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# Radionuclide Migration in Ground Water

Final Report

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Prepared by J. S. Fruchter, C. E. Cowan, D. E. Robertson, D. C. Girvin,  
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**Pacific Northwest Laboratory**  
Operated by  
Battelle Memorial Institute

Prepared for  
U.S. Nuclear Regulatory  
Commission

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Manuscript Completed: January 1985  
Date Published: March 1985

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NRC FIN B2380

## ABSTRACT

For the past several years, data on radionuclide migration in ground water at a low-level disposal site were collected. Most of the radionuclides were removed in the disposal basin and trench by either precipitation or adsorption mechanisms. However, three radionuclides  $^{60}\text{Co}$ ,  $^{106}\text{Ru}$ , and  $^{125}\text{Sb}$  showed somewhat greater than expected mobility. The elements of these three isotopes were found to be in either anionic or nonionic charge-forms. Complexes with both natural and man-made organics were implicated in the increased mobility, particularly in the case of  $^{60}\text{Co}$ . Characterization studies of the organic fraction were performed. Ruthenium-103,  $^{60}\text{Co}$ , and  $^{125}\text{Sb}$  were found to be associated with the higher molecular weight organics, particularly humic and fulvic acids with molecular weights greater than 1000. Studies were also performed that proved the hypothesis that the adsorption behavior of  $^{235}\text{Np}$  on soils of the site is dominated by adsorption on iron hydroxide. Finally, geochemical modeling of the chemical and charge form data showed the ground water to be in equilibrium with several solids that could be important in controlling the concentrations of trace elements and radionuclides.

## CONTENTS

ABSTRACT .....	iii
EXECUTIVE SUMMARY .....	ix
1.0 INTRODUCTION .....	1
2.0 PHYSICOCHEMICAL SPECIATION AND TRANSPORT OF RADIONUCLIDES IN GROUND WATER .....	3
2.1 FIELD DETERMINATION OF THE PHYSICOCHEMICAL FORM OF RADIONUCLIDES IN GROUND WATER .....	3
2.2 EXPERIMENTAL PROCEDURES .....	4
2.3 PHYSICOCHEMICAL SPECIATION OF RADIONUCLIDES .....	5
2.4 COMPARISON OF LABORATORY K <sub>ds</sub> WITH IN SITU K <sub>ds</sub> .....	8
2.5 COMPARISON OF PREDICTED AND OBSERVED RADIONUCLIDE TRANSPORT RATES .....	9
2.6 CONCLUSIONS AND RECOMMENDATIONS .....	9
3.0 CHARACTERIZATION OF HIGHER MOLECULAR WEIGHT ORGANIC SPECIES AND RADIONUCLIDES IN GROUND WATER .....	13
3.1 SAMPLE COLLECTION AND PREPARATION .....	13
3.2 ANALYSIS SCHEME FOR ORGANIC SPECIES AND RADIONUCLIDES .....	13
3.3 EVIDENCE FOR HIGHER MOLECULAR ORGANORADIONUCLIDES IN GROUND WATER .....	15
3.4 CONCLUSIONS .....	22
3.5 RECOMMENDATIONS .....	22
4.0 ADSORPTION/DESORPTION .....	25
4.1 ADSORPTION ON AMORPHIC IRON OXIDES AND SEDIMENTS .....	26
4.1.1 Amorphous Iron .....	26
4.1.2 Sediments .....	26

4.2	DESORPTION ON AMORPHIC IRON OXIDES AND SEDIMENTS .....	29
4.2.1	Amorphic Iron .....	29
4.2.2	Sediments .....	30
4.3	MODELING OF ADSORPTION/DESORPTION .....	31
4.4	CONCLUSIONS .....	31
4.5	RECOMMENDATIONS .....	33
5.0	GEOCHEMICAL MODELING .....	37
5.1	COMPARISON OF MEASURED AND PREDICTED RESULTS .....	37
5.2	CONCLUSIONS .....	39
5.3	RECOMMENDATIONS .....	39

## FIGURES

2.1	Temporal Variability of pH, Eh, Temperature, Dissolved Oxygen, Ferrous Iron, and Silica in Trench, Well, and Spring Waters .....	6
2.2	Concentrations and Physicochemical Forms of <sup>60</sup> Co in Trench, Well, and Spring Waters .....	7
3.1	Analytical Scheme for the Fractionation and Analysis of Higher Molecular Weight Organoradionuclide Complexes in Ground Water .....	14
3.2	Sephadex G-10 Fractionation and Analysis of Ground Water from Well #1 .....	16
3.3	Sephadex G-25 Fractionation and Analysis of Ground Water from Well #1 .....	17
3.4	Sephadex G-50 Fractionation and Analysis of Ground Water from Well #1 .....	18
3.5	Dialysis Fractionation and Analysis of Ground Water from Well #1 .....	20
3.6	Sephadex G-10 Fractionation and Analysis of the Lower MW Fraction from the Dialysis Fractionation .....	21
4.1	Np(V) Adsorption on Synthetic Amorphous Iron Oxyhydroxide .....	26
4.2	Np(V) Adsorption on Amorphous Fe Alluvial Sediment 2-1 .....	28
4.3	Np(V) Adsorption on Alluvial Sediments 2-2, 3-1, and 3-2 .....	29
4.4	Relation Between Np(V) Adsorption and Micro Moles of Amorphous Iron Per Liter in Suspension .....	30
4.5	Adsorption/Desorption of Np(V) on Amorphous Iron Oxyhydroxide for 3 h and 24-h Contact Time .....	31
4.6	Adsorption/Desorption Data for Np(V) on Alluvial Sediments for 192-h Contact Time .....	32

TABLES

2.1	Comparison of Laboratory-Derived and Measured Kds .....	9
2.2	Comparison of Predicted and Observed Radionuclide Transport Rates in Ground Water .....	10
5.1	Comparison of Field Observations and Calculated Species for Distribution Forms of Radionuclides at the Low-Level Waste Disposal Sites .....	38



## EXECUTIVE SUMMARY

For the past several years, staff at Pacific Northwest Laboratory have collected data concerning radionuclide migration in the ground water at a low-level disposal site and studied the physicochemical processes that control the mobility of radionuclides in the ground water. This report briefly summarizes the results obtained from this study and makes some recommendations for future research.

The effort was basically divided into four areas of research: 1) determination of the physicochemical speciation and transport of radionuclides actually in the ground water in the field, 2) characterization of organic species in the water and their potential effects on radionuclide migration, 3) laboratory study of the adsorption and desorption of neptunium on soils from the site and characteristics that control the adsorption, and 4) a preliminary effort at modeling the behavior of some of the radionuclides using the geochemical model, MINTEQA.

Study of physicochemical speciation showed that most of the radionuclides in the influent water are removed in the disposal basin and trench by either precipitation or adsorption mechanisms. Only trace amounts of several radionuclides have been observed to migrate to the seepage springs. Out of the 22 radionuclides studied, the only ones showing any mobility were Co, Tc, I, Ru, Sb, Fe, and Ni. The mobile forms were anionic and nonionic charge-forms. Typically, radionuclides that entered the disposal facility predominantly in particulate forms were observed to have higher total concentrations at the beginning of the trench than at the end, whereas radionuclides that entered the trench predominantly in soluble forms tended to be more homogeneously distributed. Data on the concentration of radionuclides in the soils from Wells #1 and #3 and the concentrations of the radionuclides in the ambient ground water were used to estimate in situ Kd (distribution coefficient) values and the velocity of the advancing radionuclide front. The estimated in situ Kd values and the velocity of the radionuclide front were in accordance with the observed behavior of  $^{60}\text{Co}$ ,  $^{90}\text{Sr}$ ,  $^{106}\text{Ru}$ ,  $^{125}\text{Sb}$ , and  $^{137}\text{Cs}$  in the ground water. The in situ Kds for Co, Ru, and Sb isotopes were found to be significantly lower than published Kds based on laboratory measurements. Complexes with both natural and manmade organic compounds in the ground water are implicated in the increased mobility of these radionuclides, particularly  $^{60}\text{Co}$ .

Part 2 of the study was undertaken to determine the nature of these organic complexes. Previous organic analyses had identified an extensive variety of low molecular weight carboxylic acids in the ground water at the site. Such components can complex radionuclides, but the interactions are generally much weaker than those of synthetic chelating agents such as EDTA. In addition, the total of the low molecular weight compounds accounted for only a small percentage of the ground water's organic content; therefore, a series of studies of high molecular weight organic species in the ground water focusing on humic and fulvic acids was undertaken. Radionuclide analyses were also performed in an effort to determine which radionuclides, if any, were associated with the high molecular weight species. These studies showed the presence of

humic/fulvic acids with nominal molecular weights ranging from several thousand to 700. There appeared to be another distribution peak with molecular weights from 300 to 700. The isotopes of Sb, Ru, and Co were found to be clearly associated with the higher molecular weight organics, particularly with humic and fulvic acids with nominal molecular weights greater than 1000. These observations strongly support the concept that the anionic form of these isotopes may result in part from organic complexation, particularly in the case of  $^{60}\text{Co}$ . Because an anionic character for this element under the conditions of this ground water was quite unexpected, we recommend that future investigations of the interactions of radionuclides in natural ground water systems characterize the organic constituents in these systems and account for the effects these organics may have on the radionuclide migration.

The third part of the study concentrated on a potentially important mechanism for retardation or removal of radionuclides in ground water: adsorption onto amorphous manganese and iron oxides and organic compounds that have a high affinity for cationic and anionic forms of radionuclides. A task was initiated to experimentally determine the adsorption behavior of  $^{235}\text{Np}$  on the sediments at the site, to test the hypothesis that iron oxides dominate the adsorption behavior, and to test the alternative hypothesis that adsorption can be described as a linear combination of the adsorption on the individual sinks. The hydroxylamine hydrochloride extraction technique together with curve stripping and sequential regression of the quantities of manganese, iron, aluminum, and silica extracted versus time were used to estimate the composition and quantity of amorphous oxide phases in the soils. Three amorphous oxide phases with differing solubility and Fe:Al:Si composition were identified. Using the estimated quantity of amorphous iron oxides in the soil, it was determined that the Np adsorption data obtained on these low organic carbon soils were consistent with the hypothesis that amorphous iron oxide fractions of the amorphous oxides in the soil determine the adsorption behavior of the neptunyl oxy-cation,  $\text{NpO}_2^+$ . Neptunium[V] is strongly bound to amorphous iron and approaches complete reversibility within 24 hours. Oxidation state analysis of Np in soil suspensions is consistent with, but does not prove, the hypothesis that Np[V] adsorbed from solution exists as Np[V] while bound to the soils.

In the final phase of the program, geochemical behavior of the influent and ground waters was modeled to identify the specific aqueous species of the radionuclides that are mobile in the ground water and to identify solid phases that may be controlling the radionuclide concentrations in the ground waters. The mobile species of the radionuclides are the anionic and nonionic oxy- and hydroxy complexes, although organic complexes may be important mobile species for iron, zinc, and cobalt. Those radionuclides that occur in the ground water predominately as the uncomplexed cation, such as cesium, cerium, and manganese, appeared to be the most greatly retarded. The ground waters were calculated to be in equilibrium with several solid phases that could be important for controlling the concentrations of trace elements and radionuclides. These solid phases include calcite, several aluminosilicates and ferrihydrite. Calcite and the feldspar appear to be dissolving in this system; however, the status of the aluminosilicates and ferrihydrite could not be evaluated based on the ground water analyses available. Future interpretive and predictive efforts for radionuclide migration in ground water can be enhanced by expanding the

capabilities of geochemical modeling codes in several areas, such as adding thermodynamic constants for organic complexes and adsorption phenomena to the data base. Further research is also needed to determine which processes control adsorption for radionuclides of interest. Improved techniques for determining redox status of key elements would also be helpful. Finally, studies to validate the models by comparing model predictions with laboratory and field data are essential.

## 1.0 INTRODUCTION

Safe disposal of radioactive wastes is one of the challenges faced today by the nuclear industry. Information presented in this report will lead to better predictions of the behavior of long-lived radionuclides in buried nuclear waste.

Predicting the environmental behavior of long-lived radionuclides will be enhanced by a better understanding of the solute forms in which radionuclides are transported in ground water. Radionuclide mobility in ground water sometimes has been underestimated when based on laboratory  $K_d$  (distribution coefficient) values (Means et al. 1978; Coles and Ramspott 1982). This is because laboratory-derived  $K_d$  values have been obtained using ideal solute tracers and a physicochemical form of the mobile radionuclide in the laboratory that is probably different from that found in the field. Other parameters not considered in the  $K_d$  experiments are the effects of long-term leaching of soil-adsorbed radionuclides by ligands and complexing agents in the ground waters.

We used the infiltrating water immediately below and surrounding a low-level disposal site to identify and evaluate the processes controlling radionuclide mobility for the purpose of developing the capability to predict radionuclide migration at potential commercial disposal sites. The specific objectives of this research project were 1) to identify the major inorganic and organic mobile species, 2) to identify and evaluate the factors that contribute to the mobility, and 3) to identify and evaluate the mechanisms that attenuate radionuclide concentrations. A deterministic geochemical model was used to interpret the data that could provide a basis for eventual prediction of radionuclide migration at other disposal sites. Developing these data and understanding the processes is necessary to identify the limitations and validity of the available data and the research outline at potential sites that would permit valid application of our results. The resulting information can be used in formulating guidelines for operating existing commercial low-level waste disposal sites, in determining essential requirements for remedial action and decommissioning, in determining long-term surveillance and maintenance requirements, and in developing criteria for selection of future burial sites.

For the past several years, staff at Pacific Northwest Laboratory have collected the available data concerning radionuclide migration in the ground water at a low-level disposal site and studied the physicochemical processes that control the mobility of radionuclides in the ground water. This report summarizes the results obtained during the study and makes some recommendations for future research. Previous activities and results are summarized in the annual reports (Robertson et al. 1981, 1983; Fruchter et al. 1984).

## REFERENCES

- D. G. Coles and L. D. Ramspott. 1982. "Migration of Ruthenium-106 in a Nevada Test Site Aquifer: Discrepancy Between Field and Laboratory Results." Science 215:1235-1236.
- J. S. Fruchter, et al. 1984. Radionuclide Migration in Ground Water: Annual Report for Fiscal Year 1983. NUREG/CR-3712, U.S. Nuclear Regulatory Commission, Washington, D.C.
- J. L. Means, D. A. Crerar, and J. O. Duguid. 1978. "Migration of Radioactive Wastes: Radionuclide Mobilization by Complexing Agents." Science 200:1477-1481.
- D. E. Robertson, A. P. Toste, K. H. Abel, and R. L. Brodzinski. 1981. Annual Progress Report for 1981, Influence of the Physicochemical Forms of Radionuclides During Migration in Ground Waters. U.S. Nuclear Regulatory Commission, Washington, D.C.
- D. E. Robertson, A. P. Toste, K. H. Abel, and R. L. Brodzinski. 1983. Radionuclide Migration in Groundwater, Annual Progress Report for 1982. NUREG/CR-3554 (PNL-4773), U.S. Nuclear Regulatory Commission, Washington, D.C.

## 2.0 PHYSICOCHEMICAL SPECIATION AND TRANSPORT OF RADIONUCLIDES IN GROUND WATER

This phase of the study addressed the characterization of the physico-chemical species of radionuclides migrating in ground waters at a low-level disposal site and the impact of chemical form on radionuclide migration rates. Our study showed that the mobile radionuclides in this ground water system exist primarily in anionic or nonionic charge-forms. The mobile radionuclides include isotopes of Co, Tc, I, Ru, Sb, Fe, and Ni. Radionuclides that remain predominantly in cationic charge-forms (e.g.,  $^{54}\text{Mn}$ ,  $^{65}\text{Zn}$ ,  $^{95}\text{Nb}$ ,  $^{95}\text{Zr}$ ,  $^{140}\text{Ba}$ ,  $^{140}\text{La}$ ,  $^{144}\text{Ce}$ ,  $^{137}\text{Cs}$ , and  $^{239}\text{Np}$ ) did not migrate significantly at this site. Strontium-90, which is predominantly cationic, was the only exception. In situ distribution coefficients (Kds) were calculated for several radionuclides and were much lower than reported laboratory-derived Kds. Using the field-measured in situ Kds, more realistic migration rates of  $^{60}\text{Co}$ ,  $^{106}\text{Ru}$ , and  $^{125}\text{Sb}$  were calculated and were in better agreement with the rapid migration rates observed in the field.

These studies point out the critical importance of physicochemical speciation of radionuclides in determining their ability to migrate from a low-level waste disposal site through the ground waters.

### 2.1 FIELD DETERMINATION OF THE PHYSICOCHEMICAL FORM OF RADIONUCLIDES IN GROUND WATER

One of the primary tools planned for use in licensing high- and low-level waste disposal sites is numerical performance assessment modeling. Such models incorporate predictions of the radionuclide movement from a waste disposal site via ground-water flow. Ground-water transport models involve the coupling of hydrologic and geochemical codes that describe the rate and direction of radionuclide movement relative to the ground-water flow. To date, no models satisfactorily perform this coupling for anything except very simple systems. More sophisticated models are currently under development, but for the present, transport calculations are frequently made by using a Kd for the element in question into the hydrodynamic transport equation. In some cases, radionuclide mobility in ground water has been under-estimated when based on this approach, particularly if laboratory-derived Kd values are used (Means et al. 1978; Jackson and Inch 1980; Killey et al. 1984; Coles and Ramspott 1982). This is because laboratory-derived Kd values have been obtained using ideal soluble tracers in chemical forms, which are not the same as the mobile forms found in the field. Also, laboratory Kds do not reflect the effects of long-term leaching of soil-adsorbed radionuclides by natural or manmade complexing substances in the ground water. These organic complexing agents can form relatively mobile chemical forms of the radionuclides.

One way to assess the accuracy of models is to compare their predictions with field observations of radionuclide transport. Studies of radionuclide

speciation, retardation, and migration in natural systems are essential in developing and testing models of isotope migration that can be used in licensing waste disposal sites.

Because the chemical speciation of radionuclides is so important in their ability to migrate in ground waters, the objective of this portion of this study has been 1) to identify and characterize the behavior of the mobile species of radionuclides migrating in a slightly radioactive ground-water plume and 2) to compare predicted radionuclide migration rates with observed field rates.

## 2.2 EXPERIMENTAL PROCEDURES

The slightly radioactive ground-water plume results from a disposal facility that consists of an unlined basin and connecting trench that receives influent water containing low levels of fission and activation products and trace amounts of transuranic radionuclides. The influent water percolates through the soil, and a small fraction of it emerges at seepage springs located some 260 m from the trench. The disposal basin and trench are very efficient in retaining most of the radionuclides, but trace amounts of a number of radionuclides existing in mobile forms migrate in the ground water from the trench to the springs.

Filtered influent water sampled at the trench and ground water sampled from monitoring wells and the seepage springs were pumped through the Battelle large volume water sampler (BLVWS) to identify the soluble, ionic charge-forms of the migrating radionuclides. The cationic, anionic, and nonionic charge-forms were absorbed by beds of cation resin, anion resin, and activated aluminum oxide in the BLVWS. The mobile species and oxidation state of several radionuclides were also studied in detail using a variety of chemical manipulations. The details of the sampling procedure for this project were published in the Fiscal Year 1982 Annual Report (Robertson et al. 1983).

At the trench, 10 to 20 L of filtered water were processed directly through the BLVWS, which consists of a 2.5-cm-thick x 15-cm-diameter bed of cation exchange resin (Dowex 50 x 8, H<sup>+</sup> form, 200-400 mesh), a 2.5-cm thick x 15-cm-diameter bed of anion exchange resin (Dowex 1 x 8, Cl<sup>-</sup> form, 200-400 mesh), and a 0.7-cm-thick x 15-cm-diameter bed of fine-grained, activated, aluminum oxide. The initial 0.4- $\mu$ m Nuclepore<sup>®</sup> filter removes radionuclides associated with particulates greater than 0.4  $\mu$ m in diameter, the resins remove soluble cationic and anionic species, and the activated aluminum oxide removes the nonionic species. The wells and springs were sampled with a larger version of the BLVWS using dual resins and aluminum oxide beds because much greater volumes of water were needed to measure the lower radionuclide concentrations. Typically, 50 to 100 L of well water and 1000 to 5000 L of spring water were processed through the sampler.

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<sup>®</sup> Nuclepore is a tradename of the Nucleopore Corporation, Pleasanton, California 94566.

Important chemical constituents of these waters that affect radionuclide speciation were also measured. Water samples were simultaneously collected for detailed measurements of temperature, pH, Eh, dissolved oxygen, alkalinity, dissolved organic carbon (DOC), major cations and anions, trace elements, and dissolved organic constituents. Temperature, pH, Eh, dissolved oxygen, and alkalinity were measured on site during the sampling. The temporal variability during 1983 of some of the most important constituents of the trench, well, and spring waters that influenced the physicochemical forms of the radionuclides is shown in Figure 2.1. In general, these waters were characterized by near-neutral pH, oxidizing Eh, near-saturated dissolved oxygen, low DOC, and moderate alkalinity. The inorganic constituents are dominated by the anions  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ , and the cations  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ , and  $\text{Na}^+$ . Sulfide concentrations in these waters were very low, normally less than 0.2 mg/L.

### 2.3 PHYSICOCHEMICAL SPECIATION OF RADIONUCLIDES

The measurement of particulate, cationic, anionic, and nonionic forms of the radionuclides in the trench, well, and spring waters showed that the migrating radionuclides were primarily those in anionic and nonionic forms. This group of mobile radionuclides included isotopes of Co, Tc, I, Ru, Sb, Fe, and Ni. Although the trench water contains predominantly cationic species of  $^{54}\text{Mn}$ ,  $^{59}\text{Fe}$ ,  $^{95}\text{Nb}$ ,  $^{140}\text{Ba}$ ,  $^{140}\text{La}$ ,  $^{137}\text{Cs}$ , and  $^{239}\text{Np}$ , the cationic forms of these radionuclides were not observed to migrate to the springs. Strontium-90 was the only radionuclide to migrate to the springs exclusively in a cationic form.

The chemical behaviors of  $^{60}\text{Co}$ ,  $^{106}\text{Ru}$ , and  $^{125}\text{Sb}$  during migration from the trench to the springs illustrate the enhanced mobility of the anionic or nonionic forms of these radionuclides and the selective removal of their particulate and cationic forms by the soil.

Cobalt-60 has been shown to be one of the most mobile radionuclides to migrate in ground waters from a variety of low-level waste disposal sites (Means et al. 1978; Killey et al. 1984; Kirby 1981; Eddy and Wilbur 1980; Stone 1982). This ubiquitous mobility appears to be related to the occurrence of the anionic cobalt species, possibly occurring as natural or manmade organic complexes (see Section 3). Figure 2.2 shows that  $^{60}\text{Co}$  in the trench water was present predominantly in particulate and cationic forms. As the water percolated through the soil to the monitoring wells and the seepage springs, the particulate and cationic forms were selectively removed and predominantly anionic  $^{60}\text{Co}$  continued migrating. Based on the relative concentrations of anionic and cationic  $^{60}\text{Co}$  in the trench and spring, the anionic  $^{60}\text{Co}$  was, on the average during 1983, about 130 times more mobile than the cationic  $^{60}\text{Co}$ .

The behavior of  $^{106}\text{Ru}$  was similar to that of  $^{60}\text{Co}$ , in that the trench water usually contained predominantly cationic  $^{106}\text{Ru}$ , which is more efficiently removed by sorption onto the soil. The anionic  $^{106}\text{Ru}$  migrated more readily to the wells and springs, and accounted for about 80% of the total soluble  $^{106}\text{Ru}$  in these waters.

Antimony-125 was very mobile in this ground-water system and exhibited a unique chemical behavior. Antimony-125 in the trench water was normally



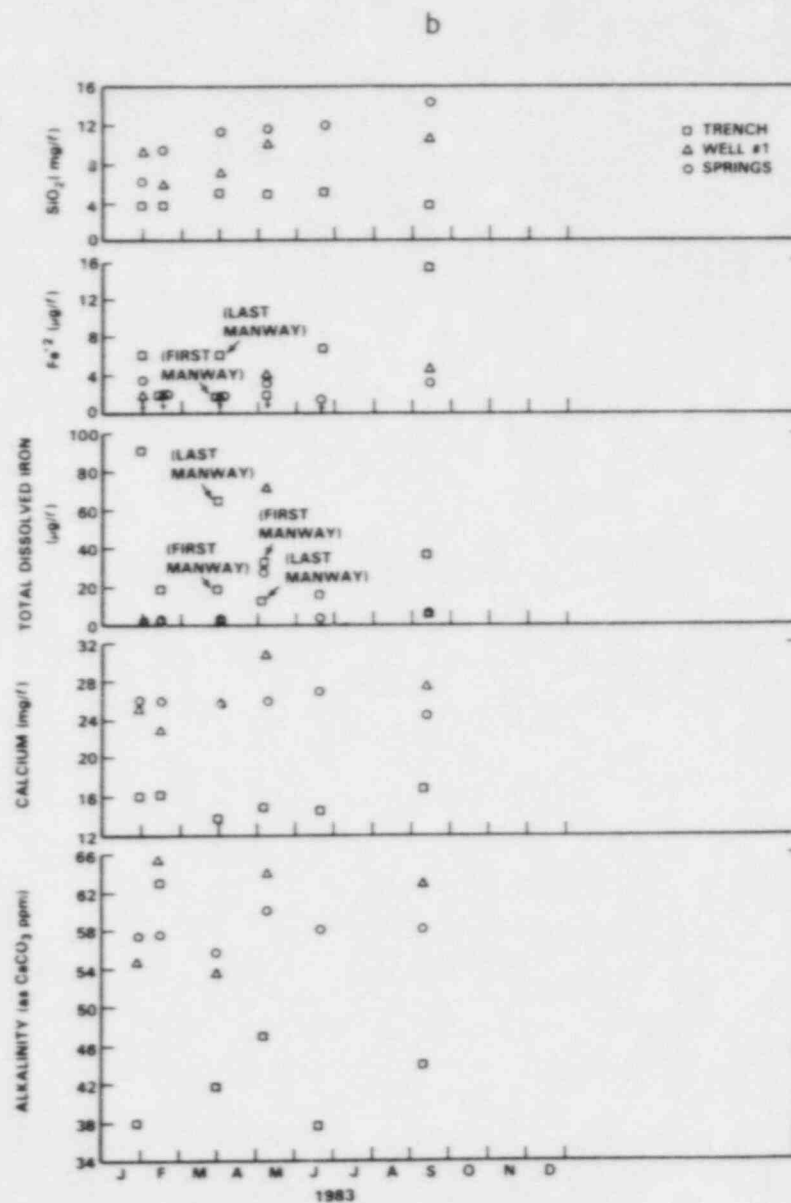
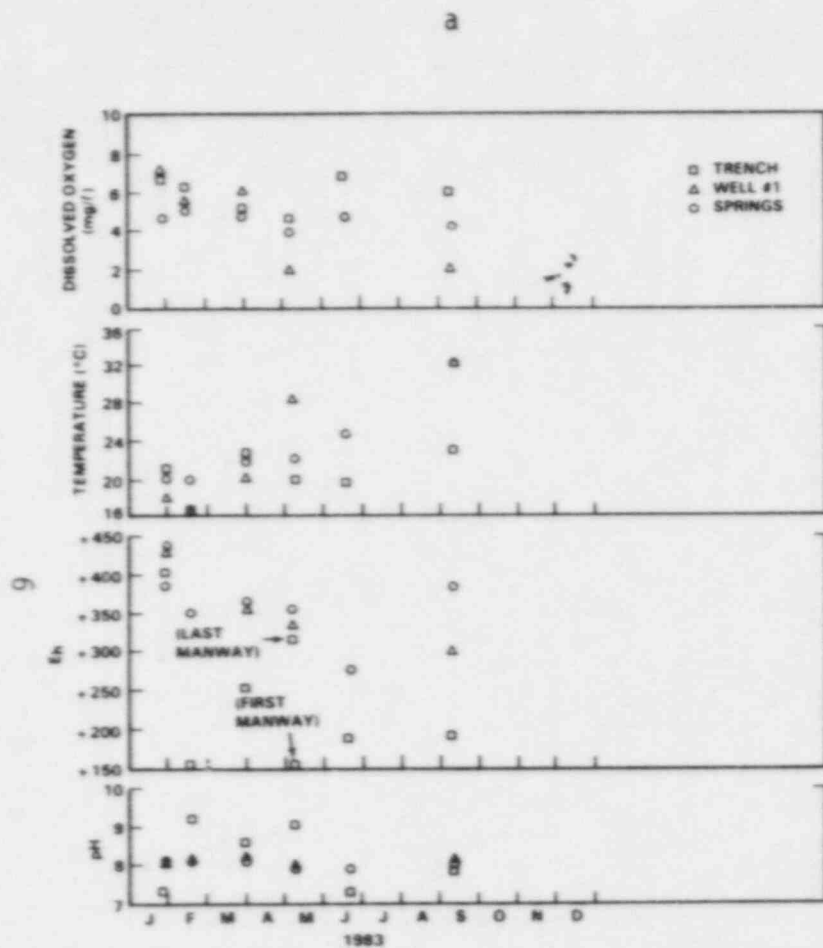


FIGURE 2.1. Temporal Variability of pH, Eh, Temperature, Dissolved Oxygen, Ferrous Iron, and Silica in Trench, Well, and Spring Waters

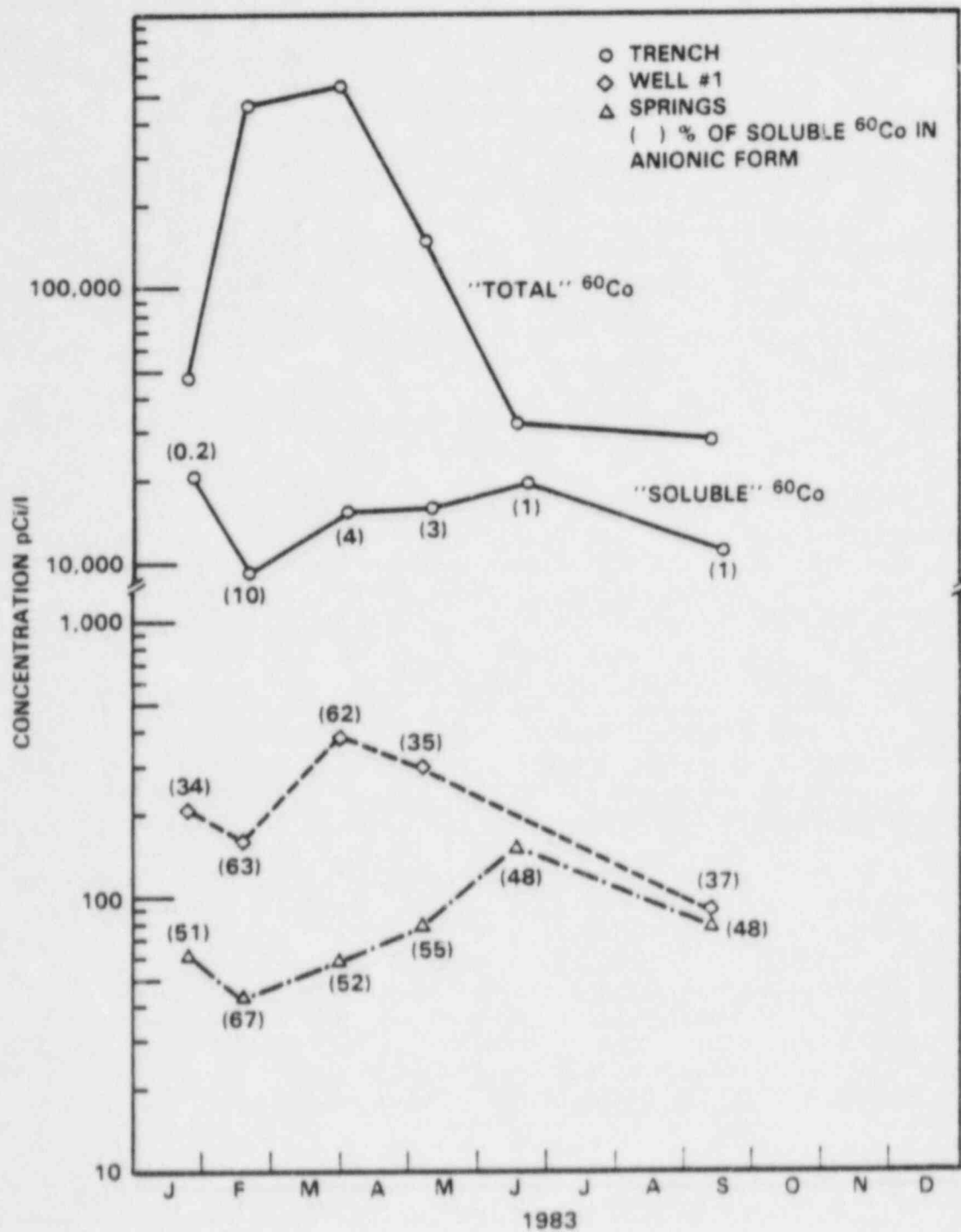


FIGURE 2.2. Concentrations and Physicochemical Forms of <sup>60</sup>Co in Trench, Well, and Spring Waters

present in a soluble anionic form, with a very small fraction being present as a soluble nonionic species. During migration in the ground water, the anionic  $^{125}\text{Sb}$  appeared to be converted to a nonionic form(s), which was also very mobile. At the springs, the  $^{125}\text{Sb}$  was typically partitioned as follows:  $76\% \pm 13\%$  nonionic,  $23\% \pm 13\%$  anionic, and generally less than 1% cationic.

Iodine-131 (8.04 days) can be a useful tracer of the long-lived  $^{129}\text{I}$  ( $1.59 \times 10^7$  year), which has been shown to be mobile in slightly contaminated ground waters (Barraclough et al. 1981; Eddy and Wilbur 1980). The radioiodine in the trench, well, and spring waters occurred predominantly in soluble anionic forms and appears to be quite mobile in this system. Further studies (Robertson et al. 1983) have shown that about 42% to 48% of the soluble anionic  $^{131}\text{I}$  is in the form of iodide ( $\text{I}^-$ ), and about 49% to 57% occurs presumably as an organically bound anionic complex.

Technetium-99 was also mobile in this ground-water system and is always present in trench, well, and spring waters in an anionic form, presumably  $\text{TcO}_4^-$ .

Iron-55,59 and  $^{63}\text{Ni}$  have migrated in trace concentrations from the trench to the springs. The soluble fraction of  $^{55,59}\text{Fe}$  and  $^{63}\text{Ni}$  in the trench water were present mainly as cationic species. However, the trace amounts of  $^{55,59}\text{Fe}$  reaching the monitoring wells and the springs are present mainly in an anionic form, whereas the  $^{63}\text{Ni}$  was usually present in both nonionic and anionic forms.

#### 2.4 COMPARISON OF LABORATORY Kds WITH IN SITU Kds

For those mobile radionuclides that migrated from the trench (e.g.,  $^{60}\text{Co}$ ,  $^{106}\text{Ru}$ ,  $^{125}\text{Sb}$ ), it was possible to measure in situ Kds at the locations where several new monitoring wells were installed in 1982. This was accomplished by measuring the radionuclide concentrations on soil samples recovered from the saturated flow depths and the concentrations in the ambient ground water at these depths. The in situ Kds were calculated by dividing the radionuclide concentrations on the soils (in pCi/g) by the radionuclide concentrations in the ambient ground water (in pCi/L).

To estimate an in situ Kd, two assumptions must be made: 1) the water and soil are in equilibrium with respect to the mobile radionuclides and 2) the water entering the trench eventually travels to the spring via the ground water intercepted by the well and does not travel by some other route. Table 2.1 shows a comparison of the measured in situ Kds with laboratory derived Kds for similar soils.

The mobile species that migrate to the monitoring wells are in chemical forms that have relatively low distribution coefficients. Laboratory-derived Kds were measured using radionuclide tracers in chloride or nitrate forms. Also, the laboratory-derived Kds did not reflect the effects of long-term leaching of soil-adsorbed radionuclides by natural or manmade organic complexing substances to which the in situ soils were exposed. The in situ Kds more accurately express the sorption capacities of the mobile forms of these radionuclides, which migrate at much faster rates than predicted from laboratory-derived Kd values.

TABLE 2.1. Comparison of Laboratory-Derived and Measured Kds

Radionuclide	Laboratory Kd	In Situ Kd for Mobile Species
$^{60}\text{Co}$	3560 (a)	9
$^{106}\text{Ru}$	400 (b)	6
$^{125}\text{Sb}$	19 (c)	4

(a) Gee and Campbell 1980

(b) Ames and Rai 1978

(c) Erdal et al. 1977; average of two sets of measurements

## 2.5 COMPARISON OF PREDICTED AND OBSERVED RADIONUCLIDE TRANSPORT RATES

The final objective of field studies of the chemical species of mobile radionuclides was to determine how well the field observations of radionuclide transport rates in ground waters compared with predicted rates based on laboratory-derived measurements. These comparisons were made using the following well-known simplified retardation equation, which ignores the effects of dispersion:

$$V_{RN} = \frac{V_{GW}}{1 + \frac{P}{n} \cdot Kd}$$

where

$V_{RN}$  = velocity of advancing radionuclide front (m/d)

$V_{GW}$  = velocity of the ground water (60 m/d) at this site

$P$  = bulk density of site soil (1.9 g/cm<sup>3</sup>)

$n$  = porosity of site soil (0.3)

$Kd$  = distribution coefficient (either laboratory-derived or in situ measured)

For radionuclides having charge-form distributions explained by inorganic complexes (e.g.,  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ ), the predicted transport rates agreed well with the field observations (see Table 2.2). However, for those radionuclides having anionic or nonionic charge-forms in the ground water that could not be explained by inorganic complexation, the observed transport rates in the field were much faster (up to 390 times faster for  $^{60}\text{Co}$ ) than predicted rates based on laboratory-derived  $Kd$  values used in the retardation equation.

## 2.6 CONCLUSIONS AND RECOMMENDATIONS

These comparisons illustrate the importance of chemical speciation on the migration of radionuclides in ground waters. The significance of dissolved organic complexing substances in the ground water has been implicated in the enhancement of mobile radionuclide species. Because very little is known concerning the effects of these organic complexing substances on the mobility of radionuclides in ground water, future studies should focus on characterizing

TABLE 2.2. Comparison of Predicted and Observed Radionuclide Transport Rates in Ground Water

Radionuclide Transport Rate in Ground Water (m/day)			
Radionuclide	Predicted <sup>(a)</sup>	Observed <sup>(b)</sup>	Ratio: $\frac{\text{Observed}}{\text{Predicted}}$
<sup>60</sup> Co	0.0028	1.1	390
<sup>106</sup> Ru	0.024	1.6	67
<sup>125</sup> Sb	0.50	2.4	~.8
<sup>137</sup> Cs	0.0042	~0.004	~1
<sup>90</sup> Sr	0.08	~0.08 <sup>(c)</sup>	~1

(a) Based on laboratory-derived Kds in Table 2.1 and references in Table 2.1

(b) Based on in situ Kds in Table 2.1, or data from Fruchter et al. (1984)

(c) Based on historical observations of <sup>90</sup>Sr detectable levels in spring water.

the role of natural or manmade dissolved organic complexing substances in ground waters. Only after an adequate understanding of the geochemistry of ground-water systems is obtained can more accurate predictions be made of radionuclide transport from waste disposal sites.

## REFERENCES

- L. L. Ames and D. Rai. 1978. "Radionuclide Interactions with Soil and Rock Media." In Vol. 1, Processes Influencing Radionuclide Mobility and Retention, EPA 521/6-78-007A, U. S. Environmental Protection Agency, Washington, D.C.
- J. T. Barraclough, B. D. Lewis, and R. C. Jensen. 1981. Hydrologic Conditions at the Idaho National Engineering Laboratory, Idaho. Emphases: 1974-1978. IDO-22060. U.S. Geological Survey, Water Resources Investigation, Open-File Report 81-526.
- D. G. Coles and L. D. Ramspott. 1982. "Migration of Ruthenium-106 in a Nevada Test Site Aquifer: Discrepancy Between Field and Laboratory Results." Science 215:1235-1236.
- P. A. Eddy and J. S. Wilbur. 1980. Radiological Status of the Groundwater Beneath the Hanford Project, January Through December, 1979. PNL-3346, Pacific Northwest Laboratory, Richland, Washington.
- B. R. Erdal, et al. 1977. "Laboratory Measurements of Radionuclide Distribution Between Selected Groundwater and Geologic Media." In Proceedings of the Task 4 Contractor Information Meeting, Waste Isolation Safety Assessment Program, R. J. Serne (Chairman). PNL-SA-6957, Pacific Northwest Laboratory, Richland, Washington.
- J. S. Fruchter, et al. 1984. Radionuclide Migration in Groundwater--Annual Report for FY 1983. NUREG/CR-3712 (PNL-5040), U.S. Nuclear Regulatory Commission, Washington, D.C.
- G. C. Gee and A. C. Campbell. 1980. Monitoring and Physical Characterization of Unsaturated Zone Transport--Laboratory Analysis. PNL-3304, Richland, Washington, Pacific Northwest Laboratory.
- R. F. Jackson and R. J. Inch. 1980. Hydrogeochemical Processes Affecting the Migration of Radionuclides in a Fluvial Sand Aquifer at the Chalk River Nuclear Laboratories. NHRI Paper No. 7, Scientific Series No. 104, National Hydrology Research Institute, Ottawa, Canada.
- R. W. D. Killey, J. O. McHugh, D. R. Champ, E. L. Cooper, and J. L. Young. 1984. "Subsurface Cobalt-60 Migration from a Low-Level Waste Disposal Site." Environmental Science and Technology 18:148-156 (1984).
- L. J. Kirby. 1981. "Migrating Radionuclides at Maxey Flats and Other Shallow Land Burial Sites." In Research Program at Maxey Flats and Consideration of Other Shallow Land Burial Sites. NUREG/CR-1832 (PNL-3510), U.S. Nuclear Regulatory Commission, Washington, D.C.
- J. L. Means, D. A. Crerar, and J. O. Duguid. 1978. "Migration of Radioactive Wastes: Radionuclide Mobilization by Complexing Agents." Science 200:147-1481.

- D. E. Robertson, A. P. Toste, K. H. Abel, and R. L. Brodzinski. 1983. Radionuclide Migration in Groundwater, Annual Progress Report for 1982, NUREG/CR-3554 (PNL-4773), U.S. Nuclear Regulatory Commission, Washington, D.C.
- J. A. Stone. 1982. "Radionuclide Migration Studies at the Savannah River Plant LLW Burial Ground--A Humid SLB Site." In Proceedings of the Fourth Annual DOE LLWMP Participants Information Meeting, Denver, Colorado.

### 3.0 CHARACTERIZATION OF HIGHER MOLECULAR WEIGHT ORGANIC SPECIES AND RADIONUCLIDES IN GROUND WATER

Organic compounds can act as ligands for radionuclides, which could potentially enhance the subsurface transport of the radionuclides in ground water and are implicated in the increased mobility of carbon radionuclide (see Section 2). The goal of this task, therefore, was to identify organic compounds that may complex or chelate radionuclides in the ground water at the low-level disposal site, thereby potentially enhancing their mobility.

Previous organic analyses have identified an extensive variety of low molecular-weight (MW) carboxylic acids in ground water at the low-level disposal site. Such compounds can complex radionuclides, but the interactions are generally much weaker compared to those of synthetic chelating agents like ethylenediaminetetraacetic acid (EDTA). Moreover, the low MW organic acids account for only a small percentage of the ground water's organic content. Consequently, in this series of studies, the higher MW organic species in the ground water have been examined, focusing on humic and fulvic acids. Radionuclide analyses have also been performed in an effort to determine which radionuclides, if any, are associated with the higher MW organic species.

#### 3.1 SAMPLE COLLECTION AND PREPARATION

Ground water was pumped from Well #1 on July 5, 1984. Well #1 is located 30 m from the trench at the low-level disposal site. The water was filtered through 0.45- $\mu$ m silver membrane filters and collected in acid-cleaned amber glass bottles. The samples were immediately transported to the laboratory where they were stored at 4°C before analysis.

#### 3.2 ANALYSIS SCHEME FOR ORGANIC SPECIES AND RADIONUCLIDES

The analytical procedure used on the samples is outlined in Figure 3.1. The filtered ground water underwent sample preparation immediately on arrival at the laboratory. Replicate aliquots of filtered water (400 mL) were concentrated to 20 mL by vacuum rotary evaporation before the dialysis and steric-exclusion fractionation into different molecular weight fractions.

For the dialysis study, 20 mL of concentrated ground water were placed in cellulose dialysis tubing with a MW = 1000 exclusion limit. The dialysis tube was sealed and placed in a beaker containing 1 L of Milli-Q purified water. The beaker was covered, and the system was magnetically stirred for 24 h. The system was then opened, and the 1 L of dialysate was decanted into an acid-cleaned glass bottle, which was refrigerated. One liter of fresh water was added to the system followed by another 24 h of stirring. The procedure was repeated again, yielding 3 L of dialysate, which was termed the lower MW fraction (MW <1000). The 3 L of dialysate were concentrated to 20 mL by vacuum evaporation and set aside for subsequent analysis. The concentrated ground water remaining inside the dialysis tube was pipetted into an acid-cleaned glass vial and labeled the high MW fraction (MW >1000).



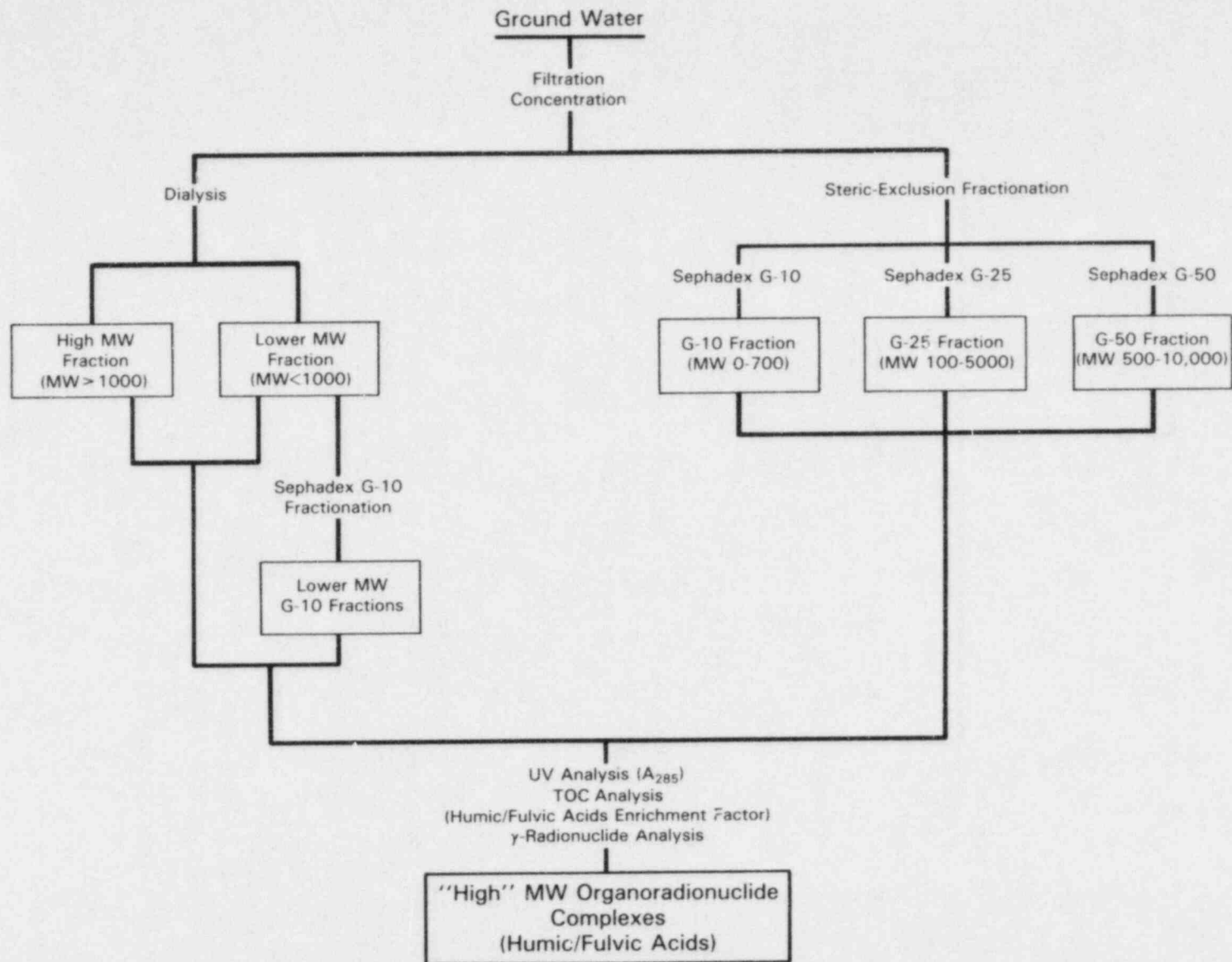


FIGURE 3.1. Analytical Scheme for the Fractionation and Analysis of Higher Molecular Weight Organoradionuclide Complexes in Ground Water

For the steric-exclusion fractionation study, three replicate samples of concentrated ground water (20 mL) were chromatographed separately on Sephadex G-10, G-25, and G-50 columns with Milli-Q purified water at a flow rate of 100 mL/h. Replicate runs were made, with and without Blue Dextran as a void volume marker. Each column was also calibrated using dextran polymers of different MWs. The column effluent was monitored by UV absorbance at 254 nm and collected into acid-cleaned flasks. A single fraction of UV-absorbing species was collected for each column run, yielding three fractions: 1) the G-10 fraction, with a nominal MW range of 0 to 700; 2) the G-25 fraction, with a nominal MW range of 100 to 5,000; and 3) the G-50 fraction, with a nominal MW range of 500 to 10,000.

The concentrated lower MW fraction ( $M < 1000$ ) from the dialysis study was further fractionated on a Sephadex G-10 column as described above. In this case, however, three fractions were collected: 1) fraction A, the first third of the chromatogram, nominally corresponding to a MW range of 700 to 1000; 2) fraction B, the middle third of the chromatogram, nominally corresponding to a MW range of 300 to 700; and 3) fraction C, the final third of the chromatogram, nominally corresponding to a MW range of  $< 300$ .

Each of the fractions obtained in the dialysis and steric-exclusion fractionations were subsequently divided into three aliquots and analyzed for their absorbance, total organic carbon (TOC) content, and  $\gamma$ -emitting radionuclide. The organic content of each fraction was analyzed for its so-called humic and fulvic acids content by computing its humic/fulvic acids enrichment factor:  $A_{285\text{nm}}/\text{TOC}$ , normalized to the value for the original well water. Aromatic residues (e.g., phenolic groups associated with naturally occurring organics), particularly humic and fulvic acids, absorb strongly in the ultraviolet region at a wavelength of 285 nm. For the radionuclide analyses, it was decided to measure the  $\gamma$ -emitting radionuclides based on past work by Robertson et al. (1983).

Some caution must be exercised when assigning MWs to organic species solely on the basis of dialysis and steric-exclusion fractionations. The dialysis tubing and the Sephadex columns were sized-calibrated using specific standards (e.g., dextrans), whose conformations may bear little resemblance to the organics in the ground-water samples. Any fractionation must be considered operational for the specific class of compounds being considered. Consequently, any MWs assigned must be considered as nominal MWs. That is not to say that such information is worthless. There is ample evidence in the literature indicating good correlation between MWs determined for humic and fulvic acids by steric-exclusion chromatography, ultra-filtration, and x-ray scattering (Thurman et al. 1982; Ogura 1974).

### 3.3 EVIDENCE FOR HIGHER MOLECULAR ORGANORADIONUCLIDES IN GROUND WATER

The results of the steric-exclusion fractionation of the ground water are summarized in Figures 3.2 through 3.4. The Sephadex G-10 chromatogram contains two distinct UV-absorbing peaks or aggregates (Figure 3.2). This column fractionated over a nominal MW range of 0 to 700. The large, early peak corresponds to large organic species with nominal MWs  $> 700$ , which passed through

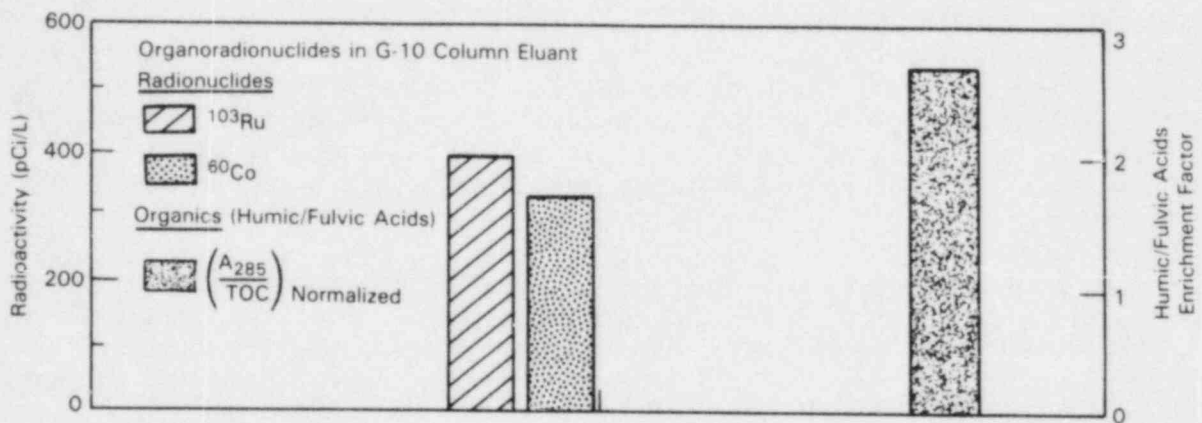
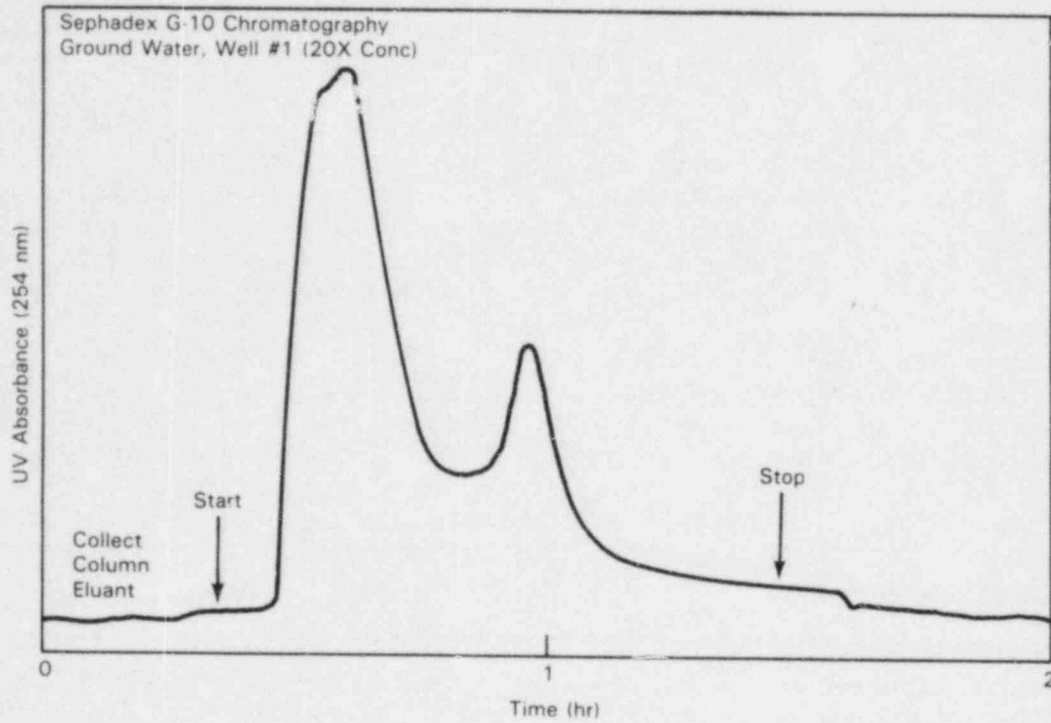


FIGURE 3.2. Sephadex G-10 Fractionation and Analysis of Ground Water from Well #1

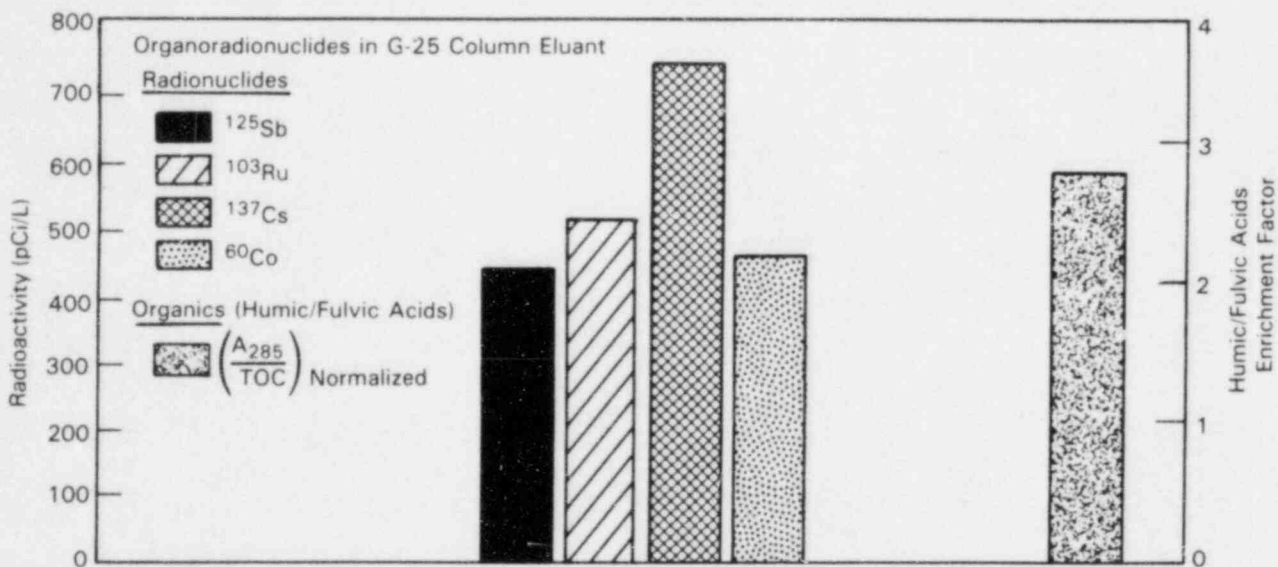
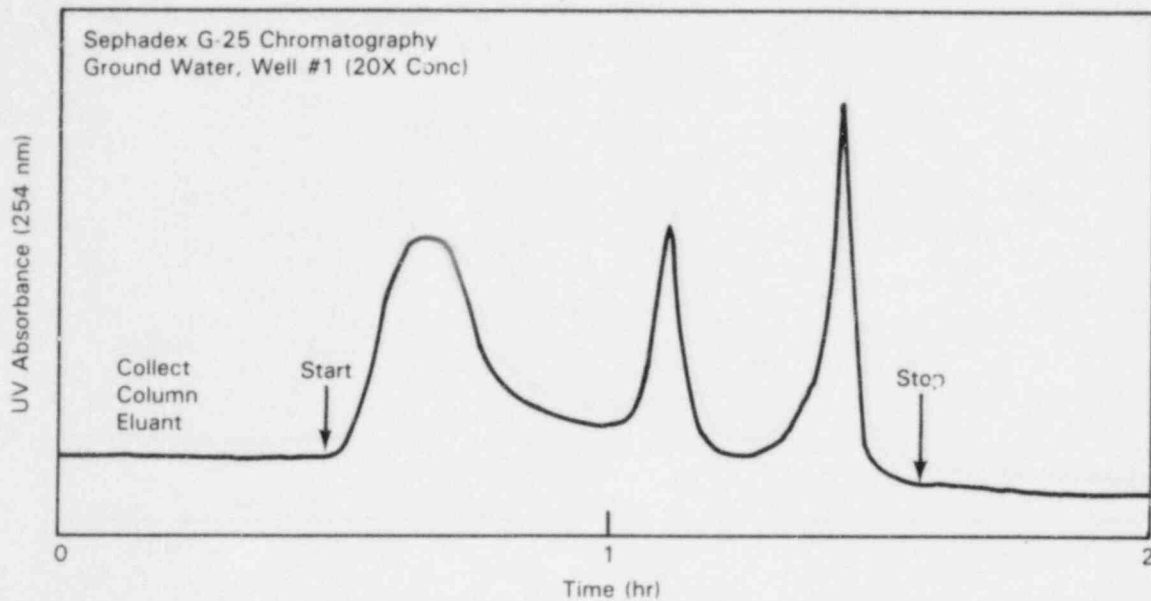


FIGURE 3.3. Sephadex G-25 Fractionation and Analysis of Ground Water from Well #1

the column unretarded. The second peak corresponded to lower MW organic species, probably in the MW range of  $<300$ , which were retarded on the column. On the basis of TOC and UV absorbance data, it is clear that the large peak accounted for 76.6% of the organic content. As Figure 3.2 illustrates, the Sephadex G-10 fractionation yielded a 2.7-fold enrichment for humic and fulvic acids. Lower MW non-UV-absorbing species were separated out. Radionuclide analyses revealed that extremely low levels of  $^{103}\text{Ru}$  and  $^{60}\text{Co}$  activity were associated with the G-10 humic/fulvic acid fraction.

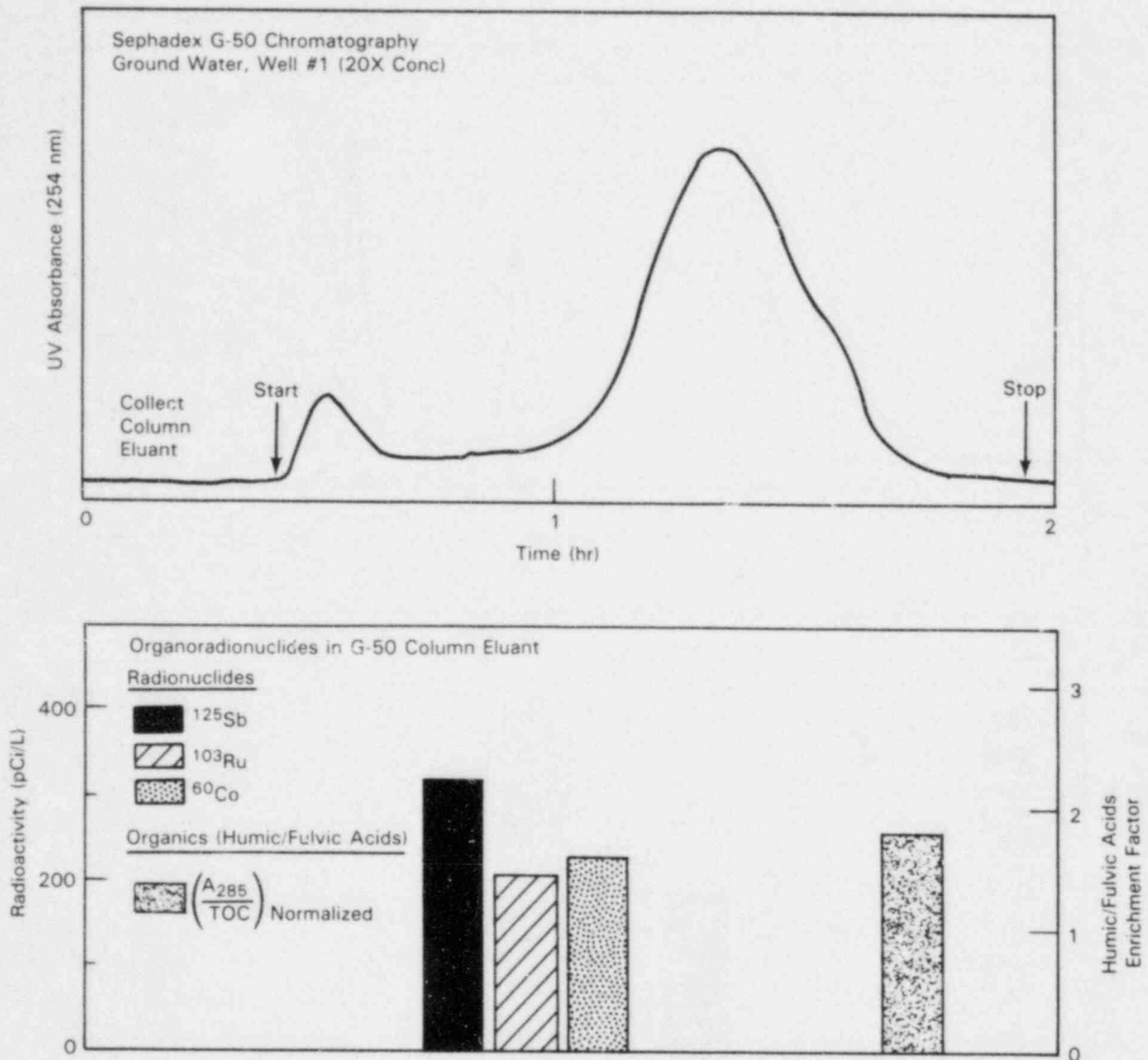


FIGURE 3.4. Sephadex G-50 Fractionation and Analysis of Ground Water from Well #1

The Sephadex G-25 fractionation yielded three distinct UV-absorbing species or aggregates (Figure 3.3). This column fractionated over a nominal range of MWs 100 to 5000. The large first peak corresponded to large organic species with MWs nominally >5000, which passed through the column; it constituted 52.4% of the G-25 fraction's organic content. The second peak corresponded to organic species (18.4% of the organic content) with nominal MWs of several thousand. The third peak (29.2% of the organic content) represented low MW species with nominal MWs of ~100 to several hundred. The Sephadex G-25 fractionation yielded a humic/fulvic acids enrichment of 2.8. Radionuclide analysis revealed measurable levels of  $^{125}\text{Sb}$ ,  $^{103}\text{Ru}$ ,  $^{137}\text{Cs}$ , and  $^{60}\text{Co}$  associated with the G-25 fraction.

The Sephadex G-50 fractionation yielded two distinct UV-absorbing species or aggregates (Figure 3.4). The first peak accounted for only 8.1% of the organic content and consisted of species with nominal MWs  $>10,000$ . The second peak accounts for 91.9% of the organics and consisted of species with nominal MWs of several thousands to a few hundred. The humic/fulvic acids enrichment of 1.8 fold for Sephadex G-50 was considerably less than that observed with Sephadex G-10 (2.7) and G-25 (2.8), suggesting that the high MW contribution to humic and fulvic acids was diminished. Radionuclide analyses revealed that some  $^{125}\text{Sb}$ ,  $^{103}\text{Ru}$ , and  $^{60}\text{Co}$  activity was associated with the G-50 fraction.

The dialysis fractionation of the ground water yielded two fractions: 1) the organic species inside the dialysis tube with nominal MWs  $>1000$ , and 2) the organic species outside the tube with nominal MWs  $<1000$  (Figure 3.5). Humic/fulvic acids enrichment factors of 1.8 and 3.1 were observed for the solutions inside and outside the dialysis tube, respectively. The high enrichment factor (3.1) associated with the lower MW fraction was undoubtedly caused by the resulting enrichment of lower MW fulvic acids in this fraction, which had a higher percentage of strong UV-absorbing groups compared to the much larger humic acids. On the basis of carbon analysis, 25% to 33% of the humic/fulvic acids appeared to have nominal MWs  $<1000$ .

Antimony-125,  $^{103}\text{Ru}$ , and  $^{60}\text{Co}$  activity were detected in both fractions, but more activity appears to be associated with the lower MW organic fraction. The lower MW fraction also contained  $^{137}\text{Cs}$  activity as well. These radionuclides may or may not be associated with the lower MW organics. They could exist as low MW inorganic species, which dialyzed through the dialysis membrane with the lower MW organics. In contrast, the  $^{125}\text{Sb}$ ,  $^{103}\text{Ru}$ , and  $^{60}\text{Co}$  activity remaining in the dialysis tube were presumably associated with the higher MW humic/fulvic acid species.

The Sephadex G-10 fractionation of the lower MW organic fraction from the dialysis fractionation is illustrated in Figure 3.6. Three distinct UV-absorbing species or aggregates were detected; the second and third peaks eluted as a doublet. The first peak (fraction A) corresponded to organic species with nominal MWs of  $\sim 700$  to  $1000$ . On the basis of the organic analysis, 47.2% of the organic content resides in this fraction. The doublet (collected as fraction B) corresponded to organics with nominal MWs of  $\sim 300$  to  $700$  and represented 52.8% the organic content.

No UV-absorbing species were detected in fraction C and the end of the chromatogram, which would be where low MW fulvic acids with MWs  $<300$  would presumably reside. The humic/fulvic acids enrichment factor for fraction C was 1.2, indicating real enrichment over the original well water. Carbon analysis indicated, however, that the organic carbon was spread over the three fractions: A, 46%; B, 34%; and C, 21%. Likely candidates for the non-UV-absorbing compounds in fraction C are the many carboxylic acids previously identified in the ground water at the disposal site (3.1, 3.4).

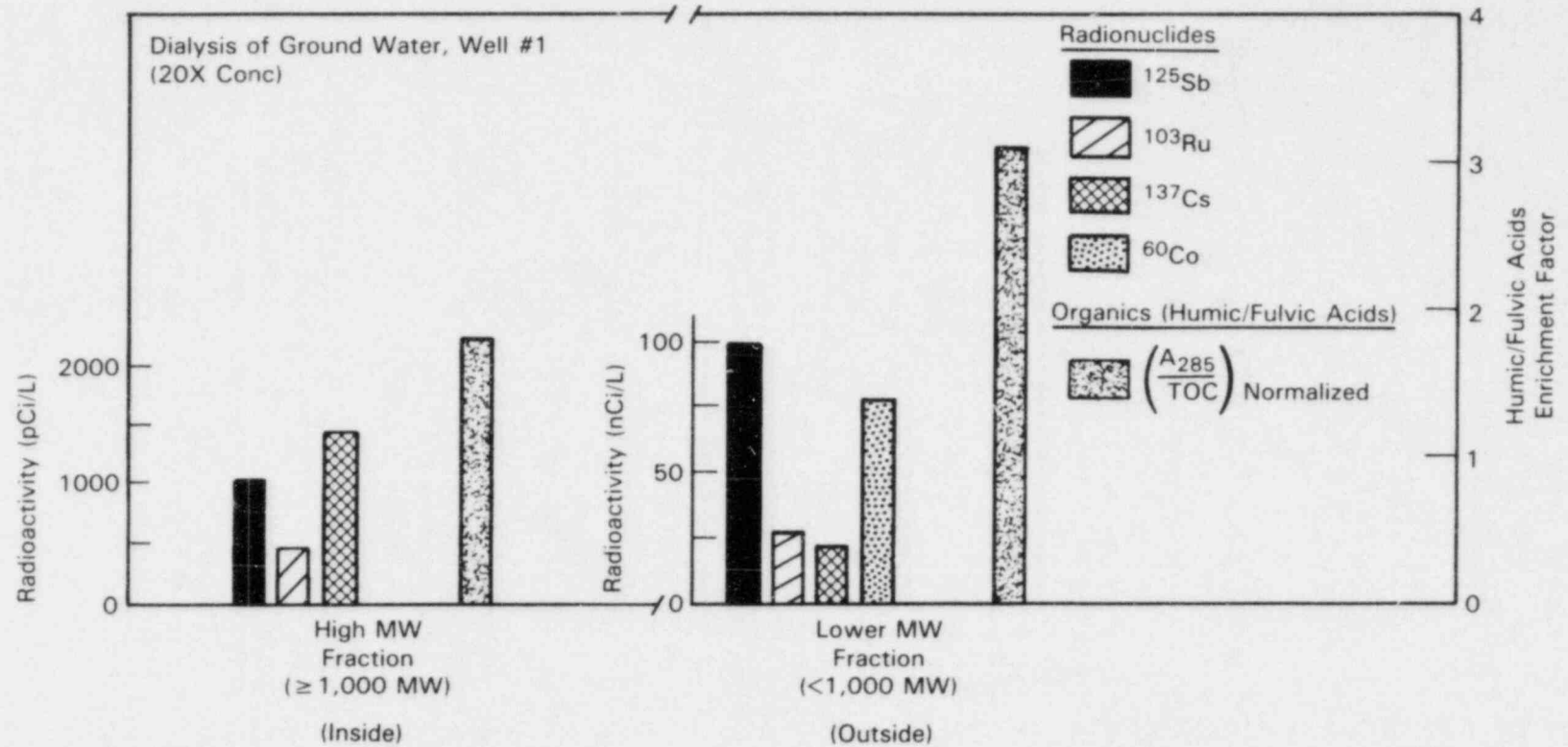


FIGURE 3.5. Dialysis Fractionation and Analysis of Ground Water from Well #1

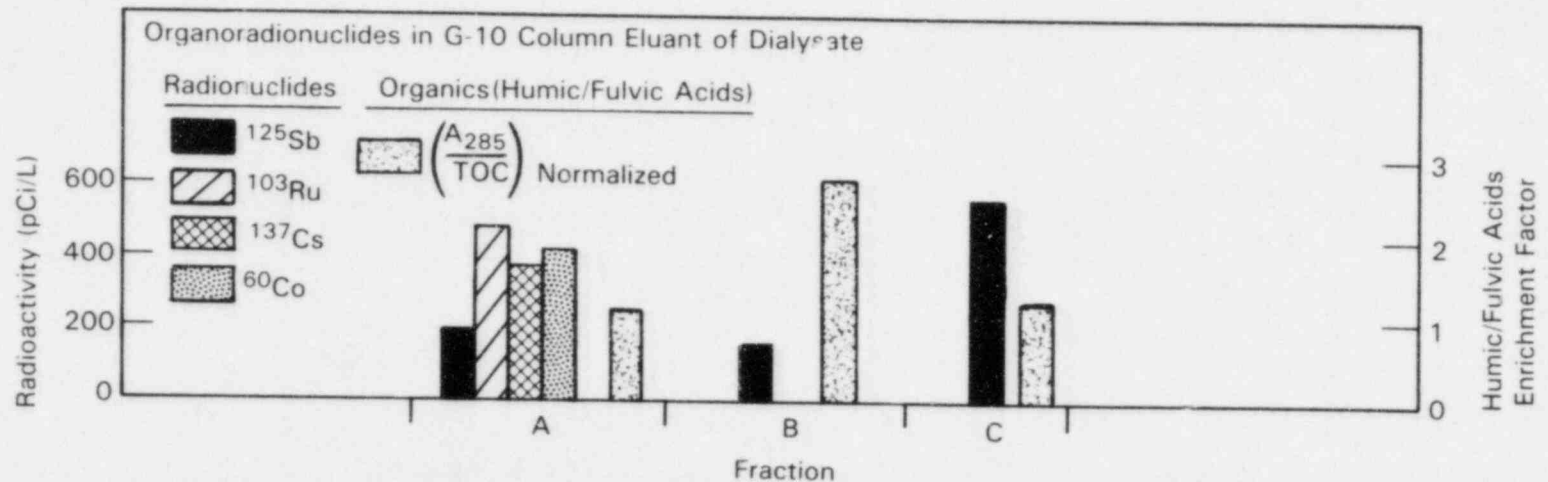
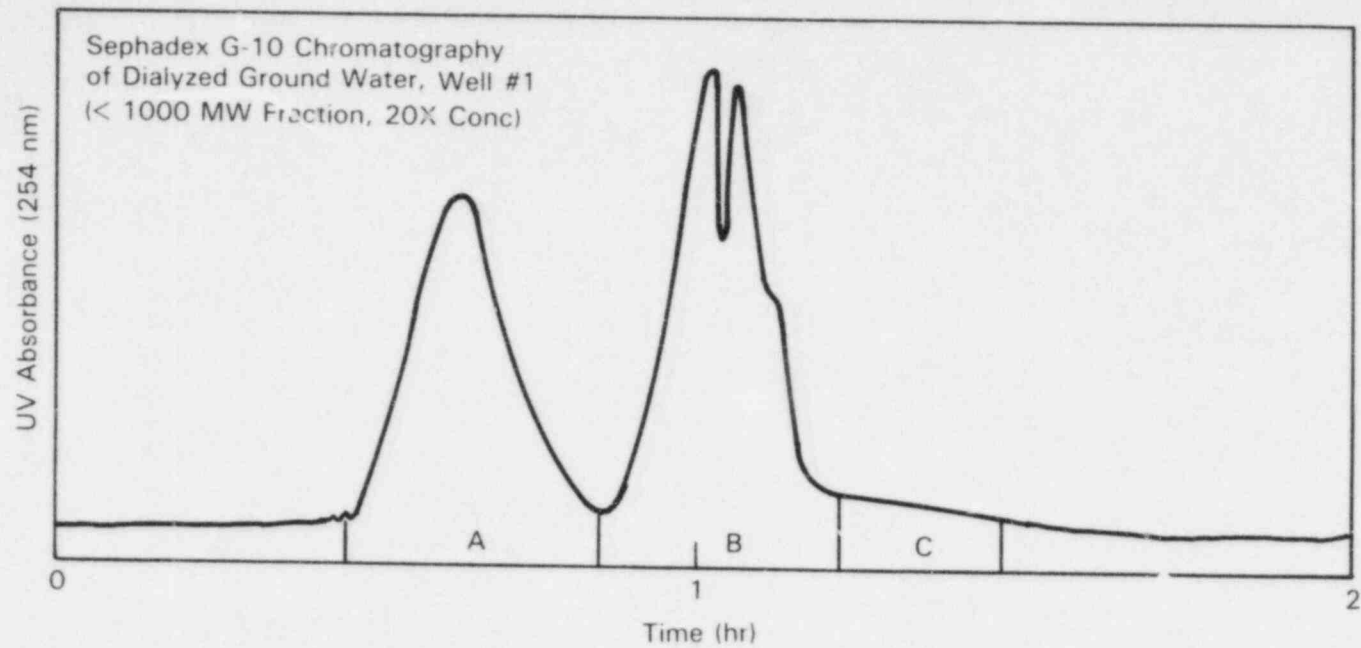


FIGURE 3.6. Sephadex G-10 Fractionation and Analysis of the Lower MW Fraction (MW <1000) from the Dialysis Fractionation



Radionuclide analyses revealed the presence of  $^{125}\text{Sb}$ ,  $^{103}\text{Ru}$ ,  $^{137}\text{Cs}$ , and  $^{60}\text{Co}$  in fraction A, but only  $^{125}\text{Sb}$  was detected in fractions B and C. It would appear that some of the radionuclides in the lower MW (<1000) dialysis fraction are indeed associated with organics having nominal (lower) MWs of ~700 to 1000.

### 3.4 CONCLUSIONS

The Sephadex and dialysis fractionation studies yielded considerable information about the humic/fulvic acids content of the ground water at the disposal site. On the basis of the Sephadex G-10 fractionation, the nominal MW range of the humic/fulvic acids fraction appears to be from a few hundred to over 10,000. However, most of the humic/fulvic acids in the ground water have nominal MWs ranging from several thousand to >700; there appears to be another distribution with MWs of 300 to 700 as well.

The radionuclide concentrations in the ground water are extremely low, but a number of important conclusions can be drawn about the potential association of radionuclides with humic and fulvic acids. On the basis of the dialysis study,  $^{125}\text{Sb}$ ,  $^{103}\text{Ru}$ , and  $^{60}\text{Co}$  are clearly associated with higher MW organics, presumably humic and fulvic acids with nominal MWs >1000. The results of the Sephadex G-50 fractionation study confirm this observation.

The results of dialysis and steric-exclusion fractionation studies agree with previous observations made on the physicochemical forms of these radionuclides (Robertson et al. 1983). Ground water collected from Well #1 in January 1983 contained anionic forms of  $^{60}\text{Co}$ ,  $^{103}\text{Ru}$ , and  $^{125}\text{Sb}$ . The  $^{103}\text{Ru}$  and  $^{125}\text{Sb}$ , in particular, were almost completely anionic. The Sephadex and dialysis studies support the hypothesis that at least some of the anionic charge forms of these three radionuclides result from organoradionuclide complexation. The absence of other radionuclides in the organic fractions (e.g.,  $^{59}\text{Fe}$ ,  $^{65}\text{Zn}$ ,  $^{63}\text{Ni}$ ) does not necessarily preclude their organic complexation. They may simply be below detection limits and/or are not strong emitters. Reexamination of the ground water at much greater concentrations could well reveal the presence of other radionuclides in the humic/fulvic acid fraction.

### 3.5 RECOMMENDATIONS

The low MW organics in the ground water at the disposal site have already been characterized. All of the species identified were naturally occurring organic acids or their diagenesis products. Synthetic, waste-derived organics (e.g., chelating agents) were not detected. Higher MW organics appeared to account for most of the ground water's organic content. In this report, an initial characterization of the higher MW organics, which account for most of the ground water is presented.

The results of this study suggest that higher MW organics are associated with some of the mobile radionuclides at the disposal site. More work needs to be done to characterize the higher MW organics at other field sites and to measure their complexing capabilities to the mobile radionuclide. Chromatographic and analytical procedures exist for isolating and purifying higher MW organics, and humic and fulvic acids in ground water. Once macro amounts of these

species are available, binding studies (e.g., dialysis and potentiometric titration) could be performed with specific radionuclides to measure binding constants, etc. Such information would provide a valuable, much needed organic data base for geochemical modeling of subsurface transport of radionuclides in soil solutions.

## REFERENCES

- N. Ogura. 1974. "Molecular Weight Fractionation of Dissolved Organic Matter in Coastal Seawater by Ultrafiltration." Marine Biology 24:305-312.
- D. Rai and R. J. Serne. 1978. Solid Phases and Solution Species of Different Elements in Geologic Environments. PNL-2651, Pacific Northwest Laboratory, Richland, Washington, 99352.
- D. E. Robertson, A. P. Toste, K. H. Abel, and R. L. Brodzinski. 1983. Radionuclide Migration in Groundwater. NUREG/CR-3554, U.S Nuclear Regulatory Commission, Washington, D.C.
- E. M. Thurman, R. L. Wershaw, R. L. Malcolm, and D. J. Pinckney. 1982. "Molecular Size of Aquatic Humic Substances." Org. Geochem. 4:27-35.
- A. P. Toste, L. J. Kirby, D. E. Robertson, K. H. Abel and R. W. Perkins. 1983. "Characterization of Radionuclide Behavior in Low-Level Waste Sites." IEEE Transactions on Nuclear Science NS-30 (1):580-585.

#### 4.0 ADSORPTION/DESORPTION

The accurate prediction or simulation of radionuclide transport in surface or ground waters requires that 1) radionuclide adsorption/desorption processes be quantitatively described (modeled) in a manner that takes into account and is compatible with changes in the geochemistry of the system and 2) the equations or information base describing adsorption/desorption is incorporated into and solved iteratively with the transport equations.

Amorphous manganese and iron oxides and organic compounds have a high adsorption affinity and may represent the phases that dominate the adsorption/desorption processes in most soils, sediments, and subsoils. For individual radionuclides, these sediment phases have distinct adsorption affinities (binding constants) and adsorption capacities (quantity of binding sites per gram of sediment). Experimental measurement of the adsorption affinity and capacity of individual sinks for a particular radionuclide, combined with the quantification of individual sinks present in a particular soil provides the information base necessary to test the validity of surface coordination modeling approaches for describing equilibrium adsorption/desorption phenomena in real soil systems.

The surface coordination model description of equilibrium adsorption/desorption is compatible with other geochemical reactions and changes in geochemical parameters that can influence radionuclide migration and fate. In its simplest form, the surface coordination approach describes the total adsorption of a radionuclide on all the sinks present in a soil as a linear combination of the adsorption on the individual sinks. The adsorption on each sink is described by the product of the adsorption affinity, the capacity of the individual sinks, and the quantity of the sink present in the soil. More complex descriptions have been used by Honeyman (1984) and Altman (1984) for systems where individual sinks exert a major influence on one another and the simple linear approach begins to break down.

The objective of this task is to 1) experimentally determine the adsorption/desorption behavior of Np(V) on the sediments considered in this study, 2) test the hypothesis that iron oxides dominate the adsorption behavior of Np(V) on these sediments, and 3) test the alternate hypothesis that Np(V) adsorption on these sediments can be described using the surface coordination reaction approach as a combination of Np adsorption on individual and quantifiable soil sinks.

If either of these hypotheses are correct and adsorption can be quantified using this approach, then data and equations describing Np(V) adsorption can be directly incorporated into a competent transport model. The ability to predict or simulate the movement and fate of Np(V) at a particular field site can be tested by quantifying the individual sink(s) that dominate adsorption/desorption in the soils at that site.

## 4.1 ADSORPTION ON AMORPHIC IRON OXIDES AND SEDIMENTS

### 4.1.1 Amorphous Iron

To test the hypothesis that Np(V) adsorption behavior in sediments is dominated by amorphous iron present in the sediment, the Np adsorption on synthetic amorphous iron oxyhydroxide was first characterized. The details of this work have been described in an earlier report (Fruchter et al. 1984). Figure 4.1 summarizes these batch adsorption experiments for several iron concentrations (solid:solution or S:S ratios). The data in Figure 4.1 were modeled (solid lines) with a single Np adsorption reaction and adsorption constant using a surface coordination model (Girvin et al. 1984). For each adsorption curve (Figure 4.1), the adsorption 'edge' is defined as the narrow band of pH for which the percent adsorption increases rapidly with pH. For the range of conditions studied, the adsorption edges occur between pH 5.5 and 6.5. For pH 9.5, the quantity of Np adsorbed approaches 100%, even in the presence of atmospheric CO<sub>2</sub> and strong aqueous carbonate complexes. The shift of the

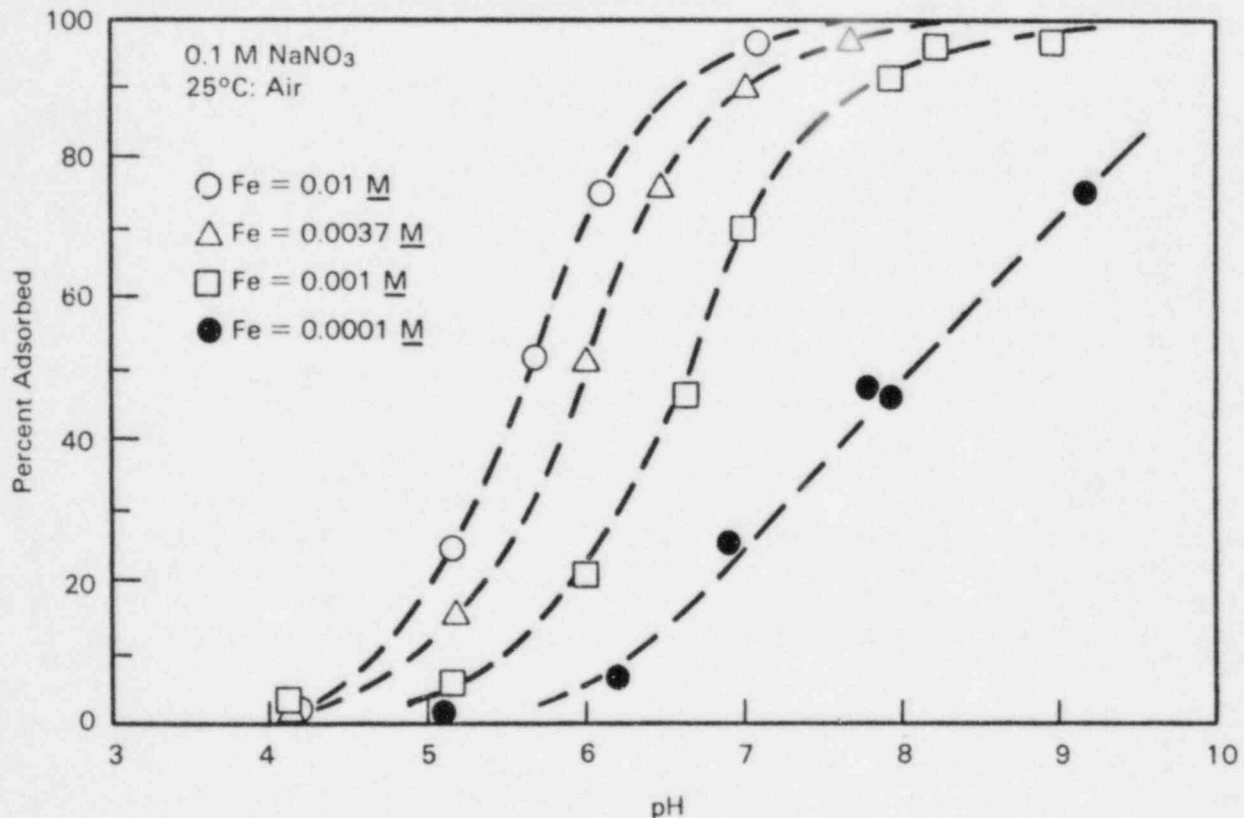


FIGURE 4.1. Np(V) Adsorption on Synthetic Amorphous Iron Oxyhydroxide. Total Np =  $4.7 \times 10^{-12}$  M. Dashed lines are model calculations.

adsorption edge to higher pH as the quantity of available iron decreases is characteristic behavior for adsorption of cations onto oxides (Leckie et al. 1980; Benjamin and Leckie 1981).

#### 4.1.2 Sediments

Data characterizing the four sediments studied here are described in Fruchter et al. (1984). The amorphous iron oxide in composite (<425  $\mu\text{m}$ ) sediment samples, 2-1, 2-2, 3-1, and 3-2, was 40, 26, 65, and 12  $\mu\text{moles Fe/g}$  of sediment, respectively. The amorphous iron oxide was measured using a rapid hydroxylamine hydrochloride extraction (Fruchter et al. 1984) and is an operational definition. Batch adsorption experiments were conducted using  $^{235}\text{Np(V)}$  at several values of pH and S:S ratios that encompass actual field conditions at the site. Sediments were pre-equilibrated for 192 to 240 h in synthetic spring water (Fruchter et al. 1984) at the desired experimental pH before the adsorption experiments were started by adding Np to the suspension of soil and spring water. A contact time of 192 h was used for all adsorption experiments. During the pre-equilibration and adsorption periods, samples were slowly rotated (end over end) except during pH adjustments (addition of strong acid or base). The quantity of Np adsorbed was determined from the  $^{235}\text{Np}$  activity remaining in solution after filtration (18 A).

The adsorption data for sediment 2-1 are shown in Figure 4.2 for several S:S ratios. (The corresponding quantities of amorphous iron in the suspensions are also given.) These data are superimposed over the data in Figure 4.1 to emphasize the similarity in the shape of the adsorption edges and the lateral shift of the edges as the quantity of amorphous iron is varied. Note that the amorphous iron in the sediment is not as effective an adsorbent (per unit weight) as the fresh synthetic amorphous iron. This may be due to a combination of factors: our operational definition of amorphous iron oxide, 2) the 192-h pre-equilibration processes, or 3) the amorphous iron in the sediment has a reduced surface area per unit weight relative to the synthetic amorphous iron.

The adsorption data for sediments 2-2, 3-1, and 3-2 are shown in Figure 4.3 for a S:S ratio of 100 g/L. Data for sediment 2-1 (100 g/L) are also plotted for comparison, and the quantity of suspended amorphous iron for each sediment is given. The similarity in the behavior of the adsorption edges for the synthetic iron and the sediments is again evident. In addition, the data for the sediments show that for a fixed pH, the percent of the total Np adsorbed increases as the amorphous iron increases. Using sediment adsorption data from Figures 4.2 and 4.3 at pH values of 7.0 and 8.0, the increase in adsorption with increasing sediment amorphous iron is clearly shown in Figure 4.4.

The adsorption data obtained to date on four sediments for several pH and S:S values are consistent with the hypothesis that amorphous iron oxide or amorphous oxides control the adsorption behavior of the neptunyl oxycation,  $\text{NpO}_2^+$ , in these sediments (because the sediment TOC concentrations are low). The hydroxylamine hydrochloride extraction data indicated that the amorphous Mn in these sediments was less than 1  $\mu\text{moles/g}$  of sediment. The cation adsorption edge for Mn oxides occurs at significantly lower pH values [ $2 < \text{pH (edge)} < 5$ ]

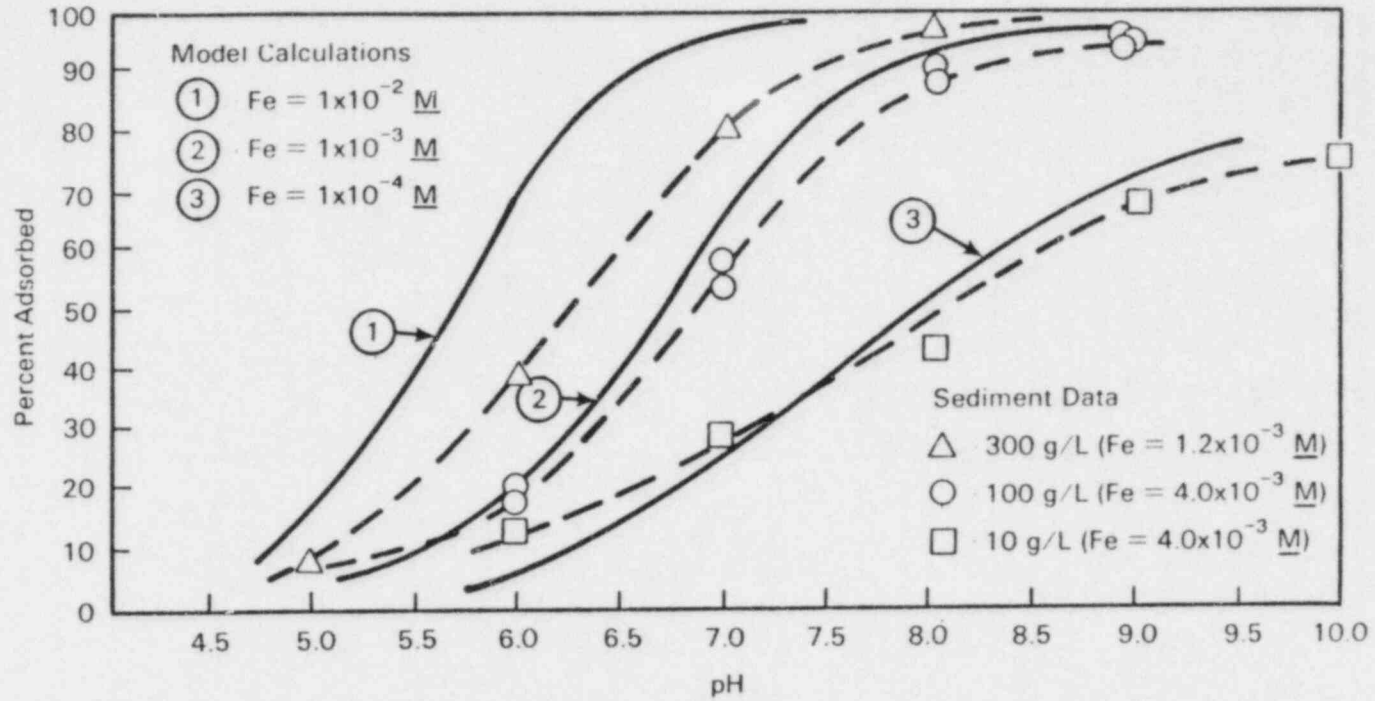


FIGURE 4.2. Np(V) Adsorption on Amorphous Fe and Alluvial Sediment 2-1

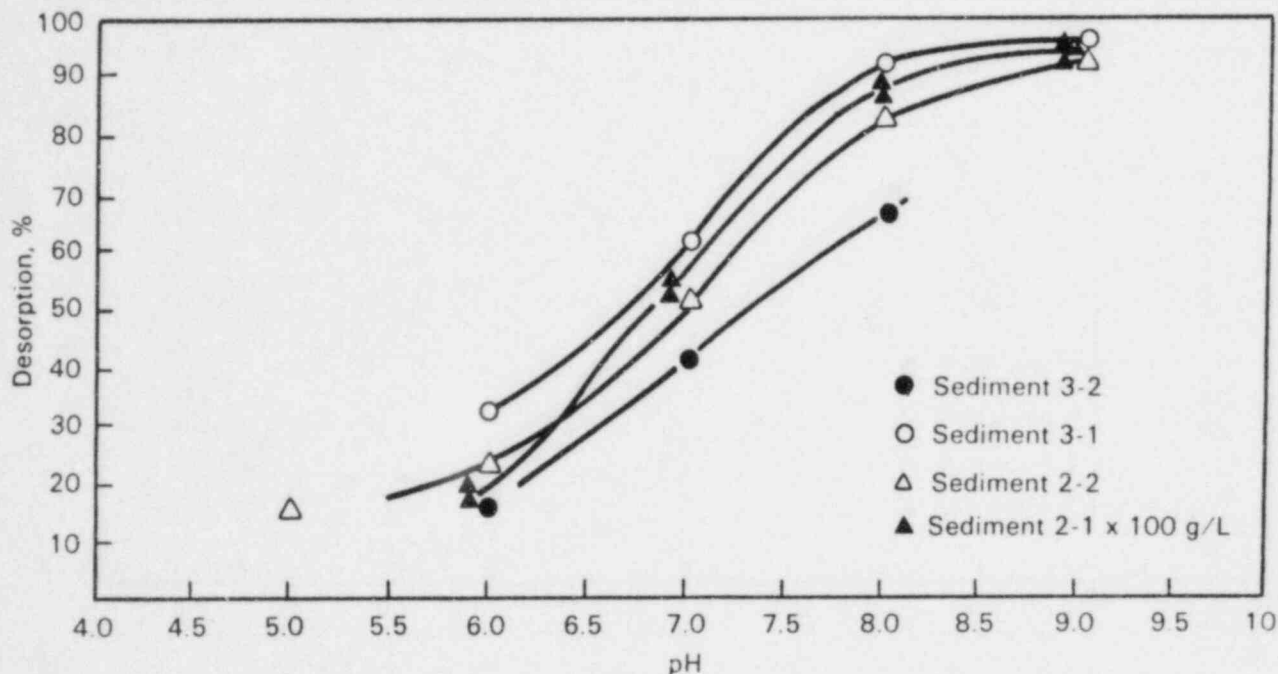


FIGURE 4.3. Np(V) Adsorption on Alluvial Sediments 2-2, 3-1, and 3-2. All data for 100 g sediment/L. Curves are hand drawn through data.

than those observed for Fe oxides [ $5 < \text{pH (edge)} < 8$ ]. Mn oxide would thus shift the edge to a lower pH. Any significant quantity of amorphous Mn oxide would thus make the Fe oxide appear to be more effective as an adsorbent. This is contrary to observations of sediment 2-1. However, the influence of Mn oxide cannot be ruled out without additional study.

#### 4.2 DESORPTION ON AMORPHIC IRON OXIDES AND SEDIMENTS

##### 4.2.1 Amorphous Iron

The reversibility of the Np adsorption reactions were examined by determining the extent of the Np desorption resulting from shifts in pH (Figure 4.5). The solid lines are 4-h adsorption curves for  $10^{-2}$  and  $10^{-3}$  M iron suspensions. Separate adsorption experiments for 3- and 24-h contact times were conducted in the  $10^{-2}$  M iron suspension. The pH of these samples was then adjusted and the desorption followed for 24 h. A large fraction of the Np was desorbed rapidly, within 3 h, from both the 3- and 24-h contact samples. This is followed by a slower desorption component, which is approaching the 4-h adsorption curve at that final pH. Despite the apparent trend, the differences in the desorption between the 3- and 24-h contact time samples are not significant because the differences are less than or equal to the experimental error of  $\pm 3\%$  on the percent adsorption scale. The data show that the adsorption and desorption rates differ and that 75% to 90% of the Np, which is going to desorb at the new pH, desorbs within 24 h. Without additional data (e.g., at 96 to



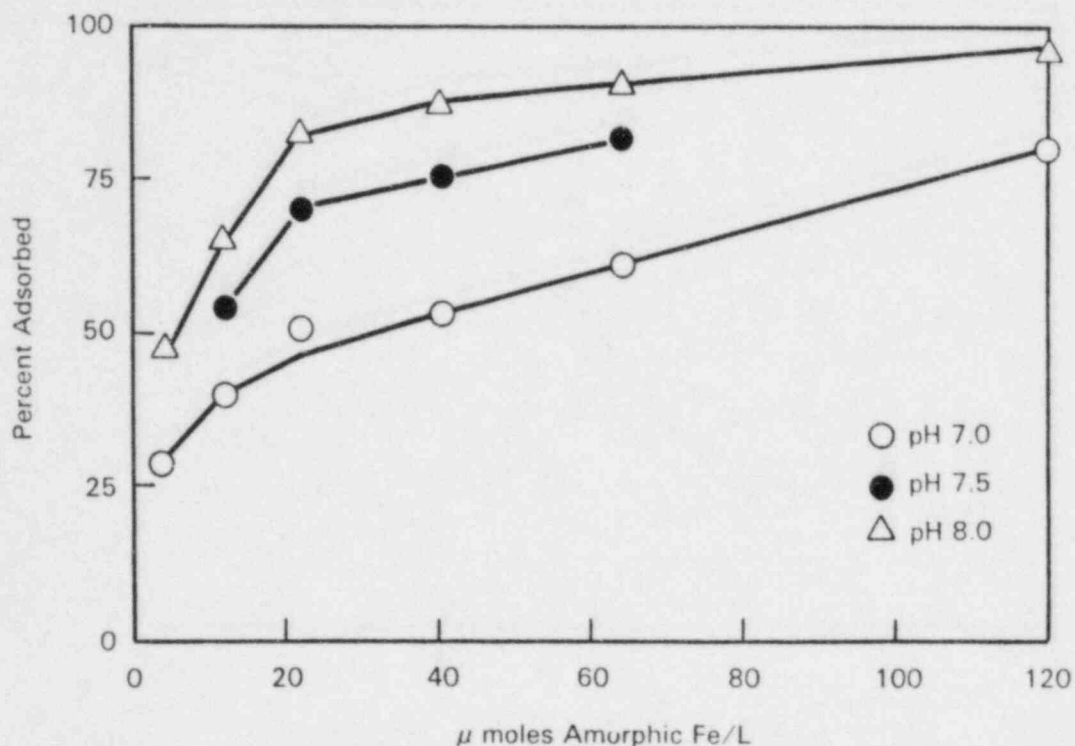


FIGURE 4.4. Relation Between Np(V) Adsorption and Micro Moles of Amorphous Iron Per Liter in Suspension. Data taken from Figures 4.2 and 4.3.

144 h), we cannot establish the complete thermodynamic reversibility of the Np(V) adsorption/desorption reaction on amorphous iron oxyhydroxide. However, these data suggest that reversibility is a reasonable first approximation.

#### 4.2.2 Sediments

The desorption experiments conducted on sediments 2-1, 2-2, 3-1, and 3-2 showed that after a 192-h contact time, at pH 8, the desorption of Np(V) between pH 6.0 and 8.0 was complete after 24 h (within the experimental error of  $\pm 4\%$  on the percent adsorption scale). These results are shown in Figure 4.6 for 100 g/L sediment suspensions. Based on this single set of experiments (run in duplicate) the adsorption of Np(V) on these sediments appears to be reversible. Note that the rate of desorption exceeds the adsorption rate (170 h) by at least a factor of six on these sediments. The experimental procedures used for desorption experiments were identical to those used for adsorption experiments, except that samples were not pre-equilibrated before adding the  $^{235}\text{Np}$ . This experimental difference was shown earlier not to affect the adsorption rate; however, it may affect the desorption rate and thus, the conclusion that the adsorption of Np(V) on these sediments is a reversible reaction. Additional experimental data are needed to eliminate this ambiguity regarding the reversibility of Np(V) on sediments.

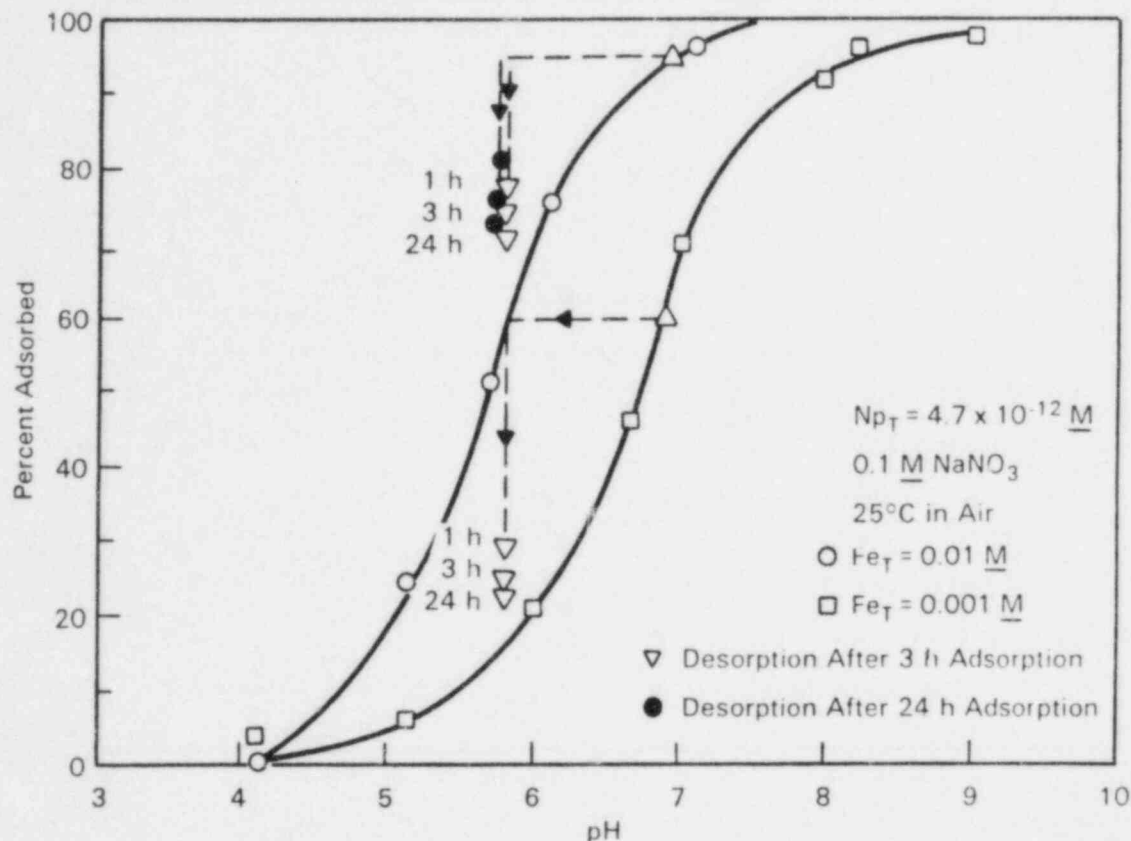


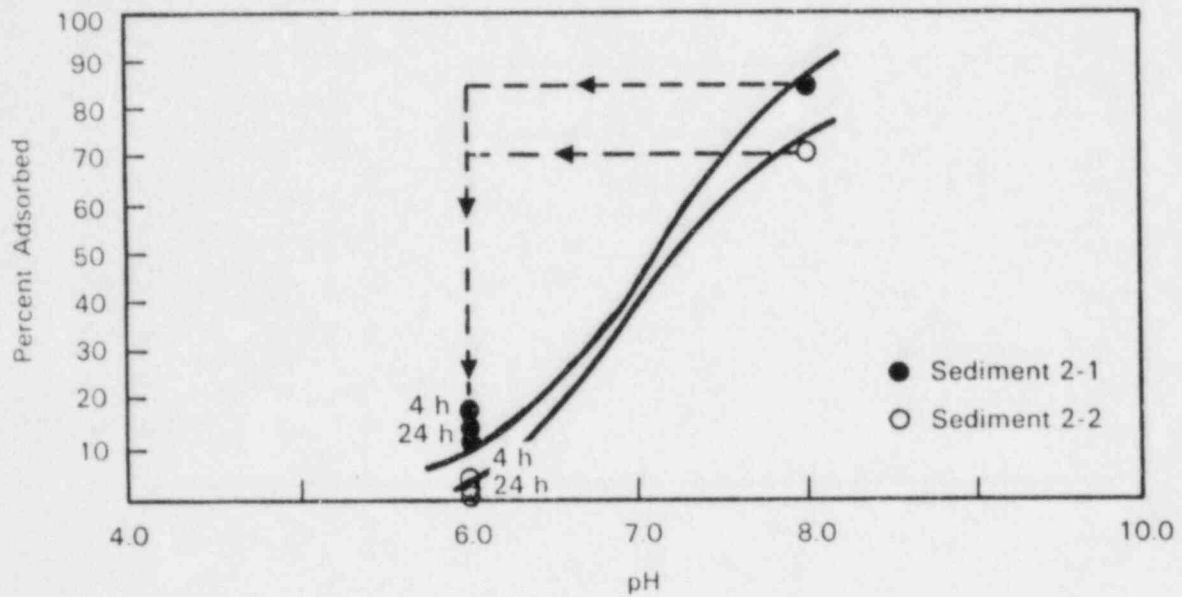
FIGURE 4.5. Adsorption/Desorption of Np(V) on Amorphous Iron Oxyhydroxide for 3-h and 24-h Contact Time. Desorption measured 1, 3 h, and 24 h after pH adjustment. Solid line is adsorption data from previous experiments. Desorption path shown by dashed lined by pH adjustment.

#### 4.3 MODELING OF ADSORPTION/DESORPTION

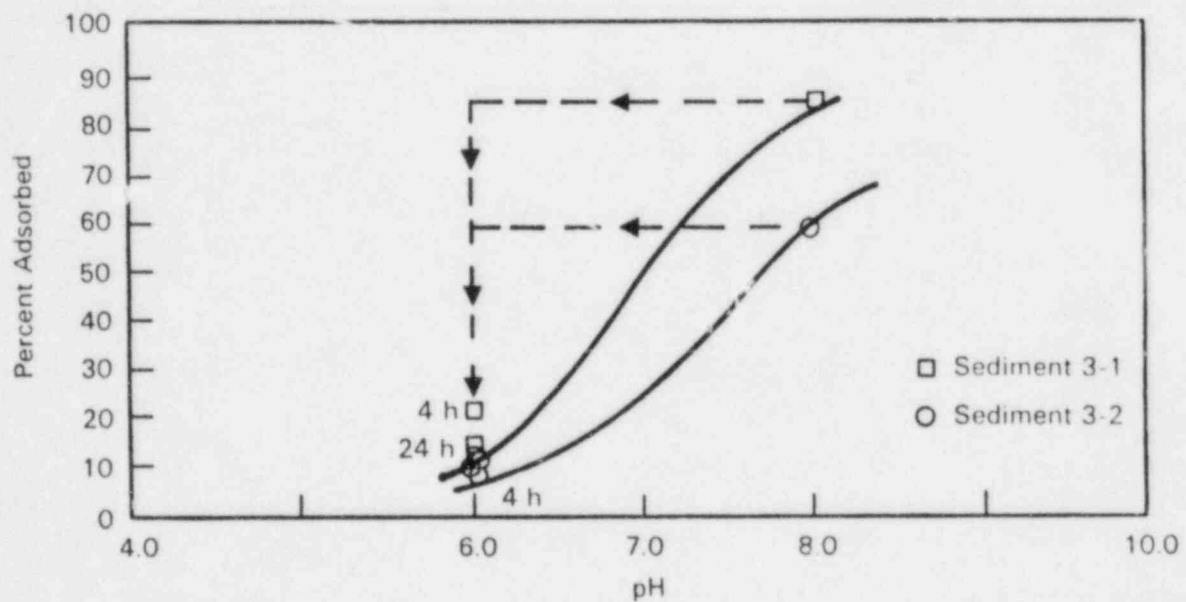
The equilibrium adsorption data for the amorphous iron oxyhydroxide has been successfully modeled using the surface coordination reaction approach as shown in Figure 4.1 and described elsewhere (Girvin et al. 1984). Preliminary adsorption data on the sediments studied suggest that the Np(V) adsorption reactions are reversible. Thus, the equilibrium adsorption data for Np(V) obtained in this study could be used in future programs to test the applicability of the surface coordination modeling approach to real systems.

#### 4.4 CONCLUSIONS

- Np[V] is strongly bound to amorphous iron oxyhydroxide ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ), and the adsorption can be described by surface coordination models of adsorption.



(a)



(b)

**FIGURE 4.6.** Adsorption/Desorption Data for Np(V) on Alluvial Sediments for 192-h Contact Time. Solid lines are adsorption curves from earlier data. The pH 8 points are adsorption data. Dashed line is pH adjusted desorption path. The points at pH 6 are desorption data after 4 and 24 h.

- Np[V] adsorption on  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  for the four sediments studied approaches complete reversibility within 24 h.
- The Np adsorption data obtained to date on four low organic carbon sediments are consistent with the hypothesis that amorphous iron oxides or amorphous oxides in the sediment determine the adsorption behavior of the neptunyl oxyocation,  $\text{NpO}_2^+$ .
- Oxidation state analysis of Np in sediment suspensions is consistent with, but does not prove, the hypothesis that Np[V] adsorbed from solution exists as Np[V] while bound to these sediments (Fruchter et al. 1984).

The results reported here strongly support our hypothesis that iron or other oxides dominate the adsorption behavior of these sediments. Competent geochemical modeling of existing data would provide significant additional insight into 1) the role played in sediments, soils, and subsoils by these oxides in controlling the attenuation of Np(V) and other radionuclides; and 2) the likelihood that quantification of oxide and other sinks (which dominate adsorption/desorption) in the soils at a given site can be used as input for adsorption models to accurately describe radionuclide attenuation in transport calculations.

#### 4.5 RECOMMENDATIONS

The information obtained from this study suggests the importance of iron and other oxide sinks in controlling the adsorption/desorption behavior of Np(V) on sediments. A continued experimental and modeling effort is needed to

- further establish the reversibility of Np(V) adsorption on sediments
- test the applicability of the surface coordination reaction approach for modeling sediment data
- determine the adsorption/desorption behavior of Np(V) on additional soils of differing character (e.g., higher organic carbon and manganese oxides and differing acidities)
- test the hypothesis that Np(V) adsorption/desorption on a wide class of soil types can be described using the surface coordination reaction approach (i.e., as a surface combination of reactions on individual and quantifiable soil sinks).

## REFERENCES

- R. S. Altman. 1984. "Copper Binding in Heterogeneous Multicomponent Aqueous Systems: Mathematical and Experimental Modeling." Ph.D. Thesis, Stanford University, Stanford, California.
- M. M. Benjamin. 1979. "Effects of Competing Metals and Complexing Ligands on Trace Metals Adsorption at the Oxide/Solution Interface." Ph.D. Thesis, Stanford University, Stanford, California.
- M. M. Benjamin and J. O. Leckie. 1981. "Multiple Site Adsorption of Cd, Cu, Zn and pH on Amorphous Iron Oxyhydroxide." J. Colloid Int. Sci. 79:209.
- G. A. Burney and R. M. Harbour. 1974. Radiochemistry of Neptunium. NAS-NS-3060, Savannah River Laboratory, Savannah, Georgia, pp. 230.
- P. R. Danesi, R. Chiarizia, G. Scibena, and G. D'Alesandro. 1971. "Stability Constants of Nitrate and Chloride Complexes of Np(IV), Np(V) and Np(VI) Ions." J. Inorg. Nucl. Chem. 33:3503-3510.
- A. R. Felmy, D. C. Girvin, and E. A. Jenne. 1984. MINTEQ - A Computer Program for Calculating Aqueous Geochemical Equilibria. EPA Report, EPA-600-3-84-032, U.S. Environmental Protection Agency, Cincinnati, Ohio.
- J. S. Fruchter, et al. 1984. Radionuclide Migration in Ground Water: Annual Report for Fiscal Year 1983. NUREG/CR-3712, U.S. Nuclear Regulatory Commission, Washington, D.C.
- D. C. Girvin, A. P. Schwab, L. L. Ames, and J. E. McGarrah. 1984. Np Adsorption on Amorphous Iron Oxyhydroxide. PNL-SA-11229, Pacific Northwest Laboratory, Richland, Washington.
- B. D. Honeyman. 1984. "Cation and Anion Adsorption at the Oxide/Solution Interface in Systems Containing Binary Mixtures of Adsorbents; An Investigation of the Concept of Adsorptive Additivity." Ph.D. Thesis, Stanford University, Stanford, California.
- F. Kraus and K. A. Nelson. 1948. The Hydrolytic Behavior of Uranium and the Transuranic Elements. AECD-1864, U.S. Atomic Energy Commission, Washington, D.C.
- J. O. Leckie, M. Benjamin, K. Hayes, G. Kaufman, and S. Altmann. 1980. Adsorption/Co-Precipitation of Trace Elements from Water with Iron Oxyhydroxide. Final Report, EPRI RP-910, Electric Power Research Institute, Palo Alto, California.
- L. Maya. 1983. "Hydrolysis and Carbonate Complexation of Dioxoneptunium (V) in 1.0 M NaClO<sub>4</sub> at 25°C." Inorg. Chem. 22:2093-2095.

- K. H. Schmidt, S. Cordon, R. C. Thompson, and J. C. Sullivan. 1980. "A Pulse Radiolysis Study of the Reduction of Neptunium (V) by the Hydrated Electron [1]." J. Inorg. Nucl. Chem. 42:611-615.
- E. P. Sevost'yanova and G. V. Khalturin. 1976. "Hydrolytic Behavior of Neptunium (V)." Radiokhimiya 18(6):870-876.

## 5.0 GEOCHEMICAL MODELING

Geochemical modeling has proven to be a valuable tool in interpreting the analytical results collected by the research staff at low-level waste burial sites. Our geochemical modeling results to date have assisted predictions of radionuclide mobility at other sites from the chemical and physical characteristics of the ground waters. As the geochemical modeling capabilities are further refined, the ability to predict the radionuclide mobility in varying environments will be enhanced.

### 5.1 COMPARISON OF MEASURED AND PREDICTED RESULTS

Analytical measurements of the concentration and charge-form of radionuclides in the ground water at this low-level waste site, using the Battelle large volume water sampler, have indicated that the mobile charge-forms of radionuclides are primarily anionic and nonionic (Robertson et al. 1981, 1983; Fruchter et al. 1984). Geochemical modeling of these waters using the radionuclide concentration, the concentration of major and trace stable-element constituents in the water, and the physical characteristics of the water, resulted in very good agreement between the analytical and calculated charge-form speciation for 13 of the 22 radionuclides studied. Comparison of field observation and calculated charge-form distribution for 13 of the radionuclides is given in Table 5.1. From the predicted aqueous speciation of these radionuclides, it was determined that those radionuclides that occurred in the water as primarily the uncomplexed cation such as cesium, cerium, and manganese were the most greatly retarded. Furthermore for the other radionuclides for which there was very good agreement between the analytical and predicted charge-form, the mobile species are the anionic oxyhydroxy complexes. For example, the mobile species of Mo, Tc, and Np are  $\text{MoO}_4^-$ ,  $\text{TcO}_4^-$ , and  $\text{NpO}_4^-$ .

For nine of the radionuclides, significant discrepancies were noted between the analytical and predicted charge-form speciation. These differences could be ascribed to organic complexation, redox disequilibria, and/or inadequate thermodynamic data. The geochemical model does not yet contain thermodynamic constants to represent the complexation of the radionuclides with natural dissolved organic matter; therefore, the role of organic complexation could not be determined quantitatively. Several of these radionuclides, however, are commonly found associated with the humic and fulvic acid fraction of the soil solution. Furthermore, recent measurements of high MW organic fractions and associated radionuclides supports the role of organic complexation for Ru, Co and Sb (see Section 3). Additional radionuclides believed to form mobile anionic organic complexes are iron, zinc, nickel, and chromium. Furthermore, these results essentially agree with those at Maxey Flats, Kentucky, where synthetic organic chelating agents increased the mobility of some radionuclides (Means et al. 1978; Rees and Cleveland 1982; Toste et al. 1983, 1984). These results suggest that if the organic acid content of the soil solution is increased, some radionuclides, such as iron, zinc, cobalt, and nickel, will become more mobile.

TABLE 5.1. Comparison of Field Observations and Calculated Species for Distribution Forms of Radionuclides at the Low-Level Waste Disposal Site

Radio-Nuclide	Field Observations		Relative Mobility	Predicted Solution Species
	Trench Water	Spring Water		
Tc	Anionic	Anionic	High	$\text{TcO}_4^-$
Np	Cationic	BD	Low	$\text{NpO}_2^+$
I	Anionic (49% Org.)	Anionic (57% Org.)	High	$\text{I}^-$
Cs	Cationic	BD	Low	$\text{Cs}^+$
Sr	Cationic	Cationic	High	$\text{Sr}^{+2}$
Ni	Cationic	Nonionic, Anionic	Low	$\text{Ni}^{+2}$ , $\text{NiOH}^-$ , $\text{Ni(OH)}_2^0$
Co	90-99% Cationic	50-75% Anionic	High	$\text{Co}^{+2}$
Ce	Cationic	BD	Low	$\text{Ce(OH)}_2^+$
Ru	30-96% Cationic	80-93% Anionic	High	$\text{Ru(OH)}_2^{+2}$
Sb	Variable	Nonionic	High	$\text{HSbO}_2^0$ , $\text{Sb(OH)}_3^0$ , $\text{Sb(OH)}_6^-$
Fe	50-70% Cationic	67% Anionic	Low	$\text{Fe}^{+2}$
Zn	80-99% Cationic	BD	Low	$\text{Zn}^{+2}$ , $\text{ZnHCO}_3^+$ , $\text{ZnSO}_4^0$ $\text{ZnCO}_3^0$ , $\text{ZnOH}^+$ , $\text{Zn(OH)}_2^0$ $\text{Zn(CO}_3)_2^{-2}$
Mn	Cationic	BD	Low	$\text{Mn}^{+2}$ , $\text{MnHCO}_3^+$ , $\text{MnSO}_4^0$

BD = Lower Than Detection Limit

In addition to potential organic complexation of Sb, the geochemical modeling also identified a potential redox disequilibrium for antimony in the ground waters. Redox disequilibrium is common in ground waters (Jenne et al. 1980; Jenne 1981); however, the redox couples are seldom measured. The results of the geochemical modeling further emphasize the need for redox couple determination in ground waters. If inorganic complexation only is considered, the geochemical modeling suggested that the antimony is oxidized during transport in the ground water in contrast to the analytical data, which suggest that



based on the charge-form distribution the antimony is reduced during the transport in the ground water. For many radionuclides, the mobility, complexation, and adsorption processes are influenced by the oxidation state of the radionuclide. For example, arsenic is much more strongly adsorbed in the As(III) oxidation state than the As(V) oxidation state.

The geochemical model was also used to determine the solid phases that are in equilibrium with or oversaturated with respect to the ground waters. This information was used to initially identify potential sorption sinks and to identify the controls that exist on the solution chemistry. Then the geochemical model was used to evaluate the analytical data by testing for oversaturation of the solution with respect to certain well-recognized solubility controls, solids known to readily precipitate from oversaturated solutions, or solids identified in the sediments. The modeling results suggest that the silicate solid phases, such as quartz and feldspars, identified in the soils by X-ray diffraction, dissolve as the water travels from the trench to the spring. The ground waters are also predicted to be in equilibrium with calcite that would control the calcium and/or carbonate concentrations in the ground water. The waters were calculated to be oversaturated with respect to aluminosilicates such as kaolinite and the aluminum oxide, gibbsite, which suggests that there is some analytical error in the aluminum determinations or organic complexation. In fact, Kennedy et al. (1974) concluded that unless a 0.1- $\mu\text{m}$  filter is used, the presence of small clay particles is quite likely to result in analytical errors. Similarly, the solutions were predicted to be oversaturated with respect to ferrihydrite, which also suggests an analytical error in the iron determinations or organic complexation and further emphasizes the need for proper filtering of the water samples before analytical measurements are made. Other potential solubility controls were identified from the geochemical modeling. These include otavite for control of the cadmium concentration, cerussite for control of the lead concentration, chloropyromorphite for the lead or phosphate,  $\text{ZnSiO}_3$  for zinc,  $\text{MnHPO}_4$  for manganese or phosphate, wulfenite for lead or molybdenum, and  $\text{CeO}_2$  for cerium.

## 5.2 CONCLUSIONS

The geochemical modeling thus permitted identification of the specific mobile and nonmobile chemical species for many radionuclides and emphasized the importance of organic complexation and redox couple measurements at future sites. Furthermore, the geochemical modeling allowed us to identify those solid phases that control the concentration of certain constituents in the ground water and which solid phases dissolve or precipitate from the waters. The geochemical modeling also identified two potential analytical problems. Thus, the geochemical modeling has proven to be an important interpretive tool and can assist in predicting the potential mobility and retardation of radionuclides at other sites.

## 5.3 RECOMMENDATIONS

Geochemical modeling proved to be a valuable interpretive tool at this site and can be used in the interpretive mode at other sites as well. However, its capabilities need to be expanded before the model can be used as a truly

predictive tool. Thermodynamic constants for describing organic complexation need to be obtained for both classes of organic compounds and individual organic compounds. The geochemical model contains adsorption models, but additional thermodynamic constants for adsorption are needed for soils and sediments. Further research is needed to identify the important controls on adsorption in soil and sediment systems and to determine the appropriate thermodynamic adsorption constants. Once these data on organic complexation and adsorption are available, the capability of the geochemical model to predict radionuclide behavior at other sites will be greatly enhanced. The confidence in the predictive capability could be increased via validation studies based on comparison of the geochemical modeling results with laboratory and field data.

## REFERENCES

- J. S. Fruchter, et al. 1984. Radionuclide Migration in Ground Water: Annual Report for Fiscal Year 1983. NUREC/CR-3712, U.S. Nuclear Regulatory Commission, Washington, D.C.
- E. A. Jenne, J. W. Ball, J. W. Burchard, P. V. Vivit, and J. H. Banks. 1980. "Geochemical Modeling: Apparent Solubility Controls on Ba, Zn, Cd, Pb and F in Waters of the Missouri Tri-State Mining Area." In Trace Substances in Environmental Health-XIV, D. D. Hemphill, ed., pp. 353-361, Univ. of Missouri, Columbia, Missouri.
- E. A. Jenne. 1981. "Speciation of Aqueous Contaminants - Role of the Geochemical Model." In Aqueous Speciation of Dissolved Contaminants, pp. 39-53, U.S. National Bureau of Standards, Gaithersburg, Maryland.
- V. C. Kennedy, G. W. Zellweger, and B. F. Jones. 1974. "Filter Pore-Size Effects on the Analysis of Al, Fe, Mn and Ti in Water." Water Resources Research 10:785-790.
- J. L. Means, D. A. Crerar, and J. O. Duguid. 1978. "Migration of Radioactive Wastes: Radionuclide Mobilization by Complexing Agents." Science 200:1477-1481.
- T. F. Rees and J. M. Cleveland. 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, pp. 41-52, International Atomic Energy Agency, Vienna, Austria.
- D. E. Robertson, A. P. Toste, K. H. Abel, and R. L. Brodzinski. 1981. Annual Progress Report for 1981, Influence of the Physicochemical Forms of Radionuclides During Migration in Ground Waters. U.S. Nuclear Regulatory Commission, Washington, D.C.
- D. E. Robertson, A. P. Toste, K. H. Abel, and R. L. Brodzinski. 1983. Radionuclide Migration in Ground Water Annual Progress Report for 1982. NUREG/CR-3554, U.S. Nuclear Regulatory Commission, Washington, D.C.
- A. P. Toste, L. J. Kirby, and T. R. Pahl. 1984. "Role of Organics in the Subsurface Migration of Radionuclides in Groundwater." In Geochemical Behavior of Disposed Radioactive Waste ACS Symposium Series No. 246, pp. 251-270, American Chemical Society, Washington, DC.
- A. P. Toste, L. J. Kirby, D. E. Robertson, K. H. Abel, and R. W. Perkins. 1983. "Characterization of Radionuclide Behavior in Low-Level Waste Sites." IEEE Transactions on Nuclear Science NS-30(1):580-585.

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6 DATE REPORT ISSUED

MONTH

YEAR

March

1985

5 AUTHOR(S)

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7 PERFORMING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code)

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8 PROJECT/TASK/WORK UNIT NUMBER

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12 SUPPLEMENTARY NOTES

13 ABSTRACT (200 words or less)

For the past several years, data on radionuclide migration in ground water at a low-level disposal site were collected. Most of the radionuclides were removed in the disposal basin and trench by either precipitation or adsorption mechanisms. However, three radionuclides <sup>60</sup>Co, <sup>106</sup>Ru, and <sup>125</sup>Sb showed somewhat greater than expected mobility. The elements of these three isotopes were found to be in either anionic or nonionic charge-forms. Complexes with both natural and man-made organics were implicated in the increased mobility, particularly in the case of <sup>60</sup>Co. Characterization studies of the organic fraction were performed. Ruthenium-103, <sup>60</sup>Co, and <sup>125</sup>Sb were found to be associated with the higher molecular weight organics, particularly humic and fulvic acids with molecular weights greater than 1000. Studies were also performed that proved the hypothesis that the adsorption behavior of <sup>235</sup>Np on soils of the site is dominated by adsorption on iron hydroxide. Finally, geochemical modeling of the chemical and charge form data showed the ground water to be in equilibrium with several solids that could be important in controlling the concentrations of trace elements and radionuclides.

14 DOCUMENT ANALYSIS - a KEYWORDS/DESCRIPTORS

radionuclide  
ground water  
migration  
speciation  
transport

b IDENTIFIERS/OPEN ENDED TERMS

15 AVAILABILITY STATEMENT

Unlimited

16 SECURITY CLASSIFICATION

(This page)

Unclassified

(This report)

Unclassified

17 NUMBER OF PAGES

18 PRICE

UNITED STATES  
NUCLEAR REGULATORY COMMISSION  
WASHINGTON, D.C. 20555

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