E-10 (V) | $>OPuO_2OH^-$ 4.14E-11 (V) | $>OPuO_2$ 1.19E-12 (V) | $>OHPuO_2OH$ 1.19E-12 (V) |
| USGS 19 | 164 | 2.8E-3 | $(>O)_2NpO_2^-$ 1.64E-6 (V) | $>OHNpO_2^+$ 1.26E-9 (V) | $>OH_2NpO_2OH^+$ 1.26E-9 (V) | $>OPuO_2OH^-$ 2.55E-11 (V) | $>OPuO_2$ 1.14E-12 (V) | $>OHPuO_2OH$ 1.14E-12 (V) |
| USGS 112 | 171 | 4.4E-3 | $(>O)_2NpO_2^-$ 1.71E-6 (V) | $>OHNpO_2^+$ 1.36E-9 (V) | $>OH_2NpO_2OH^+$ 1.36E-9 (V) | $>OPuO_2OH^-$ 4.03E-11 (V) | $>OPuO_2$ 1.75E-12 (V) | $>OHPuO_2OH$ 1.75E-12 (V) |
| RWMC Prod. | 192 | 4.3E-3 | $(>O)_2NpO_2^-$ 1.92E-6 (V) | $>ONpO_2$ 9.40E-10 (V) | $>OHNpO_2OH$ 9.40E-10 (V) | $>OPuO_2OH^-$ 4.03E-11 (V) | $>OPuO_2$ 1.16E-12 (V) | $>OHPuO_2OH$ 1.16E-12 (V) |
| USGS 87 | 197 | 4.7E-3 | $(>O)_2NpO_2^-$ 1.97E-6 (V) | $>ONpO_2$ 1.14E-9 (V) | $>OHNpO_2OH$ 1.14E-9 (V) | $>OPuO_2OH^-$ 4.43E-11 (V) | $>OPuO_2$ 1.36E-12 (V) | $>OHPuO_2OH$ 1.36E-12 (V) |
| USGS 89 | 215 | 6.3E-3 | $(>O)_2NpO_2^-$ 2.14E-6 (V) | $>ONpO_2OH^-$ 1.49E-9 (V) | $>ONpO_2$ 1.25E-9 (V) | $>OPuO_2OH^-$ 6.03E-11 (V) | $>OPuO_2$ 1.33E-12 (V) | $>OHPuO_2OH$ 1.33E-12 (V) |
| USGS 90 | 196 | 4.6E-3 | $(>O)_2NpO_2^-$ 1.96E-6 (V) | $>ONpO_2$ 1.08E-9 (V) | $>OHNpO_2OH$ 1.08E-9 (V) | $>OPuO_2OH^-$ 4.36E-11 (V) | $>OPuO_2$ 1.31E-12 (V) | $>OHPuO_2OH$ 1.31E-12 (V) |

Although the thermodynamic data base used for these calculations included Np and Pu complexes with SO_4 , NO_3 , F, and PO_4 , concentrations of these components in the water samples were not large enough for any of the resulting Pu and Np complexes to be important. Water in direct contact with the radionuclide waste, however, probably has a significantly different chemistry from that of the water samples given in table 4-4 and may have large concentrations of NO_3 , PO_4 , and other complexants. Although these complexants may increase the aqueous stability of Np and Pu, the pH and redox character of the waters also would be important variables in determining the aqueous stability, or the mobility, of Np and Pu.

The surface complexation speciation calculations reflect the aqueous speciation calculations in that the strong complexation of aqueous Pu with carbonate impedes surface complexation of Pu to the goethite surface, at least according to the thermodynamic model. Very little Pu was sorbed on the goethite surface; the aqueous solution generally contained at least 200 times more Pu ($K_r \text{ Pu} = 4.5\text{E-}3$ on average for the ground-water samples). The PHREEQC speciation calculations were repeated using identical input data, except that the Np data was omitted to determine if Np competition for surface sites affected the sorption of Pu in the previous calculations. Although the results are not shown here, the conclusion was that although Np competition did have some effect on the sorption of Pu in some water samples, Pu sorption was still very small. The largest $K_r \text{ Pu}$ value was 0.11 (for water from well USGS 89), and the values for most other water samples were one to two orders of magnitude lower.

The large concentrations of the aqueous neptunyl species relative to those of the neptunyl carbonate species, indicate a small amount of aqueous complexation by carbonate and, therefore, that Np was strongly sorbed to the goethite surface in the INEEL ground-water samples, which all had pH values of about 8. The speciation of the various water samples and of the equilibrium goethite surface generally resulted in an amount of sorbed Np that was about 200 times larger than the amount of aqueous Np; however, because of a lower pH value of 6.4 in the BLR water sample, the amount of sorbed Np in this sample was significantly smaller (a K_r value near 4).

The K_r values calculated for Np and Pu were generally proportional to the amount of goethite surface assumed present for each kg of water. If the concentration of goethite surface sites is increased by a factor of 10, the amount of Np and Pu sorption generally also will increase by a factor of 10. PHREEQC simulations confirmed this theory, except for the simulation of water from the BLR,

for which the $K_r \text{ Pu}$ value increased by a factor of 15 as a result of the tenfold increase in goethite surface (the $K_r \text{ Np}$ value increased by a factor of 10).

Because of a lack of appropriate data for the site concentrations of sediments from the INEEL, the concentration of surface sites chosen for our speciation example was derived from a calculation example given by Dzombak and Morel (1990). Field and laboratory studies of a sand and gravel aquifer at the USGS research site in Falmouth, Mass., on Cape Cod indicate that, if sediments are uniformly coated with a thin layer of iron oxyhydroxide, the site concentration is about 10^{-2} M (Davis and others, 1998). Calculations by Gary Curtis (oral commun., 1999) for the USGS research site, a sandy silt aquifer, in Bemidji, Minn. indicate a similar surface site concentration of about 10^{-2} M. If properties of the interbed sediments at the INEEL are similar to those at the Bemidji and Cape Cod sites, then the K_r values calculated in this report for both Pu and Np at the INEEL are about 2,000 times too small. If speciation calculations for the BLR sample are disregarded, and this larger surface site concentration of 10^{-2} M is combined with our speciation calculations, then a K_r value of about 4×10^4 would be applicable for Np sorption and a K_r value of 9 would be applicable for Pu sorption in the interbed sediments. These K_r values can be used to estimate the retardation of Pu or Np relative to the advective movement of water by calculation of a retardation factor (defined in equation 4.4 in section 4.3). The calculated retardation factors are 10 for Pu and 4×10^4 for Np. It is more difficult to estimate the sorption capacity and, consequently, the retardation factors applicable to the transport of Np and Pu in the INEEL basalts, but they probably would be significantly smaller than those of the interbed sediments.

Because of the lack of field or laboratory data on the amount and type of sorption sites on INEEL sediments and basalt surfaces, the speciation calculations presented here cannot be used to predict the retardation of Np and Pu. Nevertheless, the calculations indicate the very strong aqueous complexation of Pu with carbonate and the significantly stronger sorption of Np relative to that of Pu. Transport of Pu at the INEEL could be limited by the reducing conditions in the soil or ground-water environment. In reducing conditions, Pu(IV) probably would be the dominant state of Pu, instead of Pu(V) and Pu(VI), which are the stable oxidation states in oxygenated conditions. When and where present, reducing conditions probably significantly limit the mobility of Pu. Reducing conditions probably occur most commonly in the source areas of radioactive waste emplacement (because of the associated organic matter and metallic substances present) and

4-16 Review of the transport of selected radionuclides in the Interim Risk Assessment

also possibly in relatively impermeable (clayey), organic-carbon-containing zones in the interbed sediments.

Although relatively uncommon, some organic-rich zones in the interbed sediments have been found (Rightmire and Lewis, 1987a). Fe(II)-containing minerals in the basalts and in the interbeds also potentially could reduce Pu(V) and Pu(VI); in hydraulically conductive zones, however, the surface of these minerals already should have been oxidized extensively by the oxygenated ground waters. The large concentrations of DO and inorganic carbon in all ground-water samples from the INEEL used in this study indicate the possibility of Pu(V), and Pu(VI) transport in the SRP aquifer. In addition to reduction processes, other sorption and transformation processes not considered in this modeling study potentially could limit the mobility of Pu, for example: (1) the sorption of Pu(V) and Pu(VI) by calcite, and (2) the disproportionation of Pu(V) into Pu(IV) and Pu(VI) through the sorption by goethite (Keeny-Kennicutt and Morse, 1985).

4.3.2.4 Additional speciation calculations for Np and Pu

This section presents additional speciation calculations for the water samples discussed in the previous section (4.3.2.3); however, thermodynamic data for Np and Pu used in the calculations were obtained from a different data base. The same conditions that were assumed for the previous Np and Pu speciation calculations also were

assumed for these calculations. Also, for the reasons discussed in the previous section, the calculations presented here should be considered only generally illustrative of Np and Pu behavior in aqueous environments.

Thermodynamic data for aqueous Pu and Np also was obtained in the PHREEQC format from the EQ3/6 data base by David Turner (Southwest Research Institute, written commun., 1999). The EQ3/6 data base, like the ANSTO and HATCHES data bases, generally did not include any enthalpy data; consequently, the temperature dependence of Np and Pu speciation at temperatures other than 25°C could not be properly modeled. As in our previous calculations, Turner's (1995) surface complexation constants were used to simulate Pu(IV), Pu(V), and Np(V) sorption by goethite.

Table 4-8 shows the redox-state distributions calculated by using data from the ANSTO and EQ3/6 data bases. Calculations of Pu redox-state distributions based on the two data bases are significantly different: those based on the ANSTO (and HATCHES) data bases predict that the Pu was present predominantly as Pu(V), and those based on the EQ3/6 data base indicate that Pu was present predominantly as Pu(VI).

Table 4-8. Calculated aqueous Np and Pu redox-state distributions at equilibrium for selected water samples from the Idaho National Engineering and Environmental Laboratory determined using either the ANSTO or the EQ3/6 data bases

| Sampling site; Data source | % Np (V) | % Np (VI) | % Pu (IV) | % Pu (V) | % Pu (VI) |
|--------------------------------|----------|-----------|-----------|----------|-----------|
| Big Lost River; ANSTO | 93.8 | 6.23 | 10.5 | 88.6 | 0.878 |
| Big Lost River; EQ3/6 | 100 | 0.003 | 0.000 | 0.003 | 100 |
| USGS 92 (perched water); ANSTO | 33.0 | 67.0 | 0.137 | 99.8 | 0.114 |
| USGS 92 (perched water); EQ3/6 | 84.2 | 15.8 | 0.001 | 0.003 | 100 |
| NPR Test; ANSTO | 66.9 | 33.1 | 0.167 | 99.8 | 0.093 |
| NPR; EQ3/6 | 98.5 | 1.49 | 0.000 | 0.004 | 100 |
| USGS 112; ANSTO | 85.2 | 14.9 | 0.133 | 99.8 | 0.076 |
| USGS 112; EQ3/6 | 99.8 | 0.228 | 0.000 | 0.007 | 100 |
| RWMC Production; ANSTO | 65.0 | 35.0 | 0.103 | 99.8 | 0.080 |
| RWMC Production; EQ3/6 | 98.6 | 1.30 | 0.000 | 0.005 | 100 |
| USGS 89; ANSTO | 80.4 | 19.7 | 0.017 | 100 | 0.053 |
| USGS 89; EQ3/6 | 99.4 | 0.565 | 0.001 | 0.008 | 100 |

The calculations of Np redox-state distributions based on the two data bases are also significantly different. Whereas the calculations based on the EQ3/6 data base indicate that almost all the Np was present in the Np(V), those based on the ANSTO (and HATCHES) data base indicate that large amounts of Np(VI) also were present. The reasons for these differences can be determined from table 4-9, which shows the concentrations and redox states of the dominant Pu and Np species calculated on the basis of both the ANSTO and EQ3/6 data bases. The association constant in the EQ3/6 data base for the Pu(VI) species PuO_2CO_3 , the dominant aqueous Pu species in the EQ3/6 results, is 3 orders of magnitude larger than the association constant for this species in the ANSTO data base. Additionally, the Pu(V) species $\text{PuO}_2\text{CO}_3^-$, the dominant species in the ANSTO results, is not present in the EQ3/6 results. In contrast, the association constant in the EQ3/6 data base for the Np(VI) species $\text{NpO}_2(\text{CO}_3)_2^{-2}$, a dominant species in the ANSTO results, is 3 orders of magnitude smaller than the association constant for this species in the ANSTO data base. The EQ3/6 results also show the dominance of the Np(V) species NpO_2OH . The association constant in the EQ3/6 data base for this species is 2 orders of magnitude larger than the association constant in the ANSTO data base.

Because of the differences in the speciations of Np and Pu predicted by the ANSTO and EQ3/6 data bases, the K_r values calculated from the SCM data (and based on the same conditions described in section 4.3.2.3 of total surface site concentration of 5×10^{-6} mol/L) were compared. The results are presented in table 4-10.

The EQ3/6 results indicate generally 5 to 10 percent larger K_r values for Np than the ANSTO results, and consequently, greater retardation during transport. Interestingly, the K_r Pu values calculated from the EQ3/6 data were also generally larger than those calculated from the ANSTO data (except for the BLR water sample), by as much as a factor of 3.6 (for the sample from well EBR 1). If the surface site concentration increases from 5×10^{-6} mol/L to 10^{-2} mol/L and K_r values increase linearly by a factor of 2,000, the K_r Pu value for the sample from well USGS 89 would increase from 12.6, the value calculated from the ANSTO data, to 32.

The additional speciation calculations presented in this section illustrate the many uncertainties that remain concerning thermodynamic data for Pu and Np aqueous speciation. The uncertainties involved in thermodynamic modeling of Pu and Np sorption and in any predictions of Np and Pu transport by such thermodynamic models can be expected to be even greater, because the results depend not only on the aqueous thermodynamic data, but also

sorption data and the properties of the interbed sediments and basalts. Nevertheless, thermodynamic speciation results can illustrate the potential dependencies of sorption processes on aqueous and surface chemical compositions and on mineralogical parameters, and can be used to estimate the effects of compositional and mineralogical changes.

Table 4-10. K_r values of Np and Pu surface complexes on goethite for water samples from the Idaho National Engineering and Environmental Laboratory, calculated on the basis of data from the ANSTO and EQ3/6 data bases.

| Sampling site | K_r Np; ANSTO | K_r Np; EQ3/6 | K_r Pu; ANSTO | K_r Pu; EQ3/6 |
|--|--------------------|--------------------|--------------------|--------------------|
| Big Lost River below INEEL diversion | 3.69 | 3.69 | 8.1E-4 | 1.2E-05 |
| USGS 92 (perched water) | 198 | 225 | 5.5E-3 | 1.1E-02 |
| EBR 1 | 204 | 211 | 3.9E-3 | 1.4E-02 |
| NPR Test | 182 | 199 | 3.6E-3 | 4.5E-03 |
| P&W 2 | 181 | 199 | 4.6E-3 | 4.2E-03 |
| USGS 8 | 190 | 208 | 4.4E-3 | 5.5E-03 |
| USGS 19 | 164 | 176 | 2.8E-3 | 3.5E-03 |
| USGS 112 | 171 | 180 | 4.4E-3 | 4.6E-03 |
| RWMC Production | 192 | 208 | 4.3E-3 | 6.0E-03 |
| USGS 87 | 197 | 208 | 4.7E-3 | 7.7E-03 |
| USGS 89 | 215 | 222 | 6.3E-3 | 1.6E-02 |
| USGS 90 | 196 | 208 | 4.6E-3 | 7.2E-03 |

4.3.3 Summary

This section has demonstrated that speciation can be important in controlling the transport of actinides below the SDA. Critical factors involving speciation that affect actinide transport are the determination of the redox state of the actinide, determination of the aqueous species, and determination of the surface species. Redox state is especially important for determining transport of Pu and U. Pu(IV) and U(IV) are both very insoluble and, therefore, relatively immobile. However, it is difficult to assess the factors that control the oxidation state of these species in the heterogeneous environment below the SDA that consists of both fractured basalts and sedimentary interbeds. It is comparatively easier and, therefore, the primary focus of this section, to compute the effects of different aqueous compositions and different SCM's on the K_r values. The calculations were made in spite of the many

4-18 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 4-9. Concentrations and redox states of the three dominant species of Np and Pu in water samples from the Idaho National Engineering and Environmental Laboratory calculated on the basis of the ANSTO and EQ3/6 data bases

[Abbreviations: aq., aqueous; conc., concentration; st., state]

| Sampling site; data base | 1 st Np aq. conc. redox st. | 2 nd Np aq. conc. redox st. | 3 ^d Np aq. conc. redox st. | 1 st Pu aq. conc. redox st. | 2 nd Pu aq. conc. redox st. | 3 ^d Pu aq. conc. redox st. |
|---|---|--|---|---|--|--|
| Big Lost River below INEEL diversion; ANSTO | NpO_2^+ 9.15E-9 (V) | $\text{NpO}_2(\text{CO}_3)_2^{-2}$ 5.04E-10 (VI) | $\text{NpO}_2\text{CO}_3^-$ 2.29E-10 (V) | $\text{PuO}_2\text{CO}_3^-$ 8.86E-9 (V) | $\text{Pu}(\text{CO}_3)_3^{-2}$ 1.05E-9 (IV) | PuO_2CO_3 7.62E-11 (VI) |
| Big Lost River below INEEL diversion; EQ3/6 | NpO_2^+ 9.95E-9 (V) | $\text{NpO}_2\text{CO}_3^-$ 3.89E-11 (V) | NpO_2OH 1.13E-11 (V) | PuO_2CO_3 1.00E-8 (VI) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 4.50E-13 (VI) | PuO_2F_3^- 2.94E-13 (VI) |
| USGS 92 (perched water); ANSTO | $\text{NpO}_2(\text{CO}_3)_3^{-4}$ 3.65E-9 (VI) | $\text{NpO}_2(\text{CO}_3)_2^{-2}$ 3.05E-9 (VI) | $\text{NpO}_2\text{CO}_3^-$ 2.41E-9 (V) | $\text{PuO}_2\text{CO}_3^-$ 9.98E-9 (V) | $\text{Pu}(\text{CO}_3)_3^{-2}$ 1.29E-11 (IV) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 7.62E-11 (VI) |
| USGS 92 (perched water); EQ3/6 | NpO_2^+ 4.84E-9 (V) | $\text{NpO}_2\text{CO}_3^-$ 2.82E-9 (V) | $\text{NpO}_2(\text{CO}_3)_3^{-4}$ 1.58E-9 (VI) | PuO_2CO_3 9.86E-9 (VI) | $\text{PuO}_2(\text{CO}_3)_3^{-4}$ 7.46E-11 (VI) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 5.96E-11 (VI) |
| NPR Test; ANSTO | NpO_2^+ 3.52E-9 (V) | $\text{NpO}_2\text{CO}_3^-$ 3.16E-9 (V) | $\text{NpO}_2(\text{CO}_3)_2^{-2}$ 2.51E-9 (VI) | $\text{PuO}_2\text{CO}_3^-$ 9.98E-9 (V) | $\text{Pu}(\text{CO}_3)_3^{-2}$ 1.64E-11 (IV) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 7.26E-12 (VI) |
| NPR Test; EQ3/6 | NpO_2^+ 7.79E-9 (V) | $\text{NpO}_2\text{CO}_3^-$ 1.57E-9 (V) | NpO_2OH 4.74E-10 (V) | PuO_2CO_3 9.98E-9 (VI) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 1.85E-11 (VI) | $\text{PuO}_2(\text{CO}_3)_3^{-4}$ 5.53E-12 (VI) |
| USGS 112; ANSTO | NpO_2^+ 6.20E-9 (V) | $\text{NpO}_2\text{CO}_3^-$ 2.30E-9 (V) | $\text{NpO}_2(\text{CO}_3)_2^{-2}$ 1.27E-9 (VI) | $\text{PuO}_2\text{CO}_3^-$ 9.98E-9 (V) | $\text{Pu}(\text{CO}_3)_3^{-2}$ 1.32E-11 (IV) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 4.66E-12 (VI) |
| USGS 112; EQ3/6 | NpO_2^+ 8.92E-9 (VI) | $\text{NpO}_2\text{CO}_3^-$ 7.15E-10 (V) | NpO_2OH 3.27E-10 (V) | PuO_2CO_3 9.99E-9 (VI) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 7.99E-12 (VI) | $\text{PuO}_2(\text{OH})_2$ 2.14E-12 (VI) |
| RWMC Production; ANSTO | NpO_2^+ 3.360E-9 (V) | $\text{NpO}_2\text{CO}_3^-$ 3.13E-9 (V) | $\text{NpO}_2(\text{CO}_3)_2^{-2}$ 2.67E-9 (VI) | $\text{PuO}_2\text{CO}_3^-$ 9.98E-9 (V) | $\text{Pu}(\text{CO}_3)_3^{-2}$ 1.01E-11 (IV) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 6.07E-12 (VI) |
| RWMC Production; EQ3/6 | NpO_2^+ 7.84E-9 (V) | $\text{NpO}_2\text{CO}_3^-$ 1.46E-9 (V) | NpO_2OH 5.49E-10 (V) | PuO_2CO_3 9.98E-9 (VI) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 1.79E-11 (VI) | $\text{PuO}_2(\text{CO}_3)_3^{-4}$ 5.93E-12 (VI) |
| USGS 89; ANSTO | NpO_2^+ 4.37E-9 (V) | $\text{NpO}_2\text{CO}_3^-$ 3.65E-9 (V) | $\text{NpO}_2(\text{CO}_3)_2^{-2}$ 1.54E-9 (VI) | $\text{PuO}_2\text{CO}_3^-$ 1.00E-8 (V) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 3.56E-12 (VI) | $\text{Pu}(\text{CO}_3)_3^{-2}$ 1.71E-12 (IV) |
| USGS 89; EQ3/6 | NpO_2^+ 7.64E-9 (V) | $\text{NpO}_2\text{CO}_3^-$ 1.38E-9 (V) | NpO_2OH 9.08E-10 (V) | PuO_2CO_3 9.97E-9 (VI) | $\text{PuO}_2(\text{CO}_3)_2^{-2}$ 1.63E-11 (VI) | $\text{PuO}_2(\text{OH})_2$ 9.47E-12 (VI) |

uncertainties and problems with the available thermodynamic data. These limitations include a lack of consistent thermodynamic data for all important reactions, the inability to describe and quantify Pu hydroxide polymerization reactions, little knowledge of actinide complexation with natural organic matter, and lack of a site-specific surface complexation model. Despite these limitations, K_r values were calculated for 1 surface-water sample, 1 perched-water sample, and 10 ground-water samples. Even if the surface-water sample is ignored, the calculated K_r values for Am varied by 400 percent, for U by 3,000 percent, for Np by 25 percent, and for Pu by 55 percent. These variations were due only to differences in aqueous compositions among the different water samples. For Am and U, the range of K_r s also reflects variations introduced by considering several SCMs. One significant limitation of this approach is that only one water-sample analysis was available for the perched-water sample (USGS 92). This is important because (1) K_r s of Pu in water from well USGS 92 were relatively large and K_r s of U were relatively small, and (2) the transport away from the SDA may be controlled by sorption from perched water in the sedimentary interbeds.

4.4 Applicability of the local equilibrium concept to actinide transport

Distribution coefficients theoretically apply only to reversible first-order reactions at local equilibrium. Actinide sorption and desorption reactions with minerals often are affected by several kinetic processes. These include:

(1) The rate of chemical or physical sorption reactions between an actinide and a mineral surface. Generally, these reactions are relatively fast, although there is often a slow component that could require weeks to attain equilibrium.

(2) Diffusion of actinides to or from reaction sites in zones of immobile water. This diffusion increases the time required to attain equilibrium. The immobile water can be a layer on the grain surface, within crevices or pits in the grain, in dead-end pores between tightly packed grains, in fractures, or in the interlayer of expandable clay minerals. If the diffusion rate of an actinide is slow compared with the transport rate in the flowing phase, physical nonequilibrium occurs.

(3) Mineralogical changes in the sorbing phase. For example, freshly precipitated ferrihydrite has a relatively large sorption capacity because its unordered structure results in a large surface area with excess charge. As ferrihydrite recrystallizes to more ordered structures such as

goethite, surface area and sorption capacity decrease. Other slow diagenetic reactions involving clay minerals also will slowly change the sorption property of a solid.

4.4.1 Chemically-mediated kinetics

Several laboratory batch experiments have shown that sorption of actinides is characterized by a rapid initial decrease in aqueous concentration followed by a more gradual approach to equilibrium that can take weeks. Many studies have attributed this decrease in aqueous concentration as sorption without demonstrating that other processes, such as redox or precipitation, could be ignored. The rate of approach to equilibrium in laboratory experiments often is affected by experimental conditions, the nature of the solid and aqueous phases, and the type and redox state of the actinide. For example, batch experiments are conducted by using a variety of agitation techniques. Violent agitation in reciprocating shakers can slowly abrade grains and cause gradual changes in the sorbing surface that can be interpreted as chemical reaction kinetics. Other agitation methods may incompletely mix sediment and solution. Diffusion of actinides to sorption sites in unmixed sediment at the bottom of a beaker can be interpreted as slow chemical reaction kinetics.

Use of a solid phase that is not in chemical equilibrium with the aqueous phase can induce apparent actinide sorption kinetics. For example, when a rock is crushed for use in sorption experiments, weathering reactions on the fresh surface of the grains can slowly change the mineralogy of the solid and the sorption properties of the actinide (Barney, 1981).

Barney (1978) evaluated sorption of Am, Np, and Pu in batch experiments as a function of time. Crushed basalt, crushed granite, and crushed argillite were used. An initial rapid sorption reaction, complete within 5 minutes, was followed by a slow reaction that apparently resulted from changes in the composition of the rock surface. Equilibrium concentrations were not attained within 145 days. Bulk solution chemistry continued to change as a result of weathering of the freshly crushed mineral faces; therefore, it was difficult to conclude whether the slow sorption was a result of a slow reaction with a stable mineral phase or the changing mineralogy. The release of a relatively large amount of silica appeared to increase the solubility of Am and Pu. This result also complicated interpretation of the data.

Newman and others (1995) determined sorption rate constants for sorption of U by crushed basalt and a composite interbed sediment from the INEEL. The time required to reach equilibrium with crushed basalt was 61

4-20 Review of the transport of selected radionuclides in the Interim Risk Assessment

hours. The time required to reach equilibrium with the interbed sediment was 103 hours. However, more than 90 percent of the sorption by both solids took place within the first 4 hours of the experiment.

In another set of batch experiments by Friedman and Kelmers (1990), sorption of U by a soil increased throughout the 168-hour length of the experiments; however, 96 percent of the U was sorbed within the first 24 hours.

Rhodes (1957) used batch experiments to measure Pu sorption by a soil from Hanford, Wash. To attain 99.9-percent adsorption, 360 hours were required; 86 percent of the Pu was sorbed within 0.08 hours. Nelson and others (1985) noted that reaction kinetics for Pu sorption and the amount sorbed were affected by complexation with DOC. More Pu remained in the aqueous phase as the concentration of DOC increased. The time required to achieve equilibrium also increased as DOC increased.

Sheppard and others (1979) measured and noted three distinct phases in the sorption of Am and Np by four soils from the INEEL as a function of time. The first phase was a rapid quasi-exponential decrease in aqueous concentration; the second phase was a slower exponential decrease in aqueous concentration; the final phase was the stabilization of the concentration as equilibrium was attained. Their data are quantified by the number of days required for Am and Np concentrations to decrease to 37 percent of the initial concentration. For the sorption of Np, 13, 14, 39, and 52 days were required. For the sorption of Am, 51, 202, and 361 days were required. Equilibrium was attained more rapidly as the grain size of the soils increased and the cation exchange capacity decreased. The soil that equilibrated least rapidly with Am and Np had the largest clay and silt content and cation exchange capacity. This slower equilibration time could indicate exchange with ions in interlayer positions of the clay minerals and could be partially controlled by diffusion.

Rock type also has been shown to affect equilibration time for Am and Pu (Seitz and others, 1978). Equilibrium concentrations were attained relatively quickly (less than 5 hours) in carbonates such as limestone, dolomite and marble. More than 100 hours were required for equilibrium in basalts and metamorphic rocks. Equilibration times were between 5 and 100 hours in sandstone and granite. The rate of decrease in aqueous concentration generally was faster for Pu than for Am.

4.4.2 Transport-controlled kinetics

Nonequilibrium transport of solutes through porous media occurs when ground-water velocities are sufficiently fast to prevent attainment of chemical and physical

equilibrium. Transport through the interbeds at the INEEL is likely to be slow enough for reactions to approach, if not to attain, equilibrium. Transport through basalt fractures and vesicles could be too fast to allow sufficient time for equilibration.

Kumata and Vandergraaf (1998) eluted solutions spiked with Np(IV) through columns packed with highly weathered, crushed granite. At a low flow velocity of 0.03 m/d, Np was detected only in the first few centimeters of the column. As velocities increased, Np was detected farther down the column. At 0.3 m/d, Np began to elute from the column. Np(IV) is very insoluble, and transport may be indicative of a sorbed phase or of a NpO₂ colloid. Regardless of the mechanism, the experimental data show the effect of flow rate on the transport of Np.

The asymmetrical shape of breakthrough curves for Np(V) in column experiments has been modeled by using the advective-dispersive model and a first-order kinetic term to account for mass transfer of Np between the flowing phase and stagnant water in side pores (Andre and others, 1998).

Data from the Large Scale Infiltration Test (LSIT) conducted at the INEEL indicate the presence of a complex network of flowpaths in the basalt (Wood and Norrell, 1996). Transport of nonreactive tracers indicates that moisture infiltrates mostly along preferential-flow paths under unsaturated flow conditions. Transport velocities varied greatly.

Information is insufficient to reliably assess whether actinides and sediments at the INEEL are in chemical equilibrium. The chemical and physical nature of the waste at the SDA is unknown. The speciation of actinides could have an effect on equilibrium. For example, a Pu organic complex could sorb at a different rate than a Pu fluoride complex. However, previous studies at the INEEL indicate that sorption of actinides by interbed sediments is relatively rapid, and most sorption occurs within 24 hours. There is also evidence for a slower sorption process in which equilibrium could take weeks to attain; however, for the purpose of risk assessment analysis, the assumption of chemical equilibrium appears to be reasonable. Flow velocities through the interbed layers appear to be slow enough to allow time for sorption reactions to attain equilibrium.

There could be insufficient time for equilibrium to occur in basalt fractures because of faster flow velocities. Also, there is evidence from the LSIT for diffusion into zones of stagnant water, which would increase the time needed to attain equilibrium. However, because of the relatively small amount of rainfall and infiltration at the INEEL, sustained rapid flow through fractures may be

limited. The slower velocities associated with short intermittent periods of recharge could allow enough time for reactions to approach equilibrium.

4.5. Colloid-facilitated transport of actinides

Transport of actinides beneath the SDA may be enhanced by association with colloids and larger particles capable of being transported by water. This evaluation of colloid-facilitated transport is organized into three sections. The first section is a general discussion of colloid formation and mobility; the next section is a review of previous studies of actinides associated with colloids; and the final section is a discussion of evidence for colloid-facilitated transport of actinides at the INEEL.

4.5.1 Colloid definition and mobility

The definition of a colloid varies; it generally is based on size and is often an operational definition based on the techniques used to separate the solid phase from the aqueous phase. Vilks and others (1998) defined a colloid as a particle small enough to be kept in suspension by Brownian motion. Suspended particles larger than colloids require water turbulence to stay in suspension and are less likely to be transported. Particles with diameters of less than 10 μm generally are considered to be colloids (fig. 4-8 from Stumm and Morgan, 1981).

Colloids can be rock and mineral fragments, mineral precipitates and weathering products, macromolecular components of DOC such as humic substances, biocolloids such as micro-organisms, and microemulsions of nonaqueous-phase liquids (McCarthy and Zachara, 1989). Colloids can form from condensation or homogeneous nucleation of particles from dissolved species when a mineral phase is supersaturated. Colloids can form as alteration products of *in situ* minerals, or they can be transported from somewhere else.

Particles can be released into solution by various processes such as the (1) disruption of fragile aggregates by changes in ionic strength (low ionic strength tends to increase colloid stability) or by hydrodynamic force, (2) mechanical grinding of mineral surfaces, (3) mechanical disruption of secondary minerals present at mineral surfaces, and (4) release of less soluble colloids by dissolution of a more soluble matrix surrounding the colloids (Buddemeier and Hunt, 1988).

The mobility of colloids in the subsurface is controlled by the stability of the colloids in ground water, chemical interactions between colloids and immobile matrix surfaces, and hydrological and physical factors.

Particles can be removed by mechanical filtration through smaller pore spaces. Changes in aqueous chemistry can cause aggregation of colloidal particles or, if electrostatic and London-van der Waals forces are present, attachment to immobile surfaces (McDowell-Boyer and others, 1986). Colloids can be destabilized by increases in ionic strength, which result in compression of the double layer surrounding particles, by pH-induced changes in surface charge, or by the presence of strongly binding ions that decrease the net surface charge (McCarthy and Deguel-dre, 1993).

A significant problem in studying colloid mobility is ensuring that the colloids recovered from the wellbore are representative of conditions in the aquifer. Drilling redistributes material, creates fine particles, and introduces materials such as drilling mud. Sampling procedures can remove existing colloids attached to the immobile solid phase, create colloids during sampling, create colloids during separation from solution, or cause changes in the chemical and physical properties of natural colloids by altering the oxygen and carbon dioxide content, temperature, pH, Eh, and light as ground water is brought to the surface. Nucleation and precipitation of colloids on filter material can be mistakenly interpreted to indicate the presence of colloids in a water sample.

Colloids in ground water from proposed or existing nuclear waste sites have been measured. Up to 5 mg/L of colloids in water from fractured granites in Canada have been measured. They consisted of clay minerals, micas, quartz, feldspar, iron-silica oxides, and organic matter (Vilks and others, 1991). Naturally occurring colloids ranging in size from 0.050 to 1 μm in ground water from fractures in the crystalline bedrock of the Grimsel site in Switzerland have also been measured (Smith and Deguel-dre, 1993).

4.5.2 Previous studies of actinide colloid formation and transport

Am, U, Np, and Pu oxides and hydroxides can exist as colloids in ground water (McCarthy and Deguel-dre, 1993). Evidence for association of actinides with colloids comes from laboratory batch and column experiments and field studies.

4.5.2.1 Batch experiments

Formation of actinide colloids in laboratory experiments is dependent on the experimental conditions. The pH, concentration of complexing agents, including OH, CO₃, PO₄, SO₄ and F, and actinide concentration all affect whether colloids will form and at what rate. For aqueous

4-22 Review of the transport of selected radionuclides in the Interim Risk Assessment

solutions of actinides, polymers begin to form as pH increases. Increasing the pH of Pu and Am solutions with initial concentrations ranging from 1×10^{-7} to 1×10^{-11} M led to colloid formation at pH values between 7 and 9 (Ramsay, 1988).

Am solubility is smallest at a pH of 8. When Am stock solution was added to synthetic ground water, 80 percent of the Am was found to be in colloidal form; the colloids were between 0.008 and 0.450 μm in size (Vilks and Drew, 1986). Colloid formation increased over a 4-day period before stabilizing. Geochemical modeling indicated that the solubility product for AmOHCO_3 had been exceeded. In a similar experiment using saltwater, no Am colloids formed.

Adsorption of actinides by colloidal particles has been shown to affect calculated K_d s. Higgs and Rees (1986) found that Am, Np, and Pu K_d values decreased as ratios of solids to solutions increased. They attributed this behavior to increasing concentrations of colloids with adsorbed actinides moving through the 0.22- μm filters that were used to separate the solid phase from the aqueous phase. Thus, the presence of actinides on colloids in the aqueous phase led to erroneously large solution concentrations and small K_d values.

Actinides have been shown to form colloid-sized complexes with organic molecules. Sheppard and Kittrick (1983) noted the presence of Am complexes with humic acids in the 0.001- to 0.010- μm size range. Nelson and others (1985) determined that colloidal organic carbon and natural sediments used in laboratory experiments had approximately equal affinities for Pu (III+IV). Once complexed with the colloidal organic carbon, the Pu was mobile and unavailable for sorption by the natural sediments.

The association of actinides with organic carbon potentially can be an effective method for mobilization and transport from waste disposal sites. Organic material such as paper, cardboard, clothing, plastics, and other materials contaminated with radionuclides have been buried at the SDA (Humphrey and others, 1982). Vilks and others (1998) put compacted organic waste into airtight steel containers filled with water. After 18 months, the aged leachate contained 74 to 5,074 mg/L organic carbon and 5 to 110 mg/L of organic colloids. The leachate also contained large concentrations of Fe and Al, which could aggregate as colloidal particles.

Sheppard and others (1980b) measured U associated with colloidal humic molecules in the 0.001- to 0.010- μm size range. These were batch experiments with soils. Sheppard and others (1980a) found evidence for U and Am complexes with large humic acid molecules (0.010 to

0.060 μm) in water from soils. Sheppard and others (1979) found evidence for Am and Np associated with a wide range of potentially mobile soil particles in the <0.001 μm to 0.20 μm size range.

4.5.2.2 Column experiments

Colloidal transport of actinides in column experiments has been documented (Champ and others, 1982). Pu(IV) was applied as a spike to intact saturated-zone sand cores from the Chalk River Nuclear Laboratories, Ontario, and then eluted with uncontaminated ground water. Conditions were oxidizing; pH was 6.7, and HCO_3 (9.5 mg/L), SO_4 (18.5 mg/L), and Ca (6.1 mg/L) were the major ions. Small concentrations of Pu (mostly IV) were detected within 1 day of loading. The amount of Pu in column effluent increased gradually with time. At steady state, about 34 percent of the Pu in column effluent was associated with particulates (>0.450 μm), 16 percent was colloidal Pu (0.050 to 0.450 μm), 18 percent was 0.0028- to 0.050- μm sized colloidal Pu, 28 percent was associated with a molecular weight between 500 and 10,000, and 6 percent was dissolved (<500 molecular weight). When columns were cooled to 0°C, the Pu release rate decreased fourfold within 48 hours. Upon reestablishing 22°C, 20 days were required to establish original equilibrium conditions. Release of Pu associated with both colloids and particulates was totally inhibited by antibiotic treatment. Release mechanisms were discussed by Champ and others (1982), but biologically mediated release of Pu is indicated by the data.

Seitz and others (1978) eluted Am and Pu through limestone, sandstone, and tuff columns. About 0.1 percent was eluted within a couple of pore volumes. Most of the Am(III) and Pu(IV) was concentrated near the inlet port of the column. Am(III) and Pu(IV) concentrations decreased exponentially along the column length. Transport could have been associated with a colloid or as discrete colloidal hydrolysis products.

4.5.2.3 Field studies

Actinide colloids in ground water have been measured. Wastewater containing Am and Pu was disposed of in pits at Los Alamos National Laboratory in the 1940s and 1950s. Both Am and Pu in Mortandad Canyon, New Mex., several kilometers from the disposal sites, have been measured. Conductivity of ground water in this area ranges from 220 to 900 $\mu\text{S}/\text{cm}$. The Am and Pu was associated with colloids having the same chemical composition as the soil matrix (Nuttall and others, 1991).

At a location 3.4 km from the disposal pits, Pu and part of the Am were associated with 0.0025- to 0.450- μm

sized colloids. About half of the Am was associated with a low molecular weight ($<0.002 \mu\text{m}$) anionic complex of unidentified origin. Pu concentrations decreased exponentially along the flowpath. Am concentrations were variable (Penrose and others, 1990). The lithology of the disposal site is tuff, sand, silt, and clay derived from tuff. The researchers concluded that some Pu and Am could be transported by surface water during runoff events, but they stated that tritium oxide transit-time measurements indicated that most water movement took place in the subsurface.

Pu and Am colloids in the Bandelier Tuff beneath the former liquid waste disposal site at Los Alamos also have been measured. Laboratory studies found that essentially all Pu was retained within the top few millimeters of tuff core; however, in the aquifer 30 m below one disposal pit, Am and Pu concentrations as large as 5,000 Bq/kg were measured. In 1961, 20.5 m of additional water was added to this pit to change the distribution of radionuclides below the pits. Pu was found only 6.5 m below the bed, and Am was found 13.4 m (Nyhan and others, 1985).

About 5 percent of the U(VI) in ground water from the Koongarra deposit in Australia was associated with colloidal (defines as $0.0015\text{--}1.0 \mu\text{m}$) kaolinite and silica (Payne and others, 1992). The remainder of the soluble U probably was transported as carbonate complexes.

4.5.3 Evidence for colloid-facilitated transport of actinides at the Idaho National Engineering and Environmental Laboratory

Transport of actinides associated with colloids in the subsurface at the SDA has not been proven conclusively. Results, however, from field sampling and laboratory column experiments indicate that colloid-facilitated transport of actinides could occur.

4.5.3.1 Field evidence

Pu and Am in the subsurface at the INEEL have been measured. A memo from Jim Navratil to Doug Jorgensen, May 26, 1996, stated that Pu had migrated to the B-C and C-D interbeds. Possible transport mechanisms include formation of water-soluble organic or hydroxyfluoro complexes, or transport as colloids. Navratil and Jorgensen concluded that some of the reported detections of Pu were the result of analytical error or contamination.

Estes and McCurry (1994) showed that colloids are transported in the subsurface at the INEEL. Ground water was collected from USGS 45, USGS 46, and Site 14 using a straddle packer to isolate intervals. Ground water was filtered through 0.45- , 0.20- , 0.010- , and $0.02\text{-}\mu\text{m}$ mem-

brane filters. The water was supersaturated with respect to amorphous silica, calcite, and dolomite. Filters were analyzed by electron microscopy/energy dispersive X-ray spectroscopy (EDS) and point counting to determine concentration and composition. About 60 percent of the colloids were rounded and composed of Ca. About 5 percent were composed of ferrihydrite. Others were composed of Mg, Fe, Si, and Ca, and likely were clay. The authors suggested that some of the colloids could have been dislodged from fracture walls by pumping turbulence. Concentrations ranged from 2.1 to 1.8 mg/L for $>0.45 \mu\text{m}$ in size, and 2.3 to 9.8 mg/L for $<0.45 \mu\text{m}$ in size. For the 55- to 56-m depth, concentrations were 1.0, 2.7, and 6.1 mg/L for colloids of 0.20, 0.10, and $0.02 \mu\text{m}$ sizes, respectively, and 1.2 mg/l for colloids between 0.45 and $1.20 \mu\text{m}$. Concentrations and size ranges of colloids in other depth intervals were similar to those in the 55- to 56-m depth. The results show that colloids exist in ground water at the INEEL; however, pumping dislodges some of the particulates attached to the fracture wall. This disturbance could skew measurements of the natural colloid concentrations. At one site, more than three borehole volumes were purged because initial water was brownish. Fractures and vesicles in basalt from beneath the SDA contain clay minerals and even some sand and silt (Right-mire and Lewis, 1987a); although the coarse material indicates transport of particles larger than colloids, it is likely that colloidal transport also occurs.

4.5.3.2 Laboratory column experiments

Fjeld and others (1998) conducted column experiments to evaluate Pu(III+IV) and Pu(IV+V) transport in interbed sediments from the INEEL. The Pu was added to a synthetic perched ground water that contained potential complexing ligands. Batch distribution coefficient measurements indicated that Pu retardation by interbed material should be large; however, field measurements of Pu below the SDA suggested that Pu may have migrated through at least one interbed layer.

Column experiments were conducted by using interbed solids, both unwashed and washed, to remove colloids. A spike of Pu was added to the columns and then was eluted with uncontaminated ground water. The interbed material was composited from cores collected at five different depths ranging from 50 to 120 m and sieved to $<250 \mu\text{m}$. The interbed material was composed primarily of silt and clay. The synthetic ground water contained about 2000 mg/L of TDS, primarily Na, CO_3 , SO_4 , and Cl, and 1.3 mg/L of humic acid, 1.3 mg/L of EDTA, and 20 mg/L of F.

4-24 Review of the transport of selected radionuclides in the Interim Risk Assessment

Columns were 8 cm long; inside diameters were 1.5 cm. Columns were dry-packed in 1 cm intervals by tapping to consolidate the sediment. One pore volume was 5.5 mL and the flow rate was 0.3 mL/min, equivalent to a linear velocity of 6.9 m/d. From 1,000 to 2,000 pore volumes of Pu-free water was eluted after the initial Pu spike was added.

Initial Pu concentrations were about 100 Bq/mL for Pu (III+IV) and 350 Bq/mL for Pu (IV+V). The washed columns were washed at a rate of 0.3 mL/min for 24 hours at pH 8, 24 hours at pH 10.7, 24 hours at pH 12, and 48 hours at pH 8.

In the Pu(IV+V) experiments, a small peak of Pu was eluted from the unwashed column when between 1 and 2 pore volumes had been eluted. The concentration of Pu that was eluted was about 0.07 percent of the initial spike concentration. For the washed columns, the effluent peak was 0.03 percent of the initial spike concentration. These peaks were followed by a nonzero residual for the remainder of the experiment. Total recovery was 4.3 percent for unwashed and 2.7 percent for washed columns. About 33 percent was Pu(IV) and about 71 percent was Pu(V).

In the Pu(III+IV) experiments, the concentration of Pu eluted from the unwashed columns when between 1 and 10 pore volumes had been eluted was steady at almost 2 orders of magnitude larger than background concentration. This was followed by a large peak that reached a maximum at between 20 and 1,000 pore volumes and had a retardation factor of 40. Total recovery was about 60 percent. The concentration of Pu eluted from the washed column when between 1 and 20 pore volumes had been eluted was steady at 1 order of magnitude larger than background concentration. This was followed by no detectable concentration from between 30 and 90 pore volumes, a broad peak that extended from between 100 and 1000 pore volumes, and a maximum concentration between 500 and 800 pore volumes. Total recovery was 16 percent. About 48 percent was Pu(IV) and about 51 percent was Pu(III).

Pu(IV+V) was more strongly sorbed than Pu(III+IV) and sorption was stronger in the washed columns. Approximately 90 percent of the sorbed Pu(IV+V) in the washed column was in the first 2 cm of the column. About 70 percent of the sorbed Pu(IV+V) in the unwashed column was in the first 2 cm of the column. About 55 percent of the Pu(III+IV) in the washed column was in the first 2 cm, and about 15 percent of the Pu(III+IV) in the unwashed column was in the first 2 cm.

Sr also was included in the initial spike. There was little difference in the Sr concentration profiles between unwashed and washed columns. A single peak of Sr was

eluted between 50 and 500 pore volumes. There was no evidence of a high-mobility fraction.

Results of these column experiments indicate the presence of multiple physical and chemical forms of Pu having different mobilities depending on the oxidation state of the Pu and the geohydrological history of the interbed. The implication of the results, if they accurately represent field conditions, is that transport models based on a single retardation factor calculated from batch distribution coefficient measurements may not accurately reflect actinide transport in the subsurface at the SDA. In the Pu(III+IV) experiments, there was a small, high-mobility fraction, a large, moderate-mobility fraction, and a large low-mobility fraction. In the Pu(IV+V) experiments there was more sorption, but also a small high-mobility fraction.

Possible mechanisms for Pu transport in these experiments include transport as an aqueous complex with F, CO₃, EDTA, or humic acid, transport as a hydrolyzed solid, or transport as a sorbed phase on a mineral surface. The fact that more Pu(III+IV) was eluted from the unwashed column (60-percent recovery) than from the washed column (16-percent recovery) indicates that at least part of this fraction of Pu was associated with fine-grained minerals capable of being transported under these experimental conditions. Similar behavior would be expected for the Pu(IV+V) columns, yet there was only a small difference between the amount recovered from the unwashed (4.3 percent) and the washed (2.7 percent) columns. Additional data on the oxidation state of Pu in the column effluent could be used to quantify parameters for use in a solute transport model.

Newman and others (1995) also evaluated actinide transport in column experiments. Composite interbed sediment and crushed basalt were used. A spike of about one pore volume of synthetic ground water containing either Am, Pu(V), or U was added to the columns, and then 200 pore volumes of actinide-free ground water was eluted. The synthetic ground water used in these experiments was more dilute than the water used by Fjeld and others (1998). There was no added organic matter or EDTA, and F concentrations were only 0.5 mg/L. The columns were 15 cm long; inside diameters were 2.5 cm. Flow velocities were about 6 m/d.

There were peak concentrations of both Am and Pu when the first few pore volumes of all columns were eluted. The peaks for the coarser grained crushed basalt columns were much larger than those for the finer-grained sediment interbed columns. The Pu peak concentrations for the interbed columns were comparable to the Pu(IV+V) peak concentrations in interbed columns in

experiments by Fjeld and others (1998). There were no data to indicate whether Am and Pu were eluted from the columns as aqueous complexes or as colloids. In these experiments, materials that passed through a 0.2 μm filter were considered.

The flow velocities used in these experiments were probably faster than expected velocities through the interbeds beneath the SDA. Other column experiments showed that decreasing column velocity decreased the size of the eluted actinide peak; however, the location of the peak did not change.

4.5.4 Summary of colloid-facilitated transport of actinides

Evidence for the association of actinides with colloids comes from batch and column experiments and from field studies. Actinides are associated with a wide range of particle sizes, from the 500-molecular-weight range to clay sized and larger. They can exist as organic colloidal complexes and precipitates, and they can be sorbed by other minerals.

In laboratory column experiments, actinides eluted from columns packed with interbed sediments at a much faster rate than would be predicted from equilibrium sorption of aqueous species. This enhanced-mobility fraction was attributed to colloidal transport. The columns were relatively short; flow velocities through the columns were faster than expected velocities through the interbeds at the SDA but similar to expected velocities through fractured basalt. It is possible that actinide-bearing colloids migrating from the SDA could be mechanically filtered from suspension or removed by chemical or electrostatic forces. Better characterization of the colloids responsible for the enhanced breakthrough of Am and Pu observed in the column experiments is needed if this phenomenon is to be modeled. In addition, the percentage of actinides that could be associated with colloids and the percentage that could be in soluble complex form have not been determined.

The infilling of fractures and vesicles in the basalt beneath the SDA suggests the possibility of colloid transport; however, colloids at deep basalt intervals could have been transported from the surface or from interbeds immediately above the basalts. Colloids in fractures and vesicles also could have been emplaced as interbeds were forming.

One explanation for the occurrence of Pu in the B-C and C-D interbeds is that Pu mobility was enhanced by colloid transport. This explanation is consistent with both the strong association between Pu and colloids observed

in the laboratory and the evidence of the existence of colloids at the SDA. The occurrence of Pu in the B-C and C-D interbeds is also consistent with transport with small amounts of sorption. The small amount of sorption can be explained either by the formation of soluble complexes, notably CO_3^{-2} , or by slow sorption kinetics. Further study is needed to identify the geochemical characteristics of the subsurface water at the SDA, the sorption properties for the relevant variable geochemical conditions, and the geochemical and transport properties of the subsurface colloids.

4.6 Summary

The purpose of this chapter is to determine what physical and geochemical processes might be invoked to explain observed detections. Generally, three factors are likely to affect actinide transport in the unsaturated and saturated zones near the SDA. These include preferential-flow mechanisms, the effects of redox conditions on actinide speciation, and colloidal transport of actinides. Because the sorptive characteristics of colloid-sized material are poorly understood and the formation of actinide-containing colloids is dependent on solution chemistry and redox conditions, it is difficult to evaluate colloidal transport of actinides at the SDA. Preferential flow and redox conditions are summarized in the following paragraphs.

The conceptual flow model as implemented in the numerical simulator assumes that infiltration beneath the surficial sediments is gravity driven and that the infiltration rates vary in space but are generally constant in time (Magnuson and Sondrup, 1998, p. 1-5). These assumptions do not account for transport of actinides outside the SDA boundaries under the relatively low infiltration fluxes that are applied at the land surface. The presence of ^{238}Pu and $^{239,240}\text{Pu}$ (undivided) in water from well D-15 (chapter 3, this report; S.O. Magnuson, LMITCO, oral commun., 1999) indicates that the preferential-flow mechanisms described in chapter 2 of this report that can cause local increases in flux can also affect contaminant transport. Lateral movement of water and contaminants would help explain the presence of contaminants of concern (COC's) outside the SDA boundaries. Lateral movement of water also would be consistent with the documented lateral movement of concrete grout for a distance of 168 m at the SDA (Rightmire and Lewis, 1987a, p. 64). It has been noted that there are gaps in the A-B and B-C interbeds beneath the SDA (chapter 2, this report). These interbed gaps could serve as drains for infiltrating water that has reached the basalt-interbed interface and moved

4-26 Review of the transport of selected radionuclides in the Interim Risk Assessment

along the contact. The small number and seemingly random nature of radionuclide detections identified in chapter 3 of this report also indicate preferential flow in the subsurface at the SDA. These preferential-flow mechanisms add complexity to the geohydrologic system and to the computational scheme of the flow model, for example, extreme events such as flooding overwhelm the capacity of the system to transmit water through vertical fracture systems in the unsaturated zone. This incapacity forces lateral movement of water through horizontal fracture systems and could be the reason for the presence of COC's in the B-C interbed at well D-15, south of the western boundary of the SDA.

Generally, the ground water at the INEEL (and the SDA) is in oxidizing conditions: the ground water is saturated with DO and contains little organic carbon. At the SDA, a large amount of organic carbon (cardboard, wood, solvents, and other materials) and other waste was buried. As a result, it is likely that reducing conditions exist near the buried waste. These conditions will not persist indefinitely because the continual atmospheric supply of oxygen ultimately will consume all of the organic carbon associated with the waste. When this process is complete, oxidizing conditions will be reestablished. It is difficult to predict when this will occur. Am, U, Np, and Pu exist at the SDA in several different oxidation states. In this chapter, it has been shown that the transport and sorptive characteristics of these elements are affected by their oxidation state and by the redox conditions to which they are exposed. An important consideration when evaluating the mobility of these elements is whether current monitoring methods reflect long-term or transient conditions. It is possible that elements that are immobile in reducing conditions will convert to oxidation states that are mobile in oxidizing conditions. Hence, a change to oxidizing conditions could significantly affect actinide migration. For these reasons, it is necessary to have a good knowledge of the oxidation state of the COC's disposed of at the SDA and the oxidation state of any actinide detected at or near the SDA. Although the existing thermodynamic data sets are incomplete and inconsistent, surface complexation modeling techniques can help in evaluating actinide transport if the oxidation state of the element and redox conditions are known. Therefore, emphasis should be placed on identifying oxidation states and types of complexes or species formed by actinides detected at the SDA. This knowledge is necessary for the accurate prediction of actinide transport from buried waste at the SDA.

Magnuson and Sondrup (1998, section 5.4.1) discussed observed concentrations of ^{241}Am , ^{238}Pu , and $^{239,240}\text{Pu}$ in sediment from beneath disposal pit 2, the B-C

interbed, and the C-D interbed at the "triad" location, which includes wells TW-1, D-02, and 79-2 (located within 10 ft of each other in the north central part of the SDA). They compare the positive results at the B-C and C-D interbed depths to maximum model-predicted values at similar model locations and to the overall maximum values predicted by the model from all locations within the SDA. For the B-C and C-D depth intervals, the observed concentrations were 2 to 4 orders of magnitude greater than the predicted concentrations. The "triad" location is the only site in the SDA with concentrations in interbed samples larger than the minimum detection level (MDL) of 5×10^{-14} Ci/g established by the contractor's sample management office (SMO). They concluded that, because the "triad" samples were greater than predicted values, the model underestimated actinide migration at the SDA. However, they also concluded that, because of the lack of detections at other sites within the SDA, the model overpredicted migration at those sites. These conclusions seem contradictory and point out the weakness of using non-detection of actinides to confirm model predictions of values less than the MDL.

The fact that detections occurred in the subsurface at the "triad" location combined with the inability of the transport model to predict these detections indicates that there is a problem in the construction of the model. The failure of the model to predict these detections could be related to the assumptions in the conceptual model. For example, a single K_d was uniformly applied in the model. The K_d was derived from a laboratory experiment conducted on the fine-grained fraction of a composite sample using a synthetic liquid that was not representative of local water chemistry. It also was assumed that the interbeds were lithologically uniform, fine-grained material that was effective in retarding movement of contaminants. This is in spite of the limited knowledge about the characteristics and distribution of the interbeds. K_d s and their application to transport analysis is discussed extensively in chapter 5. The model may have underpredicted the actinide detections because (1) it does not adequately account for rapid movement of actinides past the interbeds by one or more of the preferential-flow mechanisms discussed in chapter 2, (2) the actinides may be in different forms resulting from different redox conditions in the source area and the area where the detections occur, or (3) the areal variability of actinide releases in the source area. The failure of the model to predict these detections indicates that significant characterization of the factors controlling actinide transport needs to be done. Particularly, data should be collected to adequately describe the variation in K_d resulting from differences in the areal distribu-

tion, thickness, and composition of the interbeds. The effects of preferential-flow mechanisms needs to be better understood. Understanding the form of the actinides is necessary to explain either their movement or lack of movement. Improving the understanding of these model variables should allow for better model predictions.

The fact that actinide measurements below the MDL occurred in all locations other than the "triad" location, and that the model predicted concentrations less than the MDL does not indicate that the model was successful in predicting actinide concentrations at those locations, it simply cannot be concluded one way or another. However, the inability to predict real detections at the "triad" location argues that the model cannot accurately predict actinide transport without a better understanding of the hydrologic system.

The occurrence of actinide concentrations larger than the MDL in the B-C and C-D interbeds at the "triad" location indicates that some form of transport is moving actinides from the SDA downward to the B-C and C-D interbeds at this location. The general decrease in ^{238}Pu concentrations with depth from the B-C interbed to the C-D interbed (from 1.18×10^{-13} to 3.22×10^{-14} Ci/g) and for ^{241}Am (8.40×10^{-13} Ci/g) and $^{239,240}\text{Pu}$ (1.07×10^{-12} Ci/g) to less than the MDL also suggests that the B-C interbed may effectively retard the migration of actinides at the SDA. The migration of actinides to the B-C interbed and the reduced migration to the C-D interbed points out that some transport mechanism is active in this system and also that some retardation mechanism is active in the B-C interbed. In order to identify and evaluate these mechanisms further, it is necessary to enhance the database through additional data collection to define the continuity of the interbeds, their hydraulic properties, their mineral-

ogical composition, and their effect on transport of actinides in this system.

The uncertainties and complexities of actinide transport and the nonuniform distribution of actinides in the environment at the SDA limit use of the data from these detections in calibration of the model. As a result, the model was calibrated by using NO_3 , which is considered to be a conservative indicator of transport in the system. The occurrence of a larger-than-background concentration of NO_3 in water from well D-15 indicates both that NO_3 can move in the unsaturated zone and that the preferential-flow mechanisms discussed in chapter 2 of this report probably operate at the SDA. However, the redox conditions near the SDA also can affect the stability of N compounds. NO_3 is the stable form of N in an oxidizing environment; however, NO_2 or NH_4 generally is more stable in a reducing environment. If NH_4 and NO_2 were removed to an oxidizing environment that contained nitrifying bacteria, then a two-step nitrification process that first converted NH_4 ion to NO_2 and then NO_2 to NO_3 would take place. In this case, N would be conservative and could be used to determine longitudinal and transverse dispersivity. On the other hand, if nitrogen were present as NO_3 in a reducing environment, it probably would undergo a N reduction process that converts NO_3 and organic carbon to CO_2 gas, water, hydroxide ion, and N_2 gas. In this case, N would not be conservative and could not be used to determine dispersivity. Therefore, sample collection to determine the distribution of NO_3 in the saturated and unsaturated zones should be expanded to include other forms of N. This would further substantiate the use of NO_3 concentrations as a conservative indicator of the movement of wastes.

5.0 Task 3: Distribution coefficients (K_ds) and their application to transport analysis

5.1 Introduction

The fate and transport of waste constituents in geologic material are dependent on chemical and physical processes that govern the distribution of constituents between the solid, stationary phase and the aqueous, mobile phase. This distribution often is quantified by an empirically determined parameter called the Distribution Coefficient (K_d). Many transport models for radionuclides use K_ds to predict the extent to which the migration of the constituent will be lessened relative to the mean ground-water velocity. Although K_ds are widely used, their application implicitly assumes that all factors affecting K_ds are constant. However, these factors, which include pH, the concentration of competing adsorbates, the concentration of complexing ligands, and the availability and types of adsorption sites, generally are not constant in field environments such as the INEEL. Therefore, K_ds may not adequately describe the transport and fate of waste constituents in some environments.

This section of the report evaluates the reliability of K_ds and their application to transport analysis at the Subsurface Disposal Area (SDA), as described in the Interim Risk Assessment (IRA) (Becker and others, 1998). The evaluation includes a review of the literature on K_ds that are specific to the SDA, as well as K_ds reported for similar subsurface sediments elsewhere. The K_ds are evaluated in terms of the existing subsurface mineralogy and aqueous geochemical conditions. The experimentally determined K_ds for Am, U, and Pu used in the IRA model are discussed in section 5.3, and the K_ds for Np from previous studies are evaluated in section 5.4

This evaluation specifically considers the K_ds used for Am, U, Np, and Pu, the experimental protocols used to determine the K_ds, and the adjustment of the reported K_ds to account for site-specific conditions such as the presence of carbonate from caliche layers. This evaluation also examines the extent to which the K_d concept may be applicable to the SDA, as well as the uncertainty associated with the K_ds used for fate and transport modeling. Many factors contribute to the uncertainty, including extrapolation of the laboratory-derived K_ds to field conditions and the effects of spatial variability of the sorbing phases.

5.2 Literature review

The actinides comprise the series of radioactive elements from actinium (atomic number 89) to lawrencium (atomic number 103). Of specific interest at the SDA are Am, U, Np, and Pu. The dominant species of these elements in ground-water systems are given in table 5-1.

Table 5-1 Important (*) and usually unimportant (**) oxidation states of some actinides in natural rock-water systems (from Langmuir, 1997)

| Actinide charge | Actinide cation (An) | Element/atomic number | | | |
|-----------------|--------------------------------|-----------------------|-------|-------|-------|
| | | U/92 | Np/93 | Pu/94 | Am/95 |
| 6+ (VI) | AnO ₂ ²⁺ | * | ** | * | |
| 5+ (V) | AnO ₂ ⁺ | ** | * | * | |
| 4+ (IV) | An ⁴⁺ | * | * | * | |
| 3+ (III) | An ³⁺ | | ** | * | * |

5.2.1 K_d basics

“K_d or not K_d, that is the question.” (Rancon, 1986).

K_ds for radionuclides on earth materials have been measured and used in environmental assessments at nuclear facilities since the early days of operations at these sites. The number of measurements has been described by Bror Jensen (1982) of Riso National Laboratory, Denmark, as “almost incalculable.” The applicability and limitations of the K_d concept will be introduced here.

Sorption processes can be studied in the laboratory by a batch method. This involves adding a known quantity of sorbate (for example, a radionuclide) to a system containing a known quantity of sorbent (for example, soil, rock). After equilibration at constant temperature, the quantity of sorbate on the solid, and that remaining in solution are measured. The initial solution concentration is varied and the equilibration and analysis process is repeated. Sorption isotherms are plots of the quantity of sorbate on a solid sorbent per unit weight of sorbent (pCi/g), versus the equilibrium solution concentration of the sorbate (pCi/mL). A typical sorption isotherm for a trace solute sorbing onto a solid is shown in figure 5-1. The maximum percentage of the solute is sorbed at the smallest sorbate concentration. A tangent drawn to the steep, initial portion of this empirical curve gives the ratio of the amount sorbed to the concentration in solution. This slope has

5-2 Review of the transport of selected radionuclides in the Interim Risk Assessment

been designated as the “distribution coefficient,” K_d (Langmuir and Mahoney, 1984) (equation 4.1). Measured K_d s are typically reported in units of mL/g or L/kg. A non-reactive sorbate will have a K_d near 0; a reactive sorbate may have a K_d of 10^2 to 10^3 or larger.

The larger the K_d , the greater the retardation of the solute. This is reflected in the retardation factor, R_F (equations 4.2 and 4.4). In laboratory column experiments where R_F is measured, K_d may be calculated by the equations above. The column method represents an alternative to the batch technique. Although the column method is more labor intensive than the batch method, it does allow for the identification of species of differing mobilities, for example, a “fast fraction,” that otherwise may be lumped in the batch method.

Distribution coefficients are typically normalized on a per unit weight of sorbent basis. However, they also may be normalized on a per-unit-of-surface-area basis (mL/m^2). The distribution coefficient in terms of surface area, K_a , is related to the more commonly used K_d by:

$$K_a = \frac{K_d}{S_A} \quad (5.1)$$

where:

S_A = specific surface area of the sorbing phase (a mineral, soil, crushed rock or any porous medium), in area per mass.

Bertetti and others (1998) have shown how surface-area measurements, as a relative measure of the number of sorption sites on a mineral surface, can be used to compare the Np(V)-sorbing properties of different materials. Whereas the K_d data in figure 5-2a suggest differing sorption properties between two types of quartz and alumina powders, normalization to surface area (fig. 5-2b) showed similar K_a s. Similar findings for U(VI) sorption on a variety of minerals have been reported by Pabalan and others (1998). Although montmorillonite K_d s over a pH range of 2 to 9 are as much as an order of magnitude larger than those for the zeolite mineral clinoptilolite, their K_a s are almost identical. For fractured media, K_a can be used in modeling the sorption of contaminants. For uncoated fractures, an estimate of the surface area of the fracture walls would be used. However, Rightmire and Lewis (1987a) have shown that many of the basalt fractures in the unsaturated zone at the SDA are coated or filled with clays, iron-stained quartz sand, calcium carbonate, and other fine-grained materials. In modeling the sorption of contaminants in these fractures, Magnuson and Sondrup (1998, p. 5-2 to 5-6) used the specific surface area of the material coating the fracture in the K_a term; extrapolating

from surficial sediment data from the SDA, this value was $20 \text{ m}^2/\text{g}$.

The K_d determined for a given constituent in the laboratory is unique to the solution properties (pH, competing ions, complexing ligands, etc.), and sorbent properties (mineralogy, organic matter content and character, surface area, etc.) being investigated. The K_d may vary with the method used to determine it—batch, column, or *in situ*—as well as with intramethod variations, such as the solid:solution ratio in batch experiments, flow rates in column experiments, and particle-size fractions measured for *in situ* experiments. Caution is necessary when results from laboratory experiments are extrapolated to field conditions. Where solution composition is variable, for example, in a contaminated ground-water system, solute transport modeling based on a single K_d may have inherent problems. Despite these limitations, K_d -based solute transport modeling has been widely used in the study of organic, inorganic, and radioactive contaminants in the subsurface (Freeze and Cherry, 1979).

In situ measurements of K_d are rare but intrinsically appealing, because sorption has occurred under field conditions. Some investigators have determined *in situ* K_d by measuring the ratio of the concentration of the radionuclide of interest in the sampled soil or rock interval, to the concentration in the sampled ground water. *In situ* measurements have included K_d s for $^{239,240}\text{Pu}$ at Enewetak Atoll (Noshkin and others, 1976), and for ^{60}Co , ^{106}Ru , and ^{125}Sb at an unnamed low-level radioactive waste disposal site (Fruchter and others, 1985). Other investigators have approached the issue of K_d s for selected transuranic elements and fission products by measuring analog radionuclides associated with natural decay series (natural analog studies). For example, U(VI) can be used as an analog for Pu(VI), and Th(IV) can be used as an analog for Pu(IV) and Np(IV). Two approaches have been used for *in situ* K_d measurement. One involves measurement of only the solute phase (Krishnaswami and others, 1982). The other involves measurement of both solid and aqueous phases, in some cases using selective extractants to identify sorbed radionuclides. There has been considerable dialog on the uses and abuses of natural analog studies in assessments of radionuclide migration (McKinley and Alexander, 1993; Ivanovich, 1993). Investigators at Los Alamos National Laboratory, the University of Southern California, and the INEEL indicate that U-series and Th-series isotopes (in an approach which appears to be similar to that of Krishnaswami and others, 1982) in the Snake River Plain (SRP) aquifer are being investigated as natural analogs of contaminant transport at the

INEEL (Luo and others, 1998; Roback and others, 1998). Details of these applications are not yet available.

K_ds generally imply retention by ion adsorption reactions—ion exchange or specific sorption—retention by the solid surface based upon its surface charge. However, solutes can be removed from solution by other processes, such as precipitation and coprecipitation, where new bulk solid phases are formed (Sposito, 1984). For example, in comparing trace metal binding constants (distribution coefficients normalized by density of exchangeable surface sites) in surficial ocean sediments from different basins, investigators excluded Mn, Fe, and Ba from consideration in sediments where enrichment appeared to be due to the formation of Mn and Fe oxides and BaSO₄, rather than to adsorption (Balistrieri and Murray 1984). The K_ds determined when an acidic, radionuclide-bearing solution comes in contact with a calcareous soil horizon may reflect the combined effects of adsorption, coprecipitation, and/or precipitation onto and in freshly precipitated Fe(III), Al, and Mn(IV) oxyhydroxides, as well as ion exchange reactions with clay minerals. Langmuir (1997, p. 356–357) refers to these as “lumped-process” or “apparent” K_ds, and presents an example of laboratory neutralization of a Th-bearing water by CaCO₃ to demonstrate the nonlinear variation in apparent K_ds from about 2 at pH 2 to about 15,000 at pH 8. These K_ds are system specific, and have limited transfer value to other systems having different conditions or compositions.

5.2.2 Sorption processes

Experimental sorption data typically are described by empirical measures such as K_d. Such empirical measures provide little information on the mechanism of sorption and are highly dependent on temporal and spatial variations in the chemical composition of the aqueous phase and in the nature and properties of the sorbing solids. Desiring a means to describe sorption in a general geochemical framework of changing water chemistry and nonuniform mineralogies, investigators have developed Surface Complexation Models (SCMs) that describe reactions between functional groups on mineral surfaces and soluble species identified by aqueous speciation models (Davis and Kent, 1990). Such SCMs have been developed to describe U(VI) sorption on ferrihydrite (Waite and others, 1994), quartz (Kohler and others, 1996), kaolinite (Turner and Sassman, 1996), and montmorillonite (Pabalan and Turner, 1997). SCMs have been used to simulate Np(V) sorption on montmorillonite (Tsukamoto and others, 1997; Turner and others, 1998), gibbsite (Del Nero and others, 1997), hematite (Kohler and others, 1999),

and magnetite and goethite (Fujita and others, 1995). Turner (1995) reviewed additional studies on actinides, including the use of SCMs to simulate the sorption of Am(III) on alumina and amorphous SiO₂, and Pu(IV, V) on alumina and goethite. Most SCM investigations have focused on monomineralic systems. Recent work by Davis and others (1998) extended the application of the surface complexation concept to complex mineral assemblages, in this case, Zn²⁺ sorption by an outwash sand, aquifer material from Cape Cod, Mass. With continued progress in the development of such models to address complex geochemical environments, in the future these models could be coupled with reactive-transport codes and used as the method of choice in performance assessment simulations of radionuclide migration at nuclear waste sites. However, currently, transport calculations used in these assessments continue to rely on empirical sorption coefficients, principally K_d (Vandergraaf and others, 1993; Turner, 1995).

As previously noted, many experimental factors can influence K_d determinations. These include:

- pH,
- Eh,
- speciation of sorbate,
- concentration of complexing or competing solutes,
- solid:solution ratio and method of phase separation at the end of an experiment,
- radionuclide concentration,
- adsorption versus desorption measurements,
- time,
- temperature, and
- properties of the sorbent, including particle size.

The thousands of batch K_ds in the literature have been determined by many laboratories, each with its own procedure. These procedures often are not well documented in the reports. Several standardized procedures have been developed for batch K_d measurements (American Society for Testing and Materials, 1987, 1993; Relyea and others, 1980). The standard batch K_d procedure of Relyea and coworkers at Pacific Northwest National Laboratory (PNNL) (1980, appendices A and B) was developed for Department of Energy’s (DOE) Office of Nuclear Waste Isolation as part of the Waste/Rock Interaction Technology (WRIT) Program. The procedure is highly detailed and contains information of specific value in radionuclide K_d measurements; for example, cautions on preparation and addition of tracer to ground water. This program also has produced recommendations on column methods for K_d measurement (Relyea and others, 1980, appendix C; Relyea, 1982). The latter report contains specific recommendations on water velocity and column dimensions.

5-4 Review of the transport of selected radionuclides in the Interim Risk Assessment

One of the goals of the WRIT Program was to produce a critically reviewed data base of K_d values for a suite of long-lived radionuclides on rocks, sediments, and minerals at candidate repository sites over a wide range of ground-water compositions (Serne and Relyea, 1981). This data base effort has not been sustained at PNNL. In recent years, there has been a strong push in the performance assessment community for reliance on site-specific K_d s, rather than literature-derived values (Krupka and others, 1999; Kaplan and Serne, 2000).

5.2.2.1 Alternatives to single K_d values

It is apparent that with all of the experimental variables noted above that can influence a K_d determination, and with the field-scale spatial variability in sorptive properties of earth materials, it is difficult to characterize a complex and dynamic transport system with a single K_d value. Investigators have suggested various means to deal with this problem:

- Turner (1995) has suggested using surface complexation models to assess the effect of critical system properties (for example, pH) for conditions beyond the range used in the sorption experiments. The calculated sorbed and aqueous-phase concentrations can be used to generate a range of K_d values predicted as a function of these variables. The range of K_d s thus developed can then be used in transport calculations to bound the simulation, rather than assuming a single case.

- Serne and Relyea (1981) considered the inability of the batch method to differentiate multiple species of a radionuclide as this method's major limitation. They recommended using at least two methods (for example, batch and column) in concert to bound radionuclide migration assessments. Such a combined approach has been used by Triay and others (1996) in evaluating sorption retardation of Np by the Yucca Mountain tuffs.

- Vandergraaf and others (1993) consider the effects of variables such as changes in mineralogy and ground-water composition on K_d s for given flowpath segments.

5.2.2.2 Importance of secondary minerals

Many lines of evidence testify as to the importance of iron (Fe^{3+}) oxides and manganese oxides as host phases for trace metals and radionuclides in undisturbed and disturbed earth materials. Many examples of this evidence are described in a report by Jenne (1998a). In summarizing priorities for future metal and radionuclide adsorption research, Everett Jenne of PNNL noted (Jenne, 1998b; p. 551): "Iron oxides are nearly always an important adsorbent in natural systems and, except for reducing conditions or the case where the Fe oxide concentration is low

or another adsorbent is relatively high, they are the dominant adsorbent."

One of the earliest investigations highlighting the importance of such phases in radionuclide retention examined soils at the solid- and liquid-radioactive waste burial grounds at Oak Ridge National Laboratory (Means and others, 1978b). Using selective extraction procedures, the investigators showed that ^{60}Co , ^{244}Cm , ^{241}Am , and ^{238}Pu (lumped) were associated predominantly with Mn oxides. The linear correlation coefficients between radionuclide concentrations and Mn oxide contents in selected soil samples ranged from 0.67 (^{244}Cm) to 0.94 (^{60}Co). For the same soils, the correlation coefficients between these radionuclides and Fe oxide content ranged from 0.12 (^{60}Co) to 0.50 (^{241}Am and ^{238}Pu). The dominant association with the Mn oxides occurred despite the fact that the Fe oxides were present at concentrations 2 to 30 times that of the Mn oxides. Like the Mn oxides, most of the Fe oxides are poorly crystalline (amorphous by X-ray diffraction). In contrast, work by Fruchter and others (1985) on alluvial sediments from the 100 N Area low-level radioactive waste disposal site at the Hanford Reservation suggested that amorphous iron oxides were the dominant sorbing phase for NpO_2^+ [Np(V)]. Np sorption increased as the amorphous Fe oxide content of the sediments increased. Evidence suggested that Mn oxides, occurring in small concentrations in these sediments, were a lesser factor in determining the extent and pH dependence of Np sorption in this system.

The presence of Fe oxides in the weathered basalts and interbeds at the INEEL often has been reported in qualitative terms. Ferrihydrite (or other unspecified Fe-bearing minerals) and Fe oxyhydroxides have been reported to be present as fracture-filling material in basalts and in the interbeds at the Idaho Nuclear Technology and Engineering Center (INTEC, formerly the Idaho Chemical Processing Plant (ICPP)) and the SDA (Estes and McCurry, 1994; Rightmire and Lewis, 1987a). Jorgensen and others (1994) noted that the reddish brown color of the A-B interbed was due to the oxidation of Fe-rich minerals, and that basalt pebbles with Fe-filled vesicles were present in the B-C interbed. Although the presence of these oxide phases has been noted, their quantitative assay and characterization in basalts, fracture fillings, and interbed sediments at the INEEL has been very limited.

Much attention has focused on bulk mineralogic analyses by X-ray diffraction (XRD) (Barraclough and others, 1976, Table A-V; Rightmire and Lewis, 1987b, table 7). In this latter example, Fe oxyhydroxides were, in some cases, removed from interbed sediment samples

from the SDA by a dithionite-citrate extraction (a standard pretreatment for XRD analysis of clay minerals). This treatment also extracts Si, Al, and Mn oxides (Jackson and others, 1986). Such treatments have been used routinely in soil and sediment XRD analysis to decrease fluorescence by the Fe oxides, and thereby improve the quality of the XRD patterns. Analysis of the extract solution for Fe and other oxide constituents can potentially quantify and characterize important radionuclide sorbents in the system. Rosentreter and others (1998) investigated U sorption on sediments from the Delmarva Peninsula in Virginia. Among the mineralogic characteristics of the sediments examined were bulk mineralogy (by optical microscopy), surface area, dithionite-citrate extractable Fe, and oxalate extractable Al. No correlation was observed between K_ds and bulk mineralogic parameters (for example, percent plagioclase feldspar). U K_ds were strongly correlated with surface area. Measured surface areas were strongly correlated with amounts of hydrous oxide coatings on the sediment (as measured by extractable Fe + Al). K_ds could be predicted by a linear regression equation combining pH with either surface area or extractable metals content. Rosentreter and others (1998) noted the importance of characterizing the spatial variability of surface area, even at sites that appeared to be mineralogically homogeneous, when attempting to describe reactive properties such as K_d. Although attention tends to focus on the Fe oxides, the surface complexation properties of Fe and Al oxides are similar, and clay minerals with pH-dependent charge sites are assumed to have surface characteristics similar to these oxides (Bradbury and Baeyens, 1993). Such pH-dependent charge sites on clay minerals are in addition to permanent charge sites that play a major role in the retention of cationic species. Future sorbent characterization research at the INEEL would benefit by focusing on secondary minerals, particularly oxides and clay minerals.

New surface spectroscopic techniques may yield information on surface species and important sorbent phases that can be useful in the development of SCMs to simulate actinide retention. For example, Duff and others (1999a) used X-ray absorption spectroscopy, in combination with microautoradiography, electron microprobe, and petrographic microscopy techniques to study the bonding environment of Pu on the zeolitic Topopah Spring Tuff sampled at Yucca Mountain. Thin sections of the tuff from the 450-m interval were exposed to a synthetic ground water spiked with Pu(V). Large concentrations of sorbed Pu were associated with smectite and Mn oxide fracture minerals. Sorption of Pu to Fe-rich regions was not observed. Both Pu(V) and Pu(VI) were observed as

sorbed species, indicating that heterogeneity is an issue in terms of Pu oxidation at the surface (Duff and others, 1999a, 1999b). In a similar experiment in which a devitrified sample from the Prow Pass Tuff was used, Pu was concentrated in the zones of altered orthopyroxenes; these zones contained amphiboles and Fe-rich amorphous materials (Vaniman and others, 1996). Reduction of Np(V) to Np(IV) at mineral surfaces in granites has been postulated as an explanation for unexpectedly large K_ds (Hadermann and Gunten, 1988); X-ray absorption spectroscopy appears to be a tool to address such questions.

CaCO₃ fills fractures and vesicles in many unsaturated zone cores from near the SDA (Rightmire and Lewis, 1987a) and has been observed to sorb U (Milton and Brown, 1987; Baudin and others, 1988), Np(V) (Morse and Choppin, 1991), and Am (Higgo and others, 1986). Rawson and others (1991) suggested that Am may be preferentially sorbed with respect to Pu or coprecipitated in calcareous surficial and interbed sediments at the SDA. Follow-up mineralogic work to investigate this possibility was noted as planned; the status of such work is currently (1999) unknown.

5.2.2.3 Role of Fe²⁺-bearing minerals

The basalts and interbed sediments at the SDA contain Fe²⁺-bearing minerals. The basalts contain pyroxenes and olivine as major mineral phases and magnetite as an accessory mineral (Knutson and others, 1990). The interbed sediments contain pyroxenes (predominantly augite) and olivine (Bartholomay, 1990b, 1990c). Bondiotti and Francis (1979) first reported the reduction of the relatively mobile species NpO₂⁺ [Np(V)] to a less soluble form (probably NpO₂ [Np(IV)] or related hydrated phase) by contact with various granites and basalts. The results of laboratory experiments, performed under O₂-free conditions, are shown in figure 5-3. That this removal from solution by the igneous rocks was associated with reduction to Np(IV) rather than sorption of Np(V), was demonstrated by extraction from the rock, followed by a separation of Np(IV) from Np(V) by precipitation with zirconium phenylarsonate. Experiments in which Pu(V) was used as the starting species showed rapid reduction to Pu(IV) by basalts, granites, and unweathered shales. These latter rocks did not reduce Np(V). Work by Meyer and others (1985) on Np(V) reduction and retention by the Umtanum Basalt from the Hanford site showed that about 90 percent of the sorbed Np was present as Np(IV), whether the system was oxic or anoxic. This suggests that the process could be operative at ferrous mineral surfaces in contact with the oxygenated ground water of the SDA subsurface environment. With prolonged oxidation of

5-6 Review of the transport of selected radionuclides in the Interim Risk Assessment

basalt surfaces by oxygenated water, all the accessible reactive ferrous iron components of the basalt likely will be oxidized, thus decreasing the impact of the retention mechanism.

Bondiotti and Francis (1979) showed that pretreatment of the Sentinel Gap Basalt (sampled north of the Hanford Reservation) with sodium hypochlorite (to oxidize Fe^{2+} to Fe^{3+}) decreased the removal of Np from solution. The pretreated oxidized basalt showed essentially no Np reduction. The removal of Np from solution by the oxidized basalt may represent sorption of Np(V) by ferric oxyhydroxides formed at ferrous mineral surfaces by the oxidizing action of the sodium hypochlorite. Column experiments in which fractured cores of unaltered and artificially, hydrothermally-altered basalts from the Hanford site showed far greater retention of Pu and Np by the unaltered basalts (Vandegrift and others, 1984). If retention of the radionuclides in the unaltered basalts is due to reduction by ferrous iron, then the lesser retention in the hydrothermally-altered basalts may reflect adsorption by ferric oxyhydroxides formed at mafic mineral surfaces during the autoclaving procedure used to alter the basalts. Petrographic descriptions done as part of the vadose-zone basalt characterization (Knutson and others, 1990) demonstrate that flow tops (and sometimes flow bottoms) are generally oxidized, showing a reddish or orange color that may penetrate about 1 m below the flow surface. On crystal faces and along grain-fracture surfaces of olivine grains there are often brassy-appearing, surface oxidation layers. Locally, oxidation of entire olivine grains may occur.

The possible reduction of actinides by mineral-bound ferrous iron received considerable attention in the Basalt Waste Isolation Program (BWIP) as a possible retardation mechanism. The preceding discussion suggests that its importance *in situ* may be lessened by oxidation of ferrous iron in water-bearing fracture and interbed zones. Its importance in the interbed sediments and basalt fracture zones at the INEEL has yet to be investigated. This geochemical process also should be considered when fresh basalts have been ground and used for K_d determinations.

Besides Fe^{2+} , other possible reductants for actinides in the subsurface environment include naturally occurring and synthetic organic substances (Bondiotti and Sweeton, 1977; Cleveland and Mullin, 1993). The speciation of Am and Pu in ground water at the SDA was investigated by Cleveland and Mullin (1993). They found that water from a perched zone at 65 m sampled at well USGS 92 within the SDA had a greater ability to retain Pu, added as a soluble, reduced [Pu(III), Pu(IV)] spike, in solution than did

any of the other water samples tested. Pu(IV) is probably the dominant Pu form in the waste buried at the SDA (Rightmire and Lewis, 1999). It also was the dominant species identified in ground water sampled at well USGS 40 near the ICPP disposal well (Rees and Cleveland, 1982). Reduction of a major fraction of the Pu(IV) to the more soluble Pu(III) oxidation state was demonstrated in these laboratory studies. Cleveland and Mullin (1993) suggested that the enhanced solubility of Pu in water from well USGS 92 was due to the reducing action of dissolved organic compounds and inorganic complexation by carbonate ions.

5.2.2.4 Influence of organic compounds on subsurface migration of actinides

Organic compounds can form complexes with actinides, which can influence both the solubility and sorption behavior of these radionuclides. The organic compounds may be naturally occurring (for example, humic and fulvic acids) or may be organic materials disposed of in the waste such as ethylenediaminetetraacetic acid (EDTA). The latter class includes degradation products of organic materials in the waste (for example, organic acids produced by the decay of cellulose).

Early work on the complexation of radionuclides by humic substances in water has been reviewed by Boggs and others (1985). The mobility of actinides may be decreased in situations where these radionuclides bind to insoluble humic materials (Boggs and others, 1985). The formation of soluble complexes may enhance transport. Figure 5-4 shows a strong inverse relation between the K_d for Np sorption onto basalt from synthetic ground water and the concentration of dissolved humic acid (a similar pattern was seen with Am). A strong inverse relation between actinide K_d s and dissolved organic carbon (DOC) has been observed in other geochemical environments—for example, in lake water receiving fallout-derived Am and Pu(III, IV) (Nelson and Orlandini, 1986). Cochrane and others (1996) showed that photo-oxidation of organic carbon in the DOC rich water of the Ob River (Russia) increased K_d s for ^{241}Am on river sediments by one to two orders of magnitude.

Recent studies by McCarthy and others (1998a, 1998b) suggest that natural organic matter may play a key role in the rapid ground-water transport of ^{241}Am and other actinides from shallow, unlined disposal trenches in fractured-shale saprolite at Oak Ridge National Laboratory. The saprolite at the Oak Ridge National Laboratory is high in clay minerals, calcite cements, and amorphous Fe- and Mn-oxides, and was expected to sorb the actinides; K_d for ^{241}Am from synthetic ground water in

the absence of natural organic matter was 8,900 dm³/kg. DOC (<1 nm in filtrate) in the shallow (8 m) ground water at the Oak Ridge site ranged from 0.45 to 0.69 mg/L (total organic carbon (TOC) in unfiltered samples ranged from 0.5 to 0.75 mg/L) (McCarthy and others, 1998a). To compare these ranges with those of ground water at the INEEL, Leenheer and Bagby (1982) reported on 77 DOC (< 0.45 μm filtrate) measurements from across the site, including wells at or near the SDA. DOC was 8.7 mg/L in well USGS 92 (depth, 64 m) and ranged from 1.6 to 8.7 mg/L in four SRP aquifer wells (USGS 87 through 90). DOC ranged from 3.3 to 13 mg/L in 10 wells monitoring background SRP aquifer water, remote from the INEEL processing or waste inputs. DOC ranged from 0.3 to 0.7 mg/L in eight SRP aquifer wells (USGS 87 through 90, USGS 117, 119, 120, and RWMC Production), listed in table 14 of Knobel and others (1992b). DOC was 0.8 mg/L in the Big Lost River (BLR) when measured on 19 November 1998. The nature of the DOC at the SDA and its ability to form stable actinide complexes needs to be investigated before the relative importance of this process in actinide migration at the site can be assessed.

The role of synthetic organic compounds in complexing and mobilizing radionuclides in shallow landfills was first reported by Means and others (1978a) for ⁶⁰Co at an intermediate-level liquid waste burial ground at Oak Ridge. This work focused on EDTA, a nonvolatile organic compound that has been specifically monitored at the SDA (Knobel and others, 1992a; Jorgensen and others, 1994). Monitoring for this compound is perhaps due to information received from the waste generators. However, many other complexants are used in decontamination and other operations in the nuclear industry. These include diethylenetriaminepentaacetic acid (DTPA), nitrilotriacetic acid (NTA), N-hydroxyethylethylenediaminetriacetic acid (HEDTA), and citric and oxalic acids (Boggs and others, 1985). Delebard and others (1984) noted that EDTA and HEDTA decreased the sorption of the radionuclides Sr, Np, Pu, and Am on Hanford sediments; HEDTA decreased sorption of ⁶⁰Co, but EDTA increased it. This latter result is seemingly in contrast to the earlier findings at Oak Ridge by Means and others (1978a). The extreme complexity of the sorption of Co(EDTA)²⁻ on Fe- and Mn-coated subsurface materials such as those at Oak Ridge, Hanford, and the INEEL, has been studied by Zachara and others (1995). The sorptive behavior of Co was shown to be linked to the oxidation of Co²⁺(EDTA)²⁻ to Co³⁺(EDTA)¹⁻ by Mn oxides in the subsurface materials, and the subsequent sorption of these different complexes by the Fe and Mn coated surfaces.

In addition to process reagents such as EDTA, organic wastes at disposal sites can contain a wide variety of materials such as plastics, rubber, paper, ion-exchange resins, and solvents. Chemical and biological degradation of these materials can release compounds that can influence actinide sorption. Cellulose materials have received considerable attention due to the large quantities of wood and cardboard used in waste packaging and rags and clothing used in decontamination. Leachates from the alkaline degradation of cellulose (as might occur in a cement matrix) were found to decrease the sorption of Pu onto cement by about two orders of magnitude. The decrease in Pu sorption is believed to be due to strong complexation of the Pu by hydroxyl groups present in compounds such as isosaccharinic acids, which result from the alkaline degradation of cellulose (Greenfield and others, 1992). Although the preceding discussion has focused on sorption for some waste disposal scenarios, organic complexes from cellulose degradation may have a more important effect on solubility of actinides than do the carbonate complexes more typically modeled during the early period following disposal (Stockman, 1998).

5.3 Evaluation of the K_ds for Am, U, and Pu used in the Interim Risk Assessment model—experimental data

The purpose of this section is to evaluate the K_ds selected and applied to the IRA for Waste Area Group 7 (WAG-7) given the known, site-specific information. K_ds used in the IRA model (Becker and others, 1998) were selected from those reported by Dicke (1997). These K_ds were determined to be the most appropriate for fate and transport modeling at this site. The intent was to maintain conservatism in the transport simulations by selecting the lowest values from a range of K_ds. This was done for Am and Pu. For U and Np, intermediate K_ds were used. K_ds for Am, U, and Pu were determined experimentally using aquifer solids from the INEEL and synthetic ground water similar in chemical composition to that from the SRP aquifer (Newman and others, 1995). K_ds for Np were selected from the literature. In this review, site-specific K_ds for Am, U, and Pu are evaluated first, followed by a discussion of the Np K_ds.

K_ds for Am, U, and Pu, reported by Dicke (1997), are based on results from batch and column experiments conducted by Goff (1994) and Newman and others (1995). Table 5-2 summarizes the K_ds in these experiments. For the interbed sediments, Dicke (1997) recommended that K_ds of 450 mL/g for Am, 6 mL/g for U, and 5,100 mL/g for Pu, be used in the IRA model. K_ds of 225 mL/g and 900 mL/g for Am, 9 mL/g for U, and 3 mL/g for Pu were

5-8 Review of the transport of selected radionuclides in the Interim Risk Assessment

recommended for sensitivity analyses in the Addendum to the Work Plan (1998).

K_{ds} also were determined for a crushed basalt. However, vesicles and fractures in basalt were assumed to be lined with minerals similar in sorption properties to those of the interbed sediment. Therefore, use of the interbed K_{ds} was suggested for modeling sorption of Am, Pu, and U in basalt. The basalt experiments and results are included in this review for the sake of completeness.

The following is an evaluation of the experimental procedures and results reported by Newman and others (1995). Some of the experiments were conducted at Clemson University (Goff, 1994). Other experiments were conducted by INEEL personnel.

5.3.1 Materials and methods

A combination of batch and column experiments were used to determine K_{ds} for Am, Pu, and U in basalt and interbed sediment.

5.3.1.1 Solid phases

5.3.1.1.1 Interbed sediments

Five interbed samples from various depths were composited, and the <0.25-mm size fraction was used for the experiments. This fraction was a sandy loam (table 5-3). Major minerals in the sand-sized fraction were pyroxene, plagioclase, quartz, olivine, and magnetite. The clay-sized fraction consisted of mica, montmorillonite, vermiculite, and chlorite. Some Mn and Fe oxide coatings were present. Cation exchange capacity was 17.39 meq/100 g.

5.3.1.1.2 Basalt

A boulder from near the SDA was used to determine K_{ds} for Am, Pu, and U in the INEEL basalt. Cores were drilled from the boulder for use in intact basalt column experiments. The remainder of the boulder was crushed for use in crushed-basalt batch and column experiments. Only the <2-mm size fraction was used. This fraction was mostly coarse sand and some silt (table 5-3). Major minerals were pyroxene, plagioclase, and olivine. The cation exchange capacity was 6.04 meq/100 g.

5.3.1.2 Aqueous phase

Synthetic ground water was used in the batch and column experiments. The water was formulated on the basis of analyses from the SRP aquifer (Wood and Low, 1986). The synthetic ground water used by Newman and others (1995) contained smaller concentrations of most constitu-

ents than did the average ground water reported by Wood and Low (1986) and smaller concentrations than have been measured in the perched water beneath the SDA (table 5-4). Actinides were added to the synthetic ground water from stock solutions. The initial chemical form of these stock solutions was: U as uranium nitrate in the VI oxidation state, Am as americium chloride in the III oxidation state, and Pu as plutonium nitrate in the IV oxidation state. Upon addition of the Pu stock solution to the synthetic ground water, the oxidation state changed. About 5 percent was Pu(III), 40 percent was Pu(IV), 50 percent was Pu(V), and 5 percent was Pu(VI). About half of the Pu(IV) was in the form of colloids greater than 0.1 μm in size.

5.3.1.3 Column experiments

5.3.1.3.1 Crushed basalt and interbed sediments—saturated

Standard procedures were used for packing the columns and conducting the leaching experiments. The crushed-basalt and interbed columns were polyvinylchloride, 15.1 cm long and 2.5 cm inside diameter. This is an adequate length:width ratio for establishing one-dimensional advective-dispersive flow.

Synthetic ground water without actinides was eluted through the columns until pH and conductivity of column effluent were the same as those of the influent. About one pore volume of synthetic ground water containing Am, U, or Pu, then was added to each column, and leached with 200 pore volumes of actinide-free ground water. ^3H also was added as a conservative tracer. Replicate columns were used for Am and U; three to five columns were used for Pu. Average pore-water velocities were 6 m/d. Velocities as slow as 0.6 m/d and as fast as 60 m/d were evaluated. Columns were saturated and leached from bottom to top.

Synthetic ground water containing Br and ^{90}Sr also was eluted through two columns packed with crushed basalt. These experiments were designed to identify any differences between transport under saturated- and unsaturated-flow conditions.

5.3.1.3.2 Intact basalt—saturated

The intact basalt cores (20.3 by 3.8 cm) were sealed in polymeric resin, then placed in polycarbonate tubes and the annular space filled with resin. They were filled and leached in the same manner as those containing unconsolidated cores. The intact basalt column experiments eluted contaminated ground water until the effluent concentrations were equal to the influent concentrations. Only ^{90}Sr and the conservative tracer Br were used.

Table 5-2. Summary of K_ds obtained using batch and column tests reported by Dicke (1997) (modified from Newman and others, 1995)

[mL/g, milliliters per gram; EDTA, ethylenediaminetetraacetic acid]

| Isotope | Media | Batch test K _d (mL/g) | Column test K _d (mL/g) | Enhanced mobility K _d (mL/g) | Recommended for risk assessment K _d (mL/g) |
|---------------------------|--------------|-------------------------------------|--------------------------------------|---|---|
| ²⁴¹ Am | Basalt | 70-280 | | 0.18 | 450** |
| ²⁴¹ Am | Interbed | 450-1,100 | | * | 450 |
| ²³⁹ Pu (total) | Basalt | | | 0.25 | 5,100** |
| ²³⁹ Pu (total) | Interbed | | | * | 5,100 |
| Pu(V) | Basalt | 70-130 | | | |
| Pu(V) | Interbed | 5,100-7,900 | | | |
| Pu(V) | Surface Soil | 7,800-22,000 | | | |
| Pu(VI) | Basalt | 12-24 | | | |
| Pu(VI) | Interbed | 110-690 | | | |
| Pu(VI) | Surface Soil | 1,800-4,900 | | | |
| Pu(EDTA) | Basalt | 0.04-0.05 | | | |
| Pu(EDTA) | Interbed | 4-5 | | | |
| Pu(EDTA) | Surface Soil | 40-490 | | | |
| ²³³ U | Basalt | 4-6 | 0.2-0.3 | | 3** |
| ²³³ U | Interbed | 3-6 | 9 | | 6 |

* Although enhanced mobility fraction was observed, it was too small to be modeled.

** The assumption was made that sorption in basalt was controlled by minerals lining the fractures and having the same sorption capacity as that of the interbed sediment.

5-10 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 5-3. Particle-size distribution for five interbed sediments and their composite, and for crushed basalt used in K_d experiments at the Idaho National Engineering and Environmental Laboratory (modified from Goff, 1994)

| Size (mm) | Interbed-1 (percent) | Interbed-2 (percent) | Interbed-3 (percent) | Interbed-4 (percent) | Interbed-5 (percent) | Composite interbed (percent) | Crushed basalt (percent) |
|-----------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|------------------------------------|-----------------------------|
| >2 | 12.7 | 33.8 | Not reported | 38.6 | 9.4 | 16.7 | Not reported |
| 1.0-2.0 | 13.9 | 16.8 | 1.6 | 17.3 | 1.9 | 12.2 | 50.6 |
| 0.5-1.0 | 12.9 | 12.4 | 3.1 | 9.8 | 1.8 | 12.2 | 26.7 |
| .25-.5 | 29.4 | 14.7 | 3.6 | 10.9 | 2.5 | 15.5 | 6.3 |
| .1-.25 | 27.6 | 26.9 | 3.9 | 9.4 | 10.2 | 20.9 | 3.9 |
| .05-.1 | 6.5 | 13.3 | 10 | 27.6 | 25.3 | 12.9 | 0.9 |
| .002-.05 | 7.8 | 13.6 | 59.5 | 22.2 | 53.4 | 22.4 | 8.5 |
| <.002 | 2 | 2.3 | 18.3 | 2.7 | 4.9 | 3.9 | 3.1 |

Table 5-4. Composition of synthetic ground water, water from the Snake River Plain aquifer, and perched and soil-zone water (from Newman and others, 1995)

[mg/L, milligrams per liter]

| Constituent | Synthetic ground water* | Snake River Plain aquifer** | | | Perched and soil zone water*** | | |
|------------------|----------------------------|-----------------------------|-------------------|------------------|--------------------------------|-------------------|-------------------|
| | Base chemistry (mg/L) | Average (mg/L) | Maximum (mg/L) | Minimum mg/L) | Average (mg/L) | Maximum (mg/L) | Minimum (mg/L) |
| Ca | 11.5 | 51 | 120 | 5.0 | 41 | 70 | 26 |
| K | 9.8 | 4 | 12 | 0 | 5.8 | 12 | 1.0 |
| Mg | 8.3 | 18 | 54 | 0.2 | 17 | 25 | 14 |
| Na | 19.7 | 26 | 140 | 4.0 | 53 | 120 | 7 |
| Cl | 18.9 | 28 | 230 | 1.8 | 41 | 81 | 14 |
| SO ₄ | 23.4 | 41 | 218 | 1.8 | 45 | 120 | 10 |
| HCO ₃ | 96.6 | 220 | 510 | 52 | 190 | 280 | 120 |
| F | 0.5 | 0.6 | 11 | 0.03 | 0.3 | 0.6 | 0.2 |
| SiO ₂ | 10.0 | 50 | 138 | 5.8 | 21 | 34 | 13 |
| pH | 8.0 | 7.8 | 9.1 | 7.0 | 8.2 | 9.1 | 7.7 |
| I(mol/l) | 0.0048 | 0.008 | 0.02 | 0.004 | | | |

*Newman and others, 1995, **Wood and Low, 1986; ***Rightmire and Lewis, 1987b (table 4-4, this report)

5.3.1.3.3 Crushed basalt—unsaturated

Unsaturated column experiments were conducted to compare K_d s from saturated and unsaturated columns. Crushed basalt was used. Columns were 25.4 cm long and 2.77 cm inside diameter. The same column was used for six unsaturated experiments and one saturated experiment. Moisture content of the columns ranged from 29 to 49 percent of saturation. Br and ^{90}Sr were added as tracers.

5.3.1.4 Batch experiments

The batch test design was adapted from the American Society for Testing Materials (ASTM) method D4319 (1993). Solid:liquid ratios were chosen to remove enough reactant so that a change in concentration could be measured. For interbed experiments conducted by Goff (1994), solid concentrations ranged from 3.5 to 150 g/L, and basalt concentrations ranged from 20 to 500 g/L. For the INEEL crushed-basalt experiments, solid concentrations ranged from 100 to 700 g/L. The aqueous and solid phases were separated by filtering through a 0.2 μm cellulose acetate filter or by centrifuging at 3,200 rpm for 20 minutes. Goff (1994) used 15-mL polystyrene centrifuge tubes. Duplicates with appropriate blanks were equilibrated for 14 time periods ranging from 5 minutes to 400 hours. INEEL personnel used 50-mL polycarbonate centrifuge tubes for Am and Pu. Before the actinides were added, basalt and sediments were prerinsed with uncontaminated ground water for two 12 hour periods.

5.3.2 Results and discussion

5.3.2.1 Batch experiments

The K_d s used in the IRA model were determined from the batch experiment results which are presented first. Results from the column experiments and other assorted experiments then follow. The following results are from batch experiments conducted at Clemson University.

K_d s for the batch experiments were calculated for 400 hours of equilibration. Equilibrium concentrations of U in the crushed basalt were attained within 61 hours, and in the interbed sediment, within 103 hours. Time required to attain equilibrium for Am and Pu was not given.

5.3.2.1.1 Am

The INEEL K_d s for ^{241}Am in interbed sediments reported by Dicke (1997) ranged from 450 to 1,100 mL/g (table 5-2). These values were obtained using initial

concentrations ranging from 3.5 to 15 Bq/mL (28 to 119 $\mu\text{g/L}$). The initial sediment concentration was 2.5 g/L. Individual K_d s for each concentration were not reported; however, it is apparent that the K_d s for Am were dependent on initial concentration. This is indicative of nonlinear sorption, where the relative amount sorbed decreases as aqueous concentration increases. Thus the largest K_d of 1,100 mL/g would represent the smallest initial concentration of 3.5 Bq/mL, and the lowest K_d of 450 mL/g represents the initial concentration of 15 Bq/mL. For Am concentrations outside the range used in these experiments, K_d s could be either larger or smaller.

Sorption of Am by the crushed basalt was also apparently nonlinear. Distribution coefficients ranged from 70 to 280 mL/g. Initial Am concentrations ranged from 1.38 to 7.34 Bq/mL (11 to 58 $\mu\text{g/L}$), and the initial sediment concentration was 12.5 g/L.

5.3.2.1.2 U

Only one initial concentration and one solid concentration were used to determine U K_d s. For the interbed sediment, a K_d of 5.1 mL/g (table 5-2) was calculated using an initial concentration of 69.05 Bq/mL and a solid concentration of 6.8 g/L. A K_d of 4.7 mL/g for the crushed basalt was calculated using an initial concentration of 5.94 Bq/mL, and a solid concentration of 200 g/L.

5.3.2.1.3 Pu

The mobility of Pu is affected by its oxidation state, which can be III, IV, V, or VI. More than one oxidation state can coexist in solution. The III and IV oxidation states predominate under reducing conditions, and the V and VI oxidation states predominate under oxidizing conditions. As was previously mentioned, the oxidation state of Pu after it had been added to the synthetic ground water was a mixture of all four, although the IV and V states dominated. To evaluate changes in oxidation state with time, a 14-day experiment was conducted in which synthetic ground water spiked with Pu(IV) was allowed to equilibrate. The amount of Pu(III, V, VI) remained relatively constant; however, within the first 24 hours, Pu(IV) activity in the solution phase decreased by 50 percent. This decrease in activity was attributed to settling of polymerized Pu(IV). Between 1 and 14 days, the Pu distribution remained relatively constant. After 14 days, the container was shaken and Pu activity increased to 90 percent of the initial value because of resuspension of most of the polymerized Pu(IV). From this experiment, it was concluded that Pu(IV) is essentially insoluble and that a K_d for this oxidation state would be inappropriate. Therefore,

5-12 Review of the transport of selected radionuclides in the Interim Risk Assessment

only the Pu(V) and Pu(VI) oxidation states were used in batch experiments to determine K_d s.

Pu(V) K_d s for the interbed sediment ranged from 5,100 to 7,900 mL/g (table 5-2). Pu(V) K_d s for a surface soil included in these experiments ranged from 7,800 to 22,000 mL/g. The smallest value of 5,100 mL/g was used in the IRA modeling. Pu(VI) K_d s were smaller, ranging from 110 to 690 mL/g for the interbed sediment, and from 1,800 to 4,900 mL/g for the surface soil. Sorption of Pu in the presence of EDTA was significantly less. In the presence of EDTA, K_d s for the interbed sediment averaged about 5 mL/g, and for the surface soil, about 400 mL/g. In these experiments, the initial Pu concentration remained constant, but the solid concentration was varied. Therefore, nonlinear sorption of Pu could not be evaluated. Sorption tended to increase with solids concentration, but the trend was not consistent. In addition, at small suspended solids concentrations, Pu remained in the initial oxidation state (either V or VI). However, at larger suspended solids concentrations, Pu(V) reduced to Pu(IV) and Pu(VI) to Pu(V). This reduction was attributed to mediation by Fe and/or Mn containing minerals.

Pu(V) K_d s for crushed basalt ranged from 70 to 130 mL/g. Pu(VI) K_d s were much smaller, ranging from 12 to 24 mL/g. Sorption of a Pu(EDTA) complex was minimal; K_d s averaged about 0.4 mL/g.

5.3.2.2 Risk assessment K_d s for Am, U, and Pu

K_d s for crushed basalt were not used in the IRA model. This decision was justified for several reasons. Crushed basalt has a high percentage of fresh mineral surfaces not present in the aquifer. These surfaces will have sorption properties that are different from those of minerals lining basalt fractures and vesicles. Also, the surface area of crushed basalt most likely will not be comparable to that of basalts in the aquifer. In addition, Barney (1981) showed that freshly crushed basalt of the Columbia River group slowly weathers during the course of laboratory experiments. K_d s measured under such conditions risk being affected by changing sorption properties.

The proposed K_d s for Am, U, and Pu in the interbed sediments should be used with caution for IRA modeling. Each K_d represents one unique measuring point in a complex geochemical environment. Combining the five interbed samples homogenized sediments that have different grain-size distributions and mineralogy. Each of these individual sediments could have different sorption properties. In addition, using the <0.25-mm size fraction eliminated 40 percent of the solids and biased the K_d toward larger values because of the greater surface area of the finer-size fraction used in the experiments.

The assumption that fractures and vesicles in the basalt have the same sorption properties as the interbed sediments may or may not be accurate. Minerals present in basalt fractures tend to be finer grained, such as clay minerals, or in the form of precipitates, such as calcite. Although these types of minerals are also present in the interbed sediments, their sorption properties may be different from those of the bulk interbed material, which also contains coarser particles of different mineralogy (sand-size grains of quartz and feldspar).

The synthetic ground water used by Newman and others (1995) contained smaller concentrations of most constituents than did the average ground water reported by Wood and Low (1986) and smaller concentrations than did perched and soil-zone water (table 5-4). Sorption of Am, U, and Pu is affected by aqueous speciation. All three actinides form aqueous CO_3 complexes. In general, sorption decreases as CO_3 concentrations increase. Thus, the K_d s determined for the synthetic ground water may be different from K_d s for perched ground water.

5.3.2.3 Column experiments

The following results are for column experiments conducted at Clemson University.

5.3.2.3.1 Interbed sediment columns

Tritium was used as a conservative tracer to evaluate column packing. Breakthrough curves for ^3H matched the shape expected for one dimensional advective-dispersive transport of a nonreactive solute (fig. 5-5). Channeling was not observed in any of the columns.

Essentially all of the Am was removed from two columns containing interbed sediment; however, there was still a small enhanced-mobility spike within the first five pore volumes (fig. 5-6). About 1.8 percent and 1.9 percent of the Am applied initially was recovered after elution of 200 pore volumes of actinide-free ground water. Most of the Am remaining in the columns was distributed in the first 3 cm.

Most of the Pu applied in the initial spike also was removed from three interbed sediment columns. There was still a small enhanced-mobility spike within the first five pore volumes (fig. 5-7). About 0.01 percent, 0.1 percent, and 0.15 percent of the applied Pu was recovered. No measurements of the distribution of the remaining Pu were reported.

About 90 and 99 percent of the applied U was recovered from two columns; however, the breakthrough curves were delayed by about 20 to 30 pore volumes (fig. 5-8). K_d s calculated from the retardation factors were 12 and 9 mL/g for the two columns studied.

One potential problem with the interbed column experiments is the increase in initial influent pH of 8 to about 8.4. Conductivity also increased. These observations, plus the fact that the influent feed solution was undersaturated with respect to calcite, indicate calcite dissolution during the column experiments. Geochemical calculations indicate that a 0.4-unit change in pH can change the K_d for U by a factor of 3 or 4. Calcite dissolution also may have an effect on Am and Pu transport in these experiments.

5.3.2.3.2 Crushed-basalt columns

Tritium was used as a conservative tracer to evaluate column packing. Breakthrough curves for ³H matched the shape expected for one-dimensional advective-dispersive transport of a nonreactive solute (fig. 5-9). Channeling was not observed in any of the columns.

After elution of 200 pore volumes of actinide-free ground water, the amount of Am recovered in effluent from two columns containing crushed basalt was 9 and 14 percent of the total concentration added initially. Most of the Am eluted between pore volumes 1 and 3, in what is referred to as an enhanced-mobility fraction (fig. 5-10). The maximum Am concentration in this fraction was about 20 percent of the influent concentration. After this initial spike, effluent concentrations became constant between 0.01 and 0.1 percent of influent concentration. Analytical detection limits were not reported. Retardation factors for the enhanced-mobility fraction in the two columns were 1.6 and 1.7, equivalent to a K_d of 0.18 mL/g (table 5-2). Gamma scans revealed that the Am remaining was distributed throughout the length of the columns.

After eluting with 200 pore volumes of actinide-free ground water, the amount of Pu recovered in effluent from five columns containing crushed basalt was 10 percent, 17 percent, 24 percent, 34 percent, and 57 percent, of the total initial concentration added. Some of the Pu eluted in an enhanced-mobility fraction between pore volumes 1 and 3, similar to the elution of Am. After the initial Pu spike, concentrations slowly decreased over 200 pore volumes (fig. 5-11). Maximum Pu concentrations in the initial spike ranged from 20 to 50 percent of the influent concentration. Retardation factors for the enhanced-mobility fractions were about 2, equivalent to a K_d of 0.25 mL/g (table 5-2). The distribution of Pu remaining in the columns was not determined.

After eluting with 200 pore volumes of actinide-free ground water, essentially all (94 and 104 percent of the total initial concentration) of the U was recovered from two columns containing crushed basalt. U concentrations in column effluent began to increase at about pore volume

1 and peaked at pore volume 2. Concentrations then slowly decreased throughout the remainder of the experiments (fig. 5-12). Retardation factors were 1.6 and 2, equivalent to K_ds of 0.2 and 0.3 mL/g (table 5-2). Maximum concentrations were 60 to 70 percent of the influent concentration. Early elution of U was assumed to be related to weak sorption of the aqueous phase as opposed to the presence of an enhanced-mobility fraction.

5.3.2.3.3 Enhanced mobility fraction

The enhanced-mobility fraction responsible for the early elution of Am and Pu (figs. 5-6, 5-7, 5-10, and 5-11) indicates that both actinides may move in the subsurface at a significantly faster rate than predicted by equilibrium-based distribution coefficients. At least three possible mechanisms could explain the enhanced mobility of Am and Pu: (1) transport as a colloid, (2) transport as a weakly sorbing aqueous complex, and (3) slow reaction kinetics.

Other researchers have found Am to be associated with colloidal material (Means and others, 1978a; Travis and Nuttall, 1985; Penrose and others, 1990; Moulin and others, 1991). Both Pu (Choppin and Stout, 1989) and Am (Nash and others, 1988) have been shown to strongly sorb on silica. It is possible that Am and Pu sorbed on fine-grained material created during the basalt crushing process. These grains then could have been removed during leaching. Colloids also could have formed in the columns by *in situ* weathering reactions of the fresh basalt. Barney (1981) observed evidence for weathering in experiments with freshly crushed basalts from the Columbia River group.

Hydrolysis products of Am and Pu could have formed colloids. It is clear from the shape of the breakthrough curves that Pu was more mobile than Am. The Pu-oxidation-state experiment showed that colloidal Pu(IV) can form in synthetic ground water. This experiment indicated that Pu(IV) and (V) were the dominant oxidation states of the initial solution. Most Pu(IV) was likely present as a colloid, and some could have been transported through the columns. The Pu(V) could have been sorbed to the stationary phase or sorbed and transported as a colloid.

The enhanced-mobility fraction also could represent transport as a mobile aqueous CO₃ complex. In a separate experiment with Pu, increasing alkalinity from 0.05 to 1.1 g/L as CaCO₃ increased the apparent enhanced-mobility fraction from 52.2 to 78 percent.

Kinetically-limited sorption could account for the enhanced-mobility fraction. In column tests with Am, increasing the flow rate from 0.6 to 60 m/d increased the enhanced-mobility fraction of Am from 1.3 to 43 percent,

5-14 Review of the transport of selected radionuclides in the Interim Risk Assessment

although the location of the peaks did not change. The faster flow rates may have increased the mass of mobile colloids or decreased contact time between actinide and sorbing material.

5.3.2.4 Additional experiments

Several other experiments were conducted to investigate various aspects of sorption in this system. These are briefly summarized in the following sections.

5.3.2.4.1 pH and ionic-strength variability

Effects of pH and ionic strength on sorption were evaluated for U in a series of batch experiments. Synthetic ground water spiked with U was used as a base solution. Ionic strength was increased from 0.004 to 0.01 and 0.02 by addition of K or CaCl₂. pH was adjusted to 6, 8, or 10. For crushed basalt, U sorption decreased with increasing Ca concentration and increasing pH. K had little effect on U sorption. At lower pH values, UO₂²⁺ and Ca²⁺ likely compete for sorption sites. As pH increases, U complexation with CO₃ results in less sorption. Trends were similar for interbed sediment but differences were not as great. No K_ds were reported; however, these data point out the dependency of sorption on ground-water composition.

5.3.2.4.2 Reproducibility of K_ds

Batch experiments were used to compare K_ds for ⁹⁰Sr sorption in experiments conducted at Clemson University and the INEEL. K_ds were comparable; however, initial differences in aqueous concentration and solids concentration did not allow a statistical evaluation. No data were provided on the reliability of Am, Pu, and U K_ds.

5.3.2.4.3 Solid:liquid ratio

K_ds measured in batch tests can decrease as suspended solids concentration increases. Possible explanations include (1) an increase in proximity of solids resulting in decreased surface area available for sorption, (2) an increase in the amount of stagnant water in grain fractures and pore spaces, resulting in more time needed for diffusion to sorption sites, and (3) an increase in the proportion of colloidal material that may not be removed by filtration, resulting in apparent greater aqueous concentrations.

⁹⁰Sr K_ds decreased from 2.8 mL/g at a solid:liquid ratio of 0.1, to 1.9 mL/g at a solid:liquid ratio of 1.9. There apparently was some effect of solid:liquid ratio on sorption, but only when solid:liquid ratios exceeded 0.7. These data do not necessarily apply to the actinides. For Pu(V) and Pu(VI) sorption by the surface soil, K_ds did decrease

as solids concentration increased; however, the data were inconclusive for the interbed sediment and crushed basalt.

5.3.2.4.4 Crushed basalt versus intact basalt

Experiments using crushed versus intact basalt were conducted only with Br and ⁹⁰Sr; however, some basic observations may be generic enough to extrapolate to Am, U, and Pu. Unfortunately, different scales were used to plot the data, so it is difficult to make direct comparisons.

Breakthrough curves for ⁹⁰Sr in crushed basalt columns were typical of those for advective-dispersive flow. ⁹⁰Sr K_ds were about 3.5 mL/g. Breakthrough curves for ⁹⁰Sr in intact basalt cores did not resemble those expected for advective-dispersive flow in one dimension. A breakthrough of about 60 percent of the initial concentration was followed by a very slow increase in concentration. Two retardation factors of about 1 were calculated, equivalent to a K_d of 0.3 mL/g. This value is significantly smaller than the K_ds for ⁹⁰Sr in the crushed basalt and interbed sediment. The larger ⁹⁰Sr K_ds indicate that transport of ⁹⁰Sr through the fractures in the intact basalt was too rapid for equilibrium sorption, or that the sorption properties of the basalt fractures were different from the sorption properties of the crushed basalt and interbed sediment.

In summary, contaminant transport in intact basalt cores did not follow traditional patterns of advective-dispersive flow models. Transport may be dominated by preferential flowpaths and diffusion into and out of the basalt matrix. When flow through fractured media is anticipated, the sorption rate constant should be compared with the hydraulic residence time to evaluate whether equilibrium conditions exist.

5.3.2.4.5 Unsaturated column experiments

Crushed-basalt columns were used for unsaturated column experiments. Water content ranged from 33 to 50 percent of saturation. Both Br and ⁹⁰Sr breakthrough curves and K_ds were similar to those in the saturated crushed basalt experiments. Newman and others (1995) concluded that saturated-column K_ds can be applied to sorption in the unsaturated zone.

5.3.3 Summary of the evaluation of K_ds for Am, U, Np, and Pu used in the Interim Risk Assessment

K_ds determined in these experiments for Am, U, and Pu are listed in table 5-2. Also listed are the K_ds recommended for use in the IRA model. Specific concerns

regarding the K_d s recommended for use in the IRA model are presented here.

(1) The concentrations of major cations and anions in the synthetic ground water used in these experiments are generally smaller than the concentrations measured in perched and infiltrating water at the SDA. This could result in underestimating the amount of aqueous complexation of Am, U, and Pu, and overpredicting sorption. Thus, the recommended K_d s could be too large. Larger concentrations of cations and anions also could increase competition for sorption sites, thereby decreasing actinide sorption. If there was calcite dissolution, as indicated by the column experiments, then the final solution composition could have been closer to that of natural waters; however, final compositions apparently were not determined.

(2) Sorption of Am as a function of aqueous concentration was apparently nonlinear. Sorption of Pu and U was probably nonlinear as well. This means that the measured K_d s are relevant only for the concentrations used in the experiments. Concentrations at the SDA that are outside of the range used in these experiments will have K_d s that are either smaller or larger than those reported here.

(3) The experimental data show that Pu sorption is highly dependent on oxidation state. The K_d recommended for IRA modeling is for Pu(V) and would not be applicable to the more mobile Pu(VI).

(4) The K_d s recommended in the IRA model are from the fine-grained fraction of one composite interbed sample that has not been shown to represent the range of sorption properties in the unsaturated zone.

(5) The assumption that sorption properties of the interbed sediments are comparable to those of the fractures in the basalts needs to be verified.

(6) The enhanced-mobility fraction responsible for the early elution of Am and Pu in the column experiments raises questions about the mechanisms responsible for transport of Am, U, and Pu. If this fraction represents transport as aqueous complexes, then the K_d s used in the IRA model are too large. If the actinides are transported as colloids, basing risk assessment on sorption-controlled transport may need to be reevaluated.

(7) In these experiments, any actinide passing through a 0.2- μ m membrane filter or removed from solu-

tion by centrifugation for 20 minutes at 3,200 rpm was considered dissolved. Other researchers have shown that neither of these procedures necessarily removes all colloids from solution. If some of the Am, U, or Pu assumed to be dissolved were present as colloids, the apparent aqueous-phase concentration would be larger, resulting in smaller calculated K_d s. From a solute transport perspective, underestimating K_d s would result in an increase in the predicted transport distance of an actinide.

5.4 Evaluation of the K_d s for Np used in the Interim Risk Assessment model—literature review

The K_d for Np used in the IRA model was 8 mL/g, based on a range of 1 to 80 mL/g. These values are from Dicke (1997) and were selected from the literature. In the Addendum to the Work Plan, a sensitivity analysis for Np was proposed using Np K_d s of 4 mL/g (half the base case) and 16 mL/g (twice the base case). For basalt, the assumption was made that fracture surfaces were lined either with fine-grained sediments or with chemical alteration products that resulted from water movement along the fractures over extended periods of time (Becker and others, 1998). Therefore, the same K_d s used to simulate sorption on sediments were used to simulate transport through basalt.

Dicke (1997) selected Np K_d s from three sources, each a compendium of K_d s from the literature (Baes and Sharp, 1983; Ticknor and Ruegger, 1989; Sheppard and Thibault, 1990). All the references in these three compendiums have been evaluated for their applicability to the INEEL. The review presented in this report is not an exhaustive review of Np sorption, but a review of those references upon which the K_d s cited by Dicke (1997) are based. The approach used in this review was to summarize the experiments and results in two different tables. Data from those references that are possibly relevant to the INEEL are summarized in table 5-5 and discussed in detail in this report. Those references not considered to be relevant to the INEEL are summarized in table 5-6. Unless specified otherwise, all experiments refer to the Np(V) oxidation state.

5-16 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 5-5. Np K_d s from references considered applicable to the Idaho National Engineering and Environmental Laboratory

[K_d s, distribution coefficients; mL/g, milliliters per gram]

| Reference | Solid phase | Location of sample | K_d s (mL/g) |
|----------------------------|--------------------------------|--------------------|----------------|
| Barney (1981) | Altered basalt | Hanford | 17-70 |
| Barney (1981) | Secondary minerals from basalt | Hanford | 13-100 |
| Barney (1982) | Sandstone | Hanford | 13-20 |
| Barney (1982) | Tuff | Hanford | 17-33 |
| Salter and others (1981b) | Secondary minerals | Hanford | 40 |
| Routson and others (1977) | Washington soils | Washington | 2.4-3.9 |
| Sheppard and others (1979) | Idaho soils | Idaho | 38-142 |
| Dicke (1997) | Literature review | Variable | 1-80 |

Table 5-6. Np K_d references not considered applicable to the Idaho National Engineering and Environmental Laboratory

[K_d s, distribution coefficients]

| Reference | Summary of experiments | Reasons for rejecting K_d s | Additional comments |
|-----------------------------|---|---|--|
| Dahlman and others (1976) | Batch Np sorption experiments on clay | Experimental conditions not applicable to those at the INEEL | |
| Nishita and others (1979) | Batch Np sorption experiments using seven soils | Inadequate data on soil properties and aqueous chemistry for comparison with the INEEL data | Np sorption increased with pH |
| Allard and others (1980) | Batch Np sorption experiments using freshly crushed individual minerals and granite | Use of individual mineral phases inappropriate for comparison with the INEEL data. Crushing not appropriate | Np sorption increased between pH 7 and 9 |
| Ames and Rai (1978) | Review of Np sorption literature | K_d s cited here described in other references | |
| Johnston and Gillham (1980) | Review of Np sorption literature | K_d s cited here described in other references | |
| Coughtrey and others (1985) | Review of Np sorption literature | K_d s cited here described in other references | |
| Nishita and others (1981) | Soils contaminated with Np, then extracted with acetate, Ca and pure water | No estimates of K_d s. Not enough data to calculate K_d s | |

Table 5-6. Np K_d references not considered applicable to the Idaho National Engineering and Environmental Laboratory—Continued

| Reference | Summary of experiments | Reasons for rejecting K _d s | Additional comments |
|------------------------------|--|--|--|
| Seitz and others (1979) | Np eluted through sandstone columns | No K _d data given | A small fraction of Np eluted with nonreactive tracer, indicating possible colloid transport or channeling of aqueous Np |
| Seitz and others (1978) | Batch Np sorption experiments using various rock types and distilled water | Solid and aqueous phases not applicable to the INEEL | |
| Anderson and others (1982) | Batch Np sorption experiments using several rock types and pure mineral phases | Solid phases not applicable to the INEEL data. Crushing inappropriate | |
| Barney (1984) | Batch Np sorption experiments using basalts and interbed materials from Hanford, Wash. | Experimental data fitted to Freundlich isotherm. No K _d data given. | |
| Bondietti and Francis (1979) | Batch Np sorption experiments using crushed igneous rocks and shales under reducing conditions | No K _d data given | Increased sorption of Np with time interpreted as kinetically controlled reduction of NpO ₂ ⁺ to NpO ₂ and increased sorption |
| Meyer and others (1983) | Recirculating column experiment with alumina | Insufficient information on aqueous phase. Solid phase not applicable to the INEEL | Np sorption increased with pH |
| Nakayama and others (1988) | Np leached through quartz-packed column. | Experimental conditions not applicable to those at the INEEL | Some Np eluted with nonreactive tracer, indicating colloidal transport |
| Salter and others (1981b) | Batch Np sorption experiments with crushed basalts | Crushed basalts not representative of Np sorption in basalt fractures at the INEEL | |
| Sheppard and others (1987) | Np eluted through soil cores from Canada | Aqueous- and solid-phase chemistries different from those at the INEEL | |
| Thibault and others (1990) | Review of Np sorption literature | K _d s cited here described in other references | |

5.4.1 Studies of potential relevance to the Idaho National Engineering and Environmental Laboratory

Routson and others (1977) conducted batch sorption experiments for ^{237}Np on subsoil samples from Washington and South Carolina. The Washington soil had a pH of 7, 0.8 mg/g CaCO_3 , a cation exchange capacity (CEC) of 4.9 meq/100 g, 10 percent silt, and 0.5 percent clay. The South Carolina soil had a pH of 5.1, <0.2 mg/g CaCO_3 , a CEC of 2.5 meq/100 g, 3.6 percent silt, and 37 percent clay. Sorption was measured in solutions with variable concentrations of $\text{Ca}(\text{NO}_3)_2$ or NaNO_3 . The initial Np concentration was 3.7 $\mu\text{Ci/L}$ for the Washington soil and 1 $\mu\text{Ci/L}$ for the South Carolina soil. The solution:solid ratio was 25 mL/10 g. Equilibration was for 24 hours, followed by centrifugation at 4,000 rpm for 3 minutes. Selected samples also were filtered through 0.01- and 0.45- μm filters; there was no difference in Np concentration.

Np K_{ds} decreased with increasing concentrations of Ca and Na. For the Washington soil, K_{ds} ranged from 0.36 mL/g in 0.2 mol Ca, to 2.4 mL/g in 0.002 mol Ca, and from 3.1 mL/g in 0.3 mol Na to 3.9 mL/g in 0.015 mol Na. For the South Carolina soil, K_{ds} ranged from 0.16 mL/g in 0.2 mol Ca to 0.25 mL/g in 0.002 mol Ca and from 0.43 mL/g in 0.2 mol Na to 0.66 mL/g in 0.002 mol Na.

K_{ds} for the stronger ionic solutions are probably unrealistic for the INEEL. In addition, water at the INEEL has a more complex chemistry than water with only Ca, Na, and NO_3 . The pH of the South Carolina soil (5.1) is much lower than that of the INEEL soils (about 8). Composition of the Washington soil appears to be similar enough to that of the INEEL soils for consideration of the Np K_{ds} . Realistic K_{ds} from the Washington study that may have some transferability to the INEEL are 2.4 mL/g in 0.002 mol Ca at a pH of 7, and possibly 3.9 mL/g in 0.015 mol Na.

A report on Np sorption by Sheppard and others (1977) is referenced in Dicke's 1997 report; however, no details concerning the experiments are given in the Sheppard report. A later journal article describing the experimental details was published by Sheppard and others (1979) and is used in this review. Several soils were used in the experiments; four of the soils were from an unknown location at the INEEL. Quality control on radionuclide purity was good. Water:soil ratios were 10 mL/g. The initial Np concentration was 0.00025 $\mu\text{Ci/mL}$, well below the concentration of any solubility products. Composition of the soils were a loam, two sandy-clay loams, and a loamy sand. Experimental data

on the effectiveness of centrifugation for particle separation show that the greater the centrifugation speed, the smaller the size of particle removed. For example, at 1,750 rpm, particles >65 nm are removed. At 7,000 rpm, particles >17 nm are removed.

Results are reported in terms of an effective distribution ratio, R^* , and were converted to K_d . For soil ID-A at pH 8.3, the K_d was 51.6 mL/g; for soil ID-B at pH 8.4, the K_d was 142 mL/g; for soil ID-C at pH 8.4, the K_d was 38 mL/g; and for soil ID-D at pH 7.7, the K_d was 38.7 mL/g. No obvious trend in K_d related to soil properties was apparent. Distilled water was used, and no final chemical composition was given. Because Idaho soils were used in these experiments, the K_{ds} are probably representative of soils at the INEEL but the experiments were limited by the use of only one Np concentration. Another limitation of the experiment was the use of low ionic-strength water which would cause overestimation of sorption.

A report by Barney (1981) describes experimentally determined K_{ds} for Np sorption on altered and unaltered basalt and on secondary minerals from Hanford. The unaltered basalt was glassy and came from the Columbia River group. The three major minerals were labradorite, augite, and magnetite. The basalt was crushed to a grain size of 20 to 50 mesh sieve number. The solid:liquid ratio was 1 g/30 mL, and pH values were 8.5 to 9.5. Suspensions were filtered through a 3-nm molecular filter. About 4 weeks were required for equilibrium, probably a result of the fresh basalt equilibrating with water. Sorption by the crushed, unaltered basalt was a function of concentration and Np oxidation state; K_{ds} ranged from 5.4 to 278 mL/g. Altered basalts contained about 40 percent vesicles and vugs filled with secondary minerals, either tuff or a clay-rich alteration. K_{ds} for altered basalts ranged from 27 to 8,688 mL/g. Secondary minerals scraped from altered basalts appeared to be primarily smectites; K_{ds} ranged from 23 to 219 mL/g.

The larger K_{ds} were the result of adding hydrazine to the experiments, which caused reduction of Np(V) to Np(IV). K_{ds} for Np(V) in unaltered basalt ranged from 2 to 20 mL/g, and averaged 8.1 ± 2.2 mL/g with NaHCO_3 , and 7.5 ± 0.4 mL/g without NaHCO_3 . K_{ds} for Np(V) in altered basalt ranged from 17 to 70 mL/g, and averaged 44 ± 20 mL/g with NaHCO_3 , and 43 ± 4 mL/g without NaHCO_3 . K_{ds} ranged for Np(V) in secondary minerals from 13 to 100 mL/g, and averaged 32 ± 8 mL/g with NaHCO_3 , and 37 ± 2 mL/g without NaHCO_3 . Because of the nonlinearity of sorption, Freundlich isotherms were fit to the data.

Barney's study (1981) is one of the more complete sorption studies experimentally. In addition, because the composition of basalt used in Barney's experiments was similar to that of the basalt at the INEEL, the secondary mineral assemblages probably are similar also. K_ds for the secondary minerals were comparable to those of the crushed, altered basalts. All these values are within the 1 to 80 mL/g range considered by Dicke (1997).

Barney (1982) conducted later experiments similar to those described in his 1981 study, but isotherms were for a sandstone and a tuff interbed. In the presence of hydrazine, Np(V) was reduced to Np(IV) and strongly sorbed; K_ds ranged from 1,000 to 5,000 mL/g. K_ds for Np(V) ranged from 13 to 20 mL/g for sandstone and 17 to 33 mL/g for tuff. This data set complements that of the 1981 study.

Salter and others (1981a) conducted experiments using secondary minerals lining and filling vesicles, vugs, and fractures in basalt of the Columbia River group underlying Hanford; 98 percent of the secondary minerals were smectites, with minor FeOOH, calcite, and silica. Surface area was 546 m²/g, and CEC was 72 meq/100 g. For an initial Np concentration of 7.47x10⁻⁸ mol, the K_d at 23°C was 36.9±7.5 mL/g and, at 63°C, was 53.5±8.8 mL/g. Water was a NaHCO₃ type with a pH of 8. The K_d for a pH 10 Na-SiO₂ type water was 160 mL/g. This was a single concentration K_d. Sediment and water used in this experiment may have been similar to those used in the INEEL experiments.

5.4.2 Summary of K_ds for Np used in the Interim Risk Assessment model

Experimental data from the literature cited in this section show that sorption of Np is a function of aqueous chemistry and solid-phase mineralogy. Most of the studies cited were for experiments conducted under oxidizing conditions, where Np(V) was the dominant oxidation state. The redox state in the unsaturated zone at the SDA is expected to be oxidizing. The two studies in which Np(V) was reduced to Np(IV) showed that much larger concentrations of Np were removed from solution, either by sorption or because of the lower solubility of Np(IV).

The dominant Np(V) species in solution in the absence of complexing ions is NpO₂⁺. Sorption is a function of pH. Sorption of Np is minimal at low pH and increases with increasing pH. This behavior is characteristic of cations. Some of the experimental evidence has shown that increasing cation concentration, especially Ca, results in competition for sorption sites and less sorption of Np. Complexation of NpO₂⁺ with anions can result in

the formation of neutral or negatively charged species such as NpO₂HCO₃⁰ and NpO₂CO₃⁻, which sorb weakly. Thus, as the concentration of these complexing ions increases, sorption of Np would be expected to decrease. Experimental data have shown that Np sorption is nonlinear. Measured K_ds decrease as the initial concentration of Np increases. Sorption of Np also varied with solid-phase mineralogy. Freshly crushed samples of minerals and rocks tended to sorb less Np than did secondary mineral assemblages.

Measured K_ds are dependent on the experimental conditions. For example, using different solid:solution ratios can result in different K_d measurements. The method of aqueous phase separation is important. Very small colloids may not be removed by centrifugation or filtration through larger pore-size filters.

The experimental data show that there is a high degree of variability in Np sorption, depending on aqueous-phase chemistry and solid-phase mineralogy. This variability argues strongly for site-specific determination of Np K_ds under geochemical conditions realistic for the INEEL. Experimental data from the Hanford studies (Barney, 1981, 1982; Salter and others, 1981a, 1981b) could be analogous to conditions at the INEEL, because basalt is the predominant rock type at both sites. The reported K_ds are comparable to those chosen by Dicke (1997) (table 5-5). On the basis of all the data evaluated in the literature, a smaller K_d of 8 mL/g for Np for use in the IRA model is not unreasonable. However, given the dependence of K_d on aqueous chemistry and solid-phase mineralogy, the sorption behavior of Np should be determined for the range of geochemical conditions specific to the INEEL.

5.5 Use and limitations of the K_d concept as applied to actinide transport at the Idaho National Engineering and Environmental Laboratory

The K_d concept has been introduced and discussed earlier in this report (section 5.2.1). The present section will compare the advantages and limitations of the K_d approach with those of speciation-based approaches in simulating radionuclide transport. Wherever possible, reference will be made regarding the possible advantages and limitations in using either one of these approaches at the INEEL site.

5.5.1 Advantages and limitations of the K_d approach in

modeling contaminant retardation

Sorption reactions are commonly a predominant cause of contaminant retardation in ground-water systems. The K_d approach in modeling such contaminant retardation has been widely implemented in computer codes that attempt to simulate the reactive transport of contaminants.

5.5.1.1 Advantages of the K_d approach

The mathematical simplicity of the K_d approach is its primary advantage. K_d s are generally assumed constant over the transport domain and timescale considered and are easily incorporated into the advection-dispersion equation as part of a constant retardation factor, R , which modifies both the dispersive and the advective terms. Consequently, a computer code used to simulate the transport of conservative, nonreactive, components can be easily modified to solve the transport equation for a reactive “retarded” component.

In addition, experimental determinations of K_d s are relatively easy to perform. K_d s obtained from batch methods in the laboratory are particularly easy to obtain. Consequently, the number of K_d measurements has been described as “almost incalculable,” as mentioned earlier in section 5.2.1. However, despite the prolific number of K_d measurements, the experimental conditions pertaining to the measurements are generally insufficiently controlled and are rarely adequately described.

5.5.1.2 Limitations of the K_d approach

Despite its advantages of simplicity, the K_d approach has many limitations. Foremost, K_d measurement or estimation techniques, whether based on laboratory measurements or field observations, rarely consider all the chemical and physical processes that may be responsible for the partitioning of a constituent between mobile and immobile phases. The partitioning generally is considered to involve a reversible sorption process, even though the constituent of interest also may have undergone partitioning due to (1) chemical processes such as solid-phase precipitation; formation of, or partitioning into, a solid-solution phase; volatilization, or (2) physical processes such as diffusion into immobile-fluid zones. Generally, comparison of the transport of a reactive tracer with that of a conservative tracer may permit accounting for retardation caused by physical processes.

Despite the assumption that K_d s generally account for partitioning caused by sorption of a constituent onto mineral surfaces, K_d s are normalized to a given mass of solid material instead of being normalized to a given solid

surface area. The effect of surface-to-mass ratios, or grain size, on K_d determinations and the effects that rock crushing may have on K_d determinations are often not accounted for. The sorptive properties of a freshly fractured rock surface, full of crystal dislocations created by the crushing process, and without the presence of any secondary minerals generated by natural weathering of the primary mineral, can be expected to differ significantly from those of an ancient, naturally weathered surface. Sorption of a constituent on the fracture surfaces of granitic or basaltic rock often is “predicted” through the use of K_d s determined from experiments performed on the crushed rock. K_d determinations rarely consider the mineralogy or physical properties of the sorbing materials, and the experiments themselves often are not described in sufficient detail.

The K_d approach inherently assumes that the sorbing mass contains an infinite number of potential sorption sites. The approach assumes that if the aqueous concentration of a constituent is increased by a given factor, the amount of sorbed constituent also will increase by the same factor, that is, the ratio of the sorbed-to-aqueous concentration will remain constant. Actual observations generally show instead that as aqueous concentrations increase, the ratio of sorbed-to-aqueous concentration tends to decrease rather than remain constant. In other words, the effective K_d tends to decrease with increasing aqueous concentrations of the constituent of interest. Following this common observation, many transport simulation computer codes now offer the possibility of simulating sorption processes using a Langmuir isotherm or Freundlich isotherm approach, instead of the linear isotherm or K_d approach. Both the Langmuir and Freundlich isotherms can simulate a decreasing ratio of sorbed-to-aqueous concentration with increasing aqueous concentration. The Langmuir isotherm also exhibits the realistic property of simulating a maximum number of sorption sites. The Freundlich isotherm does not have this capability but, in contrast to the Langmuir isotherm, the Freundlich isotherm has the capability of simulating an increasing ratio of sorbed-to-aqueous concentration with an increase in aqueous concentration. Although relatively uncommon, this behavior is sometimes exhibited by constituents undergoing ion exchange until all exchange sites are filled by the constituent. This situation occurs in the presence of another constituent that shows preferential exchange (given equal aqueous concentrations of both constituents).

These sorption models (the linear isotherm or K_d approach, the Freundlich isotherm, and the Langmuir isotherm) apply only to single components. The models do

not account for the competitive sorption by other components of the aqueous solution. The models also do not account for the aqueous speciation of the component of interest. Even though some specific aqueous species of a given component may be much more strongly sorbed than are other species of that same component, the K_d , Langmuir and Freundlich models consider only the total aqueous concentrations of the component and, therefore, ignore the thermodynamic properties of its constituent aqueous species. This major limitation is even more problematic for chemical elements with multiple oxidation states (such as U, Np, and Pu), given that different oxidation states commonly have extremely different aqueous stabilities.

The K_d , Langmuir, and Freundlich models also ignore the speciation of the sorbing surface. Although certain minerals have a relatively fixed number of sorption sites, regardless of the composition and pH of the contacting solution (notably minerals for which an ion-exchange model may be appropriate, such as certain clays and zeolites), other minerals have surface properties (such as the number of surface sites of a particular charge) that vary greatly as a function of the pH and aqueous composition of the contacting solution.

5.5.1.3 Applicability of the K_d approach to ground-water systems in chemical steady state

The K_d approach may adequately describe contaminant migration and reversible sorption in ground-water systems in which the aquifer regions occupied by the contaminant plume and by the background water each have uniform mineralogical and chemical compositions that remain uniform through the timescale of interest. In general, the reactive sorption of the contaminant of interest also must be adequately described by the local equilibrium assumption (LEA). That is, the reaction rate of the contaminant in a representative unit volume of the aquifer must be fast relative to its transport through that volume. If this is not the case, the system will not be described by two chemically and mineralogically uniform regions.

In a seminal paper, Reardon (1981) demonstrated that the K_d approach could not properly describe contaminant migration in ground-water systems undergoing dynamic chemical evolution and could not even properly describe contaminant migration in systems that were at chemical steady state. In systems at chemical steady state, K_d s may vary spatially but must be constant through time at any given point in the system. Most contaminated ground-water systems are not at chemical steady state and, instead, can be best described as dynamically evolving

systems in which effective K_d s will vary, not only spatially, but also during the time-scale of interest.

Reardon (1981) described a one-dimensional system in which ^{90}Sr , the contaminant of interest, underwent ion exchange reactions with Ca, Na, K, and Mg, which were themselves affected by the dissolution of calcite. The dissolution of calcite was described by a kinetic model, rather than by the LEA. The LEA was used, however, to describe the ion exchange reactions. Figure 5-13 shows how the effective K_d s for ^{90}Sr varied throughout the one-dimensional system, under conditions of chemical steady state, by a factor of approximately 2, as a function of the saturation index of calcite. Because the dissolution of calcite was kinetically limited (the LEA did not apply), calcite saturation was only reached approximately midway through the column. Had the calcite reacted sufficiently fast for the LEA to apply, and had initial calcite concentrations been sufficiently large so as not to be depleted anywhere in the system during the timescale of interest, K_d s would have been uniform throughout the column.

Figure 5-14 shows how the K_d s varied under conditions of dynamic chemical evolution, prior to attainment of chemical steady state. Under these conditions, K_d s varied spatially and temporally by nearly an order of magnitude.

5.5.2 Advantages and limitations of speciation-based approaches in modeling sorption reactions

In contrast to computer codes that use the K_d concept and simulate the transport of only a single component, several multispecies reactive-transport codes currently exist that offer the possibility of accounting for the wide variety of chemical reactions that can affect the transport of contaminants. These codes commonly are associated with a thermodynamic data base that is used to calculate the equilibrium state of the water and contacting surfaces, minerals, and gases in the ground-water system as a function of both time and space. The codes can simulate the mass transfers of constituents between the various phases in the system that may be needed to reach a state of equilibrium at any given point and time. Some of the codes also have the additional capability of simulating the kinetic restrictions that may prevent these equilibrium states from being reached instantaneously.

The advantage of these multispecies reactive-transport codes is that in addition to the possibility of simulating more realistically the numerous complex chemical processes that may affect the behavior and fate of contaminants, the codes are based on a set of thermodynamic

5-22 Review of the transport of selected radionuclides in the Interim Risk Assessment

constants that, in theory at least, are relatively independent of actual field conditions.

Typically, the thermodynamic constants are determined in well-controlled laboratory experiments. Although thermodynamic data describing the reaction of major cations and anions commonly present in natural water are relatively well known, at least for reactions that are sufficiently fast to have been successfully simulated under laboratory timescales, significant knowledge gaps and uncertainties exist concerning the thermodynamic properties and behavior of the elements that are of concern in contaminant transport studies. In particular, the thermodynamic properties and behavior of radionuclides (such as Am, Np, Pu and even U) are not particularly well known because of the difficulties associated with conducting accurate experiments with them.

Additionally, the thermodynamic properties of mineral surfaces are difficult to characterize in the field and even in the lab. Many uncertainties exist regarding the thermodynamic behavior of "mixtures" of surfaces and the effects caused by aging, poisoning, and recrystallization of mineral surfaces. It is also not always easy to discriminate between different processes that may be occurring, such as sorption, solid-solution formation, or recrystallization.

Finally, the simulation of chemical reactions under conditions of chemical equilibrium is often not relevant to field conditions because of kinetic limitations in the reactions of interest. Knowledge of reaction kinetics is significantly more limited and more dependent on actual field conditions than is knowledge of thermodynamic properties. Any attempt to determine reaction kinetics from field observations also is constrained by the difficulties in gaining sufficiently detailed knowledge of the physical properties of a ground-water system.

Simulations conducted with multispecies reactive-transport codes can be computationally intensive, particularly if two-dimensional or three-dimensional simulations are conducted. Unfortunately, sensitivity analyses, for which simulations must be run numerous times while only a few parameters are changed at a time, are one of the primary uses of these full-featured computer codes. Any increase in simulation complexity generally requires a significant increase in the number of simulation runs for a true understanding of the results of the simulations. Although computer time restrictions are easing, the desire to increase the complexity of contaminant transport simulations to the maximum limit of computer capabilities is always present, often to the detriment of gaining a better understanding of contaminant transport in the ground-water system being investigated.

Given these uncertainties and limitations, simple models that successfully simulate the essential properties of contaminant transport and reaction have an undeniable appeal. However, because of its many limitations, the K_d approach may be too restrictive in simulating reactive transport, and use of K_d s should be carefully examined to confirm or deny their suitability for any given field situation.

5.5.3 Uncertainties at the Idaho National Engineering and Environmental Laboratory site and their potential effects on simulation of radionuclide sorption and retardation

In addition to the uncertainties related to the conceptual models previously discussed, application of any of these conceptual models in simulating radionuclide transport at the INEEL site is limited by a lack of sufficiently detailed knowledge of the geology, hydrology, chemistry, and mineralogy of the site.

The chemistry of the water in the areas of radioactive waste disposal can be expected to differ significantly, particularly in terms of redox conditions, from the chemistry of the background water that remains unaffected by waste-disposal activities. The redox conditions in the areas of radioactive waste disposal can be expected to be more reducing and, therefore, generally less conducive to radionuclide transport (particularly for U, Np and Pu), than the oxygenated water which is predominant in the uncontaminated areas. The presence of steel and iron barrels and of detrital organic matter, such as cardboard and paper products, should generate reducing conditions. The distribution of redox conditions also is likely to be heterogeneous. Finally, large organic carbon concentrations in the waste disposal areas may lead to significantly enriched P_{CO_2} values for the water recharging through these areas. pH values also may differ significantly from background values. Large dissolved CO_3 concentrations in the recharging water could significantly increase the aqueous stability of radionuclides such as Am, U, Np, and Pu. Unfortunately, field data allowing closer examination of these hypotheses were not available for this report.

Redox conditions in the sediment interbeds also are not well documented and probably are heterogeneously distributed. It is possible that relatively impermeable, fully saturated zones of the interbeds could contain reducing water that could impede the movement of radionuclides such as U, Np, and Pu. Rightmire and Lewis (1987a) mentioned some occasional organic-rich layers in their examination of cores from the INEEL site. Relatively impermeable zones also could contain Fe(II) miner-

als, which potentially could act as reductants for U, Np, and Pu.

In addition to the uncertainties relating to the distribution of redox conditions at the INEEL site, the distribution of reactive minerals, of sorbing surfaces, of effective porosities, and of mineral-surface-to-water ratios also is likely to be heterogeneous and to differ significantly, not just between the sedimentary interbed and basalt units, but also within the units themselves.

5.5.4 One-dimensional transport simulations for U and Np

This section examines the results of some one-dimensional, multispecies reactive-transport simulations that were conducted using site and ground-water properties considered representative of the INEEL site and extends the Np and U aqueous and surface speciation results previously discussed in section 4.3.2.

5.5.4.1 U(VI) transport calculations

Multispecies reactive-solute-transport simulations were conducted to examine the variability in sorption properties that might be expected at the SDA. The approach was to use the RATEQ model (Curtis, 1999) to fit one of the breakthrough curves for U(VI) transport in laboratory columns containing sedimentary interbed material (reported by Newman and others, 1995). The adsorption of U(VI) in the columns was simulated using the SCM approach. The fitted model then was used to illustrate the range in breakthrough behavior (or retardation factors) for the different INEEL ground-water samples listed in table 4-4.

5.5.4.1.1 Calibration of the reactive-transport model

One of the challenges in applying SCMs to describe transport of adsorbing ions in aquifers is that it is difficult to characterize the adsorbing phase. One approach used to address this difficulty was to identify all the mineral surfaces present in the aquifer material and then sum the sorption onto all these sites. Davis and others (1998) referred to this approach as the component additivity approach. This approach requires detailed knowledge of the amount and adsorption properties of each adsorbing surface. This requirement is further complicated by the fact that most bulk phases are covered with surface coatings that have a different composition from that of the bulk phase. An alternative approach suggested by Davis and others (1998) is to use the same adsorption reactions and equilibrium equations as used in an SCM for a pure

solid but to estimate the required parameters from observed adsorption data on the more complex natural solid. These parameters include the adsorption equilibrium constants and the number of reactive surface sites. This second approach, termed the generalized composite approach (Davis and others, 1998), was used for the simulations discussed below.

For U(VI) transport, formulating the generalized composite approach was difficult because many SCMs have been proposed to describe U(VI) adsorption (table 4-1). These SCMs differ in the stoichiometry of H⁺, UO₂⁺², and CO₃⁻² in the adsorption reactions and in the number and types of surface sites and competing adsorbates. To adequately calibrate the SCMs, it is preferable to consider variations in all these parameters (Kohler and others, 1996). The breakthrough curves reported by Newman and others (1995), however, were conducted only for one set of chemical conditions. Therefore, it was not possible to fully calibrate the SCM used in the reactive-transport model. For the simulations reported in this section, the SCM for U(VI) adsorption onto ferrihydrite was used and only the total number of reactive sites was varied to obtain a match to the data; all the reactions, equilibrium constants, and ratio of strong to weak sites were the same as for pure ferrihydrite (Waite and others, 1994). A more complete calibration could involve modifying the equilibrium constants. Although the ferrihydrite SCM is the most complex model listed in table 4-1, it was selected because ferrihydrite can be expected to be an important sorbing surface at the SDA (section 5.2.2).

The reactive-transport model with the ferrihydrite SCM was fitted to the U(VI) breakthrough curve observed in the laboratory and originally shown as figure 13 in the report by Newman and others (1995), and reproduced in this report as figure 5-8. This fitted model then was used to illustrate the sensitivity of retardation to variations in pH and alkalinity measured in ground water at the INEEL. Columns packed with sedimentary interbed material were used in the experiments to simulate U(VI) transport in the fitted model. There were two significant problems with this data set. First, the initial U(VI) concentrations were not reported; therefore, for the sake of illustration, a value of 10⁻⁷ M was assumed. Second, the pH in the feed solution, which was undersaturated with respect to calcite, was 8.0, but the pH of the effluent was 8.48 and the specific conductivity also increased in the column. Speciation calculations showed that this rise in pH was consistent with equilibrating the feed solution with calcite. Because there is no way of knowing how the pH varied spatially and temporally in the column, transport simulations were conducted at a fixed pH. Simulations were con-

5-24 Review of the transport of selected radionuclides in the Interim Risk Assessment

ducted at pH 8.0 without calcite present and at pH 8.48 with calcite present. The two fitted breakthrough curves are shown in figure 5-15. The total site densities required to match the breakthrough curve for pH 8 and 8.48 were 1 and 2.8 mM, respectively. These values are slightly less than the value of 4.7 mM used for sand in the Cape Cod aquifer (Davis and others, 1998). Neither of the model fits reproduced the long tail illustrated by the data. One possible explanation for this long tail is that there was a small fraction of strongly sorbing sites not accounted for in the model (Kohler and others, 1996). This long tail also could be the result of other factors, including the variation in pH, slow adsorption kinetics, or adsorption from zones of immobile water.

5.5.4.1.2 Application of the surface complexation model to ground water at the Idaho National Engineering and Environmental Laboratory

RATEQ simulations using the SCM results fitted at both pH 8.0 and 8.48 were conducted for the 12 INEEL water samples summarized in table 4-4. These simulations neglected hydrodynamic dispersion but included approximately 80 to 120 solution and surface species, depending on whether PO_4 and F were included in the simulation. In performing these simulations, it was implicitly assumed that the adsorption properties in the columns packed with the interbed materials applied to each of the 12 water samples considered. This assumption is similar to that used by Magnuson and Sondrup (1998), although it has not been tested. Figure 5-16a illustrates the range in breakthrough behavior calculated from the SCM results fitted at pH 8 for all 12 water samples. In this figure, the retardation factors are equal to the pore volumes required to elute the center of mass of the U(VI) pulse. For example, U(VI) in water from well USGS 92, is slightly retarded; the retardation factor is approximately 2 to 3. In contrast, in water from the BLR, U(VI) is moderately retarded; the retardation factor is approximately 100. The retardation factors for U(VI) in the remaining water samples range from approximately 6 to 30. Even if the water from the BLR is ignored because it is a surface water and has a low pH and large p_{CO_2} , the retardation factors for U(VI) vary by a factor of more than 10. The trend of SCM results fitted at pH 8.48 is similar to that fitted at pH 8, but the retardation factors are larger. This shift results because, at the assumed pH of 8.48, more reactive sites were required to match the breakthrough curve observed in the column experiments. Again, the retardation factors vary by a factor of 10 for the INEEL ground water. For any given water composition, the two models yield retardation factors that vary by a factor of 2 to 3.

5.5.4.1.3 Comparison of one-dimensional transport simulations and calculated K_r s

Coincidentally, the site density of 1 mM required to match the U(VI) breakthrough in the column experiments at the assumed pH of 8 is the same as the site density used for the K_r s calculated for batch conditions listed in table 4-3. A comparison of the K_r s for the batch calculations for ferrihydrite in table 4-3 and the K_r values from the column simulations (calculated as $K_r = R-1$) shows a close correspondence between the batch and column approaches. This correspondence occurs because geochemical conditions for the reactive-transport simulations were nearly constant. Specifically, initial chemical conditions in the column and boundary conditions in the feed solution were the same with the exception of 10^{-7} M U(VI). The pH, therefore, remained approximately constant because calcite was ignored in the simulations for the INEEL water. Thus, the transport simulations and the batch K_r calculations were performed for the same chemical conditions. The differences in the elution order among the different water samples resulted from the variability of the chemical conditions, primarily pH and alkalinity. Overall, the retardation factors calculated from the K_r s for 1 mM ferrihydrite in table 4-3 agree well with the transport simulations. This agreement suggests that the variability in the retardation factors at the INEEL can be illustrated by considering the K_r s obtained from batch experiments.

The K_r calculated for a specific ground-water sample from a speciation model depends on the SCM used to fit the data. To examine the effect of using different SCM formulations, the SCMs for quartz, montmorillonite, goethite, and ferrihydrite were considered in greater detail. The total site density for each SCM model was varied so that the K_r equaled 20, which is approximately equal to the value observed in the Neuman column experiment (fig. 13 in the report by Newman and others, 1995). The solution composition had a pH of 8.48 and was equilibrated with calcite. Thus, the four different SCMs were forced to give the same K_r s at one solution composition that was selected to be the experimental column effluent condition. Using the site density fit just described, K_r s were calculated for the 12 INEEL water samples listed in table 4-4 and for the four different SCMs. These calculations were similar to those in table 4-3 except that the site densities for the calculations in table 5-7 were adjusted to match the column results. The results of these calculations are shown in table 5-7.

The site densities required to match the selected K_r of 20 ranged from 12 mM for quartz to 1.1 mM for goethite, reflecting the higher affinity of U(VI) for goethite. Each row in table 5-7 illustrates the range in K_r s calculated for

the different SCMs at a constant water composition. The calculated K_rs for the four SCMs typically vary by a factor of 2 to 4 in most of the water samples. Larger ranges are observed for samples from the BLR and USGS 19. These larger ranges result because of the different stoichiometries in the various SCMs coupled with the larger difference in pH and alkalinity values for these water samples relative to those for the column effluent solution or for the remaining ground-water samples.

Each column in table 5-7 illustrates the range in calculated K_rs for SCMs for different INEEL water samples. The results for quartz and montmorillonite SCMs are similar. For each sample, the difference in K_r tends to be less than 25 percent, and the minimum, median, average, and maximum values all agree closely. For the 12 INEEL water samples, the K_rs vary by a factor of 20 for these quartz and montmorillonite SCMs. Results for the two Fe phases are also similar, although for a given sample, the difference in K_r for the two SCMs varies by as much as a factor of 1.8, as in the case of USGS 19. The average K_r for the Fe phases is roughly twice that of quartz and montmorillonite. These differences result because of the differences in the stoichiometry of the adsorption reactions. In particular, the quartz and montmorillonite SCMs do not include the CO₃⁻² in the formation of the surface complex, whereas the goethite and ferrihydrite do include the CO₃⁻² in the surface complex (table 4-1). For the range of ground-water samples considered, the K_rs vary by a factor of 24 to 31 for ferrihydrite and goethite, respectively. Given that the column experiments by Newman and others (1995) considered only one solution composition, it is impossible to evaluate whether CO₃⁻² may be a part of the adsorbed complex for the INEEL sediments. Finally, the ranges in K_rs in table 5-7 were obtained by matching a site density that gave a K_r of 20 for a pH 8.48 water in equilibrium with calcite. Similar ranges in K_rs would have been obtained if the pH had been 8, but the absolute K_rs would have been smaller.

The calculated range in K_rs of 20 to 30 for U is considerably larger than the range calculated for Np (factor of 1.3) and Pu (factor of 2.0) (table 4-1). This small factor difference for Np can be explained by comparing the solution chemistry. The aqueous speciation chemistry for U(VI) is significantly more complex than for Np(V). Figure 4-2 shows that at atmospheric p_{CO_2} , and in the pH range of 7.5 to 8.4, the species UO₂(OH)₂, UO₂(CO₃)₂⁻², (UO₂)₂(CO₃)(OH)₃⁻, and UO₂(CO₃)₃⁻⁴ are present at greater than 10 percent of the total concentration at certain pH values. A similar plot of Np(V) aqueous speciation in a report by Turner and others (1998) shows that the NpO₂⁺ ion is the single dominant species up to pH 8.5,

where the NpO₂CO₃⁻ species then becomes important. The adsorption behaviors of U(VI) and Np(V) are also different. At pH values above 7, U(VI) log K_rs decrease nearly linearly with pH (fig. 4-7) because of the formation of soluble U(VI) CO₃ complexes. Adsorption of Np(V) also decreases because of the formation of soluble CO₃ complexes, but the trend of decreased adsorption starts at pH values of approximately pH 8 in the case of montmorillonite (Turner and others, 1998). Finally, the SCM for Np(V) does not include ternary surface complexes involving CO₃, although their existence has been postulated (Turner and others, 1998).

In summary, the reactive-transport calculations for U(VI) presented in this section illustrate that *if the geochemical conditions are constant*, reactive-transport simulation results can be approximated by a single K_r. Over the INEEL site, *geochemical conditions are not constant*; therefore, K_rs vary for the different water compositions. There is no clear explanation for the variations in the aqueous geochemistry; therefore, without additional detailed geochemical data, fully coupled reactive-transport simulations are not warranted. On the other hand, both the transport calculations and the batch calculations illustrate that, given the current state of our understanding of the SDA and models of adsorption properties, the calculated K_rs for U(VI) vary by a factor of 20 or more for each selected SCM just because of the variation in water composition. Adsorption properties at the SDA also may vary because of the variation in surface properties, including both the affinity for the actinide and the concentration of adsorbing sites. These variations have not been quantified and represent a gap in the data. A comparison of four different SCM results show that K_rs vary by a factor of as much as 70.

5.5.4.2 Np transport calculations

Np and Pu one-dimensional transport simulations were conducted with version 2.038 of the USGS computer code PHREEQC (Parkhurst and Appelo, 1999). Confirming results previously discussed in sections 4.3.2, Np sorbs much more strongly than Pu; and under the specific conditions of those transport simulations, Pu was not retarded significantly and, therefore, will not be discussed further. This result does not imply that Pu transport will not be retarded at the INEEL site. A greater concentration of sorbing sites (an increase by a factor of 2,000 was suggested reasonable in section 4.3.2), and the presence of possible reducing environments could cause significant retardation of Pu transport at the site. Nevertheless, many of the conclusions derived from the Np transport results presented in this section can be expected to apply to potential Pu transport.

5-26 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 5-7. Summary of U(VI) K_r s calculated for four surface complexation models calibrated to U(VI) breakthrough in column experiments at pH 8.48

[K_r , retardation coefficient; mM, millimoles per liter]

| | Quartz | Montmorillonite | Goethite | Ferrihydrite | Ratio $K_{r,max}:K_{r,min}$ |
|-----------------------------|--------|-----------------|----------|--------------|--------------------------------|
| Site density (mM) | 12 | 7.3 | 1.1 | 3.3 | |
| Big Lost River | 183 | 56 | 6,919 | 454 | 124 |
| EBR 1 | 26 | 23 | 46 | 36 | 2 |
| USGS 112 | 75 | 55 | 236 | 143 | 4 |
| USGS 8 | 17 | 14 | 45 | 31 | 3 |
| USGS 19 | 21 | 15 | 110 | 62 | 7 |
| USGS 87 | 51 | 43 | 89 | 67 | 2 |
| USGS 89 | 77 | 72 | 69 | 68 | 1 |
| USGS 90 | 43 | 36 | 80 | 59 | 2 |
| NPR test | 19 | 15 | 62 | 39 | 4 |
| P&W 2 | 43 | 61 | 104 | 70 | 2 |
| RWMC production | 25 | 22 | 58 | 41 | 3 |
| USGS 92 | 4 | 3 | 8 | 6 | 2 |
| Minimum ¹ | 4 | 3 | 8 | 6 | |
| Median | 26 | 23 | 69 | 59 | |
| Average | 36 | 33 | 82 | 56 | |
| Maximum | 77 | 72 | 236 | 143 | |
| Ratio $K_{r,max}:K_{r,min}$ | 22 | 21 | 31 | 24 | |

¹Minimum, median, average, and maximum values exclude the Big Lost River K_r values

5.5.4.2.1 Description of the Np transport simulations

The one-dimensional transport simulations were set up as follows. Water sampled from well USGS 92 (composition given in section 4.3.2), a well in the SDA, screened in a perched-water zone above the C-D interbed, was used as the background water in the one-dimensional column. The water from well USGS 92 is predominantly a NaHCO₃-rich water. The 100-m-long one-dimensional column was subdivided into 100 cells, each of which contained 1 kg H₂O (background water) and a goethite surface with 5×10^{-7} mol of surface sites per kg of H₂O and a surface area of 54 m² per kilogram of H₂O. The composition of the goethite surface at equilibrium with the composition of water from well USGS 92 was calculated by PHREEQC and used as the initial surface composition in the transport simulations. The number of surface sites was decreased by a factor of 10 from the concentration used in section 4.3.2, simply for the convenience of obtaining a retardation factor of about 20 for Np, rather than the factor of about 200 estimated in section 4.3.2. This modification resulted in a decrease by a factor of 10 in the number of timesteps that needed to be considered, thereby reducing by the same factor the time required for the transport simulations. Under these conditions, each one of the Np transport simulations presented here took 50 to 60 hours to run on an Intel Pentium-II personal computer running at 300 MHz.

A dispersivity of 10 m was assumed in the calculations. This dispersivity is probably too high by at least a factor of 10 to reasonably describe transport at the INEEL site but was used to determine whether constant retardation of Np transport still could be obtained in such a system. Simulations with lower dispersivity, or simulations with a dispersivity of 0 m, would have required significantly less (10 times less) computer time to run.

Water from well USGS 112 (composition given in section 4.3.2), a CaHCO₃-rich water modified to include 10^{-8} mol Np and 10^{-8} mol Pu, was used to simulate the infiltration of contaminated water into the column.³ The average linear ground-water velocity simulated was 10 m/yr. The infiltration of Np- and Pu-contaminated water lasted for 2,500 timesteps (250 years). After 2,500 timesteps, the aqueous solutions in the column had a uniform concentration of 10^{-8} mol Np and Pu, and the goethite surfaces were in equilibrium with these Np and Pu concentrations throughout the entire column. At that point, background water from well USGS 92 (containing no Np or Pu) was allowed to infiltrate into the column for

up to 6,000 timesteps (600 years), thereby simulating the cleanup of the column.

Water from both well USGS 92 and well USGS 112 was slightly supersaturated with respect to calcite and with respect to chalcedony. In some, but not all, simulations, these minerals were not specified as initially present in the column but were allowed to precipitate to allow the water to reach equilibrium. Any calcite precipitated was allowed to redissolve later on in the simulation if necessary.

Np and Pu thermodynamic data were added to the default PHREEQC data base from two different sources (discussion in section 4.3.2): (1) the ANSTO thermodynamic data base (provided by Marianne Guerin, 1998; Np and Pu data in that data base are identical to those contained in the HATCHES data base, Cross and Ewart, 1991), and (2) the EQ3/6 data base (provided by David Turner, Southwest Research Institute, written commun., 1999). Np and Pu surface complexation data compiled by Turner (1995) were added to both data bases. For the purposes of this report, the data bases created from the ANSTO and EQ3/6 data bases will be referred to as the "ANSTO" and "EQ3/6" data bases, even though these are not the complete ANSTO and EQ3/6 data bases.

5.5.4.2.2 Np infiltration results

Results obtained for the Np infiltration phase of the simulations (figs. 5-17 and 5-18) show that Np breakthrough at the end of the column occurred after approximately 17 pore volumes (1,700 time steps). Speciation calculations in section 4.3.2 predicted a retardation of about 20 given the sorption site concentration used in the transport simulations. The retardation of Np transport appears relatively constant in the figures, which indicates that the retardation could have been predicted using a constant K_d approach instead of the surface complexation approach. However, an appropriate K_d might have been difficult to predict.

Transport of Np was about 10 percent faster in the simulations that allowed calcite precipitation (and later redissolution) than in those that didn't allow calcite precipitation. Allowing calcite precipitation resulted in a decrease in pH of the infiltrating solution from a value of 8.4 (before calcite precipitation) to values below 7.9. This resulted in a decrease in the number of neutral and negatively charged sorption sites and, therefore, resulted in a decrease in the amount of sorbed Np (section 4.3.2.3, table 4-6, for the predominant Np surface complexes on goethite).

During the Np infiltration phase, Np transport was approximately 10 percent faster in the simulations con-

³ 10^{-8} M of ²³⁷Np corresponds to approximately 62 Bq/kg H₂O or 1,670 pCi/kg H₂O.

5-28 Review of the transport of selected radionuclides in the Interim Risk Assessment

ducted with the ANSTO data base than in those conducted with the EQ3/6 data base (figs. 5-17 and 5-18). As discussed in section 4.3.2.2, the ANSTO data base predicts that significant amounts (about 15 percent) of Np(VI) will be present in the water from well USGS 112, whereas the EQ3/6 data base predicts that essentially all the Np will be in the Np(V) state. The databases do not contain any data for Np(VI) surface complexes, only for Np(V) complexes; therefore, any aqueous Np(VI) species present become unavailable for sorptive retardation during transport.

Breakthrough curves (fig. 5-19) constructed from the results of the Np infiltration simulations for a point at the end of the 100-m-long column, using either the ANSTO or EQ3/6 data bases with or without specification of calcite equilibrium, are relatively similar to the curves that would be obtained for simulations of reactive transport with a constant K_d approach, with one significant exception. The curves for the PHREEQC simulations show an abnormally steep leading edge (the left portion of each curve), compared with the curve that would be obtained from a simulation that used a constant K_d approach. The most likely reason for this behavior is that Np exhibits relatively stronger sorption at small aqueous concentrations than at large aqueous concentrations. In other words, the effective K_d that may be applied to the PHREEQC simulation results is not constant and, instead, decreases with increasing aqueous Np concentrations (see discussion at the end of this section). The breakthrough curves for the PHREEQC simulations also clearly illustrate (1) the greater Np retardation in the simulations conducted with the EQ3/6 thermodynamic data base than with of the ANSTO data base, and (2) the greater Np retardation in the simulations conducted without specification of calcite equilibrium than in those conducted with calcite equilibrium.

5.5.4.2.3 Np cleanup results

The results of the Np cleanup phase of the simulations show surprisingly greater complexity than do the results of the Np infiltration phase (figs. 5-20, 5-21, 5-22, 5-23). The results of the simulation conducted using the ANSTO data base without specification of calcite equilibrium (fig. 5-20) show that aqueous Np concentrations decrease by about 60 percent throughout the column after flushing of one pore volume (100 timesteps) of initially Np-free water from well USGS 92. However, after flushing by this first pore volume, the rate of cleanup slows down considerably. After flushing by 25 pore volumes, aqueous Np concentrations are still near 10^{-9} mol in the center of the column, or 10 percent of the initial Np-satu-

rated condition; another 25 pore volumes (50 total) are required to halve the aqueous Np concentrations to the 0.5×10^{-9} mol level. The results of the simulation conducted using the EQ3/6 data base without specification of calcite equilibrium (fig. 5-21) show similar results to those conducted using the ANSTO data base, except that Np concentrations are reduced even more, by about 90 percent, after flushing by the first pore volume. Np concentrations after flushing with about 50 pore volumes remain at about 0.3×10^{-9} mol in the center of the column.

The simulations conducted with specification of calcite equilibrium (with either the ANSTO or EQ3/6 data bases) show faster and more even removal of the sorbed Np and faster cleanup of the contaminated column relative to the simulations conducted without specification of calcite equilibrium. This faster and more evenly distributed removal of Np is the result of the lower sorption capacity of the column for Np at lower pH values. In the results from the simulation conducted with the ANSTO data base (fig. 5-22), aqueous Np concentrations in the first 80 shifts of the cleanup phase rise as much as 5 percent above the maximum aqueous Np concentrations recorded during the Np infiltration phase. In contrast, results from the simulation conducted with the EQ3/6 data base (fig. 5-23) show only a very slight increase in aqueous Np concentrations above the 10^{-8} mol level.

The shape of breakthrough curves (fig. 5-24) constructed from the results of the Np cleanup simulations (ANSTO data base), with or without specification of calcite equilibrium, are significantly different from the shape of "normal" breakthrough curves obtained from simulations of reactive transport with a constant K_d approach. Normal breakthrough curves have, at most, one inflection point. Breakthrough curves for the PHREEQC simulations presented here show three inflection points for the simulations without specification of calcite equilibrium, and four inflection points for the simulations with specification of calcite equilibrium. In the simulations without specification of calcite equilibrium, the relatively fast initial decrease in Np aqueous concentrations, followed by the slight increase and the relatively slow subsequent decrease (caused by the larger effective K_d at small Np concentrations) could not have been modeled by using a constant K_d approach. Similarly, in the simulations with specification of calcite equilibrium, the increase in Np aqueous concentrations above the initial value of 10^{-8} mol also could not have been modeled with a constant K_d approach.

5.5.4.2.4 Np sorption isotherms for the PHREEQC surface complexation models

Np sorption isotherms were calculated on the basis of SCMs used in the PHREEQC speciation and transport simulations discussed in the previous section and in section 4.3.2. Two different types of simulations were conducted (figs. 5-25 and 5-26). In the first type, entitled "NpCl₅ addition", as much as 10⁻⁶ mol of NpCl₅ and of PuCl₅ were added in 1,000 increments of 10⁻⁹ mol to a system consisting of 1 L of water from well USGS 112, and a goethite surface with 5x10⁻⁷ mol of sorption sites preequilibrated with water from well USGS 92. In the second type of simulation, entitled "mixture of water," water from well USGS 92 and water from well USGS 112, to which 2x10⁻⁷ mol of Np and Pu had been previously added, were mixed together in various fractions and equilibrated with the goethite surface (that contained 5x10⁻⁷ mol of sorption sites preequilibrated with water from well USGS 92). Twenty-five different mixtures were created, which ranged from 1 percent of water from well USGS 112 (and 99 percent of water from well USGS 92) to 99 percent of water from well USGS 112 (and 1 percent of water from well USGS 92). The two types of simulations were run with or without specification of calcite (and chalcidony) equilibrium and with the ANSTO or the EQ3/6 thermodynamic data bases.

Results of the various isotherm simulations (figs. 5-25 and 5-26) confirm the suggestions made in the discussion of the transport simulations that the "effective" K_d for Np sorption according to the SCM is not constant and, instead, decreases with increasing aqueous Np concentrations. The results also show the significant dependence of the sorption isotherms on (1) the presence or absence of calcite equilibrium, (2) the source of the aqueous Np thermodynamic data (the ANSTO or EQ3/6 data bases), and (3) the presence or absence of water from well USGS 92 in the equilibrated systems. However, this last factor was of little importance in the simulations for which calcite equilibrium was specified. As previously observed in the transport simulations, specification of calcite equilibrium resulted in smaller concentrations of sorbed Np; use of the EQ3/6 data base instead of the ANSTO data base resulted in larger calculated concentrations of sorbed Np. Finally, the results suggest that matching the simulated isotherms with a Freundlich isotherm equation would be possible, albeit only for a given set of geochemical conditions. Any change in conditions caused, for example, by the mixing in of a background water due to normal dispersion, or to the appearance or disappearance of reactive minerals that might affect pH or Eh conditions or the concentrations of ions competing for sorption sites, would likely affect the

isotherm curve, and possibly invalidate any previously obtained match of Freundlich parameters.

5.6 Evaluation of the uncertainties associated with selected K_ds

The K_ds for Am, U, and Pu selected for the IRA model were determined using only one ground-water composition and one composite interbed sediment sample. It has been shown in chapter 4 and in earlier sections of chapter 5 of this report that K_ds for actinides can be highly dependent on the chemical and physical properties of the aqueous and solid phases. Also important is how well the laboratory experimental conditions simulate processes operating in the field. There are not enough data from WAG-7 to quantify all the uncertainties associated with the K_ds for Am, U, Np, and Pu used in the IRA model; however, some generalities can be formulated to estimate how much these K_ds could vary with changing chemical and physical properties.

The effect of aqueous chemistry on actinide sorption depends on both the actinide and its oxidation state. For example, Np(V) is the dominant oxidation state under the oxidizing conditions at WAG-7, and the primary species adsorbed is the cation NpO₂⁺. Adsorption increases with pH as the surface becomes more negatively charged. The increase is most dramatic at lower pH values and begins to plateau near 8. Because the measured pH of perched water and ground water near WAG-7 ranges between 7.8 and 8.4, these changes would be expected to have only a minor effect on Np adsorption. CaCO₃ complexes of Np also would have some effect on sorption. As CO₃⁻² concentration increases, the concentration of NpO₂CO₃⁻ and NpO₂(CO₃)₂⁻² increases, thereby decreasing the concentration of NpO₂⁺.

The thermodynamic modeling data for 11 perched-water and ground-water samples from the INEEL (table 4-7) show that relatively small changes in chemical composition can affect sorption when all other properties of the modeled system remain constant. These data are presented as molar ratios of total sorbed to total aqueous (K_p). For Np, K_ps ranged from 164 to 215. These values are dependent on the types of sorbing surface. For example, increasing the concentration of surface sites from 5.6x10⁻⁶ to 1.0x10⁻² mol per kg H₂O would increase the Np and Pu K_ps by 2,000. These calculated K_ps also can vary with the data base used in the modeling.

Pu(V) is predicted by thermodynamic modeling to be the dominant oxidation state in water at the INEEL (table 4-6). Pu forms very strong complexes with CaCO₃. In fact, most of the Pu(V) in the 11 perched-water and

5-30 Review of the transport of selected radionuclides in the Interim Risk Assessment

ground-water samples from the INEEL was calculated to be $\text{PuO}_2\text{CO}_3^-$. Because of this, sorption of Pu was computed to be minimal (table 4-7). However, the concentration of surface sites used in this model is possibly smaller than would be expected in the aquifer.

The K_d for Pu selected for the IRA model was 5,100 mL/g. The concentrations of most constituents in the synthetic ground water used in this experiment were smaller than those in most of the perched water and ground water at the INEEL (table 4-4). For example, the CO_3 concentration (96.6 mg/L) was comparable to that of the modeled ground water from well USGS 89 (table 4-4). Sorption of Pu also was greatest in this water (table 4-7). Thus, for ground water with a larger CO_3 concentration such as that from well USGS 19, the thermodynamic model indicates that the amount of Pu sorbed could decrease by 55 percent. Caution is needed when thermodynamic modeling results are extrapolated to field conditions; however, such an exercise does illustrate the uncertainty in a single K_d measurement.

Sorption of U also is dependent on the aqueous chemical composition. For example, figure 4-2a shows that a two-order-of-magnitude increase in U concentration results in a one-order-of-magnitude decrease in K_d . Increasing the ligand concentration can significantly reduce sorption of U (fig. 4-2c). Figure 4-6 shows that slight changes in pH can have a dramatic effect on the amount of U sorbed. Modeling U sorption for the 11 INEEL water samples in table 4-4 resulted in K_r s ranging from 7 to 211 for a goethite sorbent (table 4-2). Generally, sorption decreased with increasing pH and CO_3 content.

The type of surface site and value of pH also have a considerable effect on Am sorption (fig. 4-4). Formation of Am CO_3 complexes increases with CO_3 concentration resulting in less sorption. For the 11 different INEEL water samples that were modeled, K_r s varied by 400 percent.

Spatial variability in the composition of the sorbent also will have an effect on K_d s. Two important measures of sorption capacity are (1) the CEC, likely to be important for cations such as Am, and (2) the concentration of Fe oxides, likely to be important for sorption of Am, U, Np, and Pu. The K_d s selected for the IRA model (Dicke, 1997) were determined for a composite interbed material with a CEC of 17.4 meq/100 g and an Fe oxide content of 1.77 percent (Newman and others, 1995). These K_d s can be expected to decrease or increase depending on the CEC and Fe oxide content of other sediments. Bartholomay and others (1989) compiled a list of CEC measurements from previously published reports of the USGS. The data include measurements from 271 samples of interbed sed-

iments and fracture fill from the INEEL. CECs ranged from 0.9 to 42 meq/100 g, and averaged 13.6 meq/100 g. The Fe oxide content of 11 interbed samples ranged from 0.37 to 2.86 percent (Goff, 1994). Making the assumption the K_d is linearly proportional to CEC, expected minimum, maximum, and averaged K_d s for the sediments reported in Bartholomay and others (1989) can be calculated from the K_d s determined by Newman and others (1995). These values are compared in table 5-8. The average K_d s calculated for the 271 samples are comparable to the values reported by Dicke (1997); however, K_d s can be expected to be significantly smaller in coarser sediments with smaller CEC. Conversely, K_d s will be larger in finer-grained sediments with larger CEC.

Extrapolation of the laboratory-derived K_d s used in the IRA model to field conditions at WAG-7 also could introduce uncertainty in the modeling results. K_d s measured in batch experiments can decrease as the suspended solids concentration increases (section 5.3.2.4.3). ^{90}Sr K_d s for the composite WAG-7 interbed sediment decreased by 30 percent for a 19-fold increase in the solid:liquid ratio (Newman and others, 1995). The K_d s for Am, U, and Pu for the INEEL interbed experiments were determined for solid:liquid ratios ranging from 3.5 to 150 g/L (Goff, 1994). The interbed sediments in the unsaturated zone have a solid:liquid ratio of about 4,000 g/L. Thus, it is possible that the K_d s measured in the batch experiments may not adequately represent sorption in the interbeds. Newman and others (1995) measured K_d s for U in both batch and column experiments. For crushed basalt, the column K_d was more than one order of magnitude lower than the batch K_d . For the interbed sediment, the column K_d was twice as great as the batch K_d . However, it is not possible to assess the effect of solid:liquid ratio on U sorption because of variability in pH; and, possibly because of differences in U concentration between the batch and column experiments.

A great uncertainty in the K_d s selected for the IRA model concerns possible reducing microenvironments that might be found in the source area or in more impermeable zones of the saturated interbeds. These reducing environments could strongly limit the migration of Np(IV) and Pu(IV), which are only sparingly soluble.

5.7 Summary

The primary question addressed in this chapter is, "Are K_d s for Am, Np, Pu, and U that were used in the IRA model reliable and have they been applied appropriately?" The intent in selecting these K_d s was to use technically

Table 5-8. Effect of cation exchange capacity on K_ds[K_d, distribution coefficient; CEC, cation exchange capacity; meq/100 g, milliequivalents per 100 grams]

| | K _d suggested by Dicke (1997) based on CEC of 17.4 meq/100 g | K _d calculated for the smallest CEC of 0.9 meq/100 g | K _d calculated for the average CEC of 13.6 meq/100 g | K _d calculated for the largest CEC of 42 meq/100 g |
|-----------|---|---|---|---|
| Americium | 450 | 23 | 345 | 1,080 |
| Neptunium | 8 | 0.4 | 6.2 | 19 |
| Plutonium | 5,100 | 260 | 3,900 | 12,200 |
| Uranium | 6 | 0.3 | 4.6 | 14 |

defensible estimates for the K_ds and conservative estimates of other model parameters whenever “realistic” estimates were not available. It was not the intent of the IRA to present a worst case scenario. K_ds for Am, U, and Pu were determined experimentally; K_ds for Np were selected from the literature.

The K_d is a measure of the amount of a solute sorbed from solution by a solid phase. Advantages of the K_d approach are its mathematical simplicity and ease of obtaining experimental values. However, there are many limitations to the K_d approach. Generally, the K_d measured is a unique function of the aqueous and solid-phase compositions. This is especially true for inorganic solutes.

Thus, the K_d measured for sorption by a clay mineral will be different from the K_d measured for sorption by goethite. Competition for sorption sites is common. Increasing the concentration of competing solutes will decrease sorption of the solute of interest. Decreasing the concentration of competing solutes will have the opposite effect. Many ions form aqueous complexes with various ligands in solution. Changing the concentration of these ligands changes the concentration of the complex and alters the amount sorbed. Sorption is often pH dependent. Cation sorption increases with pH as the surface becomes more negatively charged. Anion sorption increases with decreasing pH as the surface becomes more positively charged. Changes in ionic strength of a solution can affect the electrical double layer surrounding particles to the extent that sorption properties change. If sorption is non-linear, K_d also will be a function of the aqueous concentration of the solute of interest.

The K_d approach may adequately describe contaminant migration and reversible sorption in ground-water

systems in which the aquifer regions occupied by the contaminant plume and by the background water each have uniform mineralogical and chemical compositions that remain uniform during the timescale of interest. In general, the reactive sorption of the contaminant of interest also must be adequately described by the local equilibrium assumption. The K_d approach generally will not properly describe contaminant migration in ground-water systems undergoing dynamic chemical evolution.

For the IRA model, a single composite of five sediment interbed samples was used in batch experiments to measure sorption of Am, U, and Pu from a synthetic ground water similar in composition to that from the SRP aquifer. Specific concerns regarding the K_ds recommended for use in the IRA model include the following:

(1) A literature survey of the CEC of 271 samples from the INEEL indicates that the sorption properties of aquifer solids can vary widely. Thus, although the K_ds measured for the IRA model may accurately represent sorption for the composite interbed sample used in the batch experiments, there is no guarantee that this sediment represents a technically defensible approach to estimating K_ds especially because the coarse-size fraction was eliminated from the composite samples.

(2) The assumption was made that sorption properties in the vesicles and fractures in the basalt were comparable to those in the sedimentary interbeds. Because these vesicles and fractures contain many minerals in common with the interbeds, this assumption may be valid but needs verification.

(3) The synthetic ground water used in these experiments was undersaturated with respect to CO₃ minerals, whereas most perched and infiltrating water at the SDA is

5-32 Review of the transport of selected radionuclides in the Interim Risk Assessment

saturated or supersaturated. Because CO_3 complexes are important in the aqueous speciation of actinides, the smaller CO_3 concentration in the synthetic ground water may have resulted in overestimating sorption. There is some evidence of calcite dissolution from the interbed sediment. The pH of effluent from column experiments increased from 8.0 to 8.4, and conductivity also increased. If calcite did dissolve in the batch experiments, then CO_3 concentrations could have increased to levels comparable to those of other water at the SDA. However, there were no data from the batch experiments to evaluate this possibility.

(4) The limited data presented in the report by Newman (1995) indicate that sorption was nonlinear; therefore, the measured K_d s apply only to the range of concentrations used in the experiments. Concentrations outside this range are likely to result in K_d s that are either smaller or larger than those reported here.

(5) The K_d of 5,100 mL/g for Pu(total) recommended for risk assessment modeling is based on experimental results for Pu(V). A K_d of 110 mL/g was measured for P(VI). Therefore, the recommended K_d for Pu(total) does not meet the stated intent to maintain technical defensibility and conservatism, unless it can be shown that Pu(VI) will not be present at WAG-7. These experiments were conducted using only one initial Pu concentration. If sorption is nonlinear, then the K_d will change with Pu concentration.

(6) A K_d for U as small as 3 mL/g was measured; therefore, the recommended K_d of 6 mL/g does not meet the stated intent to maintain technical defensibility.

(7) The cause of the enhanced-mobility fraction responsible for the early elution of Am and Pu in the column experiments needs to be resolved. If this fraction represents transport as an aqueous complex, then the K_d s

used in the IRA model are too large. If the radionuclides are transported as colloids, basing risk assessment on sorption-controlled transport may need to be reevaluated.

(8) Sorption also is dependent on the initial aqueous speciation of the actinide that enters the unsaturated zone from the disposal area. These species may be quite different from those used in the batch experiments. Therefore, K_d s could be much different.

(9) The experimental data from the literature used to select a K_d for Np show that sorption is highly dependent on aqueous-phase chemistry and solid-phase mineralogy. Given this dependency, it might be more appropriate to determine the sorption behavior of Np for the range of geochemical conditions specific to the INEEL. The literature K_d s that were evaluated ranged from 1 to 80 mL/g. Therefore, the K_d of 8 mL/g selected for risk assessment does not meet the intent to maintain technical defensibility and conservatism.

There are not enough data from WAG-7 to quantify all the uncertainty associated with the K_d s for Am, U, Np, and Pu used in the IRA model. The data presented in chapter 4 show that sorption of Am, U, Np, and Pu generally varies as a function of pH, CO_3 concentration, and sorption-site type and concentration. For 11 different water samples from the INEEL, thermodynamic modeling indicates that sorption of Am can vary by 400 percent, U by 3,000 percent, Np by 25 percent, and Pu by 55 percent. For a constant water composition, the K_d s selected for the IRA model could vary by as much as 1,500 percent for the range in concentration of surface sites measured in interbed sediment and fracture fill samples collected from the INEEL. In conclusion, the experimental conditions used to measure K_d s for the IRA model do not adequately represent the aqueous- and solid-phase variability at WAG-7.

6.0 Task 4: Transport model analysis

6.1 Introduction

The Interim Risk Assessment (IRA) model of water and contaminant transport, described by Becker and others (1998) and Magnuson and Sondrup (1998), supports the assessment of future risks to human health and safety from Subsurface Disposal Area (SDA) contaminants of potential concern (COPC's). The numerical basis of the model is the code TETRAD (Vinsome and Shook, 1993). Model output includes the aquifer contaminant concentrations that are the basis for estimates of effects on human health. This model is an essential element in predicting the effect of remedial options.

This review assesses the value and adequacy of this model as a tool for risk assessment. In this report, the term "IRA model" refers to the model used in the IRA to predict contaminant concentrations and the effects of hydrologic and chemical processes on the concentrations. This review does not evaluate the interpretation of these concentrations as risks to human health. A significant part of our evaluation is a comparison of model representations with the processes and phenomena explained in other parts of this report. Section 6.2 describes and reviews the IRA assumptions and simplifications used in setting up the numerical code. Section 6.3 describes and reviews specific aspects of the numerical code TETRAD and the calibration developed for it. Section 6.4 reviews the application of the model, especially with respect to its predictions and defensibility related to risk assessment.

This review also does not address issues that involve definition of the source term and modeling of contaminant release rates. It is clear that definition of the source term and release rates are at least as important as other issues related to the formulation of the computational scheme to predict actinide transport. As pointed out in the IRA, the source-term release-rate model has not been calibrated and remains a major deficiency that needs to be resolved (Becker and others, 1998, p. 5-38 and 7-12).

6.2 Review of significant Interim Risk Assessment assumptions and simplifications

The assumptions and simplifications used in modeling were described by Becker and others (1998) in the IRA, especially in the hydrologic descriptions in chapter 2 and the discussion of modeling assumptions in chapter 5. These assumptions and simplifications address the heterogeneity of the subsurface, possible transport mecha-

nisms, and limited interaction of water and contaminants with influences outside the Waste Area Group 7 (WAG-7) domain.

6.2.1 Hydrogeologic framework—geometrical aspects

This section discusses basic geometrical assumptions related to major components of the hydrogeologic system.

6.2.1.1 Definition and description of the model domain

In plan (horizontal) view, the SDA occupies an area with dimensions of about 1,500 m in the x direction (east to west) and as little as about 250 m to as much as about 750 m in the y direction (south to north). The additional consideration for modeling the transport of organic constituents effectively increased the modeled area to robust dimensions of 9,000 by 9,000 m (fig. 6-1).

In vertical cross section, the numerical simulator includes both the unsaturated and saturated zones. The unsaturated zone is assumed to be 175 m thick, and the saturated zone about 76 m thick. The assumed thickness of the Snake River Plain (SRP) aquifer, 76 m, is consistent with the WAG-3 and WAG-10 modeling studies (Becker and others, 1998, p. 5-66) and is supported in studies by Rodriguez and others (1997), McCarthy and others (1995), and Robertson (1974). As noted in chapter 2, these are among the smallest estimates of thickness for the SRP aquifer. Therefore, this assumption is probably conservative for predicting dilution of contaminants in the aquifer; however, dispersion and advective mixing processes in the saturated zone are not well characterized.

The plan view and vertical cross-section dimensions define a study volume that is 81 km² and 251 m thick, or about 20 km³. This block is the model domain. Within the model domain, an area of local grid refinement is defined that is 3,000 m in the x direction and 2,000 m in the y direction. Almost all of the data available for modeling are from the region of this smaller sub-domain (fig. 6-1).

The land surface is treated as if it were perfectly flat (Magnuson and Sondrup, 1998, p. 2-6). Although actual deviations from flatness are likely the main local influence on infiltration rates at the SDA, the effects of these topographic deviations are incorporated into the infiltration rates estimated by Martian (1995, p. 31) and used in the IRA model. Because there are likely no other major effects of the flat-surface assumption, its use in the model likely does not significantly affect model predictions.

The surficial sediments and sedimentary interbeds (A-B, B-C, and C-D) are assumed to have spatially variable geometric surfaces and thicknesses that affect water and contaminant movement (Becker and others, 1998, p.

6-2 Review of the transport of selected radionuclides in the Interim Risk Assessment

5-65). Although this assumption is clearly true, the specific means of representing these lithologic units in the IRA model could underestimate the degree and hydrologic effect of this variability. Uncertainties associated with this assumption are discussed further in section 6.2.1.2 on geostatistical applications. In particular, the kriging techniques used to treat this variability inherently entail smoothing that may misrepresent geometric features that deflect or concentrate water and contaminant transport. However, information that would permit a detailed treatment of these geometric features is not available and possibly not obtainable by any practical means.

Interbeds below the C-D interbed are assumed to be thin and discontinuous and to have no significant effect on flow and contaminant transport near the SDA (Becker and others, 1998, p. 5-65). In actuality, these lower interbeds are discontinuous, but they could be substantial in places (Anderson and Lewis, 1989, p. 24-31). Discontinuous interbeds could generate additional preferential flow (Magnuson and Sondrup, 1998, p. 6-5 to 6-6), for example, by the mechanism of funneled flow, but in the absence of this mechanism, they affect flow similarly to the more continuous interbeds. Although preferential flow is not treated explicitly in the model, because there are probably greater causes of preferential flow in the unsaturated zone and because interbeds are the primary sorbing media for the actinides and have a generally impeding effect, the exclusion of these units from the model probably is conservative.

6.2.1.2 Geostatistical applications

The subsurface lithology at the SDA consists of a discontinuous layer of surficial sediments that is underlain by a series of basalt flows separated by discontinuous but mappable interbeds of alluvial and eolian sediments (A-B, B-C, and C-D interbeds). The surficial sediments and interbeds correspond to the horizons of enhanced resolution in the vertical discretization of the model domain as presented by Magnuson and Sondrup (1998). The positions of the interbeds are known from borehole information that defines the elevation of the top of a given interbed and, in cases of complete penetration, its thickness. Geostatistical techniques were used to interpolate the top elevation and thickness of the three primary interbeds and the surficial sediments through the grids that discretize the model domain. A review and some extension of the geostatistical techniques used in the IRA model are presented below. This work starts from the basic geostatistical analysis of Magnuson and Sondrup (1998) and reviews the results of decisions made in their analyses and interpretations. Although this review is mostly qualitative, quanti-

tative evaluation of results are presented. The qualitative review includes a discussion of the procedural steps used in the IRA and implications inherent in geostatistical applications. The quantitative evaluations are based on cross-validation statistics that are presented in maps and tables that describe kriging standard deviations. Much of the information presented in these evaluations originated in this review because cross validation and kriging standard deviations were not reported by Magnuson and Sondrup (1998).

The data used for these quantitative evaluations were residuals obtained from detrended raw data presented in table 2-1 of Magnuson and Sondrup (1998, p. 2-2 to 2-4). The detrending procedure is briefly described and discussed below. It is important to note that the kriged estimates were not added back to the spatial trend, or retrended in our quantitative evaluations to describe variability and confidence in the kriged estimates. The number of data points available for fitting variogram models of the thickness and top elevation of the surficial sediments and sedimentary interbeds was different for each of these units. However, the number of points available for each lithologic unit was sufficient for adequate definition of most sample variograms. However, the distribution of data limit the spatial representativeness of defined sample variogram points. All data, except those for a few widely spaced points within the larger expanse of the 9,000 by 9,000 m model domain, were collected within the SDA. This necessitated the assumption that the values of the variograms defined at lags within the SDA also apply in the general model domain if the variograms are to be used in these areas. Conversely, definition of the variograms at larger lags was problematic because of the lack of data locations at these lag values.

The geostatistical analyses for each of the eight variables (top elevation and thickness of the surficial sediments, and the A-B, B-C, and C-D interbeds) consisted of three steps:

- (1) defining a polynomial drift or spatial trend for each variable (top elevation and thickness) and removing this trend to develop residuals that formed the data set for the remainder of the kriging analyses (detrending the data),
- (2) construction of variograms for the data set of residuals for each variable, and
- (3) kriging the residuals, using ordinary kriging, to grid locations and adding back the trend values computed for these locations (retrending the data).

Although justification for defining spatial trends was not readily apparent, the equations describing the trends were kept to low-order polynomials by Magnuson and

Sondrup (1998), as is generally recommended. In addition, as part of this review, the relation between the resultant residuals and the x and y coordinates were found to be free of trends. The use of residuals introduced the possibility of universal kriging as an alternative to ordinary kriging, which would have negated the need for retrending. It is not expected that the use of universal kriging methods would produce any changes to the results. Use of these alternative methods is simply mentioned because retrending and detrending procedures are handled in the actual kriging process rather than with pre- and post-processing steps.

The kriged top elevations for the surficial sediments and the three interbeds were used to place each lithologic unit in the vertical grid. The kriged thicknesses were used to describe spatial variation in the horizontal grid and to distribute the vertical thickness. It is important to note, as Magnuson and Sondrup did (1998, p. 2-9), that known areas of zero thickness were superimposed onto the kriged thickness results. The need for this is discussed in section 6.2.1.2.2.

6.2.1.2.1 Variogram construction

The variogram model and parameters for each variable are given in table 6-1 and figures 6-2 through 6-5. All variograms have stationary models within their ranges and are described by spherical, exponential, or Gaussian forms. Nugget values range from 0 to 1.6 m^2 . Most of the sill values apparently were set to the variance of the residual data sets. This systematic procedure is not uncommon. It slightly simplifies variogram modeling in that the sill is not estimated from the sample variogram points but instead is set. The effects of this procedure on results in this study are practically insignificant.

Figure 6-2b shows the variogram used by Magnuson and Sondrup for the thickness of the surficial sediments. The range of 172 m for the surficial sediment thickness reported by Magnuson and Sondrup (1998), the smallest range of any of the eight variables, is also the range they used to model the variogram. The reported ranges of all other variables (Magnuson and Sondrup 1998), except for that of the C-D interbed thickness (also used to model the variogram), are one-third of the ranges used in this review and appear to be correlation lengths. The correlation length often is cited in the literature as being a conservative range and is approximately one-third of the range used to fit the sample variogram points. Some subjective adjustment of the variogram model, such as increasing the sill or range or both, is possible. For this reason, values for the sill and range (adjusted for correlation length) reported in table 6-1, differ slightly from table 2-2 by

Magnuson and Sondrup (1998). However, it is important to note that even the most optimistic adjustment would only nominally increase the range. In a strict sense, that assumes spatial variability is well characterized within the range, additional information collected from the field can provide increased variogram range if it is collected from points located farther than the variogram range of existing point information.

The extent of the ranges of most variables in the variogram are such that kriging analyses for areas near the SDA can be an effective estimation procedure, implying that the advantages of kriging over other estimation techniques will be realized. Figures 6-2a and 6-5a show the variograms for the top elevations of the surficial sediments and the C-D interbed. Ranges for top elevations for these variograms, in contrast to those for the thickness of the surficial sediments and the C-D interbed are extended, which allows estimation of the top elevation over a much larger area. These variograms also are unusual with respect to their cross-validation statistics, as discussed below.

Outside the SDA but within the model domain, the spatial distribution of data (residuals) points for most variograms relative to the ranges of variables in the variogram eliminates kriging's special advantages in distributing spatial information; therefore, kriging becomes ineffective and estimation defaults to simple averaging of available data. Some indication of this is evident in the summary statistics presented in table 6-1, as discussed below.

The variograms for each variable were evaluated by a kriging cross-validation technique in which a data point for a location is omitted from the data set and kriging results for that location are obtained by using the subset of remaining values. The procedure is repeated for each value in the data set. Therefore, each data location will have a kriging estimate, a kriging standard deviation, and a data value. Statistics obtained from cross validation include (1) a mean estimation error defined as the difference between the data value and the kriging estimate, and (2) a root-mean-squared error ratio defined as the estimation error divided by the kriging standard deviation. Acceptable variograms are those for which cross-validation indicates a mean estimation error near zero (ensuring unbiasedness), a minimized root-mean-squared error (ensuring a small error estimate), and an average reduced root-mean-squared error near unity (ensuring consistency in the estimation accuracy).

6-4 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 6-1. Variogram models, parameters, and cross-validation statistics for thickness and top elevation variables for surficial sediments and interbeds A-B, B-C, and C-D

[Units for nugget and sill are meters squared; units for range, mean error, and root-mean-squared error are meters; ranges reported in this table were adjusted by a factor of 3 to compensate for presumed reporting of correlation length by Magnuson and Sondrup (1998) except ranges for the thickness of surficial sediments and the C-D interbed, which were reported as true ranges. Sample numbers shown in parentheses () for the thickness variable indicate the number of samples within the total sample set that represent partial penetration of the interbed. These values are reported as greater than the penetrated thickness by Magnuson and Sondrup (1998, table 2-1)]

| | | | Parameters | | | Cross-validation statistics | | |
|---------------------|-------------------|-----------------|------------|-------|-------|-----------------------------|-------------------------|---------------------------------|
| Variable | Number of samples | Variogram model | Nugget | Sill | Range | Mean error | Root-mean-squared error | Reduced root-mean-squared error |
| Surficial sediments | | | | | | | | |
| Thickness | 94 | Spherical | 1.30 | 3.90 | 176 | 0.037 | 1.621 | 0.868 |
| Top elevation | 94 | Gaussian | 0.80 | 20.30 | 3,900 | 0.170 | 3.443 | 1.424 |
| A-B interbed | | | | | | | | |
| Thickness | 94 (1) | Exponential | 0.15 | 1.03 | 330 | 0.035 | 0.603 | 0.841 |
| Top elevation | 44 | Exponential | 0.00 | 5.50 | 350 | 0.317 | 1.268 | 1.136 |
| B-C interbed | | | | | | | | |
| Thickness | 91 (3) | Exponential | 1.60 | 5.10 | 480 | -0.090 | 1.918 | 1.018 |
| Top elevation | 91 | Exponential | 0.20 | 2.80 | 450 | 0.050 | 1.045 | 1.052 |
| C-D interbed | | | | | | | | |
| Thickness | 76 (22) | Spherical | 0.00 | 8.50 | 205 | -0.078 | 2.839 | 2.244 |
| Top elevation | 76 | Gaussian | 1.00 | 11.00 | 2,900 | 0.395 | 3.120 | 1.536 |

The cross-validation statistics are shown in table 6-1. The results indicate that the mean estimation errors for some variables are smaller than the absolute value of 0.10 m. For this study, these smaller values are relatively good. Mean errors for three of the four top elevations are larger than 0.10 and, for the C-D interbed, are about 0.40. The reduced root-mean-squared errors usually are considered acceptable if they are within an interval defined as follows:

$$1 \pm 2 \sqrt{\frac{2}{\text{number of samples}}} \quad (6.1)$$

Using this reduced root-mean-squared error criterion for the variograms for the top elevation of the surficial sediments and the top elevation and thickness of the C-D interbed variables should be considered less than optimal for the region encompassed by the model domain (9,000 by 9,000 m).

6.2.1.2.2 Kriging results

The kriging standard deviation, a product of kriging theory, is a function of the geometry of the data points implemented through the variogram that is used for obtaining a kriging estimate. It is also a measure of the uncertainty associated with a kriged estimate; therefore, the kriging standard deviation is also a measure of confidence. Maps of kriging standard deviations often are presented with maps of kriging estimates so that the areas where kriging is most effective and where it is ineffective can be seen. Kriging standard deviation maps were prepared as part of this review for all variables and the results are summarized in table 6-2 and illustrated in figures 6-6 through 6-21.

Table 6-2 shows that for all variables except two (the top elevations for the surficial sediments and the C-D interbed), the kriging process was ineffective throughout about 90 percent of the 9,000 by 9,000 m model domain. In other words, although the kriging process was capable of making estimates, most of the estimates were based on simple averaging of data. In contrast, at the SDA, which represents about 5 percent of the model domain, all variables, except perhaps the top elevation of the A-B interbed (fig. 6-10) and the thickness of the C-D interbed (fig. 6-20), were effectively characterized.

Figures 6-7 and 6-9 represent the extremes for all the characterizations. The results for the top elevations of the surficial sediments, which came from a variogram with one of the longest ranges (fig. 6-1), portray relatively high confidence in kriged estimates for most of the 9,000 by 9,000 m model domain. The results for the thickness of the surficial sediments, which came from the variogram

with the shortest range (fig. 6-1), portray the highest confidence in kriged estimates for most of the SDA area; however, the full advantages of kriging were not realized for most of the model domain. These areas are characterized as those of ineffective kriging in this review and correspond to areas that are farther from any measured values than the particular variogram range.

In summary, the range of the variograms is an important factor in determining how much of the model domain will be characterized effectively by kriging. For the variables kriged by Magnuson and Sondrup (1998), only two, the top elevations for the surficial sediments and the C-D interbed, were characterized effectively for more than about 10 percent of the 9,000 by 9,000 m model domain. However, the kriging for the other variables was generally effective for most of the SDA. For areas where kriging was ineffective, estimates are essentially equivalent to those obtained from simple averaging.

It is also important to note that the kriging process introduces smoothing into the resultant estimates; therefore, for estimates of thickness, kriging will extend areas of nonzero thickness into areas of zero thickness. To preserve known gaps in the sedimentary interbeds in the SDA, Magnuson and Sondrup (1998, p. 2-9) superimposed areas of zero thickness onto kriging results.

6.2.2 Nature of materials

The effect of particular subsurface materials on water and contaminant transport is represented quantitatively in the IRA model by specific hydrologic characterizations. Table 6-3 summarizes the basic model components involved, with information on the types of measured or estimated data used to characterize them.

Magnuson and Sondrup (1998, p. 2-9) noted that the hydraulic properties used in the IRA model were delineated on the basis of lithology, and thus that their simulation represents “only contrasts in hydraulic properties between dissimilar media (sediments and fractured basalts)”. This implies the assumptions that (1) the hydraulic properties correlate strongly with directly observable features of the subsurface media, and (2) the properties are homogeneous within each lithologically identifiable layer. These assumptions allow the grouping of property characterizations (by various means) within a geomorphologically distinguishable layer. Given the small number of available measurements, these kinds of assumptions are unavoidable in the current (1999) modeling efforts, but they create serious problems in determining the reliability of model results.

6-6 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 6-2. Relative confidence in kriging estimates

[Confidence range, relative confidence in kriging estimate expressed as a percentage of maximum confidence; ineffective kriging applies to areas where the kriging process is equivalent to simple averaging]

| Variable | Confidence range | | | | Area of ineffective kriging |
|---|------------------|-----------|-----------|-----------|-----------------------------|
| | 0 to <25 | 25 to <50 | 50 to <75 | 75 to 100 | |
| Fraction of model domain in specified lithologic unit | | | | | |
| Surficial sediments | | | | | |
| Thickness | 0.02 | 0.01 | 0.01 | 0.00 | 0.97 |
| Top elevation | 0.08 | 0.22 | 0.36 | 0.33 | 0.00 |
| A-B interbed | | | | | |
| Thickness | 0.05 | 0.02 | 0.01 | 0.00 | 0.92 |
| Top elevation | 0.03 | 0.01 | 0.00 | 0.00 | 0.95 |
| B-C interbed | | | | | |
| Thickness | 0.08 | 0.03 | 0.02 | 0.01 | 0.86 |
| Top elevation | 0.07 | 0.03 | 0.01 | 0.00 | 0.89 |
| C-D interbed | | | | | |
| Thickness | 0.02 | 0.01 | 0.01 | 0.00 | 0.96 |
| Top elevation | 0.10 | 0.21 | 0.36 | 0.33 | 0.00 |

Table 6-3. Summary of hydrologic characterizations used in the Interim Risk Assessment (IRA) model (Magnuson and Sondrup (1998, see especially table 2-4). Some characterizations were adjusted in the IRA model calibration, see table 6-6, section 6.3.2 of this report)

[IRA, Interim Risk Assessment; SDA, Subsurface Disposal Area; K_{sat} , saturated hydraulic conductivity; WAG, Waste Area Group; LSIT, Large Scale Infiltration Test; COPC's, contaminants of potential concern]

| Hydrologic characterization for the IRA model | Basis of evaluation | Estimated quantities | Comments |
|---|---|---|--|
| Flow properties of surficial sediments | Neutron-measured transient water contents in 17 holes in the SDA (Bishop, 1996; Martian, 1995, UNSAT-H calibration) | K_{sat} : van Genuchten-Mualem unsaturated flow parameters | The model as constructed has little direct sensitivity to these because infiltration/recharge/runoff effects are treated separately in the infiltration model |
| Infiltration in the SDA (combined effects of climatic and hydrogeologic properties) | Neutron-measured transient water contents in 17 holes in the SDA (Bishop, 1996; Martian, 1995, UNSAT-H calibration) | Spatially and temporally variable infiltration rates at the SDA | Only two holes are in disturbed soils; uncertain contributions from historic floods; calibration data from 1994 and 1995 only |
| Flow properties of interbed sediments | WAG-3 modeling estimates; core-sample characterizations by Magnuson and McElroy (1993) | K_{sat} : van Genuchten-Mualem unsaturated flow parameters | Available data do not permit characterization at the level of accuracy and detail relevant to contaminant transport |
| Flow and transport properties of basalts in the unsaturated zone | Water and tracer data from the LSIT | Horizontal and vertical permeability; fracture porosity; longitudinal dispersivity | Selective use of data from the LSIT that supported use of a radially symmetric porous-media equivalent model |
| Flow properties of basalts in the saturated zone | WAG-10 model results; pump-test data; potentiometric-surface data | Horizontal permeability | Selective use of hydraulic head data; limited hydraulic head data to define boundary conditions; neglect of possible effects of spreading areas; determination only of ratios of permeabilities from different units |
| Contaminant transport properties of COPC's | Measured concentrations of contaminants in the aquifer | Distribution coefficients; specific-surface areas and apertures of fractures in basalts | Source-term uncertainty; use of nondetects in calibration |

6-8 Review of the transport of selected radionuclides in the Interim Risk Assessment

6.2.2.1 Means used to determine hydraulic properties

The means available to determine hydraulic properties usually involve a tradeoff between quality of results (especially directness and accuracy) and cost or convenience. Studies of large and complex regions of the subsurface, like that of the SDA, usually rely heavily on indirect methods (for example, inverse modeling, as discussed below) that typically provide results on a larger scale but with less resolution and less reliability than more direct methods. In some cases, data from more direct means are available. For example, water retention of surficial sediment cores (Shakofsky, 1993, 1995), can be measured directly, either in situ or with extracted samples. These kinds of direct measurements usually do not represent the entire range of relevant media or conditions, so it is frequently necessary to interpolate or, less desirably, to extrapolate. These procedures could be used, for example, to estimate the needed properties at different water contents or spatial positions. Another practical use of direct measurements is comparison with inverse-model results to determine whether the measurements support or invalidate the more voluminous but lower quality modeled results. The adaptation or adjustment of measurements from one medium to another, although generally less reliable than direct measurements, is adequate for some purposes. For example, hydraulic conductivity measurements for a coarse sand can be adjusted by scaling methods (Miller and Miller, 1956) to estimate the hydraulic conductivity of a similar, but finer, sand. There also are methods available for predicting certain properties from other, easier-to-measure properties. In unsaturated zone hydrology, one of the most widely used types of such methods is based on capillary bundle models (Childs and Collis-George, 1950; Mualem, 1976) that predict unsaturated hydraulic conductivity from water retention. A method of this type can be used in combination with the assumption by Magnuson and Sondrup (1998) that hydraulic properties can be based on lithology rather than individual measurements.

Most of the methods used for estimating the hydraulic properties of the various subsurface materials at the INEEL involve some form of inverse modeling. For example, the field-scale hydraulic properties of the fractured basalts were assumed to be adequately described by the inverse model results by Magnuson (1995) for the Large Scale Infiltration Test (LSIT) (Becker and others, 1998, p. 5-66). The basic scheme of inverse modeling is the systematically repeated use of a forward model, which predicts a measurable quantity (for example, water levels in a well as a function of time) from fundamental properties of the system (for example, hydraulic conductivity)

and particular input conditions (for example, infiltration as a function of time). Inverse modeling is used when the predicted quantity is already known, but the fundamental properties of the system are not. The forward model calculations are repeated with systematically varied trial values of the fundamental properties, so that the property values that lead to the most accurate output can be identified and taken as system characteristics. One common pitfall is that the results are not necessarily unique—more than one combination of input property values can lead to essentially the same output, so the system characteristics identified may not be the best possible. For example, if a deficiency in one property or in some aspect of the model framework compensates for another deficiency that has an opposing effect, then the result of the inverse modeling will be fundamentally defective in a way that may not be apparent. The reliability of inverse modeling results depends strongly on the appropriateness of applied assumptions and simplifications, for example, those concerning surface-water ground-water connections, multimodal porosity, anisotropy, and matrix diffusion. Reliability of results also requires that all significant phenomena related to contaminant transport are represented in the data used for the calibration. For example, time and space intervals and the type of measurements must not be insensitive to hydrologic processes of significance. Model calibration (discussed for the IRA model in section 6.3.2) generally involves inverse modeling in which a particular data set is chosen as a target or standard for the predicted quantities.

6.2.2.2 Fractured basalts in the unsaturated zone

Some assumptions included in the IRA model are that in the fractured porous basalts, flow is controlled by the fracture network and that the basalts can be represented adequately as equivalent to a high-permeability, low-porosity medium (Becker and others, 1998, p. 5-66). As discussed in chapter 2, such consideration of fractured media as equivalent to granular media is common. This assumption means, however, that all important transport phenomena must be encompassed by the equivalent medium. For purposes of predicting travel times, this assumption is a basic deficiency in the model and, therefore, is not a conservative assumption. Because spatially averaged behavior is inherent in the equivalent-granular-medium assumption there will be some flow paths with markedly faster transport than this assumption predicts. Unless the amount of contaminant transport in such preferential-flow paths is negligible because of factors such as dilution in the subsurface, this assumption will lead to

underpredictions of contaminant concentrations at certain points away from the source.

Various algebraic formulas can represent hydraulic properties of the medium that is taken as equivalent to the fractured, porous basalts. The IRA model uses the Brooks-Corey (1966) and van Genuchten (1980) empirical formulas for water retention curves. For the relative permeability/saturation and saturation/water potential relations for the fractures in the basalts it uses the Brooks-Corey formulas (Brooks and Corey, 1966). Both of these relations were developed and tested for use with soils, not fractured rock. However, there is precedent and support for their use with fractures, for example, the use of the Brooks-Corey formula to represent water retention in single fractures (Reitsma and Kueper, 1994). A van Genuchten curve resembles a Brooks-Corey curve but differs mainly in having a rounded rather than a sharp bend at the part of the curve representing the transition from saturation to unsaturation. Thus a van Genuchten curve could represent water retention in a fracture. For an assemblage of fractures, as in a macroscopic chunk of basalt, the resulting hydraulic properties probably would be represented reasonably by these formulas, but because the curve near the saturated-unsaturated transition probably would be more smoothly rounded, the van Genuchten formula could be a better representation. These formulas might be as suitable for fractured basalts as for soils, but for either type of medium, these representations sometimes deviate substantially from the actual properties. This deviation, which typically is a problem, for example, when the dry range is important (Nimmo, 1991), is currently a topic of controversy in the hydrologic community. Liu and others (1998) concluded that because not all fractures actively conduct water, the processes involved in conducting flow by only a few fractures "may require formulating the fracture water flow in a different way." They also noted that "Specifically, the van Genuchten (1980) and other relations... may not be valid for describing fracture water flow without suitable modification or generalization." Magnuson and Sondrup (1998, p. 2-25) also acknowledged this by noting that "Determining constitutive relationships for fractures continues to be an active research area."

The hydrogeologic properties of basalts in the unsaturated zone, (the permeability (k), anisotropy (k_v/k_h), the fracture porosity (n_f), the longitudinal dispersivity (V_L), and the Brooks-Corey parameters for unsaturated water retention and relative permeability), were determined by inverse modeling to data collected during the LSIT (Magnuson, 1995; Dunnivant and others, 1998). The LSIT was conducted by ponding water on the ground surface in a

183-m-diameter basin and monitoring for the arrival of water and conservative and reactive tracers in wells located on lines radiating outward from the center of the basin and in rings located 15, 90, and 230 m from the edge of the basin. Magnuson and Sondrup (1998) further refined the parameter values using limited borehole data on the distribution of perched water beneath the SDA and changes in the elevation of perched water over time (section 6.3.2).

Estimates for values of properties of the basalts used in the simulations by Magnuson and Sondrup (1998, table 2-4) were taken from a variety of sources. Values used as initial estimates of permeability for basalts in the unsaturated-zone portion of the model were taken from Magnuson (1995, table 4). Based on perched water-level changes directly beneath the circular infiltration pond and water-level changes at observation wells located at varying distances from the pond, Magnuson estimated the vertical permeability (k_v) to be 300 mD and the horizontal permeability (k_h) to be 90,000 mD. Magnuson (1995, p. 38) recommended a porosity of 0.03 and a k_v of 175 mD to best match B- and C-ring hydrographs and B-ring breakthrough curves in the LSIT. The values used in the IRA model for porosity and k_v , 0.05 and 300 mD, respectively, were not entirely consistent with the inverse-model results of the LSIT. Magnuson and Sondrup (1998) found it necessary to decrease k_h to 9,000 mD to recreate perched-water conditions beneath the SDA. Larger values of k_h allowed modeled percolation from the SDA to migrate rapidly downdip, and prevented the observed perched-water lenses from being simulated. The permeability estimates considered by Magnuson and Sondrup (1998) are presented in table 6-4.

The relation between relative permeability and saturation for basalts was assumed by Magnuson and Sondrup (1998) to be linear. Magnuson (1995) showed that the simulated water movement in the basalts beneath the basin of the LSIT was somewhat sensitive to the curvature in the assumed relative water-permeability/water-saturation relation; as the curvature in this relation increased, the rate of water movement slowed because the fractures had to fill to a large extent before their permeability increased sufficiently to transmit the infiltrating water (Magnuson, 1995, p. 32-37). Magnuson (1995) concluded, probably correctly, that the rate of water movement was more sensitive to the absolute (saturated) permeability than to the unsaturated hydraulic characteristics of the fractures.

6-10 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 6-4. Estimated permeability of fractured basalts at the Subsurface Disposal Area (SDA) considered for use in the Interim Risk Assessment model

[WAG, waste area group; k, permeability; mD, millidarcy; k_v , vertical permeability, k_h , horizontal permeability]

| WAG-10 model | SDA saturated-zone model | Large-Scale Infiltration Test | SDA unsaturated-zone model |
|-----------------------------|---------------------------|-------------------------------|----------------------------|
| $k_{zone53} = 168,000$ mD | $k_{low} = 153$ mD | $k_v = 300$ mD | $k_v = 300$ mD |
| $k_{zone54} = 1,800,000$ mD | $k_{medium} = 16,300$ mD | $k_h = 90,000$ mD | $k_h = 9,000$ mD |
| | $k_{high} = 1,200,000$ mD | | |
| | $k_{basalt} = 85,000$ mD | | |

As Magnuson and Sondrup (1998) noted, data on the unsaturated hydraulic characteristics of fractures are extremely limited; however, several theoretical studies indicate that the relation between water relative permeability and water saturation is nonlinear (for example, Kwicklis and others, 1998, figs. 17 and 18c). Based on the sensitivity analysis performed by Magnuson (1995), the effect of including a nonlinear relative permeability relation in the simulations would be a calibrated absolute permeability larger than otherwise would be calculated in order to compensate for the relatively small fracture permeability associated with the nonlinear curves at partial saturation. Alternatively, the effect of including a nonlinear relative permeability/saturation relation would be to hold the perched water beneath the SDA with a larger absolute permeability for the basalt (Magnuson and Sondrup, 1998).

Both Magnuson (1995) and Magnuson and Sondrup (1998, p. 2-26 to 2-27) assumed a value of 32 kPa for the Brooks-Corey fitted parameter for matric-potential scaling (A_{aw}). This implies that the average fracture aperture is 47×10^{-6} m (47 μ m), based on the capillary rise equation adapted for parallel-plate fractures (Kwicklis and Healy, 1993):

$$P_c = \Delta\rho gh = 2\sigma\cos\Theta b_f \quad (6.2)$$

where:

- P_c = capillary pressure (32,000 Pa);
- ρ = density of water (997.0 kg/m³ at standard temperature);
- g = gravitational acceleration (9.81 m/s²);
- h = height of capillary rise (m);
- σ = interfacial surface tension between water and air (75 x 10⁻³ N/m at standard temperature);

Θ = contact angle between the media and the water (typically assumed to be 0 for silica-based glasses); and b_f = fracture aperture (m).

In determining the fracture surface area for the basalts, Magnuson and Sondrup (1998, p. 5-6) assumed that the fracture porosity (ϕ_f) of the basalts is 0.05 and that the fracture apertures are 0.001 m (1,000 μ m), considerably larger than the 47 μ m apertures implied by the assumed A_{aw} value of 32 kPa, as noted above. The Magnuson and Sondrup values of ϕ_f and b_f imply that there are $\phi_f/b_f = 50$ fractures per m³ assuming that each fracture extends over a 1-m² area within a 1-m³ volume. If there are, for example, 3 mutually orthogonal fracture sets, then about 34 fractures per cubic meter contribute to permeability in any direction. Calculated from the cubic law, the permeability of a single fracture, k_f , is:

$$k_f = b_f^2/12 = (0.001)^2/12$$

$$k_f = 8.3 \times 10^{-8} \text{ m}^2 \quad (6.3)$$

and the fracture continuum permeability (k_{fc}) may be calculated as:

$$k_{fc} = (34)(8.3 \times 10^{-8} \text{ m}^2)(0.001 \text{ m/m})$$

$$k_{fc} = 2.8 \times 10^{-9} \text{ m}^2 \quad (6.4)$$

This value of k_{fc} is approximately 2,800 D or 2,800,000 mD, a value that is much larger than the k_{fc} value of 9,000 mD that Magnuson and Sondrup used in the model.

In summary, the modeled hydraulic properties of the basalts are highly simplified with respect to actual characteristics. When interpreted on the basis of simple parallel-

plate models, assumptions about the capillary properties, porosity, aperture and permeability of the fractured basalts are not entirely consistent with each other. Although these inconsistencies do not necessarily negate the conclusions of the study, improved internal consistency would give more credence and rigor to the results.

6.2.2.3 Surficial sediments

The IRA model relies for hydraulic properties of the surficial sediments on averages of Martian's (1995) inverse model results fit to neutron data from 17 shallow boreholes in the SDA. The laboratory measurements of Shakofsky (1995), summarized by Shakofsky and Nimmo (1996) and updated by Nimmo and others (1999), are useful for comparison with the inverse model results because these direct measurements were made on core samples from undisturbed soil and a simulated waste trench near the SDA. The model results differ from direct measurements in that (1) the inverse-modeled K values of Martian (1995) tend to be smaller by an order of magnitude or more, and (2) water retention remains near saturation at more extreme values of matric pressure. The second difference could also be described by saying that the Martian curves have air-entry pressures farther from zero matric pressure.

Small K might mean that the model tends to underestimate flow rates. Air-entry pressures farther from zero might mean that the model tends to overestimate the amount of soil that is near saturation (and hence would have faster flow). At any given time, these deviations might compensate for each other to some degree, but the net effect is not predictable from available information.

The hydraulic properties of the surficial sediments relate to the local hydrology in many respects. The surficial sediments are not considered to substantially impede contaminant transport, so flow rates within them probably are not a major influence on the modeled concentrations relevant to risk assessment. The properties are closely related to infiltration and recharge, but treatment of these factors in the model does not depend directly on the estimated hydraulic properties of the surficial sediments.

Another assumption is that waste at the SDA has the same hydraulic properties as the surficial sediments (Becker and others, 1998 p. 5-65). Although this is obviously not true, it is a reasonable assumption in the sense that it should not affect the WAG-7 modeling significantly. Hydraulic properties of the waste could affect source releases, but the model treats this factor in terms of the release rate in the source term. Wastes are a small fraction of the volume of the surficial layers and (except for being the source of contaminants) are not likely to signif-

icantly affect contaminant transport. The disturbances caused in the process of burial can significantly affect the hydraulic properties of the surficial sediments (Andraski, 1996; Shakofsky and Nimmo, 1996), but again, such effects are treated indirectly in the infiltration model.

6.2.2.4 Sedimentary interbeds

In a general way, properties and possible transport modes of the interbeds are similar to those of the surficial sediments. In part because they are less accessible, the interbeds have been even less completely characterized in terms of hydraulic characteristics and heterogeneity than the surficial sediments. The hydraulic properties of the sedimentary interbeds are assumed implicitly in the IRA to be adequately represented as equivalent to those of a homogeneous, isotropic, granular porous medium in which the flow is not preferential.

Magnuson and Sondrup (1998, p. 6-5) summarized the quality of the available data to characterize the hydrologic properties of the sedimentary interbeds as follows:

A-B interbed—four samples, two boreholes: "...the available samples are not adequate to hydraulically characterize the A-B interbed...A-B interbed was assigned the same hydraulic properties as the C-D interbed based on the similar lithology of the two interbeds." Vertical hydraulic conductivity varies within three orders of magnitude.

B-C interbed—six samples, five boreholes: "The samples that have been recovered are biased toward lower permeability because they are composed of finer-grained materials which are more easily recovered...the number of samples...is not adequate to hydraulically characterize the B-C interbed." Vertical hydraulic conductivity varies within six orders of magnitude.

C-D interbed—34 samples, 14 boreholes"...characterization appears adequate for the C-D interbed." The C-D interbed generally contains more clay and loam leading to better sample recovery." Vertical hydraulic conductivity ranges over seven orders of magnitude.

For the lower interbeds no samples were available.

There are potentially serious shortcomings in the assumed homogeneity of materials and flow. The interbeds in at least some places have a high degree of internal stratification and other hydraulically significant structural features (Rightmire and Lewis, 1987a; Hughes, 1993). The presence of lenses or layers of texturally contrasting materials at a vertical scale of centimeters or millimeters indicates a high likelihood that funneled flow is common in these materials. Unstable flow is also possible, and heterogeneities of the materials may cause some degree of macropore flow. Some of these preferential-flow features

6-12 Review of the transport of selected radionuclides in the Interim Risk Assessment

may channel the bulk of water and contaminant movement within a fraction of the total volume of the interbeds. The model treats preferential flow (section 2.4.3.3) only implicitly in the inferred effective hydraulic properties of the interbeds. This treatment is similar to that for flow in the basalts, though flow in the interbeds could be complicated by the possible combination of various preferential-flow modes with nonpreferential flow.

The IRA model hypothesizes a continuous impeding layer at the top of the B-C and C-D interbeds (Magnuson and Sondrup, 1998, p. 3-7), which could represent a layer of clay at the top of these interbeds, or sediment filling of fractures in the basalts immediately above the interbed. Such feature have been described (Barraclough and others, 1976), but the main reason for including these layers is to improve the match to perched-water levels in inverse modeling for model calibration (section 6.3.2.1). At least some direct observational evidence of interbed materials contradicts this hypothesis, for example textural profiles that become generally finer with increasing depth within the interbed (Rightmire and Lewis, 1987a, p. 43; Hughes, 1993, fig. 12). Some observations support a more random distribution of clays within interbeds (Rightmire and Lewis, 1987a, p. 34). These observations strongly indicate that if such interbed-capping clay layers exist near the SDA, they are not continuous. The possible nonuniqueness of inverse modeling results could account for the better matches to hydrologic data when this hypothetical clay layer is included. Alternatively, the clay layer may serve to compensate for some other, unaccounted-for mechanism that has an impeding effect.

In a study that is being done by the USGS (K.S. Perkins and J.R. Nimmo, USGS, 1999, written commun.) to develop methodologies for drilling, coring, and characterizing the hydrologic properties of the sedimentary interbeds, continuous cores of the B-C interbed were recovered from two boreholes (UZ98-1 and UZ98-2) located southwest of the SDA (fig. 6-22). The B-C interbed at this location is approximately 10.4 m thick and has two distinct sections. The upper 5 m is composed primarily of fine to coarse sands interspersed with thin, intermittent gravel layers. The lower 5.4 m is primarily a silt loam. Nineteen core samples were used to determine the unsaturated hydrologic properties of this unit. Forty samples were used to define the unit's textural characteristics, or particle-size distribution. The clay-sized fraction in eight samples from the upper section ranges from 0 to 4 percent. The clay-sized fraction in 32 samples from the lower section ranges from 4 to 23 percent; the largest clay percentages are in samples from near the base of the B-C interbed at this location.

Saturated hydraulic conductivity of the B-C interbed at the drilled location varies within four orders of magnitude, from a minimum of 0.2 mD near the bottom of the lower section to a maximum of 3,900 mD across the entire upper section. The arithmetic average of the measured saturated hydraulic conductivity for 14 samples is 12 mD. The median value for these 14 samples from the lower section is 5 mD. Measurements of saturated hydraulic conductivity in samples from the upper section do not include the effects of the thin intermittent gravel layers, indicating that the saturated hydraulic conductivity of the upper section could be much larger than the largest value measured on the core samples.

The uppermost 0.3 m of the B-C profile at the drilled location consists of a highly oxidized, reddish, baked zone of gravelly sand overlain by massive basalt. The clay-sized fraction of this upper baked zone is approximately 1 percent.

The above example illustrates that the hydrologic properties of the composite B-C interbed at the drilled location deviate markedly from the assumption that the interbeds can be treated as homogeneous, isotropic media. Characterization of the interbeds should include definition of the vertical and lateral variability of their physical, hydrologic, and chemical properties. The validity of simplifying assumptions, which are needed to represent these geologic units in the numerical simulator, cannot be established without data that can show how these basic properties vary in space.

6.2.2.5 Aquifer properties

Controls on water movement in the SRP aquifer, as described in section 2.4.4, are assumed to be consistent with the controls on water movement in the fractured basalts in the unsaturated zone (Becker and others, 1998, p. 5-66). The flow properties of the basalts in the saturated zone, specifically permeabilities, were determined largely from aquifer test data and calibration of the saturated-zone portion of the WAG-7 model to available hydraulic head data (section 6.3.2). The basalt permeabilities determined during calibration of the WAG-10 model were initially considered in the calibration but then were disregarded because they produced a poor match to the available head data and because site-specific information was available from the aquifer tests. Potential concerns with this step of the calibration process relate to (1) the neglect of the possible effects of diversion of water from the Big Lost River (BLR) into the spreading areas (section 6.2.3.3), (2) the selective use of head data that ignored indications of transient behavior in the aquifer (section 6.2.3.3), (3) the limited head data available to specify the

boundary conditions, particularly along the western and northern boundaries of the WAG-7 model, and (4) the exclusive use of prescribed heads along the boundaries and the absence of any constraints on the ground-water flux, which could allow any model that includes permeabilities in the same ratios as those determined in the calibration to match the head data equally well.

The permeability estimates for the saturated-zone portion of the model were taken initially from the WAG-10 model (McCarthy and others, 1995). These estimates were 168,000 mD for zone 53 of the WAG-10 model, which corresponded to the northeast corner of the WAG-7 model, and 1,800,000 mD for zone 54 of the WAG-10 model, which corresponded to the remainder of the WAG-7 model domain. Because Magnuson and Sondrup (1998) were unable to reproduce the observed hydraulic heads by using a two-zone model and these permeability estimates, they created a more detailed model for the saturated zone that included three shallow zones and a fourth deep zone that represented the "I" basalt. Zone 1 was a large permeability (1,200,000 mD) region that extended from the northern model boundary southward into the southern half of the SDA. Zone 2 was a medium-permeability (16,300 mD) region that extended from the southern limit of Zone 1 to the southern model boundary, except near the SDA where, locally, a small-permeability region (153 mD, Zone 3, discussed below) was assumed to extend 1,000 m south of the SDA. The permeabilities of these three zones were the arithmetic mean permeabilities of large, medium, and small permeability zones identified by Wylie and Hubbell (1994) and Wylie (1996) based on transmissivities calculated from aquifer-test data and the open intervals of the wells (Magnuson and Sondrup, 1998, fig. 2-22). Permeabilities for individual wells in the three shallow zones ranged from 4 to 1,508,700 mD. The six-order-of-magnitude variability in the permeability measurements for individual wells seems to indicate that permeability is strongly affected by different types of volcanic deposits, fissures, and dikes. In the final calibrated model, a fourth zone representing the relatively deep "I" basalt was added to the model. Based on modeling of Rodriguez and others (1997) the "I" basalt has a permeability of 85,000 mD.

The existence of the small-permeability region of Zone 3 (153 mD) in the SRP aquifer southwest of the SDA (Becker and others, 1998, p. 5-66) is supported by data from aquifer tests from eight wells that trend north-westward along the southern boundary of the SDA. Values of effective hydraulic conductivity in these wells range from about 0.003 to 0.3 m/d and are among the smallest measured values at the INEEL. Values of

hydraulic conductivity in this range are attributed by Anderson and others (1999) to concealed dikes. Dikes, if present, probably are oriented at a high angle (perpendicular) to the main direction of ground-water flow and may form local barriers to flow. As currently (1999) implemented in the IRA model, the small permeability region is assigned to the upper portion of the aquifer beneath the southern half of the SDA and affects the movement of nitrate by acting as a partial dam, that is by forcing water and dissolved nitrate in it to go around or under the small permeability region (Magnuson and Sondrup, 1998, p. 4-9). If this small permeability region is related to concealed dikes, these dikes probably extend from beneath the base of the aquifer to the top of the C-D interbed in the unsaturated zone, so that water and wastes in this area must go around or through the zone of dikes. Dikes are postulated as linear, discontinuous features in the SRP (Anderson and others, 1999). The available data strongly support the assumed small-permeability region, though its hydraulic effects are represented only approximately in the IRA model. If the actual permeability were smaller than that assumed in the model, COPC concentrations in the aquifer under the SDA likely would be greater than the model predicts.

The effective porosity of basalt probably ranges from 0.10 to 0.25 (Ackerman, 1995). Although a reasonable value of porosity of 0.05 was used for SDA flow simulations, this value is significantly less than a value of 0.21 derived from calibration of an advective transport model of the SRP aquifer system (Ackerman, 1995) and is conservative for contaminant transport.

6.2.2.6 Heterogeneity and anisotropy of hydraulic properties

The hydraulic properties within lithologic units, both basalts and interbeds, are assumed homogeneous (Becker and others, 1998, p. 5-65), as noted in section 6.2.2.1 above. The effects of this simplification are the previously mentioned omission of preferential-flow mechanisms and the impeding barrier effects that could affect contaminant transport.

Most of the subsurface is highly anisotropic (section 2.3). There are strong possibilities for small-scale (intra-layer) anisotropy, for example, where basalt fractures tend to be more vertically or horizontally oriented. Large-scale (multilayer) anisotropy is a certainty, if in no other way than because a basalt-sediment interface will have markedly different effects on horizontal and vertical flow. The net large-scale anisotropy was assessed by inverse modeling during model calibration (Becker and others, 1998, p. 3-31): horizontal K exceeded vertical K by an estimated factor of 30. The magnitude of anisotropy does not have a

6-14 Review of the transport of selected radionuclides in the Interim Risk Assessment

sound independent basis for estimation, however, which partly explains why different degrees of anisotropy have been reported by different sources (Barraclough and others 1976, p. 48; Magnuson and others, 1995). The anisotropy quantified in the IRA model is what gives the best performance of this model, but cannot be fully evaluated with respect to known properties of the subsurface.

6.2.3 Unsaturated-zone flow

6.2.3.1 Infiltration

Estimating the rates of water movement through the trenches containing the waste is essential because the likely pathway for nonvolatile contaminants to reach the underlying aquifer is dissolution by and transport with infiltrating water. These estimates were made by Martian (1995) using a computer code (UNSAT-H) and moisture profiles in the surficial sediments determined using a neutron probe at 17 shallow boreholes at the SDA. Using soil moisture data from 1994 and 1995 (Bishop, 1996), Martian (1995) first estimated the soil properties at each of the 17 boreholes and then used historical climate data in combination with the estimated soil properties to calculate daily infiltration at each borehole between 1952 and 1995. The data from 1994 and 1995 indicated that the character of the spring thaw, whether it was abrupt so as to generate runoff over partially frozen ground or slow enough to allow melting snow to infiltrate where it lay, was an important variable in determining the distribution of infiltration at the SDA. Therefore, historical information on the character of the spring thaw during 1952–95 was used to adjust the precipitation data used in the models for individual boreholes to account for the timing and amount of runoff during the spring thaw. The adjustments for individual boreholes used precipitation multipliers determined from the 1994 and 1995 calibrations, years in which the character of the spring thaw differed appreciably. Yearly infiltration rates at the 17 boreholes and detailed topographic contour maps were used to estimate spatially variable distributions of infiltration at the SDA, both temporally constant and temporally variable. The spatial average of 8.5 cm/yr was larger than the average winter precipitation of 6 cm, which Martian (1995) attributed to the drifting of snow at the SDA. In spite of the detail and thoroughness of the Martian (1995) study, significant uncertainty remains concerning infiltration at the SDA. This uncertainty arises because (1) only 2 of the 17 neutron probe access boreholes used in the calibration were located in the disturbed soils in the waste emplacement trenches (the other 15 boreholes were in the undisturbed soils between the trenches), (2) the amounts of

water that infiltrated during floods in 1962, 1969, and 1982 is uncertain, and (3) only two years of data (1994–95) were available to calibrate the infiltration model. These uncertainties were acknowledged by Magnuson and Sondrup (1998, p. 6-3).

Infiltration is assumed to be spatially and temporally variable (Becker and others, 1998, p. 5-65). This assumption is surely valid qualitatively, but like the issue of variability of subsurface properties discussed above, it is not certain whether the quantification of variability incorporated into the model is adequate to make this treatment conservative. A particular concern is whether infiltration could be concentrated at certain locations over a smaller spatial scale than covered by the grid used for this purpose (Magnuson and Sondrup, 1998, p. 2-18).

6.2.3.2 Percolation

After water infiltrates, it moves in various ways through the unsaturated zone, including vertical redistribution, deep percolation, and lateral flow. All of these have potentially significant effects on the transport of COPC's

Macropore flow, deflected or funneled flow, and unstable flow may be important modes of subsurface transport, as noted in chapter 2. For the most part, these preferential-flow features are not treated explicitly in the model. Two exceptions include (1) the incorporation of areal variations in infiltration and volatile organic compound (VOC) exchange with the aquifer, and (2) the implicit inclusion of preferential flow in the effective properties of the granular media as noted above in section 6.2.2. The treatment of areal variations in infiltration and VOC exchange with the aquifer accounts for some of the preferential flow, but at a much coarser spatial resolution than that of the preferential flowpaths. To the extent that the inverse modeling that was used to determine effective properties is based on measured data that reflect the effect of preferential flow, the resulting property values could represent preferential flow in combination with non-preferential flow. These two treatments can accommodate some effects of preferential flow, but could be inadequate for addressing issues such as travel times through the unsaturated zone and the possibility that lateral flow is a significant contaminant transport process.

As an example, the age-dating study of Busenberg and others (1993) gives evidence for significant preferential transport of solutes. In this study, concentrations of chlorofluorocarbons in the saturated zone that originated during the previous 50 years were detected. Results of this study reflect transport in both preferential and nonpreferential pathways. Busenberg and others concluded that, at

the INEEL, “most ground waters have ages of 14 to 30 years.” In comparison, the IRA model (Magnuson and Sondrup, 1998, p. 3-34 to 3-38) predicts travel times at the SDA of 23 to 216 years. The difference in travel times indicates that preferential flow, not accounted for by the model, could be significant. Magnuson and Sondrup (1998, p. 3-38) noted that the limitations of model discretization could be important in this sort of discrepancy.

6.2.3.3 Lateral flow

The numerical simulator for flow in the unsaturated and saturated zones at the SDA does not treat the effect of water diverted into the spreading areas from the BLR (Magnuson and Sondrup, 1998, p. 2-30). The spreading areas are approximately 1,500 to 1,600 m west and south of the SDA (fig. 6-22). These flood-control spreading basins were constructed in 1958, enlarged in 1984, and have been used intermittently since 1965 to regulate flow in the BLR (Bennett, 1990). A record of flow diversions into the spreading areas from January 1965 through January 2000 is shown in figure 6-23. Until recently, data have been lacking to demonstrate convincingly a direct connection between operation of the spreading areas and ground-water flow in the subsurface at the SDA. Some earlier investigators have inferred this connection as a possibility on the basis of limited unsaturated-zone, but substantial saturated-zone, data.

Because of the proximity of the spreading areas to the SDA and the large quantities of water that have been and could be diverted into these spreading areas, the effect of the spreading areas on flow and contaminant transport at the SDA needs to be evaluated. The validity of the conceptual model of flow and transport at the SDA will remain in question until these effects are determined.

Although the effect of the spreading areas on flow and transport at the SDA is not included in the IRA model, infiltration and recharge from the spreading areas are cited in the IRA as possible explanations, among others, to account for (1) the inability of the model to simulate perching at USGS 92 (implied in discussion of perched water, Magnuson and Sondrup, 1998, p. 6-4), (2) lower nitrate concentrations in perched water at USGS 92 (Magnuson and Sondrup, 1998, p. 4-4), and (3) the presence of carbon tetrachloride contamination in the SRP aquifer north and east of the SDA (Magnuson and Sondrup, 1998, p. 4-60).

Several earlier investigators hypothesized that water from the spreading areas could affect flow in both the unsaturated and saturated zones beneath the SDA. Barraclough and others (1976) proposed that recharge from these off-channel diversions could result in the formation

of a ground-water mound beneath the spreading areas, which could cause local gradients in the aquifer to change direction temporarily in response to the assimilation of the recharge water into the regional aquifer. As depicted by Barraclough and others (1976, p. 55), the subareal extent of the mound and its effect on local gradients in the saturated zone beneath the spreading areas (fig. 6-24) is apparently large enough to cause ground water in the SRP aquifer beneath the SDA to move in a north and east direction. These gradient reversals could provide a mechanism to explain the apparently incongruous presence of carbon tetrachloride in the SRP aquifer in wells upgradient to the north and east of the SDA (M14S, M7S, and M6S).

Pittman and others (1988) mapped the rise in water levels that resulted from large volumes of water that were diverted into the spreading areas between July 1981 and July 1985 (fig. 6-23). During this four-year period, more than $9.87 \times 10^8 \text{ m}^3$ of water was diverted from the BLR into the spreading areas. These diversions resulted in a net water-level rise of from 2.4 to 3 m beneath the spreading areas and from 1.8 to 2.4 m beneath the SDA (fig. 6-25). These differential head changes are much larger than local head changes that define the regional flow gradient near the SDA, and lend support to the ground-water mound hypothesis of Barraclough and others (1976).

Rightmire and Lewis (1987b) presented stable isotope data, $\delta^{18}\text{O}$ (oxygen) and $\delta^2\text{H}$ (deuterium), to show that perched water from USGS 92 could be derived, partly, from lateral flow of water in the unsaturated zone that infiltrates beneath the spreading areas. They hypothesized that water infiltrating beneath the spreading areas accumulates as a perched mound on the C-D interbed at a depth of 73 m and moves laterally about 1,500 m to the northeast beneath the SDA. Lateral migration of recharge water could dilute contaminated water that has infiltrated beneath the SDA. Dilution is one mechanism that could account for the smaller nitrate concentrations of perched water in well USGS 92.

Hubbel (1990) presented water-level records from USGS 92 and 88-02D as additional evidence to suggest that perched water-level recovery rates in USGS 92, and to a lesser extent in 88-02D, correlate with the historical record of inflows into the spreading areas.

The large diversions of water that occurred in the early to mid-1980's coincided with an anomalous 23-m rise in water levels in well USGS 88 (fig. 6-26). This monitoring well is completed in the SRP aquifer and is located midway between the spreading areas and the SDA (fig. 6-22). The water level in this well rose abruptly more than 23 m beginning in mid-1983 through late 1984 and did not return to pre-rise levels until late 1991. The water level in

6-16 Review of the transport of selected radionuclides in the Interim Risk Assessment

this well has not risen comparably since the large spreading area diversions of the early to mid-1980's. The water level in this well peaked shortly after the record monthly diversion of $6.14 \times 10^7 \text{ m}^3$ into the spreading areas in June 1984 (Bennett, 1990, p. 42). This rise is much greater than the regional rise near the SDA (fig. 6-23) and probably reflects filling of the well from spreading-area water that moved laterally in the unsaturated zone above the aquifer. The slow decline in water levels since the mid-1980's suggests that aquifer permeability in this area is very small.

To test some of these hypotheses, the USGS introduced a polyaromatic tracer (1,5 naphthalene disulfonate) into spreading areas A and B (fig. 6-22) in late June 1999 (Nimmo and others, 2002). The purpose of this experiment was to determine if it is possible for spreading-area water to move beneath the SDA. Monitoring results indicated that it is possible for water from the spreading areas to move laterally within the unsaturated zone beneath the SDA in a relatively short period of time. Test results also indicated that, at least locally, vertical movement of water through the unsaturated zone to the water table beneath the spreading areas is also rapid. The latter suggests that there could be significant gaps in the interbeds beneath the spreading areas or that, locally, the vertical permeability of the interbeds could be very large. The locations of the wells used to monitor tracer movement near the SDA are shown in figure 6-22.

The tracer was introduced into spreading area A on June 21, 1999, and into spreading area B on June 22 and 23, 1999 (fig. 6-22). This tracer was first detected in water from well USGS 92 on September 20, 91 days after its introduction into the spreading areas. This detection was followed by additional detections on October 21 and November 15, 1999. Analyses of two archived water samples from well USGS 92, dated March 30, 1999 and April 18, 1997, indicate that the tracer used in this experiment was not present in the perched water in this well prior to this test. The tracer was detected in SRP aquifer water in well USGS 120 only 9 days after tracer introduction. The tracer also was detected in perched water recovered from the basalt immediately above the B-C interbed in well USGS UZ98-2 (18 days after tracer introduction), in perched water recovered from the B-C interbed in well USGS UZ98-1 (65 days after tracer introduction), and in five boreholes completed in the B-C interbed at the LSIT. The LSIT boreholes were first sampled in December 1999, approximately 180 days after tracer introduction.

A critical assumption of the IRA model is that essentially all flow beneath the SDA originates as infiltration from local precipitation and runoff at the SDA. Within the

SDA, modeled infiltration fluxes are spatially variable and range from 0.64 cm/yr to 24.1 cm/yr for a net infiltration rate of 8.5 cm/yr. The cumulative volume of modeled infiltration at the SDA was approximately $34,300 \text{ m}^3/\text{yr}$ (Magnuson and Sondrup, 1998, p. 2-19). Outside the SDA, infiltration was assumed to be 1.0 cm/yr (Magnuson and Sondrup, 1998, p. 2-19). Although the amount of lateral flow in the unsaturated zone beneath the SDA from the spreading areas cannot be quantified on the basis of the tracer data, the magnitude of these potential fluxes could be a significant component of total flow in the unsaturated zone, and could be much larger than that derived from local precipitation and snowmelt. If the $2.71 \times 10^7 \text{ m}^3$ of water that was diverted between May 30 and July 2, 1999 is the minimum diversion necessary to initiate lateral flow in the unsaturated zone beneath the SDA, then the spreading-area diversion record (fig 6-23) indicates that many such lateral flow events have been initiated during the past 35 years.

The tracer results and other supporting information make it difficult to ignore the possibility of spreading area effects on contaminant transport beneath the SDA. Calibration of the numerical model is based on matching simulations to (1) perched-water levels, (2) nitrate concentrations in perched water and the aquifer, and (3) carbon tetrachloride concentrations in the unsaturated zone, which in turn are based on a conceptual model that is presumed to be dominated by vertical flow through the unsaturated zone. As demonstrated by the numerical simulator for the IRA, infiltration rates at the SDA are not sufficient to sustain lateral flow in the unsaturated zone on a scale large enough to transport contaminants away from the SDA. The present formulation of the IRA model guarantees that all waterborne contaminants, whether dissolved or in suspension as colloids or macromolecules, eventually will percolate through at least one of the sedimentary interbeds beneath the SDA before reaching the aquifer; therefore, the likelihood of these contaminants bypassing the deeper C-D interbed is small, although the model formulators recognize the distinct possibility that gaps could exist in the C-D interbed beneath the SDA (Magnuson and Sondrup, 1998, p. 6-2). The inability of the numerical simulator to match perching conditions at well USGS 92, the smaller nitrate concentrations in perched water at USGS 92, and the presence of carbon tetrachloride in the SRP aquifer north and east of the SDA, are all difficult to reconcile with the current (1999) conceptualization and numerical formulation of unsaturated and saturated flow at the SDA.

The significance of spreading-area recharge on model predictions of radionuclide concentrations cannot

be quantified at this time. The detection of the introduced tracer in well USGS 92 represents a single, isolated sampling point in an extremely heterogeneous and anisotropic environment. Without additional evidence of lateral flow from other locations, it is not possible at this time to determine the extent of lateral flow beneath the SDA. The detection could be only an extreme example of channeled flow. However, the possibility of widespread lateral flow cannot be discounted given the tracer detections at the LSIT site. Few deep wells are available to sample perched water and contaminants immediately above the C-D interbed. In the 1999 tracer study, only two wells were available to access water in the unsaturated zone below the B-C interbed at the SDA. Samples of perched water were collected from both wells, but the tracer was only detected in water from well USGS 92.

Lateral flow in the unsaturated zone could facilitate contaminant transport to the SRP aquifer by intercepting waterborne contaminants that otherwise would percolate into and be adsorbed by the underlying sedimentary interbeds; however, lateral movement, by itself, does not necessarily imply a greater likelihood that waterborne contaminants will be transported to the aquifer. Dilution and dispersal of waterborne contaminants over a large area could provide greater opportunity for media sorption by (1) reducing competition for sorption sites, (2) producing changes in solution chemistry that are favorable for sorption, and (3) increasing the availability of sorption sites. However, uncertainty about the lateral continuity, elevation, thickness, and hydrologic and geochemical properties of the interbeds, and uncertainty about the quantity of underflow from the spreading areas, become limiting factors on modeling a flow system where lateral flow could be a substantial component of the total flow.

6.2.4 Contaminant input and transport

6.2.4.1 Source term

The source-term and source-term release-rate model were not evaluated by the review panel. The authors of the numerical simulator and the IRA have expressed serious reservations about the lack of a qualified calibration of the source-term release-rate model (Becker and others, 1998). The review team concurs that this is a major deficiency that is at least as important as other issues related to the formulation of the computational scheme to predict radionuclide transport and needs to be resolved before completion of the Remediation Investigation and Feasibility Study (RI/FS). A brief discussion of the source term is provided in section 2.5.1 of this report, and a review of the

radionuclide sampling data at the SDA is provided in chapter 3.

6.2.4.2 Solute transport

Solute transport is described in chapters 4 and 5 of this report.

6.2.4.3 Colloid transport

Colloid transport is discussed in section 4.5 of this report.

6.2.5 Saturated-zone flow

Flow within the aquifer and interaction between the aquifer and other parts of the hydrologic system have relatively modest effects on contaminant concentrations relevant to risk assessment. Advective flow in the SRP aquifer is affected partly by aquifer thickness and porosity of the basalt flows (Ackerman, 1995). Travel time is a function of the product of thickness and porosity, and can increase or decrease with changes in thickness or porosity. As noted in section 6.2.2.5, travel time also can increase locally in small-permeability regions, such as that down-gradient from the SDA. To a first approximation, COPC concentrations in the aquifer below the SDA could be directly proportional to the travel time within the aquifer, because greater travel times directly imply that in a given time interval, less water is available for dilution of contaminants.

Water movement in the SRP aquifer is assumed to be steady, and possible episodic effects of BLR diversions to the spreading areas on flow within the unsaturated zone or the aquifer near the SDA are not included in the IRA model (Becker and others, 1998, p. 5-66). It is not known whether this omission leads to negligible error in predictions related to risk assessment, as noted by Magnuson and Sondrup (1998, p. 6-4 to 6-5) and as discussed in section 6.2.3.3 of this report.

Magnuson and Sondrup (1998) stated that simulations of flow and contaminant transport at the SDA did not consider possible local reversals in head gradients near the SDA that could result from periodic recharge from the spreading areas. However, Barraclough and others (1976) suggested that these reversals could be significant through time, and could produce periodic reversals in gradients toward the northeast and east under the SDA. If these reversals take place, they might have the additional effect of dispersing wastes derived from the SDA, such as carbon tetrachloride and nitrates, toward the northeast. According to Burgess and others (1994), concentrations of carbon tetrachloride in the aquifer are largest in the area

east of the SDA. Unless these wastes are from sources upgradient of the SDA, their distributions might be better explained in WAG-7 simulations by considering possible head reversals related to transient recharge from the spreading areas.

6.3 Review of the numerical simulator

The numerical simulator incorporates the assumptions and simplifications described in section 6.2, and allows their quantitative application. Formulation of this model was an extremely complex undertaking. This review assesses the choices made in developing and calibrating the model and the utility of the model results.

6.3.1 Description of the numerical simulator

The numerical simulations described by Magnuson and Sondrup (1998) were run with the TETRAD code. TETRAD, originally developed as an oil and geothermal reservoir simulator (Vinsome and Shook, 1993), uses numerical techniques developed over several decades of experience in reservoir simulation. The principal focus of the INEEL TETRAD simulations was the fate and transport of waste material buried at the SDA (Magnuson and Sondrup, 1998). Additional focus was defined for other phenomena, such as transport of organic constituents introduced into the subsurface from waste buried at the SDA.

TETRAD is capable of simulating the movement of an arbitrary number of components, which may be distributed among the water, gas, and oil phases in either single- or dual-porosity media. Its multiphase capabilities make it usable for both saturated and unsaturated conditions. The nonlinear component conservation equations are solved iteratively, using widely used and generally accepted numerical techniques. These numerical techniques include: (1) Newton-Raphson iteration, (2) finite-differencing techniques, (3) upstream weighting schemes of various orders for the density, permeability, mole fraction, and enthalpy terms to provide numerical stability, (4) dispersion control techniques for reducing the effects of numerical dispersion, and (5) various scaling and matrix factorization methods to provide numerical stability and flexibility in mesh design and refinement.

The modification of TETRAD to consider problems of broader hydrologic application is described by Shook (1995). The modifications included (1) the incorporation of alternative fluid property packages that describe the characteristics of fluids other than oil, gas and water (for example, dense, nonaqueous-phase liquids), (2) the equi-

librium distribution of components between phases, (3) alternative boundary conditions likely to exist in hydrologic problems, (4) phase-dependent, linear and nonlinear adsorption models, (5) decay and ingrowth of mother and daughter products from radioactive and other types of first-order decay, and (6) phase-dependent dispersive transport as a result of diffusion and mechanical dispersion, with the dispersion coefficient described by a tensor.

Direct testing of the TETRAD code was beyond the scope of this review. In published test problems, the simulation results compared favorably with the results of analytical solutions for a radially symmetric geothermal problem (Vinsome and Shook, 1993); and a two-dimensional test problem involving density-driven flow with advection, dispersion, adsorption, and decay (Shook, 1995). However, TETRAD does not have as long an established history as some older hydrologic simulators and does not yet have as broad a user base to expose its limitations.

TETRAD has several known limitations. Magnuson and Sondrup (1998, p. 5-19) expressed appropriate concern regarding the use of a single convergence criterion when simulating groups of contaminants that include parent and daughter constituents at widely varying concentrations. Although TETRAD includes methods to control numerical dispersion, these methods were not always used. As explained by Magnuson and Sondrup (1998, p. 4-9), the actual dispersion in the model calibration was a poorly characterized, inseparable mixture of numerical and hydrodynamic dispersion. It is not clear to what extent the extremely small simulated concentrations of contaminants in chapter 5, "Predictive transport simulations," and elsewhere, could have been affected by numerical dispersion.

Particle-tracking methods that would avoid problems of numerical dispersion associated with the advection-dispersion equation could be considered to supplement the simulations done so far. These methods would better illustrate simulated flowpaths than contour plots of concentration or saturation values (for example Magnuson and Sondrup, 1998, figs. 3-13 and 3-14).

Much research has been published on the applicability of the advection-dispersion equation with a constant dispersivity value for describing field-scale transport (for example, Neuman (1990), Gelhar and others (1992), and references listed therein). There seems to be a consensus that dispersivity increases with scale. As indicated by the voluminous body of recent work, this is an active area of research. The simulations of contaminant transport at the INEEL would not be expected to solve problems that have engaged the hydrologic profession for decades; however,

Table 6-5. Characteristics of TETRAD discretization (model grid shown in fig. 6-1)

| PLAN, OR HORIZONTAL, GRID | | | | | | |
|---------------------------|---------------------------|--------------|---------------------|------------|-------------------|----------------|
| Resolution level | Southwest corner location | | Cell dimensions (m) | | Number of columns | Number of rows |
| | Easting (x) | Northing (y) | Δx | Δy | | |
| 0 | 76,270 | 197,875 | 1,000 | 1,000 | 9 | 9 |
| 1 | 80,270 | 202,875 | 250 | 250 | 12 | 8 |
| 2 | 80,520 | 203,375 | 125 | 125 | 12 | 8 |
| 3 | 80,645 | 203,625 | 62.5 | 62.5 | 20 | 10 |

the major findings and hypotheses that have grown out of this earlier work provide a context for the interpretation of simulated contaminant transport at the SDA.

Initial conditions, boundary conditions, time steps, and convergence criteria used in the TETRAD modeling were not evaluated as a part of this review.

6.3.1.1 Discretization and grid refinement

Although the fate and transport processes the model simulates may be continuous, the TETRAD code requires information to represent the model domain as horizontal and vertical grids of discrete cells. The smallest cells defined in the discretization are 62.5 by 62.5 by 0.5 m and have a volume of 1,953 m³. These cells represent the finest resolution simulated within the model domain.

If the entire model domain were simulated at this finest resolution, then considerably more cells than the TETRAD code can address would be required. In addition, because current modeling philosophy often recognizes that relatively fine resolution is not necessary throughout the entire model domain, various levels of resolution often are used. Consequently, different levels of resolution were used in the discretization of the model domain and the finest levels of resolution were focused on the SDA.

There are four levels of resolution in the plan discretization; they are referred to as levels 0, 1, 2, and 3 and proceed from coarse to fine. Table 6-5 defines each level and its characteristics. Level 3 consists of cells that have a plan dimension of 62.5 by 62.5 m and is roughly centered about the SDA (fig. 6-1).

The vertical grid is structured to use the finest levels of resolution for certain horizons (surficial sediments and

three interbeds) in the vertical cross section. The vertical discretization is less systematic than the plan discretization. Briefly, it provides 0.5- to 2-m resolution to a depth of 14 m, 2 to 4 m resolution to a depth of 80 m, and 7 to 18 m resolution to a depth of 251 m.

6.3.2 Model calibration

The numerical IRA model was calibrated in a series of steps, each of which considered different hydrologic and geochemical data sets. Many of these steps involved some form of inverse modeling (section. 6.2.2.1). These steps are intended to follow generally accepted guidelines for numerical model calibration, which were summarized for example by Hill (1998, p. 34–39). The data used in the calibration, the estimated properties, and the potential concerns associated with individual steps in the calibration process are listed in table 6-6. In the calibration process described by Magnuson and Sondrup (1998, chapters 3 and 4), few parameter values or other features of the model were altered from their initially chosen specifications. Some general comments about the IRA model calibration are appropriate:

(1) The data sets varied considerably in quality and quantity, from the fairly comprehensive, high-quality data set for CCl₄ used to calibrate the gas-phase transport properties to the limited data set for perched water that was used to help determine unsaturated-zone hydrologic properties. A related concern is the uncertainty of data for background concentrations of contaminants moving beneath the SDA from upgradient locations, including those used in the calibration.

6-20 Review of the transport of selected radionuclides in the Interim Risk Assessment

Table 6-6. Summary and review of IRA model calibration steps, target data, and estimated properties used by Magnuson and Sondrup (1998, chapters 3 and 4)

[SDA, Subsurface Disposal Area; WAG, Waste Area Group; USGS, United States Geological Survey]

| Calibration step | Target data | Estimated properties of subsurface | Comments |
|---|--|---|--|
| Adjust flow and transport properties of basalts in unsaturated zone | Transient perched-water data for SDA subsurface | Horizontal and vertical permeability; fracture porosity; longitudinal dispersivity | Poor quality and quantity of perched water data; poor match of model to perched-water data |
| Estimate flow properties of basalts in saturated zone | WAG-10 model results; pump-test data; potentiometric-surface data | Horizontal permeability | Selective use of hydraulic head data; limited hydraulic head data to define boundary conditions; neglect of possible effects of spreading areas; determination only of ratios of permeabilities from different units |
| Introduce hypothetical low-permeability clay layers | Transient perched-water data for SDA subsurface | New layers, with clay-like properties, above interbeds | Poor quality and quantity of perched water data; poor match of model to perched water data; perching phenomenon is not well understood and thus may be unsuitable for use in calibration |
| Predict transport properties of nonreactive, dissolved species | Nitrate concentrations in aquifer | Liquid-phase tortuosity (for diffusion); longitudinal and transverse dispersivity | Few nitrate data available for unsaturated zone beneath the SDA; uncertainty of nitrate source term at the SDA; uncertainty of background concentration of nitrate arriving from upgradient sources; poor match of nitrate data at USGS wells |
| Predict transport properties of contaminants that move in both gas and liquid phase | Carbon tetrachloride (CCl ₄) concentrations in soil gas and vapor-extraction wells; dissolved carbon tetrachloride in perched water and ground water | Gas-phase tortuosity (for diffusion); matrix porosity of basalts; distribution coefficient for carbon tetrachloride | Source-term uncertainty; complicated factors affecting gas transport; limited perched-water data; carbon tetrachloride sources upgradient of the SDA; poor agreement between theoretical and calibrated values of gas-phase tortuosity for some geologic units; inconsistency of allowing for gas but not liquid diffusion into the matrix |
| Predict transport of contaminants of potential concern | Measured concentrations of contaminants in aquifer | Distribution coefficients; specific-surface areas and apertures of fractures in basalts | Source-term uncertainty; use of nondetections in calibration |

(2) As noted by Magnuson and Sondrup (1998) and discussed above in section 6.2.2.1, the results of the model calibration could be nonunique in that more than one combination of parameters and boundary conditions could produce comparable matches of the model results to the measured data. Magnuson and Sondrup (1998, p. 6-6) acknowledged "...the inherent non-uniqueness of almost any hydrogeological inverse model."

(3) An underemphasized aspect of the model calibration presented by Magnuson and Sondrup (1998) is the potential effect that their selected assumptions and simplifications for flow and contaminant transport could have on the estimated properties. For example, the infiltration of BLR diversions in the spreading areas southwest of the SDA could have contributed to perched water above the C-D interbed beneath the SDA and caused temporary reversals in head gradients within the aquifer (Magnuson and Sondrup, 1998, p. 6-4 to 6-5), but this was not considered in the calibration. The neglect of the potential effect of pumping from the SDA production well upgradient from the SDA probably also has affected the estimated properties. Several contaminants detected in the aquifer that could have originated from the SDA could have migrated upgradient from the SDA. The ability of the model to approximately produce results similar to the measured data at these upgradient wells could be related more to numerical dispersion in the transport solution than to a realistic representation of actual processes. Similarly, the conceptualization of the hydrologic system and how best to represent it (for example, the representation of the basalts as equivalent to a homogeneous, anisotropic, porous-medium without matrix diffusion versus a heterogeneous, anisotropic, dual-porosity continuum with matrix diffusion) ultimately determine the choice of properties to be estimated in calibration and the final values. Even a decision as fundamental as the representation of the hydrologic system as a continuum dictates the choice of properties to be optimized and determines the degree to which isolated detections of various contaminants can be considered in the calibration or predicted by the model.

(4) Because no quantitative objective function was defined for evaluating the goodness of the calibration, the evaluation is more subjective than if such a function had been defined and used. At various steps in the calibration, the model was judged to adequately match the data, although it was not obvious that it had done so. In particular, the calibrated model results do not adequately match much of the measured data for perched water in the unsaturated zone (Magnuson and Sondrup, 1998, figs. 3-23 to 3-26) or nitrate concentrations in the aquifer (figs. 4-19 to 4-22). However, these discrepancies could be unimpor-

tant if other model features, such as the source term, have overriding importance.

(5) Another problem with the lack of a quantitative objective function is that, although sensitivity studies were conducted, no formal methodology was used to quantify sensitivity or uncertainty in the model properties or to assess the propagation of uncertainty in the properties to determine their net effect on the fate of the contaminants. It is highly desirable to evaluate these uncertainties quantitatively, so that the importance of particular properties would be more apparent.

(6) As noted by Magnuson and Sondrup (1998, p. 6-2), the transport of VOC's and dissolved contaminants were most sensitive to their respective source terms rather than to hydrogeologic processes. The source terms are themselves uncertain and sensitive to assumptions concerning inventory volumes, drum failure rates, and release rates.

6.3.2.1. Calibration for unsaturated-zone hydraulics

The review panel has serious concerns about the calibration step for unsaturated-zone flow. One is the poor match of the model to the target data, as noted in comment (4) above. Another concern is that the assumed existence of low-permeability clay layers at the top of the B-C and C-D sedimentary interbeds is not fully supported by field data. Other, possibly less serious concerns are the poor quality and limited quantity of data for perched water beneath the SDA, the fact that the much larger amounts of water contained in the saturated-zone part of the SDA model could have masked mass-balance errors in the unsaturated-zone part of the model, and that the use of a radially symmetric equivalent porous-media model is supported only by a selective use of LSIT data.

6.3.2.1.1 Perched water

Calibration of the unsaturated-zone flow component of the model is based almost exclusively on matching flow simulations to short-term observations of perched water. Magnuson and Sondrup (1998, p. 3-11) used perched-water data for four locations above the B-C interbed and four locations above the C-D interbed to calibrate the unsaturated-zone flow component. For the most part, these data are rather poor. To simulate perching, two adjustments in the input were made: (1) A 1-mD clay layer with a porosity of 0.05 was assigned to the tops of the B-C and C-D interbeds, and (2) the horizontal permeability of the basalts was decreased from 90,000 to 9,000 mD. The clay layer was justified on the basis that (1) "...at some locations, a clay layer is encountered at the top of the sedimentary interbeds," and (2) "...a reduced zone of

6-22 Review of the transport of selected radionuclides in the Interim Risk Assessment

permeability at the top of the interbeds also could be considered to result from sediment infilling of fractures immediately above the interbed" (Magnuson and Sondrup, 1998, p. 3-7). These two adjustments were made assuming that all flow through the unsaturated zone beneath the SDA derives from local surface infiltration near the SDA.

Data to characterize perching are limited, and mechanisms that cause perching are poorly understood. Perched water and areas of large moisture content in the subsurface are present in just about every geologic setting beneath the SDA. No consistent pattern has emerged to predict where perching will or will not occur. Most observations indicate that perching occurs in the basalts at some locations that are not in direct contact with an underlying sedimentary interbed. Perching is most likely a manifestation of preferential flow in the basalts. Except at the contact of the basalts with the small permeability clay layer, the current formulation of the numerical simulator largely precludes any realistic simulation of lateral flow in the basalts. Lateral flow in the basalts and large fluxes in the unsaturated zone, derived from a combination of vertical infiltration within the SDA and a component of lateral flow from outside the SDA (section 6.2.3.3), could be necessary prerequisites for most perched water at the SDA.

Although perched water is important, its significance as an integrator of flow and contaminant transport processes in the unsaturated zone could be overemphasized. Instead of being a dominant and widespread phenomenon, perched water could exist primarily in isolation, where water accumulates locally into dead storage. In that case most flow in the unsaturated zone could move rapidly through the basalts and into the underlying sedimentary interbeds. Moisture distribution within the sedimentary interbeds, particularly the small permeability silty-loam units, could offer a much more realistic means of calibrating the unsaturated-zone flow component of the numerical simulator. To do this, knowledge of the moisture distribution within the interbeds and a much better definition of the hydrologic properties of the interbeds are needed. Use of interbed characteristics for this kind of calibration has not yet been seriously tried, most probably because the data are not available to do so.

The use of a small permeability clay layer to simulate perching may not be conservative. The assumption of a small permeability clay layer in the model forces lateral flow above the interbeds and thus distributes waterborne contaminants over a much larger area than might actually occur in the field. The net effect of this assumption is to provide greater opportunity for waterborne contaminants

to come into contact with a much larger volume of contaminant-sorbing media and thus to minimize the undesirable effect that competition for sorption sites would have on contaminant transport.

6.3.2.1.2 Travel time

Unsaturated-zone travel times from the ground surface to the SRP aquifer were determined in a post-audit assessment of the calibration of the unsaturated-zone flow component of the numerical simulator. Travel time estimates were not used to calibrate the numerical simulator, but rather to determine how well simulated travel times compare with other estimates based on different calculations to estimate travel time (Burns and others, 1994—50 years; and Maheras and others, 1994—20 to 70 years). These other estimates were based on assumptions of constant infiltration rate, instantaneous travel time through the fractured basalts, average thicknesses for the sedimentary interbeds, and gravity drainage under an assumed unit hydraulic gradient.

Travel times were simulated by applying an incremental pulse of water for a simulation period of 1,000 days beginning in 1952. This incremental pulse was superimposed on the spatially variable infiltration rates used in the original calibration of the numerical simulator. Arrival times were determined by tracking the time when the peak concentration of this pulse arrived at the top of the SRP aquifer. The results indicate that travel times inside the SDA range from 23 to 216 years. Except for the 216-year travel time inside the SDA, the simulated travel times were not judged to differ significantly from previous estimates; however, this is debatable. As discussed in section 6.2.3.2, evidence from the age-dating study of Busenberg and others (1993), in which concentrations of chlorofluorocarbons originating in the atmosphere within the last 50 years were detected in ground water indicated that at the INEEL the young fraction of "...most ground waters have ages of 14 to 30 years." The review team believes that these estimates differ significantly from those simulated in the IRA model.

Travel times to the SRP aquifer are sensitive to (1) the presence or absence of sedimentary interbeds, (2) the choice of properties, particularly the unsaturated hydraulic conductivity relations, used to represent the interbeds, (3) temporal and spatial variations in infiltration rates at the ground surface, (4) thickness of the interbeds, (5) representation of the interbeds as minimally conductive, homogeneous, isotropic units (section 6.2.2.4), and (6) the use of the small permeability clay layers to simulate perching. The much longer simulated travel times, when compared with other evidence, indicates that preferential

flow not accounted for by the model could be significant. These longer travel times also are consistent with the observation presented in section 6.3.2.1.1 that the assumption of the small permeability clay layers may not be conservative. The net effect of this assumption is the greater opportunity for waterborne contaminants to come into contact with a much larger volume of contaminant sorbing media, which could be what is reflected in the longer simulated travel times.

6.3.2.2. Calibration for saturated-zone hydraulics

After testing four scenarios for flow in the saturated zone at the SDA, Magnuson and Sondrup (1998, p. 3-1 to 3-6) chose the Case 4 scenario for the final simulation runs. This scenario used four permeability regions developed from data for 16 wells at the SDA and results from WAG-3 simulations (Rodriguez and others, 1997). Interpolated October 1994 hydraulic heads for an area from the Idaho Nuclear Technology and Engineering Center (INTEC) to Big Southern Butte (fig. 1) were used for boundaries of the SDA model domain. Simulated heads from Case 4 were calibrated to these interpolated heads and measured heads from 16 wells within the model domain. Two hydrostratigraphic units were assigned to the model: (1) undifferentiated basalt and sediment representing the upper part of the aquifer, and (2) basalt-flow group I, a thick basalt unit having small permeability where it has been measured at the INTEC, representing the lower part (section 6.2.2.5). An aquifer thickness of about 76 m was used for Case 4 simulations. Possible effects of discharges from the BLR to the spreading areas on flow within the aquifer (Barraclough and others, 1976) were not considered in the model (Magnuson and Sondrup, 1998).

All basalt flows in the saturated zone initially were assigned permeabilities from WAG-10 model results for Case 1 simulations. These permeabilities were adjusted into four regions for Case 4 simulations (Magnuson and Sondrup, 1998) as described in section 6.2.2.5. Model grids representing the upper part of the aquifer were divided into three permeability regions, a northern region having a permeability of 16,300 mD, a central region having a permeability of 153 mD, and a southern region having a permeability of 1,200,000 mD. On the basis of WAG-3 model results, grids representing the lower part of the aquifer were assigned a uniform permeability of 85,000 mD. This permeability region represents the inferred presence of basalt-flow group I, which tentatively was correlated from cores at the INTEC to four deep wells at the SDA on the basis of natural-gamma and lithologic logs (Anderson and Bartholomay, 1995). The permeabil-

ity region representing flow group I is the only one of the four regions that is not based on direct measurements at the SDA. Because the presence of this flow group cannot be verified by cores from the SDA, and also because the likelihood that, if present, flow group I represents a rubbly and permeable distal facies of near-vent, ponded flows at the INTEC, the justification for this permeability region is tenuous. The approximate range of hydraulic conductivity of these four permeability regions is within the range of values estimated from more than 100 aquifer tests at the INEEL (Anderson and others, 1999).

Use of interpolated October 1994 hydraulic heads for model boundaries and calibration could impart some uncertainty and bias to simulation results for the SDA. According to Magnuson and Sondrup (1998), October 1994 heads were used for the WAG-7 model because initial attempts to use the WAG-10 model boundary heads did not produce an adequate representation of water movement in the aquifer for the local-scale SDA modeling domain. Although the subsequent use of interpolated October heads improved this representation, accountability for the mass flux of water moving through the aquifer near the SDA was lost. In addition, the accuracy of any synoptic water-level map is only as good as that allowed by the number and spacing of wells available for interpretations. Although the number and spacing of wells available for this purpose is adequate at and near the SDA, it is less than desirable for outlying areas, which are critical for accurate representations of head distributions. It is desirable, therefore, to consider all available wells in interpretations. For example, USGS 13, a well southwest of the SDA that is measured only during the spring of each year, was not represented in the interpolated October 1994 heads. Use of the data for well USGS 13 significantly changes the interpolated head distribution near the Radioactive Waste Management Complex (RWMC), as shown by Bartholomay and others (1997, fig. 9).

6.3.2.3 Calibration for contaminant transport

6.3.2.3.1 Nitrate

Longitudinal and transverse dispersivity (V_L and V_T), which affect the movement of nonreactive species dissolved in the aqueous phase, were determined by using inverse modeling to match historical aquifer nitrate concentrations. Concerns with this step of the calibration process include (1) the very limited availability of nitrate data for the unsaturated zone beneath the SDA to constrain the calibration, (2) considerable uncertainty in the source term for nitrate at the SDA, (3) considerable uncertainty in the background concentration of nitrate in the ground

water because of potential nitrate sources upgradient from the SDA, (4) the poor match of the model results with measured nitrate concentrations in water from wells USGS 88 and 89, (5) the inability to distinguish the effects of dispersivity from those of the source-term release (release rate for nitrate from the source varied slowly over time), and (6) the possible augmentation, to an unknown extent, of the hydrodynamic dispersion terms by numerical dispersion in the model. These concerns are discussed in greater detail below.

Measured nitrate concentrations in the aquifer in excess of background values were presumed to reach the aquifer as a result of advection and dispersion from the SDA (Magnuson and Sondrup, 1998, p. 4-5). The quality of the nitrate data set is poor. The measured nitrate concentrations were consistently more than 50 percent larger than the selected background concentration in water from only three of eight aquifer wells, none of which are directly below the SDA, and only one significant concentration of nitrate in perched water in the unsaturated zone was reported. Although it is possible, and sometimes preferable, to use concentration data to refine model parameters for the flow properties that determine advection velocities, this was not done in this part of the calibration. Instead, velocities were calculated from the flow model calibrated to head data and the nitrate concentrations were used only to obtain estimates of the longitudinal and transverse dispersivities. This is probably the most reasonable approach given the quality of the nitrate data. The calibration process was to vary the V_L and V_T values to match historical nitrate data for four wells (Magnuson and Sondrup, 1998, fig. 4-12) and then to compare the results with those from simulations that used the same parameters to match four USGS wells (Magnuson and Sondrup, 1998, fig. 4-13). Sensitivity analyses resulted in two significant findings. First, of the four data sets used for calibration, those for M3S, an upgradient well, and M4D, a deeper downgradient well, were completely insensitive to the selected parameters and measured and simulated concentrations were equal to background concentrations. Because a wide range of parameters reproduce the measured data, these two data sets do not contribute significantly to the calibration. The second significant finding resulting from the sensitivity analyses relates to the limitations of the applicability of concentration data obtained from wells M1SA, M3S, and M10S for the purpose of model calibration. These three wells are completed near the top 25 m of the saturated zone (Magnuson and Sondrup, 1998, fig. 4-6). Any sampling of these wells could withdraw water over the entire vertical extent of the completed interval. If there was a vertical concentration gradi-

ent over the completed interval, this sampling would cause mixing of high and low concentrations in the well bore. This mixing cannot be distinguished from hydrodynamic dispersion. In fact, the zone of completion corresponds closely to a zone where large concentration gradients are simulated for the case of small values of V_L and V_T (Magnuson and Sondrup, 1998, fig. 4-16). These aquifer data could be suited only for estimating an upper bound of the dispersivities. The steep simulated gradients at a depth of 200 m also highlight a problem with the simulation approach. The selected background concentration of 700 $\mu\text{g/L}$ apparently was added after the simulations were completed, and not included in initial and boundary conditions for the simulations (Magnuson and Sondrup, 1998, figs. 4-7 to 4-11 and 4-15 to 4-18 show simulated nitrate concentrations as small as 1 $\mu\text{g/L}$). Since dispersion is most sensitive to concentration gradients, it is important to include background concentrations in the simulations because inclusion would flatten the gradient, reduce the dispersive flux, and probably increase the dispersivity values required to match the data.

A second limitation of the nitrate data set is the very limited amount of nitrate data for perched water in the unsaturated zone. Magnuson and Sondrup (1998, p. 4-5) noted that only one nitrate concentration, 925 $\mu\text{g/L}$, was reported for the perched water from well USGS 92. Simulated nitrate concentrations for water from USGS 92 were not reported. Magnuson and Sondrup (1998, p. 4-4) acknowledged that the concentration at USGS 92 could have been affected by infiltration from the spreading areas, which have an unknown nitrate concentration. This represents a gap in the data, as acknowledged by Magnuson and Sondrup, but again also raises concerns about the conceptual model because the water level in USGS 92 cannot be reproduced and the nitrate concentrations at USGS 92 are suspected to be affected by dilution.

It would be highly desirable to obtain a more complete nitrate data set for wells completed in the perched zones and in the aquifer, both within and outside the SDA. These data could improve the calibration of the flow and transport models.

6.3.2.3.2 Carbon tetrachloride

A second class of contaminants that were considered in the calibration are those that are transported in both the liquid and gas phases. Because the transport parameters affecting only aqueous-phase transport already were considered in the calibration step involving the nitrate data, the parameters calibrated during this step were restricted to those affecting gas-phase transport. These parameters were gas-phase tortuosity in the unsaturated zone (T_g) and

effective matrix porosity (n_m). Gas-phase tortuosity affects the diffusion of gas in the unsaturated zone and matrix porosity of the basalts provides additional storage for the gas-phase species and thereby slows their transport. To account for matrix diffusion, a dual-porosity model, which permits gas-phase species to diffuse into the matrix, was used in this calibration step; however, the dual-porosity model apparently was not used for simulations of radionuclide transport (Magnuson and Sondrup, 1998, p. 5-71). Dissolved aqueous-phase species were assumed not to diffuse into the matrix, even in the aquifer.

The general transport behavior of VOC's was characterized by using a relatively extensive data set for gas-phase CCl_4 in soil gas and gas-extraction wells and measured aqueous-phase CCl_4 in perched water and water from the aquifer. This step of the calibration was relatively successful despite many complicating factors affecting the transport of CCl_4 , including (1) air injection during drilling of the observation and extraction wells, (2) barometric pressure changes at the ground surface, and (3) pumping of gas-extraction wells. These processes were treated in a detailed and comprehensive manner in the calibration. Some of the concerns related to this step of the modeling are similar to those related to the previous calibration step: (1) the considerable source-term uncertainty for CCl_4 makes it difficult to uniquely identify the transport parameters, (2) the detection of CCl_4 in wells upgradient from the SDA implies temporary reversals in the hydraulic gradient due to the infiltration of water from the spreading areas or pumping from the SDA production well, or upgradient sources of CCl_4 —factors not considered by the model, (3) data for CCl_4 in perched water is limited, (4) for some hydrogeologic units, discrepancies between the initial values for I_g , estimated theoretically from the Magnuson and Sondrup model, and the final calibrated values are sufficiently large as to cast doubt about the realism of the model, and (5) time-averaged profiles of CCl_4 in the unsaturated zone that covered a relatively transient period of CCl_4 transport were compared with model results.

6.3.2.3.3 Detected contaminants of potential concern

The final step of the calibration process assessed the predictive capabilities of the calibrated model by comparing predicted concentrations of 52 COPC's with measured concentrations in the aquifer. This step required the use of contaminant-specific K_d s either measured for the materials from the site or reported in previous studies for comparable geologic materials (chapter 5). A concern with this step is that estimates of the specific-surface areas of fractures and of fracture apertures were required to adjust

the values of the K_d s to account for only partial exposure of the contaminant-bearing water to sorptive materials in parts of the model representing fractured basalts. Therefore, this step also assessed some previously uncalibrated transport parameters. Although the effects of source-term uncertainty were not examined in this step, the required modification of the initial source terms assumed in previous calibration steps suggests that source-term uncertainty for the remainder of the 52 COPC's is an unresolved issue. Alternative source terms could be expected to result in substantial differences in the simulated contaminant concentrations reported by Magnuson and Sondrup (1998). A second concern associated with this step of the calibration process is the use of nondetections and sporadic data to evaluate the predictive transport results. Data for a specific COPC were considered sporadic if the ratio of the total number of detections of that COPC to the number of wells in which the COPC was detected was five or greater (Magnuson and Sondrup, 1998, p. 5-44), that is, if most of the detections of that COPC were made in relatively few wells. If the model failed to predict the sporadic occurrences of specific COPC's, this failure was not considered a limitation of the model; rather, the fact that the model had predicted the limited transport implied by the nondetections for water from the majority of the wells was emphasized. The sporadic data could indicate, however, that preferential transport through relatively isolated pathways in the fractured basalts, which the model is unable to predict, is the predominant mode of transport.

In one instance (Becker and others, 1998, table 5-24), the simulated concentrations for ^{241}Am , ^{238}Pu , and $^{239,240}\text{Pu}$ were compared with measured concentrations in the B-C interbed. The simulated and measured concentrations of ^{241}Am agreed within an order of magnitude whereas the simulated concentrations for Pu were two to three orders of magnitude too small. These small concentrations were attributed to geochemical processes such as colloidal transport or geochemical perturbations. Although these processes could be operating, it is also possible that the continuum approach is not capable of reproducing preferential flowpaths leading to possible contamination. Another concern about these comparisons is that although some uncertainty is given for the measured concentrations, none is given for the simulated concentrations. At the small concentrations considered, even numerical truncation and rounding could be significant and should be addressed.

6.4 Model utilization

6.4.1 Sensitivity analyses

Uncertainty is inherent in subsurface flow and transport models. This is because it is impossible to fully characterize the hydrogeologic and geochemical variables that control the flow of water and transport of dissolved, reactive solutes. It is critical, therefore, that some level of uncertainty be associated with model results. Four different types of uncertainty can be identified: (1) uncertainty in the conceptual model, (2) uncertainty in the calibration parameters, (3) uncertainty in other input parameters not adjusted in calibration, and (4) numerical uncertainty. Sensitivity analyses are a sound and practical approach for addressing these four types of uncertainties and can yield two significant results. First, they can help demonstrate which processes most strongly affect transport of radionuclides, and knowledge of these processes leads to a greater intuitive understanding of the overall system. Second, they can establish some confidence levels (perhaps quantitative and formal) about the model predictions.

This section considers only the sensitivity studies conducted by Magnuson and Sondrup (1998). In most instances sensitivity analyses were conducted for the model calibration parameters only. Sensitivity analyses for evaluating the conceptual model, the uncertainty associated with other input parameters, and uncertainty associated with numerical issues are discussed in the next section. Becker and others (1998, p. 7-6) noted that the IRA is not conservative in all respects, and that sensitivity analysis would give a more precise description of the degree of conservatism.

6.4.2 Predictions

Confidence in model predictions requires a strong confidence in the adequacy of the model and also in the assumed continuation of phenomena and trends, even though they depend on factors not represented in the existing record. A quantitative, time-specific prediction is basically an extrapolation, over time, of the modeled phenomena. However, the specific, quantitative concentration of a COPC at a particular location at a specific time, such as 100 years into the future, cannot be known with confidence because (1) some of the processes that govern its transport are not understood, and (2) the calibration target data that could account indirectly for such processes are too limited in both quality and duration. Model predictions are most useful in a comparative sense in exploring

sensitivities to particular site features and management options.

A major assumption is that hydrological and meteorological conditions of the last few decades are adequately representative of the future. Another is that infiltration patterns at the SDA will not change in the future (Becker and others, 1998, p. 5-65). Assumptions like these are widely used in predictive modeling, but they are not likely to be realistic or conservative. The IRA model is based on data that typically extend back about 50 years or less. Notable exceptions include the 2 years of measured water-content profiles on which the infiltration component of the model is based. Using this 50-year data base to predict 5 years into the future would require extrapolation that exceeds the available data base by 10 percent. To predict extrapolation over the 100-year period of institutional control, twice the approximate length of the record, is much more demanding. An obvious variable is the possibility of severe climatic or geological changes. Even in the absence of such changes (which are unlikely over a 100-year period to cause major deviations outside the range of normal short-term variability), there is the problem that the last 50 years have not experienced the full range of likely meteorological or hydrologic events. For example, 1,000-year floods are not represented in the available data set, but there is a 10-percent chance that one will occur during the next 100 years. Thus, the 100-year period goes well beyond the range of available information, and extrapolation is subject to considerable uncertainty because of factors not accounted for in model development or calibration.

Although the source term includes temporal variations owing to factors such as drum failure rates, a second implicit assumption in the long-term predictions is that the geochemical conditions at the source remain constant. The current conditions at the source could be somewhat reducing because of the disposal of trash, cardboard, and metal drums. If the immediate source area is reducing, then the source term could currently be limited by the low solubility of radionuclides in the reduced forms. For example, Pu(III), Pu(IV), and U(IV) are generally recognized as being generally insoluble. If the geochemical conditions at the source become more oxidizing over time as the degradable organic carbon is exhausted, these reduced radionuclides could become oxidized and relatively mobile. In such a scenario, the source term could become stronger with time because of changes in valence state, even though the drum failure rate decreases. Temporal changes in the source term also could occur because of changes in pH and P_{CO_2} as the organic substrates in the wastes are exhausted or because of climatic changes. In

summary, the many possible changes that could occur at the source over time should be included in a complete sensitivity analysis.

Uncertainties in the predictions also arise because the adopted conceptual model does not represent the actual field conditions. Sensitivity analyses need to be conducted to examine the effect of the assumed hydrologic environment on the simulated future concentrations. Simulations could be done to examine the significance of the layering, recharge from the spreading basins, variations in interbed properties, and various other factors that can contribute to preferential flow. Preferential flow is a crucial influence that currently (1999) is poorly understood in terms of how to predict when it will occur and with what quantitative effect. Layering is not adequately represented in the model, given its importance as a possible impediment to flow, or generator of lateral flow, or configuration for preferential flow by funneling and unstable flow processes. It has been suggested that the continuum approach selected cannot account for flow features such as funneling.

Section 5.7 notes that the K_d values generally are expected to be highly uncertain for several reasons, including variations in solution composition and lack of site specific data. The impact of this uncertainty has not been considered adequately.

6.5 Summary

The IRA numerical model as implemented with the TETRAD code is a basically sound application of the current available scientific understanding of subsurface transport processes, according with standards that are accepted in the geoscientific community for models used to test hypotheses and improve the understanding of a hydrogeologic system, though not necessarily adequate for all of the applications a risk assessment might demand. For a model of such broad scope, this model was developed in a relatively short time, during which the model developers made hundreds of decisions as to what data and processes to consider. Inevitably, some decisions could be improved upon, but the review team finds few deficiencies of this type. The model developers' attempt to consider as much data in their model as they did and their overall scientific judgment in developing the model are commendable.

Limitations in the model's applicability arise mainly from (1) fundamental shortcomings inherent in any predictive modeling of a highly complex system, (2) currently inadequate scientific understanding of certain important contaminant transport processes, and (3) the

poor quality, small quantity, and often minimal relevance of the data available for characterization and calibration.

The model necessarily is based on an imperfect and highly simplified formulation of the subsurface environment and its processes. One aspect of this is that the degree of spatial detail is much more coarse in such a model than the scales of heterogeneity of properties and physical and chemical processes of the subsurface. For example, the smoothing of data, as by kriging, blurs potentially sharp contrasts between dissimilar subsurface features. The model developers recognized this problem and compensated for some of its most serious aspects by forced imposition of areas of zero interbed thickness in the model domain. Other phenomena, such as preferential flow in channels a few millimeters wide, cannot be easily compensated for. Another aspect is the time scale of applicability. Quantitative predictions of the future with this model are extrapolations of hydrogeologic data that typically extend back about 50 years. The future time over which useful extrapolations can be made from such a data set is shorter than the time scales relevant to the assessment of risks.

Significant limitations in the model's applicability arise out of hydrogeologic processes that are not well enough understood by the scientific community to predict effects of these processes on actinide transport. These chiefly concern flow behavior and chemical reactions in the unsaturated zone. Preferential flow is a process that significantly affects actinide transport, but it is poorly understood in terms of how to predict when it will occur and with what quantitative effect. It also is not known how to represent the layering of geologic materials in sufficient detail to evaluate the importance of layer contrasts as a possible impediment to flow, or a generator of lateral flow, or a configuration for preferential flow by funneling and unstable flow processes. The extent to which chemical interactions between contaminants and subsurface materials inhibit the spread of contamination is uncertain because science does not yet have an adequate theory of reactive chemical transport.

Few relevant direct measurements of subsurface properties, for example unsaturated hydraulic conductivity, are available for use in this model. The available COPC detections are also not useful for calibration, even though, in an ideal situation, measured COPC concentrations would be the data of most importance for calibration and testing. Therefore the model relies heavily on parameter values obtained through inverse modeling and less direct forms of calibration. Unfortunately, even the data used indirectly for calibration are sparse and, for the most part, have undemonstrative relevance to the transport of

6-28 Review of the transport of selected radionuclides in the Interim Risk Assessment

COPC's. Among the reasons why this relevance is not yet established are (1) that the sensitivity of COPC transport to these data was not examined, and (2) that the COPC source terms are not well established.

Despite its limitations, the IRA model has considerable value for exploring the sensitivity of projected contaminant concentrations to certain critical features of the hydrogeologic system associated with the SDA, and for testing possible consequences of alternative management strategies for assessment of their relative effectiveness. One purpose to be served in sensitivity analyses is in assessing the uncertainty of model results caused by specific deficiencies in knowledge of the subsurface transport system, for example the variation in computed COPC travel times that can be ascribed to imperfect knowledge of effective interbed permeabilities. Another purpose is in evaluating the possible effects of alterations in the system, for example whether a proposed modification of the surface-runoff management system could have significant effect on travel times. Other examples include investigating the sensitivity of projected contaminant concentrations to such hydrogeologic features as (1) alteration of infiltration fluxes associated with climatic change, (2) changes in the contaminant source term, and (3) sensitivity of projected contaminant concentrations to K_d values. The small number of sensitivity analyses completed so far in part reflects the fact that the TETRAD model, being a relatively elaborate numerical simulation code, requires considerable computer time for each run. Besides the obvious alleviation of this problem that would be afforded

by faster computers than those now available, the problem could be reduced through the development and use of simpler numerical models, perhaps working in one or two dimensions, for evaluating particular sensitivities.

Our review focuses on whether this model is defensible in various applications relevant to risk assessment. We consider defensibility in terms of whether a knowledgeable scientist would judge it to be either realistic or conservative with respect to risk-assessment applications. If the standard is to make quantitative predictions that scientists would recognize as either approximations or overestimations of the concentration of COPC's at a given point in space and time, this standard cannot be satisfied with existing science and therefore not with any particular model that has been created to date. The present state of knowledge could confirm that the predicted results are what is produced by an agreed-upon predictive procedure, but not that they will correspond to future reality. These remarks should not be taken to imply that the actual future COPC concentrations will necessarily exceed the predictions, but only that the uncertainty of the specific quantitative predictions is so high that the absolute numbers are not useful for deciding whether specific standards, in terms of specifying in advance the result of future measurements, will or will not be met. The model implemented with the TETRAD code meets prevailing scientific standards as an investigative tool, though its applicability does not extend to all aspects of risk assessment.

7.0 Summary and conclusions

This review of the Interim Risk Assessment (IRA) for Waste Area Group 7 (WAG-7) 13/14 Operable Unit focused on the fate and transport of selected actinides (Am, U, Np, and Pu) derived from mixed transuranic wastes buried in shallow pits and trenches at the Subsurface Disposal Area (SDA). This review was concerned only with the actinide data and geotechnical methodologies that were used in the numerical simulator to predict releases of the long-lived actinides to the accessible environment (the Snake River Plain (SRP) aquifer). This review did not include an evaluation of the source term or the source-term release-rate model, both of which add considerable uncertainty to an already complex problem.

The scope of this review included four topical areas: (1) Review of radionuclide sampling data at the Radioactive Waste Management Complex (Chapter 3), (2) Radionuclide transport processes (Chapter 4), (3) Distribution coefficients (K_{ds}) and their application to transport analysis (Chapter 5), and (4) Transport model analysis (Chapter 6). Each of the aforementioned chapters includes a separate summary section. Chapter 2, Conceptual model of aqueous-phase fluid flow and contaminant transport, presents background information that describes the hydrogeologic and geochemical setting of the SDA and vicinity. Chapter 2 also includes a discussion of hydrologic concepts that are considered relevant to the various review topics. The summary and conclusions presented in this chapter highlight many, but not all of the main points presented earlier. The main purpose of this chapter is to discuss the significance of the review team's findings in the context of whether or not actinide predictions can be considered to be conservative. The reader is referred to previous chapters for additional summaries that deal specifically with the topical areas covered in this review.

An implied conclusion of the IRA, as it concerns actinide transport, is that the predictions of actinide releases to the SRP aquifer are conservative. Conservative, as used in the context of the IRA, is meant to indicate that the numerical simulator predicts actinide releases that are larger than should reasonably be expected. The guiding philosophy in developing the numerical simulator was to use technically defensible estimates for the K_{ds} and conservative estimates of other model parameters wherever "realistic" estimates were not available. It was not the intent of the IRA to present a worst-case scenario.

In the case of the actinides and many other aqueous-phase contaminants, calibration control is poor for both the flow component and the transport component of the numerical simulator. No attempt was made, and appropriately so, to calibrate the numerical simulator to actinide detections in the field. The limited number of detections, their sporadic and seemingly random nature, and uncertainty over whether or not these detections represent dissolved-phase transport preclude their use for this purpose. The review team concurs with the principal investigators of the IRA that using these detections for calibration purposes is of limited value. However, to imply (as was done in the IRA, Becker and others, 1998, p. 5-61) that nondetections of actinides predicted by the model are consistent with field evidence can be misleading because model predictions are below minimum detection levels. Thus, it is not possible to demonstrate objectively whether or not the present numerical simulator over or underpredicts actinide releases to the SRP aquifer. The lack of calibration control for the actinides places greater importance and emphasis on demonstrating the reliability and validity of other aspects of the numerical simulator, as discussed in following paragraphs.

The numerical simulator is developed around a conceptual model that incorporates a number of assumptions. Any assessment of model predictions must consider the validity of the conceptual model that was used to guide the formulation of the numerical simulator, the reliability of calibration controls that were used to adjust input parameters and to test the model's capability to match the historical record, and the validity of other assumptions that were used to simplify the real-world problem. Data quality and completeness largely determine the confidence that can be placed in the model's predictive capability. Of necessity, subjective judgment or professional opinion was used in the present study to supplement or substitute for the lack of data. In doing so, the distinction between what falls inside the categories of conservative, realistic, or technically defensible and what falls outside is often blurred. This is particularly evident in the way that K_{ds} were determined and used in the numerical simulator.

All numerical models rely to some degree on the need to simplify the real-world problem. Simplification is required either to minimize computational requirements or to represent complex systems and processes at scales that are capable of integrating the effects of many smaller scale features and interactions. Simplification invariably reduces the problem to studying how temporally averaged and spatially averaged representations interact. Often,

7-2 Review of the transport of selected radionuclides in the Interim Risk Assessment

simplification will degrade, or in some cases, eliminate opportunities to calibrate the simulator. Care is required to ensure that the transformation from the real world to the simulated world preserves the critical elements of the problem being studied and that the simplification process does not inadvertently compromise valuable calibration opportunities that would further reduce confidence in the risk estimates. This point was made in the IRA (Becker and others, 1998, p. 7-6). Loss of calibration opportunity is a trade-off that results from simplification and the use (or overuse) of conservative assumptions.

The conceptual model of flow in the unsaturated zone beneath the SDA assumes that all flow is derived from surface infiltration and runoff within the immediate vicinity of the SDA. Infiltration is spatially and temporally variable across the SDA. Water infiltrating through the shallow surficial sediments and buried waste is redistributed as it comes into contact with the underlying basalts. If the surficial sediments are not present beneath the buried wastes, then downward percolation into the underlying basalts proceeds unimpeded, without lateral redistribution. Flow into and through the basalts underlying the surficial sediments occurs primarily as vertical flow with little or no lateral redistribution within the basalts themselves. Lateral and vertical flow occurs at the contact between the basalts and underlying sedimentary interbeds. Locally, perched water may form at the contact between the basalts and underlying sedimentary interbeds if the vertical flux exceeds the downward percolation capacity of the interbeds and the horizontal permeability of the basalts. Lateral flows derived from seepage in the spreading areas or from the Big Lost River were not considered as sources of water that could contribute to flow in the unsaturated zone or to the formation of perched water.

There is considerable uncertainty over how the exclusion of lateral flow from outside the SDA affects actinide predictions. The decision to do so was based on the lack of compelling evidence (at least not until 1999) to do otherwise, and perhaps because of lack of data to determine what component of the total flux should be assigned to flow derived from outside the SDA. Exclusion of lateral flow in the unsaturated zone from outside the SDA may represent a significant departure from real-world conditions. If so, then interpretations of field data that were used to adjust input parameters to calibrate the numerical simulator or to test its predictive capability may be seriously compromised. Until the issue of lateral flow from outside the SDA is resolved, the reliability of the numerical simulator to predict the fate and transport of contaminants in the subsurface will remain controversial.

Assuming that other aspects of the current conceptual model are applicable, predictions of actinide releases, as presented in the IRA, are presumed to be conservative for the following reasons: (1) K_{ds} that were chosen for actinide transport were at the low end of the range of values that were available from laboratory tests or derived from the literature, (2) gaps in the interbeds and surficial sediments were included to provide preferential pathways for the migration of actinides, (3) the sorption capacity of the basalt matrix in both the unsaturated and saturated zones was assumed to be zero, (4) the thin and discontinuous interbeds located between the C-D interbed and the SRP aquifer were excluded from the numerical simulations, and (5) only the upper portion (76 m) of the total thickness of the SRP aquifer was assumed to be available for mixing and dilution of contaminants. By design, assumptions (3) and (4) are truly conservative treatments that require no additional clarification. Assumption (2) is conservative to the extent that all gaps in the interbeds, within the areal extent of the flow field that could potentially contain waterborne contaminants, are known. Assumption (5) may be conservative, but dispersion and advective mixing processes in the saturated zone are not well characterized. Laboratory- and literature-derived K_{ds} to support assumption (1) lack rigorous definition, may not be applicable to a chemically evolving, mixed-waste environment, and apply only to dissolved-phase transport.

The preceding assumptions constitute the primary basis for implying that predictions of actinide releases to the SRP aquifer are conservative. Additional assumptions were included in the numerical simulator to simplify the computational scheme, improve agreement with certain field observations, or accommodate data limitations. Examples of these assumptions are: (1) representation of the basalts as a homogeneous, anisotropic, equivalent porous media, (2) use of a low-permeability clay layer at the tops of the interbeds and the base of the surficial sediments to simulate perching, (3) assignment of hydrologic properties to the sedimentary interbeds on the basis of lithologic similarity and representation of the interbeds as low-permeability, homogeneous, isotropic units, all with nearly identical hydrologic properties, (4) use of laboratory-derived K_{ds} that are based on tests that do not consider how the actinides may behave in the field in the presence of other mixed wastes, and (5) use of K_{ds} that presume that the capacity of the media to sorb contaminants is infinite, that sorption characteristics of the media are constant, and that there is no competition for sorption sites from other contaminants that may be present.

The effects of these additional assumptions on actinide predictions are difficult to assess. Assumptions based on incomplete data or lack of data are difficult to defend and are particularly vulnerable to criticism. As a minimum, these assumptions point out the lack of rigor attendant to various aspects of the present study. Assumptions (4) and (5) fall into this category. The validity of the other assumptions and their effect on actinide predictions depend on the quality and completeness of the supporting data and on how these and other assumptions were implemented and subsequently evaluated in the numerical simulator. Sensitivity analyses normally are used to evaluate the significance of assumptions on model predictions; however, these analyses were not included in the present version of the IRA and supporting documentation. Nevertheless, a qualitative critique of these secondary assumptions and their effect on the numerical simulator is presented.

(1) Representation of the hydrologic properties of the basalts—Flow in the basalts is very complex. The representation of the basalts as an equivalent, homogeneous, anisotropic, porous media largely precludes realistic simulations of preferential flow within these units. This is a tradeoff resulting from the need to simplify. Results from inverse modeling of data from the Large-Scale Infiltration Test were used to determine equivalent porous-media properties for the basalts to represent the large-scale anisotropy and heterogeneity of these units in a manner appropriate for use in the numerical simulator. This approach is a commonly used and accepted practice, even though nonunique solutions are possible. For modeling purposes, anisotropy of the basalts is represented by a 30:1 (reduced from 300:1 to simulate perching) contrast between horizontal and vertical permeability. Homogeneity of the basalts is embodied in the representation of these units as a low-porosity, high-permeability equivalent porous media. In reality, these flow units are extremely heterogeneous and anisotropic. It is highly unlikely that the true permeability distribution of the basalt flows will ever be known at a scale that would be appropriate for use in the numerical simulator to predict precisely where actinides will migrate. For purposes of the IRA, this may not be necessary if other means (discussed later under topic (3)—hydrologic properties of the sedimentary interbeds) are available to determine the cumulative effect of preferential flow in the basalts. The present modeling effort suggests that the movement of waterborne contaminants in the unsaturated zone will be confined to a relatively small area that lies beneath the immediate vicinity of the SDA. Thus, it is assumed that all

contaminants eventually will contact one or more of the primary sedimentary interbeds beneath the SDA before arriving at the SRP aquifer. This hypothesis needs to be tested. Noteworthy from the perspective of conservatism, the numerical simulator does not assign any capacity to the basalt matrix to sorb contaminants in the unsaturated and saturated zones. This is a conservative assumption that should result in overpredicting actinide releases.

(2) Simulation of perched water—Calibration of the unsaturated-flow component of the numerical simulator relies almost exclusively on simulating perching that has been observed at various locations beneath the SDA. The presence of perched water is appealing because these sites offer an opportunity to sample for waterborne contaminants. The assumption is made that perching mechanisms tend to integrate the flow and contaminant transport history to the point where the perched-water body is formed. To some extent this is true, but if other sources of water outside the contributing area of the SDA are present, then the interpretation of sampling results can be misleading. Lateral flow from outside the boundaries of the SDA may lead to underestimates of contaminant releases because of dilution, dispersion, and facilitated transport of waterborne contaminants that are derived from infiltration within the SDA.

Data to characterize perching phenomena are limited and the mechanisms that lead to perching are poorly understood. Perched water and areas of elevated moisture content in the subsurface have been encountered in almost every geologic setting beneath the SDA. No consistent pattern has emerged to predict where perching will or will not occur. The sedimentary interbeds are presumed to play a major role in this process; however, most observations indicate that perching occurs in the basalts at locations that are not in direct contact with the underlying sedimentary interbeds. The inclusion of a low-permeability clay layer at the tops of the major sedimentary interbeds and at the base of the surficial sediments was needed to simulate perching and redistribute vertical flow. These adjustments were made assuming that all flow through the unsaturated zone beneath the SDA is derived from surface infiltration at the SDA. As mentioned previously, lateral flow from the spreading areas or from seepage in the Big Lost River was not considered as a source of water that could account for the local accumulation of perched water. Larger fluxes in the unsaturated zone, derived perhaps from outside the vicinity of the SDA, may be a necessary prerequisite for most perched-water occurrences.

Although perching is important, its significance as an integrator of flow and contaminant transport processes in

7-4 Review of the transport of selected radionuclides in the Interim Risk Assessment

the unsaturated zone may be overemphasized. A different perspective of perching might suggest that it simply reflects isolated areas where water accumulates locally into dead storage and that most flow in the unsaturated zone actually moves rapidly through the basalts and into the underlying sedimentary interbeds.

The use of a low-permeability clay layer to simulate perching may not be conservative. The low-permeability clay layer forces lateral flow to occur above the interbeds and thus distributes waterborne contaminants over a much larger area than might actually occur in the field. The net effect of this assumption is to provide greater opportunity for waterborne contaminants to come into contact with a much larger volume of contaminant-sorbing media, thus minimizing the deleterious effect that competition for sorption sites would have on contaminant transport. The assumption, as implemented, presumes that there are no known gaps in the C-D interbed in the immediate vicinity of the SDA to facilitate rapid transport to the SRP aquifer. Care must be taken not to overinterpret the significance of perched water in deference to other possibilities that are less obvious but may be more meaningful for characterizing flow in the unsaturated zone.

(3) Hydrologic properties of the sedimentary interbeds—Numerical simulations indicate that the downward flux of water beneath the SDA is not uniformly distributed. This is indicated by the lateral and vertical variability in simulated water saturations within individual interbeds and between interbeds. This is a realistic portrayal of moisture distribution in the unsaturated zone. Moisture distribution patterns that are predicted by the numerical simulator are a consequence of (1) variations in the spatial and temporal distribution of infiltration at the ground surface, (2) differences in the vertical and horizontal permeability assigned to the basalts, (3) contrasts in permeability between the basalts, the interbeds, and clay layers used to simulate perching, and (4) geometric variations in the elevation, attitude, thickness, and continuity of the modeled units, particularly the interbeds. Unfortunately, there are few data to determine how well these simulated moisture distributions represent actual field conditions.

Moisture distribution within the sedimentary interbeds, particularly the low-permeability, silty-loam units, may offer the best opportunity to calibrate the unsaturated-zone flow component of the numerical simulator. As a minimum, moisture distribution within these units may provide the information needed to determine whether flux in the unsaturated zone is derived exclusively from infiltration at the SDA, or if it includes an outside component that needs to be addressed in the

numerical simulations. To do this, realistic representation of the hydrologic properties of the interbeds is needed to avoid compromising the calibration opportunity afforded by this approach. The use of the interbeds in this manner has not yet been explored or exploited to its full potential; most probably because the data are not available to do so. Flux across these units can be estimated if ambient saturations and the moisture characteristic curves for these units are known.

Temporal and spatial variations in the saturation of the sedimentary interbeds can be estimated either from *in situ* measurements of matric potential, borehole measurements using properly calibrated neutron-activation probes, or laboratory measurements of core. All these methods complement each other and should be considered together. Core measurements of the hydrologic properties and ambient moisture content of the sedimentary interbeds, particularly the silty-loam units, are especially desirable.

(4) Applicability of laboratory-derived K_d s—One of the major assumptions used to defend actinide predictions as conservative is derived from the fact that the K_d s used in the numerical simulator were chosen from the low end of the range of laboratory- and literature-derived values. The intent of this decision is clear; however, the quality and completeness of the available data are insufficient to demonstrate that the K_d s were selected from a representative population of test results that are reasonably representative of the site and the influence of a chemically evolving, mixed-waste environment. The K_d s used for Am, U, and Pu transport were derived from a limited number of batch tests of a single, composite, sedimentary interbed sample. This sample was prepared from a mixture of five samples with different physical and chemical properties. Forty percent of the bulk sample (the coarse fraction) was eliminated from the batch tests, possibly biasing the results toward higher K_d s because of the greater surface area represented by the finer size fraction. Furthermore, the batch tests were conducted using synthetic water containing concentrations of major cations and anions that were generally smaller than those measured in ground water and perched water near the SDA. The lower ionic strength of the solution reduces competition for available sorbing sites and leads to larger K_d estimates. The synthetic water also was undersaturated with respect to calcite, even though calcite is a common mineral phase in the sedimentary interbeds. This is a potentially serious departure from actual field conditions, because aqueous stability and mobility of the actinides may be enhanced by the formation of weakly-sorbing carbonate complexes.

The importance of carbonate complexation is demonstrated in the thermodynamic modeling that was conducted as part of this review. Formation of carbonate complexes also was suggested, along with colloidal transport, as possible explanations for the early elution of a “fast fraction” that was observed in the column experiments for Am and Pu referenced in this review.

Although the K_d s used in the numerical simulator were selected from the lower end of the range of these laboratory-derived measurements, it is not obvious that the limited data and experimental protocols provide adequate opportunity to demonstrate that these K_d s are reasonably conservative or technically defensible.

7-6 Review of the transport of selected radionuclides in the Interim Risk Assessment

References Cited

- Ackerman, D.J., 1995, Analysis of steady-state flow and advective transport in the eastern Snake River Plain aquifer system, Idaho: U.S. Geological Survey Water-Resources Investigations Report 94-4257 (DOE/ID-22120), 25 p.
- Ackerman, D.J., 1991, Transmissivity of the Snake River Plain aquifer at the Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Water-Resources Investigations Report 91-4058 (DOE/ID-22097), 35 p.
- Allard, B., Beall, G.W., and Krajewski, T., 1980, The sorption of actinides in igneous rocks: *Nuclear Technology*, v. 49, no. 3, p. 474-480.
- American Society for Testing and Materials, 1996, Standard practice for intralaboratory quality control procedures and a discussion on reporting low-level data: ASTM D-4210-89 (reapproved 1996), 8 p.
- American Society for Testing and Materials, 1987, Standard test methods for 24-h batch-type measurement of contaminant sorption by soils and sediments: ASTM D-4646-87, 4 p.
- Ames, L. L., and Rai, D., 1978, Radionuclide interactions with soil and rock media, volume 1: Processes influencing radionuclide mobility and retention, element chemistry and geochemistry, conclusions and evaluation: EPA 520/6-78-007, p. 3-101 to 3-107.
- Anderson, K., Torstenfelt, B., and Allard, B., 1982, Sorption behavior of long-lived radionuclides in igneous rock, in *Environmental Migration of Long-Lived Radionuclides*: International Atomic Energy Agency, IAEA-SM/257/20, p. 111-131.
- Anderson, M.P., and Woessner, W.W., 1992, Applied groundwater modeling—Simulation of flow and advective transport: San Diego, Harcourt Brace Jovanovich, 289 p.
- Anderson, S.R., Ackerman, D.J., Liszewski, M.J., and Freiburger, R.M., 1996, Stratigraphic data for wells at and near the Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Open-File Report 96-248 (DOE/ID-22127), 27 p., 1 diskette.
- Anderson, S.R., and Bartholomay, R.C., 1995, Use of natural-gamma logs and cores for determining stratigraphic relations of basalt and sediment at the Radioactive Waste Management Complex, Idaho National Engineering Laboratory, Idaho: *Journal of the Idaho Academy of Science*, v. 31, no. 1, p. 1-10.
- Anderson, S.R., Kuntz, M.A., and Davis, L.C., 1999, Geologic controls of hydraulic conductivity in the Snake River Plain aquifer at and near the Idaho National Engineering and Environmental Laboratory, Idaho: U.S. Geological Survey Water-Resources Investigations Report 99-4033 (DOE/ID-22155), 38 p.
- Anderson, S.R., and Lewis, B.D., 1989, Stratigraphy of the unsaturated zone at the Radioactive Waste Management Complex, Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Water-Resources Investigations Report 89-4065 (DOE/ID-22080), 54 p.
- Anderson, S.R., and Liszewski, M.J., 1997, Stratigraphy of the unsaturated zone and the Snake River Plain aquifer at and near the Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Water-Resources Investigations Report 97-4183 (DOE/ID-22142), 65 p.
- Andraski, B.J., 1996, Properties and variability of soil and trench fill at an arid waste-burial site: *Soil Science Society American Journal*, v. 60, p. 54-66.
- Andre, C., Sardin, M., Vitorge, P., and Faure, M.H., 1998, Analysis of breakthrough curves of Np(V) in clayey sand packed column in terms of mass transfer kinetics: *Journal of Contaminant Hydrology*, v. 35, p. 161-173.
- Baes, C.F., III, and Sharp, R.D., 1983, A proposal for estimation of soil leaching and leaching constants for use in assessment models: *Journal of Environmental Quality*, v. 12, no. 1, p. 17-28.
- Baker, R.S., and Hillel, Daniel, 1991, Laboratory tests of a theory of fingering during infiltration into layered soils comment and reply: *Soil Science Society of America Journal*, v. 55, no. 3, p. 896-897.
- Balistrieri, L.S., and Murray, J.W., 1984, Marine scavenging—Trace metal adsorption by interfacial sediment from MANOP site H1: *Geochimica et Cosmochimica Acta*, v. 48, p. 921-929.
- Barney, G.S., 1978, The kinetics and reversibility of radionuclide sorption reactions with rocks: *Proceedings of the Task 4, Waste Isolation Safety Assessment Program*, Battelle, Pacific Northwest Lab., RHO-ST-19, p. 161-218.
- Barney, G.S., 1981, Radionuclide reactions with groundwater and basalts from Columbia River basalt formations: US DOE report RHO-SA-217, Rockwell International, Richland, Wash., 44 p.
- Barney, G.S., 1982, Radionuclide sorption on basalt-interbed materials, FY 1981 Annual Report: Basalt Waste Isolation Project, Rockwell International Report, U.S. Department of Energy RHO-BW-ST-35P, [variously paged].
- Barney, G.S., 1984, Radionuclide sorption and desorption reactions with interbed materials from the Columbia River basalt formation, in Barney, B.S., Navratil, J.D., and Schulz, W.W., eds, *Geochemical behavior of disposed radioactive waste*, American Chemical Society Symposium Series 246, p. 3-23.
- Barraclough, J.T., Robertson, J.B., and Janzer, V.J., 1976, Hydrology of the solid waste burial ground, as related to the potential migration of radionuclides, Idaho National Engineering Laboratory, with a section on drilling and sample analyses, by Saindon, L.G.: U.S. Geological Survey Open-File Report 76-471 (IDO-22056), 183 p.
- Barrie, S.L., and Haney, D.F., 1997, Sampling and analysis plan for routine monitoring of operable unit 7-06, section 2 (Specific objectives and data uses): INEL-94/0027 rev. 6, [variously paged].
- Bartholomay, R.C., 1998, Distribution of selected radiochemical and chemical constituents in perched ground

ref-2 Review of the transport of selected radionuclides in the Interim Risk Assessment

- water, Idaho National Engineering Laboratory, Idaho, 1992–95: U.S. Geological Survey Water-Resources Investigations Report 98–4026 (DOE/ID–22145), 59 p.
- Bartholomay, R.C., 1990c, Mineralogical correlation of surficial sediment from area drainages with selected sedimentary interbeds at the Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Water-Resources Investigations Report 90–4147 (DOE/ID–22092), 18 p.
- Bartholomay, R.C., 1990b, Mineralogy, petrology, and grain size of surficial sediment from the Big Lost River, Little Lost River and Birch Creek drainages, Idaho National Engineering Laboratory, Idaho: Idaho State University, M.S. thesis, 118 p.
- Bartholomay, R.C., 1990a, Digitized geophysical logs for selected wells on or near the Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Open-File Report 90–366 (DOE/ID–22088), 347 p.
- Bartholomay, R.C., Knobel, L.L., and Davis, L.C., 1989, Mineralogy and grain size of surficial sediment from the Big Lost River drainage and vicinity, with chemical and physical characteristics of geologic materials from selected sites at the Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Open-File Report 89–384 (DOE/ID–22081), 74 p.
- Bartholomay, R.C., Tucker, B.J., Ackerman, D.J., and Liszewski, M.J., 1997, Hydrologic conditions and distribution of selected radiochemical and chemical constituents in water, Snake River Plain aquifer, Idaho National Engineering Laboratory, Idaho, 1992 through 1995: U.S. Geological Survey Water-Resources Investigations Report 97–4086 (DOE/ID–22137), 57 p.
- Baudin, G., Billon, A., and Petit, J.C., 1988, Technical aspects of the French R and D programme devoted to radionuclide migration in the geosphere—A review: *Radioactive Waste Management and the Nuclear Fuel Cycle*, v. 10, p. 81–113.
- Baumer, A.R., Flynn, S.C., Thompson, R.G., and Watkins, C.S., 1997, Quality assurance project plan for Waste Area Groups 1, 2, 3, 4, 5, 6, 7, 10 and Inactive Sites: Lockheed Martin Idaho Technologies Company, DOE/ID–10587 (formerly INEL–95/0086), rev. 5, [variously paged].
- Beasley, T.M., Kelley, J.M., Bond, L.A., Rivera, W., Jr., Liszewski, M.J., and Orlandini, K.A., 1998, Heavy element radionuclides (Pu, Np, U) and ¹³⁷Cs in soils collected from the Idaho National Engineering and Environmental Laboratory and other sites in Idaho, Montana, and Wyoming: U.S. Department of Energy, EML–599, 74 p.
- Bear, J., 1978, *Hydraulics of groundwater*, New York, McGraw-Hill, 569 p.
- Becker, B.H., Bensen, T.A., Blackmore, C.S., Burns, D.E., Burton, B.N., Hampton, N.L., Huntley, R.M., Jones, R.M., Jorgensen, D., Magnuson, S.O., Shapiro, C., VanHorn, R.L., 1996, Work plan for Operable Unit 7-13/14; Waste Area Group 7 comprehensive remedial investigation/ feasibility study: Lockheed Martin Idaho Technologies Company, INEL–95/0343, rev. 0, [variously paged].
- Becker, B.H., Burgess, J.D., Holdren, K.J., Jorgensen, D.K., Magnuson, S.O., and Sundrup, A.J., 1998, Interim risk assessment and contaminant screening for the Waste Area Group 7 remedial investigation: Lockheed Martin Idaho Technologies Company, DOE/ID–10569, Draft rev. 2, [variously paged].
- Bennett, C.M., 1990, Streamflow losses and ground-water level changes along the Big Lost River at the Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Water-Resources Investigations Report 90–4067 (DOE/ID–22091), 49 p.
- Bertetti, F.P., Pabalan, R.T., and Almendarez, M.G., 1998, Studies of neptunium sorption on quartz, clinoptilolite, montmorillonite, and α -Alumina in Jenne, E.A., ed., *Adsorption of metals: Geomedia, Academic Press*, p. 131–148.
- Bishop, C.W., 1991, Hydraulic properties of vesicular basalt: University of Arizona, M.S. Thesis, 115 p.
- Bishop, C.W., 1996, Soil moisture monitoring results at the Radioactive Waste Management Complex of the Idaho National Engineering Laboratory, FY-96, FY-95, and FY-94: Lockheed Martin Idaho Technologies Company, INEL–96/297, [variously paged]
- Boggs, S., Jr., Livermore, D., and Seitz, M.G., 1985, Humic substances in natural waters and their complexation with trace metals and radionuclides—a review: Argonne National Laboratory, ANL–84–78, 110 p.
- Bondiatti, E.A., and Francis, C.W., 1979, Geologic migration potentials of technetium-99 and neptunium-237: *Science*, v. 203, p. 1,337–1,340.
- Bondiatti, E.A., and Sweeton, F.H., 1977, Transuranic speciation in the environment, in White, M.G. and Dunaway, P.B., eds., *Transuranics in Natural Environments: Energy Research and Development Administration*, p. 449–476.
- Bradbury, M.H., and Baeyens, B., 1993, A general application of surface complexation to modeling radionuclide sorption in natural systems: *Journal of Colloid and Interface Science*, v. 158, p. 364–371.
- Brooks, R.H., and Corey, A.T., 1996, Properties of porous media affecting fluid flow: *Journal of Irrigation Drainage Division, American Society of Engineering*, v. 92, p. 61–87.
- Buddemeier, R.W., and Hunt, J.R., 1988, Transport of colloidal contaminants in groundwater—radionuclide migration at the Nevada Test Site: *Applied Geochemistry*, v. 3, p. 535–548.
- Burgess, J.D., Higgs, B.D., and Wood, T.R., 1994, WAG 7 groundwater pathway track 2 summary report: EG&G Idaho, Inc., EGG–ER–10731, [variously paged].
- Burgus, W.H., and Maestas, S.E., 1976, A further investigation of subsurface radioactivity at the Radioactive Waste Management Complex, Idaho National Engineering Laboratory: U.S. Energy Research and Development Administration, INEL Report IDO–10065, 36 p.
- Burns, D.E., Becker, B.H., Huntly, R.M., Loehr, C.A., Rood, S.M., Sinton, P., and Smith, T.H., 1994, Revised preliminary scoping risk assessment for waste pits, trenches, and soil vaults at the Subsurface Disposal Area, Idaho National

- Engineering and Environmental Laboratory, EG&G Idaho, Inc., EGG-ER-11395.
- Busenberg, E., Plummer, L.N., Bartholomay, R.C., and Wayland, J.E., 1998, Chlorofluorocarbons, sulfur hexafluoride, and dissolved permanent gases in ground water from selected sites at and near the Idaho National Engineering and Environmental Laboratory, Idaho, 1994 through 1997: U.S. Geological Survey Open-File Report 98-274 (DOE/ID-22151), 72 p.
- Busenberg, E., Weeks, E.P., Plummer, L.N., and Bartholomay, R.C., 1993, Age dating ground water by use of chlorofluorocarbons (CCl_3F and CCl_2F_2), and distribution of chlorofluorocarbons in the unsaturated zone, Snake River Plain aquifer, Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Water-Resources Investigations Report 93-4054 (DOE/ID-22107), 47 p.
- Carnall, W.T., and Choppin, G.R., 1983, Plutonium Chemistry: American Chemical Society, Washington D.C., American Chemical Society Symposium Series 216, 484 p.
- Casey, F.X., Logsdon, S.D., Horton, R., and Jaynes, D.B., 1997, Immobile water content and mass exchange coefficient of a field soil: Soil Science Society American Journal, v. 61, p. 1,030-1,036.
- Cecil, L.D., 1989, Reporting of radionuclide data of environmental concern, *in* Pedersen, G.L., and Smith, M.M., compilers, U.S. Geological Survey Second National Symposium on Water Quality, Abstracts of the Technical Sessions, Orlando, Fla, November 12-17, 1989: U.S. Geological Survey Open File Report 89-409, 2 p.
- Cecil, L.D., Orr, B.R., Norton, Teddy, and Anderson, S.R., 1991, Formation of perched ground-water zones and concentrations of selected chemical constituents in water, Idaho National Engineering Laboratory, Idaho 1986-88: U.S. Geological Survey Water-Resources Investigations Report 91-4166 (DOE/ID-22100), 53 p.
- Cecil, L.D., Pittman, J.R., Beasley, T.M., Kubik, P.W., Sharma, P., Fehn U., and Gove, H.E., 1992, Water infiltration rates in the unsaturated zone at the Idaho National Engineering Laboratory estimated from chlorine-36 and tritium profiles, and neutron logging: Water-Rock Interaction, Balkema, Rotterdam, p. 709-714.
- Champ, D.R., Merritt, W.F., and Young, J.L., 1982, Potential for the rapid transport of plutonium in groundwater as demonstrated by core column studies, *in* Lutze, W., ed., Scientific basis for nuclear waste management, 7 June 1982, Materials Research Society, V., p. 745-754.
- Childs, E.C., and Collis-George, N., 1950, The permeability of porous materials: Proceedings Royal Society of London, v. 201A, p. 392-405.
- Choppin, G.R., and Allard, B., 1985, Complexes of actinides with naturally occurring organic compounds, Handbook on the Physics and Chemistry of the Actinides, Elsevier Science Publishers, p. 407-429.
- Choppin, G.R., and Stout, B.E., 1989, Actinide behavior in natural waters: The Science of the Total Environment., v. 83, p. 203-216.
- Cleveland, J.M., 1979, The chemistry of plutonium: American Nuclear Society, La Grange Park, Ill., 653 p.
- Cleveland J.M., and Mullin, A.H., 1993, Speciation of plutonium and americium in ground waters from the Radioactive Waste Management Complex, Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Water-Resources Investigations Report 93-4035, 9 p.
- Cochran, J.K., Fisher, N., and Moran, S.B., 1996, Transport and fate of radionuclides in the Ob River Estuarine System: Arctic Nuclear Waste Assessment Program Summary FY 1995, Office of Naval Research, ONR-32296-16, p. 62-76.
- Colello, J.J., Rosentreter, J.J., Bartholomay, R.C., and Liszewski, M.J., 1998, Strontium distribution coefficients of basalt core samples from the Idaho National Engineering and Environmental Laboratory, Idaho: U.S. Geological Survey Water-Resources Investigations Report 98-4256 (DOE/ID-22153), 68 p.
- Collins, B.L., 1999, Federal Government Coordination on Standards: Standardization News, v. 27, no. 5, p. 20-21.
- Coughtrey, P.J., Jackson, D., Jones, C.H., Kane, P., and Thorne, M.C., 1985 Radionuclide distribution and transport in terrestrial and aquatic ecosystems—A critical review of data: A.A. Balkema, Netherlands, 359 p.
- Cross, J.E., and Ewart, F.T., 1991, HATCHES—A Thermodynamic Database and Management System: Radiochimica Acta 52/53, p. 421-422.
- Currie, L.A., 1984, Lower limits of detection—definition and elaboration of a proposed position for radiological effluent and environmental measurements: U.S. Nuclear Regulatory Commission, NUREG/CR-4007, 139 p.
- Dahlman, R.C., Bondietti, E.A., and Eyman, L.D., 1976, Biological pathways and chemical behavior of plutonium and other actinides in the environment, *in* Friedman, A.M., ed., Environmental behavior of the actinide elements: American Chemical Society Symposium Series no. 35, p. 47-80.
- Dames and Moore, 1992, Compilation and summarization of the Subsurface Disposal Area radionuclide transport data at the Radioactive Waste Management Complex: U.S. Department of Energy, INEL Report EGG-ER-10546, 75 p.
- Davis, J.A., and Leckie, J.O., 1978, Surface ionization and complexation at the oxide/water interface. II. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions. J Colloid Interface Sci, 67, p. 90-107.
- Davis, J.A., and Kent, D.B., 1990, Surface complexation modeling in aqueous geochemistry: Reviews in Mineralogy, v. 23, p. 177-260.
- Davis, J.A., Coston, J.A., Kent, D.B., and Fuller, C.C., 1998, Application of the surface complexation concept to complex mineral assemblages: Environmental Science and Technology, v. 32, p. 2,820-2,828.
- Davis, L.C., and Pittman, J.R., 1990, Hydrological, meteorological, and geohydrological data for an unsaturated zone study near the Radioactive Waste Management Complex, Idaho National Engineering Laboratory,

ref-4 Review of the transport of selected radionuclides in the Interim Risk Assessment

- Idaho—1987: U.S. Geological Survey Open-File Report 90–114 (DOE/ID–22086), 208 p.
- Davis, L.C., Hannula, S.R., and Bowers, Beverly, 1997, Procedures for use of, and drill cores and cuttings available for study at, the Lithologic Core Storage Library, Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Open-File Report 97–124 (DOE/ID–22135), 31 p.
- de Rooij, G.H., Warrick, A.W., and Gielen, J.L.W., 1995, Steady flow from a disc source above a shallow water table: *Journal of Hydrology*, p. 37–55.
- Dekker, L.W. and Ritsema, C.J., 1994, How water moves in a water repellent sandy soil. 1. Potential and actual water repellency: *Water Resources Research*, v. 30, p. 2,507–2,517.
- Del Nero, M., Made, B., Bontems, G., and Clement, A., 1997, Adsorption of neptunium (V) on hydrargilite: *Radiochimica Acta*, v. 76, p. 219–228.
- Delegard, C.H., Barney, G.S., and Gallagher, S.A., 1984, Effects of Hanford high-level waste components on the solubility and sorption of cobalt, strontium, neptunium, plutonium, and americium: American Chemical Society Symposium Series 246, Seattle, Wash., 1983, p. 95–112.
- Dicke, C.A., 1997, Distribution coefficients and contaminant solubilities for the Waste Area Group 7 baseline risk assessment: Lockheed Martin Idaho Technologies Company, INEL/EXT–97–00201, [variously paged].
- Diment, G.A., Watson, K.K., and Blennerhassett, P.J., 1982, Stability analysis of water movement in unsaturated porous materials—1. Theoretical considerations: *Water Resources Research*, v. 18, p. 1,248–1,254.
- Duff, M.C., Hunter, D.B., Triay, I.R., Bertsch, P.M., Reed, D.T., Sutton, S.R., Shea-McCarthy, G., Kitten, J., Eng, P., Chipera, S.J., and Vaniman, D.T., 1999a, Mineral associations and average oxidation states of sorbed Pu on tuff: *Environmental Science and Technology* v. 33, no. 13, p. 2,163–2,169.
- Duff, M.C., Newville, M., Hunter, D.B., Bertsch, P.M., Sutton, S.R., Triay, I.R., Vaniman, D.T., Eng, P., and Rivers, M.L., 1999b, Micro-XAS studies with sorbed plutonium on tuff: *Journal of Synchrotron Radiation*, v. 6, p. 350–352.
- Dunnivant, F.M., Newman, M.E., Bishop, C.W., Burgess, D., Giles, J.R., Higgs, B.D., Hubbell, J.M., Neher, E., Norell, G.T., Pfeifer, M.C., Porro, I., Starr, R.C., and Wylie, A.H., 1998, Water and radioactive tracer flow in a heterogeneous field-scale system: *Groundwater*, v. 36, no. 6, p. 949–958.
- Dzombak, D.A., and Morel, F.M.M., 1990, *Surface Complexation Modeling—Hydrous Ferric Oxide*: John Wiley and Sons, New York, 393 p.
- Estes, M., and McCurry, M., 1994, Concentrations and compositions of colloidal particles in groundwater near the ICPP, Idaho National Engineering Laboratory, Idaho: *Hydrogeology Waste Disposal: Science and Politics Proceedings*, 30th Symposium Engineer's Geology of Geotechnical Engineering, Pocatello, Idaho, 1994, p. 165–179.
- Faybishenko, B., 1999, Evidence of chaotic behavior in flow through fractured rocks, and how we might use chaos theory in fractured rock hydrogeology: *Proceedings—Dynamics of Fluids in Fractured Rocks*, Berkeley, Calif., 1999, p. 207–218.
- Fjeld, R.A., Coates, J.T., Elzerman, A.W., and Navratil, J.D., 1998, Column studies of plutonium transport in sedimentary interbeds from the Snake River Plain: *Proceedings of Waste Management 98 Symposium*, Tuscon, Ariz., 7 p.
- Flury, M., Fluhler, H., Jury, W.A., and Leuenberger, J., 1994, Susceptibility of soils to preferential flow of water—A field study: *Water Resources Research*, v. 30, no. 7, p. 1,945–1,954.
- Forman, S.L., Smith, R.P., Hackett, W.R., Tullis, J.A., and McDaniel, P.A., 1993, Timing of late Quaternary glaciations in the western United States based on the age of loess on the eastern Snake River Plain, Idaho: *Quaternary Research*, v. 40, p. 30–37.
- Freeze, R.A., and Cherry, J.A., 1979, *Groundwater*: Englewood Cliffs, N.J., Prentice Hall, 604 p.
- Friedman, H.A., and Kelmers, A.D., 1990, Laboratory measurement of radionuclide sorption in solid waste storage area 6 soil/groundwater systems: ORNL/TM–10561, 22 p.
- Fruchter, J.S., Cowan, C.E., Robertson, D.E., Grivin, D.C., Jenne, E.A., Toste, A.P., and Abel, K.H., 1985, Radionuclide migration in ground water: Pacific Northwest Laboratory, NUREG/CR–4030 PNL–5299, 41 p.
- Fujita, T., Tsukamoto, M., Ohe, T., Nakayama, S., and Sakamoto, Y., 1995, Modeling of neptunium (V) sorption behavior onto iron-containing minerals: *Materials Research Society Symposium Proceedings*, v. 353, p. 965–972.
- Gelhar, L.W., Welty, C., and Rehfeldt, K.R., 1992, A critical review of data on field-scale dispersion in aquifers: *Water Resources Research*, v. 28, no. 7, p. 1,955–1,974.
- Ghodrati, M., and Jury, W.A., 1992, A field study of the effects of soil structure and irrigation method on preferential flow of pesticides in unsaturated soil: *Journal of Contaminant Hydrology*, v. 11, p. 101–125.
- Gianniny, G.L., Geslin, J.K., Link, P.K., and Thackray, G.D., 1997, Quaternary surficial sediments near Test Area North (TAN), northeastern Snake River Plain—an actualistic guide to aquifer characterization: *Symposium on Engineering Geology and Geotechnical Engineering*, 32d, Boise, Idaho, March 26–28, 1997, *Proceedings*, p. 29–44.
- Glass, R.J., Parlange, J.Y., and Steenhuis, T.S., 1989a, Wetting front instability—1. Theoretical discussion and dimensional analysis: *Water Resources Research*, v. 25, no. 6, p. 1,187–1,194.
- Glass, R.J., Parlange, J.Y., and Steenhuis, T.S., 1989b, Wetting front instability—2. Experimental determination of relationships between system parameters and two-dimensional unstable flow field behavior in initially dry porous media: *Water Resources Research*, v. 25, no. 6, p. 1,198–1,207.
- Glass, R.J., Steenhuis T.S., and Parlange, J.Y., 1988, Wetting front instability as a rapid and far-reaching hydrologic

- process in the vadose zone: *Journal of Contaminant Hydrology*, v. 3, p. 207–226.
- Goff, R.W., 1994, The sorption of select radionuclides on basalt and interbed material of the Snake River Plain in southern Idaho: Clemson University, M.S. Thesis, 131 p.
- Greenfield, B.F., Moreton, A.D., Spindler, M.W., Williams, S.J., and Woodwark, D.R., 1992, The effects of the degradation of organic materials in the near field of a radioactive waste repository: *Materials Research Society Symposium Proceedings, Scientific Basis for Nuclear Waste Management XV*, Strasbourg, France, 1991, p. 299–306.
- Grenthe, I., J. Fuger, R.J. Lemire, A.B. Muller, C. Nguyen-Trung, and Hwassner, 1992, *Chemical Thermodynamics of Uranium*. Elsevier, Amsterdam, 716 p.
- Griffioen, J.W., Barry, D.A., Parlange, J.Y., 1998, Interpretation of two-region model parameters: *Water Resources Research*, v. 34, no. 3, p. 373–384.
- Hadermann, J., and Gunten, H.R.V., 1988, Radionuclide migration in the geosphere—Swiss research activities in laboratory and field experiments and in model validation: *Radioactive Waste Management and the Nuclear Fuel Cycle*, v. 10, p. 233–255.
- Healy, R.W., 1990, Simulation of solute transport in variably saturated porous media with supplemental information on modifications to the U.S. Geological Survey's computer program VS2D: U.S. Geological Survey Water-Resources Investigations Report 90–4025, 125 p.
- Hendrickx, J.M. and Yao, T., 1998, Prediction of wetting front instability in homogenous soils—an empirical approach: *American Geophysical*, 1998 Fall meeting, 361 p.
- Higgo, J.J.W., and Rees, L.V.C., 1986, Adsorption of actinides by marine sediments—Effect of the sediment/seawater ratio on the measured distribution ratio: *Environmental Science Technology*, v. 20, no. 5, p. 483–490.
- Higgo, J.J.W., Cole, T., Rees, L.V.C., and Cronan, D.S., 1986, The relationship between effective diffusion coefficients and distribution ratios in deep sea sediments, *in* Sibley, T.H., and Myttenaere, C., eds., *Application of Distribution Coefficients to Radiological Assessment Models*: Elsevier Applied Science Publishers, p. 166–180.
- Hill, M.C., 1998, Methods and guidelines for effective model calibration: U.S. Geological Survey Water-Resources Investigations Report 98–4005, 90 p.
- Hillel, D., and Baker, R.S., 1988, A descriptive theory of fingering during infiltration into layered soils: *Soil Science*, v. 146, p. 51–56.
- Hoxie, D.T., 1989, A conceptual model for the unsaturated-zone hydrogeologic system, Yucca Mountain, Nevada, in Laul, J.C., Van Luik, A.E., and Alexander, D.H., eds., *Nuclear waste management, 1988: Perspectives on National and International Programs and Technology; Part II, Radioactive Waste Management and the Nuclear Fuel Cycle*, 13 (1-4), p. 63–75.
- Hsi C.K.D. and Langmuir, D., 1985, Adsorption of uranyl onto ferric oxyhydroxides—Application of the surface complexation site-binding model. *Geochim. Cosmochim. Acta*, v. 49, p. 1,931–1,941.
- Hubbell, J.M., 1990, Perched ground water at the Radioactive Waste Management Complex: U.S. Department of Energy, EDF–VVED–ER–098, EG&G Idaho, Inc., 30 p.
- Hubbell, J.M., Hull, L.C., Humphrey, T.G., Pittman, J.R., and Fischer, P.R., 1987, Subsurface investigations program at the Radio-active Waste Management Complex of the Idaho National Engineering Laboratory, Annual Progress Report, FY-1986, U.S. Department of Energy, DOE/ID–10153, [variously paged].
- Hughes, J.D., 1993, Analysis of characteristics of sedimentary interbeds at the Radioactive Waste Management Complex, Idaho National Engineering Laboratory, Idaho: Idaho State University, M.S. Thesis, 74 p., 2 plates.
- Humphrey, T.G., 1980, Subsurface migration of radionuclides at the Radioactive Waste Management Complex, 1978: U.S. Department of Energy, INEL Report EGG–2026, 44 p.
- Humphrey, T.G., and Tingey, F.H., 1978, The subsurface migration of radionuclides at the Radioactive Waste Management Complex, 1976–1977: U.S. Department of Energy, INEL Report TREE–1171, 98 p.
- Humphrey, T.G., Smith, T.H., and Pope, M.C., 1982, Projected subsurface migration of radionuclides from buried Idaho National Engineering Laboratory transuranic waste: *Nuclear Technology*, v. 58, p. 136–149.
- Ivanovich, M., 1993, Response to McKinley and Alexander (1993): *Journal of Contaminant Hydrology*, v. 13, p. 263–266.
- Jackson, M.L., Lim, C.H., and Zelazny, L.W., 1986, Oxides, hydroxides, and aluminosilicates, *in* Klute, A., ed., *Methods of Soil Analysis, Part 1, Physical and Mineralogical Methods* (2d ed.): American Society of Agronomy, Soil Science Society of America, p. 101–150.
- Jaynes, D.B., Logsdon, S.D., and Horton, R., 1995, Field method for measuring mobile/immobile water content and solute transfer rate coefficient: *Soil Science Society of America Journal*, v. 59, p. 352–356.
- Jenne, E.A., ed., 1998a, *Adsorption of Metals*: Geomedia, San Diego, Academic Press, 583 p.
- Jenne, E.A., 1998b, Priorities for future metal adsorption research: *in* Jenne, E.A., ed., *Adsorption of Metals*: Geomedia: Academic Press, p. 549–560.
- Jensen, B.S., 1982, The migration of radionuclides with ground water. A discussion of the relevance of the input parameters used in model calculations: *Materials Research Society Fifth International Symposium on the Scientific Basis for Nuclear Waste*, Berlin, Germany, 1982, p. 765–774.
- Jensen, M.P., Nash, K.L., Morss, L.R., Appelman, E.A., and Schmidt, M.A., 1996, Immobilization of actinides in geomedia by phosphate precipitation, *in* Gaffney, J.S., Marley, N.A., and Clark, S.B., eds.: *Humic and Fulvic Acids—Isolation, Structure and Environmental Role*, American Chemical Society, Washington, D.C., American Chemical Society, ACS Symposium Series 651, chap. 17, p. 272–285.

ref-6 Review of the transport of selected radionuclides in the Interim Risk Assessment

- Johnston, H.M., and Gillham, R.W., 1980, A review of selected radionuclide distribution coefficients of geologic materials: Atomic Energy of Canada, Pinawa, Manitoba ROE 1LO, Technical Record TR-90, p. 24-83.
- Jorgensen, D.J., Kuhns, D.J., King, J.J., and Loehr, C.A., 1994, WAG-7 Operable Unit (OU) 7-02 Acid Pit Track 2 Summary Report: EG&G Idaho Inc., EGG-ERD-10242, [variously paged].
- Jury, W.A., and Wang, Zhi, 1999, Recent developments and unresolved problems in vadose zone hydrology and contaminant transport: Proceedings, Dynamics of Fluids in Fractured Rocks, Berkeley, Calif.; p. 103-104.
- Keeny-Kennicutt, W.L., and Morse, J.W., 1985, The redox chemistry of Pu(V)O₂⁺ interaction with common mineral surfaces in dilute solutions and seawater: *Geochimica et Cosmochimica Acta*, v. 49, p. 2,577-2,588.
- Kersting, A.B., Efurud, D.W., Finnegan, D.L., Rokop, D.J., Smith, D.K., and Thompson, J.L., 1999, Migration of plutonium in groundwater at the Nevada Test Site, *Nature*, v. 397, p. 56-59.
- Knobel, L.L., Bartholomay, R.C., Cecil, L.D., Tucker, B.J., and Wegner, S.J., 1992, Chemical constituents in the dissolved and suspended fractions of ground water from selected sites, Idaho National Engineering Laboratory and vicinity, Idaho, 1989: U.S. Geological Survey Open-File Report 92-51 (DOE/ID-22101), 56 p.
- Knobel, L.L., Bartholomay, R.C., and Orr, B.R., 1997, Preliminary delineation of natural geochemical reactions, Snake River Plain aquifer system, Idaho National Engineering Laboratory and vicinity, Idaho: U.S. Geological Survey Water-Resources Investigations Report 97-4093 (DOE/ID-22139), 52 p.
- Knobel, L.L., Cecil, L.D., and Wood, T.R., 1995, Chemical composition of selected core samples, Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey, Open-File Report 95-748 (DOE/ID-22126), 59 p.
- Knobel, L.L., and Mann, L.J., 1988, Radionuclides in ground water at the Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Open-File Report 88-731 (DOE/ID-22077), 37 p.
- Knutson, C.F., McCormick, K.A., Crocker, J.C., Glenn, M.A., and Fishel, M.L., 1992, 3D RWMC vadose zone modeling (including FY-89 to FY-90 basalt characterization results): EG&G Idaho, Inc., EGG-ERD-10246 [variously paged].
- Knutson, C.F., McCormick, K.A., Smith, R.P., Hackett, W.R., O'Brien, J.P., and Crocker, J.C., 1990, FY-89 Report RWMC vadose zone basalt characterization: EG&G Idaho, Inc., EGG-WM-8949 [variously paged].
- Kohler, M., Curtis, G.P., Kent, D.B., and Davis, J.A., 1996, Experimental investigation and modeling of uranium (VI) transport under variable chemical conditions: *Water Resources Research*, v. 32, p. 3,539-3,551.
- Kohler, M., Honeyman, B.D., and Leckie, J.O., 1999, Neptunium (V) sorption on hematite (α -Fe₂O₃) in aqueous suspension—The effect of CO₂: *Radiochimica Acta* (in press).
- Krishnaswami, S., Graustein, W.C., and Turekian, K.K., 1982, Radium, thorium and radioactive lead isotopes in groundwaters—Application to the in situ determination of adsorption-desorption rate constants and retardation factors: *Water Resources Research*, v. 18, p. 1,663-1,675.
- Kumata, M., and Vandergraaf, T.T., 1998, Experimental study on neptunium migration under in situ geochemical conditions: *Journal of Contaminant Hydrology*, v. 35, p. 31-40.
- Kung, K.J.S., 1990a, Preferential flow in a sandy vadose zone-1. Field observation: *Geoderma*, v. 46, p. 51-58.
- Kung, K.J.S., 1990b, Preferential flow in a sandy vadose zone-2. Mechanism and implications: *Geoderma*, v. 46, p. 59-71.
- Kuntz, M.A., 1992, A model-based perspective of basaltic volcanism, eastern Snake River Plain, Idaho, in Link, P.K., Kuntz, M.A., and Platt, L.B., eds., *Regional geology of eastern Idaho and western Wyoming*: Geological Society of America Memoir 179, p. 289-304.
- Kuntz, M.A., Covington, H.R., and Schorr, L.J., 1992, An overview of basaltic volcanism of the eastern Snake River Plain, Idaho, in Link, P.K., Kuntz, M.A., and Platt, L.B., eds., *Regional geology of eastern Idaho and western Wyoming*: Geological Society of America Memoir 179, p. 227-267.
- Kuntz, M.A., and Dalrymple, G.B., 1979, Geology, geochronology, and potential volcanic hazards in the Lava Ridge-Hells Half Acre area, eastern Snake River Plain, Idaho: U.S. Geological Survey Open-File Report 79-1657, 66 p.
- Kuntz, M.A., Dalrymple, G.B., Champion, D.E., and Doherty, D.J., 1980, Petrography, age, and paleomagnetism of volcanic rocks at the Radioactive Waste Management Complex, Idaho National Engineering Laboratory, Idaho, with an evaluation of potential volcanic hazards: U.S. Geological Survey Open-File Report 80-388, 63 p.
- Kuntz, M.A., Skipp, Betty, Lanphere, M.A., Scott, W.E., Pierce, K.L., Dalrymple, G.B., Champion, D.E., Embree, G.F., Page, W.R., Morgan, L.A., Smith, R.P., Hackett, W.R., and Rodgers, D.W., 1994, Geologic map of the Idaho National Engineering Laboratory and adjoining areas, eastern Idaho: U.S. Geological Survey Miscellaneous Investigations Map I-2330, scale 1:100,000.
- Kwicklis, E.M., Thamir, F., Healy, R.W., and Hampson, D., 1998, Numerical simulation of air- and water- flow experiments in a block of variably saturated, fractured tuff from Yucca Mountain, Nevada: U.S. Geological Survey Water-Resources Investigations Report 97-4274., 64 p.
- Laney, P.T., Minkin, S.C., Baca, R.G., McElroy, D.L., Hubbell, J.M., Hull, L.C., Russell, B.F., Stormberg, G.J., and Pittman, J.T., 1988, Annual Progress Report, FY-1987, Subsurface investigations program at the Radioactive Waste Management Complex of the Idaho National Engineering Laboratory: U.S. Department of Energy, INEL Report DOE/ID-10183, 153 p.
- Langmuir, D., 1997, *Aqueous Environmental Geochemistry: Upper Saddle River, NJ, Prentice Hall Inc*, 600 p.

- Langmuir, D., and Mahoney, J., 1984, Chemical equilibrium and kinetics of geochemical processes in ground water studies: Proceedings of the First Canadian/American Conference on Hydrogeology, practical applications of ground water geochemistry, Banff, Alberta, Canada, p. 69–95.
- Lappala, E.G., Healy, R.W., and Weeks, E.P., 1987, Documentation of computer program VS2D to solve the equations of fluid flow in variably saturated porous media: U.S. Geological Survey Water-Resources Investigations Report 83–4099, 184 p.
- Leenheer, J.A., and Bagby, J.C., 1982, Organic solutes in ground water at the Idaho National Engineering Laboratory: U.S. Geological Survey Water-Resources Investigation 82–15 (IDO–22061), 39 p.
- Liszewski, M.J., and Mann, L.J., 1993, Concentrations of 23 trace elements in ground water and surface water at and near the Idaho National Engineering Laboratory, Idaho, 1988–91: U.S. Geological Survey Open-File Report 93–126 (DOE/ID–22110), 44 p.
- Liszewski, M.J., Rosentreter, J.J., and Miller, K.E., 1997, Strontium distribution coefficients of surficial sediment samples at the Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Water-Resources Investigations Report 97–4044 (DOE/ID–22140), 33 p.
- Liszewski, M.J., Rosentreter, J.J., Miller, K.E., and Bartholomay, R.C., 2000, Chemical and physical factors affecting strontium distribution coefficients of surficial sediment samples at the Idaho National Engineering and Environmental Laboratory, Idaho: Environmental Geology, v.39, no. 3/4, p. 411–426.
- Liu, H.H., Doughty, C., and Bodvarson, G.S., 1998, An active fracture model for unsaturated flow and transport in fractured rocks: Water Resource Research, v. 34, no. 10, p. 2,633–2,646.
- Lockheed Martin Idaho Technologies Co., 1995, WAG-7 comprehensive RI/BRA model calibration data—June 1995 report, [variously paged].
- Loehr, C.A., Einerson, J.J., and Jorgensen, D.K., 1993, SDA core analysis summary, 1971–89: INEL report ER–WAG7–36 (rev. 1), 146 p.
- Luo, S., Ku, T., Roback, R., Murrell, M., and McLing, T., 1998, Assessing in situ radionuclide transport based on uranium-series disequilibria in groundwater: EOS Transactions, American Geophysical Union, v. 79(45), Fall Meeting Supplement, H32F–06, p. F354.
- Luxmoore, R.J., 1981, Micro-, meso-, and macroporosity of soil: Soil Science Society American Journal, v. 45, no. 3, p. 671–672.
- Ma, L., and Selim, H.M., 1997, Evaluation of nonequilibrium models for predicting atrazine transport in soils: Soil Science Society American Journal, v. 6, p. 1,299–1,307.
- Ma, L., and Selim, H.M., 1996, Solute transport in soils under conditions of variable flow velocities: Water Resources Research, v. 32, no. 11, p. 3,277–3,283.
- Magnuson, S.O., 1995, Inverse modeling for field-scale hydrologic and transport parameters of fractured basalt, INEL–95/0637, Idaho National Engineering Laboratory: Lockheed Idaho Technologies Company, Idaho Falls, Idaho, 41 p.
- Magnuson, S.O., McElroy, D.L., 1993, Estimation of infiltration from in situ moisture content and representative moisture characteristics curves for the 30', 110', and 240' interbeds: Engineering Design File, EDF-RWM-93-001, 17 p.
- Magnuson, S.O., and Sondrup, A.J., 1998, Development, calibration, and predictive results of a simulator for subsurface pathway fate and transport of aqueous- and gaseous-phase contaminants in the Subsurface Disposal Area at the Idaho National Engineering and Environmental Laboratory, INEEL/EXT–97–00609, Idaho National Engineering Laboratory, Lockheed Martin Idaho Technologies Company, Idaho Falls, Idaho, 222 p.
- Maheras, S.J., Rood, A.S., Magnuson, S.O., Sussman, M.E., and Bhatt, R.N., 1994, Radioactive Waste Management Complex low-level waste radiological performance assessment: EG&G Idaho, Inc., EGG–WM–8773, 308 p.
- Mann, L.J., 1986, Hydraulic properties of rock units and chemical quality of water for INEL-1—a 10,365-foot deep test hole drilled at the Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Water-Resources Investigations Report 86–4020 (IDO–22070), 23 p.
- Mann, L.J., and Knobel, L.L., 1988, Concentrations of nine trace metals in ground water at the Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Open-File Report 88–332 (DOE/ID–22075), 17 p.
- Markham, O.D., 1978, Activation and fission products in the environment near the Idaho National Engineering Laboratory Radioactive Waste Management Complex: U.S. Department of Energy, IDO–12095, 19 p.
- Martian, P., 1995, UNSAT-H infiltration model calibration at the Subsurface Disposal Area, Idaho National Engineering Laboratory, Lockheed Martin Idaho Technologies Company Report INEL–95/0596, 38 p.
- McCarthy, J.F., and Degueudre, C., 1993, Sampling and characterization of colloids and particles in groundwater for studying their role in contaminant transport: Environmental Particles, v. 2, p. 247–315.
- McCarthy, J.F., and Zachara, J.M., 1989, Subsurface transport of contaminants: Environmental Science and Technology, v. 23, no. 5, p. 496–502.
- McCarthy, J.F., Czerwinski, K.R., Sanford, W.E., Jardine, P.M., and Marsh, J.D., 1998a, Mobilization of transuranic radionuclides from disposal trenches by natural organic matter: Journal of Contaminant Hydrology, v. 30, p. 49–77.
- McCarthy, J.F., Sanford, W.E., and Stafford, P.L., 1998b, Lanthanide field tracers demonstrate enhanced transport of transuranic radionuclides by natural organic matter: Environmental Science and Technology, v. 32, p. 3,901–3,906.

ref-8 Review of the transport of selected radionuclides in the Interim Risk Assessment

- McCarthy, J.M., and McElroy, D.L., 1995, SDA hydraulic characterization data compilation—surficial sediments and interbeds: Lockheed Martin Idaho Technologies Company, Engineering Design File ER-WAG7-71, INEL-95/130, 108 p.
- McCarthy, J.M., Arnett, R.C., Neupauer, R.M., Rohe, M.J., and Smith, C., 1995, Development of a regional groundwater flow model for the area of the Idaho National Engineering Laboratory, Eastern Snake River Plain Aquifer: Lockheed Martin Idaho Technologies Company, INEL-95/0169, rev 1, 208 p.
- McDowell-Boyer, L.M., Hunt, J.R., and Sitar, N., 1986, Particle transport through porous media: *Water Resources Research*, v. 22, no. 13, p. 1,901-1,921.
- McElroy, D.L., Rawson, S.A., Hubbell, J.M., Minkin, S.C., Baca, R.G., Vigil, M.J., Bonzon, C.J., Landon, J.L., Laney, P.T., Pittman, J.R., Anderson, S.R., and Davis, L.C., 1989, Site characterization program at the Radioactive Waste Management Complex of the Idaho National Engineering Laboratory: Annual Progress Report, FY-1988 (draft), EG&G Idaho, Inc., 53 p.
- McKinley, J.P., Zachara, J.M., Smith, S.C., and Turner, G.D., 1995, The influence of uranyl hydrolysis and multiple site-binding reactions on adsorption of U(VI) to montmorillonite., *Clays Clay Miner.*, v. 43, p. 1,299-1,307.
- McKinley, I.G., and Alexander, W.R., 1993, Assessment of radionuclide retardation—Uses and abuses of natural analogue studies: *Journal of Contaminant Hydrology*, v. 13, p. 249-259.
- Means, J.L., Crerar, D.A., and Duguid, J.O., 1978a, Migration of radioactive wastes—Radionuclide mobilization by complexing agents: *Science*, v. 200, p. 1,477-1,481.
- Means, J.L., Crerar, D.A., Borcsik, M.P., and Duguid, J.O., 1978b, Adsorption of Co and selected actinides by Mn and Fe oxides in soils and sediments: *Geochimica Acta*, v. 42, p. 1,763-1,773.
- Meyer, R.E., Arnold, W.D., Case, F., Shiao, S.Y., and Palmer, D.A., 1983, Valence effects on adsorption: U.S. Nuclear Regulatory Agency NUREG/CR-2863, ORNL-5905, 24 p.
- Meyer, R.E., Arnold, W.D., Kelmers, A.D., Kessler, J.H., Clark, R.J., Johnson, J., Young, G.C., Case, F.I., and Westmoreland, C.G., 1985, Technetium and neptunium reactions in basalt/groundwater systems: Proceedings of the Materials Research Society Symposia on the Scientific Basis for Nuclear Waste Management VIII, Boston, Mass., 1985, p. 333-342.
- Miller, D.E., and Gardner, W.R., 1962, Water infiltration into stratified soil: *Soil Science Society of American Proceedings*, v. 26, p. 115-119.
- Miller, E.E., and Miller, R.D., 1956, Physical theory for capillary flow phenomena: *Journal of Applied Physics*: v. 27, p. 324-332.
- Milton, G.M., and Brown, R.M., 1987, Adsorption of uranium from groundwater by common fracture secondary minerals: *Canadian Journal of Earth Science*, v. 24, p. 1,321-1,328.
- Montazer, P., and Wilson, W. E., 1984, Conceptual hydrologic model of flow in the unsaturated zone, Yucca Mountain, Nevada: U.S. Geological Survey Water-Resources Investigation Report 84-4345, 55 p.
- Morse, J.W., and Choppin, G.R., 1991, The chemistry of transuranic elements in natural waters: *Reviews in Aquatic Sciences*, v. 4, p. 1-22.
- Morse, L.H., and McCurry, Michael, 1997, Possible correlations between basalt alteration and the effective base of the Snake River Plain aquifer at the INEEL: Symposium on engineering geology and geotechnical engineering, 32d, Boise, Idaho, March 26-28, 1997, Proceedings, p. 1-13.
- Moulin, V., Labonne, N., and Theyssier, M., 1991, Retention properties of silica colloids for actinides: *Migration 1991, Abstracts*, v. 77.
- Moulin, V., Robouch, P., Vitorge, P., Allard, B., 1988, Environmental Behaviour of Americium(III) in Natural Waters. *Radiochim. Acta*. v., 44/45, no. 1, p. 33-37.
- Moulin, V.M., Moulin, C.M., and Dran, J.C., 1996, Role of humic substances and colloids in the behavior of radiotoxic elements in relation to nuclear waste disposal—confinement or enhancement of migration, in Gaffney, J.S., Marley, N.A., and Clark, S.B., eds., *Humic and Fulvic Acids—Isolation, Structure and Environmental Role*: American Chemical Society, Washington D.C., American Chemical Society, ACS Symposium Series 651, chap. 16, p. 259-271.
- Mualem, Y., 1976, A new model for predicting the hydraulic conductivity of unsaturated porous media: *Water Resources Research*, v. 12, p. 593-622.
- Nace, R.L., Deutsch, Morris, and Voegeli, P.T., 1956, Geography, geology, and water resources of the National Reactor Testing Station, Idaho, part 2, geography and geology: U.S. Atomic Energy Commission Publication IDO-22033, 225 p.
- Nakayama, S., Arimoto, H., Yamada, N., Moriyama, H., and Higashi, K., 1988, Column experiments on migration behavior of neptunium (V): *Radiochimica Acta*, v. 44/45, p. 179-188.
- Nash, K.L., Cleveland, J.M., and Rees, T.F., 1988, Speciation patterns of actinides in natural water: A laboratory investigation: *Journal of Environmental Radioactivity*, v. 7, p. 131-157.
- Nelson, D.M., and Orlandini, K.A., 1986, The role of natural dissolved organic compounds in determining the concentrations of americium in natural waters, in Bulman, R.A., and Cooper, J.R., eds., *Speciation of fission and activation products in the environment*: Elsevier Applied Science Publishers, p. 262-268.
- Nelson, D.M., Penrose, W.R., Karttunen, J.O., and Mehlhaff, P., 1985, Effects of dissolved organic carbon on the adsorption properties of plutonium in natural waters: *Environmental Sciences Technology*, v. 19, no. 2, p. 127-131.
- Neuman, S.P., 1990, Universal scaling of hydraulic conductivities and dispersivities in geologic media: *Water Resources Research*, v. 26, no. 8, p. 1,749-1,758.

- Newman, M.E., Porro, I., Scott, R., Dunnivant, F.M., Goff, R.W., Blevins, M.D., Ince, S.M., Leyba, J.D., DeVol, T.A., Elzerman, A.W., and Fjeld, R.A., 1995, Evaluation of the mobility of Am, Cs, Co, Pu, Sr, and U through INEL basalt and interbed materials: Summary report of the INEL/Clemson University laboratory studies, ER-WAG7-82, INEL-95/282, [variously paged].
- Nicholl, M.J., Glass, R.J., and Wheatcraft, S.W., 1994, Gravity-driven infiltration instability in initially dry nonhorizontal fractures: *Water Resource Research*, v. 30, no. 6, p. 2,533-2,546.
- Nimmo, J.R., 1991, Comment on the treatment of residual water content, *in* Luckner, L. and others, A consistent set of parametric models for the two-phase flow of immiscible fluids in the subsurface: *Water Resources Research*, v. 27, p. 661-662.
- Nimmo, J.R., Perkins, K.S., Rose, P.A., Rousseau, J.P., Orr, B.R., Twining, B.V., and Anderson, S.R., 2002, Km-scale rapid transport of naphthalene sulfonate tracer in the unsaturated zone at the Idaho National Engineering and Environmental Laboratory: *Vadose Zone Journal*, v. 1, no. 1, p. 89-101.
- Nimmo, J.R., Shakofsky, S.M., Kaminsky, J.F., and Lords, G.S., 1999, Laboratory and field hydrologic characterization of the shallow subsurface at an Idaho National Engineering and Environmental Laboratory waste-disposal site: U.S. Geological Survey Water-Resources Investigations Report 99-4263, 31 p.
- Nishita, H., Wallace, A., Romney, E.M., and Schulz, R.K., 1979, Effect of soil type on the extractability of ^{237}Np , ^{239}Pu , ^{241}Am , and ^{244}Cm as a function of pH: U.S. Nuclear Regulatory Commission NUREG/Cr-0997, UCLA 12-1192, 32 p.
- Nishita, H., Wallace, A., Romney, E.M., and Kinnear, J., 1981, Relationship between the chemical extractability of several transuranic elements from soils and their uptake by wheat plants: *Soil Science*, v. 132, p. 60-65.
- Nitao, J., and Buscheck, T., 1991, Infiltration of a liquid front in an unsaturated, fractured porous medium: *Water Resources Research*, v. 27, no. 8, p. 2,099-2,112.
- Noshkin, V.E., Wong, K.M., Marsh, K., Eagle, R., Holladay, G., and Buddemeier, R.W., 1976, Plutonium radionuclides in the groundwaters at Enewetak Atoll: Proceedings of the Symposium on Transuranium Nuclides in the Environment, San Francisco, Calif., 17-21 November 1975, p. 517-543.
- Nuttall, H.E., Jain, R., and Fertelli, Y., 1991, Radiocolloid transport in saturated and unsaturated fractures: Proceedings of the 2nd Annual International Conference on High Level Radioactive Waste Management, Las Vegas, Nev., 28 April, p. 189-196.
- Nyhan, J.W., Drennon, B.J., Abeele, W.V., Wheeler, M.L., Purtymun, W.D., Trujillo, G., Herrera, W.J., and Booth, J.W., 1985, Distribution of plutonium and americium beneath a 33-yr-old liquid waste disposal site: *Journal of Environmental Quality*, v. 14, no 4, p. 501-508.
- Olmsted, F.H., 1962, Chemical and physical character of ground water in the National Reactor Testing Station, Idaho: U.S. Atomic Energy Commission Publication IDO-22043, 81 p.
- Or, Dani, 1996, Wetting-induced soil structural changes the theory of liquid phase sintering: *Water Resources Research*, v. 32, no. 10, p. 3,041-3,049.
- Pabalan, R.T., and Turner, D.R., 1997, Uranium (6+) sorption on montmorillonite: Experimental and surface complexation modeling study: *Aquatic Geochemistry*, v. 2, p. 203-226.
- Pabalan, R.T., Turner, D.R., Bertetti, F.P., and Prikryl, J.D., 1998, Uranium VI sorption onto selected mineral surfaces, *in* Jenne, E.A., ed., Adsorption of Metals by Geomedia: Academic Press, p. 99-130.
- Pace, M.N., Rosentreter, J.J., and Bartholomay, R.C., 1999, Strontium distribution coefficients of selected core samples from the Idaho National Engineering and Environmental Laboratory, Idaho: U.S. Geological Survey Water-Resources Investigations Report 99-4145, 55 p.
- Parkhurst, D., and Appelo, A., 1999, User's guide to PHREEQC (Version 2) - A computer program for speciation, reaction-path, 1-D transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312 p.
- Parlange, J.Y., and Hillel, D.E., 1976, Theoretical analysis of wetting front instability in soils: *Soil Science*, v. 122, p. 236-239.
- Payne, T.E., Edis, R., and Seo, T., 1992, Radionuclide transport by groundwater colloids at the Koongarra uranium deposit: Proceedings of Material Resource Society Symposium, v. 257, p. 481-488.
- Penrose, W.R., Polzer, W.L., Essington, E.H., Nelson, D.M., and Orlandini, K.A., 1990, Mobility of plutonium and americium through a shallow aquifer in a semiarid region: *Environmental Science Technology*, v. 24, no. 2, p. 228-234.
- Persoff, P., and Pruess, R.J., 1995, Two-phase flow visualization and relative permeability measurement in natural rough-walled rock fractures: *Water Resources Research*, v. 31, no. 5, p. 1,171-1,186.
- Philip, J.R., and Forrester, R.I., 1975, Steady infiltration from buried, surface, and perched point and line sources in heterogeneous soils, II, flow details and discussion: *Soil Science Society of America Proceedings*, v. 39, no. 3, p. 408-414.
- Phillips, F., 1994, Environmental tracers for water movement in desert soils of the American Southwest: *Soil Science Society of America Journal*, v. 58, p. 15-24.
- Pittman, J.R., Jensen, R.G., and Fischer, P.R., 1988, Hydraulic conditions at the Idaho National Engineering Laboratory, 1982 to 1985: U.S. Geological Survey Water-Resources Investigations Report 89-4003 (DOE/ID-22078), 73 p.
- Pruess, K., 1998, On water seepage and fast preferential flow in heterogeneous, unsaturated rock fractures: *Journal of Contaminant Hydrology*, v. 30, p. 333-362.
- Raats, P.A.C., 1973, Steady upward and downward flows in a class of unsaturated soils: *Soil Science*, v. 115, p. 409-413.

ref-10 Review of the transport of selected radionuclides in the Interim Risk Assessment

- Ramsay, J.D.F., 1988, The role of colloids in the release of radionuclides from nuclear waste: *Radiochimica Acta*, v. 44/45, p. 165–170.
- Rancon, D., 1986, Influence of concentration distributions in solid medium on the assessment of radioelement distribution between the liquid and solid phases, *in* Sibley, T.H., and Myttenaere, C., eds., *Application of distribution coefficients to radiological assessment models*: Elsevier Applied Science Publishers, p. 64–71.
- Rathburn, S.L., 1993, Pleistocene cataclysmic flooding along the Big Lost River, east-central Idaho: *Geomorphology*, v. 8, p. 305–319.
- Rawson, S.A., and Hubbell, J.M., 1989, Geochemical controls on the composition of soil pore waters beneath a mixed waste disposal site in the unsaturated zone, *in* FOCUS'89, Nuclear waste isolation in the unsaturated zone: American Nuclear Society, Las Vegas, Nev., March 1989, Proceedings, p. 241–247.
- Rawson, S.A., Walton, J.C., and Baca, R.G., 1991, Migration of actinides from a transuranic waste disposal site in the vadose zone: *Radiochimica Acta*, v. 53, p. 477–486.
- Reardon, E.J., 1981, Kds - Can they be used to describe reversible ion sorption reaction in contaminant migration?: *Ground Water*, v. 19, no. 3, p. 279–286.
- Reed, M.F., and Bartholomay, R.C., 1994, Mineralogy of selected sedimentary interbeds at or near the Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Open-File Report 94–374 (DOE/ID–22116), 19 p.
- Reed, M.F., Bartholomay, R.C., and Hughes, S.S., 1997, Geochemistry and stratigraphic correlation of basalt lavas beneath the Idaho Chemical Processing Plant, Idaho National Engineering Laboratory: *Environmental Geology*, v. 30, p. 108–118.
- Reedy, O.C., Jardine, P.M., Wilson, G.V., and Selim, H.M., 1996, Quantifying the diffusive mass transfer of nonreactive solutes in columns of fractured saprolite using flow interruption: *Soil Science Society of America Journal*, v. 60, p. 1,376–1,384.
- Rees, T.F., and Cleveland, J.M., 1982, Characterization of plutonium in waters at Maxey Flats, Kentucky, and near the Idaho Chemical Processing Plant, Idaho: *in* Environmental migration of long-lived radionuclides: International Atomic Energy Agency, IAEA–SM–257/66, p. 41–52
- Reitsma, S., and Kueper, B.H., 1994, Colloid transport in unsaturated porous media: *Water Resources Research*, v. 30, no. 4, p. 857–864.
- Relyea, J.F., 1982, Theoretical and experimental consideration for the use of the column method for determining retardation factors: *Radioactive Waste Management and the Nuclear Fuel Cycle*, v. 3, p. 151–166.
- Relyea, J.F., Serne, R.J., and Rai, D., 1980, Methods for determining radionuclide retardation factors— Status Report: Pacific Northwest Laboratory, Richland, Wash., PNL–3349, UC–70, 65 p.
- Rhodes, D.W., 1957, Adsorption of plutonium by soil: *Soil Science*, v. 84, p. 465–471.
- Richards, L.A., 1931, Capillary conduction of liquids through porous mediums: *Physics*, v. 1, p. 318–333.
- Righetto, L., Bidoglio, G., Azimonti, G., and Bellebono, I.R., 1988, Surface interactions of actinides with alumina colloids, *Radiochimica Acta*, vol. 44/45, p. 73–75.
- Rightmire, C.T., 1984, Description and hydrogeologic implications of cored sedimentary material from the 1975 drilling program at the Radioactive Waste Management Complex, Idaho: U.S. Geological Survey Water-Resources Investigations Report 84–4071 (IDO–22067), 33 p.
- Rightmire, C.T., and Lewis, B.D., 1987a, Geologic data collected and analytical procedures used during a geochemical investigation of the unsaturated zone, Radioactive Waste Management Complex, Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Open-File Report 87–246 (DOE/ID–22072), 83 p.
- Rightmire, C.T., and Lewis, B.D., 1987b, Hydrogeology and geochemistry of the unsaturated zone, Radioactive Waste Management Complex, Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Water-Resources Investigations Report 87–4198 (DOE/ID–22073), 89 p.
- Rightmire, C.T., and Lewis, B.D., 1999, Influence of the geochemical environment on radionuclide migration in the unsaturated zone, Radioactive Waste Management Complex, Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Open-File Report (in press).
- Ritsema, C.J., and Dekker, L.W., 1994, How water moves in water repellent sandy soil, 2. Dynamics of fingered flow: *Water Resources Research*, v. 30, p. 2,519–2,531.
- Ritsema, C.J., Dekker, L.W., Nieber, J.L., and Steenhuis, T.S., 1998, Modeling and field evidence of finger formation and finger recurrence in a water repellent sandy soil: *Water Resources Research*, v. 34, no. 4, p. 555–567.
- Roback, R.C., Murrell, M.T., Nunn, A., Luo, S., Ku, T.L., and McLing, T., 1998, Uranium and thorium series isotopes in fresh groundwater at the INEEL: EOS Transactions, American Geophysical Union, v. 79(45), Fall Meeting Supplement, p. F343.
- Robertson, J.B., 1974, Digital modeling of radioactive and chemical waste transport in the Snake River Plain aquifer at the National Reactor Testing Station, Idaho: U.S. Geological Survey Open-File Report (IDO–22054), 41 p.
- Robertson, J.B., Schoen, R., and Barraclough, J.T., 1974, The influence of liquid waste disposal on the geochemistry of water at the National Reactor Testing Station, Idaho: U.S. Geological Survey Open- File Report, IDO–22053, 231 p.
- Rodgers, D.R., Hackett, W.R., and Ore, H.T., 1990, Extension of the Yellowstone Plateau, eastern Snake River Plain, and Owyhee plateau: *Geology*, v. 18, p. 1,138–1,141.
- Rodriguez, R.R., Schafer, A.L., McCarthy, J.M., Martian, P., Burns, D.E., Raunig, D.E., Burch, N.A., and VanHorn, R.L., 1997, Comprehensive RI/FS for the ICPP OU 3–13 at the INEEL: RI/BRA Report (Draft Final), DOE/ID–10534, rev. 0, 3,617 p.
- Rosentreter, J.J., Quarder, H.S., Smith, R.W., and McLing, T., 1998, Uranium sorption onto natural sands as a function of

- sediment characteristics and solution pH, *in* Jenne, E.A., ed., Adsorption of metals: Geomedia: Academic Press, p. 181–192.
- Routson, R.C., Jansen, G., and Robinson, A.V., 1977, ²⁴¹Am, ²³⁷Np, and ⁹⁹Tc sorption on two United States subsoils from differing weathering intensity areas: *Health Physics*, v. 33, p. 311–317.
- Russell, Bertrand, 1948, *Human knowledge, its scope and limits*: New York, Simon and Schuster, 524 p.
- Russo, D., Zaidel, J., and Laufer, A., 1998, Numerical analysis of flow and transport in a three-dimensional partially saturated heterogeneous soil: *Water Resources Research*, v. 34, no. 6, p. 1,451–1,468.
- Salter, P.F., Ames, L.L., and McGarrah, J.E., 1981b, The sorption behavior of selected radionuclides on Columbia River basalts: Pacific Northwest Laboratories RHO–BWI–LD–48, [variously paged].
- Salter, P.F., Ames, L.L., and McGarrah, J.E., 1981a, Sorption of selected radionuclides on secondary minerals associated with the Columbia River basalts: Pacific Northwest Laboratories RHO–BWI–LD–43, 40 p.
- Salvucci, 1996, Series solution for Richards equation under concentration boundary conditions and uniform initial condition: *Water Resources Research*, v. 32, no. 8, p. 2,401–2,407.
- Scanlon, B., Tyler, S.W., and Wierenga, P.J., 1997, Hydrologic issues in arid, unsaturated systems and implications for contaminant transport: *Reviews of Geophysics*, v. 35, p. 461–490.
- Seitz, M.G., Rickert, P.G., Fried, S.M., Friedman, A.M., and Steindler, M.J., 1979, Migratory properties of some nuclear waste elements in geologic media: *Nuclear Technology*, v. 44, p. 284–296.
- Seitz, M.G., Rickert, P.G., Fried, S.M., Friedman, A.M., and Steindler, M.J., 1978, Studies of nuclear-waste migration in geologic media: ANL–78–8, Argonne National Laboratories, Ill., 32 p.
- Selker, J.S., Parlange, J.Y., Steenhuis, T.S., Baker, R.S., and Hillel, D., 1991, Laboratory tests of a theory of fingering during infiltration into layered soils; comment and reply: *Soil Science Society of America Journal*, 55 (3), p. 896–897.
- Selker, J.S., Parlange, J.Y., and Steenhuis, T.S., 1992a, Fingering flow in two dimensions—Measurement of matric potential: *Water Resources Research*, v. 28, no. 9, p. 2,523–2,528.
- Selker, J.S., Parlange, J.Y., and Steenhuis, T.S., 1992b, Laboratory tests of a theory of fingering during infiltration into layered soils—comment and reply: *Soil Science Society of America Journal*, v. 55, no. 3, p. 896–897.
- Serne, R.J., and Relyea, J.F., 1981, The status of radionuclide sorption-desorption studies performed by the WRIT program, *in* Hofmann, P.L., and Breslin, J.J., eds., *The technology of high level nuclear waste disposal* (v. 1): U.S. Department of Energy, DOE/TIC–4621, p. 203–254.
- Shakofsky, S.M., 1993, Changes in the hydraulic properties of a soil caused by construction of a waste trench at a radioactive waste disposal site: M.S. thesis, San Jose State University, 53 p.
- Shakofsky, S.M., 1995, Changes in soil hydraulic properties caused by construction of a simulated waste trench at the Idaho National Engineering Laboratory Idaho: U.S. Geological Survey Water-Resources Investigations Report 95–4058 (DOE/ID–22121), 26 p.
- Shakofsky, S.M., and Nimmo, J.R., 1996, Unsaturated zone properties at a waste disposal site at the Idaho National Engineering Laboratory, *in* Morganwalp, D.W., and Aronson, D.A., eds., *U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting*, Colorado Springs, Colo., 1993: U.S. Geological Survey Water-Resources Investigations Report 94–4015, p. 949–953.
- Sheppard, J.C., Campbell, M.J., Cheng, T., and Kittrick, J.A., 1980b, Retention of radionuclides by mobile humic compounds and soil particles: *Environmental Science Technology*, v. 14, no. 11, p. 1,349–1,353.
- Sheppard, J.C., Campbell, M.J., Kittrick, J., and Cheng, T., 1980a, Investigation of the transport of actinide-bearing soil colloids in the soil-aquatic environment: U.S. Department of Energy, DOE/EV/73012–5, [variously paged].
- Sheppard, J.C., Campbell, M.J., Kittrick, J.A., and Hardt, T.L., 1979, Retention of neptunium, americium, and curium by diffusible soil particles: *Environmental Science Technology*, v. 13, no. 6, p. 680–684.
- Sheppard, J.C., and Kittrick, J.A., 1983, Factors influencing the transport of actinides in the groundwater environment: U.S. Department of Energy, DOE/EV/73012–3, 40 p.
- Sheppard, J.C., Kittrick, J.A., Campbell, M.J., and Hardt, T.L., 1977, Determination of distribution ratios and diffusion coefficients of neptunium, americium, and curium in soil-aquatic environments: Washington State University, Pullman, Wash., RLO–2221–T–12–3, 22 p.
- Sheppard, M.I., and Thibault, D.H., 1990, Default soil solid/liquid partition coefficients, K_{ds}, for four major soil types: *Health Physics*, v. 59, no. 4, p. 471–482.
- Sheppard, M.I., Thibault, D.H., and Mitchell, J.H., 1987, Element leaching and capillary rise in sandy soil cores—Experimental results: *Journal of Environmental Quality*, v. 16, no. 3, p. 273–284.
- Shook, G.M., 1995, Development of an environmental simulator from existing petroleum technology: Lockheed Martin Idaho Technologies Company INEL–94/0283, 30 p.
- Sill, C.W., 1987, Precipitation of actinides as fluorides or hydroxides for high-resolution alpha spectrometry: *Nuclear and Chemical Waste Management*, v. 7, p. 201–215.
- Sill, C.W., and Sill, D.S., 1989, Determination of actinides in nuclear wastes and reference materials for ores and mill tailings: *Waste Management*, v. 9, p. 219–229.
- Silva, R.J., Bidoglio, G., Rand, M.H., Robouch, P., Wanner, H., and Puigdomenech, I., 1995, *Chemical Thermodynamics of Americium*, Elsevier, Amsterdam, 392 p.

ref-12 Review of the transport of selected radionuclides in the Interim Risk Assessment

- Smith, P.A., and Degueudre, C., 1993, Colloid-facilitated transport of radionuclides through fractured media: *Journal of Contaminant Hydrology*, v. 13, p. 143–166.
- Smith, R.P., Jackson, S.M., and Hackett, W.R., 1996, Paleoseismology and seismic hazards evaluations in extensional volcanic terrains: *Journal of Geophysical Research*, v. 101, no. B3, p. 6,277–6,292.
- Soll, W., and Birdsell K., 1998, The influence of coatings and fills on flow in fractured, unsaturated tuff porous media systems: *Water Resources Research*, v. 34, no. 2, p. 193–202.
- Sposito, G., 1984, *The Surface Chemistry of Soils*: New York, NY, Oxford University Press, 234 p.
- Steenhuis, T.S., Parlange, J.Y., and Aburine, S.A., 1995, Preferential flow in structured and sandy soils—Consequences for modeling and monitoring, in Wilson, L.G., and others, eds., *Handbook of vadose zone characterization and monitoring*: Boca Raton, FL, Lewis, p. 61–77.
- Stephens, D.B., 1996, *Vadose zone hydrology*: Boca Raton, FL, Lewis, 347 p.
- Stockman, H.W., 1998, Long-term modeling of plutonium solubility at a desert disposal site, including CO₂ diffusion, cellulose decay, and chelation: *Journal of Soil Contamination*, v. 7, p. 615–647.
- Stothoff, S.A., 1997, Sensitivity of long-term bare soil infiltration simulations to hydraulic properties in an arid environment: *Water Resources Research*, v. 33, no. 4, p. 547–558.
- Stout, M.Z., and Nichols, J., 1977, Mineralogy and petrology of Quaternary lavas from the Snake River Plain, Idaho: *Canadian Journal of Earth Sciences*, v. 14, p. 2,140–2,156.
- Striegl, R.G., Prudic, D.E., Duval, J.S., Healy, R.W., Landa, E.R., Pollock, D.W., Thorstenson, D.C. and Weeks, E.P., 1996, Factors affecting tritium and ¹⁴C carbon distributions in the unsaturated zone near the low-level radioactive-waste burial site south of Beatty, Nevada: U.S. Geological Survey Open- File Report 96–110, 16 p.
- Stumm, W., and Morgan, J.J., 1981, *Aquatic chemistry*: John Wiley & Sons, New York, 780 p.
- Su, G.W., Geller, J.T., Pruess, K., and Wen, F., 1999, Experimental studies of water seepage and intermittent flow in unsaturated, rough-walled fractures: *Water Resources Research*, v. 35, no. 4, p. 1,019–1,037.
- Thibault, D.H., Sheppard, M.I., and Smith, P.A., 1990, A critical compilation and review of default soil solid/liquid partition coefficients, K_d, for use in environmental assessments: AECL–10125, Atomic Energy of Canada Limited, 115 p.
- Ticknor, K.V., and Ruegger, B., 1989, *A Guide to the NEA's Sorption DataBase, Version 2.0*, 19 p.
- Tokunaga, T.K., and Wan, J., 1997, Water film flow along fracture surfaces of porous rock: *Water Resources Research*, v. 33, no. 6, p. 1,287–1,295.
- Travis, B.J., and Nuttall, H.E., 1985, Analysis of colloidal transport, in Werne, L.O., ed., *Materials Research Society Symposium Proceedings: Scientific Basis for Nuclear Waste Management—IX*, Pittsburgh, Pa, MRS, p. 737–745.
- Triay, I.R., Furlano, A.C., Weaver, S.C., Chipera, S.J., and Bish, D.L., 1996, Comparison of neptunium sorption results using batch and column techniques: Los Alamos National Laboratory, LA–12958–MS, 30 p.
- Tripathi, V.S., 1983, *Uranium transport modelling: geochemical data and sub-models*, PhD. dissertation, Stanford University.
- Tsukamoto, M., Fujita, T., and Ohe, T., 1997, Surface complexation modeling for description of actinide sorption at the buffer materials/water interface: *Journal of Nuclear Materials*, v. 248, p. 333–337.
- Tucker, B.J., and Orr, B.R., 1998, Distribution of selected radiochemical and chemical constituents in water from perched ground water, Idaho National Engineering Laboratory, Idaho, 1989–91: U.S. Geological Survey Water-Resources Investigations Report 98–4028 (DOE/ID–22144), 62 p.
- Turner, D.R., 1995, A uniform approach to surface complexation modeling of radionuclide sorption: Center for Nuclear Waste Regulatory Analyses, San Antonio Texas, Nuclear Regulatory Commission Contract NRC–02–93–005, 118 p.
- Turner, D.R., and Sassman, S.A., 1996, Approaches to sorption modeling for high-level waste performance assessment: *Journal of Contaminant Hydrology*, v. 21, p. 311–332.
- Turner, D.R., Pabalan, R.T., and Bertetti, F.P., 1998, Neptunium (V) sorption on montmorillonite—An experimental and surface complexation modeling study: *Clay and Clay Minerals*, v. 46, no. 3, p. 256–269.
- Turner, J., 1999, A standards view from Capital Hill: *Standardization News*, v. 27, no. 5, p. 18–19.
- U.S. Department of Energy, 1998, Addendum to the work plan for the Operable Unit 7–13/14 Waste Area Group 7 Comprehensive Remedial Investigation/Feasibility Study: U.S. Department of Energy DOE/ID–10622, Draft rev. 2, [variously paged].
- U.S. Environmental Protection Agency, 1980, *Interim guidelines and specifications for preparing Quality Assurance Project Plans*: U.S. Environmental Protection Agency QAMS–005/80, [variously paged].
- U.S. Geological Survey, 1998, Significant issues to be resolved to support and defend the Interim Risk Assessment and additional work required to resolve those issues—Task 5, Independent technical review of the Interim Risk Assessment Radioactive Waste Management Complex WAG 7–13/14 Operable Unit: U.S. Geological Survey Letter Report, 19 p.
- van Genuchten, M.T., 1980, A closed-form equation for predicting the hydraulic conductivity of unsaturated soils: *Soil Science Society of America Journal*, v. 44, no. 5, p. 892–898.
- van Genuchten, M.T., and Wierenga, P.J., 1976, Mass transfer studies in sorbing porous media, I. Analytical solutions: *Soil Science Society of America Journal*, v. 40, p. 473–480.
- Vandegrift, G.F., Bowers, D.L., Gerding, T.J., Fried, S.M., and Wilbur, C.K., 1984, Interaction of groundwater and basalt fissure surfaces and its effect on the migration of actinides:

- American Chemical Society Symposium Series 246, Seattle, Wash., p. 229–247.
- Vandergraaf, T.T., Ticknor, K.V., and Melnyk, T.W., 1993, The selection of sorption database for the geosphere model in the Canadian Nuclear Fuel Waste Management Program: *Journal of Contaminant Hydrology*, v. 13, p. 327–345.
- Vaniman, D., Furlano, A., Chipera, S., Thompson, J., and Triay, I., 1996, Microautoradiography in studies of Pu (V) sorption by trace and fracture minerals in tuff: *Materials Research Society Symposium Proceedings*, v. 412, p. 639–646.
- Vilks, P., and Drew, D.J., 1986, The effect of colloids on actinide migration, p. 667–673.
- Vilks, P., Bachinski, D.B., and Vandergraaf, T.T., 1991, The role of particulates in radionuclide transport: *Proceedings 3rd International Symposium Advanced Nuclear Energy Research*, Mito City, Japan, 13–15 March, p. 394–401.
- Vilks, P., Caron, F., and Haas, M.K., 1998, Potential for the formation and migration of colloidal material from a near-surface waste disposal site: *Applied Geochemistry*, v. 13, p. 31–42.
- Vinsome, P.K.W., and Shook, G.M., 1993, Multi-purpose simulation: *Journal of Petroleum Science and Engineering*, v. 9, p. 29–38.
- Voegeli, P.T., and Deutsch, Morris, 1953, Geology, water supply, and waste disposal at sites 11 and 11A, burial ground D, and vicinity, National Reactor Testing Station, Idaho: U.S. Atomic Energy Commission Publication (IDO–22027), 42 p.
- Waite, T.D., Davis, J.A., Payne, T.E., Waychunas, G.A., and Xu, N., 1994, Uranium (VI) adsorption to ferrihydrite—Application of a surface complexation model: *Geochimica et Cosmochimica Acta*, v. 58, p. 5,465–5,478.
- Wang, Z., Feyen, J., van Genuchten, M.T., and Nielsen, D.R., 1998a, Air entrapment effects on infiltration rate and flow instability: *Water Resources Research*, v. 34, no. 2, p. 213–222.
- Wang, Z., Feyen, J., and Ritsema, C.J., 1998b, Susceptibility and predictability of conditions for preferential flow: *Water Resources Research*, v. 34, no. 9, p. 2,169–2,182.
- Wang, Z., Feyen, J., and Elrick, D.E., 1998c, Prediction of fingering in porous media: *Water Resources Research*, v. 34, no. 9, p. 2,183–2,190.
- Welhan, J.A., and Wylie, A., 1997, Stochastic modeling of hydraulic conductivity in the Snake River Plain aquifer—evaluation of lithologic controls at the core and borehole scales: *Symposium on Engineering Geology and Geotechnical Engineering*, 32d, Boise, Idaho, March 26–28, 1997, *Proceedings*, p. 93–107.
- Whitehead, R.L., 1992, Geohydrologic framework of the Snake River Plain regional aquifer system, Idaho and eastern Oregon: U.S. Geological Survey Professional Paper 1408–B, 32 p., 6 pls.
- Wolery, T.J., 1992a, EQ3/6, A software package for geochemical modeling of aqueous systems: Package overview and installation guide (Version 7.0): UCRL–MA–110662–PT–I, Lawrence Livermore National Laboratory, Livermore, Calif.
- Wolery, T.J., 1992b, EQ3NR, A computer program for geochemical aqueous speciation-solubility calculations—Theoretical manual, user's guide and related documentation (Version 7.0): UCRL–MA–110662–PT–III, Lawrence Livermore National Laboratory, Livermore, Calif.
- Wolery, T.J., and Daveler, S.A., 1992, EQ6, A computer program for reaction path modeling of aqueous geochemical systems: Theoretical manual, user's guide and related documentation (Version 7.0): UCRL–MA–110662–PT–IV, Lawrence Livermore National Laboratory, Livermore, Calif.
- Wood, T.R., and Norrell, G.T., 1996, Integrated large-scale aquifer pumping and infiltration tests, groundwater pathways: Summary report, INEL–96/0256, p. 5-18 to 5-48.
- Wood, W.W., and Low, W.H., 1986, Aqueous geochemistry and diagenesis in the Eastern Snake River Plain aquifer system, Idaho: *Geologic Society of America Bulletin*, v. 97, p. 1,456–1,466.
- Wylie, A.H., 1996, Pumping Test of Pit 9 Production Wells: Engineering Design File INEL–96/171, Lockheed Martin Idaho Technologies Company.
- Wylie, A.H., and Hubbell, J.M., 1994, Aquifer testing of wells M1S, M3S, M4D, M6S, M7S, and M10S at the Radioactive Waste Management Complex: EG&G Idaho, Inc., Engineering Design File 14ER–WAG7–26, rev. 1, 127 p.
- Wylie, A.H., McCarthy, J.M., Neher, E., and Higgs, B.D., 1995, Large-scale aquifer pumping test results: Lockheed Martin Idaho Technology, Engineering Design File Report ER–WAG7–56, 138 p.
- Yao, T., and Hendrickx, J.M.H., 1996, Stability of wetting fronts in dry homogeneous soils under low infiltration rates: *Soil Science Society of America Journal*, v. 60, no. 1, p. 20–28.
- Zachara, J.M., Gassman, P.L., Smith, S.C., and Taylor, D., 1995, Oxidation and adsorption of Co (II) EDTA2-complexes in subsurface materials with iron and manganese oxide grain coatings: *Geochimica et Cosmochimica Acta*, v. 59, p. 4,449–4,463.

Appendix

SIGNIFICANT ISSUES TO BE RESOLVED TO SUPPORT
AND DEFEND THE INTERIM RISK ASSESSMENT
AND ADDITIONAL WORK REQUIRED TO
RESOLVE THOSE ISSUES

Prepared by the U.S. Geological Survey

In fulfillment of Task 5 requirements of the

INDEPENDENT TECHNICAL REVIEW
OF THE INTERIM RISK ASSESSMENT
RADIOACTIVE WASTE MANAGEMENT COMPLEX
WAG 7-13/14 OPERABLE UNITS

October 15, 1998

CONTENTS

I. Introduction 3

 Background 3

 Purpose and scope 3

II. Review of additional work from the Addendum that is related to hydrologic transport

 of contaminants 3

 Perched-water and soil-moisture monitoring data 4

 Installation of instruments to collect leachate, vapor concentrations, and moisture
 measurements and installation of lysimeters near soil vaults 4

 Installation of upgradient aquifer-monitoring wells 5

 Actinide migration mechanisms 5

III. Significant issues not identified or emphasized in the Addendum 5

 Hydraulic and geochemical characterization of the sedimentary interbeds 5

 Laboratory performance and data quality objectives 7

IV. Recommendations for additional work to resolve significant issues 7

 Corehole drilling and testing program 7

 Scope 8

 Objectives 9

 Laboratory technical review and data quality objectives 9

V. Summary 10

 References cited 10

SIGNIFICANT ISSUES TO BE RESOLVED TO SUPPORT AND DEFEND THE IRA, AND ADDITIONAL WORK REQUIRED TO RESOLVE THOSE ISSUES, RWMC WAG 7-13/14 OPERABLE UNIT

By Joseph P. Rousseau, Brennon R. Orr, and LeRoy L. Knobel

I. Introduction

Background. The IRA and Contaminant Screening for the WAG-7 RI/FS (Becker and others, 1998) was prepared for the DOE by LMITCO in support of the WAG-7 comprehensive RI/FS. The purpose of the IRA was to preserve a formal record of work completed in support of the RI/FS. The draft Addendum to the Work Plan for the WAG-7-13/14 Operable Unit Comprehensive RI/FS (DOE, 1998) defined revised strategies and additional requirements for conducting the WAG-7 comprehensive RI/FS. These two reports and supporting documents will be used in completion of the draft ROD for remediation of WAG-7 by December 2002. The DOE, in order to prepare for ROD negotiations with the EPA and the State of Idaho, requested that the USGS conduct an independent technical review of the IRA, the Addendum, and associated documents.

Purpose and Scope. Modification A005 to Contract Number DE-A107-97ID13556 between the DOE and USGS, dated July 16, 1998, established additional work to be accomplished by the USGS in support of the independent technical review, as requested by the DOE. Five tasks were identified in the proposal for work. Task 1 provides a review of radionuclide data supporting the IRA, Task 2 discusses radionuclide transport processes pertinent to the Subsurface Disposal Area (SDA), Task 3 addresses K_{ds} and their application to transport analysis, and Task 4 discusses transport model analysis. These tasks, to be completed by July 15, 1999, will provide a detailed review of primary and secondary documents associated with the IRA.

Task 5 (deliverable report to be provided to the DOE by October 15, 1998) of this technical review is intended to provide timely interim guidance to several questions. First, what are the most significant issues that need to be resolved to support and defend the IRA? Second, what additional work is immediately required to resolve those issues? This interim guidance is offered to provide sufficient lead time to resolve those issues within the timeframe of the draft ROD (2002).

As part of Task 5, preliminary reviews were conducted of the IRA (Becker and others, 1998), results of the LSIT (Wood and Norrell, 1996), K_{ds} and contaminant solubilities for the WAG-7 Baseline Risk Assessment (Dicke, 1997), and the flow and transport model (Magnuson and Sondrup, 1998). Additionally, planned work elements were evaluated that were identified in the Addendum to the Work Plan (DOE/ID, March 1998). This review focused primarily on data needs rather than on analytical approaches.

II. Review of Additional Work from the Addendum that is Related to Hydrologic Transport of Contaminants

Data quality objectives (DQOs) listed in the Addendum (DOE, 1998, table 3-3) evaluated activities needed to satisfy 1996 workplan data gaps. The USGS evaluated only those DQOs that pertain to hydrologic transport of contaminants as highlighted in italics. Data gaps identified in the Addendum are summarized after each DQO.

Identify distributions of interbed soil contaminants in the unsaturated zone to help determine whether contaminants in the aquifer are derived from the SDA or an upgradient source. This DQO was to be accomplished by analyzing for contaminants in spatially distributed samples from the A-B, B-C, and C-D interbeds. This DQO was not satisfied because interbed sample results were inadequate. Pu geochemistry experiments were inconclusive and additional experiments have been defined. No determination was made about spurious detections of actinides in the C-D interbed. Perched-water monitoring continues to evaluate migration. Additional interbed sampling is not planned.

Identify distributions of water contaminants in the unsaturated zone to help determine whether contaminants in the aquifer are derived from the SDA or an upgradient source. Monitoring work is in progress. The contractor is planning to expand the monitoring network with lysimeters near soil vaults and in waste zones.

Identify contaminant concentrations in the aquifer to help determine whether contaminants in the aquifer are derived from the SDA or an upgradient source. Determination of contaminant source using analyses of ^3H and NO_3 plumes proved to be inconclusive. Data were inadequate to calibrate IRA models or to differentiate upgradient sources of contaminants.

Data gaps that warrant further data collection and research were identified from analysis of these DQOs. Planned work elements to meet the need for additional data were summarized in table 3-4 of the Addendum. Work elements listed in table 3-4 that pertain to hydrologic transport of contaminants and our assessment of the adequacy of these elements to fill data gaps are summarized as follows.

Perched-water and soil-moisture monitoring data (sections 4.3.7, and 4.1.4). These data focused primarily on the surficial sediments and called for quarterly monitoring of unsaturated-zone soil water and perched water over an extended time.

Continued perched-water monitoring is appropriate, as are additional experiments to define the presence of actinides in the B-C interbed. The emphasis in the Addendum appears to be on perched water within the surficial sediments. This work certainly is important, provides a better understanding of the contaminant source term, and should be continued.

In addition, deeper interbed sampling and installation of appropriately designed lysimeters are needed, not only to differentiate contaminant sources, but also to assess the role of the interbeds in the transport of contaminants. Historically, much of the deeper sampling within the boundary of the SDA has taken place from well USGS 92. The limited areal sampling is not adequate to describe the distribution of radioactive and organic chemical contaminants in water in the vadose zone, both inside and outside the SDA. Additional sampling points may become available if a corehole-drilling program is undertaken as proposed in section IV of this report. Coreholes constructed as part of the proposed drilling program could be instrumented to expand the present monitoring network.

Installation of instruments to collect leachate, vapor concentrations, and moisture measurements (section 4.3.8) and installation of lysimeters near soil vaults (section 4.3.9). Additional suction lysimeters with appropriate backfill material to collect water samples, tensiometers to monitor infiltration rates, and time-domain reflectometry waveguides to measure soil-moisture content will be installed in new shallow coreholes and drill holes.

This work again is focused solely on the surficial sediments and will provide valuable information concerning contaminant transport. However, the limited capability to collect water samples from underlying interbeds or to measure moisture content and infiltration within interbeds precludes assessment of the role of these interbeds in vertical or lateral transport of contaminants. Additional sampling points may become available if a corehole drilling program

is undertaken as proposed in section IV of this report. Coreholes constructed as part of this proposed program could be instrumented to assist in determining the extent of contaminant migration in the unsaturated zone.

Installation of upgradient aquifer-monitoring wells (sections 4.3.10, 4.4.1). Installation of five additional upgradient, aquifer-monitoring wells was planned to identify contaminant concentrations in the aquifer, to delineate the upgradient areal extent of the CCl_4 plume in the unsaturated zone, to define background water chemistry by long-term monitoring, to provide data for calibration of fate and transport models, and to differentiate between contaminant sources.

Inconclusive analyses of ^3H and NO_3 plumes clearly illustrated the need for additional upgradient wells completed in the SRP aquifer. Four of these wells have been constructed by LMITCO and have been included in the WAG-7 monitoring programs. A fifth well is planned by the USGS in FY 1999. These wells will provide valuable upgradient water-level and water-chemistry data. We strongly endorse the implementation of this work element. The process used to locate these wells was technically sound and was designed to provide the information identified by the data gap analysis. We encourage continued monitoring of these wells to provide information to better differentiate between contaminant sources.

Actinide migration mechanisms (section 4.4.5). Work elements include peer review of actinide K_d data by qualified experts, inventory of U and Pu species in samples sent to the INEEL, modeling of transport mechanisms, modeling of actinide speciation, column tests, replication of previous colloid transport work, experiments to determine adsorption of actinide complexes onto colloids, and confirmation of the effects of Pu oxidation states on transport.

The work elements identified in the Addendum to examine actinide migration mechanisms need to be accomplished. We believe that successful completion of these elements is dependent on detailed determination of bulk and clay lithology and mineralogy in the sedimentary interbeds underlying the SDA. Intact samples from proposed corehole drilling may provide additional opportunity to conduct K_d analyses that are more representative of the deeper interbeds.

III. Significant Issues Not Identified or Emphasized in the Addendum

Hydraulic and Geochemical Characterization of the Sedimentary Interbeds. We believe that the hydraulic and geochemical properties of the sedimentary interbeds are not adequately characterized to meet the needs of a comprehensive risk assessment for radionuclide migration. Only a limited number of samples were available from the A-B, B-C, and C-D interbeds to characterize the hydraulic and geochemical properties of these units. Investigators, involved in the development and calibration of a predictive simulator for the transport of contaminants in the subsurface at the SDA (Magnuson and Sondrup, 1998, p. 6-5), also have acknowledged the lack of adequate data. Considerable, and perhaps undue, reliance has been placed on a few measurements and qualitative observations to describe the hydrogeologic properties of all the sedimentary interbeds in the WAG-7 model domain, both within and outside the SDA. The extent and reliability of these data as reported by Magnuson and Sondrup (1998, p. 6-5) and McCarthy and McElroy (1995, table 3.2.1-3) are summarized as follows:

Surficial sediments – 350 samples from both disturbed and undisturbed locations: “...characterization is of high quality and shows that there is substantial spatial variability in hydraulic properties...” Vertical hydraulic conductivity varies over four orders of magnitude (McCarthy and McElroy, 1995, p. 3-13).

A-B interbed – 4 samples, 2 boreholes: “...available samples are not adequate to hydraulically characterize the A-B interbed.” “...A-B interbed was assigned the same hydraulic properties as the C-D interbed based on the similar lithology of the two interbeds.” Vertical hydraulic conductivity varies over three orders of magnitude.

B-C interbed – 6 samples, 5 boreholes: “...number of samples...not adequate to hydraulically characterize the B-C interbed.” “The samples that have been recovered are biased toward lower permeability because they are composed of finer-grained materials which are more easily recovered.” Vertical hydraulic conductivity varies over six orders of magnitude.

C-D interbed – 34 samples, 14 boreholes: “...characterization appears adequate for the C-D interbed.” “The C-D interbed generally contains more clay and loam leading to better sample recovery.” Vertical hydraulic conductivity varies over seven orders of magnitude.

Lower interbeds – no samples.

The lack of adequate hydraulic data for the sedimentary interbeds within the SDA is due in large part to difficulty in obtaining complete core samples from these loosely consolidated units. Geochemical and lithologic data for the sedimentary interbeds are inadequate for the same reason. Outside the SDA, borehole coverage is extremely limited as well, and definition of the hydraulic and geochemical properties and of the generalized stratigraphy of these units is practically nonexistent.

Within the immediate vicinity of the SDA, the composite thickness, elevations, and orientations of the individual interbeds are, for the most part, well defined. Minor exceptions may be present, particularly in areas of the SDA where borehole coverage is limited (Magnuson and Sondrup, 1998, p. 6-2). Outside the SDA, definition of the sedimentary interbed stratigraphy is based only on a few widely spaced boreholes, and implications on subsurface flow and transport modeling at the SDA are uncertain.

Understanding the role of the sedimentary interbeds in retarding the migration of radionuclides from the SDA to the SRP aquifer requires much more rigorous definition of the hydraulic and geochemical properties of these units than is currently available. The interbeds, at best, are imperfect hydrologic barriers. In general, rapid downward movement of water through the fractured basalts in the unsaturated zone is retarded at interbed boundaries or above sediment- or precipitate-filled fractures near the base of the basalts that are in contact with these interbeds. This process was observed and documented in the controlled, Large Scale Infiltration Test (LSIT) south of the SDA (Wood and Norrell, 1998). Most of the flow through the unsaturated zone is in fractures and narrow, preferential channels in the basalt. This preferential flow can transport contaminants much faster than more uniform piston flow can. Interbeds may be a major retarding influence if they act to spread out and homogenize the preferential flow that enters from the basalt fractures. Alternatively, they may have little effect if flow locally is channeled and directed over or around the layer boundaries until a breach in the vertical flow barrier is encountered.

The contaminant retardation efficiency of the sedimentary interbeds depends largely on the flux within and across these units and on the cation exchange capacity (CECs) of these units. Maximum retardation efficiency is achieved if flow occurs through the sedimentary interbeds. During periods of high infiltration, lateral flow above the sedimentary interbeds may be a significant component of the total flow, and contaminant retardation efficiency may be much less than might otherwise prevail because flow would occur primarily in the basalts. This aspect of the role of the sedimentary interbeds on radionuclide migration in the unsaturated zone has not been adequately addressed, perhaps because of the lack of sufficient data with which to generate meaningful simulations.

The current predictive simulator for subsurface pathway on contaminant fate and transport does not include the possible effects of episodic infiltration in the spreading areas on contaminant transport at the SDA (Magnuson and Sondrup, 1998, p. 2-30). Rightmire and Lewis (1987) documented the possibility of significant lateral flow in the unsaturated zone beneath the SDA from infiltration of Big Lost River (BLR) diversions into the spreading areas south and west of the SDA. In this earlier study of the hydrogeology and geochemistry of the unsaturated zone at the SDA, perched water samples that were collected from above the C-D interbed at USGS 92 were shown to be depleted in the stable isotopes deuterium and ^{18}O , suggesting that this water was derived from recharge in the spreading areas and not from vertical infiltration in the SDA. In contrast, the stable isotopic signatures from perched water above the shallower B-C interbed

in well 77-2 at the SDA indicated an evaporative influence, suggesting that the source was infiltration of local meteoric water. Furthermore, the historical record of perched-water levels in USGS 92, dating back to 1972, correlates remarkably well with the records of BLR diversions into the spreading areas (Joel Hubbell, LMITCO, oral commun., 1998). Lateral flow in the unsaturated zone, possibly originating from episodic recharge in the spreading areas, also may be responsible for the observed CCl_4 plume in the SRP aquifer north and east of the SDA.

The manner in which water moves within, on, and through the sedimentary interbeds in transit to the SRP aquifer may: (1) accelerate or retard contaminant transport, (2) concentrate or dilute contaminants, and (3) determine whether flow primarily is vertical or horizontal. It is therefore important that sufficient data be made available so that critical simplifying assumptions, needed for the final formulation of the predictive simulator for subsurface pathway, can be adequately defended.

A corehole drilling program to provide better and more defensible definition of the role of the sedimentary interbeds in contaminant migration processes at the SDA is presented in section IV. The drilling of these coreholes will also provide additional opportunities to help satisfy some of the DQOs identified in the Addendum as discussed in section II. Additionally, the proposed drilling program will provide a unique opportunity to expand on the Rightmire and Lewis (1987) study of the hydrogeology and geochemistry of the unsaturated zone at the SDA.

Laboratory Performance and DQOs. The sporadic detections of contaminants at some sample sites, many of which are at the method detection limit, combined with the fact that detections frequently are unconfirmed by quality assurance samples, indicate that problems may be associated with sample collection methods, sample handling in the laboratory, analytical methods, processing of raw analytical data, or reporting of analytical results. In addition, the previous use of more than one laboratory creates difficulty in comparing detections near the method detection limit. Resolution of these data discrepancies is critical to understanding the movement of contaminants in the unsaturated zone. Examples of problematic data follow (uncertainties are reported as one estimated sample standard deviation; units are in picocuries per liter)

| <u>Well</u> | <u>Date</u> | <u>Laboratory</u> | <u>Radionuclide</u> | <u>Sample type</u> | <u>Concentration</u> |
|-------------|-------------|-------------------|---------------------|--------------------|----------------------|
| M4D | Nov 1993 | Barringer | Pu-239, -240 | Filtered | ND |
| | | | | Duplicate, F | 1.3±.3 |
| | | | | Unfiltered | ND |
| | | | | Duplicate, U | ND |

[Problem—Inability to reproduce a result that was well above the analytical method detection limit]

| | | | | | |
|-----|----------|-----|--------|-------------|---------|
| M3S | Oct 1997 | EPI | Am-241 | Unfiltered | .04±.01 |
| | | | | Reanalysis. | 02±.02 |

[Problem—Reporting results less than the analytical method detection limit as positive results]

| | | | | | |
|-----|----------|---------|--------|-----------------|----------|
| M1S | May 1998 | EPI | Am-241 | Primary | 2.0±.1 |
| | | EPI | | Replicate-split | ND |
| | | EPI | | Replicate-split | ND |
| | | Paragon | | Replicate-split | 04±.02 |
| | | Paragon | | Replicate-split | 003±.011 |
| | | OS lab | | Co-sample | <0.05 |

[Problem—Inability of the same lab and other labs to reproduce a result that was well above the analytical method detection limit]

IV. Recommendations for Additional Work to Resolve Significant Issues

Two specific programs are recommended to resolve significant issues identified in section III. These consist of a comprehensive, integrated corehole-drilling program and a laboratory technical review.

Corehole-drilling and testing program.—The hydraulic and geochemical properties of sedimentary interbeds beneath the SDA have not been adequately addressed in the IRA, Addendum, and ancillary documentation. A comprehensive, integrated corehole-drilling program is needed to resolve issues related to the transport of contaminants

app-8 Review of the transport of selected radionuclides in the Interim Risk Assessment

through the unsaturated zone and the effect of episodic recharge in the spreading areas on lateral movement of water in the unsaturated zone. Two key assumptions are essential to the successful execution of the recommended program: (1) The corehole-drilling program will provide complete, relatively undisturbed cores from the land surface through the C-D interbed at many widely dispersed sites within the WAG-7 model domain, and (2) if perched water is encountered during drilling operations, representative water samples will be immediately collected for chemical, isotopic, and contaminant analyses, particularly in the vicinity of the RWMC.

Techniques for obtaining relatively undisturbed core from unconsolidated sediments presently are being developed. These techniques can provide the samples needed to characterize hydraulic and geochemical properties of the A-B, B-C, and C-D interbeds. The inability to obtain these samples has been a major shortcoming of previous drilling efforts.

Scope

The scope of a corehole-drilling program needed to adequately characterize the hydraulic and geochemical properties of the sedimentary interbeds includes the following work elements.

- Approximately 24 to 36 coreholes will be dry-core drilled to collect core (hole size approximately 13 cm) from the land surface through the C-D interbed, with an average depth of approximately 90 m. These coreholes will be located to best sample the interbeds within the WAG-7 model domain, to include sites that will provide information at the SDA, between the SDA and the spreading areas, and to the northeast where contaminants have been detected in the unsaturated zone and aquifer. Corehole-drilling operations will include reaming of the corehole after coring through the B-C interbed and installation of steel casing across the B-C interbed to advance the corehole to the target depth.

- Sedimentary interbed core will be recovered and preserved in Lexan⁴ liners.

- Perched water will be sampled immediately when encountered during drilling operations.

- Geophysical logs will be run in each corehole; log suites will include gamma, neutron, and density logs.

- Video logs will be run in each corehole.

- Each corehole will be prepared for followup monitoring, instrumentation, abandonment, and future deepening to support additional work needed to meet DQOs identified in section II.

- Hydraulic testing and geochemical analyses will be conducted on recovered cores, particularly those of the sedimentary interbeds and the basalt-interbed contacts. Laboratory tests of interbed core samples will provide spatial and vertical characterization of hydraulic and hydrochemical properties of the A-B, B-C, and C-D interbeds. These properties are needed to evaluate contaminant transport through the interbeds, potential for lateral flow from the spreading areas, and lateral migration of contaminants to the northeast of the SDA. Laboratory tests of the hydraulic properties of interbed cores should include detailed profiles of grain size, permeability, and water content. Laboratory tests of hydrochemical properties should include detailed profiles of the interbed mineralogy and interstitial water chemistry. The interbed mineralogy should include a detailed breakdown of the clay minerals present and their relative proportions. In addition, interbed samples could be used to satisfy DQOs calling for further tests for K_d s and actinide transport as noted in section II of this report.

⁴Use of brand names does not constitute endorsement by the USGS

Objectives

Implementation of this integrated corehole-drilling program will achieve the following objectives and can be completed in sufficient time to meet milestone dates associated with the WAG-7 ROD.

- Better definition of perching and lateral flow mechanisms within the basalt and sedimentary interbeds.
- Importance of episodic recharge from the spreading areas relative to contaminant transport in the unsaturated zone at the SDA.
- Better definition of the hydraulic properties of the sedimentary interbeds and the basalt/interbed contacts. These properties include permeability, porosity, and moisture content.
- Better resolution of the spatial continuity, thickness, and orientation of sedimentary interbeds within the WAG-7 model domain.
- Definition of the clay mineralogy within each interbed.
- Development of a defensible methodology to assign representative cation-exchange capacities to the sedimentary interbeds.

Laboratory Technical Review and DQOs. —The use of more than one laboratory for radiochemical analytical work that supports the ROD for remediation of WAG-7 is undesirable and makes comparison of data difficult. Review of past laboratory technical procedures to eliminate historical spurious radiochemical data is not feasible. A technical review is needed to eliminate future uncertainty over the reliability of laboratory analytical procedures. A consistent means of reporting data also needs to be established.

- A single laboratory should be selected to analyze all the data under a consistent set of DQOs. The selected laboratory should be contracted for the duration of the data collection process and should be audited on a routine basis.
- An independent audit of the selected laboratory should be conducted prior to awarding the contract. The preselection audit should be jointly conducted by independent parties such as DOE, USGS, INEEL Oversight Committee, and EPA. The audit should be conducted under the auspices of the guidelines contained in “Manual for the Certification of Laboratories Analyzing Drinking Water. Criteria and Procedures. Quality Assurance. Third Edition, April 1990. EPA/570/9-90/008.”
- The audit should include an on-site visit, and the selected laboratory should participate in appropriate round-robin programs such as those conducted by EPA and DOE (RESL).
- For reporting low-level data, we recommend that the approach that was documented by L.A. Currie (1984) be adopted. This approach is described in ASTM *Standard Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data*”, D 4210-89 (Reapproved 1996).

V. Summary

The purpose of Task 5 of the Independent Technical Review of the IRA was to identify the most significant issues that need to be resolved to support the draft ROD for site remediation by December 2002 and to provide interim guidance to DOE on what work will be required to resolve those issues.

We have reviewed the DQOs identified by LMITCO in their draft Addendum and concur with their proposed work program to meet those DQOs. We have identified two additional issues that need to be resolved prior to finalizing the IRA. These issues involve: (1) inadequate definition of the role of the sedimentary interbeds in contaminant transport processes, and (2) uncertainty over the reliability of the analytical procedures used to determine the presence of radionuclides in the ground water at the SDA.

An integrated corehole-drilling and hydrologic-testing program should be undertaken at the earliest possible date to provide adequate characterization of the geochemical and hydraulic properties of the sedimentary interbeds within the WAG-7 model simulation domain. The proposed drilling and testing program can be completed in time to meet the draft ROD target negotiation date of December 2002. The drilling of these coreholes will provide additional opportunities to help meet some of the DQOs identified in the Addendum to the Work Plan for WAG-7.

Any uncertainties over the reliability of the analytical procedures used to determine whether radionuclide contaminants are present in the ground water at the SDA need to be resolved at the earliest possible date. Although it may not be possible to correct past deficiencies, it is essential that future ground water sampling and associated laboratory analyses be conducted in a manner that provides a consistent and defensible data base.

References Cited

- American Society for Testing Materials, 1996, Standard practice for intralaboratory quality control procedures and a discussion on reporting low-level data, ASTM D 4210-89.
- Becker, B.H., Burgess, J.D., Holdren, K.J., Jorgensen, D.K., Magnuson, S.O., and Sondrup, A.J., 1998, Interim Risk Assessment and Contaminant Screening for the Waste Area Group 7 Remedial Investigation: Lockheed Martin Idaho Technologies Company, DOE/ID-10569, Draft Revision 2, variously paged.
- Currie, L.A., 1984, Lower limit of detection—definition and elaboration of a proposed position for radiological effluent and environmental measurements: U.S. Nuclear Regulatory Commission, NUREG/CR-4077, 139 p.
- Dicke, C.A., 1997, Distribution coefficients and contaminant solubilities for the Waste Area Group 7 Baseline Risk Assessment: Lockheed Martin Idaho Technologies Company INEEL/EXT-97-00201, variously paged.
- Magnuson, S.O., and Sondrup, A.J., 1998, Development, calibration, and predictive results of a simulator for subsurface pathway fate and transport of aqueous- and gaseous-phase contaminants in the Subsurface Disposal Area at the Idaho National Engineering and Environmental Laboratory: Lockheed Martin Idaho Technologies Company, INEEL/EXT-97-00609, variously paged.
- McCarthy, J.M., and McElroy, D.L., 1995, Hydraulic characterization data compilation: Surficial sediments and interbeds: EG&G Idaho, Inc., Engineering Design File EDF INEL-95/130, variously paged.
- Rightmire, C.T. and Lewis, B.D., 1987, Hydrogeology and geochemistry of the unsaturated zone, Radioactive Waste Management Complex, Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Water-Resources Investigations Report 87-4198 (DOE/ID-22073), 89 p.
- U.S. Department of Energy, 1998, Addendum to the Work Plan for the Operable Unit 7-13/14 Waste Area Group 7 Comprehensive Remedial Investigation/Feasibility Study: Draft Revision 2, DOE/ID-10622, variously paged.
- Wood, T.R. and Norrell, G.T., 1996, Integrated large-scale aquifer pumping and infiltration tests: Lockheed Martin Idaho Technologies Company, INEL-96-0256, variously paged.