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Characterization of Radionuclide-Chelating Agent Complexes Found in Low-Level Radioactive Decontamination Waste

Literature Review

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Pacific Northwest National Laboratory
Operated by
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Abstract

Under the regulations outlined in 10 CFR 61, the U.S. Nuclear Regulatory Commission is responsible for regulating the safe land disposal of low-level radioactive wastes that may contain organic chelating agents. Such agents include ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), picolinic acid, oxalic acid, and citric acid, and can form radionuclide-chelate complexes that may enhance the migration of radionuclides from disposal sites.

Data from the available literature indicate that chelates, most notably picolinate and EDTA, can leach from solidified decontamination wastes in moderate concentration (i.e., 1-100 ppm) and can potentially complex certain radionuclides in the leachates. The effects of the formation of such radionuclide-chelate complexes on the migration of radionuclides in groundwater systems is still difficult to quantitatively predict owing to the dependence of such migration on several factors including the chemical composition of the groundwater, the specific adsorbing surfaces present in the soils, and the ability of microorganisms to biodegrade the chelates. However, in general it appears that both EDTA and DTPA have the potential to mobilize radionuclides from waste disposal sites because such chelates can leach in moderate concentration, form strong radionuclide-chelate complexes, and can be recalcitrant to biodegradation. It also appears that oxalic acid and citric acid will not greatly enhance the mobility of radionuclides from waste disposal sites because these chelates do not appear to leach in high concentration, tend to form relatively weak radionuclide-chelate complexes, and can be readily biodegraded. In the case of picolinic acid, insufficient data are available on adsorption, complexation of key radionuclides (such as the actinides), and biodegradation to make definitive predictions, although the available data indicate that picolinic acid can chelate certain radionuclides in the leachates.

Contents

Figures

Tables

Executive Summary

A variety of chemical decontamination processes are used to remove the build-up of radioactive-activated metals and corrosion products from the cooling systems of nuclear power plants. All of these decontamination processes use chelating agents, such as ethylenediaminetetraacetic acid (EDTA), picolinic acid, oxalic acid, citric acid, and less frequently, diethylenetriaminepentaacetic acid (DTPA), to complex the released radionuclides. The complexed radionuclides and any excess uncomplexed chelates are then removed onto cation- or anion-exchange resins. The U.S. Nuclear Regulatory Commission (NRC), as defined in 10 CFR 61, is responsible for regulating the disposal of such wastes, including providing regulatory criteria for the co-disposal of organic chelating agents that have the potential to enhance the migration of radionuclides away from disposal sites.

One of the principal pathways for radionuclides migrating away from a disposal site is contact with infiltrating recharge water. The presence of chelating agents in the wastes could enhance the subsequent migration of radionuclides in groundwaters if 1) sufficient quantities of chelating agents can leach from the wastes, 2) the leached chelating agents form strong radionuclide-chelate complexes, 3) the chelating agents or the radionuclide-chelate complexes do not adsorb to soils or sediments, and 4) the leached chelating agents or radionuclide-chelate complexes do not undergo degradation processes, such as biodegradation, that destroy the chelating agents.

Therefore, this literature review was focused on the following areas: 1) the nature and composition of reactor decontamination solutions; 2) the leaching chemistry studies of the solidified decontamination wastes; 3) the aqueous complexation of radionuclides, including the thermodynamic data available for calculating the stability of radionuclide-chelate complexes and analytical methods for identifying specific radionuclide-chelate complexes; 4) the adsorption of chelating agents and metal-chelate complexes in soils or specific soil components (i.e., oxides and clay minerals); and 5) the biodegradation of the chelates and radionuclide-chelate complexes present in decontamination solutions.

In reviewing the leaching and decontamination chemistry studies, it appears that the principal decontamination processes currently used are the following: 1) the low-oxidation-state metal ions (LOMI) process, which is used in about 65 percent of the current power plant decontaminations and uses picolinic and formic acid; 2) the CAN-DEREM process, which uses EDTA and citric acid; and 3) the CITROX process, which uses citric and oxalic acids. Based upon the few studies completed, it appears that organic chelating agents can leach moderately from solidified cements and can increase radionuclide and transition-metal leach rates by factors of 10 to 100. The resulting leach rates still appear to be low, possibly because of the importance of pH-dependent precipitation reactions. In addition, some of these waste forms appear to be physically unstable in low-ionic-strength solutions.

The review of the thermodynamic data available for aqueous complexation reactions of chelates with metals and radionuclides focused on tabulating the data for metal-chelate complexes of EDTA, DTPA, picolinic acid, oxalic acid, and citric acid with selected radionuclides (i.e., neutron activation products, fission products, and actinides). A critical evaluation of these data was not performed because several such reviews have been published recently. Few data more recent than the latest critical review (i.e., Smith and Martell 1989) were

found. Therefore, the majority of the data were compiled from the published critical reviews. As expected, this tabulation revealed that a large amount of data is available for metal complexes with all of the ligands of interest in this study, although fewer data are available for DTPA and picolinic acid than for the other chelates. Unfortunately, far fewer data are available for the actinide-chelate complexes that could be present in the decontamination wastes. Based upon these data, it appears that the most important complexes involve EDTA and picolinic acid. Oxalic acid and citric acid do not appear to be present in sufficiently high concentration or to be sufficiently strong chelating agents to form important metal-chelate complexes.

Analytical methods for identifying radionuclide-chelate complexes in the leachate solutions are complicated by the low concentrations of chelates and metals found in the reviewed studies that unfortunately only include data on cement solidified spent resins while current practice is to dispose of the spent resins directly in high integrity containers. We can not predict what the expected concentrations/ radioactivity of the chelating agents, stable metals and radionuclides would be in leachates from the resins themselves. Although appropriate analytical procedures are still being developed, some promising techniques are becoming available. One such technique under development couples liquid chromatography/mass spectrometry (LC/MS) with inductively coupled mass spectrometry (ICP/MS) to allow the simultaneous determination of organic and metal components. Other techniques are also being investigated. Such direct analytical determinations, once passed the development stage, could complement the thermodynamic calculations in identifying the specific radionuclide-chelate complexes of concern.

Much research has been done on the adsorption of EDTA, oxalic and citric acids and their metal complexes to soils and specific soil components; such as oxides. Less work has been done on DTPA, and only a few studies have been conducted with picolinic acid. The adsorption of these chelates and their metal complexes, especially on oxides, can be highly pH dependent and all of the chelates can undergo what is termed "ligand-like" adsorption [i.e., adsorption of the chelates is strongest at low pH, decreases rapidly in the neutral pH region, and can be negligible at high pH (>8)]. In general, relatively high concentrations of oxalic acid and citric acid are required to complex and mobilize metal ions in soils or soil components. These adsorption/desorption reactions for oxalate and citrate complexes do not appear to have any significant kinetic hindrance, and there is little or no evidence for the adsorption of oxalate-metal or citrate-metal complexes. Owing to the stronger thermodynamic stability of EDTA-metal aqueous complexes, EDTA can, at higher pH values and relatively low chelate concentrations, reduce metal adsorption onto soils or soil components. However, there is very good evidence for the adsorption of EDTA-metal complexes, particularly on Fe and Al oxides. This metal-chelate adsorption can retard, rather than enhance, the migration of radionuclides in soils and sediments. In addition, certain metal-EDTA complexes, most notably Ni-EDTA, appear to be kinetically inert and do not react rapidly with other competing ions in solution. These factors make it especially difficult to quantitatively predict the effects of EDTA on radionuclide transport in soils or sediments. Similar effects appear to be possible for the adsorption of DTPA, or possibly DTPA-metal complexes, although the data are much more limited. In the case of picolinic acid, very few studies have been conducted, and it is difficult to reach general conclusions. However, based on the few studies that have been done, it appears that adsorption of picolinate-metal complexes does not occur because both the amine and carboxylic acid functional groups of the picolinate ion prefer to bond to the adsorbent surface leaving no binding site on the ligand to adsorb metals, and that the formation of kinetically inert picolinate-metal complexes is unlikely. That is, when adsorption does occur, the picolinate molecule uses all its binding sites (2) to bond with the solid surface in preference to remaining bonded to the metal in the aqueous complex. However, further research in this area is required.

A variety of factors can influence the biodegradation of chelating agents and metal(radionuclide)-chelate complexes: 1) the presence of microorganisms capable of degrading the chelates; 2) the adsorption of the chelates to soils or sediments; 3) the aqueous speciation or complexation of the chelates; and 4) specific groundwater conditions, such as the pH and the organic carbon content of the water. In general, it appears that because citrate and oxalate are naturally present in some environmental systems, microorganisms capable of degrading these acids should be generally present. Picolinate is normally not present in the environment, but structural pyridine analogs do exist, suggesting that picolinate-degradative pathways should also exist. There is no structural analog for EDTA in environmental systems, and this fact may account for EDTA's general recalcitrance to biodegradation in many environmental systems.

The need for an accurate and adequately complete water analysis as input data for a model is one of the most important factors to obtaining accurate modeling results. Inadequate solution analyses, such as limited number of analyzed constituents, accuracy of data, and lack of sampling and analytical error uncertainties are common problems. As with most types of computer modeling techniques, "garbage in equals garbage out" also applies to the application of chemical equilibrium models to aqueous speciation and mass transfer calculations. In the rare cases when the user has a complete and accurate water analysis other limitations include 1) an inadequate conceptual model that ignores the existence of certain aqueous species, sorbed species, and/or solids containing elements and/or ligands of interest (such as complexation of metals by dissolved organic compounds); 2) the lack of thermodynamic data for known aqueous species, sorbed species, and/or solids of interest; 3) the lack of internal consistency between parameters within a single thermodynamic database as well as between databases used by different models, and 4) inadequate theoretical understanding and formulation of certain processes, such as absence of models and/or data for sorption, kinetic rates, and solid solution; calculations in high-ionic strength solutions; and disequilibrium between redox couples.

Because thermodynamic databases are a critical component to accurately model aqueous speciation and solubility in soil/water systems, the more knowledgeable the user is with a model's database in terms of the completeness and accuracy of its data, the more likely the results will be correct. Unfortunately, most users cannot be experts with respect to the measurement and derivation of thermodynamic data nor can they afford to do a critical review of thermodynamic data for all aqueous species and solids containing elements of interest to their modeling applications. In these cases, the user should thoroughly document the database used when reporting results of aqueous speciation and solubility modeling calculations.

At present, the geochemical codes MINTEQ and HYDRAQL appear to have the most robust adsorption algorithms and most complete data bases for organic ligand-radionuclide complexes. These models will be used in future modeling endeavors associated with this project.

Field data that show significant concentrations of radionuclides migrating with an apparent anomalously enhanced rate away from disposal units are scarce. No such studies are available for commercial low-level disposal facilities. At two defense waste facilities (Chalk River, Ontario and Oak Ridge, Tennessee) enhanced ^{60}Co migration has been observed beyond 50 meters from the burial trenches. In the former instance the cobalt appears to be associated with natural dissolved organics from neighboring swamps. In the latter case the cobalt appears to be bound to EDTA, likely present in the original waste stream.

Foreword

The objectives of the overall project are to accomplish the following tasks:

- determine the importance of radionuclide-chelating complexes in leachates obtained from leaching studies of decontamination low-level waste from nuclear power stations
- perform thermodynamic calculations to identify important radionuclide-chelate complexes and validate experimental test results with, if possible, direct experimental evidence for the existence of the complexes
- determine or propose chemical structures for the radionuclide-chelate complexes
- determine sorption behavior of selected free radionuclides, uncomplexed chelates, and radionuclide-chelate complexes on soils and important adsorbing surfaces in soils
- experimentally determine thermodynamic data for important radionuclide-chelating complexes for which data are unavailable
- modify existing geochemical models to include thermodynamic, and if possible, kinetic data for radionuclide-chelating complexes
- validate geochemical calculations using actual leachate and soils data.

This literature review, the first product of the project, addresses the first bulleted task and tabulates available knowledge on bulleted tasks two through four. Specifically the literature review was conducted to provide data and information on radionuclide-chelating agent complexes expected to be formed during decontamination of commercial power stations and subsequently disposed in commercial low-level radioactive waste disposal facilities. Information was obtained on the chemistry of decontamination including types of chelating agents used, types and quantities of radionuclides and stable transition metals removed from the power station piping and amounts of these constituents loaded onto resins and the ultimate fate of the radionuclides, metals, free ligands and ligand-radionuclide complexes during waste leaching. Using the leach solution characteristics, a review and analysis of available analytical methods that might be used to directly measure the metal (radionuclide)-ligand complex itself was performed. In addition the thermodynamic and kinetic data for metal ligand complex formation were tabulated. Such data will be used later in the program to predict the fate of radionuclide-chelating agent complexes in subsurface environments. The adsorption and biodegradation tendencies of the metal(radionuclide)-ligand complexes were also tabulated. Chemical models and codes that could use the thermodynamic and adsorption data for future calculations of fate were also described. Finally, the literature review tabulates available citations where organic chelating agents have been suspected of being the cause of enhanced migration of radionuclides from burial grounds.

The review surveys the literature on chemical decontamination processes used to remove the build-up of radioactive-activated metals and corrosion products from the cooling systems of nuclear power plants. All of these decontamination processes use chelating agents to complex the released radionuclides. The complexed radionuclides and any excess uncomplexed chelates are then removed onto cation- or anion-exchange resins. The U.S. Nuclear Regulatory Commission (NRC) is responsible for regulating the disposal of such wastes, including providing regulatory criteria for the co-disposal of organic chelating agents that have the potential to enhance the migration of radionuclides away from disposal sites. One of the principal pathways for radionuclides migrating away from a disposal site is contact with infiltrating recharge water. The presence of chelating agents in the wastes could enhance the subsequent migration of radionuclides in groundwaters in specified situations.

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Abbreviations

BNL	Brookhaven National Laboratory
BWR	boiling water reactor
DSS-1	double-shell slurry-1
DSSF	double-shell slurry feed
DTPA	diethylenetriaminepentaacetic acid
EDTA	ethylenediaminetetraacetic acid
ESD	element-selective detector
GC	gas chromatography
HEDTA	hydroxyethylenediaminetetraacetic acid
HIC	high-integrity container
HPLC	high-performance liquid chromatography
ICP/MS	inductively coupled plasma/mass spectrometry
INEL	Idaho National Engineering Laboratory
LC	liquid chromatography
LI	leachability index
LLW	low-level radioactive waste
LOMI	low-oxidation-state metal ions
MS	mass spectrometry
NCRW	neutralized cladding removal waste
NTA	nitrilotriacetate
PIC	paired-ion chromatography
PNL	Pacific Northwest Laboratory
PWR	pressurized water reactor
SEM	scanning electron microscopy
TRU	transuranic elements

1 Introduction

Regulations governing the burial of low-level radioactive wastes (LLW) produced by commercial entities (as opposed to the U.S. Department of Defense and the U.S. Department of Energy) are set forth in 10 CFR 61. Within Subpart D of this regulation, specific mention is made to licensees to evaluate the impacts of the presence of chelating agents.

Organic complexes of radionuclides have been implicated in several instances as enhancing the mobility of radionuclides such as ^{60}Co, ^{238}Pu, ^{241}Am, and ^{90}Sr from shallow-land burial grounds at Oak Ridge, Tennessee (Means et al. 1978; Means and Alexander 1981) and at Maxey Flats, Kentucky (Polzer et al. 1982; O'Donnell 1983; Dayal et al. 1986). Organic chelates, such as EDTA and picolinic acid, have also been shown to leach from solidified decontamination wastes from nuclear power stations (McIsaac and Mandler 1989). Thus, chelating agents present in decontamination wastes could enhance the migration of radionuclides away from sites where such wastes are disposed.

Chemical decontamination is an effective means of removing the build-up of activated metals and other radioactive components that can occur in the cooling systems of nuclear power plants. This build-up of radioactive elements is primarily associated with corrosion products, such as Fe/Ni chromites, chromic oxides, Ni ferrites, and ferric oxides, which are deposited as films in the cooling systems. Removal of such oxide films can significantly reduce the occupational radiation exposure received by personnel while performing maintenance tasks and improve the thermal hydraulic performance of the cooling system.

Three principal chemical decontamination processes are currently used: the low-oxidation-state metal ions (LOMI) process (Shaw and Wood 1985; Swan et al. 1987; Smee et al. 1986), the CAN-DEREM process (Speranzini et al. 1990); and the CITROX process. Two other processes are less commonly used: the DOW NS-1 process (McIsaac and Mandler 1989) and the CAN-DECON process (Speranzini et al. 1990). Some decontamination processes are typically used in conjunction with pre-oxidation steps. These steps involve alternate applications of reducing/complexing agents to dissolve the Fe-oxide coatings and to complex the released radionuclides, and of strong oxidizing agents (such as alkaline permanganate) to oxidize Cr present in the Fe/Ni chromites and to loosen or break up these deposits. The added reducing or complexing agents and oxidizing solutions are then removed by either cation- or anion-exchange resins. These resins constitute the principal waste from the decontamination process and are commonly mixed with cement for stabilization and then disposed. Current disposal practices emphasize placing the solidified wastes or dewatered resins directly in high-integrity containers.

The principal organic chelating/ complexing agents present in the decontamination solutions, listed with their associated process, are as follows: 1) citric acid-oxalic acid (CITROX), 2) formic acid-picolinic acid (LOMI), 3) citric acid-ethylenediaminetetraacetic acid (EDTA) (CAN-DEREM), and 4) citric and oxalic acids and diethylenetriaminepentaacetic acid (DTPA) and EDTA (DOW NS-1). This literature review is principally concerned with the radionuclides and chelating agents that can be leached from the disposed wastes and the potential for these chelates to enhance or retard migration of the leached radionuclides through surrounding soils and sediments.

The radionuclides and metal ions of primary concern include neutron activation products (isotopes of Co, Cr, Fe, Mn, and Ni), fission products (Cs, Sb, and Sr), actinide elements (Am, Cm, and Pu), and major components of groundwaters and soils (Al, Ca, Mg). The major cations present in the groundwaters are important because they can displace the hazardous radionuclides from the organic chelates.

Introduction

To address the effects of the chelates on the leaching and migration of radionuclides from waste forms requires knowledge of 1) the quantities of chelates and metals that potentially could be leached from the waste forms; 2) the ability of the chelates to bind the released metals in aqueous solution; 3) the ability of the soils or sediments to adsorb the chelates or radionuclide-chelate complexes; and 4) the identification of processes, such as biodegradation, that can break down or degrade the released chelates. Therefore, this review includes four sections: decontamination concerns and treatment and disposal of spent resins, aqueous complexation of radionuclides, adsorption of chelates and radionuclide-chelate complexes, and biodegradation of chelates and radionuclide-chelate complexes. All of these factors are important in determining the potential for the chelating agents to affect the leaching of waste forms and the migration of radionuclides in soils and sediments. The section on the aqueous complexation of radionuclides includes a review of the data available for performing thermodynamic equilibrium calculations and a review of analytical methods for identifying radionuclide-organic complexation. In addition, two sections are included that discuss chemical models/codes that use the thermodynamic and adsorption data to predict radionuclide fate and discuss literature where organic chelating agents have been suspected of causing enhanced migration, respectively.

To gather information on these subjects, Pacific Northwest Laboratory(a) (PNL) staff conducted searches of the following computer databases:

- Chemical Abstracts, 1967 to 1992
- Energy Science and Technology Database, 1974 to 1992
- Nuclear Science Abstracts, 1948 to 1976
- U.S. Department of Defense Research On-line System (DROLS).

Staff emphasized the Chemical Abstracts database and references from 1980 to the present. Some of the sources reviewed, but not cited in text, are listed in Appendix A. Further, the annual workshop proceedings of the EPRI (Electrical Power Research Institute) sponsored meetings on chemical decontamination proved to be quite valuable.

The purpose of this literature review was to identify and tabulate information on radionuclide-chelating complexes expected to be formed during the decontamination of operating nuclear power stations and disposed in commercial low-level radioactive waste disposal facilities. One chapter summarizes the data on studies that examine the extent of radionuclide-chelating agent complexes' impact on the mobility of radionuclides in grooundwater systems at low-level waste sites. Another chapter discusses analytical methods that might be useful in directly measuring the radionuclide-chelating agent complexes that may leach from disposed decontamination wastes. The literature review contains a chapter and appendix on thermodynamic data that is available and useful for predicting radionuclide-chelating agent complex formation. A final chapter discusses conceptual models and computer codes that can be used to predict the behavior and transport of radionuclide-chelating agent complexes in groundwater/soil systems. Emphasis is placed on the following chelates (EDTA, DTPA, picolinic acid, oxalic acid, and citric acid). Therefore, references on leaching or migration of metal ions or radionuclides in the absence of chelates were not reviewed. The reader is referred to previous reviews in this area (Rai et al. 1984a,b; Ames and Rai 1978; Onishi et al. 1981; Coughtrey et al. 1983-1984) for information on unchelated metal ions.

(a) PNL is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

2 Decontamination Concerns and Processes for Reactors and Components

Over the past twenty years the nuclear power industry has found it necessary to remove radioactive impurities from the piping and structures outside of the core. This need is driven by several circumstances including 1) increased inspection and maintenance activities (e.g., to monitor/prevent stress corrosion cracking and to replace welds and valves that are the most likely points of failure) as reactor operating lifetimes increase; 2) more stringent limits on allowable doses to plant workers as regulatory agencies and scientific organizations acquire information on the exposure effects on humans; and 3) the desire to improve heat transfer percentages in reactor operation. Decontamination of reactor systems is necessary because fluids circulating through the reactor's heat transfer apparatus contain suspended particulates and dissolved species that can become radioactive through the capture of neutrons that flux out of the core. The primary sources of the particulates and dissolved species are usually corrosion products from the metal pipes and equipment through which fluids circulate. A second source of radioactive contaminants are leaks of fission products directly from fuel elements into the fluids that cool the elements and core.

The average value of a man-rem of exposure to a plant worker has been estimated to be $5000. By performing decontamination prior to maintenance activities, a power-generating company can save 0.5 to 5 million dollars in personnel exposure costs. As a rule of thumb, decontamination is justified when piping within the reactor recirculation system exceeds 300 millirads per hour. Periodic decontaminations are necessary because piping will re-contaminate at a rate of about 100 to 150 millirads per effective full-power year. Thus at average plant efficiencies, decontamination is considered every 2 to 4 years (Vandergriff 1988; Smee and Beaman 1988).

Currently, several operating nuclear plants are considering decontamination of the entire reactor system, including the core. Several plants are petitioning the NRC to perform decommissioning of the core with the fuel remaining in place. It appears that the NRC will allow a full-system decommissioning of the Indian Point pressurized water reactor (PWR) using the CAN-DEREM process and the Brunswick boiling water reactor (BWR) using the LOMI process. It is unclear whether the full decontaminations will be performed with the fuel in the core. A complete core decontamination will likely generate a volume of final waste an order of magnitude larger than the waste generated by past external-to-the-core cooling system decontaminations, thereby increasing the percentage of resin-laden decontamination waste being buried in commercial low-level radioactive waste (LLW) burial grounds.

2.1 Formation of the Corrosion Products

Shaw and Wood (1985) state that 80 percent of PWR activation products form from corrosion of the Inconel-600 alloys found in PWR steam generators and 20 percent from corrosion of stainless steel 304 piping. The bulk of the PWR activation products redeposit on the surfaces of the steam generators. For BWR systems, the feed-water heaters and drains are the sources of material to be activated, and the bulk of the activated material ends up redeposited in the cooling water recirculation piping system.

When the irradiated particles and dissolved species reattach to piping and equipment outside of the shielded core, plant workers can be exposed during inspection and maintenance tasks. Typical doses for piping in PWR reactors level off at several hundred millirad per hour after several years of operation without decontamination (Sellers 1983). Doses for similar situations in BWR plants can continue to increase if decontaminations are not performed. For comparison, doses within the reactor core reach 10^9 millirad per hour. Current whole-body dose limits for radiological workers range from 2,000 to 5,000 millirem per year. Past limits were 12,000 millirem per year. Assuming the exposed dose is wholly caused by gamma ray emission (a reasonable assumption for this nuclear plant scenario), a worker would receive the allowable annual dose in twenty to thirty hours. Recent decontaminations of BWR components have been performed at a total worker exposure of 2.8 to 4.8 rem (2800 to 4800 millirem), whereas estimated dose removed by decontamination ranges from 50 to 1000 rem with a median value of about 350 rem (Schmeidmiller 1993; Valvasori 1993).

Table 2.1 lists the most common radioisotopes found in the waste solutions/solids generated after decontamination activities. The table identifies each isotope, its mode of production, and its primary types of decay. Power-plant-worker exposure is most sensitive to isotopes that decay with high-energy gamma emissions. The highest activity-level isotope generated is ^{60}Co, which is also the greatest dose contributor because of its two high-energy gamma emissions. Actual measurements of the radionuclide content in spent resins are shown in Table 2.15.

The source or parent material for most of these isotopes are metal-like elements (Cr, Fe, Mn, Ni, Co, Sn) found in the alloys or as impurities in the steel pipes. The fission products and ^{241}Pu come from uranium fuel. The radionuclides are redeposited onto and into corrosion products within the reactor system. The nature of the corrosion products vary from the type of reactor (PWR is a reducing environment and BWR is an oxidizing environment), the place within the system [micro environments differ such as dissolved O_2 content being 10 ppm right out of the core and only 0.06 ppm in the steam drum at Winfrith (Bradbury et al. 1981)], and position versus the base metal (pipe) surface. In the latter case nuclides directly adjacent to the pipe surface are within a relatively more reducing environment than nuclides deposited several atomic layers out in the corrosion product. The build-up of corrosion product with differing composition occurs with time of reactor operation; thus, one could say the composition varies with time. These variable micro environments and fundamental differences in PWR and BWR cooling water chemistry lead to a variety of corrosion products with disparate characteristics.

Table 2.1 Common radioisotopes deposited in power plant systems

Isotope	t1/2	Mode of Decay	Mode of Production	Natural Abundance of Parent Isotope
^{51}Cr	27.8d	EC; Gamma (.320 Mev)	^{50}Cr (n, γ)	^{50}Cr 4.3%
^{54}Mn	30.3d	EC; Gamma (.835 Mev)	^{56}Fe (d, α)	^{56}Fe 91.7%
^{55}Fe	2.7y	EC	^{54}Fe (n, γ)	^{54}Fe 5.8%
^{58}Co	71.3d	EC; Gamma (.810 Mev)	^{55}Mn (α, γ)	^{55}Mn 100%
^{59}Fe	44.5d	Beta; Gamma (1.09 Mev) (1.29 Mev)	^{58}Fe (n, γ)	^{58}Fe 0.3%
^{60}Co	5.26y	Beta; Gamma (1.17 Mev) (1.33 Mev)	^{59}Co (n, γ)	^{59}Co 100%
^{63}Ni	92y	Beta	^{62}Ni (n, γ)	^{62}Ni 3.7%
^{65}Zn	244d	EC; Gamma (1.12 Mev)	^{64}Zn (n, γ)	^{64}Zn 48.9%
^{90}Sr	27.7y	Beta	Fission	
^{103}Ru	39d	Beta; Gamma (.497 Mev)	Fission	
^{125}Sb	2.7y	Beta; Gamma (.427 Mev) (.599 Mev)	^{124}Sn (n, γ)	^{124}Sn 6.0%
^{137}Cs	30.0y	Beta; Gamma (.667 Mev)	Fission	
^{241}Pu	14.7y	Beta; Gamma (.145 Mev)	^{238}U (3n, γ)	^{238}U 99.7%

Therefore a single approach for decontamination cannot be used, and efficiencies for any given approach will vary from reactor to reactor and among locations within any given reactor. This variability has lead to the use of sequential decontamination processes that use two or more steps and chemical schemes or the repetition of several cycles of fresh reagent between vigorous flushing to remove corrosion products. Characteristics of the deposited corrosion products will be described next, followed by a discussion of several widely used decontamination processes.

2.2 Characteristics of the Corrosion Products

Detailed studies of the type and nature of corrosion products formed on power plant materials have been performed on actual parts removed from reactors and on test coupons purposefully inserted into reactor systems. A condensation of various facts taken from Smee et al. (1986); Velmurugan et al. (1991); Shaw and Wood (1985); Ayres (1971); Bradbury et al. (1981, 1983a,b); and Davis (1983) follows. The corrosion product on base metal reactor parts such as pipes forms very hard, adherent inner layers when the base metal (Fe and Fe-Ni alloys) corrodes in situ. The outer layers are generally more porous and more loosely held and are formed by deposition of suspended fine particles and precipitation of dissolved cations. Because of the inherent chemical differences in water chemistry between PWRs (reducing) and BWRs (oxidizing), the minerals formed also differ. Table 2.2 identifies the typical inner and outer layers of corrosion product for the two reactor types. The PWR corrosion product is rich in Cr(III), the reduced form of Cr. This material is especially resistant to dissolving in common decontamination reagents. The BWR corrosion product is highly oxidized on the outside layer with Fe found only as Fe(III). Deeper within the inner layer of BWR corrosion product, Fe is found as the mixed Fe(II) - Fe(III) oxide, magnetite.

Magnetite is also found in the outer layer of PWR corrosion product, again showing PWR's more reduced environment. The activation metals (^{58}Co, ^{60}Co, ^{54}Mn, and ^{63}Ni) are divalent cations that will replace Fe(II) in the chromite structures of PWR and magnetite structures in both reactor types. In BWRs Cr(III) will substitute into both the inner and outer oxide layers for Fe(III) in Ni ferrites and hematite, respectively, but much less Cr is found in BWR corrosion product. Bradbury et al. (1981) found the Cr content of corrosion product from oxidized areas at the Winfrith steam generating heavy water reactor to be 10 percent, while reduced-zone corrosion product contained up to 60 percent Cr.

2.3 Decontamination Processes

An ideal decontamination process would fulfill the following criteria: 1) could be used without having to dismantle reactor system components or install complicated temporary equipment; 2) would rapidly remove the activation products without

Table 2.2 Description of corrosion product layers

Location	Pressurized Water Reactor		Boiling Water Reactor	
	Formula	Type	Formula	Type
Inner layer	Cr_2O_3	Chromite	Fe_3O_4	Magnetite
Inner layer	$FeO \cdot Cr_2O_3$	Chromite	$NiO \cdot Fe_2O_3$	Ni ferrite
Inner layer	$NiO \cdot Cr_2O_3$	Chromite		
Outer layer	Fe_3O_4	Magnetite	Fe_2O_3	Hematite
Outer layer	$NiO \cdot Fe_2O_3$	Nickel ferrite		

dissolving, corroding, or otherwise harming the existing metal components that must return to service; 3) would prevent the reprecipitation of the corrosion product prior to removal from the reactor system; 4) would allow easy removal of the activation products into a form suitable for disposal; and 5) would allow regeneration and reuse of the decontamination reagents. Furthermore, the entire process must be performed within several days to a week so that the reactor can be restarted, and workers should receive a much smaller dose during the decontamination and waste disposal process than they would have received during reactor maintenance if a decontamination had not been performed. Key concerns have been the impact of decontamination operations on the future stability of reactor materials and systems, the volume and toxicity of waste products after disposal, and assurance that there will be a significant net long-term occupational dose reduction.

In the early 1970s decontamination exercises inevitably used high concentrations of aqueous reagents (organic acids and chelating agents at 5 to 20 percent by weight) to dissolve or loosen the corrosion product. Subsequent flushing of the reactor components resulted in a mixed (high suspended solids and high dissolved solids) slurry that was awkward to treat for disposal. Peters (1991) estimates that this concentrated decontamination methodology would consume 1 to 6×10^7 grams of reagents. The concentrated processes are harsh on the reactor components and can cause rapid and significant corrosion. The waste slurry resists easy evaporation or ion-exchange clean-up.

According to Miller et al. (1988), the first dilute reagent decontamination was performed in 1979 at the Vermont Yankee plant. In the late 1970s and early 1980s, a dilute process called CAN-DECON was widely used in the United States. Speranzini et al. (1990) identify 24 CAN-DECON uses (19 BWR and 5 PWR) in the United States between 1979 and 1984. An incident at the Peach Bottom-2 Nuclear Reactor when a post decontamination inspection showed 50 μm-deep, intergranular attack caused concerns about enhanced stress corrosion cracking. Soon after this discovery, two other dilute (~0.1 to 0.2 percent by weight) aqueous processes, CITROX and LOMI, and a modified CAN-DECON process named CAN-DEREM have been used for recent decontaminations. Most of the decontamination recipes used at nuclear power plants are proprietary and licensed with specific restrictions on releasing exact details. Staff found a large variation in the quantity of details in publicly available literature obtained for this literature review. Staff did not canvass utilities or vendors to determine how frequently each decontamination process has been used, but some data for the years 1991-1993 from two vendors are reported in Table 2.3. A list of dilute decontamination processes and the key ingredients that have been publicly identified are shown in Table 2.4. Both tables also include preoxidation processes to condition Cr(III)-rich oxides for subsequent decontamination. As shown in Table 2.3, many decontaminations rely on several repetitive sequences of a decontamination cycle to remove corrosion products. Table 2.3 also lists the curies of radionuclides removed and volume of spent resins produced that require disposal. Details may be found in Schmeidmiller (1993) and Valvasori (1993).

2.3.1 CAN-DECON Process

This dilute decontamination process was patented by Atomic Energy of Canada Limited in the early 1970s (Speranzini et al. 1990, 1993). This process has now been replaced by the CAN-DEREM process (see Subsection 2.3.2). The CAN-DECON process is described here to provide background information on the currently used CAN-DERAM process. In the CAN-DECON process the solvent contains a mixture of citric, oxalic, and EDTA acids at a total ligand concentration of 0.1 to 0.2 percent by weight. Velmurugan et al. (1991) describe a similar decontamination solution used in India that is 0.03 percent citric, 0.03 percent oxalic, and 0.01 percent EDTA acids and has pH between 2.1 and 2.3. The solvent is circulated within the reactor system at temperatures between 85° to 120°C for 24 to 72 hours. During circulation, the solvent is continuously run through a filter and cation-exchange column where particulates and cationic activation products (e.g., ^{60}Co, ^{54}Mn, and ^{63}Ni), fission products (e.g., ^{90}Sr and ^{137}Cs), and dissolved metals

Table 2.3 Recent (1991-1993) decontamination activities by two U.S. vendors

	Decon Types			
Reactor Type	**CITROX (C)**	**CAN-DECON (CD)**	**CAN-DEREM (CR)**	**LOMI (L)**
BWR	6	0	3	23
PWR	4	1	2	0

Details

BWR (Sequence of Steps)	**Curies Removed**	**Resin Wastes (ft^3)**
C-AP-C[a]	4.7	138
L	75	270
L-AP-L	50	301
L-AP-L	14	300
L-AP-L	22.7	180
L	13.1	0.5
L-AP-L	44.5	105
C	3.3	240
L-AP-L	121	345
L-AP-L	32	180
L-L-AP-L-AP-L	94	300
L	3	57
L-AP-L	123	182
L-AP-L	229	200
L	110	154
L[b]	49	
CR-AP-CR	19	240
CR[b]	10	
L-AP-L	75	179
CR[b]	17	
L-L	51	150
PWR (Sequence of Steps)		
C-AP-C	32	180
AP-C-AP-C-AP-C	0.4	20
C-AP-C	0.4	15
CR-AP-OX-CR-AP-OX-CR[c]	4.3	NA[d]
C-AP-C-AP-C	88	496
CR-AP-CR-AP-CR	1	20
CD-AP-CD-AP-CD	1	20

(a) AP = Alkaline permanganate.
(b) Two separate areas were decontaminated using different techniques and all spent resins were commingled.
(c) OX = Oxalic acid rinse.
(d) NA = Not available.

Table 2.4 Dilute decontamination processes

Name	Principle Ingredients	Decontamination (D) or Preoxidation (P)
CITROX	Oxalic acid, citric acid	D
CAN-DECON	Oxalic acid, citric acid, and EDTA	D
CAN-DEREM	Citric acid and EDTA	D
DOW NS-1	DTPA, citric acid, oxalic acid and EDTA	D
LOMI	V formate, formic acid, picolinic acid, and Na hydroxide	D
AP (alkaline permanganate)	Na hydroxide and K permanganate	P
NP (nitric acid permanganate)	Nitric acid and K permanganate	P
APAC	Na hydroxide, K permanganate, oxalic acid and ammonium citrate	P/D

(i.e., Fe^{2+} and Ni^{2+}) are removed respectively with regeneration of the H_4Y (EDTA acid with exchange sites re-protonated). During dissolution of corrosion products, the cationic activation products and dissolved metals form H_2MY complexes where two protons are lost when the chelate binds the divalent metal. This keeps the metals from re-precipitating or readsorbing onto the reactor components. The cation-exchange resin (H^+ form) can out compete EDTA for the divalent metal and regenerates H_4Y. Oxalic acid ($H_2C_2O_4$) is a mild reductant and can release electrons that react with ferric and mixed ferrous/ferric oxides to solubilize ferrous ions. Pertinent reactions are shown in Table 2.5. The overall reaction of interest that describes the mass transport of Fe-oxide corrosion product from the reactor pipes to the ion-exchange resin outside the reactor is a combination of equations 1, 2, 4, and 5 or 1, 3, 4, and 5 (Table 2.5) as follows:

$$H_2C_2O_4 + Fe_3O_4 + 6R{:}H \leftrightarrows 2CO_2 + 3R_2{:}Fe + 4H_2O \text{ for magnetite and} \tag{1}$$

$$H_2C_2O_4 + Fe_2O_3 + 4R{:}H \leftrightarrows 2CO_2 + 2R_2{:}Fe + 3H_2O \text{ for hematite.} \tag{2}$$

The overall reactions consume oxalic acid, but regenerate EDTA. Apparently the citric acid helps maintain pH and hinders the formation of ferrous oxalate, a rather insoluble compound. In the acid environment, CO_2 gas dissolves to an equilibrium value and then exsolves any excess. The activation metals mimic the ferrous ions and become adsorbed onto the cation-exchange resin. At the end of the recirculation of the decontamination, all of the solvent is run through a mixed-bed (cation-anion) resin to remove the citric and EDTA acids, any excess oxalic acid (all on the anion-exchange portion of the mixed bed), and any residual cations on the cation-exchange resin. In practice the reagents are added to the coolant water stream as a concentrated solid slurry. They quickly dissolve in the overall system. There are also a few residual particulates including ferrous oxalate that are removed onto submicron filters prior to the final mixed-bed ion exchange cleansing. Some HFe(III)Y complexes, where Y = EDTA, are formed that do not easily disassociate when percolated through the cation exchange column, resulting in a small loss of this reagent with time. At the completion of the decontamination, non-labile HM(III)Y complexes are captured on the anion portion of the mixed-bed resin. CAN-DECON requires less volume of exchange resins for system clean-up than other techniques because metal

Table 2.5 CAN-DECON mechanisms

Description	Chemical Equation	No.
Oxalic acid oxidation	$H_2C_2O_4 \text{-----}> 2CO_2 + 2H^+ + 2e^-$	1
Fe oxide reduction	$8H^+ + Fe_3O_4 + 2e^- \text{------}> 3Fe^{2+} + 4H_2O$	2
	$6H^+ + Fe_2O_3 + 2e^- \text{------}> 2Fe^{2+} + 3H_2O$	3
Fe complexation	$Fe^{2+} + H_4Y \text{------}> H_2[FeY] + 2H^+$	4
Resin recapture of Fe	$H_2(FeY) + 2\,R{:}H \text{------}> R_2{:}Fe + H_4Y$	5
POSSIBLE SIDE REACTIONS		
Base metal oxidation	$Fe^\circ \text{------}> Fe^{2+} + 2e^-$	6
Proton reduction	$2H^+ + 2e^- \text{------}> H_2$	7

salts or hydroxides are not added for pH control and the main chelator EDTA is regenerated for continuous cycling without the need to add additional chemicals. The CAN-DECON process is not effective at dissolving Cr-rich Fe oxides ($FeO \cdot Cr_2O_3$) or Cr_2O_3 itself. In this regard CAN-DECON is inferior to the LOMI process. A separate process called preoxidation (noted in Table 2.4 with the letter P) must be performed before CAN-DECON or between two CAN-DECON repetitive cycles to effectively remove Cr-rich deposits.

Table 2.6 lists summary data on five separate CAN-DECON operations performed in the early 1980s at reactors in the United States (data extracted from Davis 1983). In general the CAN-DECON process is good for carbon steel components but not preferred for systems with large amounts of stainless steel.

2.3.2 CAN-DEREM Process

The CAN-DECON process fell into disfavor in 1984 when 50-μm deep intergranular attack was noticed on Peach Bottom-2 piping after decontamination. Lab testing suggested that oxalic acid was the reagent causing this base metal attack. The CAN-DEREM process was thus created by removing the oxalic acid, leaving citric and EDTA acids as the active ingredients. Numerous laboratory tests (Speranzini et al. 1990, 1993) showed the revised recipe to be effective. In late 1989 three steam generator heaters at Beaver Valley 1 were cleaned using combined Na hydroxide/permanganate preoxidation and CAN-DEREM (0.1 percent by weight at 120°C for 6-24 hours). Recently, Speranzini et al. (1993) have shown that the oxidation steps between applications of CAN-DEREM generate four to eight times more of the spent-resin waste than the decontamination steps. Therefore, methods to improve the preoxidation steps (keep MnO_4 from decomposing) are under active investigation. The use of Zn^{2+} in reactor cooling water heaters at Beaver Valley 1 were cleaned using combined Na hydroxide/permanganate preoxidation and CAN-DEREM (0.1 percent by weight at 120°C for 6-24 hours). Table 2.3 shows at least five recent uses of the CAN-DEREM process. Recent improvements are its use at 90 to 95°C for 8-10 hours at concentrations below 0.1% chelators.

Table 2.6 CAN-DECON operations

Brunswick 2			Nine Mile Point			Brunswick 1			Vermont Yankee 2 Campaigns (1979, 1981)		
Element / Nuclide	Stable Metals Removed (g)	Nuclides Removed (Ci)	Element/ Nuclide	Stable Metals Removed (g)	Nuclides Removed (Ci)	Element / Nuclide	Stable Metals Removed (g)	Nuclides Removed (Ci)	Element/ Nuclide	Stable Metals Removed (g)	Nuclides Removed (Ci)
Fe	6,020		Fe	4,800		Fe	17,350		Fe	3,040, 6,314	
Cr	32		Cr	83		Ni	260		Cr	60, 356	
Cu	50		Eu	23		Mn	165		Cu	350, 66	
Ni	49		Ni	296		Co	6		Ni	60, 262	
Mn	35		Mn	24		Cu	2		Mn	10, —	
Na	97		Co	18		Cr	0.5		^{51}Cr		0.06, 0.03
^{51}Cr		8.0	^{51}Cr		–	^{60}Co		3.6	^{60}Co		1.4, 2.4
^{60}Co		3.0	^{60}Co		34.1	^{51}Cr		3.0	^{54}Mn		0.06, 0.47
^{54}Mn		2.4	^{54}Mn		2.0	^{54}Mn		1.7	^{58}Co		0.01, 0.3
^{58}Co		0.9	^{58}Co		2.0	^{58}Co		0.6	^{59}Fe		–, 0.09
^{59}Fe		0.9	^{59}Fe		0.3	^{59}Fe		0.2	^{65}Zn		0.7, 1.8
^{137}Cs		0.6	^{134}Cs		0.06	^{65}Zn		0.08	^{131}I		0.06, <0.01
^{65}Zn		0.5	^{113}Sn		0.01						
^{131}I		0.2	^{141}Ce		0.17						
^{122}Sb		0.05	^{124,125}Sb		0.13						

It is not apparent why CAN-DEREM should be as effective as CAN-DECON if one removes the mild reducing agent oxalic acid. Without a reducing agent the ferric-oxide-containing corrosion product should not be readily dissolved, kept soluble, or form easily ion-exchangeable H_2FeY complexes of EDTA. Ferric oxide will dissolve in acid systems by reactions

$$8H^+ + Fe_3O_4 \leftrightarrows Fe^{2+} + 2Fe^{3+} + 4H_2O \text{ and} \tag{3}$$

$$6H^+ + Fe_2O_3 \leftrightarrows 2Fe^{3+} + 3H_2O \tag{4}$$

However, the ferric ions supposedly form very strong HFe(III)Y complexes with EDTA that are not readily broken apart by percolation through strong acid cation-exchange resins. Perhaps the $Fe(III)Y^-$ complex is removed at the end of the cleanup by the anion resin or perhaps another reductant such as hydrazine or base metal corrosion ($Fe^\circ + 2Fe^{3+} \rightarrow 3Fe^{2+}$) provides the electrons necessary to reduce all ferric ions. If the latter were occurring, it would seem that CAN-DEREM would be harsher than CAN-DECON on the base metal corrosion. Ayres (1971) states that citric acid-EDTA solutions at pH values 6-8 work well on steel if temperatures are elevated to 90°C or higher.

Recently, Speranzini et al. (1993) have shown that the oxidation steps between applications of CAN-DEREM generate four to eight times more of the spent-resin waste than the decontamination steps. Therefore, methods to improve the preoxidation steps (keep MnO_4 from decomposing) are under active investigation. The use of Zn^{2+} in reactor cooling water allows the removal of ^{60}Co without the need for permanganates. This will improve decontaminations using CAN-DEREM because the oxidation step generates most of the spent resin. The CAN-DEREM process in a five-step sequence is being considered for a full reactor-system decontamination in the United States.

2.3.3 CITROX Process

Decontamination processes that use only citric and oxalic acids as the active ingredients have been and continue to be used at the time of this literature review. At first the process used a concentrated solution, but in the 1980s, dilute versions were employed. Specific articles describing dilute CITROX campaigns were not found in the open literature. The process was developed and is licensed by Pacific Nuclear Services, Inc. for application in both PWR and BWR. CITROX is generally used in conjunction with pre-oxidation steps AP (or NP. It appears that TURCO, a commercial cleaning agent, is a trade name for the citric-oxalic solution. Bradbury et al. (1981) discuss some applications of a 6 percent-by-weight solution to decontaminate the Winfrith reactor in the United Kingdom. Given knowledge of the chemical processes described for the CAN-DECON solvent, we speculate that CITROX would perform as follows. Oxalic acid would act as a mild reductant to reduce ferric-oxide-containing corrosion product. The acid conditions would keep ferrous and divalent cationic activation metals in solution. The remaining oxalate and citric anions would also complex the metals and keep them in solution. The oxalate and citrate complexes are much weaker than metal-EDTA complexes and thus should readily break apart when flushed through cation-exchange columns. The weak metal-ligand complexes formed by oxalate and citrate anions may account for CITROX having started as a concentrated decontamination solution in order to effectively keep divalent metals in solution. Because CITROX decontaminations will not attack Cr-rich oxide corrosion products, it is often paired with pre-oxidation processes. For final clean-up the spent reagents are flushed through cation and mixed-bed resins to scavenge soluble cations and spent CITROX reagents and residual corrosion products, respectively. Based on Table 2.3, it appears that CITROX is still used in both BWR and PWR decontaminations, especially in concert with the AP preoxidation process.

2.3.4 NS-1 Process

The Dow Chemical Company (DOW) patented a decontamination process named NS-1 that uses a combination of DTPA, EDTA, and citric acid. The process is no longer used, but wastes from the process have been produced and the process was included in this review for completeness. Specific articles were not found in the open literature that describe the chemical reactions and performance attributes of this solvent. Because the NS-1 does not contain the mild reductant oxalic acid the solvent must rely upon acid dissolution of ferric-bearing corrosion product. Both DTPA and EDTA form very stable complexes with divalent and trivalent cations. The trivalent cation-ligand complexes may not be readily broken apart by cation-exchange resins typically used to remove the activation products from spent solvent. The NS-1 process is also known to generate a large amount of spent resin in comparison to other decontamination processes. The NS-1 process for decontamination is often packaged with another DOW waste solidification process that uses polyester styrene polymer to encapsulate high percentages of solid wastes, such as evaporator salts and spent ion-exchange resins. The basic processes that make NS-1 effective must be similar to the CAN-DEREM process, where oxalic acid is not present.

2.3.5 LOMI Process

A relatively new dilute-solution decontamination process has been amply discussed in the open literature and appears to be the most popular decontamination process marketed today. The January 9, 1992 issue of Nuclear Waste News (p. 15) states that LOMI decontaminations account for 90 percent of current and planned decontaminations in the United

States. The process is named LOMI (low oxidation metallic ion). The commercial process uses vanadous [V(II)] cation to rapidly reduce ferric-oxide-bearing corrosion product. The vanadous cation is added to a solution of picolinic acid as a vanadous formate in excess formic acid. This reagent, vanadous formate, is produced using V_2O_5 in the presence of formic acid by electrolytic reduction. The original V(V) is reduced through the V(III) intermediate. Formic acid keeps $V(OH)_3$ from precipitating prior to its being reduced further to V(II). The organic acids (formic and picolinic) maintain slightly acid conditions, while picolinate anions complex the divalent Fe, activation products, and trivalent-spent V cations (V^{3+}). The metal-picolinate complexes remain in solution and are readily broken apart by cation exchange resins. If the organic acid ligands were not present, released metals and V^{3+} could reprecipitate. At the end of decontamination, spent acids, formic and picolinic, are removed by anion exchange resins used within mixed-bed exchange resins. LOMI provides the following advantages: 1) very rapid reduction/dissolution of corrosion products, including those with nickel ferrite and Cr up to 20 percent by weight; 2) no significant localized attack on base metal surfaces; 3) no particulate by-products formed; and 4) rapid removal of dissolved corrosion products, spent solutes, and excess reagents. Specific details are documented in Davis (1983); Bradbury et al. (1981, 1983a,b, 1986); Vargo and Remark (1990); Swan et al. (1987); and Larrick et al. (1990).

Details of the LOMI process follow. Solutions of picolinic acid, Na hydroxide or ammonium hydroxide, and traces of hydrazine (an oxygen getter) are circulated through reactor piping and heated to 80° to 95°C. Once the aqueous system is low in oxygen, 0.25 M vanadous formate solution is injected until the overall V concentration is 0.005 to 0.03 M. More base is injected to bring the pH of the aqueous solution to 3.5 to 4.5 (one article claims a pH of 6 is tolerable). The vanadous ion can rapidly (minutes to a few hours) reduce and dissolve the oxide corrosion product. The picolinic acid present in excess of the V at a ratio of about 6:1 on the molar basis forms soluble complexes with the dissolved metals and spent V(III). The used solution is then circulated through a mixed bed or sequential train of cation- and then anion-resin beds. The cation-exchange bed removes spent V(III) corrosion products (Fe^{2+}, Co^{2+}, Ni^{2+}, etc.) and Na^+ used to buffer the system. The anion-exchange resin removes formate and picolinate anions. Recent improvements to the LOMI process include 1) a new vanadous formate product with much less excess formic acid present (therefore less anion-exchange resin is needed); 2) availability of high-capacity, weak-base anion- exchange resins that retain formate and picolinate anions; 3) regeneration of V(II) from electrochemical reduction of V(III) (Bradbury et al. 1986); and 4) regeneration of exchange resins and concentration of metal as solid wastes by the ELOMIX (Electrochemical LOMI Ion EXchange) (Bradbury 1981) process. During the ELOMIX process, cation-exchange resin is placed in an electrochemical cell and separated from the anode and cathode by a semi-permeable membrane. The cell's electric field pulls cations out of the resin towards the cathode where they precipitate as metals onto a filter that is readily disposed. The metal precipitates are much more stable than spent organic exchange resins. The anode generates H^+ that replaces the cations on the cation resin (the exact process used to regenerate cation resins). The final waste generated is only 10 percent of the normal LOMI process. Recall that the standard LOMI decontaminations produce 1.5 to 3 times as much spent resin as CAN-DEREM.

The redox couple for V(II)/V(III) in the presence of picolinic acid is - 0.41 volts versus the hydrogen electrode. This value is about the same as the Cr(II)/Cr(III) couple and thus LOMI is incapable of reducing chromic oxides or very Cr-rich oxide corrosion products. A reagent based on chromous [Cr(II)] metal in picolinic acid has been investigated but was found to react very quickly with water, such that Cr(II) disappeared and $H_2(g)$ formed. This consumed the active ingredient before the corrosion product was reduced and dissolved. It is not known why V(II) doesn't react as rapidly in water and disappear. If this reaction were occurring rapidly, LOMI would not be useful either.

Interestingly, the formic acid and formate anion ($HCOO^-$) is a boon in high-radiation fields because it readily reacts with H• or OH• radicals to form a species CO_2^- that regenerates the V(II) LOMI active ingredient by the following two reactions

$$HCOO^- + H\bullet \rightarrow CO_2^- + H_2 \text{ or } HCOO^- + OH\bullet \rightarrow CO_2^- + H_2 \qquad (5)$$

$$CO_2^- + V(pic)_3 \rightarrow V(pic)_3^- + CO_2(g) \qquad (6)$$

Currently most decontaminations performed since the mid 1980s have used the LOMI process. Typical LOMI decontaminations used the masses of reagents and produced the masses/activities of major corrosion products listed in Table 2.7. Three typical LOMI decontaminations were described in detail in the literature reviewed. One decontamination proceeded as follows. The first LOMI flush was performed at 90°C for 4 hours. The spent solution was circulated through a mixed-bed ion-exchange resin for 4.5 hours at temperatures between 66 and 95°C to remove contaminants. A preoxidation step was then carried out using nitric acid permanganate (NP) for 8 hours at 95°C. The spent NP was rinsed from the cooling system using an oxalic acid rinse at 70°C for 4.5 hours (to remove MnO_2 deposits and destroy leftover MnO_4). A second LOMI decontamination was performed at 90°C for 3 hours. The spent LOMI was then flushed through a mixed-bed resin at 90° dropping to 60°C over a 2-hour period. The cooling system was then ready for restart (see Hudson et al. 1988).

A second decontamination (again using LOMI, NP, and oxalic acid) was completed within 64 hours from initial hook up, system heating, and final spent-solution clean-up on mixed-bed resins. The actual time involved from injection of the first LOMI reagents until completion of the second LOMI reagent contact was 44 hours. Eighty-six percent of the total radioactivity removed came out during the first LOMI step, 12% during the NP-oxalic acid steps, and 2% during the second LOMI step (see Vandergriff 1988).

The third LOMI decontamination for which adequate details are present is found in the next section and Table 2.8. The LOMI-AP-LOMI process is being considered for a full reactor decontamination of a U.S. reactor in the near future.

2.4 Preoxidation Steps

Chromium-rich oxide corrosion products are quite resistant to dissolution by any of the decontamination solutions/processes discussed. Cr(III) does not readily reduce to Cr(II), as does Fe(III) reduce to Fe (II). On the other hand, Cr(III) is readily oxidized to Cr(VI), which forms a very soluble chromate species, CrO_4^{2-}. Therefore, reactor piping and components are often pre-treated with an oxidation step to loosen the corrosion product layer and selectively remove Cr.

The active oxidizing agent used to oxidize Cr is K permanganate, $KMnO_4$. Two solvent-mixture processes are commonly employed: an acidic mixture, nitric acid/permanganate (called NP); and an alkaline mixture, Na hydroxide/permanganate (called AP). In either case, Swan et al. (1987) state that the rate of reaction saturates when MnO_4^- reaches a concentration of $3x10^{-3}$ M (~500 ppm $KMnO_4$). Also there is not an advantage to raising temperatures above 90°C. After the preoxidation step, the spent solvent can be mixed with anion-exchange resins to sequester excess MnO_4^- and dissolved CrO_4^{2-}, but there has been concern about highly exothermic reactions between permanganate and organic exchange resins. More commonly, any excess MnO_4^- is reduced by the addition of oxalic acid, which converts permanganate to soluble Mn(II), which is removed by running the spent preoxidation solution through cation exchange resins. Net reactions in the preoxidation and rinse steps are

$$2OH^- + Cr_2O_3 + 2KMnO_4 \rightleftharpoons 2CrO_4^{2-} + 2MnO_2 + 2K^+ + H_2O \qquad (7)$$

$$MnO_2 + (COOH)_2 \rightleftharpoons 2CO_2 + 2OH^- + Mn^{2+} \qquad (8)$$

$$6H^+ + 2KMnO_4 + 5\,(COOH)_2 \rightleftharpoons 2K^+ + 2Mn^{2+} + 10CO_2 + 8H_2O \qquad (9)$$

Table 2.7 LOMI mass balance

Reagents	Smee et al. (1986) Mass (Kg)	Davis (1983) Mass (Kg)	Moles[a]	EPRI (1991) Mass (Kg)
V(II)	172	300	5.8×10^3	180
Formic Acid	310	1500	3.3×10^4	457
NaOH	340	650	1.6×10^4	360
Picolinic Acid	1250	4000	3.3×10^4	2700
Products				
Fe	137	300	5.3×10^3	
^{60}Co	---	3×10^3(Ci)	---	
Total Curies	1780			
Resins				
Cation	1.76×10^{4}[b]	---	---	1.8×10^{4}[b]
Anion	1.05×10^4	---	---	1.7×10^4
Mixed bed	0.37×10^4	---	---	0.4×10^4

(a) Swan et al. (1987) suggest that the typical molar ratio is 1:6:10 for V(II), picolinic acid, and formic acid per mole of ferric Fe removed. This differs slightly from Table 2.8 values of 1.1:6.2:6.2. Newer formulations are known to reduce the usage of formic acid.

(b) Liters of resins.

Table 2.8 FitzPatrick reactor decontamination

	Removed	Activity	Time
System Heatup	--	--	9.0
LOMI 1 (6 mM V^{2t})	--	--	6.5
Ion Exchange	15.3	52.8	6.0
NP (1.3 ppm $KMnO_4$)	1.2	2.1	5.0
Oxalic Rinse (0.7 ppm)	--	--	4.5
Ion Exchange	1.3	5.4	4.0
LOMI 2 (25 mM V^{2t})	--	--	3.5
Ion Exchange	2.0	1.1	5.5
Backflush	--	--	4.0
Final Ion Exchange/Drain	--	--	8.0
Total	19.8	61.4	56

Swan et al. (1987) state that the acid (NP) process dissolves chromites and ferrites better than the alkaline (AP) process, but Cr(VI) is much more soluble under alkaline conditions. Bradbury et al. (1983a,b) suggest that the NP process is most effective at cleaning stainless steel. Table 2.3 suggests that the AP process is favored in the last several years.

Vargo and Remark (1990) and Hudson et al. (1988) describe a decontamination campaign of the James A. FitzPatrick plant in 1988 where a nitric acid preoxidation step was used between two LOMI treatments. Corrosion product with contents in the range of 12-14 percent Cr were readily removed. The $KMnO_4$ solution used was 0.13 percent by weight. The pH was 2.5 with nitric acid. After treatment 670 ppm oxalic acid was added to decompose excess permanganate. The solution was cleaned by flushing it through a cation resin to collect Mn(II) and an anion exchange resin to clean any remaining oxalate. After removing the spent preoxidizing solution, a final LOMI step was performed for 3.5 hours. Table 2.8 lists the amount of metal (Fe, Cr, Ni, etc.) removed and the radioactivity (mostly ^{60}Co) removed in this four-step process. The piping was back flushed and drained. The total decontamination took 56 hours to complete. The total spent resin generated was 236 ft^3.

Smee et al. (1986) describe a decontamination of the Connecticut Yankee reactor piping that used an alkaline permanganate, then an acid permanganate preoxidation, followed by a CAN-DECON step. The masses and activities of corrosion and activation corrosion product removed are shown in Table 2.9. There was one mention of a coupled pre-oxidation decontamination process called APAC (alkaline permanganate ammonium citrate). It is a combined AP pre-oxidation, and a CITROX decontamination.

2.5 Summary of Decontamination Options

In summary, staff found that soft- or dilute-solution decontaminations are now favored over concentrated-solution decontaminations of reactor systems. The LOMI, CITROX and CAN-DEREM are the processes currently being used to decontaminate facilities in the United States. The dilute solutions are percolated through ion-exchange resins to remove the metallic activation and corrosion products and anionic-spent organic acids/complexing agents. The loaded exchange resins, after some dewatering, become the waste that must be further treated or packaged for disposal. The ion-exchange resins generally consist of organic polymers with relatively high densities of fixed positive or negative charges. The decontamination solutions load the resins with the following cations: Fe(II), Fe(III), Ni(II), Co(II), Mn(II), K, Cr(III), and Na, and the anions: NO_3^-, CrO_4^{2-}, citrate, oxalate, picolinate, formate, and EDTA.

The following section describes issues related to ion-exchange-resin stability, processing for disposal, and most importantly, fate after disposal. Currently, spent resins are usually dewatered and placed directly into high-integrity containers (HICs). Commonly used HICs have high-density polyethylene liners overpacked with concrete, cement, or Ferralium alloy. In the recent past spent resins were solidified directly into cementitious waste forms that used high density plastic liners for the outer container or HICs. The cementitious solidification binders often included pozzolanic materials and sometimes small additions of proprietary ingredients to increase hardening. Less commonly used HICs have solidification binders consisting of bitumen (asphalt) or polymer (vinyl ester styrene).

2.6 Treatment and Disposal of Spent Resins

Investigations on the long-term compatibility of spent resins used to remove decontamination reagents and activation/corrosion products dissolved from reactor systems must address several issues. When resins are directly placed in HICs, material compatibility must be determined. The resins contain strong acids or bases, dependent upon whether they are

Table 2.9 Connecticut Yankee decontamination

STEPS

1. Add 0.1% $KMnO_4$/0.01% NaOH, pH=11 [6 h at 90-95°C (AP)]
2. Add nitric acid until pH=2.5 [6 h at 90-95°C (NP)]
3. Add 0.2% oxalic acid [3 h at 90° decompose excess MnO_4]
4. Remove spent reagents and dissolved corrosion product through mixed-bed resin
5. Add 0.1% LND-101A, pH=2.5 [15h at 100°C (CAN-DECON)]
6. Remove spent reagents and dissolved corrosion product through 2:1 anion/cation mixed-bed resin.

Total resin used is 2,900 liters.

Metal Removed (kg)		Activity Removed (Ci)	
Fe	8.0	^{60}Co	61.8
Ni	7.3	^{58}Co	46.9
Cr	4.1	^{54}Mn	5.2
		Others	4.1
TOTAL	19.4	TOTAL	118.6

cation- or anion-exchange resins. Mixed-bed resins may contain both labile H^+ and OH^-, dependent on the extent of their removal by competing ions removed from the decontamination solutions. Resins loaded with activation products, unused oxidizing agents (MnO_4^-), or unused reducing agents [oxalates, V(II)] can generate gases, absorb or exude water, and further react with net increases or decreases in volume (shrinking and swelling).

Kempf and Soo (1989) describe three incidents when resins reacted vigorously. In one event when resins were being dewatered, a self-generated thermal excursion occurred and temperatures reached 185°C. In two other instances, resins packed into HICs apparently generated gases during transport to burial grounds. The gas over-pressurization led to HIC lids lifting off the containers. Several publications discuss concerns about adverse reactions between ion-exchange resins and permanganate anions left from preoxidation of Cr-rich corrosion products (a larger problem for PWR reactors).

Commonly used resins in the 1980's were Amberlite (Rohm and Haas) IRN-77 (a strong-acid, cation-exchange resin), Amberlite (Rohm and Haas) IRN-78 (a strong-base, anion-exchange resin), and IONAC (Sybron) A-365 (a weak-base, anion-exchange resin). Today Sybron resins appear to be most prevalent.

Resins that have not been loaded with wastes (H^+ saturated or OH^- saturated for cation and anion resins, respectively) hold 47-70 percent moisture. When used to scavenge ions out of decontamination solutions, spent resins hold only 33-47 percent water. It thus appears that spent resins will shrink somewhat when compared to fresh resins. Conversely, if spent resins react during storage or disposal, they may absorb available water and swell, causing pressurization problems.

Kempf and Soo (1989) contacted partially loaded resins (with picolinic/EDTA acids for the anion resins and ferrous ions for the cation resin) with solutions of K permanganate and nitric acid. The loaded cation-exchange resin [50-100 percent Fe(II)] did not show any reaction. On the other hand, loaded anion-exchange resins showed some exothermic reaction when either reagent was contacted. Nitric acid reacted slightly more than permanganate. Whitish precipitate formed that may be picolinic or EDTA acids.

Kempf and Soo (1989) also investigated the corrosivity of these moist resins on common metals and alloys. Test were performed with and without irradiation in a ^{60}Co facility that generated 10^4 rad per hour doses. Tests were run for over a year such that total doses of 10^8 rads were absorbed. Irradiation of sealed resin packages causes an initial drop in overall gas pressure as O_2 is consumed. Soon pressure slowly increases as reducing gases (H_2, CO, etc.) are formed.

Metals contacting the moist resins either show no corrosion (Ferralium and Ticode-12), some attack when irradiated (austenitic stainless steel), or moderate attack under all conditions (carbon steel). The exact nature of attack appears to be H^+ sites on the cation-resin beads touching the metal surface and oxidizing atoms of Fe° metal to Fe(II).

High-density polyethylene containers showed no reaction with moist resins under irradiation because O_2 is removed. Plastic/resin contacts in air show some long-term cracking from O_2 attack on the plastic.

It is not clear from the few reviewed laboratory studies what the long-term fate of resins and their adsorbed decontamination reagents and reactor corrosion products will be if disposed directly in metal or plastic HICs. Gas formation, swelling, metal corrosion, and oxidation-induced plastic cracking do occur at measurable rates under several realistic storage/disposal environments.

The fate of spent resins that are solidified prior to disposal has been the topic of several investigations. Specific publications reviewed include Akers et al. (1993); Ferrara (1991); Keiling and Marx (1991); McIsaac et al. (1992), Morcos et al. (1992); Neilson and Columbo (1982); Piciulo and Adams (1985); Piciulo et al. (1985, 1986); Premuzic and Manaktala (1984); and Soo and Milian (1991).

Brookhaven National Laboratory (BNL) scientists have been investigating solidification of ion-exchange resins into cement for over ten years. Although none of the BNL work described below was performed on actual commercial reactor wastes, the work is useful to our interests and therefore some discussion is presented. Neilson and Columbo (1982) solidified exchange resins that had been soaked with various simple inorganic salt solutions and mixtures of salts [Na_2SO_4, $CaCl_2$, $Al(NO_3)_3$]. Scanning electron microscopy (SEM) was used to investigate the surface of the resin beads solidified in cement. During cement hydration, it appeared that the resin beads had shrunk away from the cement. Alternatively, the shrinkage may have occurred as the beads dried out under the vacuum conditions required in the SEM. The cation-exchange resins react with wet cement. Cement-borne cations Ca(II), Al(III), and Si(IV) replace some of the cations originally loaded onto the resins, and Si(IV) appears to replace the sulfur from the sulfonate (SO_3) group on the resins. Post-mortem studies of waste forms that had broken apart while immersed in water showed that it was the cation resins that swelled and cracked the cement waste forms. Standard Portland cement, high-alumina cement, and modified gypsum-based cement were all studied. The leach rates of three radionuclides from these cementitious wastes were measured. Cesium leached much faster than Sr and Co from all three waste forms. The high-alumina cement was less prone to swelling than the other two but still leached more Cs than standard Portland cement. Neilson and Columbo found that loading the cement with greater than 25 percent (by dry weight) exchange resins caused the solidified forms to swell and break apart during water leaching.

Other BNL investigators studied the solidification of decontamination process, spent ion-exchange resins. Emphasis was placed on developing mix recipes to produce water-resistant waste forms and to measure the leach rates of the organic chelating agents used in the CITROX, LOMI, CAN-DECON, and NS-1 decontamination processes previously described. Piciulo and Adams (1985) and Piciulo et al. (1985, 1986) loaded two anion-exchange resins, Amberlite IRN-78 (a strong-base resin), and IONAC A-365 (a weak-base resin, Cl-loaded pH = 5.5), and one strong-acid, cation-exchange resin, Amberlite IRN-77, with decontamination reagents. A mixed-bed resin was created by mixing two parts anion resin with one part cation resin. The resins were loaded to about 50 percent of their exchange capacity with the decontamination reagents. The IONAC A-365 anion resin was used for LOMI (picolinic and formic acid) tests, while the IRN-78 anion resin was used to adsorb the other decontamination reagents. Note that the reagents were not subjected to corrosion products and the possibility of further reaction in reactor piping systems before being cleansed by exchange onto resins.

The partially loaded resins were then solidified with two binders in separate tests, either Portland type I or DOW polyester-styrene polymer. The resin/water/binder ratios used to solidify the resins are not stated in the three references. For the cement waste forms, the resin/water slurry is first treated with Na hydroxide to create pH = 12 conditions. For the polymer solidified samples, resin-water slurries were pre-treated to pH = 9.5 with HCl prior to mixing. The cylindrical, waste-form specimens, 2-inch diameter by 4-inch height, were leached in deionized water using the ANS 16.1 protocol for 90 days (ANS 1986). Leach results, described in terms of the leachability index (LI defined as - log of the effective diffusion coefficient when expressed in cm^2/s units), are shown in Table 2.10. The data suggest several trends. Most importantly, the organic reagents do not leach faster than other studied radionuclides such as Cs, Sr, and Co. In fact, Cs leaches faster when solidified in these two waste forms than when originally present in evaporated salts. In general, the polymer waste form is more leach resistant than cement. (For leachability indices the larger the value the better the waste form.) Premuzic and Manaktala (1984) show other data for Dow polymer solidification of NS-1 concentrated solution where leach indices for Fe and Ni are greater than 10.5. The LOMI solution and its individual reagents, picolinic and formic acids, leach faster than do CAN-DECON, CITROX, and NS-1 reagents. Generally there is no difference in leach rates for wastes containing only anion resins and those containing both anion and cation resins. Oxalic acid leaches more slowly out of cement than other organic reagents, probably because it forms insoluble Ca oxalates with the high-Ca content in cement.

After 90 days of leaching, only a few percent of reagents such as EDTA, oxalic, and citric acids were leached from the waste forms. Up to 13 percent of the picolinic acid in the LOMI solution-loaded resins leached. Assuming homogeneous mixing within the solids, the percentages that leached equate to depleting the content of the outer 0.3 to 1.5 mm of the waste form surface in 90 days. As typically found for solidified wastes, the leach rates of contaminants slow down with time such that extrapolations to longer times based on short-term ANS 16.1 data should lead to over-estimating release, provided the waste forms do not fall apart during prolonged immersion.

Soo and Milian (1991) summarized many years of work on solidification of cation exchange, anion exchange, and mixed-bed exchange resins into cementitious waste forms. Again we reiterate that the work was performed on fresh reagents and not actual decontamination waste for commercial reactors. The main thrust was to develop water-resistant and physically strong waste forms. Compressive strength testing and 90-day immersion tests were performed on specimens fabricated at numerous resin, water, and cement ratios. Resins studied include the cation-exchange resin Amberlite

Table 2.10 Leach rates for resin-bound organic decontamination reagents from solid wastes

Reagent	Resin	Waste Form Leachability Index (LI)	
		Cement	Polymer
EDTA	MB[(a)]	10.1	>13.0
	AN[(b)]	10.3	13.0
EDTA in mix of equimolar oxalic, citric, EDTA	AN	10.5	--
	MB	10.5	--
Oxalic acid	AM	12.6	--
	MB	--	10.3
Oxalic in mix of equimolar oxalic, citric, EDTA	AN	10.9	--
	MB	11.5	--
Citric acid	AN	10.9	--
	MB	--	--
Citric in mix of equimolar oxalic, citric, EDTA	AM	9.8	--
	MB	10.2	--
Picolinic Acid	AN	9.2	12.4
	MB	9.2	9.8
Picolinic in LOMI	AN	8.6	9.1
(PA and formic acid)	MB	8.8	8.5
Formic Acid	AN	--	--
	MB	8.5	--
Formic in LOMI	AN	8.4	--
	MB	8.3	--
LND - 101 A[(c)]			
Reagent A	AN	10.3	--
B	AN	10.5	--
C	AN	9.8	--

(a) MB = Mixed-bed resin (two parts anion and one part cation).
(b) AN = Anion-exchange resin (IRN-78 for the EDTA, citric, and oxalic acids, and IONAC A-365 for the LOMI reagents.
(c) This reagent is proprietary; reagents within it are not identified in the referenced reports. Other literature identifies the reagents as CAN-DECON, a mix of oxalic, EDTA, and citric acids. We do not know which order BNL used in labeling them A, B, and C.

IRN-77 (loaded with H^+, Na^+, and Fe^{2+}), the anion-exchange resin Amberlite IRN-78 (loaded with Cl, CAN-DECON and CITROX reagents), and IONAC-A-365 (loaded with LOMI reagents). Summary observations include the fact that stable/intact cement waste forms were created only when the weight percent of dewatered resins remained below 30 percent. In general, the loading had to be dropped as low as 12.5 percent to ensure consistently stable waste forms. On a more quantifiable and production basis, the waste-to-cement ratios must be kept at 0.66 to 1.07, where waste is the summed weight of dewatered resin and water. Soo and Milian believe that waste form problems occur because the resins rehydrate slowly as the cement continues to imbibe water during hydration. The resin beads swell and crack the cement. The authors found that cation resins swell less than anion resins when resins are pretreated to get the pH of their slurries within the range of 7 to 9. In general, resins present in cement retard the cement hardening for awhile. Cation-exchange resins loaded with ferric ion are especially set-retarding. Sulfate anions in cement easily replace picolinate anions on anion resin sites but formate anions resist exchange. The replacement of picolinate causes 0 to 13 percent volume shrinkage in the anion resin. Calcium, and to a lesser extent, Al^{3+} and Si^{4+} cations from the cement, will replace Na^{+} and Fe^{2+} ions on cation- or mixed-bed resins loaded during spent decontamination solution cleanup.

Exact correlations among all the variables studied were not obvious, consistent, or readily understandable. A few generalities were offered by the authors. Waste-form strength increases and swelling decreases when the cement hardens rapidly. The lower the ratio of waste resins and water to cement binder, the better the solid product. This is likely caused by a lower-porosity product being less capable of absorbing water. Loading the product with resins at <12.5 percent by weight (dewatered resins) is recommended. It is wise to keep heat of hydration low so that resins do not dehydrate while the cements are curing. Leach rates and physical disintegration occur more rapidly in deionized water than in natural water, probably because the cement and resin pores draw fresh water inward under osmotic forces. The authors warn that all of their findings may not apply to the specialized, proprietary, vendor solidification processes. Vendors using proprietary additives often claim that they can adequately solidify up to 50 percent by weight of dewatered resins.

2.7 Leach Testing of Cement Solidified Spent Resins

Researchers at Idaho National Engineering Laboratory (INEL) obtained several decontamination waste streams and cementitious, solidified decontamination waste forms from commercial reactor operators. Laboratory tests were performed to measure compressive strengths of the cementitious waste forms, their physical stability when immersed in water, and the individual leach rates of various species within the waste forms.

Table 2.11 lists the source and nature of waste streams and final solidified products and types of chemical characterizations that have been performed. Details can be found in McIsaac and Akers (1991), Morcos et al. (1992), Akers et al. (1993a,b; 1994a,b), McIsaac and Mandler (1989), McIsaac et al. (1991, 1992) and McIsaac (1993). Most of the samples of solidified waste were 2-inch-diameter by 4-inch-high right cylinders that had been cured at room temperature.

A few FitzPatrick reactor samples were cured at 49°C for four hours prior to final curing at room temperature. Total cure times for the solid wastes prior to leaching ranged from 119 days for FitzPatrick samples to >900 days for Peach Bottom 3 solid wastes. The chemical composition of the unsolidified resin wastes for three of the reactor decontaminations are shown in Table 2.12. The units for the values are activity or mass per gram of water saturated resin. The leach indices for these three (Brunswick, FitzPatrick and Peach Bottom-3) solidified waste forms are reported in Table 2.13.

All of the Brunswick-1 cement waste forms leached in low-ionic-strength waters (i.e., all but the seawater) completely broke apart. The FitzPatrick samples cured at room temperature showed significant cracking, and the specimens cured at 49°C for four hours early in the 119-d cure completely broke-up. Swelling of the resin beads after the waste forms imbibe water is the likely cause. The three Peach Bottom-3 specimens that were leach tested in deionized water did not break up during the leaching although the INEL reports show only 5 days of leach results.

General observations on specific species leaching for the Brunswick and FitzPatrick samples (both waste forms broke apart during the 90 to 388 day long tests) follow. The Brunswick cation-resin-bearing cement contains much higher activities of nuclides than the mixed-bed resin cement waste (6.7 vs 0.4 μCi/g resin). This is predictable because the cation resin strips out the metallic nuclides (^{54}Mn, ^{55}Fe, ^{60}Co, and ^{63}Ni, etc.) prior to the decontamination solution reaching the mixed-bed resin that removes the organic ligands, Cr(VI), and remaining cations. The FitzPatrick mixed-bed resin activity at 9.0 μCi/g was somewhat higher than that of the Brunswick resins, but the same isotopes dominated.

Table 2.11 Description of decontamination wastes studied at INEL

Waste Stream	Characterization	Solidified Waste Form	Leachant
Brunswick-1 (CITROX/AP/CITROX cation exchange resin Purolite NRW-37)	Nuclide content and stable metals content	Portland cement/Pozzolan	Deionized water Barnwell groundwater Hanford groundwater Seawater
Brunswick-1 (CITROX/AP/CITROX mixed bed exchange resin 6.5% Purolite C-100-H, 58.5% Purolite A-600OH and 35% Purolite NRW-37)	Nuclide content and stable metals content	Portland cement/Pozzolan	Deionized water Barnwell groundwater Hanford groundwater Seawater
FitzPatrick (LOMI waste resins 80% Ionac C-267 and 20% Ionac A-365)	Nuclide content and stable metals content	Portland cement/Pozzolan	Deionized water Barnwell groundwater Hanford groundwater Seawater
Peach Bottom Unit 3 (LOMI-NP-LOMI waste resins-10% IONAC A-365 anion and 90% IONAC C-267 cation)	Nuclide content and stable components	Portland cement/Pozzolan	Deionized water
Millstone-1 F33 (CAN-DECON waste resins Rohm and Haas IRN-77 and IRN-78)	Nuclide content and stable components	Portland cement	Deionized water
Millstone-1 F201 (CAN-DECON waste resins Rohm and Haas IRN-77 and IRN-78)	Nuclide content and stable components	Portland cement	Deionized water
Peach Bottom-2 (CAN-DECON waste resins Rohm and Haas IRN-77 and IRN-78)	Nuclide content and stable components	Portland cement/Pozzalan	Deionized water
Pilgrim (NS-1 decon waste resins not specified)	Nuclide content and stable components	Portland cement/Pozzalan	Deionized water
Cooper (AP/CITROX decon: waste resins mixed bed 10% Purolite C-100-H and 90% Purolite A-600)	Nuclide content and stable components	Portland cement/Pozzolan	Deionized water
Cooper (AP/CITROX decon: waste resin cation Purolite NRW-37)	Nuclide content and stable components	Portland cement/Pozzolan	Deionized water
Indian Point-3 (LOMI waste resins Ionac A-365 and Rohm and Haas IRN-77)	Nuclide content and stable components	Portland cement/Pozzolan	Deionized water

Total transuranic (TRU) isotopes were low: 2.1×10^{-3} and 6.7×10^{-2} μCi/g for Brunswick and FitzPatrick, respectively. The dominant TRU isotope in both cases was ^{241}Pu. All leachates from the cement waste forms, except seawater, showed highly alkaline pH values (11.4 to 12.5), dependent upon contact time. The cause for the high leachate pH values is undoubtedly the dissolution of $Ca(OH)_2$ from the cement. Seawater pH values are slightly lower because of its higher buffering capacity and because a large surface rind of $CaCO_3$ formed on the cement specimens that likely slows release of most constituents, including OH^- from the waste form interior. The release of transition metals, and by inference transuranics, does not depend on whether the waste form remains intact or crumbles into small pieces. This suggests that their release is not controlled by diffusion out of the solid but is controlled by pH-dependent solubility reactions. From Table 2.13 it is apparent that release of transition metal radionuclides (Mn, Fe, Co, and Ni) is higher from cements containing anion-exchange resins loaded with organic acid complexing agents than from cements containing only cation-exchange resins. Leachability indices decrease (leach diffusion coefficients increase) about two orders of magnitude when organic acid complexing agents are present in the cement waste forms. Despite the observed increase in leaching from wastes containing organic complexants, the absolute values for release remain quite low, De

Table 2.12 Composition of spent resins (μCi/g and μg/g)

	Brunswick - 1 Resins		FitzPatrick	Peach Bottom
Constituent	Cation	Mixed Bed	Mixed Bed	Mixed Bed
^{51}Cr	ND[a]	ND	0.43	ND
^{54}Mn	0.53	0.022	1.25	0.044
^{55}Fe	2.8	0.15	0.03	1.35
^{59}Fe	<0.07	<0.01	0.47	ND
^{57}Co	ND	ND	0.005	ND
^{58}Co	0.06	0.003	1.3	ND
^{60}Co	2.65	0.13	4.91	4.64
^{63}Ni	0.07	0.006	0.027	0.076
^{65}Zn	0.04	0.002	0.292	0.59
^{90}Sr	0.001	0.0008	8x10^{-5}	2.2x10^{-5}
^{95}Zr	<0.01	<0.005	0.006	NA
^{95}Nb	ND	ND	0.014	NA
^{113}Sn	ND	ND	0.007	NA
^{125}Sb	0.001	0.005	0.011	0.017
^{134}Cs	<0.0003	<7x10^{-5}	0.01	ND
^{137}Cs	0.014	0.0004	0.02	0.004
^{238}Pu	2.6x10^{-7}[b]	7.9x10^{-8}[b]	2.5x10^{-5}	6.6x10^{-5}
^{239}Pu	2.0x10^{-7}	6.9x10^{-8}	4.5x10^{-5}	2.2x10^{-5}
^{241}Am	b	b	3.7x10^{-5}	5.2x10^{-5}
^{242}Cm	1.2x10^{-8}	3.0x10^{-8}	4.1x10^{-5}	9.5x10^{-6}
^{244}Cm	2.6x10^{-8}	5.0x10^{-9}	4.3x10^{-6}	1.3x10^{-4}
^{241}Pu	NA[c]	NA	NA	0.018
^{14}C	NA	NA	NA	8.7
^{99}Tc	NA	NA	NA	0.037
^{129}I	NA	NA	NA	<5x10^{-6}
Cr	450	1580	195	650
Fe	6400	690	2380	3000
Co	208	297	256	NA
Ni	730	64	116	730
Zn	NA	NA	NA	158
Oxalic acid	NA	20000	NA	NA
Citric acid	NA	41000	NA	NA
Picolinic Acid	NA	NA	NA	<0.63

(a) ND = Not detected (below detection limit).
(b) Analysis is total ^{238}Pu + ^{241}Am.
(c) NA = Not analyzed.

Table 2.13 Leachability indices for species from solidified waste forms into groundwaters (see Table 2.11 for description)

	Brunswick - 1		FitzPatrick	Peach Bottom
Constituent	Cation Resin	Mixed Bed	Mixed Bed	LOMI Resins[a]
^{54}Mn	>16	>12.7	12.7 - 14.6	NR[b]
^{55}Fe	14.8 - 16.6	12.9 - 14.1	10.9 - 12.0	9.7-12.9 ave. 12.2
^{58}Co	>11.5	>8.3	10.4 - 11.1	NR
^{60}Co	16.3 - 16.7	13.5 - 13.8	10.3 - 10.8	10.9-11.4 ave. 11.4
^{63}Ni	11.0 - 11.6	11.0 -12.4	NR	10.3-14.3 ave. 10.4
^{65}Zn	>13.2	>9.8	11.0 -12.9	NR
^{90}Sr	10.9 - 12.8	10.9- >12.9	NR	9.3-11.2 ave. 10.9
^{125}Sb	>10.6	10.8 - 11.0	>10.8	10.4
^{134}Cs	>9.6	>8.1	6.6 - 6.9	NR
^{137}Cs	10.1 - 10.7	7.2 - 8.5	6.7 - 7.0	9.3
^{14}C	NR	NR	NR	12.1-14.4 ave. 13.5
^{99}Tc	NR	NR	NR	10.1-11.5 ave. 11.0
Cr	>9.7	>10.5	>11.2	9.3-9.5 ave. 9.4
Fe	>10.3	>8.3	>11.5	13.0-14.7 ave. 14.4
Co	>7.7	>7.8	>10.0	8.6-8.7 ave. 8.6
Ni	>8.9	>6.5	9.5 - 10.2	8.7-9.1 ave. 8.9
Oxalic Acid	NR	10.3 - 10.6	NA[c]	NA
Citric Acid	NR	10.4 - 11.2	NA	NA
Picolinic Acid	NA	NA	7.2 - 8.5	9.3 ave. 9.3

(a) Leached in deionized water, not groundwaters.
(b) NR = Not reported; constituent found in waste but leachate not analyzed.
(c) NA = Not analyzed; constituent not found in waste.

values $<10^{-10}$ cm^2/s. Picolinic acid appears to leach much faster than citric and oxalic acids. As mentioned, Ca oxalate solubility may limit the release of oxalic acid. The INEL data on the release of organic complexing agents from actual reactor solidified decontamination wastes agree with the BNL data on simulated decontamination wastes. Both studies show that picolinic acid leaches faster than citric, oxalic, and EDTA acids.

Alkaline earth (^{90}Sr), alkali metals (^{137}Cs), and ^{125}Sb do not show sensitivity to the presence or absence of organic acids in the solidified wastes. On an absolute scale, Cs leaches two to three orders of magnitude faster than Sr and the transition metals.

Other studies on leaching of contaminants from actual decontamination wastes solidified in cement (Portland type I or mixtures of cement and additives) using deionized water only have been performed at INEL. Details have been extracted from McIsaac and Mandler (1989), and Akers et al. (1994a,b). Small, solidified waste specimens were obtained by dip sampling out of the large disposal containers prior to cement hardening. Samples of the spent resins were also obtained and characterized for chemical and radionuclide contents. Solidified sample description is presented in Table 2.14. The Peach Bottom-2 samples are not the same as those identified as Peach Bottom-3 in Tables 2.11 - 2.13. Characteristics of the spent resins prior to solidification are shown in Table 2.15. The resultant leach data expressed as leachability indices are shown in Table 2.16. From Table 2.15 it can be seen that ^{54}Mn, ^{55}Fe, ^{58}Co, ^{60}Co, and ^{63}Ni represent the major radioactivity bound to resins. Small amounts of the fission products ^{137}Cs, ^{125}Sb, and ^{90}Sr are also present. Transuranic activities are predominantly ^{241}Pu. Large amounts of Fe and Ni (approaching mg/cm^3 of resin) and trace amounts of Cr and Co (tens of μg/cm^3 of resin) are bound to the cation- and mixed-bed resins. Mixed-bed resins used to cleanse spent CAN-DECON solutions contain mg/cm^3 of resin concentrations of oxalic, citric, and EDTA acids, while mixed-bed resins used to cleanse LOMI solutions contain mg/cm^3 of resin concentrations of picolinic and formic acids. Cation resins contain less than 1 percent as much organic ligands.

Leach studies that used deionized water as the leachant show faster release of constituents during the first several days followed by slow decreases in leaching out to 90 days. This initial rapid release followed by a gradually slowing release is quite common for solidified waste studies (e.g., Serne and Wood 1990). The leachability indices shown in Table 2.16 show very little leaching of transition metals and ^{241} Pu, the dominant TRU nuclide. Release of ^{90}Sr is intermediate and release of ^{137}Cs is fastest. The total amount of transition metal and TRU nuclide or stable metal released from the small (2-inch diameter x 4-inch height) specimens in 90 days would have been present in the surface 0.03- to 0.5-mm layer. Conversely more than 70 percent of the specimens released their total inventory of ^{137}Cs within 90 days. Release rates for transition metals (both stable and radioactive) did not increase dramatically for specimens that developed cracks and sloughed off some particulates, except for those specimens of Cooper Power Plant waste that completely deteriorated within hours. This suggests that solubility reactions and not diffusion may control their release. The INEL authors caution that some of the early release data (LIs in Table 2.16) for the Cooper cation-resin solid waste form are biased because the leachate samples were not filtered and the solid waste specimens were actively crumbling with the formation of fine particulates during the first several samplings.

The release of organic reagents from CAN-DECON and CITROX processes are intermediate compared to transition metals and ^{137}Cs. The release of organics from the Pilgrim Reactor (NS-1 process) and Indian Point-3 (LOMI process) was larger. Up to 30 to 80 percent of these reagents were released in 90 days. This is about one-half the rate of ^{137}Cs and 10 to 100 times faster than the release of transition metals.

Table 2.14 Description of cement-solidified resin waste samples from decontamination processes

Sample Identification and Process				Solidified Waste Form				
Sample Identification	Decon Process	Cure Time (Days)	Waste Type	Diameter x Height (cm)	Surface Area (cm^2)	Mass (g)	Volume (cm^3)	Durability During Leaching (~90 days)
Millstone-1 F33	CAN-DECON	684	Rohm and Haas (R&H) IRN-77 and IRN-78	4.8 x 5.1	107	114.3	84.9	3 to 5% broke off
Millstone-1 F201	CAN-DECON	684	R&H IRN-77 & IRN-78	4.8 x 6.2	115	125.9	93.5	3 to 5% broke off
Peach Bottom-2	CAN-DECON	571	R&H IRN-77 & IRN-78	4.8 x 8.9	169	207.7	158.4	remained intact
Pilgrim	NS-1	654	NA[a]	4.8 x 9.2	173	215.2	164.1	remained intact
Cooper (mixed bed)	AP/CITROX	710	10% Purolite C-100-H, 90% Purolite A-600	4.4 x 9.5	164	205.2	147.8	total crumbling in 1 hour
Cooper (cation)	AP/CITROX	802	Purolite NRW-37	4.4 x 10.2	173	215.6	157.7	total crumbling in 8 hours
Indian Point-3	LOMI	539	IONAC A-365, R&H IRN-77 + cation resin from radwaste	4.6 x 9.5	171	202.5	158.6	remained intact

(a) NA = Not available.

Table 2.15 Chemical composition of spent resins [nuclides expressed as μCi/cm^3 settled wet resin; chemicals expressed as μg/cm^3 (same conditions)]

Constituent	Indian Point-3	Cooper Mixed-Bed	Cooper Cation	Millstone	Pilgrim	Peach Bottom-2
^{3}H	5.1×10^{-4}	3.8×10^{-4}	3.9×10^{-6}	1.1×10^{-3}	2.1×10^{-5}	2.6×10^{-2}
^{14}C	4.8×10^{-5} [a]	$<1 \times 10^{-5}$ [a]	$<1 \times 10^{-5}$ [a]	3.6×10^{-5} [a]	5×10^{-5} [a]	ND[c]
^{54}Mn	4.8×10^{-1}	1.4×10^{-1}	1.0	2.4	3.8×10^{-1}	1.7×10^{-1}
^{55}Fe	1.7	4.0×10^{-1}	5.7	20	2.7	ND
^{57}Co	4.4×10^{-2}	ND[c]	ND	ND	ND	ND
^{58}Co	22.5	3.9×10^{-2}	7.1×10^{-1}	5×10^{-1}	9×10^{-2}	ND
^{60}Co	3.9	7.3×10^{-1}	6.7	7.8	5.2	11.8
^{63}Ni	4.8	3.6×10^{-1}	10.3	8.7×10^{-1}	2.8×10^{-1}	ND
^{90}Sr	1.3×10^{-4}	2.0×10^{-4}	7×10^{-5}	5.9×10^{-4}	1.5×10^{-4}	1.6×10^{-5}
^{95}Nb	ND	9×10^{-3}	ND	ND	ND	ND
^{99}Tc	NA	1.1×10^{-4}	3×10^{-5}	ND	2.2×10^{-5}	ND
^{129}I	$<1 \times 10^{-5}$	$<3 \times 10^{-5}$	$<4 \times 10^{-5}$	$<2 \times 10^{-6}$	$<2 \times 10^{-6}$	ND
^{125}Sb	9.3×10^{-4}	4.2×10^{-2}	$<2 \times 10^{-4}$	1.6×10^{-1}	8.4×10^{-3}	$<6 \times 10^{-5}$
^{137}Cs	1.3×10^{-1}	2.1×10^{-4}	$<2 \times 10^{-4}$	2.1×10^{-3}	3×10^{-2}	$2{,}8 \times 10^{-3}$
^{238}Pu	1.2×10^{-5}	3.1×10^{-5}	7.7×10^{-5}	4.9×10^{-3}	2.2×10^{-4}	ND
$^{239/240}$Pu	1.3×10^{-5}	1.5×10^{-5}	3×10^{-5}	2.6×10^{-3}	3.1×10^{-4}	ND
^{241}Pu	4.9×10^{-2}	2.2×10^{-2}	1.0×10^{-2}	3.5×10^{-1}	3.5×10^{-2}	5.1×10^{-3}
^{241}Am	9.4×10^{-6}	2.4×10^{-5}	1.1×10^{-4}	4.0×10^{-3}	5.3×10^{-6}	ND
^{242}Cm	1.9×10^{-4}	6.4×10^{-5}	6.8×10^{-5}	4.1×10^{-4}	1.7×10^{-5}	ND
^{244}Cm	1.1×10^{-5}	6.6×10^{-5}	8.1×10^{-5}	3.4×10^{-3}	1.4×10^{-5}	ND
Fe	660	520	11,000	5,800	1,100	NA[b]
Ni	710	74	1,200	2,100	140	NA
Co	<12	<15	60	16	9.6	NA
Cr	90	NA	300	350	NA	NA
Oxalic acid	NP[d]	16,200	270	7,400	290	5,900
Citric acid	NP	25,000	96	6,300	3,000	5100
EDTA	NP	NP	NP	6,100	3,700	4,900
DTPA	NP	NP	NP	NP	360	NP
Formic acid	4,000[e]	NP	NP	NP	NP	NP
Picolinic acid	4,100	NP	NP	NP	NP	NP

(a) ^{14}C data are expressed as μCi/cm^3 of dry resin.
(b) NA = Not analyzed (potentially present but not looked for).
(c) ND = Not detected (below an unspecified detection limit).
(d) NP = Not present in waste; thus not analyzed.
(e) Formic acid not analyzed; estimate based on picolinic acid concentration.

Table 2.16 Leachability indices for species in solid wastes

Constituent	Indian Point-3	Cooper Mixed Bed	Cooper Cation	Millstone F-33	Millstone F-201	Pilgrim	Peach Bottom-2
^{54}Mn	13.8 to 16.5	~12.7	10.5 to 14.3	13.4 to 15.4	13.3 to 16.2	>10.1 to 13.2	11.9 to >13.4
^{55}Fe	12.5 to 16.3	10 to 11.5	8.7 to 11.5	NA[a]	13.6 to 16.9	14.9 to 17.5	NA
^{60}Co	12.5 to 13.6	11.9 to 14.9	12.5 to 14.6	12.7 to 14.6	12.2 to 14.0	8.7 to 10.0	12.6 to 13.1
^{63}Ni	12.8 to 14.5	13.6 to 15.3	12.0 to 15.3	NA	10.5 to 11.8	6.5 to 7.7	NA
^{90}Sr	8.0 to 9.3	10.2 to 11.8	fast release	NA	7.5 to 8.5	7.2 to 9.5	>8.6 to 9.8
^{125}Sb	>9.5 to >12.2	10.1 to 12.5	3.7 to 6.3	11.1 to 13.6	10.8 to 13.4	>7.1 to 8.5	ND[b]
^{137}Cs	6.4 to 7.4	fast release	fast release	5.8 to 6.5	5.9 to 6.6	>10.4 to 13.4	7.6 to 7.9
^{241}Pu	>11.1 to >13.9	>10.3 to <12.8	>10.2 to >12.8	NA	>13 to >16	>11.5 to <13.5	79.5 to >11.1
Stable Metals							
Cr	>9.6 to >11.7	NA	6.0 to 11.0[c]	NA	>10.8 to >12.8	ND	NA
Fe	10.7 to <13.4	>10.6 to >12.5	5.2 to >13.2[c]	NA	>13.3 to >15.3	>12.0 to >14.0	NA
Co	ND	ND	6.1 to >9.2[c]	NA	>6.8 to >8.8	>6.5 to >8.5	NA
Ni	9.5 to 11.1	7.6 to >9.4	5.7 to 11.7[c]	NA	10.1 to 11.6	6.3 to 7.6	NA
Organic Regents							
Oxalic	NP[d]	8.8 to 11.8	ND	9.4 to 11.7	9.4 to 9.6	6.5 to 7.6	9.4 to 11.7
Citric	NP	8.8 to 12.3	6.5 to 7.3	9.2 to 11.3	9.3 to 11.0	5.6 to 7.5	8.7 to 11.7
EDTA	NP	NP	NP	7.6 to 8.9	7.9 to 8.6	5.3 to 6.7	8.1 to 11.6
DPTA	NP	NP	NP	NP	NP	6.8 to 8.1	NP
Formic	6.5 to 7.2	NP	NP	NP	NP	NP	NP
Picolinic	6.7 to 7.6	NP	NP	NP	NP	NP	NP

(a) NA = Potentially present but not analyzed.
(b) ND = Below an unspecified detection limit.
(c) The small LI value at the start of tests is likely biased by particulates.
(d) NP = Not present, thus not analyzed.

The results of McIsaac and Mandler (1989) are similar to other INEL studies on CITROX and LOMI solidified wastes and simulated decontamination studies performed at Brookhaven National Laboratory. The LOMI reagent, picolinic acid, leaches faster than CAN-DECON or CITROX reagents.

The release of transition metals (activation products and stable element corrosion products) and actinides from cement solidified wastes is very low (LIs >10 and normally ~12). The presence of co-leached organic reagents does increase transition metal release by a factor of 10 and in a few situations by two orders of magnitude. The release of ^{90}Sr and especially ^{137}Cs is significantly higher than transition metals. The presence of co-leaching organic decontamination reagents does not affect Sr or Cs release.

2.8 Leaching of Chelating Agents from Cement

One other study of the release of organic ligands and their impact on the release of radionuclides from cement solidified waste forms was found. Ferrara (1991) performed laboratory tests on a simulated low-level nuclear waste [$NaNO_3$ salts solidified in cement with and without the presence of chelating agents (EDTA and citric acid being of interest to our review)]. The waste forms were leached in deionized water and several brines (NaCl, $MgCl_2$, and mixed $MgCl_2$, $MgSO_4$, KCl, and NaCl) of interest to the Federal Republic of Germany nuclear waste disposal program in bedded salts.

The cement waste forms (small 50-cm^3 cylinders) were made using 310 g cement, Portland type I/II, 50 g $NaNO_3$, and 140 g water. Trace quantities (either 0.3 g or 1.5 g Na-EDTA or 0.2 g or 1.5 g Na citrate) of organic ligands, 40 μCi ^{137}Cs, and 12 μCi ^{60}Co were also added to several waste forms so that the effects of ligands on radionuclide release could be determined.

The cement waste forms were cured for two to three months prior to the leach tests. Each 50-cm^3 waste form was immersed in 300 ml of leachant (deionized water or one of three brines). The tests were static in that leachant was not replaced. At 1, 2, 4, 8, and 22 weeks of immersion, a few milliliters of solution were removed, filtered through 0.0018-μm membranes, and the radionuclide- and organic-ligand contents measured.

The release of ^{137}Cs after 22 weeks was nearly 40 percent of the original inventory regardless of the amount and type (or absence) of organic ligand present in the cement. The amount of ^{60}Co leached in all tests was below detection limits. The release of EDTA after 22 weeks was about 1 percent, while the citrate release was below detection limits. A rather insensitive titration method was used to measure ligand release so one should not assume that citrate was not released. One can assume that the release was minor (<1 percent of inventory) and perhaps is controlled by an insoluble compound. Fractional release of EDTA is constant at the two starting inventories, suggesting that there is no solubility control for EDTA in cement.

In other batch "solubility" tests, 2 to 3 g of crushed cement laden with chelants and radionuclides were immersed in the same leachants (30 ml). The amounts of chelating agent released after three, four, and five weeks were determined. For the deionized water leach tests, additional ^{60}Co and stable Co were added to the solution to determine Co solubility. Equilibrium was achieved within the three-week sampling period. The EDTA concentration in the deionized water leachate was 2.4×10^{-4} and 4.5×10^{-5} M for the original EDTA inventories of 0.3 percent and 0.03 percent within the cement. These values are much below the expected EDTA solubility in cement leachate. The authors suggest adsorption of EDTA on the cement as the cause. Citrate concentrations were below the detection limit $<1 \times 10^{-5}$ M, suggesting that Ca citrate may be insoluble. Cobalt in the presence of cement-water leachates was very low ($\sim 1 \times 10^{-6}$ M). The presence or absence of chelating agents did not influence cobalt solution concentrations.

In simple solutions of 1 percent chelates and pH = 12.5 with Na hydroxide, Co concentrations are much higher when citrate or EDTA are present. That is, when no solid cement or high-Ca solution concentrations are present, Co-ligand complexes readily form and increase Co solution concentrations. When cement is present, either Co adsorbs onto the solid or the high-Ca solution concentration outcompetes Co for the EDTA ligand, and the free Co precipitates or adsorbs onto the cements. [The cement released high Ca and Na concentrations (1.4×10^{-2} and 8×10^{-2} M) and buffered the pH to 12.5.] See Section 3.2 for discussions of thermodynamic calculations to predict these changes. Table 2.17 shows actual data presented in Ferrara (1991).

Table 2.17 Concentration of cobalt in high-pH leachates

	Co Concentration (M)	
Complexing Agent	With Cement	No Cement
None	$<1 \times 10^{-5}$	1.6×10^{-4}
EDTA	4×10^{-5}	2.8×10^{-2}
Citric Acid	4×10^{-5}	1.8×10^{-2}
Oxalic Acid	$<1 \times 10^{-5}$	$<1 \times 10^{-5}$

2.9 Summary of Leach Results for Species from Cement Solidified Spent Resins

The following summary paraphrases important concluding remarks in the last of the INEL studies on leaching of cement solidified spent decontamination resins and where appropriate mentions corroborating facts from the few other studies that were reviewed. The LOMI reagents (picolinic and formic acids) leach faster than EDTA , while citric and oxalic acids leach slowest. Transition metal radionuclides and corrosion products (stable metals) leach very slowly from solidified cements. Stable nickel leaches faster than stable iron, cobalt and chromium. For radionuclides iodine and cesium leach fastest followed by Sr, Ni, Tc, Co, Fe and ^{14}C. The presence of the organic chelating agents in leachates does increase radionuclide and transition-metal release by a factor of 10 to 100, but the transition-metal radionuclides' leach rates still remain quite low. For example, when expressed as leachability indices, transition metal radionuclides (Fe, Ni, Cr, Mn, etc.) leach with LIs between 10 and 12 in the presence of organic ligands and 12 to >13 when ligands are not present. Non transition- metal radionuclides that are believed to not form strong complexes with the ligands (^{90}Sr and ^{137}Cs) leach faster with LIs from 7 to 10 and 6 to 8, respectively. Table 2.18 summarizes the INEL data presented in Akers et al. (1994b).

Many of the solidified waste specimens physically broke apart during the INEL leach testing, apparently from resin-bead, rehydration-induced swelling. The release rates of transition metal radionuclides do not increase dramatically when waste forms degrade, suggesting that solubility processes are more important than diffusion. The release of organic ligands does increase some with specimen disintegration, and the release of ^{137}Cs is significantly increased.

Many of the INEL reports list the actual concentrations/activities of organic ligands, stable transition metals, and radionuclides in leachates from 90-day ANS 16.1 leach tests. In general, formic and picolinic acids reach concentrations between 10 and a few hundred parts per million, EDTA concentrations are 1 to 100 ppm, citric acid concentrations are 1 to 30 ppm, and oxalic acid concentrations are 1 to 2 ppm. Transition metal concentrations are generally <0.05 ppm with a few data points in the low parts per million range. Radionuclide activities are 0.01 to 10 μCi/L for transition metals.

Table 2.18 Summary of INEL leach data for cement-solidified spent resins (LI's)

		Constituents Leached						Stable Metals		Radionuclides			
Sample ID	Decon Type	Picolinic Acid	Formic Acid	Oxalic Acid	Citric Acid	EDTA	DPTA	Fe	Ni	^{137}Cs	^{60}Co	^{55}Fe	^{63}Ni
Indian Point 3	LOMI	6.9	6.7	NP[(a)]	NP	NP	NP	>12.1	10.1	6.7	12.8	14.6	13.5
FitzPatrick	LOMI	7.5	--[(b)]	NP	NP	NP	NP	>12.0	9.4	7.1	10.5	11.6	8.9
Peach Bottom 3	LOMI	9.3	--	NP	NP	NP	NP	14.4	8.9	--	11.4	12.2	10.4
Cooper (Mixed Bed)	CITROX	NP	NP	10.2	10.5	NP	NP	>11.2	>8.1	5.9	12.8	10.3	13.9
Brunswick (Mixed Bed)	CITROX	NP	NP	11.0	11.5	NP	NP	>10.5	>8.5	7.9	13.2	11.0	12.3
Millstone F-33	CAN-DECON	NP	NP	10.1	10.8	8.3	NP	--	--	6.1	13.6	--	--
Millstone F-201	CAN-DECON	NP	NP	9.5	10.4	8.3	NP	>14.0	10.7	6.1	13.2	14.9	11.1
Peach Bottom 2	CAN-DECON	NP	NP	10.1	10.0	9.0	NP	--	--	7.8	12.8	--	--
Pilgrim	NS-1	NP	NP	7.2	6.5	5.7	7.5	--	6.9	12.1	9.2	16.1	7.1

a) NP = not present, thus not analyzed.
b) -- = not reported.

All the INEL leach data will be used to perform speciation calculations to help determine whether the observed leaching of transition metals and radionuclides are controlled by formation of stable radionuclide-chelating complexes. These thermodynamic calculations will be the topic of the second report to be produced in this project. The speciation calculations will also allow predictions on the probable speciation of radionuclides in soil porewater after the leachate leaves the burial ground. At the moment speciation calculations are our only means at determining the importance of radionuclide-chelating agent complexes because none of the available data specifically differentiates the complex species from the total organic ligand, stable metal or radionuclide present in the leachates and spent resins prior to leaching. Section 3.1 and 3.2 discuss the thermodynamic data available and the methodology to perform the speciation calculations. Section 3.3 discusses the state-of-the-art analytical techniques for attempting to determine the radionuclide-organic ligand complexes directly.

3 Aqueous Complexation of Radionuclides

The ability of organic chelating agents to influence the migration of radionuclides in soils or sediments is fundamentally tied to the aqueous radionuclide-chelate complexes that can form and the strength of such complexes. Therefore, it is of fundamental importance that the aqueous radionuclide-chelate complexes be identified and their concentrations determined in the leaching solutions. There are basically two methods for determining the concentrations of radionuclide-organic chelate complexes in aqueous solutions: 1) thermodynamic equilibrium calculations using stability constants for the metal ions with the chelates, inorganic ligands (such as SO_4 and CO_3), and competing cations (e.g., Ca^{2+}, Mg^{2+}); and 2) direct analytical identification of radionuclide-organic chelates. The direct identification of radionuclide-chelate complexes in leachate solutions is important not only in establishing the presence of these complexes but also in validating the thermodynamic calculations. The thermodynamic calculations are also useful for identifying possible radionuclide-chelate complexes and providing information on the strength of these complexes. The strength of the formed complexes is important in predicting the fate of the chelated metals as they migrate through soils and sediments.

This section reviews the analytical methods for identifying organic ligands and chelate-radionuclide complexes in radioactive wastes, along with the available thermodynamic data for performing the thermodynamic equilibrium calculations to identify possible radionuclide-chelate complexes. Information on the reaction kinetics of these complexes with soils or sediments is discussed in Section 4.

3.1 Availability of Thermodynamic Data

The available thermodynamic data were reviewed for the formation of metal complexes with the protonated and unprotonated forms of citric acid, diethylenetriaminepentaacetic acid (DTPA), ethylenediaminetetraacetic acid (EDTA), oxalic acid, and picolinic acid. The following metals were included in the review: Am, Ca, Cm, Co, Cr, Cs, Fe, Mg, Mn, Nb, Ni, Pu, Sr, Sn, Zn, and Zr. These ligands and metals were chosen based on their presence in decontamination wastes from nuclear reactors or their natural occurrence in groundwater. The objective of this task was to compile these data, identify important data that are unavailable, and identify readily apparent inconsistencies or errors among the data. A critical review of these data was beyond the scope of this work.

Several critical compilations of thermodynamic stability-constant data (Sillen and Martell 1964, 1971; Martell and Smith 1974, 1977, 1982, and 1989) have been performed and provided most of the data discussed in this section. In addition, a computerized database literature search was conducted to provide recent (post 1989) supplementary data unavailable from the critical compilations. This search provided only a few additional data not already tabulated in the critical compilations.

The data are arranged and discussed in five sections, one for each of the protonated forms of the ligand of interest. Data for each metal are discussed in these sections. The reported values were assumed to be reasonably reliable if they met all of the following criteria: 1) at least two, independent, stability-constant studies were conducted for a particular metal-ligand system; 2) results of the studies are consistent; and 3) the studies do not have any obvious problems noted in the critical reviews. It should be noted, however, that this does not guarantee reliability. Stability-constant determinations are often problematic. In complicated systems important species are sometimes misidentified or omitted, and in some cases, the studies can be fraught with experimental difficulties. In some cases it is possible that different investigators have repeated the same errors, resulting in comparable but incorrect results. However, because the vast majority of the data compiled here are derived from critical reviews, the chances of these kinds of errors are reduced.

3.1.1 EDTA

Table B.1 in Appendix B is a compilation of the available data for EDTA complexation. EDTA complexation data for Cs are apparently unavailable at this time.

At least two studies of EDTA complexation were available and consistent for the following metals: Al, Ca, Co(II), Co(III), Fe(II), Fe(III), Mg, Mn(II), Ni, Pu(VI), Sr, Zn, and Zr. Only one set of data is available for Am, Cm, Cr(III), Nb(V), Pu(V). There are also data available for Pu(III) and Pu(IV), but large discrepancies appear to exist in these data.

For the readily hydrolyzable metals, Al(III), Cr(III), Fe(III), Mn(III), and Zr(IV), very strong ML complexes are formed with EDTA, where M represents the bare metal ion and L represents the fully deprotonated form of EDTA (L^{4-}). EDTA complexes of the form MH_xL^{4-x}, where x represents the number of H^+ ions attached to EDTA, are also formed with these metals. Stability constants for these complexes are considerably lower than those for the ML complexes. These metals also tend to form mixed hydrolysis species $[M(OH)_xL]$, where x can be an integer between 1 and 3. Data are not available for the MHL species for Zr^{4+}.

The trivalent actinides, Am(III), Cm(III), and Pu(III), also form very stable ML complexes. Stability constants for the MHL or $M(OH)_xL$ species are not available. As indicated before, the Pu(III) data are uncertain.

With EDTA, Co(III) forms extremely strong ML complexes. In addition, data are available for the MHL complex; however, this constant appears to be inexplicably low relative to the ML constant. Stability constants are not available for the $M(OH)_xL$ complex for Co(III).

The divalent transition metals, Co(II), Fe(II), Mn(II), Ni(II), and Zn(II), also form ML complexes with EDTA that have large stability constants. Data are also available for the MHL and $M(OH)_xL$ complexes. However, data are not available for the $M(OH)_xL$ complexes for Co(II) and Mn(II). Stability-constant data are also available for the MH_2L complexes for Co(II), Ni(II), and Zn(II). These complexes are quite weak.

The alkaline earth metals, Ca^{2+}, Mg^{2+}, and Sr^{2+}, form ML complexes with EDTA that are quite strong. They are, however, considerably less stable than the transition metal-ligand complexes previously discussed. Data are also reported for alkaline-earth MHL complexes, but these complexes appear to be relatively weak.

Although it appears that Pu^{4+} will form strong complexes with EDTA, the data remain uncertain. PuO_2^+ forms ML and MHL complexes with EDTA that are similar in strength to the alkaline earth metals. Only one set of data is currently available for PuO_2^+.

Very little data are available for Nb^{5+}. The stability constant for the reaction of $Nb(OH)_2^{3+} + L^{4-} = Nb(OH)_2L^-$ is quite large, log K = 40.8. However, it is difficult to determine the significance of this species because the hydrolysis constants for Nb^{5+} are known only for the conversion of $Nb(OH)_5^0$ to $Nb(OH)_4^+$ and $Nb(OH)_6^-$.

3.1.2 DTPA

Table B.2 in Appendix B is a compilation of the available data for DTPA complexation. Although DTPA forms complexes that tend to be somewhat stronger than those of EDTA, fewer data are available for DTPA. Data for DTPA complexation for Cr, Cs, Nb, Pu, and Co(III) are apparently unavailable at this time.

At least two studies of DTPA complexation were available, consistent, and considered to be reliable for the following metals: Al(III), Am(III), Ca, Cm(III), Co(II), Fe(II), Fe(III), Mg, Mn(II), Ni, Sr, Zn, and Zr.

As with EDTA, DTPA (H_5L) forms very strong complexes of the form ML with the readily hydrolyzable metals, Al(III), Fe(III), and Zr(IV). DTPA complexes of the form MHL are also formed by these metals. Stability constants for the MHL complexes are considerably lower than those for the ML complexes. Data are not available for the MHL species for Zr(IV). These metals also tend to form mixed hydrolysis species [$M(OH)_xL$], where x can be 1 or 2.

The trivalent actinides, Am(III) and Cm(III), form very stable ML complexes. Stability constants for the MHL or $M(OH)_xL$ species are not available.

The divalent transition metals, Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+}, also form ML complexes with DTPA that have large stability constants. These metals tend to form very stable MHL complexes also. Data for the $M(OH)_xL$ complexes, where x is 1 or 2, are available for Fe^{2+}. Stability-constant data are available for the MH_2L complexes for Co^{2+}, Ni^{2+}, and Zn^{2+}. These complexes are relatively weak.

The alkaline earth metals, Ca^{2+}, Mg^{2+}, and Sr^{2+}, form ML complexes that are quite strong. They are, however, of considerably lower stability than the complexes of transition and actinide metals previously discussed. These alkaline earth metals also form MHL complexes that are considerably stable.

3.1.3 Picolinic Acid

Table B.3 in Appendix B is a compilation of the available data for picolinic acid complexation. Picolinic acid complexation data for Al, Am, Cu, Cs, Nb, Zr, Co, Mn, Pu(III), Pu(IV), and Pu(V) are apparently unavailable at this time.

At least two studies of picolinic acid complexation were available and consistent for the following metals: Ca, Co(II), Fe(III), Mg(II), Mn(II) Ni, Sr, and Zn. Only one set of data is available for Cr(III), Fe(II), and Pu(IV). Although data for Am(III) and Cm(III) are not available, stability constants for picolinic acid are available for the trivalent lanthanide ions (Yoneda et al. 1965; Gritman et al. 1977). As a result of the analogous behavior of the trivalent lanthanides and trivalent actinides, it will be possible to estimate data for Am(III) and Cm(III) (Krauskopf 1986; Cantrell 1988; Rai et al. 1992; Felmy et al. 1989).

For the readily hydrolyzable metals, Cr(III) and Fe(III), moderately strong complexes of the form ML_2 are reported for picolinic acid (HL). Data are also available for the $M(OH)L_2$ species for Fe^{3+}. Data for the ML complex for these metals are not available.

The divalent transition metals, Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+}, form ML, ML_2, and ML_3 complexes with picolinic acid that have fairly large stability constants. The alkaline earth cations, Ca^{2+}, Mg^{2+}, and Sr^{2+}, form ML and ML_2 complexes that are fairly weak. PuO_2^{2+} forms both ML and MHL complexes with picolinic acid. The ML complex is fairly strong.

By inference to lanthanides, the trivalent actinides form ML, ML_2, and ML_3 complexes of weak to moderate stability. For example, the data of Gritman et al. (1977) indicate that logarithms of the stability constants for the formation of the ML complex range from 3.2 for La to 4.1 for Lu at 25°C and 0.5 ionic strength. By analogy, it is expected that Am(III), Cm(III), and Pu(III) will form picolinate complexes of similar stability.

3.1.4 Oxalic Acid

Table B.4 in Appendix B is a compilation of the available data for oxalic acid complexation. Oxalic complexation data for Cs, Co(III), and Pu(IV) are apparently unavailable at this time.

At least two studies of oxalic acid complexation were available and consistent for the following metals: Al, Am, Ca, Co(II), Co(III), Cm(III), Fe(III), Mg, Mn(II), Ni, Pu(IV), Sr(II), Zn, and Zr. Only one set of data is available for Cr(III), Fe(II), Mn(III), Nb(V), and Pu(III). Large discrepancies exist between the available data for Pu(VI) complexes.

For the readily hydrolyzable metals, Al(III), Cr(III), Fe(III), and Zr(IV), strong ML complexes are formed with oxalic acid (H_2L). Oxalic acid also forms ML_2 and ML_3 complexes with these metals. MHL complexes are known for Al(III) and Fe(III). $M(OH)L_2$ and $M(OH)_2L_2$ complexes are known for Cr(III).

The trivalent actinides, Am(III), Cm(III), and Pu(III), also form relatively stable ML, ML_2, and ML_3 complexes. The Pu(III) stability constants are much greater than those of Am(III) and Cm(III), suggesting that the Pu(III) stability constants may be overestimated.

Plutonium(IV) forms strong complexes with oxalic acid. Complexes of the form $M(L)_x$, where x is 1 through 4, are known. Data are available for the ML and ML_2 complexes of Pu(VI); however, as indicated earlier, large discrepancies exist among the data.

The divalent transition metals, Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+}, form ML complexes of moderate stability with oxalic acid. The ML_2, ML_3, MHL, and $M(HL)_2$ species can also form with metals. The $M(HL)_x$ complexes are weak.

The alkaline earth metals, Ca^{2+}, Mg^{2+}, and Sr^{2+}, form ML and ML_2, complexes that have moderate to weak stability. Weak MHL and $M(HL)_2$ complexes have also been reported.

Few data are available for Nb(V). Stability constants are available for the formation of the following complexes: $Nb(OH)_4L^-$, $Nb(OH)_4HL^0$, $Nb(OH)_2L_2^-$, and $Nb(OH)_2L_3^{3-}$. Comparisons of the available data are difficult because different species apparently were present and very different ionic strengths were used in these studies.

3.1.5 Citric Acid

Table B.5 in Appendix B is a compilation of the available data for citric acid complexation. Citrate acid complexation data for Co(III), Pu(V), and Pu(VI) are apparently unavailable at this time.

At least two studies of citric acid complexation were available and consistent for the following metals: Al, Am(III), Ca, Co(II), Cs, Fe(II), Fe(III), Mg, Mn(II), Ni, Pu(IV), Sr, Zn, and Zr. Only one set of data is available for Cm(III), Cr(III), Nb(V), and Pu(III) complexes. The Cm(III) data are consistent with the Am(III) data. According to Cleveland (1979), the Pu(III) data do not appear to be reliable.

For the readily hydrolyzable metals, Al(III), Cr(III), Fe(III), and Zr(IV), strong complexes are formed with citric acid (H_4L). Stability constants for complexes of the form ML and MHL are available for Al(III), Cr(III), and Fe(III). MOHL stability constants are available for Al^{3+} and Cr^{3+}. Additional data for the complexes $M(HL)_2$, MH_2L, and MLHL are known for Al(III). Data are also exist for the MH_2L and M(OH)HL complexes of Fe(III). For Zr^{4+}, data are available only for the MH_2L and MH_3L complexes.

The trivalent actinides, Am(III), Cm(III), and Pu(III), also form very stable citric acid complexes. For Am(III), data are available for the following complexes: ML, MHL, $M(HL)_2$, MH_2L, and $M(HL)H_2L$. For Cm(III), data are available for the MHL, $M(HL)_2$, and $M(HL)H_2L$ complexes. Stability constant data for Pu(III) include the MHL, $M(H_3L)_2$, and $M(H_3L)_3$ species; however, as indicated before, these data are uncertain.

Data available for citric acid complexation for Pu(IV) indicate that strong complexes form. Data are available for only the MHL and $M(HL)_2$ complexes.

The divalent transition metals, Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+}, also form citric acid complexes that are fairly strong. Complexes of the form ML, MHL, MH_2L, and MH_3L are known. The stability of these complexes decreases with increasing degree of protonation of citrate. Data are not available for the ML complex with Fe(II). Other complexes for which data are available include M(OH)L and $M(HL)H_2L$ for Fe^{2+}; $M(HL)_2$, M(OH)L, and $M(HL)H_2L$ for Ni^{2+} ; and $M(HL)_2$ and M(OH)HL for Zn(II).

Moderately strong complexes with citric acid are formed with the alkaline earth metals, Ca^{2+}, Mg^{2+}, and Sr^{2+}. The complexes formed include MHL, $M(HL)_2$, MH_2L, $M(H_2L)_2$, and MH_3L. Data are not available for the $M(H_2L)_2$ complex with Mg^{2+}, and only data for the MHL complex are available for Sr^{2+}.

Again, very few stability-constant determinations have been made for Nb(V). Data are available for the formation of the M(OH)HL and $M(OH)_4H_3L$ species.

3.1.6 Summary

A large number of stability constants are available for the EDTA, DTPA, picolinic acid, oxalic acid, and citric acid complexes with the metals of interest in this study, although somewhat fewer data are available for DTPA and picolinic acid than for the other chelates. These data have been critically reviewed and evaluated several times and no effort was made in this study to repeat such evaluations. However, there are still discrepancies in some of these data, particularly for the actinide elements. EDTA, DTPA, and picolinic acid form stronger complexes than do oxalic acid and citric acid. However, this fact alone does not mean that the effects of oxalic and citric acid complexation on the metal ions of interest in this study are unimportant. To assess the overall importance of these ligands in binding the metal ions also requires knowledge of the total ligand concentrations in the leachates. If one ligand, such as oxalic acid, is present in far greater quantity than a stronger binding ligand, such as EDTA, it is possible that the oxalic acid complexes could still predominate, though as discussed in Section 3, citric and oxalic acids do not tend to leach from exchange resins bound in cementitious waste forms. To assess the effects of both stability and concentration requires that thermodynamic modeling calculations be performed using actual or estimated leachate metal and ligand concentrations.

3.2 Speciation of Decontamination Waste Leachates

As an exercise, the thermodynamic data tabulated in this review were entered into the database of the chemical equilibrium model HYDRAQL (Papelis et al. 1988) and preliminary speciation calculations performed on selected decontamination waste leachates analyzed by McIsaac and Mandler (1989). The results of this preliminary analysis showed that organic chelates, especially EDTA and picolinic acid present in solidified decontamination wastes, are capable of complexing several of the radionuclides present in the waste leachates. This preliminary analysis showed that organic chelate complexes of Am, Co, Mn, Ni, Sr, and Zn could be the dominant aqueous species in the leachates. Examples of these calculations are shown in Figures 3.1 and 3.2 for Co and Ni species in a LOMI leachate containing picolinic acid. Clearly, such chelates can effectively complex certain radionuclides in these leachates even at high pH values. More detailed and extensive modeling analysis of these leachates need to be performed to verify these preliminary results.

3.3 Analysis of Radionuclide-Organic Complexes in Low-Level Waste

Methods for analyzing organics, including chelators and acids in mixed waste (either low level or high level) that is in controlled containment, are reviewed in this section. This includes waste generated by commercial, research, and defense facilities. A discussion of literature relating primarily to the specific analysis of radionuclide-chelating complexes is also included.

3.3.1 Analytical Methods

Gas Chromatography Techniques. Gas chromatography (GC) is the predominant method for analysis of organics in nuclear waste. The analyses of a variety of organic compounds in a variety of nuclear wastes have been described by Lucke et al. (1991); Grant et al. (in submission); Toste et al. (1987a,b, and 1988); and Toste and Lechner-Fish (1989). The analysis techniques involved GC/flame ionization detection (FID) and GC/mass spectrometry (MS). Matrices analyzed included neutralized cladding removal waste (NCRW), double-shell slurry-1 (DSS-1) waste, double-shell slurry feed (DSSF) waste, pressurized water reactor (PWR) waste, and boiling water reactor (BWR) waste. Four classes of organics (volatile, basic, acidic, and neutral) were analyzed by U.S. Environmental Protection Agency (EPA) methods that were modified for use in a hot cell or radiation hood. A fifth class of organics was also analyzed: hydrophilic organic acids, including chelating agents, for which there are no accepted EPA methods.

The presence of chelators in nuclear waste has been a particular concern. Chelators and their degradation products must be derivatized prior to analysis by GC. Because the chelators [e.g., ethylenediaminetetraacetic acid (EDTA), hydroxyethylenediaminetetraacetic acid (HEDTA), nitrilotriacetate (NTA)] have more than one carboxylic acid functional group, there is a potential for a varying degree of derivatization. Conditions must be monitored carefully so that complete derivatization takes place. Carboxylic acid groups can be methylated by reaction with boron trifluoride/methanol. Other derivatization methods have also been evaluated. These include methylation with diazomethane, butylation with butanol/HCl, and silylation with bis(trimethylsilyl)trifluoroacetamide (BSTFA) (Campbell et al. 1992b). In addition, reactions of chelators with chloroethanol/HCl to form the chloroethyl ester have also been studied (Campbell et al. 1992b). Chelator degradation and rearrangement products have been determined by GC linked with Fourier transform infrared spectrometry. This technique demonstrated the formation of lactams by some of the chelator fragments present in some of the mixed-waste samples. Gas chromatography linked with high-resolution mass spectrometry has also shown the presence of nitrosoamine-type compounds; this implies an interaction between the chelators and the inorganic components found in mixed waste.

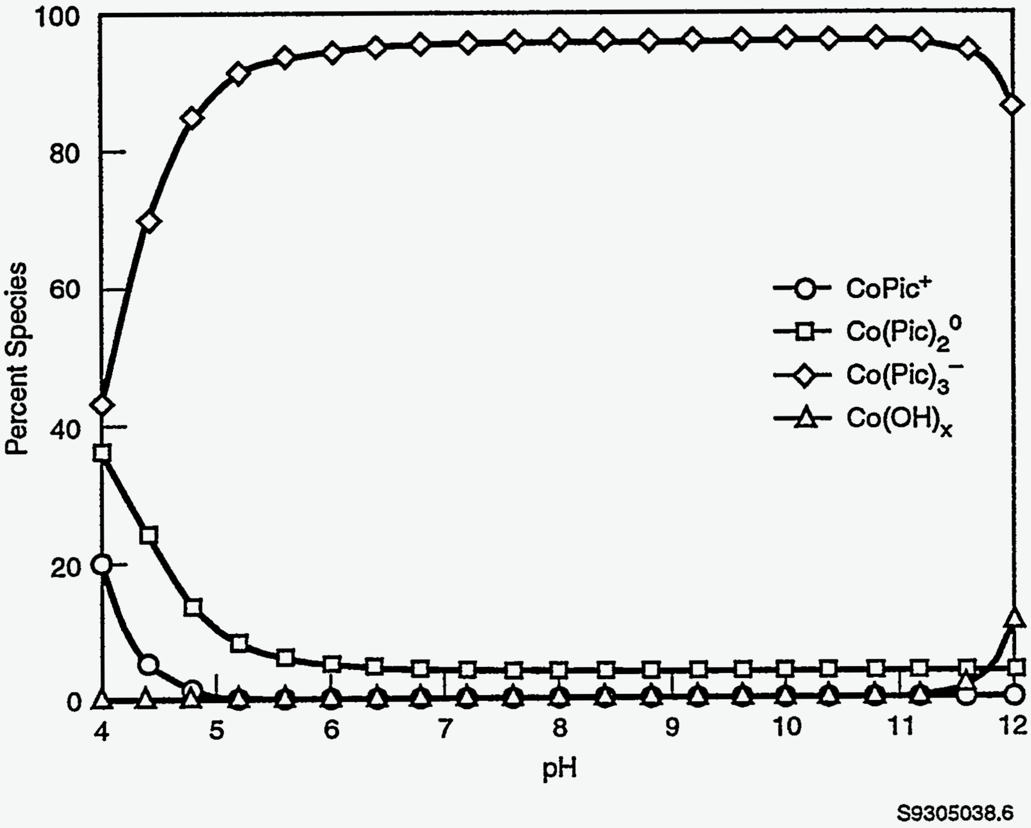

Figure 3.1 Cobalt speciation in FitzPatrick leachate (McIsaac and Mandler 1989). Initial Ca concentration from dissolution of portlandite. Equilibrium maintained with $CaCO_3$, $Al(OH)_3$, and $Fe(OH)_3$ as the pH varied.

Typical detection limits of chelators in complex aqueous waste streams by derivatization GC are 5 to 10 ppm.

High-Performance Liquid Chromatography. High-performance liquid chromatography (HPLC) analysis of nuclear wastes is used predominantly to analyze for chelators and low-molecular-weight organic acids. The advantage of HPLC analysis over GC is that the chelators do not need to be derivatized; the aqueous phase can be analyzed directly. Typically, chelators are analyzed by paired-ion chromatography (PIC) on C_{18} columns. The PIC reagents are usually dodecyltrimethylammonium bromide or tetrabutylammonium hydroxide (Toste et al. 1987c). The complexed metal may be added to the mobile phase or the sample (Grace and Co. 1988).

Most of the HPLC work done so far has been on simulated or synthetic waste, a mixture created in the laboratory to resemble mixed waste found in nuclear waste storage tanks. Using simulated waste, the interrelationship of chelators with other waste constituents can be studied (Toste et al. 1987c). The degrading effects of uranium on EDTA in simulated waste have been monitored by HPLC (Unger et al. 1987).

Some studies have been done using different chromatographic stationary phases and eliminating the reagents associated with PIC for the analysis of chelators. Eliminating the PIC reagents would make HPLC more amenable to detection by MS.

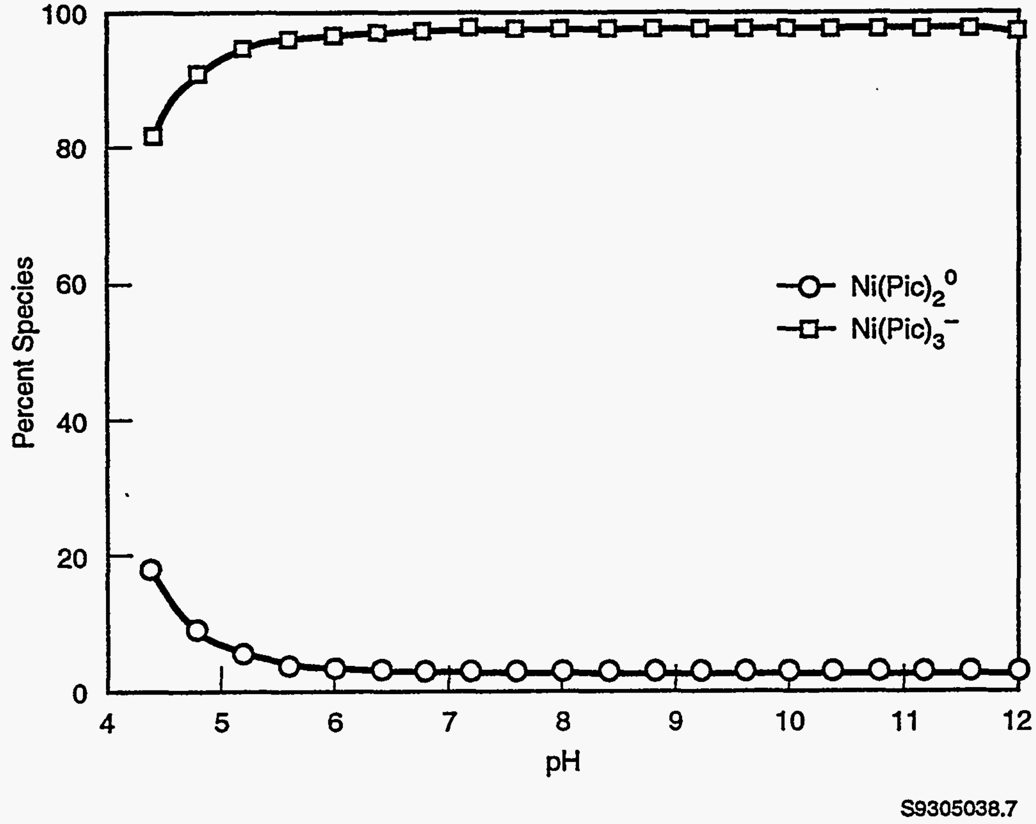

Figure 3.2 Nickel speciation in FitzPatrick leachate (McIsaac and Mandler 1989). Initial Ca concentration from dissolution of portlandite. Equilibrium maintained with $CaCO_3$, $Al(OH)_3$, and $Fe(OH)_3$ as the pH varied.

Because chelators are polar organic compounds, they are not well retained on C_{18} columns without the PIC reagent. Thus, more polar stationary phases such as anion exchange, anion exclusion, amino diol, and cyano have been studied (Toste et al. 1987c; Grace and Co. 1988; Unger et al. 1987; Metcalf 1981). Amon et al. (1992) found that the resolution of EDTA and HEDTA declined in the following order: amino > anion exclusion > cyano >> diol column. They also found that the chromatography on these columns was not as robust as PIC. In addition, resolution and capacity decreased with repetitive injections.

3.3.2 Techniques for Identifying Specific Radionuclide-Chelate Complexes

A generalized approach used by Olson et al. (1988) for the analysis of organometallic compounds in waste is illustrated in Figure 3.3. The sample is introduced, with or without derivatization as necessary, into a chromatographic system (gas chromatograph or liquid chromatograph) that is coupled to an element selective detector (ESD), such as a graphite furnace atomic absorption spectrophotometer, flame photometric detector, or mass spectrometer.

Olson et al. (1988) described simultaneous ultratrace molecular speciation of methylmercury and tin components in mining-discharge sediments using a novel purge-and-trap gas chromatograph coupled with dual flame photometric (Sn) and AA

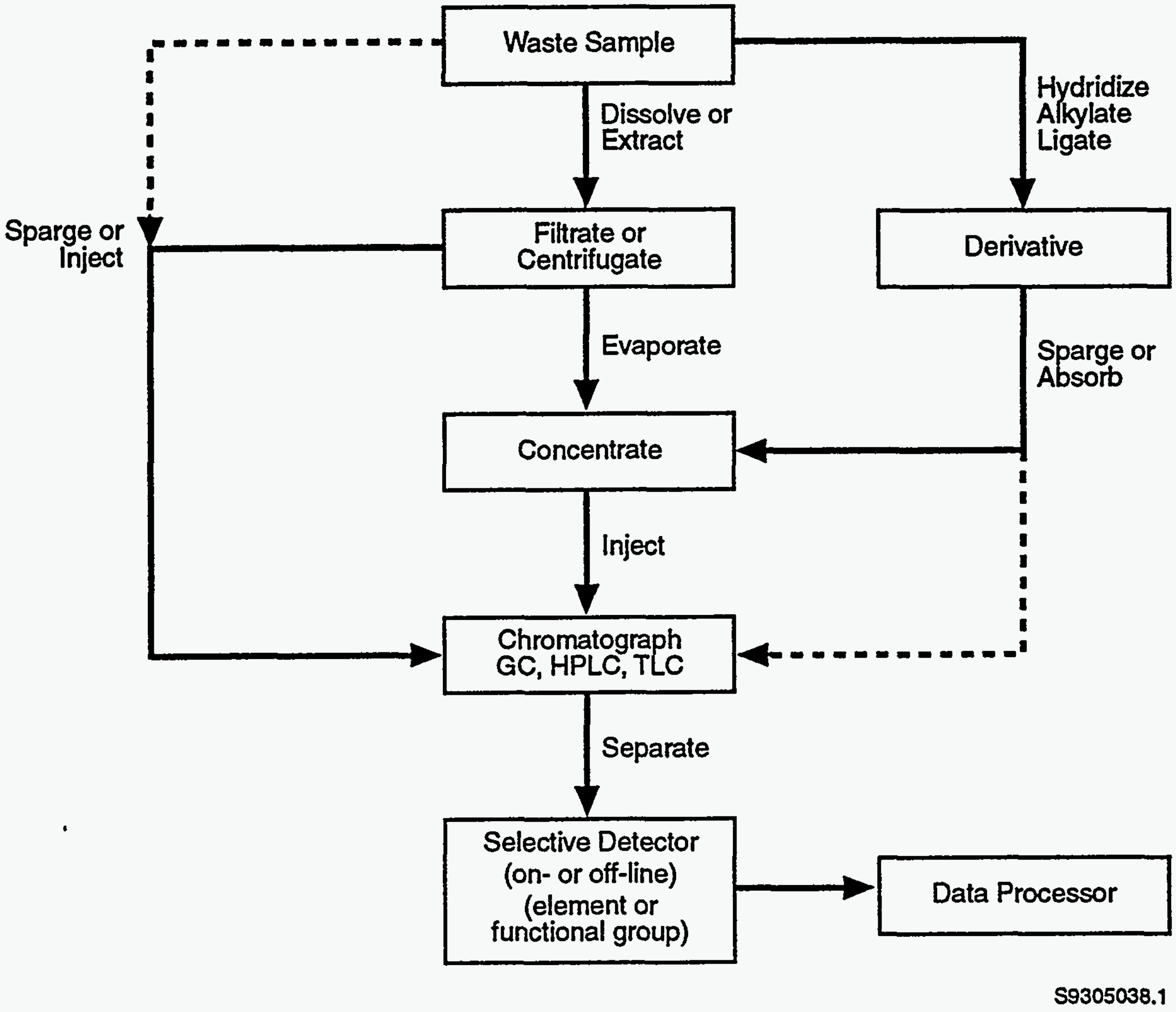

Figure 3.3 Generalized approach used by Olson et al. (1988)

(Hg) detectors. Other applications included GC-ESD or HPLC-ESD systems to speciate organometals in marine sediments, biological sludges, tissues, aquatic microlayers, and atmospheres. An alternate approach relying on nondestructive ultratrace chemical speciation was also studied. These nondestructive techniques included microscopic Fourier transform infrared spectroscopy and the use of unique metal-specific fluorogenic ligands to decorate the complex test matrix for assay by microscopic epifluorescence spectrophotometric imaging. None of the techniques listed above have been applied to the analysis of radionuclide-chelator complexes in mixed hazardous wastes.

Pacific Northwest Laboratory staff have shown that thermospray LC/MS is a promising technique for analyzing small organic acids, with the exception of oxalic acid, in mixed waste. Standards for several of the acids were analyzed, and the base peak in most cases was $(M+H)^+$. A waste sample from tank 101-SY on the Hanford Site was analyzed using thermospray LC/MS. The total ion chromatogram is shown in Figure 3.4. The extracted ion plots for citric acid (M/Z 193), glycolic acid (M/Z 95), and acetic acid (M/Z 97) are illustrated in Figure 3.5. The extracted ions were determined by analyzing standards of the free acids (uncomplexed).

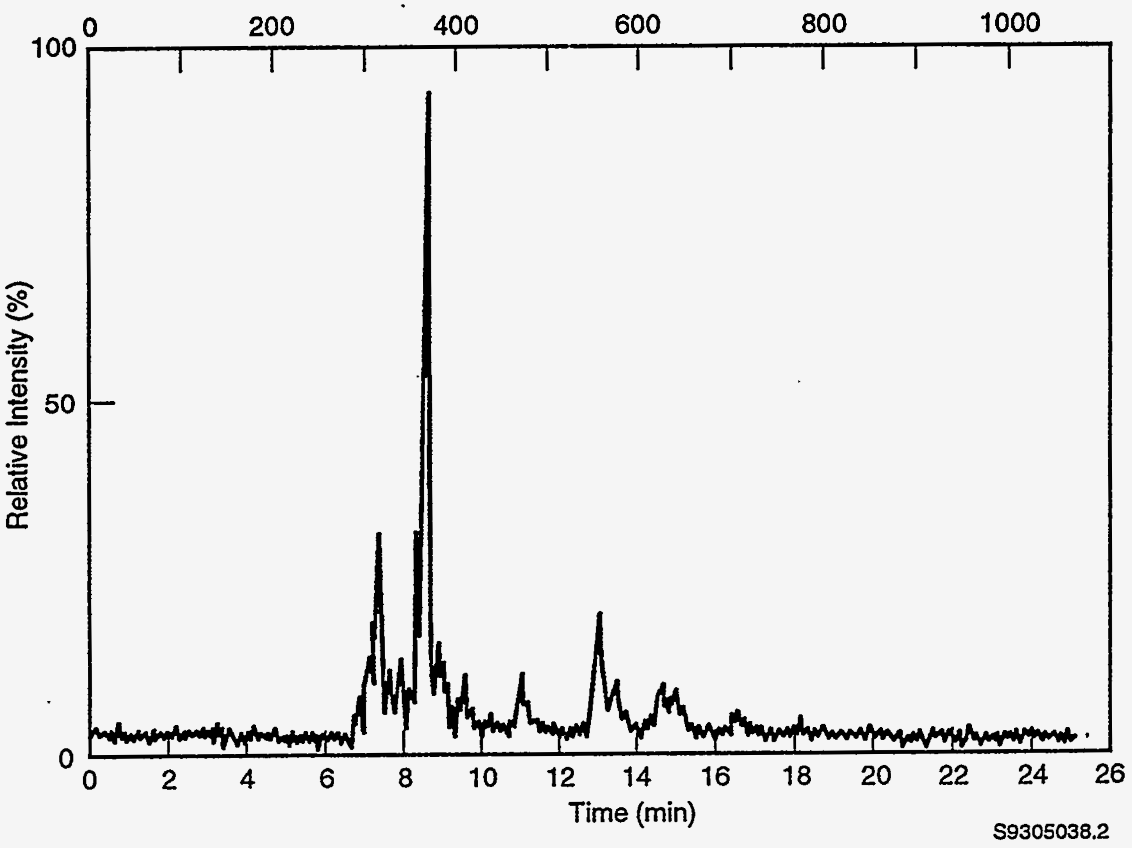

Figure 3.4 Total ion LC/MS chromatogram of actual waste sample

An LC/MS method also was developed for the analysis of complexed metal-chelators. In a preliminary study using thermospray LC/MS, Cu(EDTA) and Cu(HEDTA) were separated. The total ion chromatogram is shown in Figure 3.6. The corresponding mass spectra are shown in Figure 3.7a and b. The technique appears to be promising for determining the organic portion of the metal complex. The next step is to determine the metal portion of the metal complex. Inductively coupled plasma/mass spectrometry (ICP/MS) has been used extensively at PNL for the analysis of inorganics and radionuclide mixtures. Preliminary results indicate that coupling LC/MS to ICP/MS will allow the organic portion and metal component of the complex to be determined almost simultaneously. The effluent after the LC section can be split prior to entering in the mass spectrometer and the ICP/MS.

Other techniques, such as electrospray MS, capillary zone electrophoresis MS, and frit-fast atom bombardment, are also being investigated as methods for identifying the organic portion of the complex while still being coupled to ICP/MS. Preliminary studies using negative ion electrospray MS to analyze the free acids indicate that the base peak in most instances is $(M-H)^-$. The next step is the analysis of the complexed metal acid-ligand. A fast separation, based on micellar electrokinetic chromatography with a cationic surfactant, has also been developed that is capable of resolving the copper complexes of HEDTA, NTA, DTPA, ethylenediaminetriacetate (ED3A), and EDTA in under 6.5 minutes. Detection limits are on the order of 40 picograms. Separations based on micellar electrokinetic capillary chromatography have been

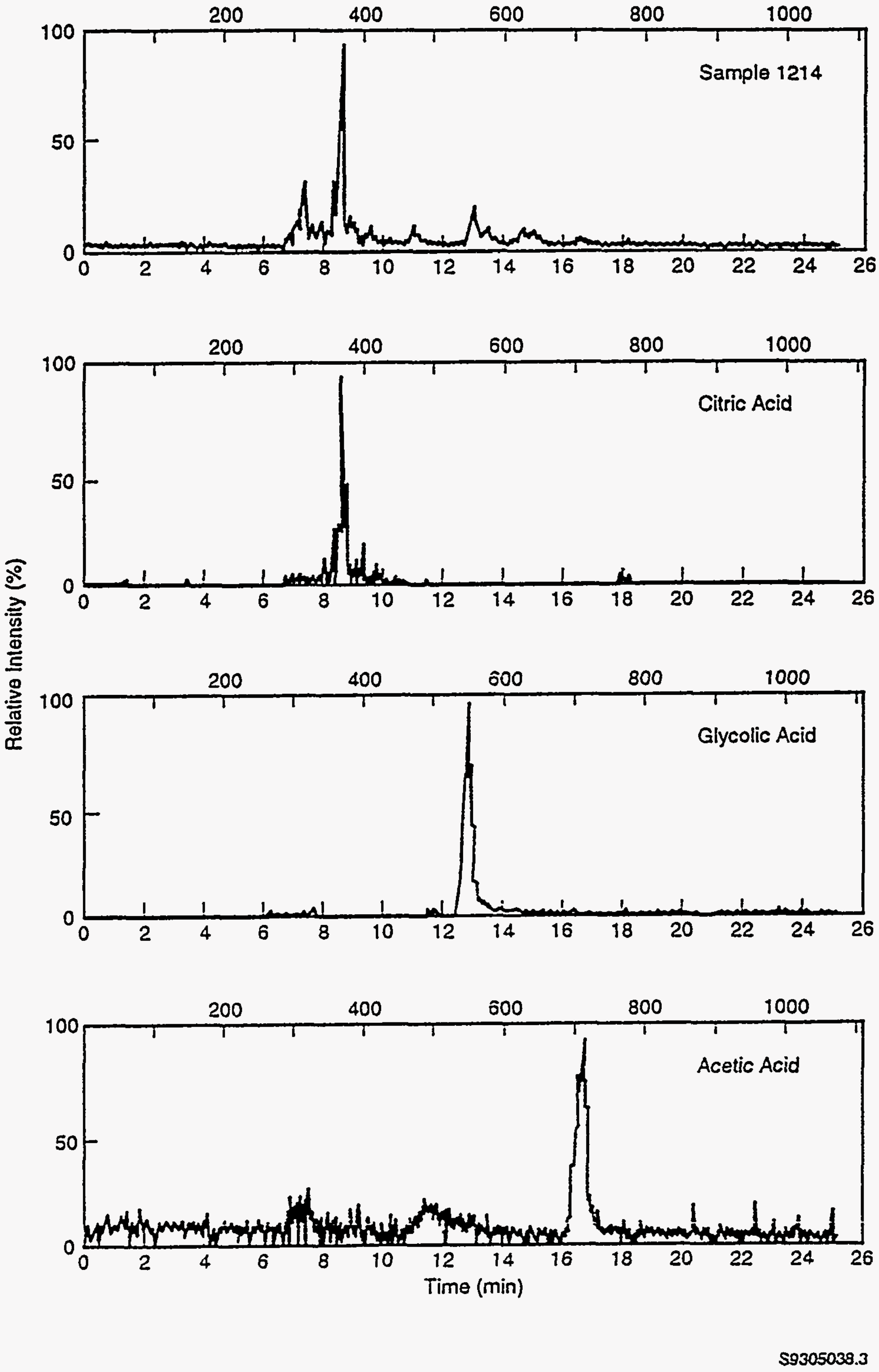

Figure 3.5 Total ion LC/MS chromatogram and extracted ion plots for citric, glycolic, and acetic acids in waste sample

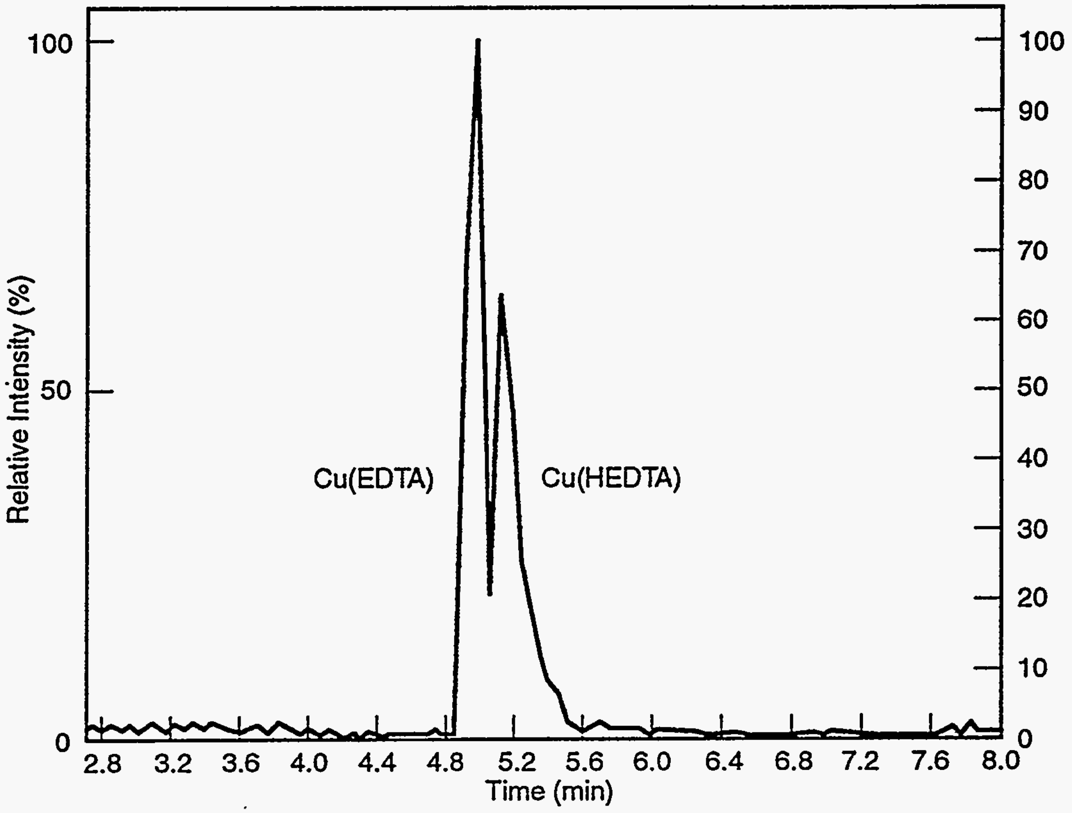

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Figure 3.6 Total ion LC/MS chromatogram of Cu(HEDTA) and Cu(EDTA)

successful in resolving mixed metal complexes of EDTA. Initial studies have focused on separating Fe(III), Co(III), and Cr(III) complexes of EDTA. Further work is needed to interface with the mass spectrometer and develop compatible mobile phases.

High-resolution microcolumn HPLC has been applied to a variety of complex environmental (Means et al. 1978) and biological samples (Toste and Myers 1986) providing separations that cannot be achieved within the resolution constraints imposed by columns of conventional dimensions (Harvey et al. 1991). In addition to the enhanced resolution, microcolumn separations offer a number of inherent advantages, including minute sample volume requirements, enhanced mass-flow detection sensitivity, and the feasibility of utilizing exotic mobile phases.

Importantly, the low flow rates characteristic of microcolumn HPLC greatly simplify introduction of the column eluant to mass spectrometric analyzers. Microcolumn technology may be coupled with LC/MS and ICP/MS to simultaneously determine the identity of inorganic and organic components.

Pacific Northwest Laboratory staff have performed some preliminary studies on several copper-complexed chelators with thermospray LC/MS (Campbell et al. 1991, 1992a). The results are encouraging, but much work is needed to make LC/MS

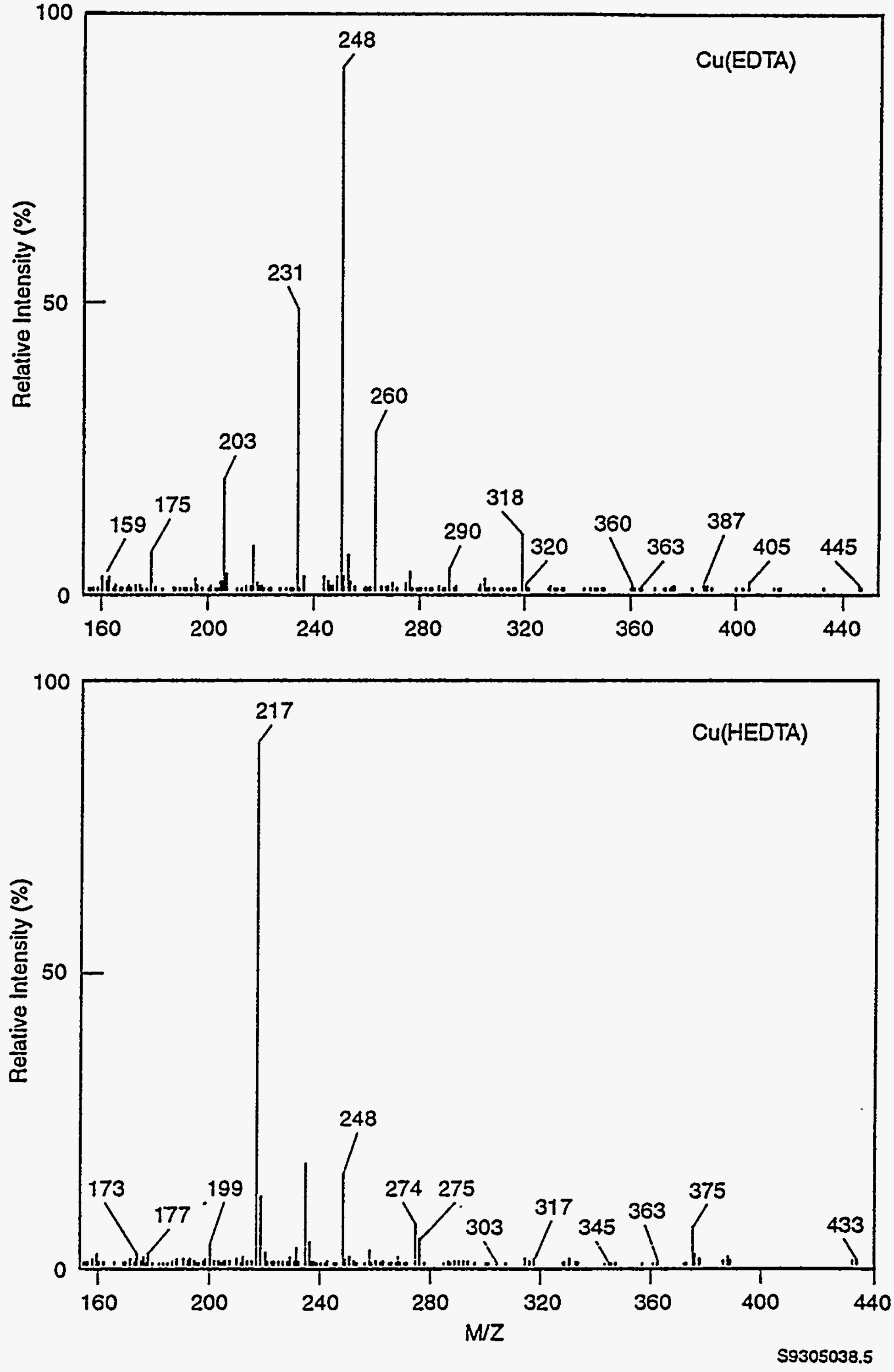

Figure 3.7 Mass spectra of Cu(EDTA) and Cu(HEDTA), obtained by using thermospray LC/MS

a viable technique for the organic portion (chelator). There has been little work to couple LC/MS and ICP/MS for the analysis of metal complexes; the metal will be identified by ICP/MS and the corresponding organic moiety by LC/MS. The concept of microcolumn LC/MS and ICP/MS for the nearly simultaneous determination of the identity of inorganic and organic components is at the forefront of science and technology.

3.3.3 Conclusions

With the exception of the method-development activities at PNL, and to a lesser extent at Oak Ridge National Laboratory, only a very small body of work exists relating to organic analysis in highly radioactive wastes. In addition, there are few references to any methods for the analysis of organometallic compounds in waste. For the most part, the literature deals with the analysis of components on the EPA priority pollutant list. The other analytes that have been thoroughly studied include the chelators, e.g., EDTA and HEDTA. Methods for detecting these radioactive waste components, which are of prime interest in this study, have been developed, primarily at PNL, and are available for application to radioactive waste samples.

4 Adsorption of Chelates and Radionuclide-Chelate Complexes

The ability of soils or sediments to adsorb the free, uncomplexed chelating agents, the uncomplexed radionuclides, or radionuclide-chelate complexes is a key factor in determining the effects of chelating agents on the transport of radionuclides away from low-level waste disposal sites. The adsorption of the uncomplexed chelating agents, uncomplexed radionuclides, and the radionuclide-chelate complexes must all be understood because equilibrium can exist between these species; therefore, adsorption of uncomplexed species can alter the apparent effects of the introduced chelating agents. This section reviews the literature on the sorption of uncomplexed chelating agents and radionuclides in the presence of chelating agents, including data on adsorption onto oxides, clay minerals and natural soils and sediments.

4.1 Background

The adsorption of uncomplexed radionuclides, uncomplexed chelating agents, and radionuclide-chelate complexes are difficult to predict, owing to numerous factors, such as the pH, concentration of competing ions, and concentration of chelating agents, which can affect adsorption of the radionuclides or radionuclide-chelate complexes in soils and sediments.

As examples, Table 4.1 shows the apparent K_d values for Co measured on an illitic soil as a function of the solution pH in the absence of chelating agents. As expected, the adsorption of uncomplexed Co is highly pH dependent with the highest adsorption(a) occurring at higher pH values. Tables 4.2 and 4.3 show the effects of the adsorbent concentration and the effects of competing cations, respectively, on the adsorption of Co on the same soil in the absence of chelating agents. Clearly, all three of these factors (i.e., pH, competing ions, adsorbent concentration) can affect the adsorption of the uncomplexed Co on the same soil. Differences between soils and the presence of chelating agents further complicate the situation.

Difference in adsorption between soils can result because a variety of adsorbing surfaces can be present as part of the soil particles or exist as coatings on the surface of the soil particles. These adsorbing surfaces include Fe and Al oxides, surface-bound organic material, and clay minerals such as kaolinite and montmorillonite. Each of these adsorbing surfaces can have a variety of different adsorption sites and/or different functional groups responsible for the adsorption of the solutes. The surface properties of the hydrous Fe and Al oxides are particularly important given that 1) these oxides can occur as coatings on the surface of the soil particles, and 2) clay minerals such as kaolinite and montmorillonite have Al-oxide edge sites that show adsorptive properties similar to those of hydrous Al oxides (James and Parks 1982; Zachara et al. 1988). The surface properties of hydrous Fe and Al oxides have been studied extensively (e.g., Davis and Leckie 1978a,b; Schindler 1981; Stumm et al. 1980; Kummert and Stumm 1980; Benjamin and Leckie 1981a,b; Hingston 1981a,b; Balistrieri and Murray 1987; Zachara et al. 1987, 1988, 1989a,b; Liang and Morgan 1990). Their surface properties are affected by changes in pH, ionic strength, adsorbed metal ions, and adsorbed inorganic and organic ligands. These studies and numerous others attempt to describe the surface properties of oxides and clay-mineral edge sites by assuming the formation of protonated or deprotonated surface species (FeOH, FeO^-,

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(a) The K_d values at higher pH values can be affected by the precipitation of a Co-containing solid phase such as $Co(OH)_2(c)$.

Table 4.1 **The effects of solution on the adsorption of cobalt on an illitic soil (data of Bangash et al. 1992)**

pH	K_d (cm^3/g)
3	5.27
4	6.59
5	10.4
6	17.3
7	263
8	4120
9	6820
10	9560

Table 4.2 **The effects of adsorbent (soil) concentration on the adsorption of cobalt on an illitic soil (data of Bangash et al. 1992)**

Adsorbent concentration (g/dm^3)	K_d (cm^3/g)
0.5	770
1.0	908
2.0	960
5.0	1930
10	4520
20	5570
30	5670
40	5920
50	5540
60	5420
70	4540
80	3090

Table 4.3 The effects of the concentration of ions on the adsorption of cobalt on an illitic soil (data of Bangash et al. 1992)

Cation concentration (eq/dm^3)	$K_d(cm^3/g)$
Na^+	
0.01	4060
0.1	3910
1	2630
3	2570
K^+	
0.01	2750
0.1	1610
1	911
3	744
Mg^{2+}	
0.01	2490
0.1	745
1	297
3	138
Ca^{2+}	
0.01	2470
0.1	572
1	49
3	43

$FeOH_2^+$, $AlOH$, AlO^-), which describe the surface charge and can act as adsorbing sites for inorganic and organic solutes. Introduction of these surface species with other surface complexes (such as SO^--Cd^{2+} and SOH-$HCrO_4^-$, where S represents the adsorbent solid matrix) has been used to describe the pH-dependent adsorption of a large variety of inorganic and organic ligands, including some of the ligands of interest in this study such as ethylenediaminetetraacetic acid (EDTA) (Rubio and Matijevic 1979; Chang et al. 1983; Blesa et al. 1984; Bowers and Huang 1986), oxalic acid (Mesuere and Fish 1992a,b; Balistrieri and Murray 1987), and picolinic acid (Davis and Leckie 1978a). In these studies the adsorption reactions of the specific chelates are described by the formation of coordinated surface species (Figure 4.1).

Besides adsorption, the organic chelates of concern in this study [EDTA, diethylenetriaminepentaacetic acid (DTPA), picolinic acid, citric acid, and oxalic acid] can undergo a variety of reactions with these surfaces including breakdown or hydrolysis at the surface, dissolution of the surface by forming aqueous complexes (Torres et al. 1989 and 1990), or even oxidation/reduction reactions at the surface (e.g., Fe oxides) (Santos et al. 1990; Torres et al. 1990). All of these reactions can complicate the interpretation of the data in radionuclide-organic chelate adsorption studies.

With these fundamental factors in mind, the following section reviews literature on the interactions of EDTA, DTPA, picolinic acid, oxalic acid, citric acid and metal complexes formed with these chelating agents with heterogeneous soils and sediments and the specific adsorbing surfaces (i.e., oxides and clay minerals) present in these natural materials.

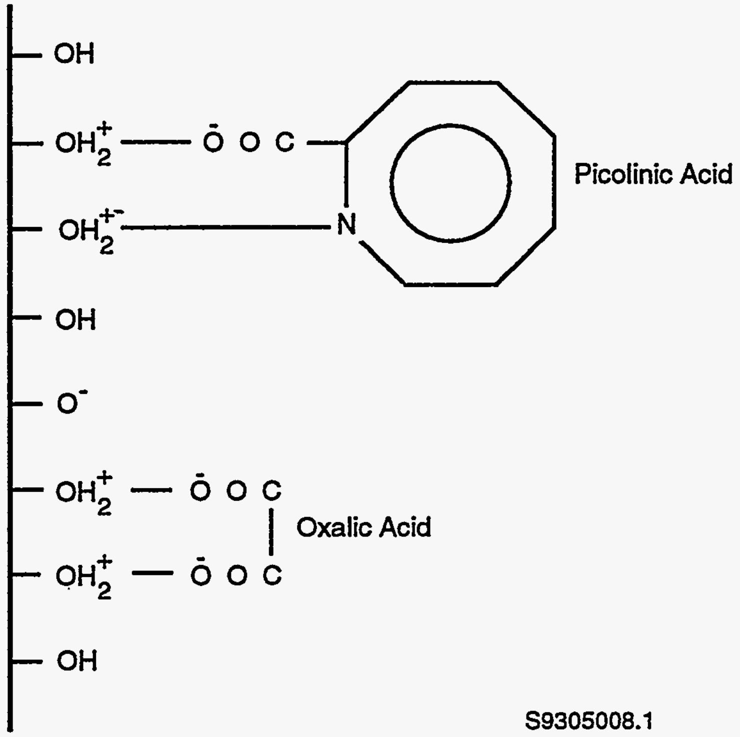

Figure 4.1 Schematic representation of possible surface-complexation reactions at the oxide/water interface

4.2 Adsorption of EDTA and EDTA-Metal Complexes

The adsorption of EDTA and several metal-EDTA complexes have been investigated on a variety of adsorbing surfaces including Fe oxides (Bryce et al. 1994; Szecsody et al. 1994; Zachara et al. 1995b; Blesa et al. 1984; Bowers and Higgs 1987; Chang et al. 1983; Chubin and Street 1981; Rubio and Matijevic 1979; Rueda et al. 1985; Swanson 1984, 1985, 1986; Torres 1987); Al oxides (Bowers and Huang 1986, 1987; Chubin and Street 1981; Girvin et al. 1993; Huang and Lin 1981; Plavsic et al. 1980); zeolites and/or clay minerals (Chubin and Street 1981; Huang et al. 1988; Maest et al. 1985; Swanson 1984, 1985, 1986); and soils and sediments (Zachara et al. 1995a, 1995b; Assaad and Awad 1981; Bangash et al. 1992; Bowers and Higgs 1987; Dyanand and Sinha 1979; Elliott and Denneny 1982; Erich et al. 1987; Haigh et al. 1991; Jones et al. 1983; Lahov and Zipori 1978; Lindsay and Norvell 1969; Slavek and Pickering 1981; Swanson 1981, 1982a,b, 1983).

In the case of the adsorption of uncomplexed EDTA(a) onto oxides, all of the results appear to be reasonably consistent. The adsorption of uncomplexed EDTA is pH dependent and exhibits what is termed "ligand-like" or "anionic-like" behavior. Sorption of uncomplexed EDTA is greatest at pH values lower than 5, decreases in the intermediate pH range of 5 to 8, and becomes negligible at pH values greater than 10. The exact pH dependence is a function of the

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(a) In these experiments it is difficult to distinguish between the adsorption of the uncomplexed ligand and the formation/adsorption of Fe-EDTA complexes in iron oxide suspension or Al-EDTA in aluminum oxide suspensions.

specific sorbent (Fe or Al oxide) and the oxide/EDTA ratio in the experiments. The adsorption of EDTA onto kaolinite (Swanson 1985) is also pH dependent and, based on a limited number of points over the pH range (5-7), appears to have a similar, though somewhat less, pH-dependent adsorption to that seen on Al oxide (Bowers and Huang 1986; Huang and Lin 1981). This adsorption of "uncomplexed" EDTA is important for two reasons: 1) adsorption of chelates can prevent their migration through soils and hence reduce their possibility of mobilizing radionuclides; and 2) as will be discussed, molecules of adsorbed EDTA have free, functional groups (i.e., functional groups not bound to the surface), which can bind complex metals to the surface-bound EDTA and thereby retard the migration of metal ions.

The influence of EDTA on the adsorption of metals and other cations has been examined for several different metallic elements, primarily Co (Szecsody et al. 1994; Zachara et al. 1995a, 1995b; Huang and Lin 1981; Girvin et al. 1993; Maest et al. 1985; Jones et al. 1983; Swanson 1981, 1982a,b, 1983; Bangash et al. 1992); Ni (Bowers and Huang 1986, 1987; Bryce et al. 1994; Swanson 1981, 1982a,b, 1983, 1984, 1985, 1986; Zachara et al. 1995a); Zn (Bowers and Higgs 1987; Bowers and Huang 1986, 1987; Huang et al. 1988; Slavek and Pickering 1981); Cu (Bowers and Huang 1986,); Cd (Swanson 1984, 1985, 1986; Chubin and Street 1981; Elliott and Denneny 1982); and Sr (Maest et al. 1985; Swanson 1981; Haigh et al. 1991). Far less work has been done on long-lived actinide elements such as Am (Swanson 1985, 1986); Pu (Swanson 1984, 1985, 1986; Polzer et al. 1982); U (Haigh et al. 1991; Maest et al. 1985); Np (Haigh et al. 1991); and actinide analogs, e.g., Eu (Swanson 1981; Haigh et al. 1991).

One of the key factors in most of these studies was whether or not the metal-EDTA complexes adsorbed or whether the results could be explained by solely considering aqueous complexation reactions. This issue is important because the adsorption of EDTA to the surface occurs at lower pH values than the adsorption of the free metal ions. The adsorbed EDTA then appears to have free functional groups to bind the metal ions to the surface.(a) Thus the introduction of a strong complexing ligand such as EDTA can have the unexpected result of increasing the metal adsorption at pH values lower than 7, where the free metal ions would not be strongly adsorbed. This adsorption of metals to surface-bound EDTA and adsorption of metal-EDTA complexes have been demonstrated clearly for Cd, Cu, Ni, Pb, and Zn on Al oxides (Bowers and Huang 1986, 1987), Co on Al and Fe oxides and natural subsurface materials (Szecsody et al. 1994; Zachara et al. 1995a, 1995b; Huang and Lin 1981; Girvin et al. 1993), and Ni, Cd, and Pu onto amorphous Fe oxide (Swanson 1985, 1986; Bryce et al. 1994). Unfortunately, with a few exceptions (Szecsody et al. 1994; Zachara et al. 1995a, 1995b; Bryce et al. 1994; Bowers and Huang 1986; Blesa et al. 1984; Rubio and Matijevic 1979; Huang and Lin 1981; Girvin et al. 1993), little work has been done on developing mechanistic site-binding models with which to quantitatively describe the adsorption of EDTA or metal-EDTA complexes, even on relatively simple oxide surfaces, and the work of Zachara et al. (1995a, 1995b) is the only work done which has applied this approach to heterogeneous soil systems. Such work is needed to develop more quantitative and generic models for predicting the influence of EDTA or other chelates on the adsorption of radionuclides.

In the studies of clay minerals or soils, the effect of the added EDTA appears to invariably decrease the observed metal adsorption, and until recently very little evidence was available for the adsorption of metal-EDTA complexes in heterogeneous soil systems. In most studies, the reasons for these observed decreases in adsorption are not always apparent because the pH and amount of competing cations are often not clearly defined in the studies with actual soils. The reporting of pH values is particularly important because adsorption of metal-EDTA complexes can occur only at pH values lower than 7. Many of the studies of metal adsorption in the presence of EDTA were conducted at higher pH

(a) It is operationally difficult to separate the direct binding of metal-EDTA complexes originally in solution from the two-step adsorption of free EDTA and subsequent complexation of metal ions by surface-bound EDTA.

values where the adsorption of metal-EDTA complexes would not be expected to occur. Therefore as expected, these studies have shown significantly decreased adsorption as a result of the formation of strong aqueous complexes.

Recent work in which Co(II)EDTA^{2-} sorption onto eight sand-textured subsurface materials (Zachara et al. 1995a, 1995b) was studied has significantly increased our understanding of the mechanisms for the observed decreases in adsorption at higher pH and has demonstrated that total metal adsorption can actually increase at lower pH values. Figure 4.2 is a plot of K_d values determined for various species in the Co^{2+}-EDTA-sediment system determined by Zachara et al. (1995b) for a well characterized sediment (Oyster 1.5-m). It was shown that Co(II)EDTA^{2-}complex sorbs as an anion on most sediments, with sorption increasing as pH decreased. Compared to free Co^{2+}, the Co(II)EDTA^{2-} complex shows greater adsorption below pH 6 and less adsorption at higher pH. Therefore, the net effect of EDTA complexation on Co mobility depends on the pH of the system. Multiple lines of evidence indicated that the dominant sorbents in natural subsurface sediments were Fe and Al oxides.

Solution analysis coupled with modeling of aqueous speciation and Al- and Fe-phase solubility indicated that dissociation of Co(II)EDTA^{2-} was promoted by Al^{3+} and Fe^{3+} that were liberated from the sediments by either proton- or ligand-promoted dissolution. This dissociation, which was not complete, yielded a multicomponent mixture of Co^{2+}, Co(II)EDTA^{2-}, AlEDTA^{-}, and FeEDTA^{-}. Surface-complexation modeling showed that surface speciation evolved from one dominated by surface complexes with CaEDTA^{2-}, and Co(II)EDTA^{2-} at intermediate pH to one dominated by complexes with AlEDTA^{-}, and FeEDTA^{-} at lower pH. It was determined that the coupled dissolution, exchange, and surface-complexation reactions impart complex kinetic behavior to the subsurface transport of Co(II)EDTA^{2-}. Retardation coefficients, aqueous speciation, and the transport velocities of Co^{2+} relative to EDTA will change with transport distance, residence time and geochemical conditions such as pH and major ion concentrations.

In addition to the complexities outlined above regarding the effect of EDTA on Co^{2+} adsorption onto soils, it has been demonstrated that manganeses oxides occurring as grain coatings in subsurface sediments are responsible for oxidation of Co(II)EDTA^{2-} to Co(III)EDTA^{-} (Zachara et al.1995b). It was found that Co(III)EDTA^{-} was much less strongly adsorbed than its divalent analog (Co(II)EDTA^{2-}) and as a result the highest sorption of Co^{2+} was noted in sediments which contained the lowest concentration of secondary oxides.

Other key factors influencing the behavior of metal adsorption in the presence of EDTA are the kinetics of the reactions among the aqueous metal-EDTA complexes and the kinetics of the reactions that occur at the adsorbed surface. The formation of unreactive, chelated metal species in solution can be an important effect because such complexes will not react with competing ions (such as Ca, Al, or Fe species) present in solution. Such competing ions can prevent migration of the radionuclides at higher pH values by displacing the radionuclides from the EDTA complexes.

The importance of the formation of "kinetically inert"(a) aqueous metal-EDTA complexes was demonstrated by Swanson (1985, 1986) for Ni-EDTA but not for Am-EDTA or Cd-EDTA complexes. Thus the formation of such inert complexes appears to be highly metal-ligand specific and difficult to predict.

One other kinetic or rate process of importance is the change with time in metal adsorption that can occur when metal-EDTA complexes are adsorbed onto the surfaces of oxides (Swanson 1985, 1986). These results indicate that

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(a) Kinetically inert complexes are strong aqueous complexes that do not dissociate or react with competing ions even if such reactions are thermodynamically favorable.

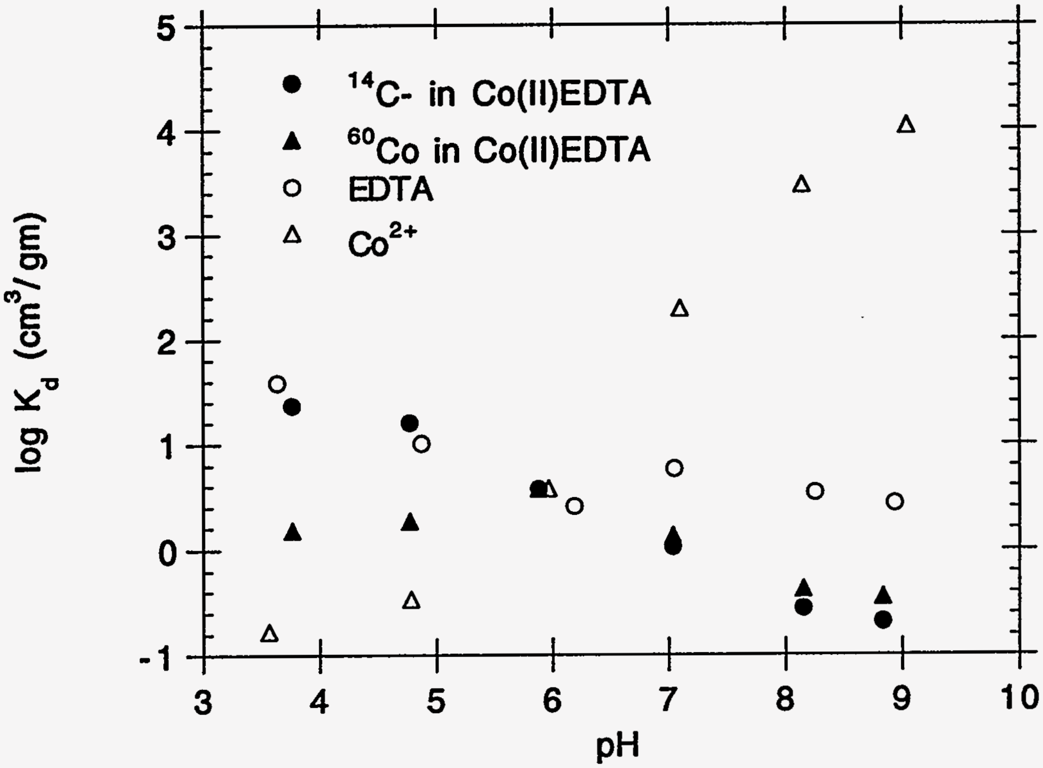

Figure 4.2 K_d values determined for various species in the Co^{2+}-EDTA-sediment system for a well characterized sediment (Oyster 1.5-m), Zachara et al. (1995b)

adsorbed metal-EDTA complexes, specifically Ni-EDTA complexes, can break down with time-releasing the metal to solution. Such results have also been found for the adsorption of other metal-EDTA complexes onto Fe oxide (Zachara et al. 1995a, 1995b) and are believed to result from the slow displacement of the metal ion from the EDTA complex by Al^{3+} and Fe^{3+} present in the oxide surfaces.

In the recent work of Bryce et al. (1994) it was determined that in the ternary nickel/EDTA/hydrous ferric oxide system, the sequence of addition of components strongly affected the fraction of nickel which was adsorbed, but did not affect the fraction of EDTA adsorbed. Addition of a preformed $NiEDTA^{2-}$ complex resulted in ligand like adsorption behavior onto hydrous ferric oxide, similar to that observed by Zachara et al.(1995a, 1995b) for the $Co(II)EDTA^{2-}$ complex. If either the EDTA or Ni were added first, the fraction of nickel which was adsorbed was initially high, followed by a slow decrease in the fraction of adsorbed Ni over time. This was attributed to the desorption of nickel as the $NiEDTA^{2-}$ complex slowly formed in solution. Adsorption of nickel was high when either EDTA or Ni was added first because the adsorption of both of these free components was rapid and EDTA and Ni did not compete with each other for adsorption sites. These results suggest that an equilibrium model may not always be appropriate for modeling transport of radionuclide-chelating agent complexes from low level waste disposal sites, especially if the chelating agents and the radionuclides are transported from the sites at different times.

In summary, EDTA can adsorb strongly onto oxide surfaces at lower pH values where metal ions usually do not adsorb. This adsorbed EDTA can complex metal ions and result in the removal of radionuclides from solution under pH conditions where adsorption of the uncomplexed metal ions is not expected to occur. At higher pH values EDTA is not adsorbed and can prevent adsorption of metal ions or radionuclides by forming strong aqueous complexes. In addition, certain metal-EDTA complexes appear to be kinetically inert and do not react rapidly with other competing ions in solution, thus enhancing the potential for these ions to migrate through soils and sediments at neutral to basic pH values.

4.3 Adsorption of Picolinic Acid and Picolinate-Metal Complexes

The adsorption of picolinic acid and metal-picolinic complexes has been studied far less than EDTA. The adsorption of picolinic acid has been studied on amorphous Fe oxide (Davis and Leckie 1978b; Swanson 1986); hematite (Pope et al. 1981); and on two field soils (Nicholls and Evans 1991a,b). The adsorption of picolinic acid, similar to that of EDTA, onto Fe oxides is highly pH dependent and follows classical ligand-like behavior. Picolinic acid adsorption is highest at the low pH range of 4 to 5, rapidly decreases in the intermediate pH range of 5 to 7, and becomes negligible at pH values higher than 8. The exact adsorption edge is dependent on the picolinic acid/oxide ratio in the experiments. A similar trend is also seen in the adsorption experiments on soils (Nicholls and Evans 1991a,b), except that the adsorption on these two soils decreased rapidly at pH values less than 5, possibly because of the dissolution of metal oxide coatings or other soil components at these lower pH values.

The influence of picolinic acid on the adsorption of metal ions has been little studied, but the existing data appear to be consistent. In studying the effect of picolinic acid on the adsorption of Cu(II) onto amorphous Fe oxide, Davis and Leckie (1978b) found that the influence of picolinic acid on the adsorption of Cu could be predicted by simply considering the formation of aqueous Cu-picolinate complexes. They found no evidence for the formation or adsorption of Cu-picolinate complexes. Their hypothesis was that both the amine and carboxylic acid functional groups on picolinic acid are coordinated to the Fe-oxide surface (see Figure 4.1), leaving no exposed functional groups to complex the metal ions in solution, as was hypothesized for EDTA. Their hypothesis was at least partially confirmed by Swanson (1986), who studied the adsorption of nickel and americium on amorphous Fe oxide in the presence of picolinic acid, and the adsorption of Ni, Cd, and Am onto kaolinite in the presence of picolinic acid. Swanson (1986) found no evidence for the adsorption of metal-picolinate complexes onto Fe oxide. Again, the effect of picolinate seems to be related only to the formation of aqueous complexes. This same effect was also seen in the kaolinite adsorption studies for Cd and Am. The only possible evidence for adsorption of metal-picolinate complexes was found in the adsorption studies of Ni onto kaolinite. At pH values lower than 5, the adsorption of Ni was greater in the system with picolinic acid than in the experiments without picolinic acid, indicating the possible adsorption of a Ni-picolinic acid complex. However, this result is based only on three data points at low adsorption densities. In general, it appears that the effect of picolinic acid on the adsorption of metal ions is related only to the formation of aqueous complex species. Formation of any adsorbed metal-picolinate complexes appears to be a minor effect, if it occurs at all.

4.4 Adsorption of DTPA and DTPA-Metal Complexes

The adsorption of DTPA or DTPA metal complexes has been studied on several different soils. The metal ions studied include Co (Bangash et al. 1992; Swanson 1981, 1982a,b); Ni (Swanson 1981); Zn (Lindsay and Norvell 1969; Kuo and Mikkelsen 1980); Cs and Sr (Swanson 1981, 1982a,b); rare-earth elements (Swanson 1981, 1982a,b; Jester et al. 1987), and Pu (Wildung and Garland 1974). In addition, the migration of Fe-DTPA chelates (Erich et al. 1987; Dyanand and Sinha 1980) and the adsorption of DTPA onto Fe oxides (Chang et al. 1983) have been studied.

The studies on Fe oxides (Chang et al. 1983) indicate that DTPA adsorption follows the same ligand-like adsorption as does EDTA, indicating the possibility that adsorption of metal-DTPA complexes could occur. However the studies in soil systems, similar to those for EDTA, do not show any conclusive evidence for adsorption of metal-DTPA complexes, although almost all of these experiments were conducted at higher pH values (8-10), where adsorption of metal-DTPA complexes would not be expected to occur. As expected at these higher pH values, the decreased adsorption of metal ions in the presence of DTPA appears to be primarily related to the increased aqueous complexation of the metal ions. Further studies of oxides, clay minerals, and soils at lower pH values are required to evaluate the possible importance of adsorption of metal-DTPA complexes.

No conclusive information was found on the "kinetic inertness" of metal-DTPA complexes or the rates of different adsorption reactions.

4.5 Adsorption of Oxalic Acid and Oxalate-Metal Complexes

Oxalic acid is a naturally occurring organic ligand that forms much weaker aqueous metal complexes than do EDTA, DTPA, and picolinic acid. As a result, the influence of oxalic acid on the adsorption of metal ions is expected to be less at the same ligand concentration than that observed for EDTA, DTPA, or picolinic acid. The adsorption of oxalic acid has been studied on a wide range of oxides, clay minerals, and soils, principally because these ligands are naturally occurring and present in many soils and sediments.

On Fe oxides, oxalic acid exhibits classical ligand-like behavior with adsorption predominating at pH values lower than 5, decreasing in the intermediate pH range from 5 to 8, and becoming negligible at pH values higher than 9 to 10 (Mesuere and Fish 1992a,b; Balistrieri and Murray 1987; Kallay and Matijevic 1985; Zhang et al. 1985). The influence of oxalate on the adsorption of other metals and ligands onto Fe oxides has also been studied, including selenite (Balistrieri and Chao 1987), chromate (Mesuere and Fish 1992a), sulfate (Inskeep 1989; Balistrieri and Murray 1987), Ca and Mg (Balistrieri and Murray 1987), Ni (Swanson 1984), and Cd (Lamy et al. 1991).

These results show that in the case of anion adsorption, oxalate can compete for surface adsorption sites with other anions, such as sulfate, chromate, and selenite, and thereby reduce the adsorption of these constituents. Site-binding models have been developed to describe these competitive adsorption reactions and the adsorption of uncomplexed oxalic acid onto Fe oxides (Mesuere and Fish 1992a,b; Balistrieri and Chao 1987; Balistrieri and Murray 1987; Kallay and Matijevic 1985).

In the case of metal adsorption onto Fe oxides, i.e., Cd and Zn, the effects of oxalic acid seem to be primarily related to the aqueous complexation of these metals by oxalate. Thus, the concentration of oxalate must be orders of magnitude greater than the concentration of EDTA or picolinate to have the same effect on the adsorption of metal ions such as Ni (Swanson 1984). No compelling evidence is available for the adsorption of metal-oxalate complexes onto Fe oxides.

The adsorption of oxalate and the influence of oxalate on the adsorption of anions or metal ions have been studied on a variety of clay minerals, including kaolinite, montmorillonite, and illite, and on natural soil materials (Chairidchai and Ritchie 1990; Evans and Zelazny 1990; Kafkafi et al. 1988; Nicholls and Evans 1991a,b; Means et al. 1983; Swanson 1982a,b; Bangash et al. 1992; Elliott and Denneny 1982). The results of these studies indicate at least the same qualitative behavior of oxalate adsorption as that found for the Fe oxides: i.e., 1) pH-dependent and ligand-like adsorption (Nicholls and Evans 1991a,b); 2) enhanced desorption or release of anions such as phosphate (Kafkafi et al. 1988) and sulfate (Evans and Zelazny 1990); and 3) decreased adsorption of metal ions such as Zn (Chairidchai and Ritchie 1990); Co (Swanson 1982a,b; Means et al. 1983; Bangash et al. 1992); Cd (Elliott and Denneny 1982); and Cs and Sr (Means et al. 1983). As was found for the Fe oxides, the effects of oxalate on the adsorption of these metal ions was significantly less than the effects of stronger complexing agents such as EDTA. Therefore, much larger concentrations of oxalate are required to have the same complexation or desorption effects on the metal ions as does EDTA.

One further point, Means et al. (1983) found an unusually large decrease in the adsorption of uranium, presumably as U(VI), onto kaolinite and montmorillonite, but not illite, in the presence of oxalate at about pH 5. The reasons for these results are unclear, but indicate the possibility for oxalate to mobilize uranium species.

4.6 Adsorption of Citric Acid and Citrate-Metal Complexes

Citric acid, similar to oxalic acid, is a naturally occurring organic ligand that forms much weaker aqueous metal complexes than either EDTA, DTPA, or picolinic acid. The adsorption of citric acid has been studied on a variety of solid surfaces including Fe and Al oxides (Swanson 1986; Zhang and Matijevic 1984; Zhang et al. 1985; Chubin and Street 1981; Kallay and Matijevic 1985; Balistrieri and Chao 1987); and soils and clay minerals (Chubin and Street 1981; Bangash et al. 1992; Slavek and Pickering 1981; Swanson 1981, 1982a,b; Chairidchai and Ritchie 1990; Kafkafi et al. 1988).

The adsorption of citric acid onto Fe oxides shows the same qualitative trends as oxalic acid adsorption onto Fe oxides: pH-dependent ligand-like adsorption (Zhang et al. 1985; Kallay and Matijevic 1985) and enhanced desorption of anionic species such as selenite (Balistrieri and Chao 1987) and sulfate (Inskeep 1989). The effects of citrate on the adsorption of metal ions such as nickel (Swanson 1986) are complicated by the dissolution of the Fe oxide adsorbent (Swanson 1986; Zhang et al. 1985) and the rapid decomposition of the citric acid complexant (Swanson 1986). Kallay and Matijevic (1985) have proposed a site-binding model to explain the adsorption of citric acid onto hematite, which includes the adsorption of the L^{3-} and the HL^{2-} species. No definitive evidence is available for the adsorption of metal-citrate complexes.

The studies on the effects of citric acid on metal adsorption onto soils or clay minerals appear to be highly dependent on the ratio of soil/clay mineral to added citric acid (Bangash et al. 1992). Some investigators (Chubin and Street 1981) have noted very little effect of added citric acid on metal adsorption, while others (Slavek and Pickering 1981) have noted very large decreases in metal adsorption after the addition of citric acid.

In summary it appears that 1) citric acid appears to react rapidly with metal ions to form soluble complexes; 2) citric acid can react with soil components such as Fe oxide or Ca and Mg present in the soil, and these reactions can displace metal ions from the citric acid; 3) relatively high concentrations of citric acid are required to significantly decrease metal adsorption onto soils and soil minerals; and 4) citric acid can decompose in the adsorption experiments.

4.7 Summary

First, it appears that at higher pH values (i.e., >8) where the uncomplexed chelating agents are not adsorbed, the stronger complexing capability of EDTA, DTPA, and picolinic acid can decrease the adsorption of metal ions more than citric acid or oxalic acid by forming stronger aqueous complexes. This effect has been demonstrated by Bangash et al. (1992) for Co adsorption on an illitic soil (Table 4.4), where it required approximately 100 times as much citric or oxalic acid as EDTA/DTPA to have the same effect on Co adsorption. As indicated in Section 3, such high concentrations of oxalic or citric acid are unlikely to leach from cementitious waste forms.

Table 4.4 The effects of chelating agents on the adsorption of cobalt on an illitic soil (data of Bangash et al. 1992)

Ligand concentration (mol/dm^3)	K_d (cm^3/g)
None	6860
EDTA	
1.0×10^{-6}	4880
1.0×10^{-5}	988
1.0×10^{-4}	77
1.0×10^{-3}	0.6
DTPA	
1.0×10^{-6}	2620
1.0×10^{-5}	712
1.0×10^{-4}	79
1.0×10^{-3}	0.3
Oxalic	
1.0×10^{-4}	1270
1.0×10^{-3}	1070
Citric	
1.0×10^{-4}	771
1.0×10^{-3}	173

Second, the adsorption of all of the uncomplexed chelates in this study is pH dependent, especially on oxide surfaces, and appears to be ligand-like with maximum adsorption occurring at lower pH values (i.e., <7).

Third, adsorption of metal-chelate complexes can occur in the EDTA and DTPA systems but not for oxalic acid, citric acid, or picolinic acid, although the data on picolinic acid are limited. The adsorption of these metal-EDTA/DTPA complexes occurs at lower pH values where strong metal adsorption usually does not occur. As a result, adsorption of such complexes could enhance the adsorption of metal ions even in the presence of a strong chelate such as EDTA in acidic geochemical environments, which are relatively rare at most shallow-land burial sites.

Finally, certain metal-EDTA complexes, most notably Ni-EDTA, appear to be relatively inert and do not react rapidly with other competing ions in the solution. Such inertness could enhance the migration of these chelated metals because other ions in the groundwater, such as Ca, Fe or Al species, would not displace the metal ion from the chelate.

5 Biodegradation of Chelates and Radionuclide-Chelate Complexes

Biodegradation of organic chelates and metal-chelate complexes is one of the principal factors that can prevent or reduce the ability of chelates to transport metal ions and radionuclides through soils and sediments. The rates of biodegradation of chelate and metal-chelate complexes depend on many factors, including the specific ligands and metal-ligand complexes present, the specific strains of bacteria present, the availability of other sources of organic carbon, the sorption of chelates and metal-chelate complexes, extremes in pH, and metal concentration. This section reviews the available literature on the biodegradation of ethylenediaminetetraacetic acid (EDTA), picolinic acid, citric acid, and oxalic acid, and other information on diethylenetriaminepentaacetic acid (DTPA), nitrilotriacetate acid (NTA), and picolinic acid analogs (e.g., nicotinic acid) under different environmental conditions. The difficulties and problems encountered in such studies are emphasized.

5.1 Biodegradation of EDTA

Varying rates of aerobic EDTA biodegradation have been found for soils (Means et al. 1980; Tiedje 1975, 1977); sediments (Tiedje 1975, 1977); deep subsurface sediments (Bolton et al. 1993); and an aerated lagoon (Belly et al. 1975). However, EDTA appears to be recalcitrant to biodegradation under anoxic conditions (Tiedje 1975, 1977; Bolton et al. 1993). Only one study has compared the degradability of several synthetic chelates in soil and found biodegradability decreased in the order nitrilotriacetate > ethylenediaminetetraacetate ≈ diethylenediaminepentaacetate (Means et al. 1980). Synthetic chelate degradation can occur in subsurface sediments from great depths (Bolton et al. 1993). Surface soil and subsurface sediments from five formations (36- to 376-m depth) were collected near Allendale, South Carolina. Aerobic mineralization of ^{14}C-labeled EDTA, DTPA, and NTA occurred in select sediments, indicating that subsurface microorganisms can degrade chelates, while chelates may be relatively stable in strata where limited mineralization occurs. The chelates were not mineralized more rapidly or to a greater extent in the surface soil than in the subsurface sediments. The relative order of chelate persistence was EDTA > DTPA > NTA, with the maximum amount mineralized during 115 days at 15, 26, and 43 percent, respectively. Maximum mineralization of all three chelates did not occur in the same sediment, indicating that different microbial populations were responsible for the degradation of each chelate. Mineralization of chelates was minimal under denitrifying conditions and was reduced when additional soluble carbon was added. There was no relationship between chelate mineralization and the adsorption of chelates to sediments or the aqueous speciation of the chelates. However, rates of chelate degradation were quite low, and degradation studies were conducted over long time periods (>100 days).

Additional carbon compounds present with the chelates can influence chelate degradation. Soil samples had increased degradation of EDTA when soluble organic compounds were added (Tiedje 1977; Means et al. 1980), suggesting that co-metabolism of EDTA occurred. However, subsurface sediments had decreased DTPA, EDTA, and NTA degradation when a mixture of soluble carbon compounds was added (acetate, citrate, glutamate, and succinate) at 10 μg/ml (Bolton et al. 1993). This suggests that after soluble carbon augmentation, subsurface sediments may degrade chelates differently than does surface soil. A microbial consortium (group of microorganisms) was able to biodegrade EDTA at approximately 5×10^{-8} concentration (Belly et al. 1975). Several amino acids and sugars decrease EDTA biodegradation when added to the consortium (Belly et al. 1975), indicating catabolite repression occurs. However, when the EDTA concentration was increased, or NTA or ethylenediamine were added, ^{14}C-EDTA mineralization increased. Thus isolates able to utilize EDTA as a sole source of carbon respond to normal physiological control.

Biodegradation

Microbial consortia and microbial isolates have been studied for their ability to degrade EDTA. A microbial consortium from an aerated lagoon (Belly et al. 1975), an *Agrobacterium* sp. isolated from a treatment facility (Lauff et al. 1990), and a microbial consortium and a bacterial isolate from sewage (Nörtemann 1992), all of which received EDTA, were able to degrade EDTA as a sole source of carbon and energy. The proposed pathway for the degradation of EDTA by a microbial consortium from an aerated lagoon results in the release of degradative intermediates of EDTA, which can also complex metals (Belly et al. 1975). These degradative intermediates may include ethylenediaminetriacetate (ED3A), ethylenediaminediacetate (N, N-EDDA, and N, N'-EDDA), ethylenediaminemonoacetate (EDMA), and ethylenediamine. All the proposed steps in the degradative pathway for EDTA occur via oxidation of the C-N bond, presumably by a series of monooxygenases and the release of glyoxylate. Thus, the degradative intermediates produced sequentially include ED3A; N, N-EDDA and/or N, N'-EDDA; EDMA, and ethylenediamine (Figure 5.1).

Most of the work on the degradation of chelates in the environment and by microorganisms (some cited above) has not specified or controlled the aqueous speciation of the chelate, so that the metal-chelate complex degraded was not known and may have changed during the experiment. Thus it is not possible to identify the metal-chelate complexes that were degraded by reviewing the results of these studies. In addition, metal toxicity may have influenced chelate degradation. Thus, current understanding is limited on how the aqueous speciation of the chelate will influence its degradation. The aqueous speciation of chelates varies depending on pH and the concentrations and types of metal ions present. Metals and protons compete for the chelate at low pH, while at higher pH, hydroxyl and carbonate ions compete with the chelate for the metal ions. Thus these multiple equilibria will dictate the form of the chelate available for degradation.

Some work has been conducted on how the complexed metal influences chelate degradation (mainly NTA) in soils (Tiedje and Mason 1974); sediments (Bolton et al. 1993); waters (Swisher et al. 1974); sewage (Madsen and Alexander 1985; Swisher et al. 1967); and with microorganisms (Firestone and Tiedje 1975; Madsen and Alexander 1985). A study of DTPA, EDTA, and NTA mineralization in terrestrial subsurface sediments (Bolton et al. 1993) has demonstrated through aqueous speciation modeling (Felmy et al. 1984) that the form of the chelate in solution varied among the surface soil and subsurface sediments. In this study 80 percent of the EDTA in solution was either $CaEDTA^{2-}$, $FeEDTA^{-}$, $HEDTA^{3-}$, or $H2EDTA^{2-}$, while more than half of the NTA was present in solution as $Ca\text{-}NTA^{-}$, Fe-NTA, $FeOHNTA^{-}$, or $HNTA^{2-}$. Variations in the aqueous speciation of EDTA or NTA did not appear to influence their long-term (i.e., >100 days) mineralization; however, the proportions of EDTA- or NTA-complexing metals other than Ca and Fe were minimal (Bolton et al. 1993).

Few studies have been conducted to ascertain the effects of microbial consortia or isolates on how the complexed metal influences EDTA degradation. Lauff et al. (1990) isolated an *Agrobacterium* sp. that apparently could degrade only $FeEDTA^{-}$. However they did not model their aqueous system to predict the forms of EDTA present. Also, they did not investigate the degradability of EDTA directly, but rather found no growth of the organism with the concentration of EDTA in excess of Fe. A study has investigated the mineralization of various metal-NTA complexes by an NTA-degrading bacterium under conditions in which the NTA was predominantly present as the metal-NTA complex. The order for the rates of mineralization of various metal-NTA complexes was free acid of NTA > Fe-NTA = Co-NTA > Al-NTA > Cu-NTA > Ni-NTA. The differences observed in the rates of mineralization of NTA were not accounted for by the toxicity of the complexed metal. Also, the degradability of the various metal-NTA complexes was not related to the thermodynamic stability constants for the various metal-chelate complexes, implying that factor(s) other than the strength of the metal-chelate complex control the degradation of NTA by this *Pseudomonas* strain.

Madsen and Alexander (1985) isolated a *Listeria* sp. from sewage that degraded $Ca\text{-}NTA^{-}$, but not $FeOHNTA^{-}$, $Mg\text{-}NTA^{-}$, or $HNTA^{2-}$. They used the aqueous speciation model MINEQL (Westall et al. 1976) to calculate the aqueous speciation of their nutrient solutions. Madsen and Alexander (1985) stated that the dependence of NTA mineralization on Ca may have

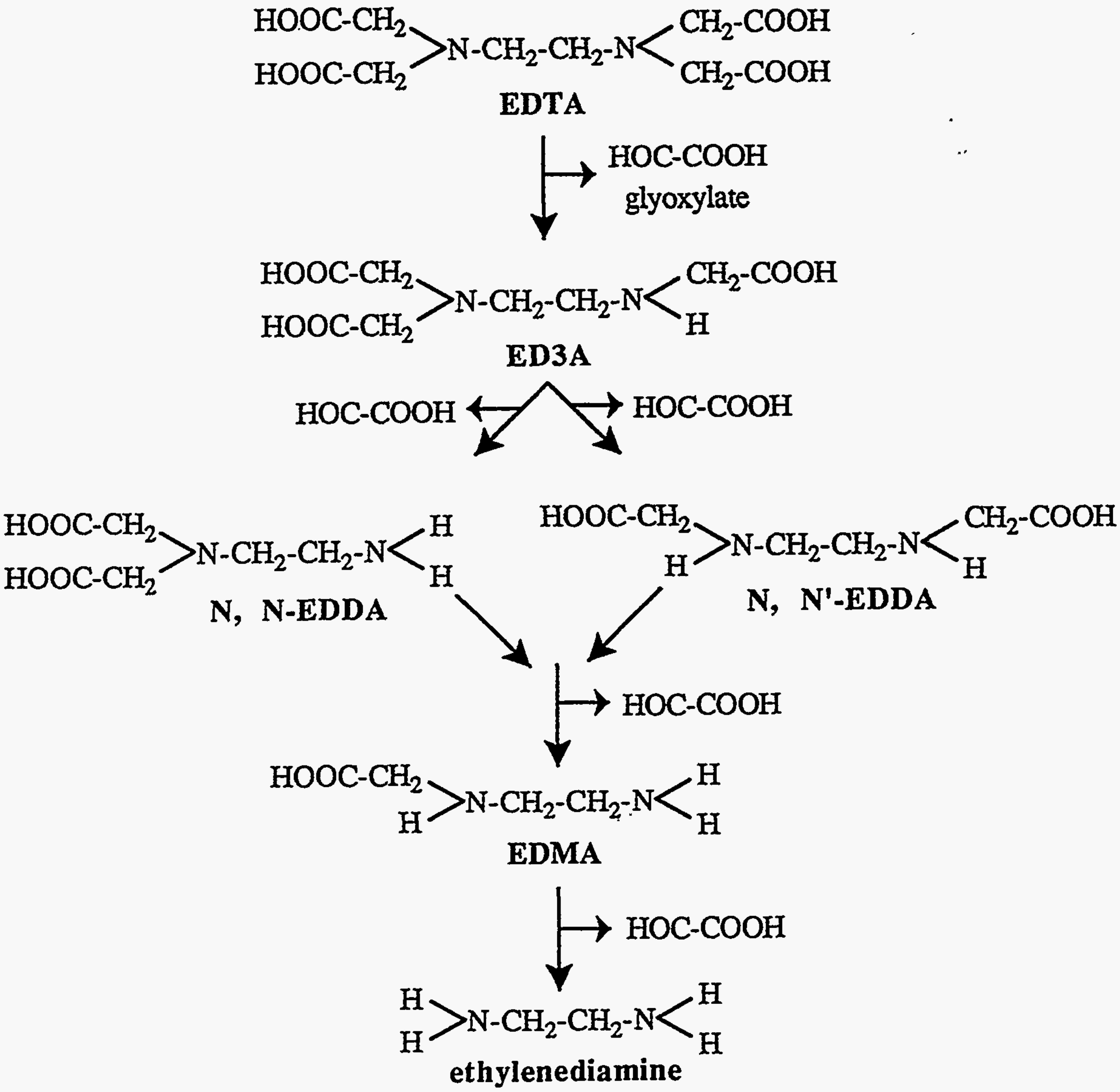

Figure 5.1 Proposed EDTA degradative pathway utilized by a microbial consortium (Belly et al. 1975)

been overlooked by earlier investigators. Bolton et al. (1993a) conducted aqueous speciation calculations with the computer code MINTEQ (Felmy et al. 1984), using the actual metal content (including Ca and Mg) of their experimental systems determined with ICP-AES. The concentrations of Ca and Mg in their experimental systems did not alter the speciation of the NTA. Thus, Bolton et al. (1993a) showed that *Pseudomonas* sp. ATCC 29600 mineralizes NTA when various metal-NTA complexes were present, whereas the *Listeria* sp. mineralized NTA only when the Ca-NTA complex was present (Madsen and Alexander 1985). This indicates that different NTA-degrading microorganisms may have differing specificities for various metal-NTA complexes.

5.2 Biodegradation of Citric Acid

Citric acid is a normal constituent of bacterial metabolism as a central component of the tricarboxylic acid cycle, otherwise known as the citric acid or Kreb's cycle (Gottschalk 1986). As such, citric acid is not an unusual compound for bacterial cells to metabolize. Because citrate is an important component of microbial metabolism, once citrate enters the cell, it is unlikely that degradative intermediates are released into solution under aerobic conditions. Anaerobic degradation of citrate may result in the release of acetate into solution and the oxaloacetate produced is further decarboxylated to yield pyruvate. Pyruvate is then metabolized via various pathways depending on the microbial species (Gottschalk 1986). Although citrate is usually readily metabolized by microorganisms, citrate in the environment is usually not present in the acid form, but rather as metal-citrate complexes. The presence of metals and the predominance of specific metal-citrate complexes can alter the degradability of citrate (Brynhildsen and Rosswall 1989; Francis and Dodge 1993; Francis et al. 1992; Madsen and Alexander 1985).

Madsen and Alexander (1985) studied metal-citrate complex degradation in sewage and by isolates from sewage using the aqueous speciation model MINEQL (Westall et al. 1976) to calculate the distribution of metal-citrate complexes in their experiments. They found that sewage microorganisms did not mineralize Mg-citrate but did mineralize Fe-, Al-, Ca-, and free-acid citrate at concentrations ranging from 0.1 to 0.001 μg/ml. They isolated the citrate-degrading isolates *Pseudomonas* sp. and *Pseudomonas pseudoalcaligenes* from the sewage. The *Pseudomonas* sp. degraded the Fe- and Ca-citrate, but not the Al-, Mg-, or H-citrate, while the *Pseudomonas pseudoalcaligenes* degraded the Ca-, Fe-, Al-, and H-citrate, but mineralized only 15 percent of the Mg-citrate. Thus different microorganisms may have different abilities to degrade different metal-citrate complexes or even the free acid of citrate (i.e., uncomplexed). Toxicity of the metal did not influence the physiology of the microorganisms as demonstrated by no difference in glucose mineralization in the presence of the various metal-citrate complexes or a no-citrate control.

Brynhildsen and Rosswall (1989) used the approach of Madsen and Alexander (1985) to prepare their experimental solutions so that 95 percent of the citrate would be present as specific metal-citrate complex. They used a *Klebsiella* sp. isolated from sewage to study the degradation of Cd-, Cu-, Mg-, Zn-, and uncomplexed citrate at approximately 0.14 μM. Uncomplexed citrate and Mg-citrate were rapidly degraded at almost the same rate with only approximately 20 percent of the citrate carbon remaining in solution. When Cu-, Zn-, or Cu-citrate complexes were present, approximately 95, 86, and 77 percent of the citrate carbon remained in solution, demonstrating much less citrate degradation in the presence of these metals. The presence of the metals was not toxic to glucose mineralization, suggesting that metal toxicity was not a factor in limiting citrate degradation, but rather that the metal being complexed by the citrate was limiting citrate degradation.

Francis et al. (1992) and Francis and Dodge (1993) used a *Pseudomonas fluorescens*, which was isolated from a leachate sample from the low-level radioactive waste disposal site at West Valley, New York, to study metal-citrate degradation. Francis et al. (1992) proposed that the stereochemical form of the citrate with the metal [i.e., bidentate (two carboxylic acid groups of citrate) for Ca-, Ni-, and Fe(III)-citrate; tridentate (two carboxylic acid groups and the hydroxyl group of citrate) for Cd-, Cu-, Fe(II)-, and Pb-citrate; and a bis complex (two citrate, both tridentate) for $(UO_2)_2$-citrate$_2$] dictated the degradability of the various metal-citrate complexes. They found various rates of metal-citrate degradation (1:1 metal-citrate complex) at 0.52 mM concentrations. Citrate was readily degraded in the presence of Ca, Fe(III), and Ni. Citrate was not degraded in the presence of equal molar Cd, Cu, Pb, or U. Francis et al. (1992) stated that metal toxicity was not likely because adding the undegradable metal-citrate complex to free citrate resulted in degradation of the free citrate. They did not investigate the influence of the various metal-citrate complexes on the degradation of an uncomplexing organic such as glucose. At this high a concentration (0.52 mM), metal toxicity was likely a factor in limited metal-citrate degradation.

It is difficult to interpret their data and ensure that specific metal-citrate complexes were the dominant form of citrate in solution because they did not conduct aqueous speciation calculations, their experimental systems were at a high concentration, and their metal-citrate ratio was 1:1.

In addition to the complexed metal, adsorption of citrate and its removal from solution can decrease its biodegradability. Gordon and Millero (1985) found a significant decrease in 2 μM citrate degradation by *Vibrio alginolyticus* when the sorbent hydroxyapatite was present. Citrate was rapidly adsorbed to the hydroxyapatite, limiting the solution concentration available for degradation. It is likely that the adsorption of citrate decreased its rate of degradation. Their experiments were conducted in seawater at pH 8. There may have been different forms of citrate present in the control (no hydroxyapatite) than when the hydroxyapatite was present because no aqueous speciation calculations were conducted.

5.3 Biodegradation of Oxalic Acid

Oxalate is a two-carbon dicarboxylic acid, which some microorganisms can use as a sole source of carbon and energy (Gottschalk 1986). *Pseudomonas oxalaticus* was found to oxidize oxalate to CO_2 via oxalyl-CoA and formate (Gottschalk 1986). There have not been many recent studies of the biodegradation of oxalate in the environment or by microorganisms. Madsen and Alexander (1985) studied oxalate degradation by sewage microorganisms using aqueous speciation modeling (Westall et al. 1976) to calculate the distribution of metal-oxalate complexes in their experiments. They found that sewage microorganisms did not mineralize Mg-oxalate at 0.001 μg/ml, but did readily mineralize it as the concentration increased to 0.01 and 0.1 μg/ml. Thus the degradability of oxalate in the environment may be concentration dependent. The rates of degradation for Al-, Fe-, and H-oxalate were similar and fast at all three concentrations. Calcium-oxalate was mineralized readily, but more slowly than Al-, Fe-, or H-oxalates, and much more rapidly than Mg-oxalate.

Madsen and Alexander (1985) isolated two oxalate-degrading microorganisms from sewage, including *Pseudomonas alcaligenes* and an *Alcaligenes* sp., and inoculated various metal-oxalate containing media. The *Pseudomonas alcaligenes* mineralized Al-, Ca-, Fe-, and H-oxalate at the same fast rate, but mineralized Mg-oxalate at a significantly slower rate. The *Alcaligenes* sp. mineralized Ca-oxalate most readily, followed respectively by Fe-oxalate, Mg-oxalate and Al-oxalate, and H-oxalate. Formic acid was used to determine if the various metal-oxalate complexes influenced the physiology of the microorganisms. The mineralization of formic acid was not affected by the presence of various metal-oxalate complexes for the *Pseudomonas alcaligenes*. This suggests that metal-oxalate toxicity was not a factor limiting oxalate degradation. The *Alcaligenes* sp., however, was subject to some inhibition in formate mineralization by the presence of various metal-oxalate complexes. This difference in degradability of different metal-oxalate complexes for *Pseudomonas alcaligenes* and an *Alcaligenes* sp. demonstrate that there is strain selectivity for the degradation of various metal-oxalate complexes.

5.4 Biodegradation of Picolinic Acid

Picolinic acid belongs to a class of compounds that have in common a pyridine ring. A number of pyridines and pyridine derivatives are naturally occurring, but many are of anthropogenic origin. Many of the processes used for the production of synthetic fuels result in the production of pyridines. Examples include coal gasification and oil shale retorting (Sims and Summers 1985). Also, a variety of pyridines and pyridine derivatives have been used as solvents for a wide variety of industrial applications. For these reasons there has been considerable interest in the microbial degradation of this class of compounds.

Specifically, biodegradation of picolinic acid (2-pyridinecarboxylic acid) has been of interest because of its activity as an inhibitor of sporulation in bacteria and because of its close structural relationship to the herbicide Picloram (Figure 5.2a) and as a photolytic product of the herbicide Diquat (Figure 5.2b) (Smith and Grove 1969).

Although pyridine is resistant to electrophilic substitution reactions because of the electronegativity of the N atom in this heterocycle, the presence of carboxyl in picolinic acid activates the ring towards enzymatic nucleophilic attack. Thus, based on its electrochemistry, picolinic acid should be susceptible to enzymatic attack by aerobic and anaerobic microorganisms. Another reason that picolinic acid would be expected to be readily degraded by microorganisms stems from the fact that it is an essential cofactor of the coenzymes nicotinamide adenine dinucleotide (NAD+) (Figure 5.2c) and nicotinamide adenine dinucleotide phosphate (NADP+), essential carriers of reducing equivalents in cellular metabolism.

Pyridine carboxylic acids appear to be quite susceptible to aerobic biodegradation in soil with the parent compound disappearing in usually less than 7 days (Sims and Summers 1985). Ohsugi et al. (1981) isolated 20 strains of bacteria from soil enrichment cultures that could grow on and degrade picolinic acid. A variety of aerobic and anaerobic bacteria have also been isolated that can grow on and degrade nicotinic acid (Behrman and Stanier 1957).

In general, the aerobic attack of the pyridine ring of picolinate is via nucleophilic attack by -OH derived from water, followed by introduction of a second hydroxyl by monooxygenase attack or by nucleophilic substitution at electron-deficient sites. As an example, the pathway for the metabolism of picolinate by a *Bacillus* sp., isolated from soil, is presented in Figure 5.3.

Metabolites similar to those in Figure 5.3 were identified as transformation products of picolinic acid degradation by an *Aerococcus* sp. (Dagley and Johnson 1963). An *Arthrobacter* sp. was isolated from garden soil that was capable of growing on picolinic acid as a sole carbon and energy source and produced 6-hydroxy-picolinic acid as a metabolite (Tate and Ensign 1974). An unidentified Gram-negative coccus was isolated from soil that could utilize picolinic acid and nicotinic acid as sole sources of carbon, nitrogen, and energy (Shukla et al. 1977).

Picolinic acid and its derivatives can form complexes with some metals; for example, Picloram forms weak complexes with Fe(III) and Cu(II) but strong, insoluble complexes with Fe(II) and Ni(II), and has been postulated as a mechanism for removal of this herbicide from contaminated groundwater (Michaud and Hoggard 1988). The influence of these complexes on the biodegradation of picolinic acid is unknown.

Pyridine and pyridine derivatives have also been shown to be degraded under anaerobic conditions. The initial step in metabolism can be either ring reduction or ring hydroxylation (Berry et al. 1987). Although few studies have directly investigated the anaerobic biodegradation of picolinic acid, insights can be gained from research on nicotinate. A bacterium identified as *Clostridium barkeri* was isolated from Potomac River sediments using anaerobic enrichment techniques and was found to ferment nicotinate (Pastan et al. 1964). The proposed degradation pathway is shown in Figure 5.4.

An anaerobic bacterium that utilizes sulfate as the terminal electron acceptor (i.e., a sulfate-reducing bacterium), which completely mineralized nicotinate, was isolated from marine mud samples (Imhoff-Stuckle and Pfennig 1983). Although there was no attempt to identify intermediates, it was suspected that conversion to 6-hydroxynicotinate was the first step in nicotinate degradation by this organism.

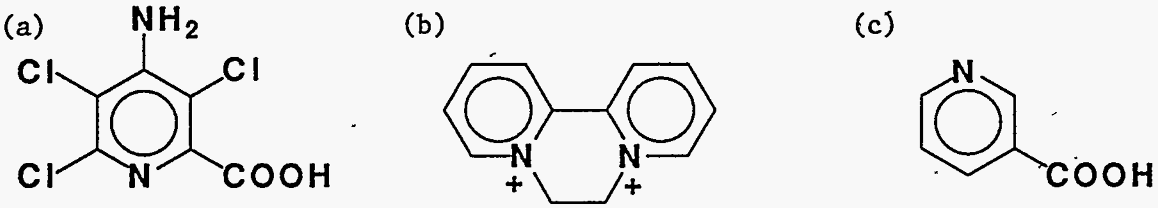

Figure 5.2 Structures of Diquat, Nicotinate, and Picloram

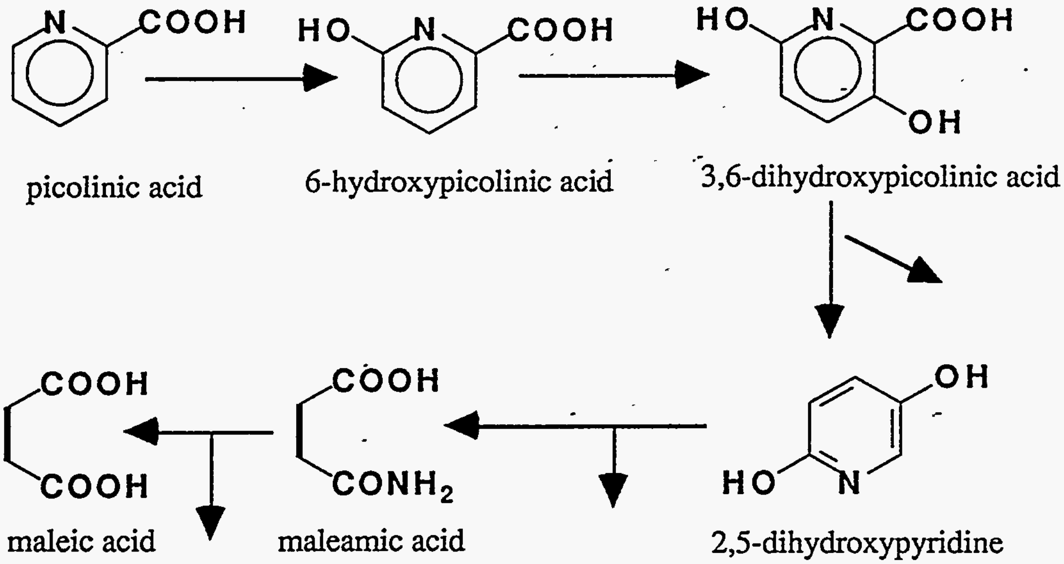

Figure 5.3 Picolinate biodegradation pathway utilized by a *Bacillus* sp. (Shukla and Kaul 1973)

In general, picolinate will most likely degrade in aerobic soils and sediments and probably will be degraded in anaerobic environments also, based on studies with its structural analog, nicotinic acid. However, further research is needed to confirm that picolinate will be degraded under anaerobic conditions and to identify the responsible functional groups of microorganisms.

The factors likely to control picolinate fate in the environment include the presence of microorganisms capable of degrading the compound, concentration, pH, and bioavailability. The concentration of picolinate, if too high, can be toxic or inhibitory to the microorganisms. Alternatively, if the concentration is too low, it may be below the threshold or concentration at which microorganisms can effectively metabolize the compound. Extremes of pH can also be detrimental to the biodegradation of organic compounds, although many microorganisms are adapted to life at extreme pH. Another factor that can influence the biodegradation of organic compounds in soils and sediments is their sorption to mineral and organic particles. For example, the rate of biodegradation of quinoline sorbed to smectite clay has been shown to be controlled by the rate of desorption from the clay (Smith et al. 1992). Finally, little or no information is available regarding

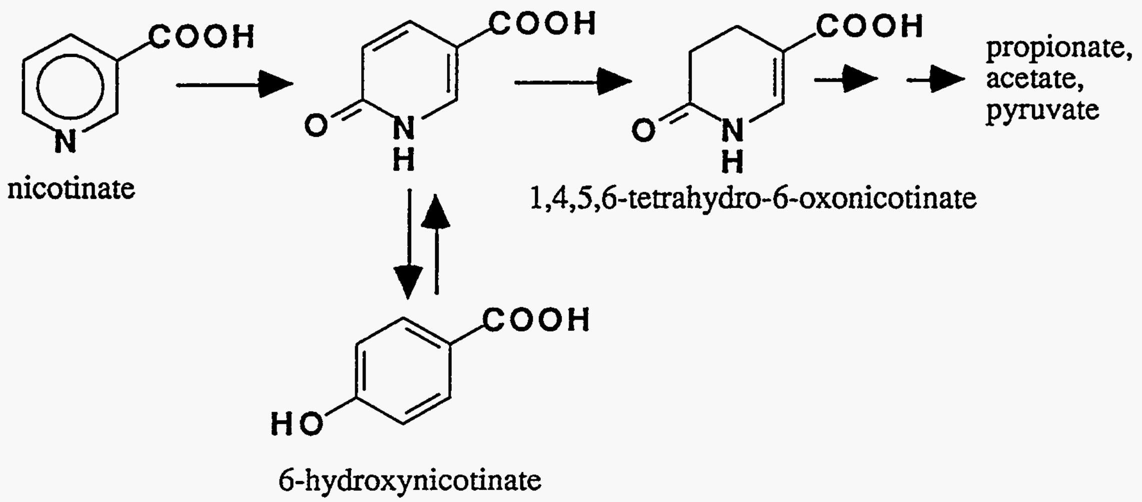

Figure 5.4 Pathway of nicotinate fermentation by *Clostridium barkeri*

the susceptibility of metal-picolinate complexes to enzymatic attack by aerobic or anaerobic microorganisms. We speculate, based on analogy to the synthetic chelating agents NTA and EDTA, that different metal-picolinate complexes will vary in the rate and extent to which they are degraded.

5.5 Summary

The factors likely to control the fate of organic compounds in the environment are 1) the presence of microorganisms capable of degrading the compound, 2) environmental conditions conducive to degradation, 2) concentration, and 4) bioavailability. It is not unusual for microorganisms to be exposed to citrate and oxalate in the environment, and microorganisms able to degrade these acids should generally be present. Picolinate normally is not present in the environment, but structural analogs are present, suggesting that picolinate-degradative pathways may exist or evolve over time. There is no structural analog for EDTA or DTPA in the environment, which may explain their recalcitrance in most soils and sediments. Microorganisms generally degrade organic contaminants within a range of environmental conditions; however, microorganisms are constantly being found to function at extremes of moisture content (e.g., desiccation), temperature (e.g., hot springs), pH, and nutrient availability (e.g., oligotrophic conditions). The concentration of organic compounds, if it is too high, can be toxic or inhibitory to microorganisms. This is known to occur with EDTA (Eagon and Carson 1965) and may also occur with picolinate, citrate, and oxalate. Alternatively, if the concentration is too low, it may be below the threshold concentration at which microorganisms can effectively metabolize the compound. The biodegradation of organic compounds in soils and sediments is also influenced by their sorption to mineral and organic surfaces. For example, sorption of citrate to hydroxyapatite limited its degradation (Gordon and Millero 1985). Limited information is available on the effects of sorption on degradation for EDTA, DTPA, oxalate, or picolinate, but we hypothesize decreased degradation when sorption occurs. A final factor influencing the bioavailability of EDTA, citrate, DTPA, oxalate, and picolinate is their aqueous speciation, i.e., the form available in solution to the microorganism. The degradability of citrate and oxalate can be limited when specific metals are complexed. Although the information for EDTA, DTPA and picolinate is limited, we hypothesize that this is also true for them. Thus the presence of specific metal-citrate, oxalate, EDTA, DTPA, or picolinate complexes may extend the half-life of the organic ligand in the environment and perhaps enhance metal transport if the metal-ligand complex adsorbs to sediment/soil less than the uncomplexed metal does.

6 Chemical Models for Predicting the Behavior of Radionuclide-Chelate Complexes in Soil/Water Systems

Chemical equilibrium models[a] may be used to calculate the reactions of radionuclides, chelating agents, and radionuclide-chelate complexes in aqueous solutions, such as leachates and ground water, and how the resulting dissolved compounds may interact with soil mineral phases. This information is used to predict the leaching and transport of radionuclide-chelate complexes in soil/water systems associated with disposal facilities for low-level radioactive waste (LLW). Thermodynamic, kinetic, and sorption data for radionuclide-chelate complexes, as reviewed in previous chapters, are required components in the databases used by these chemical models. This chapter reviews chemical models that may be used to evaluate the behavior of radionuclide-chelate complexes in soil/water systems.

The speciation or chemical form of dissolved radionuclides is generally the single most important factor governing their ability to migrate in surface-water, soil, and ground-water systems. For these complex, heterogeneous systems, radionuclide speciation is commonly determined using a chemical equilibrium model and a database of reaction stoichiometries and associated thermodynamic constants for aqueous species containing the radionuclides of interest. The chemical equilibrium models use the principles of equilibrium thermodynamics[b] to solve the distribution of the total dissolved mass of a radionuclide (e.g., Pu^{IV}) between its various uncomplexed (e.g, Pu^{4+}), inorganically-complexed (e.g., $PuOH^{3+}$, $PuSO_4^{2+}$), and organically-complexed (e.g., Pu^{IV}-EDTA) aqueous species. For very simple geochemical systems, personal-computer spreadsheet software can be used to solve the necessary equations to calculate aqueous speciation. However, for most systems, dedicated computerized models that run on a variety of platforms from high-end personal-computer processors to mainframe computers are required to solve the complex assemblages of chemical reactions.

As a result, chemical equilibrium models used to calculate aqueous chemical equilibria are invaluable tools for predicting the masses of dissolved radionuclides, chelating agents and radionuclide-chelate complexes. This information is in turn used to assess the behavior and migration potential of dissolved radionuclides in soil/water systems. This speciation information is valuable for conducting performance assessments (PAs) of low-level radioactive waste (LLW) disposal facilities used for the disposal of decontamination wastes containing radionuclides and chelating agents.

6.1 Chemical Equilibrium Models

The development and application of chemical equilibrium models to calculate the aqueous speciation of radioactive and other hazardous contaminants in soil/water systems has been extensive. Several compilations of technical papers provide valuable perspectives on the development, application, and limitations of chemical equilibrium models. Although there are a large number of models available in the technical community, most chemical equilibrium models share several common capabilities and fit into one of two general categories of models.

(a) For the sake of brevity, the term "chemical equilibrium models" will refer to all computerized models used to calculate reactions involving aqueous species, solids, and gases in chemical and geochemical systems at equilibrium conditions and/or with kinetic constraints. The user should be aware that some "chemical equilibrium models" include kinetic rate data to model some aqueous speciation, redox, or solubility reactions as a function of equilibration time.

(b) The use of thermodynamic principles to calculate aqueous equilibria in soil/water systems is described in numerous sources, including Garrels and Christ (1965), Lindsay (1979), Morel (1983), Nordstrom and Munoz (1985), and Stumm and Morgan (1981).

6.1.1 General Sources of Information

Two important sources of published papers pertaining to the development and application of chemical models are the proceedings from special symposia sponsored by the American Chemical Society. These include the proceedings edited by Jenne (1979b) and Melchior and Bassett (1990). At the time of publication, the papers published in these proceedings represented the state of knowledge for various topics related to chemical modeling, and several of these papers continue to be regularly cited in today's modeling literature. Papers contained in these proceedings and the references cited therein are a valuable reference source of information on chemical modeling. The papers cover a wide range of topics that include:

- development, documentation, validation, and verification comparison of available chemical models and their associated thermodynamic database

- application of chemical models to modeling equilibrium and mass transfer (i.e., solubility) processes, contaminant transport, surface chemistry, and organic compounds

- advancements in the thermodynamics of aqueous systems, ion interactions, solid solutions of mineral precipitates, mineral and gas solubilities

- advancements in the kinetic rates for aqueous/mineral systems.

The beginning of each proceedings includes a detailed overview paper by the editors of the proceedings. The overview by Jenne (1979a) contains discussions of technical goals; approaches; priorities; and problem issues, such as, organic ligands, redox-dependent speciation, thermodynamic data, time scales, error estimates, system characterization, adequacy of literature reviews, need for interdisciplinary approaches, and graduate training. Topics covered in the overview by Bassett and Melchior (1990) included developments in aqueous theory (e.g., ion association, ion hydration, and ion interaction); model applications; surface chemistry; model sensitivities to sampling, errors, analytical errors, computational errors, redox potential, and reaction metastability; advancements in thermodynamic and kinetic data for organic compounds, macromolecules, cosolvents, and partitioning of organic molecules; and coupling of chemical and hydrological models.

Several conferences have also been held that have focused on the development of geochemical models, improvement of their thermodynamic databases, application of these models to the disposal of LLW and high-level radioactive waste (HLW), and identification of key geochemical data needs pertaining to the improvement of these models. Examples include conferences that had been sponsored by the U.S. Nuclear Regulatory Commission (NRC), such as those described in the published proceedings by Alexander and Birchard (1984), Erdal (1985), and Jacobs and Whately (1985).

Numerous papers describing chemical modeling studies related to radioactive waste disposal are presented each year and published in proceedings from the annual symposia entitled "Scientific Basis for Nuclear Waste Management." These symposia are organized by the Materials Research Society. Readers are encouraged to peruse the indices for the proceedings published for each of these meetings since 1978 for studies related to the chemical modeling of radionuclides that may be released from LLW and HLW source-term components and then transported in ground-water systems.

Another valuable source of information includes the papers published in the proceedings from the international conferences entitled "Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere," which are referred to as the MIGRATION meetings. Papers from "MIGRATION '93," which was the fourth and most recent conference in this series, are published in Adloff et al. (1994). Proceedings from this and earlier MIGRATION meetings have also been published in special issues of *Radiochimica Acta* in 1988, 1991, 1992, and 1994, and the *Journal of Contaminant Hydrology* in 1993.

6.1.2 Types of Chemical Equilibrium Models

Table 6.1 contains a partial list of chemical equilibrium models that have been described in the literature. Although no attempt was made to make this list all inclusive, Table 6.1 nonetheless demonstrates the extensive number of chemical equilibrium models that exist. Numerous reviews of chemical equilibrium models have been published. Serne et al. (1990, chapter 3) reviews the status of chemical models. They summarized reviews of chemical models that had been published as of 1990, sources and issues related to thermodynamic databases, validation(a) testing of chemical models, and issues regarding future development and application of chemical models and their databases. Some of the more extensive model reviews described by Serne et al. (1990) include those by Jenne (1981), Kincaid and Morrey (1984), Kincaid et al. (1984), Morrey et al. (1986), Mercer et al. (1981), Nordstrom and Ball (1984), Nordstrom and Munoz (1985), Nordstrom et al. (1979), Potter (1979). Mangold and Tsang (1991) is another model review published since Serne et al. (1990). In addition to chemical equilibrium models, the review by Mangold and Tsang also includes discussions of hydrological models and hydrochemical (i.e., coupled aqueous chemical/hydrological transport) models.

Chemical equilibrium models can be divided into two general categories: 1) speciation-solubility models, and 2) reaction path models. All speciation-solubility models include the capabilities to calculate the distribution of aqueous species for a water composition specified by the user and the degree of saturation [i.e., saturation index (SI)] of the speciated composition of that aqueous solution with respect to the solids in the model's thermodynamic database. Aqueous speciation identifies the compositions, masses, and activities of the various uncomplexed and inorganically and organically complexed ions that comprise the total dissolved mass of each element listed in the water composition. The calculated aqueous species are based on the reactions and associated thermodynamic constants included in each model's thermodynamic database. The saturation index calculations indicate if the specified water composition is oversaturated (i.e., $SI > 0$), at equilibrium (i.e., $SI \approx 0$), or undersaturated (i.e., $SI < 0$) with respect to each solid in the database. If a particular solid is near equilibrium, it is a possible solubility control for the concentrations of one or more of its constituent elements in the water composition

Table 6.1 Examples of some chemical equilibrium models described in the literature

ADSORP
AION
AQ/SALT
ASAME
BALANCE
CHEMIST
CHEMTRN
COMICS
DISSOL
ECES
ECHEM
EHMSYS
EQ3
EQ3NR
EQ6
EQBRAT
EQUIL
EQUILIB
EVAPOR
FASTCALC
FASTPATH
GEOCHEM
GIBBS
HALTAFALL
HITEQ
HYDRAQL
IONPAIR
KATKHE
KATKLE1
MICROQL
MINEQL
MINEQL2
MINTEQ
MINTEQA2
MIRE
MIX2
NOPAIR
PATHCALC
PATHI
PHREEQE
REDEQL
REDEQL.EPAK
REDEQL2
RIVEQL
SEAWAT
SENECA
SENECA2
SIAS
SOLGASWATER
SOLMNEQ
SOLVEQ
SYSTAB
THERMAL
WATCH1
WATCHEM
WATEQ
WATEQ2
WATEQ3
WATEQF
WATEQFC
WATSPEC

(a) Silling (1983) defines validation as the "assurance that a model as embodied in a computerized model is a correct representation of the process or system for which it is intended." In contrast to validation, Silling (1983) defines verification as the "assurance that a computerized model correctly performs the operations specified in a numerical model."

selected for modeling. Some speciation-solubility models also include the capabilities to calculate mass transfer(a) between a single initial and final state, that results from mineral precipitation/dissolution, gas solubility, and/or adsorption/desorption equilibria.

The speciation-solubility category of models includes HYDRAQL (Papelis et al. 1988), MINTEQA2 (Allison et al. 1991), and its predecessor versions described by Felmy et al. (1984, MINTEQ), Peterson et al. (1987, MINTEQ), Brown and Allison (1987, MINTEQA1). The HYDRAQL model is being used for aqueous speciation calculations being completed as part of the project that supported this literature review. It is a direct descendent of MINEQL model (Westall et al. 1976). The MINTEQ model has also been used on NRC-supported projects, such as Krupka et al. (1994), MacKinnon and Sullivan (1994), Peterson et al. (1986), and Peterson et al. (1984). The model was originally constructed by combining the mathematical structure of the MINEQL model with the thermodynamic database and geochemical attributes of the WATEQ3 model (Ball et al. 1981a). The reader is referred to the references and user guides listed above for details regarding the use of these models, types and examples of geochemical equilibria calculations possible with this category of models, and the underlying equations on which speciation-solubility models are based.

Reaction path models comprise the second category of chemical equilibrium models. All reaction path models include the capabilities to calculate aqueous speciation and the degree of saturation of aqueous solutions, but also permit the simulation of mass transfer due to precipitation/dissolution of minerals or adsorption/desorption onto mineral surfaces as a function of reaction progress. Computationally, one unit of reaction progress means that one unit of gaseous or solid reactant (e.g., a nuclear-waste form) has reacted with an aqueous solution containing solid phases with which the solution is already in equilibrium. At each step of reaction progress, the model calculates the changes or path of mineral and gaseous solubility equilibria that constrain the composition of the aqueous solution, the masses of minerals precipitated and/or dissolved to attain equilibrium, and the resulting composition of the aqueous solution.

Examples of reaction path models include PHREEQE (Parkhurst et al. 1980) and EQ3/EQ6 (Wolery and Daveler 1992; Wolery 1979, 1983; Jackson 1988). These models have been used extensively in studies related to the disposal of radioactive waste. These applications have included studies supported by the NRC, such Murphy and Pabalan (1994) and Sverjensky (1992).

6.2 Thermodynamic Databases

An extensive number of tabulations and critical reviews of thermodynamic data have been published during the last 30 years. These publications contain thermodynamic data for a large range of compounds needed to model soil/water systems, including data for uncomplexed, inorganically-complexed, and organically-complexed aqueous species; elements; naturally-occurring minerals; solids of environmental interest that do not normally occur in nature (e.g., amorphous $PuO_2{\cdot}H_2O$); liquids; and gases. The availability of thermodynamic data for organically-complexed aqueous species, as noted in Chapter 3, is considerably limited when compared to that available for uncomplexed and inorganically-complexed aqueous species. Nordstrom and Munoz (1985, Appendix F) list the references for more than 206 compilations of thermodynamic data. Several tabulations commonly cited as important sources of data for thermodynamic databases used in chemical equilibrium models are listed in Table 6.2.

6.2.1 Radionuclide-Chelate Complexes

The availability of thermodynamic data (e.g., $\Delta G^{\circ}_{r,298}$ or log $K^{\circ}_{r,298}$) for radionuclide-chelate reactions in databases used for chemical equilibrium codes is particularly important to the objectives of the study supporting this literature review. Overall, users should assume that the thermodynamic databases associated with most publicly-available versions of chemical

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(a) Mass transfer is defined here as the transfer of mass between two or more phases that includes an aqueous solution, such as the mass change resulting from the precipitation of a mineral. On the other hand, mass transport is defined as the time-dependent movement of one or more solutes during fluid flow.

Table 6.2 Examples of compilations of thermodynamic data that have been used to develop the databases for chemical equilibrium models

Title	Reference
The Hydrolysis of Cations	Baes and Mesmer (1976)
JANAF Thermochemical Tables. Third Edition.	
Part I. (Al-Co)	Chase et al. (1985a)
Part II. (Cr-Zr)	Chase et al. (1985b)
CODATA: Key Values for Thermodynamics	Cox et al. (1989)
Chemical Thermodynamics Series. Volume 1:	Grenthe et al. (1992)
Chemical Thermodynamics of Uranium	
Summary and Critique of the Thermodynamic Properties of Rock-Forming Minerals	Helgeson et al. (1978) and other references by Helgeson as cited in Nordstrom and Munoz (1985)
Critical Stability Constants.	
Volume 1: Amino Acids	Martell and Smith (1974)
Volume 3: Other Organic Ligands	Martell and Smith (1977)
Volume 4: Inorganic Complexes	Martell and Smith (1976)
Volume 5. First Supplement	Martell and Smith (1982)
Volume 6. Second Supplement	Martell and Smith (1989)
Handbook of Thermodynamic Data	Naumov et al. (1974)
The Chemical Thermodynamics of Actinide Elements and Compounds	
Part 1. The Actinide Elements	Oetting et al. (1976)
Part 2. The Actinide Aqueous Ions	Fuger and Oetting (1976)
Part 3. Miscellaneous Actinide Compounds	Cordfunke and O'Hare (1978)
The Chemical Thermodynamics of Actinide Elements and Compounds	
Part 8. The Actinide Halides	Fuger et al. (1983)
Part 12. The Actinide Aqueous Inorganic Complexes	Fuger et al. (1992)
Thermodynamic Tables for Nuclear Waste Isolation: Aqueous Solutions Database	Phillips et al. (1988)
Thermodynamic Properties of Minerals and Related Substances at 298.15K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures	Robie et al. (1978)
Selection of Standard Free Energies of Formation for Use in Soil Chemistry	Sadiq and Lindsay (1979) and supplements by Sadiq and Lindsay (1981) and Elrashidi and Lindsay (1984)

Table 6.2 (contd)

Title	Reference
The NBS Tables of Chemical Thermodynamic Properties. Selected values for Inorganic and C_1 and C_2 Organic Substances in SI Units	Wagman et al. (1982)

equilibrium codes are limited with respect to reactions and thermodynamic data for radionuclide-chelate complexes. This limitation results from several factors. Firstly, the amount of thermodynamic data available for radionuclide-chelate reactions and the number of experimental studies supporting these values are considerably less than the data and studies available for radionuclide complexes containing inorganic ligands, such as hydroxide, carbonate, phosphate, and sulfate. This factor is evident from number of studies and data identified in Section 3.1 for complexation reactions involving EDT, DTPA, picolinic acid, oxalic acid, and citric acid.

Secondly, the thermodynamic databases for chemical equilibrium codes also evolve not only based on the availability of thermodynamic data, but, as importantly, on the chemical environments to which these modeling tools have been applied. In general, the early applications included modeling the availability of mineral nutrients in soils and sediments; metal concentration processes in geological environments, such as ore deposits; and the corrosion of metals. Application of these techniques to the behavior of radionuclides and, more specifically, radionuclide-chelate complexes in soil/water systems is relatively a more recent objective. Therefore, databases required for these latter applications lag behind the databases developed, refined, and documented for the earlier modeling studies.

Once a particular chemical equilibrium code or group of codes is selected for the types of modeling studies anticipated at a user's organization, the user will typically extend the thermodynamic database to include the constituents important for their applications. Because of research, funding, and/or publication priorities, individual database development efforts are not commonly reported in the open literature or made available to all potential users.

An inventory of the databases for all codes in Table 6.1 is not possible, especially given that users typically tailor a database to their specific application needs. However, a review of the organic reactions included in the databases for MINTEQA2 (Allison et al. 1991), HYDRAQL (Papelis et al. 1988), EQ3NR/EQ6 (Wolery and Daveler 1992), and PHREEQE (Parkhurst et al. 1980) provides a perspective of the extent and differences in their contents relative to radionuclide elements and organic ligands. The metals considered important to low-level radioactive decontamination wastes, as identified in Section 3.1, include Al, Am, Ca, Cm, Co, Cr, Cs, Fe, Mg, Mn, Nb, Ni, Np, Pu, Sr, Sn, Tc, Zn, and Zr. These elements were chosen because of their presence in decontamination wastes from nuclear reactors or their natural occurrence in aqueous systems.

Of the four codes identified above, MINTEQA2 (Version 3.11) (Allison et al. 1991), as distributed by the U.S. Environmental Protection Agency, contains the most extensive organic database. The EPA-version of MINTEQA2, however, does not include all of the metals, especially radionuclide elements, identified above. Table 6.3 lists the organic ligands and those metals in the list above that are in the MINTEQA2 database.(a) From these organic ligands and metals, Table 6.3 also identifies those metal-organic complexes for which reactions and the associated thermodynamic values are included in the database of the EPA-version of MINTEQA2.

(a) The MINTEQA2 database has been modified on other NRC projects to include the radionuclides Am, Co, Cs, Np, Pu, Sn, and Zr. The focus of these modifications, however, was not low-level radioactive decontamination wastes and the inclusion of reactions for radionuclide-chelate complexes.

Table 6.3 List of reactions in MINTEQA2 (Version 3.11) involving organic ligands and metals of significance to low-level radioactive decontamination wastes. [The EPA-version of MINTEQA2 does not contain the metals Am, Cm, Co, Cs, Nb, Pu, Sn, and Zr.]

Organic Ligands	Metals								
	Al	Ca	Cr	Fe	Mg	Mn	Ni	Sr	Zn
Chelating agents:									
n-butylamine									
citrate	x		x	x	x	x			x
diethylamine							x		x
dimethylamine									
EDTA[(a)]	x		x	x	x		x	x	x
ethylenediamine		x		x	x	x	x		x
glutamate							x		x
glycine			x				x		x
hexylamine									
methylamine									
2-methyl pyridine							x		
3-methyl pyridine							x		x
4-methyl pyridine							x		
iso-propylamine							x		x
n-propylamine							x		x
NTA[b]									
phthalate		x	x				x		x
salicylate							x		
tartrate									
tri-methylamine									
tributylphosphate									
valerate		x	x				x		
Other organic ligands:									
acetate	x			x		x			x
benzoate	x			x		x			x
butyrate	x	x	x	x		x			x

Table 6.3 (contd)

	Metals								
Organic Ligands	Al	Ca	Cr	Fe	Mg	Mn	Ni	Sr	Zn
iso-butyrate			x	x			x		
formate									
fulvate									
humate									
propanoate		x	x	x	x		x		x
iso-valerate		x	x			x			

(a) EDTA ≡ ethylenediaminetetraacetic acid
(b) NTA ≡ nitrilotriacetate

The HYDRAQL code (Papelis et al. 1988) also includes an extensive number of organic ligands. The version of the HYDRAQL being used by our PNL project staff includes the organic chelating agents acetylacetone, alanine, arginine, citrate, cysteine, EDT, glycine, histidine, leucine, lysine, nitrilotriacetate (NTA), oxalate, pentetate, picolinate, proline, salicylate, serine, and tartrate, and the organic ligand acetate. Of the metals listed above, the database includes Am, Ca, Co, Cr, Cs, Fe, Mg, Mn, Ni, Sr, Sn, Zn, and Zr. The database, however, contains a limited number of reactions and associated thermodynamic data for metal-organic complexes. These include complexes for Ca-EDT, Mg-EDT, and Fe-acetate.

The extent of organic complexes in the thermodynamic databases for the versions of the EQ3NR/EQ6 (Wolery and Daveler 1992) and PHREEQE (Parkhurst et al. 1980) codes used by PNL staff in our group ranges from severely limited to null. Version 3245R54 of the EQ3NR/EQ6 database contains only two organic ligands, acetate and ortho-phthalate. Of the metals considered important to low-level radioactive decontamination wastes, this version of the EQ3NR/EQ6 database includes data for the complexes Ca-acetate, Fe-acetate, Mg-acetate, Sr-acetate, and Ca-ortho-phthalate. Our copy of PHREEQE database contains no organic ligands.

6.2.2 General Considerations

Databases of chemical equilibria models need to contain thermodynamic data for all important uncomplexed, inorganically-complexed, and organically-complexed aqueous species of radionuclides of interest as well as geologically- and environmentally-relevant elements to adequately calculate the behavior of radionuclide-chelate complexes in soil/water systems. Depending on how a modeling problem is conceptualized, different dissolved elements in the soil/water system may compete with the radionuclides of interest for the available mass of a dissolved chelating compound. Similarly, the mass of a individual radionuclide will be distributed between all of its uncomplexed, inorganically-complexed (e.g., hydroxyl, carbonate, sulfate, phosphate, etc.), and organically-complexed aqueous species. If a reaction for an important aqueous species is missing in the database and/or its thermodynamic constants are not known, then the estimated distribution of aqueous species for any dissolved element will be incorrect and could, in turn, affect the species distributions calculated for the other elements considered in the modeling problem.

The selection of a "best" set of thermodynamic values from these sources is a technically and logistically challenging effort. Because new thermodynamic data, especially for constituents of environmental interest such as radionuclides, are constantly being reported in the literature, the developer of a model's database must review recently published literature and attempt to assimilate any new values with those in existing compilations. Issues related to this selection and evaluation process are discussed in Nordstrom and Munoz (1985, Chapter 12). The critical evaluation and selection of thermodynamic data for incorporation into an existing database requires a understanding of the general solution chemistry and phase stability relationships of solids associated with a particular cationic and/or anionic constituent.

The developer must also be cognizant of the criteria initially used by the compiler to review and select the source data for the published tabulations. Because selection criteria and data analysis methods may differ between different tabulations of thermodynamic data, major sources of error may occur if the values accepted from different sources are not internally consistent. The example presented by Serne et al. (1990) involves the selection of thermodynamic data for aqueous complexes and solids containing phosphorus. Two different reference states can be used for elemental phosphorus [white or red phosphorus; for example, see Wagman et al. (1982) and Robie et al. (1978)]. If thermodynamic data are selected for radionuclide phosphate complexes from tabulations based on different reference states of phosphorus, inconsistencies of approximately 1.3 kcal per phosphorus atom per formula unit would result in the Gibbs free energies of formation at 25°C for the two sets of values.

6.3 Applications of Chemical Equilibrium Models to Radioactive Waste Issues

Chemical equilibrium models have been applied to a wide range of radioactive-waste disposal problems. Chemical modeling has been applied to many research topics associated with mission areas of the NRC. These include regulatory issues, such as land or geologic disposal of uranium mill tailings, LLW, decommissioning wastes, and HLW. Examples of chemical modeling studies supported by the NRC include the following:

- chemical modeling of contaminants in plumes migrating from uranium mill tailings waste impounds [e.g., Peterson et al. (1986) and references therein]
- chemical modeling of long term stability of earthern materials in contact with acidic tailings [e.g., Peterson et al. (1984) and references therein]
- estimating solubility-controlled concentration limits for radionuclides released from source-term components at LLW disposal facilities [e.g., Campbell and McCartin (1994), Krupka et al. (1994), and work in progress]
- coupling of geochemistry to computerized LLW source-term release models [e.g., MacKinnon and Sullivan (1994) and work in progress]
- analysis of the ionic nature and distribution of aqueous species of radionuclides released in decontamination solutions from nuclear reactor components[(a)]
- proposed tool to help assess the environmental availability of uranium in soils and sediments associated with decommissioning sites [e.g., Amonette et al. (1994, p.27-29)]
- chemical modeling of the geochemistry and migration of uranium, thorium, and other related elements at field sites studied as natural analogues to geological repositories for HLW disposal, such as the Alligator Rivers Analogue Project in Australia [e.g., Sverjensky (1992), Payne et al. (1992)], and Peña Blanca in Mexico [e.g., Murphy et al. (1991), Murphy and Pearcy (1992), and work in progress]
- chemical modeling in support of confirmatory analyses related to the characterization studies of Yucca Mountain in Nevada as a possible geologic HLW repository [e.g., Murphy and Pabalan (1994) and work in progress]
- mechanistic modeling of adsorption of radionuclides on soil components, such as adsorption of uranium on hydrated iron oxide (Waite et al. 1994) and sorption database development (Turner 1993).

(a) Unpublished 1994 draft report prepared by K. M. Krupka (PNL) for P. R. Reed (NRC).

6.4 Summary

The selection of a chemical equilibrium model is typically based more on the capabilities of the model, such as the availability of a surface complexation model to calculate sorption or ion-interaction model to calculate equilibria in high-ionic strength brines, than on concerns of computational accuracy of the model. Most models are currently at the stage of development that computational accuracy of the algorithms used to solve the chemical equilibria is usually not an issue. However, the need for an accurate and adequately complete water analysis as input data for a model is one of most important factors to obtaining accurate modeling results. As with most types of computer modeling techniques, "garbage in equals garbage out" also applies to the application of chemical equilibrium models to aqueous speciation and mass transfer calculations.

Another major source of discrepancy results from the thermodynamic databases used in the chemical equilibrium models. The limitations associated with these thermodynamic databases can in general be attributed to three factors: 1) the absence of aqueous species, sorbed species, and/or solids containing elements and/or ligands of interest; 2) the lack of thermodynamic data for known aqueous species, sorbed species, and/or solids of interest; and 3) the lack of internal consistency between parameters within a single thermodynamic database as well as between databases used by different models. This source of discrepancy has been revealed in comparison studies of different chemical equilibrium models. For example, a comparison study (INTERA 1983) of the PHREEQE and EQ3/EQ6 reaction path models demonstrated that the results of aqueous speciation and solubility calculations are identical when two models of different heritage and development history are used with thermodynamic databases containing the same reactions and associated thermodynamic constants. As will be discussed below, the importance of a model's thermodynamic database in generating consistent modeling results was also shown by Nordstrom et al. (1979) in the results of a comparison study reported for 14 chemical models.

Jenne (1981) and Nordstrom et al. (1979) discuss the limitations of using chemical equilibrium models. Although these reviews are somewhat dated, the issues identified by these authors are equally relevant to today's model development efforts and application studies. Jenne (1981) discusses the various applications and limitations of speciation-solubility and reaction path models. These limitations include the following:

- inadequate, critical evaluations of available thermodynamic data
- incompetence of models for particular applications due to a lack of thermodynamic aqueous species and solids containing elements of interest, such as complexation of metals by dissolved organic compounds, and data to calculate aqueous equilibria at elevated temperatures
- inadequate theoretical understanding and formulation of certain processes, such as absence of models and/or data for sorption, kinetic rates, and solid solution; calculations in high-ionic strength solutions; and disequilibrium between redox couples
- inadequate solution analyses, such as limited number of analyzed constituents, accuracy of data, and lack of sampling and analytical error uncertainties.

Nordstrom et al. (1979) is a commonly cited review of chemical equilibrium models. They discuss the major categories of modeling approaches used to calculate geochemical equilibria in aqueous solutions. Tables I and II in Nordstrom et al. (1979) list the characteristics of 14 chemical models and their associated thermodynamic databases. This model information was supplied by model users as part of a questionnaire that they were asked to complete. As part of this effort, Nordstrom et al. asked the users to complete and report the results of two test cases (analyses of a dilute river-water and an average sea-water). Nordstrom et al. used the results from these test cases to examine the consistency of these chemical equilibrium models and their thermodynamic databases. Reasons for the discrepancies between the results from the different geochemical reaction models were discussed. Nordstrom et al. emphasized that the adequacy of the thermodynamic database used with each model was the biggest source of discrepancy in the results reviewed for the river-water and sea-water test cases. Other potential limitations that resulted in discrepancies included:

- inadequacy of the assumptions on which the model is based
- inconsistency and inadequacy of the activity coefficient equations
- inaccurate assumptions about the redox state of aqueous systems
- inadequacy of the aqueous species considered in a model
- inconsistency in methods used to handle the input of solution carbonate and/or alkalinity values
- inadequacy of temperature corrections

Because thermodynamic databases are a critical component to accurately model aqueous speciation and solubility in soil/water systems, the more knowledgeable the user is with a model's database in terms of the completeness and accuracy of its data, the more likely the results will be correct. Unfortunately, most users cannot be experts with respect to the measurement and derivation of thermodynamic data nor can they afford to do a critical review of thermodynamic data for all aqueous species and solids containing elements of interest to their modeling applications. In these cases, the user should thoroughly document the database used when reporting results of aqueous speciation and solubility modeling calculations.5

7 Observations of Enhanced Radionuclide Migration Attributed to Organic Ligands

7.1 Introduction

As mentioned in previous sections, the transport properties of radionuclides and regulated trace metals present in commercial low-level nuclear wastes are controlled by their speciation distribution in vadose-zone sediment pore water and groundwaters. There are two processes involving organic matter that can influence trace contaminant migration through sediments and groundwater surrounding shallow-land burial sites. The most frequently discussed process is organic ligand (both man-made chelators used for decontamination/clean up and natural plant degradation products) - metallic radionuclide or trace metal complexation. These complexation reactions result in two significant changes in trace contaminant mobility. First, water soluble organic-contaminant complexes significantly increase the concentration of many metallic contaminants that can be found in natural groundwaters. Many metallic radionuclides exhibit low solubility in groundwaters that are devoid of organic ligands and that exhibit neutral to slightly basic pH values. The presence of soluble organic ligands can significantly increase the observed solution concentrations of metallic radionuclides and trace metals (i.e., increase solubility). Further, the organic ligand-metal complex species generally exhibit a net negative surface charge. Metal ion (i.e., cation) adsorption onto sediments/soil is strong because of the electrostatic attraction forces between the opposite charged molecules. When the metal (cation) complexes with an organic ligand to form neutral or anionic molecules, the electrostatic forces between the solute and sediment surface either disappear or become repulsive. Thus, organic-metal complexes generally exhibit diminished adsorption properties onto sediments and migration tendencies are increased. The combination of increased solubility and decreased adsorption potential both lead to increases in migration potential.

A second but lesser discussed process is the ability of insoluble organic matter (e.g., high molecular weight humic acids and humin) present in soils to sequester contaminants, both metallic and non-metallic (e.g., ^{129}I). The adsorption of metallic contaminants onto insoluble humic acids is akin to the complexation reactions just discussed for soluble ligands. The ligands contain electron-pair-donor sites (e.g., COO^-, NH_2) that attract the electron deficient metals. The tendency for trace anions such as I^- to adsorb onto organic matter in soils is less well understood. One explanation is that the complex organic molecules contain surface sites with partial charge imbalances (net positive charged sites) that attract anions. It is also useful to note that organics present in sediment often occur as coatings over the inorganic rock grains and thus exhibit a large surface area that encourages surface reactions.

Whatever the cause, the tendency for contaminants to become adsorbed onto insoluble organic matter within sediments and soils lowers migration potential. Thus, whether the interactions of contaminants with organic matter are beneficial or deleterious to stopping migration depends on the particular geochemical circumstance.

A third effect of organics on trace contaminant migration occurs when organic material with inherent reducing capacity changes the redox condition of the soil/sediments. Certain dissolved organic molecules (e.g., polyhydric phenols) are known to reduce manganese oxides (e.g., pyrolusite, MnO_2) that generally are strong adsorbers of trace metals and metallic radionuclides. When the manganese oxides are reduced, they solubilize (Mn^{2+} released to solution) and release the previously bound metals. Dissolved organic material with reducing capacity likely can also reduce redox sensitive elements such as Pu, Np, and Tc. Reduction of these radionuclides generally leads to decreased mobility via precipitation reactions. Again, the key to assessing the fraction of a contaminant that will remain in the aqueous phase is determined by the many competing bio-geo-chemical processes occurring in the natural system, which are theoretically quantified via equilibrium constant expressions, such as described in Section 3.2.

7.2 Chelate vs Complex

Free metal ions in groundwaters are fully solvated (i.e., all the coordination sites are filled by water molecules or other ligands). When a complex is formed, one or more water molecules or existing ligands are displaced. The number of water molecules or ligands that can be coordinated to a metal ion is typically 6 for alkaline earth and transition metals and increases to 8, 10 or 12 for larger and more highly charged lanthanides and actinides.

When a metal ion is coordinated simultaneously to more than one donor group of the same organic ligand, the complex becomes a heterocyclic ring. This special configuration is called a chelate to distinguish the species from complexes where the ligand binds metals with only one donor group. Chelates often differ markedly in stability from complexes. As more donor groups in a particular ligand bind to a metal ion, more ring structures form and the chelate stability increases. One theoretical explanation for the increased stability is the significant increase in entropy that occurs when solvated water or other ligands are displaced (placed back into the bulk solution). For each chelate ring formed, the Gibbs free energy of reaction decreases such that the stability constant increases by a factor of about 100.

The increased stability of ring-structure complexes (chelates) causes the complex to remain intact even at very low concentrations of metals and ligands in solution (see Martell 1971 p. 245-246 for more detail). Generally, normal complexes, even those with high stability constants, show significant dissociation back to free metal cations and ligands when large dilution occurs.

From a practical standpoint, the salient point from this description of the differences in chelates and complexes is the increased stability of the fully coordinated metal-chelate. Once formed, the metal chelate can remain stable even when the solution is diluted. Thus, when man-made chelating agents are used to decontaminate nuclear facilities, the concentrations of both the chelate and radionuclide are relatively high. This promotes metal-chelate formation. Upon being mixed (diluted) during waste-form production (e.g., solidification into cement) or during trench leachate production, metal chelates can remain stable beyond the capabilities of "normal" complexes. The further dilution that occurs as trench water mixes with pore waters and groundwaters has the tendency to cause further dissociation of complexes. Only the most stable complexes (i.e., chelates) will remain intact in the environment outside disposal facilities. Much of the data available from field studies where organo-metallic complexation is suspected as the cause of enhanced radionuclide mobility infer that man-made chelating agents used originally to decontaminate facilities are the driving force: That is, the organic-metallic association occurred prior to disposal and survived the diluting processes that occur subsequently. The few data that corroborate this conceptual model are provided in Sections 7.3 and 7.4.

The following two sections will discuss the findings of selected articles that provide experimental and field data directly related to LLW disposal.

7.3 Selected Experimental Studies

The following discussion provides some details on organic-radionuclide interactions as an introduction to the complicated interplay of these constituents in natural environments. The first two articles discuss association and dissociation reactions between radionuclides and humic material.

Swanson (1981, 1982 a,b, 1983, 1984, and 1985) performed numerous laboratory experiments to evaluate the effects of several organic complexants on radionuclide migration potential through soils and pure oxide and clay components of soils. His large database of empirical observations is difficult to sort and somewhat confounded by variable container adsorption, filter membrane adsorption, apparent degradation of organic complexants versus time, and apparent slow kinetics with first order rate half-lives of weeks to months. It is difficult to quantify the effects of organic complexants on contaminant mobility because of the numerous factors that are important, such as strength of the complex versus competing ions, whether the complex or complexant itself adsorbs onto the soil substrates, the strength of the adsorption reactions between the free (uncomplexed) contaminant and the soil substrate, the stability of the organic ligand to degradation (chemical or biological), kinetic factors and whether the contaminant-ligand were complexed prior to introduction into the groundwater system.

After analyzing Swanson's data, it is difficult to find a few succinct statements but we offer these observations. Such empirical tests are very difficult to analyze when only total ligand concentrations at the start of the experiment are given. Complete solution analyses and speciation calculations via computer code are required to unravel the empirical data. In general, the test results show some adsorption of the contaminants studied as long as the complexants' total concentrations were 10^{-5}M or less. In fact, for the three soil systems studied, long-term K_d values for the above conditions generally remain near values for the system when no organics are present or at values of 30 mL/g or above. A K_d of 30 mL/g represents considerable adsorption. In only a few cases are K_d values less than 30 mL/g. These cases include Ni-EDTA complexes contacting Hanford and Oak Ridge soils, and Ni-EDTA complexes contacting Hanford soil. The key seems to be that these complexes are rather inert to decomposition, and at normal pH values for the given soils, the complex does not adsorb. That is, the degradation kinetics of the complex are slow and the complex doesn't adsorb. Free EDTA adsorbs somewhat onto Savannah River and Oak Ridge soils. The EDTA K_d value drops from 45 to 20 mL/g as the total EDTA concentration in a 30 mL to 1 g soil slurry rises from $2x10^{-7}$ to $1x10^{-6}$M. The Oak Ridge and Savannah River soils also appear to adsorb somewhat Ni and Co -EDTA complexes that formed prior to contacting the soils. During the several month-long tests, significant portions of organic complexes, such as EDTA and citrate, were found to decompose into other (assumed simpler) molecules.

The most critical situation that promotes mobility occurs when an organometallic complex is inert to dissociation and does not adsorb onto soil substrates and the free organic ligand (uncomplexed ligand) does not degrade (biologically). Generally, if the kinetics of complex association and dissociation are rapid, the metal will eventually be stripped away from the ligand and adsorb onto the soil because of competition with other more concentrated metals, or because of ligand decomposition. Finally, adsorption of the complex itself can occur for many organometallic-complex and soil combinations, as discussed in Section 4, especially Zachara et al. (1995 a,b).

Some radionuclides may not form strong complexes with natural organic ligands or man-made chelating agents. Swanson (1981), Czyscinski and Weiss (1981), and Dayal et al. (1984 a,b), among others, show such is the case for Cs and Sr. Other nuclides that may not form strong organic complexes, that are long-lived, and that often are identified as potential human dose problems in performance assessment calculations include ^{237}Np (in its [V] valence state), ^{99}Tc, and ^{129}I.

One article was reviewed on the effects of organics on neptunium adsorption. Lieser and Muhlenweg (1988) studied neptunium (10^{-5} to 10^{-9}M) adsorption in seven sediment-groundwater systems from Gorlebañ, Germany. Under oxidizing conditions (Eh≥350 mV), there was minor Np adsorption; K_d = 1 to 6 mL/g. Addition of 10^{-4} to 10^{-2}M EDTA to the groundwater did not affect Np adsorption. The authors suggest that NpO_2^+ [Np(V)] does not form stable complexes with EDTA. Under reducing conditions, Eh≤130 mV Np adsorption was generally quite high (K_d>1000 mL/g), except for one groundwater/sediment system with 13 mg/L DOC.

Addition of 10^{-4}M EDTA to the seven slurries (under reducing conditions) did not change adsorption properties, but addition of 10^{-2}M EDTA did lower adsorption of Np to K_d values between 10 and 100 mL/g. The authors suggest that Np(IV) (Np^{4+}) ions form stable complexes with EDTA but these complexes do exhibit some adsorption. The near-surface groundwater-sediment test shows Np(IV) colloids, which the authors inferred to be humic acid colloids. Colloidal migration was observed in laboratory column tests. Variable adsorption of Np could be expected under reducing conditions if colloids (organic or inorganic) are present. At normal concentrations found in LLW trench leachates, Lieser and Muhlenweg (1988) found that EDTA appears to have little effect on Np migration under oxidizing or reducing conditions.

Lieser and Bauscher (1988) studied technetium (10^{-6}M) adsorption in two soil-groundwater systems from Germany. Under oxidizing conditions (Eh>310 mV and Eh>140 mV at pH values 4 and 7, respectively) there was no adsorption. After establishing reducing conditions, a K_d value of 10^3 mL/g was obtained (i.e., large adsorption). Similar tests were performed in the presence of 10^{-3}M EDTA. For oxidized tests there was no difference (i.e., Tc again showed no adsorption). For anaerobic tests the presence of EDTA temporarily inhibited adsorption. After 7 days, the K_d values were 2 and 170 mL/g for the two systems but after 60 days the K_d values reached values around 10^3 mL/g, just like the tests without EDTA. Tc (V), an intermediate product during reduction, is known to form strong EDTA complexes. The authors suggest that EDTA slows down the final reduction process to Tc (IV) but does not stop it. That is, the EDTA acts as a kinetic delay factor to Tc (VII) reduction to Tc (IV). No mention is made of analyses to be certain that the groundwaters still contained 10^{-3}M EDTA after 60 days. It is possible that EDTA degraded or that EDTA-Tc complexes slowly adsorb on soils and that the actual observations are more complicated than the authors infer.

It is nearly impossible to succinctly summarize the cited experimental data on the effects of organics on the mobility of contaminants that are present in LLW. The variables and their interactions are many. Migration potential depends on site-specific conditions and to generalize would require the capability to perform thermodynamic speciation calculations on the heterogeneous system (i.e., contaminants, solution and solid adsorbents). Further, kinetic information appears to be required if residence times less than several weeks or months are important. The current state of codes to perform such calculations was discussed in Section 6.

Currently, the only practical approach available would be to study migration at existing disposal sites (site-specific studies) or to limit the range of experimental studies to the hydro-bio-geochemical conditions present at existing or planned disposal sites. The final subsection of this section reviews available field data from existing burial sites pertinent to the effects of organics on contaminant mobility.

7.4 Field Studies

Robertson et al. (1983), Fruchter et al. (1984), and Fruchter et al. (1985) discuss numerous measurements of radionuclide total content and charge form species distributions, total organic content, carboxylic acid content of low molecular weight organic fractions, and radionuclide (γ emitters) associations with high molecular weight organics (humic substances) in well waters, spring waters and Hanford Reservation DOE defense LLW-liquid wastes discharged to a disposal trench. The trench is located 260 m away from the banks of the Columbia River, where the springs are located. The two wells are between the trench and the springs, at distances of 30 and 73 m from the trench.

High volume water samplers with sequential beds of ion exchange and adsorbing layers of Al_2O_3 were used to concentrate the radionuclides from various waters. Total radionuclide contents and fractions present as cationic, anionic, or neutral species were measured.

Four of the more mobile nuclides (determined by relatively small decreases in activity from intermediate wells to the river bank) were ^{60}Co, ^{125}Sb, ^{131}I, and ^{103,106}Ru. Table 7.1 gives some data on radionuclides contents. A large percentage of all four nuclides are present in the groundwaters as anions and or nonionic species. Based on sediment concentrations from the wells and well water activities, in situ K_d values for ^{60}Co, ^{106}Ru and ^{125}Sb are 9, 6, and 4 mL/g. These values, especially the ^{60}Co value, are considered lower than values found in laboratory tests. The authors suggest that dissolved organic matter could be increasing their mobility.

Organic analyses of low molecular weight hydrophilic compounds in the trench waters and groundwaters found numerous mono- di-, oxygenated- and aromatic-carboxylic acids at low μg/L concentrations. The low molecular weight carboxylic acids are normal products excreted by microbes in soils. The total concentration of these acids only constitutes a few percent of the total dissolved organic content of the waters. Thus, the authors suggest high molecular weight organics are likely more important [note: there is a discrepancy in the TOC reported in Fruchter et al. (1984) for water samples for which organics and TOC values are reported in appendices where detailed chemical compositions are found. The values reported in the text are higher by 4 to 30 times. If so, the low molecular weight organics may constitute much more than a few percent of the total organic carbon in the waters.]

In Fruchter et al. (1985), a water sample from the well closest to the disposal crib (well #1) was taken specifically for organic-radionuclide analyses. First, the sample was concentrated 20 times by evaporation. Next, the concentrate was dialyzed three times in deionized water to remove (membrane MW exclusion ~1000) lower molecular weight organics. In addition, steric-exclusion chromatography (using Sephadex G-10, G-25 and G-50 columns) was performed on the concentrated groundwater (undialyzed) and the solution that was outside the dialysis bag (lower than 1000 MW). Using UV and γ-ray analyses of fractions from the Sephadex columns, the authors studied association of radionuclides with organic matter. The "high MW" dialyzed fraction contains ^{125}Sb, ^{103}Ru, ^{60}Co, and ^{137}Cs. No quantitative mass balance discussion is provided to trace the radionuclide concentrations in the various fractions back to the starting groundwater. Radionuclides were definitely present in samples where species should be larger than 1000 MW. The authors recommended further characterization. Radionuclide concentration in all fractions were always below 100 pCi/L, based on the original groundwater (i.e., compensating for the 20-fold concentration).

Jones, Serne and Toste (1988) report that a very small portion (<0.1%) of ^{60}Co present in solidified commercial LLW placed in Hanford sediments has been found to migrate to the bottom of lysimeter drains (55 cm below the waste forms) in less than three years. ^{60}Co and ^{3}H activity were detected in the drainage within one year after water was first collected. The ^{60}Co content in the drainage water averages about 6×10^4 pCi/L but has peaked as high as 1×10^6 pCi/L. The ^{60}Co in the drainage water does not adsorb significantly to any of the cation exchange resins, anion exchange resins, or Al_2O_3, used by Robertson et al. (1983) in the field studies just discussed. Detailed organic analyses of the original liquid waste streams prior to solidification show the presence of chelating agents (e.g., EDTA), their degration products and numerous carboxylic acids. The authors infer that some ^{60}Co-EDTA originally present in the liquid waste stream remains intact through solidification, leaching and migration through the sediment.

Table 7.1. Radionuclide activities observed in field water samples (pCi/L)

	Springs (260 m)	Well 3 (73 m)	Well 1 (30 m)	Trench (0 m)
^{60}Co	43-15	120-170	90-380	0.5 to 4.7×10^5
^{106}Ru	32-130	66-86	110-400	1.4 to 3.5×10^3
^{125}Sb	63-140	22	100-230	280 to 350
^{131}I	32-710	5-7	25-11,000	0.9 to 3.2×10^4

Effects of Organics

A large effort was expended to investigate the fate of radionuclides disposed in trenches at an inactive commercial LLW disposal facility at Maxey Flats, Kentucky. Numerous reports and others cited therein mention organic-radionuclide complexation and discuss potential effects on radionuclide migration. The reports authored or edited by Kirby [e.g., Kirby 1984, 1991) and Kirby and Rickard (1984)], reports by Fowler, et al. (1983), Fowler and Polzer (1988), Francis et al. (1980) and Cleveland and Rees (1981) were reviewed in particular.

Trench waters at Maxey Flats commonly contain total dissolved organic carbon between 100 and 7,000 mg/L. Specific analyses of the trench waters for EDTA and HEDTA have shown that they and suspected degradation products are present at concentrations between 0.1 and 20 mg/L, a small percentage of the total organic carbon content. Cleveland and Rees (1981) speculate that EDTA -Pu complexes may be the cause of rather high solution activities of ^{238}Pu and ^{239,240}Pu; 1,000 to 87,000 pCi/L and 10 to 8,300 pCi/L, respectively. Kirby (1984) also reports that concentrations of EDTA and major chemicals remains fairly constant over the 6-m distance away from the trench. However, radionuclide concentrations tend to decrease over the 6-m distance, often decreasing up to 10 to 20 times the activities in the trenches.

Specific steric exclusion chromatography coupled with GC-MS and radionuclide analyses suggest that several radionuclides do associate with the chelating agents in trench waters. But none of the Maxey Flats studies show radionuclides, excepting ^{3}H, traveling in groundwater considerable distance (e.g., >50 m) and reaching the boundaries of the disposal site. Within Kirby (1984), Polzer et al. discuss a plausible mechanism for the dissociation of Pu-EDTA (or any radionuclide-organic complex) when trench waters interact with native soil. Polzer et al. show how Fe present in pore waters can better compete with trace concentrations of radionuclides to complex the EDTA and release the radionuclides. Again, thermodynamic mass action relationships can be used to show dissociation of radionuclide-complexes should occur. Excepting situations where kinetics hinder dissociation (see previous section and Swanson references), one should expect common soil solution cations (Fe, Mn, Ca, Mg, etc.) to eventually force radionuclide-organic complexes to dissociate.

Several reports describe field observations at the Chalk River nuclear site in northwest Ontario, Canada. We review four articles in particular: Jackson and Inch (1983), Killey et al. (1984) and Robertson et al. (1987, 1989).

Jackson and Inch (1983), Bergeron et al. (1987), Champ et al. (1984), and Robertson et al. (1984, 1986, 1987, 1989) discuss migration of ^{90}Sr from a low-level liquid waste disposal facility through a shallow sandy aquifer. In 25 years ^{90}Sr has moved downgradient (based on ~500 pCi/g isopleths on the aquifer soil) about 200 m, which is calculated to be ~3% of the velocity of the groundwater. Strontium-90 in solution is predominately cationic (98%) as expected. About 80% of the adsorbed ^{90}Sr is ion exchangeable and the remaining 20% appears to be adsorbed to oxide minerals. No organic interactions are identified.

In contrast, Killey et al. (1984) found that ^{60}Co migrating from a nearby liquid waste disposal site through the sandy aquifer has been discharging into a nearby stream (~135 m from the disposal pit) at significant activities (600-1100 pCi/L) for many years.

In situ K_d values for the ^{60}Co are quite variable (0.5 to 130 mL/g), dependent upon sampling location. Prior to 1962, known complexing agents (oxalic and tartaric acids) were routinely disposed in the pit. The pH of the contaminated groundwater is 4.6 to 5.8 (about 10 times more acidic than ambient groundwaters). Numerous characterizations of the ^{60}Co in the groundwater and adsorbed on the sediments have been performed. These include speciation, ultrafiltration, steric exclusion chromatography, electrophoresis, solvent extraction, UV treatment, and high performance liquid chromatography on the water and sediment-water and sediment-reagent leachates.

The adsorbed ^{60}Co appears to be associated mainly with ferromagnesian minerals and the clays biotite and vermiculite. Only about 10% of the adsorbed ^{60}Co is ion exchangeable and only about 5-35% is leached when amorphous iron coatings are dissolved.

Because the groundwater characterization techniques might alter speciation, several techniques were used to investigate the speciation. Charge-form studies and electrophoresis suggest that dissolved ^{60}Co is present as an anion. Steric exclusion chromatography results were not interpretable because the ^{60}Co appeared to adsorb on the Bio-Gel P-2 column. Ultrafiltration through various membranes showed the ^{60}Co species' size to distribute as 15% less than 500 MW, 45% as 500 to 1000 MW and 40% as greater than 1000 MW. Organics of natural origin in the ambient groundwater tended to be found in the 500 to 1000 MW size range. UV irradiation destroys the anionic behavior of the ^{60}Co in contaminated groundwater suggesting association to organic matter. Solvent extraction with water-immiscible solvents did not remove the complex suggesting that if it is organic, that the organic ligand is quite polar and hydrophilic.

An experiment where cationic ^{57}Co was added to contaminated groundwater showed little exchange between ^{57}Co and ^{60}Co. That is, the ^{57}Co remained cationic and the ^{60}Co remained anionic. The assumed ^{60}Co complex is thus not labile (i.e., the complex doesn't dissociate rapidly). Liquid chromatography shows that ^{60}Co elutes in the same aliquots as an organic species with strong UV light absorbing properties. When uncontaminated groundwater is leached through contaminated sediments, only the soluble ^{60}Co present in the original pore waters is leached. Altogether, the data were interpreted by the authors as ^{60}Co likely being complexed to natural organics (e.g., fulvic acids) present in the groundwater at concentrations below 2 mg/L.

Means et al. (1976, 1978) report the first field evidence of radionuclide migration enhanced by organic complexes. In particular, water samples taken from shallow wells about 67 m from Trench 7 at the Oak Ridge, Tennessee, DOE defense waste burial ground showed between 0.7×10^5 and 3×10^5 pCi/L of ^{60}Co. The ^{60}Co was **not** cationic as 90-95% passed through a cation-exchange column. Gel-permeation (steric exclusion) chromatography of concentrated groundwater showed ^{60}Co (~90%) was associated to organics with molecular weight below 700. A small fraction (5 to 10%) was associated with higher molecular weight organics later identified by infrared analyses as humic substances. The <700-MW fraction was further concentrated and treated and finally analyzed by GC-MS. Using EDTA standards, the ^{60}Co was found to be associated with EDTA. The original concentration of EDTA in the well waters with elevated ^{60}Co was about 3.4×10^{-7}M or ~0.1 mg/L. The authors further discuss the fact that EDTA is resistant to decomposition by radiation, slowly biodegrades in the environment, and is commonly used in nuclear facility decontamination.

In situ K_d values for ^{60}Co in the vicinity of Trench 7 were 7 to 65 mL/g at the groundwater pH values of 6.0 to 8.5. Comparable weathered shale in the region adsorbed ^{60}Co in the free-cationic state extensively, and yielded a K_d of 70,000 mL/g. When 1×10^{-5} M EDTA was added to the shale, a K_d of only 2.9 mL/g was found. At the observed EDTA concentration, 3.4×10^{-7}M, we would expect slightly higher values as the field results show.

Means and Alexander (1981) review the biogeochemistry of three common chelating agents - EDTA, NTA and DTPA. Although EDTA is fairly resistant to biodegradation, photolytic degradation has been reported by some as quite rapid. Thus, EDTA is not expected in surface waters where sunlight is active.

In summary, field data that show significant concentrations (nCi/L or greater) of radionuclides migrating in groundwaters substantial distances (>50 m) from disposal units are few. But one must acknowledge that the available database is not large, especially for commercial LLW burial facilities. In two instances (Chalk River and Oak Ridge), ^{60}Co migration beyond 50 m at activities above 1 nCi/L have been reported in this section. In the former instance

(Killey et al. 1984), ^{60}Co appears associated with natural dissolved organics with molecular weights above 500. In the latter case (Means et al. 1978), significantly higher activities of ^{60}Co (10^5 pCi/L) were found in groundwaters 67 m from a trench and the ^{60}Co appeared to be bound to EDTA.

Several other reports are available that discuss the apparent enhancement of radionuclide solubility in waters within trenches that have high organic contents and radionuclide activities. These studies infer or directly show organic-radionuclide complexation, but they address transport through neighboring soils only qualitatively. These qualitative studies show that the radioactivity decreases. The decreases are likely caused by competition by the more abundant cations (Ca, Mg, Fe, Mn, etc.) for the available organic ligands. ^{60}Co-EDTA appears to be a particularity non-reacting complex (chelate) with very slow reaction dissociation kinetics. The reader is referred to a past NRC literature review (Serne et al. 1990 Section 4.0) for details.

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Appendix A

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Appendix B

Stability Constant Data

Tables

B. Stability Constant Data

Table B.1. EDTA stability constant data

The logarithms of the constants for the equilibria indicated are shown, along with ionic strength and temperature and the reference. The references are as follows: 1) Martell and Smith (1974); 2) Martell and Smith (1977); 3) Martell and Smith (1982); 4) Martell and Smith (1989); 5) Sillen and Martell (1964); 6) Sillen and Martell (1971); and 7) Cleveland (1979).

	EDTA (H_4L)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
Al				
$Al^{3+} + L^{4-} \rightleftharpoons AlL^{-}$	16.5	0.1	25	1
	16.3	0.1	25	1
	16.11	0.1	15	5
	16.7	0.1	20	6
	16.5	0.1	25	6
	16.01	0.2	25	6
$Al^{3+} + HL^{3-} \rightleftharpoons AlHL^{0}$	3.4	0.1	25	6
$AlL^{-} + H^{+} \rightleftharpoons AlHL^{0}$	2.5	0.1	25	1
	2.0	0.1	15	5
	2.5	0.1	20	1
	2.77	0.1	20	6
	2.63	0.2	25	6
$AlOHL^{2-} + H^{+} \rightleftharpoons AlL^{-} + H_2O$	5.83	0.1	25	1
	5.89	0.1	20	1
	5.16	0.1	15	5
	5.87	0.2	25	6
$Al^{3+} + L^{4-} + OH^{-} \rightleftharpoons AlOHL^{2-}$	25.04	0.1	20	6
$AlL^{-} + OH^{-} \rightleftharpoons AlOHL^{2-}$	8.0	0.1	25	6
$Al(OH)_2L^{3-} + H^{+} \rightleftharpoons AlOHL^{2-} + H_2O$	10.31	0.2	25	6

Table B.1. (Continued)

	EDTA (H_4L)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
<u>Am(III)</u>				
$Am^{3+} + L^{4-} \rightleftharpoons AmL^{-}$	17.8	0.1	25	1, 4
	16.4	0.5	25	4
	18.2	0.1	25	5
<u>Ca</u>				
$Ca^{2+} + L^{4-} \rightleftharpoons CaL^{2-}$	10.61	0.1	25	1, 3
	10.69	0.1	20	1
	9.68	1.0	25	1, 3, 4
	10.65	0.1	25	4
	10.97	0.1	25	4
	9.68	0.5	25	4
	11.00	0.0	25	3
	12.42	0.0	25	4
	10.7	0.1	25	5
	10.85	0.1	21.7	5
	10.42	0.1	25.3	5
	10.59	0.1	20	5
	10.57	0.1	25	5
	10.59	0.1	30	6
$CaL^{2-} + H^{+} \rightleftharpoons CaHL^{-}$	3.18	0.1	20	1, 4
	3.1	0.1	25	4
	3.51	0.1	20	5, 6
<u>Co(II)</u>				
$Co^{2+} + L^{4-} \rightleftharpoons CoL^{2-}$	16.26	0.1	25	1
	16.45	0.1	25	4
	16.21	0.1	20	5
	15.4	0.1	30	5
	16.31	0.1	20	5, 6
	16.55	0.1	20	6
	16.5	0.1	20	6
	15.71	0.2	25	6
	16.14	0.2	25	6

Table B.1. (Continued)

	EDTA (H_4L)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
$Co^{2+} + HL^{3-} \rightleftharpoons CoHL^-$	9.15	0.1	20	5, 6
	8.66	1.0	NI[a]	5
$CoL^{2-} + H^+ \rightleftharpoons CoHL^-$	3.0	0.1	25	1, 4
	3.0	1.0	25	1, 4
	2.93	0.0	25	1
$CoHL^- + H^+ \rightleftharpoons CoH_2L^-$	1.7	1.0	25	4
<u>Co(III)</u>				
$Co^{3+} + L^{4-} \rightleftharpoons CoL^-$	41.4	0.1	25	1, 4
	40.7	1.0	25	1
	36	0.1	20	5
	40.6	0.2	25	6
$CoL^- + H^+ \rightleftharpoons CoHL^0$	3.0	0.1	20	1, 4
<u>Cm(III)</u>				
$Cm^{3+} + L^{4-} \rightleftharpoons CmL^-$	18.1	0.1	25	1, 4
	16.7	0.5	25	4
	16.9	1.0	25	4
	18.5	0.1	25	5
<u>Cr(III)</u>				
$Cr^{3+} + L^{4-} \rightleftharpoons CrL^-$	23.4	0.1	20	1, 6
$CrL^- + H^+ \rightleftharpoons CrHL^0$	1.95	0.1	20	1
$CrOHL^{2-} + H^+ \rightleftharpoons CrL^- + H_2O$	7.39	0.1	20	1

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[a] NI = Not indicated by author; assumed to be room temperature.

Table B.1. (Continued)

	EDTA (H_4L)			
Equilibria	Constant	Ionic Strength	Temperature	Reference
Cs (no data)				
Fe(II)				
$Fe^{2+} + L^{4-} \rightleftharpoons FeL^{2-}$	14.27	0.1	25	1, 4
	14.32	0.1	20	1
	14.33	0.1	20	5
	14.33	0.1	25	5
	14.2	0.1	20	6
$Fe^{2+} + HL^{3-} \rightleftharpoons FeHL^{-}$	6.86	0.1	20	5, 6
$FeL^{2-} + H^{+} \rightleftharpoons FeHL^{-}$	2.7	0.1	25	1, 4
	2.75	0.1	20	1
	1.31	0.1	20	5
$FeL^{2-} + OH^{-} \rightleftharpoons FeOHL^{3-}$	4.9	0.1	25	5
$FeOHL^{3-} + OH^{-} \rightleftharpoons Fe(OH)_2L^{4-}$	4.1	0.1	25	5
$FeOHL^{3-} + H^{+} \rightleftharpoons FeL^{2-} + H_2O$	9.07	0.1	20	1, 4
$Fe(OH)_2L^{4-} + H^{+} \rightleftharpoons FeOHL^{3-} + H_2O$	9.84	0.1	20	1, 4
Fe(III)				
$Fe^{3+} + L^{4-} \rightleftharpoons FeL^{-}$	25.0	0.1	25	1, 3
	25.1	0.1	20	1
	25.15	1.0	20	1, 6
	25.1	0.1	25	4, 5, 6
	23.9	1.0	25	4
	25.7	1.0	25	5
$Fe^{3+} + HL^{3-} \rightleftharpoons FeHL^{0}$	16.2	0.1	20	5
	15.2	1.0	25	6

Table B.1. (Continued)

	EDTA (H_4L)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
$FeL^- + OH^- \rightleftharpoons FeOHL^{2-}$	7.1	1.0	25	6
	6.5	0.1	20	6
$Fe^{3+} + L^{4-} + OH^- \rightleftharpoons FeOHL^{2-}$	34	0.1	20	6
$FeL^- + H^+ \rightleftharpoons FeHL^0$	1.3	0.1	20	1, 3, 6
	1.3	0.1	25	4
$FeOHL^{2-} + H^+ \rightleftharpoons FeL^- + H_2O$	7.49	0.1	20	1, 3, 5
	7.53	1.0	25	1, 3, 5
	7.37	0.1	25	4, 5
$FeOHL^{2-} + OH^- \rightleftharpoons Fe(OH)_2L^{3-}$	4.53	0.1	25	5
$Fe(OH)_2L^{3-} + OH^- \rightleftharpoons Fe(OH)_3L^{4-}$	1.5	0.1	25	5
$Fe(OH)_2L^{3-} + H^+ \rightleftharpoons FeOHL^{2-} + H_2O$	9.41	0.1	20	1, 3, 5
$(FeOHL)_2{}^{4-} + 2H^+ \rightleftharpoons 2FeL^- + 2H_2O$	12.21	1.0	25	1, 3, 4, 5
$2FeOHL^{2-} \rightleftharpoons (FeOHL)_2{}^{4-}$	2.8	1.0	25	1, 3, 4, 5
<u>Mg</u>				
$Mg^{2+} + L^{4-} \rightleftharpoons MgL^{2-}$	8.83	0.1	25	1, 3
	8.79	0.1	20	1
	9.12	0.0	20	1
	8.85	0.1	25	4
	9.13	0.1	25	4
	8.67	0.5	25	4
	8.69	0.1	20	5, 6
	8.9	0.1	25	5
	8.64	0.1	25.3	5
$Mg^{2+} + HL^{3-} \rightleftharpoons MgHL^-$	2.28	0.1	20	5, 6
$MgL^{2-} + H^+ \rightleftharpoons MgHL^-$	3.85	0.1	20	1, 3, 4
	4.0	0.1	25	4

Table B.1. (Continued)

Equilibria	Constant	Ionic Strength	Temperature	Reference
	EDTA (H_4L)			
Mn(II)				
$Mn^{2+} + L^{4-} \rightleftharpoons MnL^{2-}$	13.81	0.1	25	1, 5
	13.87	0.1	20	1
	13.88	0.1	25	1
	13.98	0.1	21.7	5
	13.58	0.1	20	5
	14.04	0.1	20	5, 6
	12.88	0.1	20	6
	14.5	0.1	20	6
	13.64	0.2	25	6
$Mn^{2+} + HL^{3-} \rightleftharpoons MnHL^{-}$	6.9	0.1	20	5, 6
$MnL^{2-} + H^{+} \rightleftharpoons MnHL^{-}$	3.1	0.1	25	1, 4
	3.1	0.1	20	1
	0.47	0.1	20	5
Nb(V)				
$Nb(OH)_2^{3+} + L^{4-} \rightleftharpoons Nb(OH)_2L^{-}$	40.78	1.0	20	6

Table B.1. (Continued)

	EDTA (H_4L)			
Equilibria	Constant	Ionic Strength	Temperature	Reference
<u>Ni</u>				
$Ni^{2+} + L^{4-} \rightleftharpoons NiL^{2-}$	18.52	0.1	25	1
	18.62	0.1	20	1, 5, 6
	18.4	0.1	25	4
	18.56	0.1	20	5
	17.5	0.1	30	5
	18.36	0.1	20	6
	18.12	0.2	25	6
$Ni^{2+} + HL^{3-} \rightleftharpoons NiHL^{-}$	11.56	0.1	20	5, 6
	11.62	1.0	NI[a]	5
$NiL^{2-} + H^{+} \rightleftharpoons NiHL^{-}$	3.2	0.1	25	1
	3.2	0.1	20	1
	3.1	0.1	25	4
	3.0	1.0	25	4
	5.20	0.1	20	5
$NiHL^{-} + H^{+} \rightleftharpoons NiH_2L^{0}$	0.9	1.0	25	4
$NiL^{2-} + OH^{-} \rightleftharpoons NiOHL^{3-}$	1.8	0.1	20	1
	0.41	1.0	NI	5
$NiOHL^{3-} + H^{+} \rightleftharpoons NiL^{2-} + H_2O$	11.9	0.1	25	4
	12.92	1.0	25	4
<u>Pu(III)</u>				
$Pu^{3+} + L^{4-} \rightleftharpoons PuL^{-}$	18.12	0.1	20	5
	25.75	0.1	20	6
	17.1	0.1	NI	7
<u>Pu(IV)</u>				
$Pu^{4+} + L^{4-} \rightleftharpoons PuL^{0}$	17.66	0.1	20	5
	26.1	?	25	6
	17.1	0.1	NI	7

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[a] NI = Not indicated by author; assumed to be room temperature.

Table B.1. (Continued)

	EDTA (H_4L)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
$Pu^{4+} + H_2L^{2-} \rightleftharpoons PuL^0 + 2H^+$	24.2	0.1	NI[a]	7
<u>Pu(V)</u>				
$PuO_2^+ + L^{4-} \rightleftharpoons PuO_2L^{3-}$	10.2	0.05	20	6
$PuO_2^+ + HL^{3-} \rightleftharpoons PuO_2HL^{2-}$	4.80	0.1	25	1
<u>Pu(VI)</u>				
$PuO_2^{2+} + L^{4-} \rightleftharpoons PuO_2L^{2-}$	16.39	0.1	20	5
	16.02	0.1	20	7
<u>Sr</u>				
$Sr^{2+} + L^{4-} \rightleftharpoons SrL^{2-}$	8.68	0.1	25	1
	8.73	0.1	20	1
	8.80	0.0	20	1
	8.74	0.1	25	4, 5
	8.53	0.1	25.3	5
	8.63	0.1	20	5
	8.42	0.165	22	6
	8.80	0.1	30	6

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[a] NI = Not indicated by author; assumed to be room temperature.

Table B.1. (Continued)

	EDTA (H_4L)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
$Sr^{2+} + HL^{3-} \rightleftharpoons SrHL^{-}$	2.30	0.1	20	5
$SrL^{2-} + H^{+} \rightleftharpoons SrHL^{-}$	3.93	0.1	20	1, 4
Zn				
$Zn^{2+} + L^{4-} \rightleftharpoons ZnL^{2-}$	16.44	0.1	25	1, 3, 5
	14.87	3.0	25	3
	16.5	0.1	25	4, 5
	15.7	1.0	25	4
	18.0	0.0	25	4
	15.7	0.5	25	4
	16.69	0.1	21.7	5
	16.26	0.1	20	5, 6
	15.3	0.1	30	5
	17.5	0.1	20	6
	15.94	0.2	25	6
$Zn^{2+} + HL^{3-} \rightleftharpoons ZnHL^{-}$	9.0	0.1	20	6
$ZnL^{2-} + H^{+} \rightleftharpoons ZnHL^{-}$	3.0	0.1	25	1, 3, 5
	3.10	3.0	25	3, 5
	2.8	1.0	25	5
$ZnHL^{-} + H^{+} \rightleftharpoons ZnH_2L^{0}$	1.2	1.0	25	5
$ZnL^{2-} + OH^{-} \rightleftharpoons ZnOHL^{3-}$	2.1	0.1	25	1, 3
$ZnOHL^{3-} + H^{+} \rightleftharpoons ZnL^{2-} + H_2O$	11.6	0.1	25	5
	11.97	1.0	25	5

Table B.1. (Continued)

Equilibria	EDTA (H_4L) Constant	Ionic Strength	Temperature	Reference
Zr(IV)				
$Zr^{4+} + L^{4-} \rightleftharpoons ZrL^0$	29.4	0.1	25	1, 3
	29.5	0.2	20	1
	27.7	1.0	20	1, 3, 6
	32.8	0.0	25	3
	19.4	0.1	25	5
	29.9	0.1	25	5
	29.5	0.1	20	6
	28.5	1.0	20	6
	29.0	0.23	NI[a]	6
	29.0	1.2	20	6
$ZrL^0 + OH^- \rightleftharpoons ZrOHL^-$	7.9	1.0	20	6
$ZrOHL^- + H^+ \rightleftharpoons ZrL^0 + H_2O$	6.2	0.1	25	1, 3, 5
	6.1	1.0	25	1, 3
$2ZrOHL^- \rightleftharpoons Zr_2(OH)_2L^{2-}$	3.5	0.1	25	1, 3, 5

[a] NI = Not indicated by author; assumed to be room temperature.

Table B.2. DTPA stability constant data

The logarithms of the constants for the equilibria indicated are shown, along with ionic strength and temperature and the reference. The references are as follows: 1) Martell and Smith (1974); 2) Martell and Smith (1977); 3) Martell and Smith (1982); 4) Martell and Smith (1989); 5) Sillen and Martell (1964); and 6) Sillen and Martell (1971).

	DTPA (H_5L)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
Al				
$Al^{3+} + L^{5-} \rightleftharpoons AlL^{2-}$	18.7	0.1	25	1, 6
	18.6	0.1	20	1
	18.4	0.1	20	6
$Al^{3+} + HL^{4-} \rightleftharpoons AlHL^{-}$	4.3	0.1	25	6
$AlL^{2-} + H^{+} \rightleftharpoons AlHL^{-}$	4.3	0.1	25	1
	4.63	0.1	20	1, 6
$AlL^{2-} + OH^{-} \rightleftharpoons AlOHL^{3-}$	6.6	0.1	25	1, 6
Am(III)				
$Am^{3+} + L^{5-} \rightleftharpoons AmL^{2-}$	22.92	0.1	25	1, 6
	23.1	0.1	25	4
$Am^{3+} + HL^{4-} \rightleftharpoons AmHL^{-}$	14.06	0.1	25	4
Ca				
$Ca^{2+} + L^{5-} \rightleftharpoons CaL^{3-}$	10.75	0.1	25	1
	10.83	0.1	20	1
	9.98	0.1	25	5
	10.63	0.1	20	5
	10.89	0.1	20	5
	10.74	0.1	25	5
	10.7	0.1	25	5
	10.6	0.1	25	6

Table B.2. (Continued)

	DTPA (H_5L)			
Equilibria	Constant	Ionic Strength	Temperature	Reference
$Ca^{2+} + HL^{4-} \rightleftharpoons CaHL^{2-}$	6.11	0.1	25	1
	6.11	0.1	20	1
	6.42	0.1	20	1
$CaL^{3-} + Ca^{2+} \rightleftharpoons Ca_2L^-$	1.6	0.1	25	1
	1.98	0.1	20	1, 5
<u>Cm(III)</u>				
$Cm^{3+} + L^{5-} \rightleftharpoons CmL^{2-}$	23.0	0.1	25	1
	23.5	0.1	25	4
	22.99	0.1	25	6
$Cm^{3+} + HL^{4-} \rightleftharpoons CmHL^-$	14.43	0.1	25	4
<u>Co(II)</u>				
$Co^{2+} + L^{5-} \rightleftharpoons CoL^{3-}$	19.15	0.1	25	1
	19.27	0.1	20	1, 6
	19.00	0.1	20	5
	18.4	0.1	25	5
	19.72	0.0	18-22	6
$Co^{2+} + HL^{4-} \rightleftharpoons CoHL^{2-}$	13.43	0.1	20	5
	11.89	0.0	18-22	6
$CoL^{3-} + H^+ \rightleftharpoons CoHL^{2-}$	4.94	0.1	25	1
	4.74	0.1	20	1
$CoHL^{2-} + H^+ \rightleftharpoons CoH_2L^-$	3.22	0.1	25	1
$CoL^{3-} + Co^{2+} \rightleftharpoons Co_2L^-$	3.74	0.1	25	1
	3.51	0.1	20	1, 6
<u>Cr(III)</u> (no data)				
<u>Cs</u> (no data)				

Table B.2. (Continued)

	DTPA (H_5L)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
Fe(II)				
$Fe^{2+} + L^{5-} \rightleftharpoons FeL^{3-}$	16.4	0.1	25	1
	16.5	0.1	20	1
	16.55	0.1	20	5
	15.97	0.1	20	5
	16.5	0.1	25	5
$Fe^{2+} + HL^{4-} \rightleftharpoons FeHL^{2-}$	10.71	0.1	20	5
$FeL^{3-} + H^+ \rightleftharpoons FeHL^{2-}$	5.30	0.1	25	1, 5
	5.35	0.1	20	1
$FeL^{3-} + OH^- \rightleftharpoons FeOHL^{4-}$	5.01	0.1	25	1, 5
$FeOHL^{4-} + OH^- \rightleftharpoons Fe(OH)_2L^{5-}$	4.37	0.1	25	1, 5
$FeL^{3-} + Fe^{2+} \rightleftharpoons Fe_2L^-$	2.98	0.1	25	1, 5
Fe(III)				
$Fe^{3+} + L^{5-} \rightleftharpoons FeL^{2-}$	28.0	0.1	20	1
	28.6	0.1	25	1
	27.50	0.1	20	5
	27.3	0.1	20	6
$Fe^{3+} + HL^{4-} \rightleftharpoons FeHL^-$	19.48	0.1	25	5
$FeL^{2-} + H^+ \rightleftharpoons FeHL^-$	3.56	0.1	25	1, 5
	3.58	0.1	20	1, 6
$FeL^{2-} + OH^- \rightleftharpoons FeOHL^{3-}$	4.12	0.1	25	1, 5
	3.9	0.1	20	1, 6

Table B.2. (Continued)

Equilibria	DTPA (H_5L)			
	Constant	Ionic Strength	Temperature	Reference
Mg				
$Mg^{2+} + L^{5-} \rightleftharpoons MgL^{3-}$	9.34	0.1	25	1
	9.30	0.1	20	1
	9.3	0.1	25	6
$MgL^{3-} + H^+ \rightleftharpoons MgHL^{2-}$	6.85	0.1	25	1
	7.09	0.1	20	1
Mn(II)				
$Mn^{2+} + L^{5-} \rightleftharpoons MnL^{3-}$	15.51	0.1	25	1
	15.60	0.1	20	1, 5
	15.13	0.1	20	5
	15.1	0.1	25	1
	15.5	0.1	25	1
$Mn^{2+} + HL^{4-} \rightleftharpoons MnHL^{2-}$	8.63	0.1	20	1
$MnL^{3-} + H^+ \rightleftharpoons MnHL^{2-}$	4.40	0.1	25	1
	4.64	0.1	20	1
$MnL^{3-} + Mn^{2+} \rightleftharpoons Mn_2L^-$	2.09	0.1	20	1, 5
Nb(V) (no data)				
Ni				
$Ni^{2+} + L^{5-} \rightleftharpoons NiL^{3-}$	20.17	0.1	25	1
	20.32	0.1	20	1, 5
	20.21	0.1	20	5
	20.10	0.1	20	5
	20.2	0.1	25	5
$Ni^{2+} + HL^{4-} \rightleftharpoons NiHL^{2-}$	15.26	0.1	20	5

Table B.2. (Continued)

Equilibria	DTPA (H_5L)			
	Constant	Ionic Strength	Temperature	Reference
$NiL^{3-} + H^+ \rightleftharpoons NiHL^{2-}$	5.67	0.1	25	1
	5.62	0.1	20	1
$NiHL^{2-} + H^+ \rightleftharpoons NiH_2L^-$	3.02	0.1	25	1
$NiL^{3-} + Ni^{2+} \rightleftharpoons Ni_2L^-$	5.59	0.1	25	1
	5.41	0.1	20	1, 5
Pu (no data)				
Sr				
$Sr^{2+} + L^{5-} \rightleftharpoons SrL^{3-}$	9.68	0.1	25	1
	9.77	0.1	20	1
	9.68	0.1	20	5
	9.57	0.165	22	6
$SrL^{3-} + H^+ \rightleftharpoons SrHL^{2-}$	5.4	0.1	25	1
	5.69	0.1	20	1

Table B.2. (Continued)

Equilibria	DTPA (H_5L)			
	Constant	Ionic Strength	Temperature	Reference
Zn				
$Zn^{2+} + L^{5-} \rightleftharpoons ZnL^{3-}$	18.29	0.1	25	1
	18.40	0.1	20	1, 5
	18.3	0.1	25	5
	18.8	0.1	25	5
	18.17	0.1	20	5
	18.75	0.1	20	5
	18.73	0.0	18-22	6
$Zn^{2+} + HL^{4-} \rightleftharpoons ZnHL^{2-}$	13.40	0.1	20	1
$ZnL^{3-} + H^+ \rightleftharpoons ZnHL^{2-}$	5.60	0.1	25	1
	5.43	0.1	20	1
$ZnHL^{2-} + H^+ \rightleftharpoons ZnH_2L^-$	3.06	0.1	25	1
$ZnL^{3-} + Zn^{2+} \rightleftharpoons Zn_2L^-$	4.48	0.1	25	1
	4.36	0.1	20	1, 5
Zr(IV)				
$Zr^{4+} + L^{5-} \rightleftharpoons ZrL^-$	35.8	0.23	20	1
	36.9	1.0	20	1, 6
	35.81	0.23	NI[a]	6
	33.96	0.39	20	6
$ZrL^- + OH^- \rightleftharpoons ZrOHL^{2-}$	8.1	1.0	20	1, 6
$Zr^{4+} + H_5L \rightleftharpoons ZrL^- + 5H^+$	5.67	1.0	NI	6
	3.63	2.0	NI	6

[a] NI = Not indicated by author; assumed to be room temperature.

Table B.3. Picolinic acid stability constant data

The logarithms of the constants for the equilibria indicated are shown, along with ionic strength and temperature and the reference. The references are as follows: 1) Martell and Smith (1974); 2) Martell and Smith (1977); 3) Martell and Smith (1982); 4) Martell and Smith (1989); 5) Sillen and Martell (1964); and 6) Sillen and Martell (1971).

	Picolinic Acid (HL)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
Al (no data)				
Am(III) (no data)				
Ca				
$Ca^{2+} + L^- \rightleftharpoons CaL^+$	1.81	0.1	20	1, 5
	2.22	0.0	25	1, 4, 5
	1.80	0.1	25	4
	2.5	0.1	25	5
$Ca^{2+} + 2L^- \rightleftharpoons CaL_2^0$	3.79	0.0	25	1, 4, 5
Cm(III) (no data)				
Co				
$Co^{2+} + L^- \rightleftharpoons CoL^+$	5.74	0.1	20	1, 5
	4.69	0.0	25	5
	6.0	0.02	25	5
$Co^{2+} + 2L^- \rightleftharpoons CoL_2^0$	10.44	0.1	20	1, 5
	10.53	0.0	25	1
	10.8	0.02	25	5
$Co^{2+} + 3L^- \rightleftharpoons CoL_3^-$	14.09	0.1	20	1, 5
Cr(III)				
$Cr^{3+} + 2L^- \rightleftharpoons CrL_2^+$	10.22	0.5	25	6

Table B.3. (Continued)

	Picolinic Acid (HL)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
Cs (no data)				
Fe(II)				
$Fe^{2+} + L^- \rightleftharpoons FeL^+$	4.90	0.1	20	1, 5
$Fe^{2+} + 2L^- \rightleftharpoons FeL_2^0$	9.00	0.1	20	1, 5
$Fe^{2+} + 3L^- \rightleftharpoons FeL_3^-$	12.30	0.1	20	1, 5
	11.30	0.2	25	6
Fe(III)				
$Fe^{3+} + 2L^- \rightleftharpoons FeL_2^+$	12.80	0.1	20	1
	12.80	0.1	25	5
	12.88	0.1	20	6
$FeOHL_2^0 + H^+ \rightleftharpoons FeL_2^+ + H_2O$	2.96	0.1	20	1
$2FeOHL^+ \rightleftharpoons Fe_2(OH)_2L_2^{2+}$	3.06	0.1	20	1
$Fe^{3+} + 2L^- + OH^- \rightleftharpoons FeOHL_2^0$	23.84	0.1	25	5
	23.92	0.1	20	6
$2Fe^{3+} + 4L^- + 2OH^- \rightleftharpoons Fe_2(OH)_2L_4^0$	50.76	0.1	25	5
	50.72	0.1	20	6
$FeOHL_2^0 + H^+ \rightleftharpoons FeL_2^+ + H_2O$	2.96	0.1	25	5
$2FeOHL_2^0 \rightleftharpoons Fe_2(OH)_2L_4^0$	3.06	0.1	25	5
Mg				
$Mg^{2+} + L^- \rightleftharpoons MgL^+$	2.20	0.1	20	1, 5
	2.58	0.0	25	1, 5
	2.21	0.1	25	4
	2.58	0.0	25	4
	2.5	0.1	25	5

Table B.3. (Continued)

	Picolinic Acid (HL)			
Equilibria	Constant	Ionic Strength	Temperature	Reference
$Mg^{2+} + 2L^- \rightleftharpoons MgL_2^0$	3.95	0.0	25	1, 4, 5
Mn(II)				
$Mn^{2+} + L^- \rightleftharpoons MnL^+$	3.57	0.1	20	1, 5
	3.88	0.0	25	1, 5
	3.6	NI[a]	22	5
$Mn^{2+} + 2L^- \rightleftharpoons MnL_2^0$	6.32	0.1	20	1, 5
	7.08	0.0	25	1, 5
	4.6	NI	22	5
$Mn^{2+} + 3L^- \rightleftharpoons MnL_3^-$	8.1	0.1	20	1, 5
Nb(V) (no data)				
Ni				
$Ni^{2+} + L^- \rightleftharpoons NiL^+$	6.80	0.1	20	1, 5
	7.63	0.0	25	1, 3, 5
	6.72	0.1	25	3
	6.6	1.0	25	3
	6.4	0.1	25	5
	6.68	0.001	25	5
	5.9	0.02	25	5
$Ni^{2+} + 2L^- \rightleftharpoons NiL_2^0$	12.58	0.1	20	1, 5
	12.45	0.0	25	1, 3, 5
	12.44	0.1	25	3
	12.2	1.0	25	3
	11.9	0.1	25	5
	12.66	0.001	25	5
	11.3	0.02	25	5
$Ni^{2+} + 3L^- \rightleftharpoons NiL_3^-$	17.22	0.1	20	1, 5
	17.07	0.1	25	3
	16.7	1.0	25	3
	17.78	0.001	25	5

[a] NI = Ionic strength not indicated by author.

Table B.3. (Continued)

	Picolinic Acid (HL)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
Pu(VI)				
$PuO_2^{2+} + L^- \rightleftharpoons PuO_2L^+$	4.58	0.1	25	1
$PuO_2L^+ + H^+ \rightleftharpoons PuO_2HL^{2+}$	5.22	0.1	25	1
Sr				
$Sr^{2+} + L^- \rightleftharpoons SrL^+$	1.70	0.1	20	1, 5
	1.79	0.0	25	1, 4, 6
	1.69	0.1	25	4
	2.4	0.1	25	5
$Sr^{2+} + 2L^- \rightleftharpoons SrL_2^0$	2.98	0.0	25	1, 4, 6
Zn				
$Zn^{2+} + L^- \rightleftharpoons ZnL^+$	5.30	0.1	20	1, 5
	5.75	0.0	25	1, 3, 5
	5.25	0.1	25	3
	5.1	1.0	25	3
	5.12	0.1	25	5
$Zn^{2+} + 2L^- \rightleftharpoons ZnL_2^0$	9.62	0.1	20	1, 5
	10.01	0.0	25	1, 3, 5
	9.52	0.1	25	3
	9.3	1.0	25	3
$Zn^{2+} + 3L^- \rightleftharpoons ZnL_3^-$	12.92	0.1	20	1, 5
	12.75	0.1	25	3
	12.5	1.0	25	3
$ZnL^+ + L^- \rightleftharpoons ZnL_2^0$	6.08	0.1	25	6
Zr(IV) (no data)				

Table B.4. Oxalic acid stability constant data

The logarithms of the constants for the equilibria indicated are shown, along with ionic strength and temperature and the reference. The references are as follows: 1) Martell and Smith (1974); 2) Martell and Smith (1977); 3) Martell and Smith (1982); 4) Martell and Smith (1989); 5) Sillen and Martell (1964); 6) Sillen and Martell (1971); and 8) Konecny (1967).

	Oxalic Acid (H_2L)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
<u>Al</u>				
$Al^{3+} + L^{2-} \rightleftharpoons AlL^+$	6.1	1.0	25	2, 4
	5.97	0.5	25	4
$Al^{3+} + 2L^{2-} \rightleftharpoons AlL_2^-$	11.09	1.0	25	2, 4
	10.93	0.5	25	4
	13	0.0	18	5
$AlL^+ + L^{2-} \rightleftharpoons AlL_2^-$	5.45	1.0	32	5
$Al^{3+} + 3L^{2-} \rightleftharpoons AlL_3^{3-}$	15.12	1.0	25	2, 4
	15.97	0.5	25	4
	14.88	0.5	25	4
	16.3	0.0	18	5
	15.60	0.1	20	6
$AlL_2^- + L^{2-} \rightleftharpoons AlL_3^{3-}$	3.69	1.0	32	5
$AlL^+ + H^+ \rightleftharpoons AlHL^{2+}$	0.0	0.5	25	4
$3Al^{3+} + 3L^{2-} + 3H_2O \rightleftharpoons Al_3(OH)_3L_3^0 + 3H^+$	9.34	0.5	25	4
$2Al^{3+} + 4L^{2-} + 2H_2O \rightleftharpoons Al_2(OH)_2L_4^{4-} + 2H^+$	13.54	0.5	25	4
<u>Am(III)</u>				
$Am^{3+} + L^{2-} \rightleftharpoons AmL^+$	5.25	0.1	25	2
	4.63	1.0	25	2, 6
	4.82	0.5	25	2, 6
	5.99	0.2	20-25	6
	6.15	0.1	25	6

Table B.4. (Continued)

	Oxalic Acid (H_2L)			
Equilibria	Constant	Ionic Strength	Temperature	Reference
$Am^{3+} + 2L^{2-} \rightleftharpoons AmL_2^-$	8.85	0.1	25	2
	8.35	1.0	25	2, 6
	8.60	0.5	25	2, 6
	10.15	0.2	20-25	6
	10.54	0.1	25	6
$Am^{3+} + 3L^{2-} \rightleftharpoons AmL_3^{3-}$	11.15	1.0	25	2, 6
<u>Ca</u>				
$Ca^{2+} + L^{2-} \rightleftharpoons CaL^0$	1.66	1.0	25	2
	3.00	0.0	25	2
	2.46	0.1	37	4
	2.36	0.15	37	4
	3.19	0.0	25	4
	2.22	0.5	37	5
	3.27	0.0	37	5
	3.0	0.1	25	5
	3.00	0.0	18	5
$Ca^{2+} + 2L^{2-} \rightleftharpoons CaL_2^{2-}$	2.69	1.0	25	2, 6
$Ca^{2+} + HL^- \rightleftharpoons CaHL^+$	1.38	0.1	25	2
	1.84	0.0	25	2
$Ca^{2+} + 2HL^- \rightleftharpoons Ca(HL)_2^0$	1.8	0.1	25	2
<u>Cm(III)</u>				
$Cm^{3+} + L^{2-} \rightleftharpoons CmL^+$	5.25	0.1	25	2
	5.96	0.2	20-25	6
	4.80	0.5	25	6
$Cm^{3+} + 2L^{2-} \rightleftharpoons CmL_2^-$	8.85	0.1	25	2
	10.15	0.2	20-25	6
	8.61	0.5	25	6
$Cm^{3+} + 3L^{2-} \rightleftharpoons CmL_3^{3-}$	11.15	1.0	25	2, 6

Table B.4. (Continued)

	Oxalic Acid (H_2L)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
Co(II)				
$Co^{2+} + L^{2-} \rightleftharpoons CoL^0$	3.84	0.1	25	2
	3.25	1.0	25	2
	4.72	0.0	25	2, 3
	3.85	0.1	25	3
	3.29	1.0	25	3
	4.7	0.1	25	5
	4.7	0.0	25	5
	4.49	NI[a]	NI[b]	5
	4.49	NI[a]	NI[b]	5
	3.72	0.16	25	5
	4.79	0.0	25	5
	4.64	0.0	25	6
	4.69	0.0	25	6
	4.75	0.0	25	6
	3.87	0.1	20	6
$Co^{2+} + 2L^{2-} \rightleftharpoons CoL_2^{2-}$	5.60	1.0	25	2
	7.0	0.0	25	2
	5.9	1.0	25	3
	6.9	0.0	25	3
	6.7	0.0	25	5
	6.64	NI[a]	NI[b]	5
	6.66	NI[a]	NI[b]	5
	6.03	0.16	25	5
	6.79	0.1	20	6
	7.15	0.0	25	6
	6.91	0.0	25	6
$Co^{2+} + 3L^{2-} \rightleftharpoons CoL_3^{4-}$	8.13	NI[a]	NI[b]	5
	9.7	NI[a]	18	5
$Co^{2+} + HL^{-} \rightleftharpoons CoHL^{+}$	1.61	0.1	25	2, 3
	1.61	NI[a]	NI[b]	5
	1.66	0.16	25	5

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[a] NI = Ionic strength not indicated by author.

[b] NI = Not indicated by author; assumed to be room temperature.

Table B.4. (Continued)

Equilibria	Oxalic Acid (H_2L)			
	Constant	Ionic Strength	Temperature	Reference
$Co^{2+} + 2HL^- \rightleftharpoons Co(HL)_2^0$	2.89	0.1	25	2, 3
	2.89	NI[a]	NI[b]	5
	2.91	0.16	25	5
<u>Cr(III)</u>				
$Cr^{3+} + L^{2-} \rightleftharpoons CrL^+$	5.34	0.1	25	6
$CrL^+ + L^{2-} \rightleftharpoons CrL_2^-$	5.17	0.1	25	6
$CrL_2^- + L^{2-} \rightleftharpoons CrL_3^{3-}$	5.47	1.0	32	5
	4.93	0.1	25	6
$CrOHL_2^{2-} + H^+ \rightleftharpoons CrL_2^- + H_2O$	7.34	0.1	4	3
$Cr(OH)_2L_2^{3-} + H^+ \rightleftharpoons CrOHL_2^{2-} + H_2O$	9.55	0.1	4	3
<u>Cs</u> (no data)				
<u>Fe(II)</u>				
$Fe^{2+} + L^{2-} \rightleftharpoons FeL^0$	3.05	1.0	25	2, 6
$Fe^{2+} + 2L^{2-} \rightleftharpoons FeL_2^{2-}$	5.15	1.0	25	2, 6
	4.52	0.5	25	5
$Fe^{2+} + 3L^{2-} \rightleftharpoons FeL_3^{4-}$	5.22	0.5	25	5
<u>Fe(III)</u>				
$Fe^{3+} + L^{2-} \rightleftharpoons FeL^+$	7.53	0.5	25	2, 6
	7.59	1.0	25	2, 6
	7.74	3.0	25	2, 6
	7.58	1.0	25	3
	7.54	0.5	NI[b]	6
	7.39	0.5	25	6

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[a] NI = Ionic strength not indicated by author.
[b] NI = Not indicated by author; assumed to be room temperature.

Table B.4. (Continued)

Equilibria	Oxalic Acid (H_2L)			
	Constant	**Ionic Strength**	**Temperature**	**Reference**
$Fe^{3+} + 2L^{2-} \rightleftharpoons FeL_2^-$	13.64	0.5	25	2, 6
	13.81	1.0	25	3
	14.59	0.5	NI[a]	6
$Fe^{3+} + 3L^{2-} \rightleftharpoons FeL_3^{3-}$	18.49	0.5	25	2, 6
	18.6	1.0	25	3
	17.96	0.5	25	5
	20.0	0.5	NI	6
	20.46	0.1	20	6
$Fe^{3+} + HL^- \rightleftharpoons FeHL^{2+}$	4.35	0.5	25	2, 6
	4.27	0.0	25	6
$FeL_2^- + L^{2-} \rightleftharpoons FeL_3^{3-}$	4.77	1.0	32	5
$FeOH^{2+} + HL^- \rightleftharpoons FeL^+ + H_2O$	6.83	1.0	25	6
<u>Mg</u>				
$Mg^{2+} + L^{2-} \rightleftharpoons MgL^0$	2.76	0.1	20	2, 3, 5
	3.43	0.0	25	2
	2.67	0.15	37	3
	3.42	0.0	18	3, 5
	2.52	0.5	37	3
	3.59	0.0	37	3
	2.55	0.2	25	5
	2.65	0.7	NI	5
	2.28	0.62	37	5
	3.41	0.0	37	5
	2.61	0.2	23	6
	2.39	0.1	20	6
$Mg^{2+} + 2L^{2-} \rightleftharpoons MgL_2^{2-}$	4.24	0.1	25	2
	4.38	0.0	25	5
	4.24	0.09	25	6

[a] NI = Not indicated by author; assumed to be room temperature.

Table B.4. (Continued)

Equilibria	Oxalic Acid (H_2L) Constant	Ionic Strength	Temperature	Reference
Mn(II)				
$Mn^{2+} + L^{2-} \rightleftharpoons MnL^0$	3.2	0.1	25	2
	3.95	0.0	25	2
	3.9	0.1	25	5
	3.89	0.0	18	5
	3.82	0.0	25	5
	3.92	0.0	15	5
	3.97	0.0	25	5
	3.96	0.0	25	5, 6
	3.75	0.1	20	6
$Mn^{2+} + 2L^{2-} \rightleftharpoons MnL_2^{2-}$	4.4	0.1	25	2
	5.80	0.1	25	5
	5.25	0.0	25	5
Nb(V)				
$Nb(OH)_4^+ + H_2L \rightleftharpoons Nb(OH)_4HL^0 + H^+$	3.55	6.0	20	6
$Nb(OH)_4^+ + 2H_2L \rightleftharpoons Nb(OH)_2L_2^- + 2H^+ + 2H_2O$	5.13	6.0	20	6
$Nb(OH)_4^+ + 2HL^- \rightleftharpoons Nb(OH)_2L_2^- + 2H_2O$	12.11	0.5	25	6
$Nb(OH)_4^+ + 2HL^- + L^{2-} \rightleftharpoons Nb(OH)_2L_3^{3-} + 2H_2O$	17.15	0.5	25	6
$Nb(OH)_4^+ + L^{2-} \rightleftharpoons Nb(OH)_4L^-$	3.08	3.5	20	8

Table B.4. (Continued)

	Oxalic Acid (H_2L)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
Ni				
$Ni^{2+} + L^{2-} \rightleftharpoons NiL^0$	5.16	0.0	25	2, 3, 5, 6
	3.7	1.0	25	3
	5.3	0.1	25	5
$Ni^{2+} + 2L^{2-} \rightleftharpoons NiL_2^{2-}$	6.6	1.0	25	3
	6.51	0.0	25	5
	7.64	0.1	25	5
	7.64	2.0	25	6
	7.88	0.1	20	6
Pu(III)				
$Pu^{3+} + L^{2-} \rightleftharpoons PuL^+$	9.31	NI[a]	NI[b]	5
$Pu^{3+} + 2L^{2-} \rightleftharpoons PuL_2^-$	18.70	NI[a]	NI[b]	5
$Pu^{3+} + 3L^{2-} \rightleftharpoons PuL_3^{3-}$	28.62	NI[a]	NI[b]	5
Pu(IV)				
$Pu^{4+} + L^{2-} \rightleftharpoons PuL^{2+}$	8.30	4.0	25	4
	8.74	1.0	20	5
$Pu^{4+} + 2L^{2-} \rightleftharpoons PuL_2^0$	14.9	4.0	25	4
	16.91	1.0	20	5
$Pu^{4+} + 3L^{2-} \rightleftharpoons PuL_3^{2-}$	23.39	1.0	20	5
$Pu^{4+} + 4L^{2-} \rightleftharpoons PuL_4^{4-}$	27.50	1.0	20	5
Pu(VI)				
$PuO_2^{2+} + L^{2-} \rightleftharpoons PuO_2L^0$	9.4	1.0	20	2
	6.66	NI[a]	20	6

[a] NI = Ionic strength not indicated by author.
[b] NI = Not indicated by author; assumed to be room temperature.

Table B.4. (Continued)

	Oxalic Acid (H_2L)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
$PuO_2^{2+} + 2L^{2-} \rightleftharpoons PuO_2L_2^{2-}$	11.4	NI[a]	20	6
<u>Sr</u>				
$Sr^{2+} + L^{2-} \rightleftharpoons SrL^0$	1.25	1.0	25	2, 6
	2.54	0.0	25	2, 5
$Sr^{2+} + 2L^{2-} \rightleftharpoons SrL_2^{2-}$	1.90	1.0	25	2, 6
$Sr^{2+} + HL^- \rightleftharpoons SrHL^+$	1.11	0.1	25	2
$Sr^{2+} + 2HL^- \rightleftharpoons Sr(HL)_2^0$	1.7	0.1	25	2
<u>Zn</u>				
$Zn^{2+} + L^{2-} \rightleftharpoons ZnL^0$	3.88	0.16	25	2
	3.43	1.0	25	2
	4.87	0.0	25	2
	4.9	0.1	25	2
	3.88	0.1	25	5
	4.68	0.0	25	5
	5.00	0.0	25	5
	4.89	0.0	18	5
	4.85	0.0	25	6
	3.44	1.0	25	6
$Zn^{2+} + 2L^{2-} \rightleftharpoons ZnL_2^{2-}$	6.40	0.16	25	2
	6.16	1.0	25	2
	7.65	0.0	25	2
	7.11	0.1	25	2
	6.40	0.1	25	5
	7.60	0.1	25	5
	7.04	0.0	25	5
	7.36	0.0	25	5
	7.59	0.1	20	6
	7.55	0.0	20	6
	6.48	1.0	25	6

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[a] NI = Ionic strength not indicated by author.

Table B.4. (Continued)

Equilibria	Oxalic Acid (H_2L) Constant	Ionic Strength	Temperature	Reference
$Zn^{2+} + HL^- \rightleftharpoons ZnHL^+$	1.72	0.1	25	2, 5
$Zn^{2+} + 2HL^- \rightleftharpoons Zn(HL)_2^0$	3.12	0.1	25	2, 5
<u>Zr(IV)</u>				
$Zr^{4+} + L^{2-} \rightleftharpoons ZrL^{2+}$	9.80	NI[a]	NI[b]	5
	11.2	1.0	20	6
	10.26	1.0	18-20	6
$Zr^{4+} + 2L^{2-} \rightleftharpoons ZrL_2^0$	17.14	NI[a]	NI[b]	5
	20.3	1.0	20	6
$Zr^{4+} + 3L^{2-} \rightleftharpoons ZrL_3^{2-}$	20.88	NI[a]	NI[b]	5
$Zr^{4+} + 4L^{2-} \rightleftharpoons ZrL_4^{4-}$	21.17	NI[a]	NI[b]	5
$Zr^{4+} + H_2L \rightleftharpoons ZrL^{2+} + 2H^+$	5.50	2.0	NI[b]	6
$Zr^{4+} + 2H_2L \rightleftharpoons ZrL_2^{2+} + 4H^+$	9.70	2.0	NI[b]	6

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[a] NI = Ionic strength not indicated by author.
[b] NI = Not indicated by author; assumed to be room temperature.

Table B.5. Citric acid stability constant data

The logarithms of the constants for the equilibria indicated are shown, along with ionic strength and temperature and the reference. The references are as follows: 1) Martell and Smith (1974); 2) Martell and Smith (1977); 3) Martell and Smith (1982); 4) Martell and Smith (1989); 5) Sillen and Martell (1964); 6) Sillen and Martell (1971); 7) Cleveland (1979); and 8) Konecny (1967).

	Citric Acid (H_4L)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
<u>Al</u>				
$Al^{3+} + HL^{3-} \rightleftharpoons AlHL^0$	7.98	0.1	25	4
	7.87	0.15	37	4
	7.14	0.5	25	4
$Al^{3+} + 2HL^{3-} \rightleftharpoons Al(HL)_2{}^{3-}$	11.7	0.5	25	4
$Al^{3+} + H_2L^{2-} \rightleftharpoons AlH_2L^+$	5.21	0.1	25	4
	4.55	0.15	37	4
	4.17	0.5	25	4
$Al^{3+} + H_4L \rightleftharpoons AlHL^0 + 3H^+$	-4.7	0.25	33	6
$AlL^- + H^+ \rightleftharpoons AlHL^0$	3.31	0.1	25	4
	3.23	0.15	37	4
	3.5	0.25	33	6
$AlL^- + HL^{3-} \rightleftharpoons AlLHL^{4-}$	4.2	0.15	37	4
$AlOHL^{2-} + H^+ \rightleftharpoons AlL^- + H_2O$	6.8	0.25	33	6
<u>Am(III)</u>				
$Am^{3+} + HL^{3-} \rightleftharpoons AmHL^0$	7.74	0.1	25	2
	6.96	1.0	25	2
$Am^{3+} + 2HL^{3-} \rightleftharpoons Am(HL)_2{}^{3-}$	10.9	0.1	25	2
	10.3	1.0	25	2
$Am^{3+} + H_2L^{2-} \rightleftharpoons AmH_2L^+$	4.53	1.0	25	2
$AmL^- + H^+ \rightleftharpoons AmHL^0$	5.61	1.0	25	2
$AmHL^0 + H_2L^{2-} \rightleftharpoons Am(HL)H_2L^{2-}$	2.5	0.1	25	2

Table B.5. (Continued)

	Citric Acid (H_4L)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
<u>Ca</u>				
$Ca^{2+} + HL^{3-} \rightleftharpoons CaHL^{-}$	3.50	0.1	25	2
	3.18	0.16	25	2, 5
	4.68	0.0	25	2, 5
	3.55	0.1	20	2, 6
	3.45	0.1	25	4
	3.30	0.15	37	4
	3.64	0.1	25	4
	3.49	0.15	37	4
	4.85	0.0	25	4, 5
	4.90	0.0	25	5
	4.84	0.0	25	5
	3.17	0.15	25	5
	3.22	0.16	22-23	5
	3.20	0.15	28	5
	3.4	0.25	33	6
$Ca^{2+} + 2HL^{3-} \rightleftharpoons Ca(HL)_2^{4-}$	8.02	0.0	25	5
$Ca^{2+} + H_2L^{2-} \rightleftharpoons CaH_2L^0$	2.10	0.1	20	2, 6
	3.09	0.0	25	2, 5
	2.13	0.1	25	4
	1.89	0.15	37	4
	2.93	0.0	25	4
	3.05	0.0	25	5
	3.29	0.0	25	5
$Ca^{2+} + 2H_2L^{2-} \rightleftharpoons Ca(H_2L)_2^{2-}$	6.79	0.0	25	5
$Ca^{2+} + H_3L^{-} \rightleftharpoons CaH_3L^{+}$	1.05	0.1	20	2, 6
	1.10	0.0	25	2, 5
	1.0	0.1	25	4
	1.15	0.0	25	5

Table B.5. (Continued)

	Citric Acid (H_4L)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
Cm(III)				
$Cm^{3+} + HL^{3-} \rightleftharpoons CmHL^0$	7.74	0.1	25	2
$Cm^{3+} + 2HL^{3-} \rightleftharpoons Cm(HL)_2{}^{3-}$	10.9	0.1	25	2
$CmHL^0 + H_2L^{2-} \rightleftharpoons Cm(HL)H_2L^{2-}$	2.5	0.1	25	2
Co(II)				
$Co^{2+} + L^{4-} \rightleftharpoons CoL^{2-}$	7.08	2.0	25	5
$Co^{2+} + HL^{3-} \rightleftharpoons CoHL^-$	5.00	0.1	20	2, 3
	4.83	0.16	25	2
	4.89	0.1	25	3
	4.83	0.06	25	5
	4.16	0.16	25	5
	4.51	0.2	NI[a]	5
	4.83	0.15	25	5
	4.41	2.0	25	5
	4.7	0.16	25	5
	5.00	0.1	20	6
$Co^{2+} + H_2L^{2-} \rightleftharpoons CoH_2L^0$	3.02	0.1	20	2, 3
	3.19	0.16	25	2
	3.19	0.1	25	3
	3.19	0.06	25	5
	3.19	0.15	25	5
	3.02	0.1	20	6
$Co^{2+} + H_3L^- \rightleftharpoons CoH_3L^+$	1.25	0.1	20	2, 3, 6
$Co^{2+} + H_4L \rightleftharpoons CoH_2L^0 + 2H^+$	-4.1	0.25	33	6
$CoHL^- + H^+ \rightleftharpoons CoH_2L^0$	4.2	0.25	33	6
$CoL^{2-} + H^+ \rightleftharpoons CoHL^-$	8.0	0.25	33	6

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[a] NI = Not indicated by author; assumed to be room temperature.

Table B.5. (Continued)

Equilibria	Constant	Ionic Strength	Temperature	Reference
	Citric Acid (H_4L)			
Cr(III)				
$Cr^{3+} + H_4L \rightleftharpoons CrHL^0 + 3H^+$	-5.55	0.1	22-25	6
$CrL^- + H^+ \rightleftharpoons CrHL^0$	5.3	0.1	22-25	6
$CrOHL^{2-} + H^+ \rightleftharpoons CrL^- + H_2O$	6.5	0.1	22-25	6
Cs				
$Cs^+ + HL^{3-} \rightleftharpoons CsHL^{2-}$	0.32	0.1	25	2, 4, 6
	0.47	0.15	37	4
Fe(II)				
$Fe^{2+} + HL^{3-} \rightleftharpoons FeHL^-$	4.4	0.1	20	2, 6
	4.8	0.1	25	3, 4
	4.56	0.15	37	3, 4
	4.4	0.1	20	3, 4
	4.70	0.15	37	4
	3.08	1.0	25	5
$Fe^{2+} + H_2L^{2-} \rightleftharpoons FeH_2L^0$	2.65	0.1	20	2
	2.98	0.1	25	3
	3.10	0.15	37	3, 4
	2.65	0.1	20	3, 4, 6
	2.9	0.1	25	4
	2.6	3.0	25	4
	2.12	1.0	25	5
$Fe^{2+} + H_3L^- \rightleftharpoons FeH_3L^+$	1.1	0.15	37	4
$FeHL^- + H_2L^{2-} \rightleftharpoons Fe(HL)H_2L^{3-}$	1.73	0.15	37	3
$Fe_2(OH)_2(HL)_2{}^{4-} + 2H^+ \rightleftharpoons 2Fe^{2+} + 2HL^{3-} + 2H_2O$	5.4	0.15	37	3
$2Fe^{2+} + 2HL^{3-} \rightleftharpoons Fe_2L_2{}^{4-} + 2H^+$	-5.4	0.15	37	4

Table B.5. (Continued)

Equilibria	Citric Acid (H_4L)			
	Constant	Ionic Strength	Temperature	Reference
$FeL^{2-} + H_2O \rightleftharpoons Fe(OH)L^{3-} + H^+$	-0.5	1.0	25	5
Fe(III)				
$Fe^{3+} + L^{4-} \rightleftharpoons FeL^-$	25	0.1	24	5
$Fe^{3+} + HL^{3-} \rightleftharpoons FeHL^0$	11.50	0.1	20	2
	11.2	0.1	25	3
	11.4	0.1	20	3, 6
	11.85	1.0	25	5
	11.7	0.1	24	5
	12.5	0.1	NI[a]	5
	11.56	0.1	20	6
$Fe^{3+} + HL^{3-} \rightleftharpoons FeL^- + H^+$	9.46	0.1	24	5
$Fe_2L_2^{2-} + 2H^+ \rightleftharpoons 2FeL^- + 2H^+$	1.6	0.1	20	2
$Fe^{3+} + H_2L^{2-} \rightleftharpoons FeH_2L^+$	6.7	0.1	25	3
	6.3	1.0	25	5
	6.31	1.0	NI	5
$Fe^{3+} + HL^{3-} + H_2O \rightleftharpoons Fe(OH)HL^- + H^+$	8.5	0.1	25	3
$2Fe^{3+} + 2HL^{3-} + 2H_2O \rightleftharpoons Fe_2(OH)_2(HL)_2^{2-} + 2H^+$	21.2	0.1	20	3, 6
$FeHL^0 + 3H^+ \rightleftharpoons Fe^{3+} + H_4L$	1.82	0.1	24	5
$FeL^- + H^+ \rightleftharpoons FeHL^0$	1.92	0.1	24	5

[a] NI = Not indicated by author; assumed to be room temperature.

Table B.5. (Continued)

Equilibria	Citric Acid (H_4L)			
	Constant	Ionic Strength	Temperature	Reference
Mg				
$Mg^{2+} + HL^{3-} \rightleftharpoons MgHL^-$	3.37	0.1	25	2
	3.25	0.16	25	2
	3.87	0.1	25	2
	3.40	0.1	20	2, 6
	3.45	0.1	25	4
	3.34	0.15	37	4
	4.84	0.0	25	4
	3.66	0.1	25	4
	3.54	0.15	37	4
	3.2	0.16	25	5
	3.29	0.15	NI[a]	5
	3.29	0.09	25	5
	3.16	0.1	25	6
	3.96	0.0	25	6
	3.6	0.1	32	6
	3.73	0.1	25	2, 6
$Mg^{2+} + H_2L^{2-} \rightleftharpoons MgH_2L^0$	1.92	0.1	25	2
	1.60	0.16	25	2
	1.84	0.1	20	2, 6
	1.81	0.1	25	4
	1.66	0.15	37	4
	2.59	0.0	25	4
	1.60	0.15	NI	5
	1.60	0.09	25	5
	1.85	0.1	25	6
$Mg^{2+} + H_3L^- \rightleftharpoons MgH_3L^+$	0.84	0.1	20	2, 6
	0.7	0.1	25	4

[a] NI = Not indicated by author; assumed to be room temperature.

Table B.5. (Continued)

	Citric Acid (H_4L)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
<u>Mn(II)</u>				
$Mn^{2+} + HL^{3-} \rightleftharpoons MnHL^-$	4.15	0.1	25	2
	3.70	0.16	25	2
	3.70	0.1	25	3
	3.80	0.15	37	3, 4
	4.15	0.1	25	3, 4
	3.76	0.1	25	4
	3.81	0.1	25	4
	3.93	0.15	37	4
	3.54	0.16	25	5
	3.67	0.15	25	5
	3.72	0.15	25	6
$Mn^{2+} + H_2L^{2-} \rightleftharpoons MnH_2L^0$	2.16	0.1	25	2
	2.08	0.1	25	3
	2.22	0.15	37	3, 4
	2.16	0.1	25	3
	2.3	0.1	25	4
	2.08	0.15	25	5
	2.08	0.15	25	5
$Mn^{2+} + H_3L^- \rightleftharpoons MnH_3L^+$	1.5	0.15	37	4
$2Mn^{2+} + 2HL^{3-} \rightleftharpoons 2MnL_2^{4-} + 2H^+$	-6.3	0.1	25	4
	-5.73	0.15	37	4
$Mn_2(OH)_2(HL)_2^{4-} + 2H^+ \rightleftharpoons 2Mn^{2+} + 2HL^{3-} + 2H_2O$	5.73	0.15	37	3
$Mn^{2+} + H_4L \rightleftharpoons MnH_2L^0 + 2H^+$	-4.9	0.25	33	6
$MnHL^- + H^+ \rightleftharpoons MnH_2L^0$	4.7	0.25	33	6
$MnL^{2-} + H^+ \rightleftharpoons MnHL^-$	8.5	0.25	33	6

Table B.5. (Continued)

Equilibria	Citric Acid (H_4L)			
	Constant	Ionic Strength	Temperature	Reference
Nb(V)				
$Nb(OH)_4^+ + H_4L \rightleftharpoons Nb(OH)_4H_3L^0 + H^+$	2.94	4.5	20	6
$Nb(OH)_4^+ + HL^{3-} \rightleftharpoons Nb(OH)_4HL^{2-}$	2.53	3.5	20	8
Ni				
$Ni^{2+} + HL^{3-} \rightleftharpoons NiHL^-$	5.40	0.1	20	2
	5.11	0.16	25	2
	5.35	0.1	25	3
	5.40	0.1	20	3, 6
	5.17	0.1	25	4
	5.25	0.1	25	4
	5.56	0.1	25	4
	5.10	0.025	32.5	5
	5.11	0.15	25	5
	4.99	2.0	25	5
	5.11	0.15	25	5
$Ni^{2+} + 2HL^{3-} \rightleftharpoons Ni(HL)_2^{4-}$	8.11	0.1	25	4
	8.58	0.1	25	4
$Ni^{2+} + H_2L^{2-} \rightleftharpoons NiH_2L^0$	3.30	0.1	20	2
	3.19	0.16	25	2
	3.25	0.1	25	3, 4
	3.30	0.1	20	3, 6
	3.48	0.1	25	4
	3.37	0.025	32.5	5
	3.19	0.15	25	5
$Ni^{2+} + H_3L^- \rightleftharpoons NiH_3L^+$	1.75	0.1	20	2
	1.75	0.1	20	3, 6
	1.8	0.1	25	4
$Ni_2(OH)_2(HL)_2^{4-} + 2H^+ \rightleftharpoons 2Ni^{2+} + 2HL^{3-} + 2H_2O$	4.71	0.1	25	3
$NiH_2L^0 + HL^- \rightleftharpoons Ni(H_2L)HL^{3-}$	4.4	0.1	25	4
	4.61	0.1	25	4

Table B.5. (Continued)

	Citric Acid (H_4L)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
$2Ni^{2+} + 2HL^{3-} \rightleftharpoons Ni_2L_2^{4-} + 2H^+$	-3.96	0.1	25	4
	-4.32	0.1	25	4
$NiLOH^{3-} + H^+ \rightleftharpoons NiHL^{2-}$	7.87	0.025	32.5	5
$Ni^{2+} + H_4L \rightleftharpoons NiH_2L^0 + 2H^+$	-4.1	0.25	32	6
$NiHL^- + H^+ \rightleftharpoons NiH_2L^0$	3.7	0.25	32	6
$NiL^{2-} + H^+ \rightleftharpoons NiHL^-$	7.9	0.25	32	6
	7.9	NI[a]	35	6
Pu(III)				
$Pu^{3+} + HL^{3-} \rightleftharpoons PuHL^0$	8.9	<0.05	NI[b]	7
$Pu^{3+} + 2H_3L^- \rightleftharpoons Pu(H_3L)_2^+ + 3H^+$	6.6	<0.05	NI[b]	7
$Pu^{3+} + 3H_3L^- \rightleftharpoons Pu(H_3L)_3^0$	10.1	<0.50	NI[b]	7
Pu(IV)				
$Pu^{4+} + HL^{3-} \rightleftharpoons PuHL^+$	15.2	0.5	25	6
	15.7	0.5	25	6
$Pu^{4+} + 2HL^{3-} \rightleftharpoons Pu(HL)_2^{2-}$	30.1	0.5	25	6
	29.5	0.5	25	6

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[a] NI = Ionic strength not indicated by author.

[b] NI = Not indicated by author; assumed to be room temperature.

Table B.5. (Continued)

	Citric Acid (H_4L)			
Equilibria	**Constant**	**Ionic Strength**	**Temperature**	**Reference**
Sr				
$Sr^{2+} + HL^{3-} \rightleftharpoons SrHL^{-}$	3.05	0.1	25	2
	2.81	0.16	25	2
	4.11	0.0	25	2
	3.02	0.1	25	4
	3.23	0.1	25	4
	2.85	0.16	25	5
	2.2	1.05	25	5
	2.90	0.15	25	5
	2.70	0.16	25	5
	2.7	0.16	37	5
	2.7	0.25	32	6
	2.24	1.0	22	6
Zn				
$Zn^{2+} + L^{3-} \rightleftharpoons ZnL^{2-}$	7.5	0.1	18-20	6
$Zn^{2+} + HL^{3-} \rightleftharpoons ZnHL^{-}$	4.98	0.1	20	2, 6
	4.70	0.16	25	2
	4.27	0.5	25	2
	4.86	0.1	25	3
	5.27	0.15	37	3
	4.94	0.1	20	3
	4.27	0.5	25	3
	4.76	0.1	25	4
	4.27	0.5	25	4
	4.83	0.1	25	4
	4.79	0.1	30	4
	4.85	0.15	25	5
	4.71	0.16	25	5
	4.25	2.0	25	5
$Zn^{2+} + 2HL^{3-} \rightleftharpoons Zn(HL)_2^{4-}$	5.90	0.5	25	2,3

Table B.5. (Continued)

Equilibria	Citric Acid (H_4L)			
	Constant	Ionic Strength	Temperature	Reference
$Zn^{2+} + H_2L^{2-} \rightleftharpoons ZnH_2L^0$	2.98	0.1	20	2, 3, 6
	2.94	0.5	25	2, 3
	3.87	0.1	25	3
	2.78	0.1	25	4
	2.49	0.5	25	4
	2.96	0.15	25	5
	3.00	0.1	18-20	5
$Zn^{2+} + H_3L^- \rightleftharpoons ZnH_3L^+$	1.25	0.1	20	2, 3, 6
	1.3	0.1	25	4
$Zn^{2+} + H_4L \rightleftharpoons ZnH_2L^0 + 2H^+$	-3.66	0.05	25	6
$2Zn^{2+} + 2HL^{3-} + 2H_2O \rightleftharpoons Zn_2(OH)_2(HL)_2^{4-} + 2H^+$	2.94	0.1	25	3
$2Zn^{2+} + 2HL^{3-} \rightleftharpoons Zn_2L_2^{4-} + 2H^+$	-2.94	0.1	25	4
$Zn(OH)^0 + HL^{3-} \rightleftharpoons Zn(OH)(HL)^{2-} + OH^-$	9.4	NI[a]	NI[b]	5
$ZnHL^- + OH^- \rightleftharpoons Zn(OH)(HL)^{2-}$	5.6	0.04-0.4	25	6
$ZnHL^- + OH^- \rightleftharpoons ZnL^{2-} + H_2O$	5.5	0.3	25	6
$Zn^{2+} + H_4L \rightleftharpoons ZnH_2L^0 + H^+$	-4.2	0.25	33	6
$ZnHL^- + H^+ \rightleftharpoons ZnH_2L^0$	4.3	0.25	33	6
$ZnL^{2-} + H^+ \rightleftharpoons ZnHL^-$	7.7	0.25	33	6
Zr(IV)				
$Zr^{4+} + H_2L^{2-} \rightleftharpoons ZrH_2L^{2+}$	10.78	1.0	18-20	6
$Zr^{4+} + H_4L \rightleftharpoons ZrH_3L^{3+} + H^+$	3.87	1.0	NI[b]	6
	3.12	2.0	NI[b]	6

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[a] NI = Ionic strength not indicated by author.
[b] NI = Not indicated by author; assumed to be room temperature.

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P.R. Reed, NRC Project Manager

11. ABSTRACT (200 words or less)

The U.S. Nuclear Regulatory Commission is responsible for regulating the safe land disposal of low-level radioactive wastes that may contain organic chelating agents. Such agents include EDTA, DTPA, picolinic acid, and citric acid, which can form radionuclide-chelate complexes that may enhance the migration of radionuclides from disposal sites. Data from the available literature indicate that chelates can leach from solidified decontamination wastes in moderate concentration and can potentially complex certain radionuclides in the leachates. The effects of the formation of such radionuclide-chelate complexes on the migration of radionuclides in groundwater systems is still difficult to quantitatively predict. However, in general it appears that both EDTA and DTPA have the potential to mobilize radionuclides from waste disposal sites because such chelates can leach in moderate concentration, form strong radionuclide-chelate complexes, and can be recalcitrant to biodegradation. It also appears that oxalic acid and citric acid will not greatly enhance the mobility of radionuclides from waste disposal sites because these chelates do not appear to leach in high concentration, tend to form relatively weak radionuclide-chelate complexes, and can be readily biodegraded. In the case of picolinic acid, insufficient data are available to make definitive predictions.

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