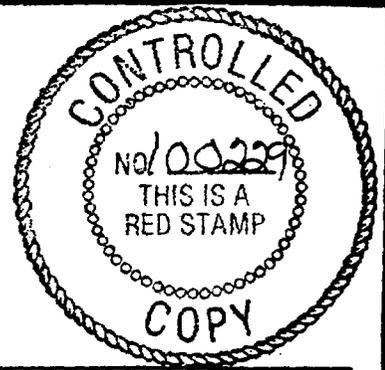


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DISSOLVED SPECIES CONCENTRATION LIMITS  
AND  
COLLOID BEHAVIOR

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ABSTRACT

This report describes the rationale and approach for two geochemical site characterization studies for the proposed deep geologic repository for high-level nuclear waste at Yucca Mountain, Nevada. The first study is Dissolved Species Concentration Limits (SCP No. 8.3.1.3.5.1) and consists of three discrete activities; Radionuclide Solubility Measurements, Radionuclide Speciation, and Solubility Modeling. The Solubility Measurement activity will provide solubility limits for dissolved species of important radionuclides (e.g., Np, Pu, and Am) found in the waste to be emplaced at the proposed repository under conditions that are characteristic of the repository and along flow paths to the accessible environment. The experiments described in this activity are meant to satisfy the requirements of the NRC technical position on high-level waste isolation. The Speciation activity will identify the important species of radionuclides under site-specific conditions and determine their thermodynamic formation constants. The intent of this activity is to provide the necessary data to enable reliable predictions of radionuclide solubility and speciation under potentially important site-specific conditions for which these properties have not been empirically determined. The Solubility Modeling activity will employ an existing thermodynamic code (EQ3/6) to carry out predictions of radionuclide solubility and speciation. This will be done to fill in any data gaps where empirical determinations have not been made. The Modeling activity will utilize the existing EQ3/6 data base, but with augmentations provided by the Solubility Measurements and Speciation activities and other external sources of validated radionuclide thermodynamic data.

The second study is Colloid Behavior (SCP No. 8.3.1.3.5.2). This study consists of a single activity, Colloid Formation, Characterization, and Stability. This activity will determine the chemical and physical properties of radiocolloids, and study their formation and stability. Two radionuclides that form colloids, plutonium and americium, have been identified for investigation. If new solubility and speciation data indicate that colloidal neptunium is important, this colloid will also be investigated.

The results of these two studies will be used to assess radionuclide releases to the accessible environment and the existence of favorable or potentially adverse conditions at the site. It will also provide input to other geochemical site characterization studies concerned with radionuclide sorption and dynamic transport processes.

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## GLOSSARY OF ACRONYMS AND ABBREVIATIONS

<b>TERM</b>	<b>MEANING</b>
APS	Autocorrelated Photon Spectroscopy
CFR	Code of Federal Regulations
CPC	Controlled Potential Coulometry
DCR	Diffraction Controlled Resonator
DOE	Department of Energy
DP	Detailed Technical Procedure
EMF	Electromotive Force
EPA	Environmental Protection Agency
EQ3/6	Thermodynamic Modeling Code
FTIR	Fourier-Transform Infrared Spectroscopy
HDEHP	di(2-ethylhexyl) phosphoric acid
INC	Isotope and Nuclear Chemistry Division
JCPDS	Joint Committee on Powder Diffraction Standards
LANL	Los Alamos National Laboratory
LBL	Lawrence Berkeley Laboratory
LIF	Laser Induced Fluorescence Spectroscopy
LSV	Linear Sweep Voltammetry
NAA	Neutron Activation Analysis
NIST	National Institute of Standards and Testing
NQA-1	National Quality Assurance-1
NRC	Nuclear Regulatory Commission
NTS	Nevada Test Site
PAS	Photoacoustic Spectroscopy
PDL	Pulsed Dye Laser
PDS	Photothermal Deflection Spectroscopy
ppm	parts per million
QA	Quality Assurance
SCP	Site Characterization Plan
SEM	Scanning Electron Microscopy
TTA	Thenoyl-trifluoro-acetone
WEX	Wavelength Extender
XAS	X-ray Absorption Spectroscopy
YAG	Yttrium Aluminum Garnet
YMP	Yucca Mountain Project

## 1.0 PURPOSE AND OBJECTIVES OF STUDIES

This study plan describes two of the studies included in Investigation 8.3.1.3.5, Studies to Provide the Information Required on Radionuclide Retardation by Precipitation Processes along Flow Paths to the Accessible Environment. These studies are required by the Site Characterization Plan (SCP) (DOE, 1988) before licensing and construction of a proposed repository for high-level radioactive waste at Yucca Mountain, Nevada. The purpose of these studies, Dissolved Species Concentration Limits (Study 8.3.1.3.5.1) and Colloid Behavior (Study 8.3.1.3.5.2), is to supply data for calculating radionuclide transport along potential transport pathways from the repository to the accessible environment. These calculations are needed to address the overall system performance objective for radionuclide releases in 10 CFR 60.112 (NRC, 1988) (Issue 1.1, Total System Performance, SCP Section 8.3.5.13), to make findings on the postclosure system guidelines and the technical guidelines for geochemistry in 10 CFR 960.3-1-5 (DOE, 1988) (Issue 1.9, Higher-Level Findings--Postclosure, SCP Section 8.3.5.18), and to address the siting criteria of 10 CFR 60.122 (Issue 1.8, NRC Siting Criteria, SCP Section 8.3.5.17). Specifically, Issue 1.1 requires estimates of the means and standard deviations of the solubility limits of radionuclide-bearing compounds under the water chemistry conditions expected at the site.

Water moving through the emplacement area toward the accessible environment can transport radionuclides in two ways: either as dissolved species in the water or as particulate material (i.e., natural colloidal materials or radiocolloids) carried by the water. This investigation will supply data and models that can be used to calculate the concentration limits of dissolved radionuclides in local water at the Yucca Mountain site. These concentration limits will be used directly by performance assessment models of radionuclide transport. This investigation will also supply data and models that describe the formation and stability of radiocolloids in local water. This information will be used in assessing the likelihood of colloid transport (Investigation 8.3.1.3.7, Studies to Provide the Information Required on Radionuclide Retardation by All Processes along Flow Paths to the Accessible Environment). It will also be used in the calculations for Issue 1.1, Total System Performance. Radionuclide solubility and speciation data and models will also be used to support modeling of sorptive behavior as a function of water chemistry and radionuclide chemistry (Investigation 8.3.1.3.4, Studies to Provide the Information Required on Radionuclide Retardation by Sorption Processes along Flow Paths to the Accessible Environment).

It is not practical to measure the solubilities of all radionuclides that may exist in radioactive waste under all conditions that may occur at the repository or along flowpaths to the accessible environment. Therefore, the technical approach used to select radionuclides for solubility measurements and to select the conditions of these measurements is based on three criteria:

- radionuclides present in quantities that are large in comparison with Environmental Protection Agency (EPA) release limits (40 CFR 191, Appendix A, Table I);
- radionuclides that are likely to reach solubility limits during transport based on current knowledge of radionuclide chemistry and expected repository conditions; and
- conditions for solubility experiments that will bound expected conditions at the repository or along flow paths to the accessible environment.

The radionuclides of primary concern are discussed in SCP Section 4.1.3.1.1, Key Radionuclides. A review of the chemistry of important radionuclides is also given in SCP Section 4.1.3.4, Processes Affecting Radionuclide Concentrations and Speciation in Solution. These sections, along with descriptions of the expected ground water chemistry (SCP Section 4.1.2, Ground Water Chemistry) and changes in water chemistry resulting from waste emplacement (SCP Section 4.2, Geochemical Effects of Waste Emplacement), form the basis for the selection

of the solubility experiments discussed below. The initial emphasis is on solubility and speciation for americium, plutonium, and neptunium. Measurements are also planned for uranium, thorium, radium, zirconium, tin, and nickel. The latter elements are included in the testing program so that the concentrations can be used as upper bounds for transport assessments.

Investigation 8.3.1.3.5, Studies to Provide the Information Required on Radionuclide Retardation by Precipitation Processes along Flow Paths to the Accessible Environment, consists of two distinct studies. The goal of the first study, Study 8.3.1.3.5.1, Dissolved Species Concentration Limits, is to comply with the NRC's position paper (1984) by providing solubility data (concentration limits) for dissolved species of important radionuclides under conditions that are characteristic of the repository and along flow paths to the accessible environment, and to provide a predictive capability for solubility under conditions for which solubility has not been empirically determined. The results of this study will be used in the assessment of radionuclide releases to the accessible environment and to assess the existence of favorable or potentially adverse conditions at the site.

Study 8.3.1.3.5.1, Dissolved Species Concentration Limits, will consist of three separate activities. These activities are Solubility Measurements (8.3.1.3.5.1.1), Speciation Measurements (8.3.1.3.5.1.2), and Solubility Modeling (8.3.1.3.5.1.3). The objective of the solubility measurements activity is first to measure the solubilities of important radionuclides under closely controlled experimental conditions. The objective of the speciation measurements activity is to identify important aqueous species of radionuclides and to determine their formation constants under prescribed conditions. The formation constants (sometimes referred to by the more generic term equilibrium constants) define the equilibria that exist between the radionuclide and its complexes in solution. This activity will be necessary when data are unavailable from sources outside the Yucca Mountain Project (YMP) or when verification of the validity of available data is required. This activity will be conducted concurrently with Activity 8.3.1.3.5.1.1, Solubility Measurements, and is intended to fill any data gaps so that a complete body of solubility data can be adequately tested by thermodynamic modeling. The objective of Activity 8.3.1.3.5.1.3, Solubility Modeling, is to implement the thermodynamic models and determine the data needed to calculate radionuclide solubilities over the entire range of conditions expected at the repository site. It is clear that there is a significant interdependence of all three activities in this study and that all are vital for the success of the study.

The second study, Colloid Behavior (8.3.1.3.5.2), will focus on understanding the behavior of radiocolloids. Within the context of this study plan, radiocolloids are defined as colloidal aggregates composed of radionuclides and/or simple complexes of radionuclides. These should be distinguished from complex colloids that are composed of clay or other particulate matter onto which radionuclides are sorbed. Complex colloids are considered in detail in Study 8.3.1.3.4.1 (Batch Sorption) under Activity 8.3.1.3.4.1.4 (Sorption on Particulates and Colloids). The transport properties of these complex colloids are also considered in Study 8.3.1.3.6.1 (Dynamic Transport) under Activity 8.3.1.3.6.1.5 (Filtration). The interface to these Studies is discussed below. The goal of this study is to determine the stability of radiocolloids under site-specific conditions at the repository or along flow paths to the accessible environment. The results will be used in the assessment of radionuclide releases to the accessible environment and to assess the existence of favorable or potentially adverse conditions at the site. This study plan considers only one activity in the Colloid Behavior study: Colloid Formation, Characterization, and Stability (Activity 8.3.1.3.5.2.1). The objective of this activity is to determine the conditions that are favorable to the formation and stabilization of the radiocolloids and to characterize the physical and chemical properties of these colloids. The information obtained in this activity will be used specifically by Issue 1.1 (Total System Performance) and Investigations 8.3.1.3.4 (Studies to Provide the Information Required on Radionuclide Retardation by Sorption Processes along Flow Paths to the Accessible Environment) and 8.3.1.3.6 (Studies to Provide the Information Required on Radionuclide Retardation by Dispersive, Diffusive, and Advective Transport Processes along

Flow Paths to the Accessible Environment). Colloid Modeling (Activity 8.3.1.3.5.2.2) will be included under the domain of the Solubility Modeling Activity (8.3.1.3.5.1.3).

In selecting these experiments, we have also considered the generic technical position entitled "Determination of Radionuclide Solubility in Ground Water for Assessment of High-Level Waste Isolation" (NRC, 1984). This technical position serves as guidance in the preparation of detailed plans for experiments to determine radionuclide solubility. It requires that if radionuclide solubility is used as a factor in limiting radionuclide release, experiments must be designed to determine solubility under site-specific conditions. The experiments discussed in this study plan are meant to satisfy the requirements of the NRC's technical position.

The various parameters that influence solubility can be divided into three groups:

- those parameters that define the conditions controlling solubility (water chemistry, temperature, and radiation field),
- those parameters that define radionuclide behavior (radionuclide chemistry, colloid behavior, and kinetic data), and
- those parameters necessary to understand precipitation processes (models).

The primary areas of choice in designing solubility experiments involve the conditions of the experiment and the elements chosen. Five specific parameters have been considered in designing the experiments for the solubility studies: (1) water composition, including pH and Eh (speciation of redox-sensitive radionuclides), (2) temperature, (3) identity of the solid that controls solubility, (4) the presence of other solids, and (5) radiation effects, such as radiolysis. Solubilities that represent upper limits on radionuclide concentrations are of primary concern in defining the experiments. However, solubility data alone, without an understanding of the basic thermodynamic processes that determine the solubilities are of limited value. Thus, our approach is intended to stress an understanding through speciation determinations. Thermodynamic modeling will also be used to help understand the solubility and speciation behavior of the radionuclides in the multicomponent aqueous systems found in the Yucca Mountain environment.

An important part of this investigation is modeling the solubility and speciation of radionuclides (SCP Section 4.1.3.4, Processes Affecting Waste Element Concentration in Solution). Modeling will be used for two purposes: (1) to assess the importance of the various parameters that influence solubility and speciation (e.g., water composition) and (2) to calculate solubilities under conditions not directly covered by the solubility experiments. Existing models of solubility and speciation of radionuclides are based primarily on equilibrium methods. This emphasis will continue. Equilibrium models require thermodynamic data for solids that are likely to precipitate and for aqueous species that may be present in the water. We are deriving these data from literature sources, from other sources within the Yucca Mountain Project (e.g., SCP Section 8.3.5.10.3.2), and from the solubility and speciation data collected as part of this investigation. Nonequilibrium or kinetic models will be used as needed to describe certain aspects of radionuclide solubility.

Movement of natural radiocolloids is a transport mechanism that may be active under conditions at the Yucca Mountain site that may limit the effectiveness of the sorption barrier in retarding migration. To assess the potential for colloid transport (Investigation 8.3.1.3.4, Studies to Provide the Information Required on Radionuclide Retardation by All Processes along Flow Paths to the Accessible Environment), information is needed about the likelihood of colloid formation under extant water chemistry conditions at the Yucca Mountain site and the stability of colloids once formed. Two radionuclides that may form stable colloids under these conditions have been identified: plutonium and americium (SCP Section 4.1.3.4). Because these nuclides also contribute significantly to the radioactivity of the waste inventory, we plan to examine their potential for colloid formation and to perform stability experiments.

## 2.0 RATIONALE FOR SPECIES CONCENTRATION LIMITS AND COLLOID BEHAVIOR STUDIES

### 2.1 Rationale for Dissolved Species Concentration Limits

We will determine the solubilities of certain radionuclides in the far-field environment. The radionuclides studied will be those found in the waste to be emplaced at Yucca Mountain. Certain experiments will be conducted in samples of ground water obtained at the Yucca Mountain site. The results will be used to determine whether the site is suitable for disposal of radioactive waste. First, we will measure the upper limit of concentrations of the various ionic and colloidal radionuclides. These data alone will not be sufficient because ground water conditions (e.g., temperature, Eh, and pH) may change; therefore, we will also determine the actual species present and the equilibrium quotients of the various reactions. In this manner, thermodynamic data will be obtained that can be used in solubility modeling to calculate solubility limits under any possible conditions at the repository site, including both the near and far field. This approach includes an assessment of the solubility limits of colloidal radionuclides. The rationale and justification for each of these tasks are outlined in more detail in the sections below.

#### 2.1.1 Rationale for Radionuclide Solubility Measurements (Activity 8.3.1.3.5.1.1)

Radionuclide concentrations in water passing through the emplacement area can be limited by two mechanisms: low dissolution rates of the solid waste form or solubilities of individual radionuclides. If solid waste dissolution rates are low enough, it may not be necessary to depend on solubilities to limit radionuclide concentrations. However, the solid waste forms have not yet been determined, and therefore the dissolution rates of the solid waste are unknown. (Note however that information on the water chemistry at the potential emplacement horizon in the near field will be determined in Study 8.3.4.2.4.1 Rock-Water Interactions at Elevated Temperatures.) Determination of radionuclide solubility provides an upper bound on radionuclide concentrations in solution and provides a basis for extrapolation to long-term behavior. These concentration limits may be higher than those obtained from solid waste dissolution rates for many important radionuclides. Only if the rate of ground water flow through the waste is sufficiently slow to permit saturation of the water with radionuclides will the solution concentrations approach the solubility limits. Therefore, an assessment of radionuclide release rates using a saturation-limited dissolution model represents the most conservative approach possible.

As radionuclides are transported from the emplacement area to the far field along flow paths to the accessible environment, changing water chemistry (pH, Eh, oxidation state, and concentrations of complexing species) due to degradation of either the engineered barrier system or the geological barrier can alter solubilities. A knowledge of radionuclide solubilities under the conditions along possible flow paths is necessary to assess this scenario. Investigation 8.3.1.3.1, Studies to Provide Information on Water Chemistry Within the Potential Emplacement Horizon and along Potential Flow Paths, provides information on flow path conditions.

Long times are frequently required to reach steady-state conditions for radionuclide solubility/dissolution. For this reason every conceivable solubility determination cannot be investigated. We will select radionuclides, ground water, pH, Eh, and temperature to bracket the expected range of conditions by choosing parameters that represent lower and upper limits.

##### 2.1.1.1 Radionuclides

The radionuclides selected will be limited to nuclides with solubility-limited dissolution rates (sparingly soluble). Americium, neptunium, plutonium, thorium, uranium, radium, nickel, tin, and zirconium will be investigated in this study. Cesium, technetium, strontium, iodine, and carbon have such large solubilities (determined from the literature data base) under the conditions

expected at Yucca Mountain that their dissolution rates are limited by the dissolution rate of the waste, and therefore these nuclides will not be considered in this activity.

#### 2.1.1.2 Water Compositions and Temperatures

Ideally, water samples with compositions that bracket the range of waters expected in the vicinity of Yucca Mountain should be chosen for solubility and speciation measurements. Much of the needed information concerning the water composition in the unsaturated zone will come from Study 8.3.1.2.2.7 (Unsaturated Zone Hydrochemistry). The present strategy calls for the use of two waters that are currently available from the saturated zones at the site for the initial solubility experiments. Then, as information on the water composition in the unsaturated zone becomes available, it will be compared with the composition data for the two saturated waters. If the water compositions are sufficiently disparate to lead to probable significant differences in solubilities (i.e., higher levels that would potentially jeopardize solubility as a barrier to migration), then synthetic unsaturated-zone waters will be prepared and used for additional solubility determinations. Note that the variation in solubility based on changes in water composition will be tested to the extent possible with existing thermodynamic data to determine if additional solubility determinations with synthetic unsaturated-zone water are warranted. In this way, it should be possible to avoid an excessively large suite of experimental determinations.

For the initial solubility experiments, the two waters available from the site are Well J-13 water and Well UE-25p#1 water. Well J-13 water taps the Topopah Spring Member tuff which contains the repository horizon. Thus, this water was initially expected to be representative of the water composition of the unsaturated zone near the proposed emplacement area (Ogard and Kerrisk, 1984; Kerrisk, 1987). However, preliminary results of Yang et al. (1988) indicate that unsaturated-zone water has approximately three times greater ionic strength than Well J-13 water. Well UE-25p#1 taps the carbonate aquifer that underlies the emplacement horizon. This water has an ionic strength and total carbonate content higher by approximately an order of magnitude than Well J-13 water. Well UE-25p#1 water represents natural water with the highest concentrations of dissolved species expected in the vicinity of Yucca Mountain (Kerrisk, 1987). The water from both wells is oxidizing. Generally, radionuclide solubility studies under oxidizing conditions lead to higher solubilities for a number of radionuclides than would occur under mildly or strongly reducing conditions. Thus, these tests will provide conservative results. Note also that the preliminary data of Yang et al. (1988) on the unsaturated-zone waters place the dissolved species concentration between that of Well J-13 and Well UE-25p#1. Thus, the choice of these two waters for the initial experiments appears reasonable based on preliminary data.

In addition, solubility measurements will be done in dilute sodium perchlorate electrolyte. These measurements will provide data for a) a relatively simple system where only hydrolysis occurs and only oxides or hydroxide precipitates are being formed, and b) scenarios in which dilute waters reenter the repository after the thermal period.

The perchlorate electrolyte is used because the perchlorate anion,  $\text{ClO}_4^-$ , is a hard base with low tendency to coordinate (Cotton and Wilkinson, 1988), though some cases have been established where a small complexation between perchlorate ions and metal ions occur. However, these interactions are the exception rather than the rule (Hartley et al., 1988). This is demonstrated by the many reported studies for the actinide hydrolysis reaction (Freeman and Keller, 1991) that are carried out in perchlorate medium with concentrations ranging from very dilute (~0.1 M) to concentrated (~5 M).

An additional variable in the groundwater composition is the possible presence of dissolved species derived from the waste package and other engineered barrier components. Tests on the reactions of Well J-13 water with the host rock and on the metals from which the waste container

may be fabricated (SCP Section 8.3.5.9.2, Information Need 1.4.2, Material Properties of the Container) were initiated as part of the waste package task of the YMP (Oversby, 1985). Only small changes in water composition associated with the contact of Well J-13 water with the metals tested have been found. However, small changes in critical constituents (e.g., redox-buffering agents) can significantly impact solubilities. If changes in the concentrations of critical components are observed in the experiments to determine waste-package dissolution properties, the solubility conditions outlined in this study must be re-evaluated and changed as necessary. Here, too, an attempt will be made to predict the change in solubilities of radionuclides as a result of the changes in water composition using existing thermodynamic data before experimental solubility determinations are initiated so that the number of empirical determinations can be kept to an acceptable level.

The maximum temperature of the host rock in which liquid water is present is expected to be limited by the boiling point of water at Yucca Mountain (95°C). The solubility experiments that use Well J-13 water will be conducted at temperatures between 25 and 90°C. This span covers the range from pre-emplacment temperatures to the maximum temperature at which solubility would be important. For Well UE-25p#1 water, solubility tests will be limited to a maximum temperature of 60°C. Maximum temperatures in the saturated zone under the emplacement area and those along flow paths away from the emplacement area are expected to be less than 60 °C (Johnstone et al., 1984).

#### 2.1.1.3 Constraints on Solubility Studies

The solubility of radionuclides in solutions of near-neutral pH and relatively low carbonate concentration (total carbonate from 0 to about 0.1 M) is generally controlled by solids containing hydroxides and/or carbonates. The formation of hydroxide and carbonate solids depends on the activity of  $H^+$  [ $a(H^+)$ ] in solution; therefore, accurate solubility measurements require continuous control of  $a(H^+)$ . The conventional measure of  $a(H^+)$  is pH. Strictly, pH is defined operationally to yield a quantity that is easily and reproducibly measured and approximately equally to  $-\log a[H^+]$ . For solutions of low ionic strength and pH values in the range 2 - 12, the operational definition is within 0.02 units of  $-\log a(H^+)$  (Levine, 1978). For the purpose of solubility determinations, standard deviations in pH of 0.2 unit should be satisfactory for these near-neutral solutions. If the solubility tests show a stronger pH dependence, the pH will be controlled more tightly, if possible.

The accuracy of measured pH values is controlled by (1) the accuracy of the standard buffer solutions certified by the National Institute of Standards and Technology (NIST), which are used to standardize the pH electrodes, and (2) the degradation of the pH electrodes in the time between calibrations. The accuracy of a newly restandardized pH electrode will be set by valid standard buffer solutions, which should not exceed 0.01 pH unit. pH electrodes degrade when continuously in contact with the solution. Semiweekly restandardization will limit the resulting degradations to between 0.05 at 25°C and 0.1 pH unit at 90°C.

The solution concentrations of the radionuclides are determined by radionuclide counting (alpha, beta, and gamma counting) of solution aliquots. Determination of concentrations requires accurate measurement of volume and counting rates. Volumes are measured with calibrated digital pipettes and Class A volumetric pipettes and glassware having tolerances better than 1.5% (Eppendorf, Shugar 1990). Given sufficient counting time, counting rates can be measured to very high precisions. Their accuracy is limited by the accuracy of commercially available NIST-certified standard sources (typically 2 to 3%). These combined accuracies lead to an accuracy of about 5% for the concentration determination.

Radionuclide counting will be done to a precision of 5% whenever possible within reasonable counting times. For trace-level concentrations relatively long counting times may be required to reach this level of precision, and sample counting to a lower precision may become necessary.

Table 1 lists counting times in minutes of a 1 mL sample of  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$ , and  $^{243}\text{Am}$  that are necessary to reach 5%, 20%, and 50% precision at  $10^{-10}$ ,  $10^{-9}$ , and  $10^{-8}$  M, respectively. If the solubility tests indicate that a higher precision than the initially chosen one is needed to refine solubility limits, the sample will be re-counted over a longer time.

TABLE 1  
 PRECISION AS A FUNCTION OF COUNTING TIME AND SOLUTION CONCENTRATION <sup>a</sup>

Nuclide		Counting Time (minutes) <sup>b</sup>		
		$10^{-10}$ M	$10^{-9}$ M	$10^{-8}$ M
$^{237}\text{Np}$	5%	43,127	4,313	431
	20%	2,695	270	27
	50%	431	43	5
$^{239}\text{Pu}$	5%	486	47	5
	20%	31	3	1
	50%	5	1	<<1
$^{243}\text{Am}$	5%	149	15	2
	20%	10	1	<<1
	50%	1	<<1	<<1

<sup>a</sup>1 mL sample, 100% counting efficiency.

<sup>b</sup> $2\sigma$  values.

### 2.1.2 Rationale for the Study of Radionuclide Speciation (Activity 8.3.1.3.5.1.2)

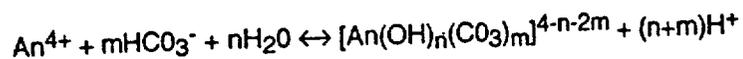
The study of speciation of radionuclides is fundamentally important to the determination of radionuclide solubility in the ground water at Yucca Mountain. Speciation is strictly defined as (1) the identification of the radionuclide, (2) the determination of its oxidation state, and (3) the formula and/or structure of the ionic and/or solid complex [i.e., the stoichiometry of the ion as complexed by OH ions (e.g., hydrolysis) and/or by other ligands (e.g., carbonate, fluoride, phosphate)]. Speciation can be determined to a lesser degree by, for example, deducing only the oxidation state of the radionuclide in question.

Although direct solubility measurements (Activity 8.3.1.3.5.1.1) will provide limits for the concentrations of important radionuclides under certain specific ground water conditions, they cannot possibly provide concentration limits for all foreseeable ground water conditions. Therefore, a basic thermodynamic characterization of radionuclide speciation is needed to bridge any gaps in the data acquired from direct solubility determinations and to provide the fundamental thermodynamic constants needed for modeling solubility under conditions that are not specifically considered in the solubility determination. In the speciation study, we will attempt to identify the important complexes of the radionuclides (e.g., oxidation states, formula and/or structure of the ionic or solid complex, and extent of hydration or complexation) that are likely to form under the prevailing ground water conditions (e.g., temperature, pH, Eh, and concentration of complexing agents) at the Nevada Test Site (NTS). The speciation study will also attempt to determine the formation constants for these complexes.

### 2.1.2.1 Rationale for Approach to Speciation Activity

Ogard and Kerrisk (1984) report that carbonate ions are a principal potential complexing agent in the ground water at the NTS, which has carbonate ion concentrations as high as  $3 \times 10^{-3}$  M. Actinides, which typically have quite low solubilities in near-neutral solutions, can be complexed by carbonate ligands to form species that have increased solubility limits (Allard, 1982). For this reason, the speciation study will focus on the carbonate complexes of the important radionuclides. If Activity 8.3.1.3.5.1.1 (Solubility Measurements) and Activity 8.3.1.3.5.1.3 (Solubility Modeling) identify other important complexing agents, such as fluoride, phosphate, and humates, speciation studies for these other agents will be considered.

Carbonate ion speciation of the actinides under solution conditions such as those expected in the far field involves equilibria such as



where An refers to an actinide element.

It is difficult to study these equilibria directly using conventional methods because, at environmentally relevant pH values, the concentration of  $\text{An}^{4+}$  is extremely low. These experimental difficulties can be overcome in several ways. We are currently pursuing two of the more promising approaches. First, we have developed modern, ultrasensitive, laser-based spectroscopic techniques (Tait et al., 1993; Berg et al., 1991a and b). These techniques include the absorption-based probes known as photoacoustic spectroscopy (PAS), the related method of photothermal deflection spectroscopy (PDS), and the complementary, emission-based probe known as laser-induced fluorescence (LIF) spectroscopy. Because of the extreme sensitivity of these methods, speciation data can be obtained directly for solutions having site-specific characteristics (Stumpe et al., 1984; Eiswirth et al., 1985; Bennett et al., 1992). The second approach is the method of competitive complexation (Hobart et al., 1986a and b). This method uses conventional (transmission-based) electronic absorption spectroscopy to obtain speciation data. For some radionuclides such as plutonium and americium, this approach requires some deviations from the actual solution conditions and compositions expected for the ground water at the repository site so that sufficiently high concentrations of the radionuclide species can be maintained. However, for the more soluble radionuclides such as uranium and neptunium, this method is directly applicable under site-specific conditions in many cases. The principal advantage of this method is experimental expediency in that the spectroscopic techniques are well established and straightforward in implementation. Therefore, scoping experiments can be carried out with minimal expenditure of resources. In addition, this method will provide valuable spectral signatures for speciation at higher concentrations, which can be used to assist in interpretation of speciation data obtained from other methods.

Both the methods based on advanced laser spectroscopic probes (PAS, PDS, and LIF) and the competitive complexation method rely on information contained in the electronic absorption band structure of the radionuclide species to characterize speciation. The principal electronic transitions that give rise to these characteristic absorption bands are Laporte-forbidden f-f transitions. Although these transitions do not involve bonding electrons, the energies, intensities, and numbers of transitions in the total absorption spectrum change in a very sensitive way in response to perturbations induced by the coordination environment (i.e., the ligand field) of the radionuclide ion. Thus, different species of the same metal ion possess distinctive absorption spectra. However, because the spectral transitions are in general parity-forbidden, the intensities are extremely low ( $\epsilon \leq 50 \text{ M}^{-1} \text{ cm}^{-1}$  is not uncommon). This fact, coupled with the inherent low solubility of these species under solution conditions in the ground water, is the cause of the formidable experimental challenge to the characterization of speciation in these

systems.

The principal advantage of the methods based on advanced laser-based spectroscopic probes lies in the extreme sensitivity of the detection schemes. In general, photothermal effects occur when light is absorbed by any state of matter (solid, liquid, or gas) and the absorbed energy is subsequently converted into heat as a result of radiationless deactivation. The evolved heat produces two prominent effects. One is a thermal expansion that creates an acoustic pressure wave, which is the effect used in PAS. The second is the generation of a gradient in the index of refraction in the medium surrounding the absorber. This gradient can be probed optically and is the basis of PDS. Photoacoustic and photothermal deflection spectroscopies result when these two effects are engendered by monochromatic light tuned through a wavelength range of interest. The acoustic signal is detected using a very sensitive pressure-transducing device such as a piezoelectric crystal. The index-of-refraction gradient is determined by precisely measuring the deflection of the light beam from a small probe laser. Thus, the only difference between PAS and PDS is in the method of detection of the evolved heat. In both cases, the magnitude of the measured signal as a function of excitation wavelength is directly related to the absorption spectrum of the illuminated sample. The extreme sensitivity of these two techniques results when a high-intensity, short-duration, pulsed laser is used to excite the samples and the analytical signal is measured using gated detection methods. Laser-induced fluorescence spectroscopy is simply analytical fluorimetry that uses the special properties of pulsed laser excitation to gain sensitivity and resolution. It can be seen that PAS, PDS, and LIF are exactly complementary techniques. If a sample loses the energy of excitation by emitting light, there is little thermal effect, and LIF is the appropriate tool for analysis. Conversely, if the excitation energy is readily lost as heat, little light is emitted, and PAS and PDS are the best methods.

PAS and PDS offer the same advantage for enhanced sensitivity relative to conventional transmission-based absorption spectroscopic probes as do LIF and other emission-based spectroscopic probes. This advantage is that both PAS and PDS are true zero-background analytical tools; that is, the analytical signal is measured against a negligible background signal. This method contrasts with conventional absorption methods in which the analytical signal is derived from the small difference between two large light levels. In addition, laser-excited PAS and PDS (and LIF) are particularly effective for analytes with narrow absorption transitions because the absorption bands can be scanned using a single laser dye. Accordingly, these techniques are ideally suited for the study of actinide speciation because the electronic spectra for these species are dominated by the characteristically narrow f-f transitions.

Photoacoustic and photothermal deflection spectroscopies and LIF have what may legitimately be called ultimate sensitivity. It has been demonstrated that LIF can detect as few as eight molecules of a substance in solution. However, most of these measurements (excluding vibrational PAS and PDS) involve probing electronic spectroscopic transitions and, as such, are notoriously difficult to relate a priori to specific structural (speciation) features. The spectra are quite sensitive to structure, but the relationships between spectral signatures and structures must generally be established empirically. Accordingly, part of our task will be to establish these spectral signatures for the actinide species extant under environmentally relevant conditions. We will use existing and new analytical data that have been derived from using competitive complexation and other methods (see below) to establish spectral signatures for radionuclides that exist at higher concentrations than those expected in the natural environment. Using PAS and PDS, we will perform serial dilution studies ranging from high concentrations to those of environmental significance. This approach will enable us to track the evolution of speciation down to environmentally significant conditions and/or the detection limits of the techniques. Implicit in all this work is the necessity of modeling the spectral properties of complex mixtures of species to assist in assigning spectral signatures and in assessing the contributions of each species to the total spectroscopic signal.

For the studies based on the competitive complexation method, the citrate ion has been chosen as the competitive complexing agent. Previous work with the actinides has shown that the carbonate ion competes successfully with the citrate ion for the coordination sites on the actinide ions. The competitive complexation method involves three stages of investigation: (1) the study of the pure carbonate systems, (2) the study of the pure citrate systems, and (3) the study of the mixed carbonate/citrate systems. All three stages are necessary so that the formation constants for the carbonate complexes (Equation 1) can be expressed in terms of the principal radionuclide species present in aqueous solutions (e.g.  $An^{4+}$ ). Some results for the pure carbonate and citrate complexations of the actinides already exist in the literature. The present study will confirm and extend the previous work for the first two stages.

This approach to the determination of the identity of the radionuclide species and their formation constants often necessitates some deviation from site-specific conditions at the repository. In particular, the concentrations of the radionuclides such as plutonium and americium in the test solutions will have to be significantly higher than those likely to be present in the ground water because of the relative insensitivity of conventional electronic absorption spectroscopy. To permit a reliable determination of the speciation and thermodynamic constants, the concentrations of the various species must be large enough to provide easily measurable absorbance values. However, by determining thermodynamic data, the behavior of the radionuclides can, in principle, be extrapolated to any regime. These studies will also provide species-specific spectral signature data for use in interpreting results obtained by other methods.

Two valuable adjuncts to the laser spectroscopic and competitive complexation methods described above are x-ray absorption spectroscopy (XAS) and nuclear magnetic resonance (NMR) spectroscopy. These techniques enable the direct determination of structural information (coordination numbers, ligand identities, bond distances, valence) for species in solution, allowing, in principle, for a complete unambiguous specification of speciation. The conventional XAS technique is applicable at the millimolar concentration level for the actinides (Combes et al., 1992), and advanced detection methods can likely extend this range down to the micromolar level. Likewise,  $^1H$ ,  $^{13}C$ , and  $^{17}O$  NMR techniques are readily applicable at the millimolar level for radionuclides (Strom et al., 1981; Aberg et al., 1983a and b; Ferri et al., 1988), and can be extended to lower levels by using more powerful magnetic fields. These lower detection limits are still not sufficiently sensitive for directly probing many of the actinide species that exist under environmentally relevant conditions. However, the combination of competitive complexation methods (high concentrations), XAS and NMR methods (high and intermediate concentrations), and PAS, PDS, and LIF methods (intermediate and low concentrations) should provide a complete description of radionuclide speciation.

Other experimental methods of studying radionuclide speciation are also available, including potentiometric electromotive force (EMF) determinations as a function of complexant concentration and pH, solvent extraction, ion exchange chromatography, solubility, and enthalpy titrations. None of these methods is without certain limitations and drawbacks as discussed by Newton and Sullivan (1985). Nonetheless, all are potentially useful for this speciation study, and a continuing appraisal of the progress made with the competitive complexation and PAS, PDS, and LIF methods vis-a-vis the possibility of applying these other methods seems most prudent at present.

As described below, many of the detailed tests and analyses that make up this speciation study are under development. As this activity evolves, we will change the methods and approaches as necessary to obtain the information needed in the most practical manner. At present, we expect to conduct all of the proposed experiments (with the exception of x-ray absorption spectroscopy) at Los Alamos National Laboratory (LANL). In addition, it is expected that site-specific data on the speciation of the radionuclides of interest can be obtained through simulation of anticipated repository conditions. Therefore, this activity should have no direct impact on the proposed Yucca

Mountain site, with the exception of the potential need for ground water samples from the site. Although the expected results from this activity are needed by several other activities and information needs (Section 1), the results are not needed for the initiation of any other YMP activity. Thus, there are no specific time constraints on this activity. The required level of accuracy, where meaningful and appropriate, and the precision for most of the measurements in this activity are conservatively estimated at ~5%. At this level, the data will be valid and significant to the issues and information needs. In all cases, we will endeavor to obtain results with the highest possible levels of statistical significance.

#### 2.1.2.2 Constraints on the Speciation Activity

It is impractical to study speciation for all of the radionuclides that may be present in the waste to be emplaced at the repository. For this reason, the primary guidance for choosing which radionuclides to study will come from the EPA listing on release limits [40 CFR 191, Appendix A, Table 1 (EPA, 1987)]. Potential candidates for speciation studies will be those radionuclides that are expected to be present in the repository in quantities that are large in comparison with their EPA release limits. The potential list of radionuclides will be further constrained to include only those that are likely, based on present knowledge of radionuclide chemistry and expected repository conditions, to have ground water concentrations that are limited by solubility during transport. Additional guidance in selecting candidate radionuclides for speciation studies will come from Activities 8.3.1.3.5.1.1, Solubility Measurements, and 8.3.1.3.5.1.3, Solubility Modeling. The initial emphasis for the speciation studies, based on the above criteria, will be on neptunium, plutonium, and americium. Subsequent studies will be conducted as necessary for uranium, thorium, radium, zirconium, tin, and nickel. Note that the speciation and complexation properties of many of the radionuclides in this second tier are already fairly well understood (see, for example Martell and Smith, 1982) because there are stable nuclides (Zr, Sn, and Ni) that can easily be handled, or because the radionuclides have low specific activities (Th and U) that greatly simplify handling. Thus, additional speciation studies for this second tier should be limited in scope and are presently scheduled for the final two years of the Speciation task. Speciation determinations for all radionuclides enumerated above can be conducted using the suite of techniques described in Section 2.1.2.1.

It is also impractical to carry out speciation studies under all conditions that may occur at the repository and along all flow paths to the accessible environment. For this reason, experimental conditions for the speciation studies (concentration of radionuclides, temperature, pH, Eh, and concentration of complexing agents) will be chosen (in consultation with investigators in Study 8.3.1.2.2.7 Unsaturated Zone Hydrochemistry) to provide the soundest possible thermodynamic results, which, in some cases, may require that data be collected under conditions that are not typical of those expected at the repository site. However, reliable thermodynamic results will also allow extrapolation with minimal uncertainty of radionuclide solubilities and other properties to site-specific conditions.

#### 2.1.3 Rationale for Solubility Modeling Studies (Activity 8.3.1.3.5.1.3)

Solubility modeling analysis has two purposes: (1) to assess the importance of the various parameters that influence the solubility and speciation of radionuclides (for example, ground water chemistry) and (2) to calculate the solubilities of radionuclides under conditions that are not directly covered by Solubility Measurements (Activity 8.3.1.3.5.1.1) and Speciation Measurement (Activity 8.3.1.3.5.1.2).

The primary environmental parameters that control solubility and speciation are ground water chemistry, ground water temperature, and radiation. The ranges of these parameters that will be covered in this analysis are governed by the conditions expected at the proposed Yucca Mountain repository and along flow paths to the accessible environment (Ogard and Kerrisk,

1984; Kerrisk, 1987).

The conditions covered by the solubility modeling analysis are the same as those outlined by Kerrisk (1985) for solubility measurements. Table 2 summarizes these conditions. The sensitivity of the solubility of important radionuclides to variations in ground water chemistry and temperatures within the ranges listed in Table 2 will be evaluated. If it is experimentally determined (see Section 3.1.1.5) that radiation is a significant parameter, attempts will be made to evaluate the sensitivity to variation in the radiation field. Input will also be obtained from Study 8.3.1.3.1 Groundwater Chemistry Modeling to insure that all potential groundwater chemistries are considered in modeling radionuclide speciation.

2.1.3.1 Rationale and Justification for the Approach Used to Model Solubility

The initial approach to modeling solubility and speciation is to use an equilibrium (thermodynamic) model. The model chosen is the EQ3/6 chemical equilibrium computer program ( Wolery, 1983; Wolery et al., 1988). Modeling solubility and speciation involves a two-step process: (1) validating the model and the thermodynamic data that support the model by comparing calculated solubilities and aqueous species concentrations of radionuclides with results from well-controlled experiments and (2) using the validated model to calculate solubilities as needed for sensitivity analyses or for support of performance assessment.

TABLE 2  
 ENVIRONMENTAL CONDITIONS FOR SOLUBILITY MODELING

Parameter	Range
Water Chemistry	Simple neutral electrolyte (NaClO <sub>4</sub> ) through complex, multi-ion solution approximating Well UE-25p# 1water.
pH	5 to 11
Temperature	20 to 95°C
Redox Conditions	0 to 500 mV vs NHE
Radiation	Alpha activity from waste element isotopes. The effect of radiation is actually incorporated into the pH / Eh ranges.*

\*Kerrisk (1985)

Using EQ3/6 to calculate radionuclide solubilities requires a set of thermodynamic data for the major aqueous species and the solids that could precipitate for each radionuclide of interest, as well as data for the constituents of the ground water at Yucca Mountain. These data are obtained by analyzing the results of speciation and solubility experiments involving the radionuclides, by performing theoretical calculations, and by making comparisons with elements whose chemical behavior is similar. Many of the data needed have been obtained from the chemical literature. An evaluation of this literature data base, modification of existing data, and the addition of new data

found to be needed to model solubility represent a major part of this modeling activity. A significant amount of data base evaluation and modification has taken place (Wolery et al., 1989) under the auspices of the Geochemical Modeling and Database Development Activity (WBS 1.2.1.4.5) at Lawrence Livermore National Laboratory. However, this work has not emphasized radionuclides.

It is not certain at this time whether equilibrium models will describe the solubility of all important radionuclides. Models involving kinetic behavior or other non-equilibrium phenomena may be required to adequately model observed behavior. Non-equilibrium models will require additional input information including rate constants and reaction mechanisms. It is improbable that all necessary input data can be collected under the experimental activities in this Study Plan. If non-equilibrium modeling appears necessary, it will only be implemented using assumptions concerning missing input data, and conclusions drawn from the results of the non-equilibrium modeling will be qualified with respect to the level of approximation and the projected impact of the approximate result.

In addition to solubility, speciation, and thermodynamic data obtained from the literature and other sources within the Yucca Mountain Project (SCP Section 8.3.5.10.3.2), solubilities of important radionuclides obtained from solubility measurements (Activity 8.3.1.3.5.1.1) and formation constants of important aqueous species obtained from speciation measurements (Activity 8.3.5.3.5.1.2) are needed to perform the analyses described here. Data are also needed that describe the expected conditions at the repository and along flow paths to the far field. The most important environmental information is groundwater chemistry (SCP Sections 8.3.1.2.2.7.2, 8.3.1.2.2.4.8, and 8.3.4.2.4.1.3).

#### 2.1.3.2 Constraints on the Solubility Modeling Study

Solubility modeling depends on site characterization activities to define existing and expected future conditions at Yucca Mountain. Solubility calculations used in these models will be validated only for the range of environmental conditions covered by Solubility Measurements (Activity 8.3.1.3.5.1.1) and Speciation (8.3.1.3.5.1.2). Small extrapolations are possible for ground water compositions or temperatures different from those from which the data have been derived. Equilibrium modeling is limited by the assumption that, over the time scale of interest, chemical equilibrium exists in the system. This limitation is relieved to some extent by the validation process. Solubility and speciation measurements will identify the solids controlling solubility. This experimental work, used in conjunction with assumed equilibrium in the aqueous phase, allows application of this technique.

The Solubility Modeling activity is presently scheduled to begin in FY94. This starting date anticipates the availability of a version of EQ3/6 that has undergone software quality assurance review. This starting date will be timely enough to accomplish the necessary interfaces and provide the needed support for Activities 8.3.1.3.5.1.1 and 8.3.1.3.5.1.2. However, if initiation of modeling studies is further postponed, or if the modeling code must be qualified, the schedule for Activity 8.3.1.3.5.1.2 in particular will need to be adjusted.

#### 2.2 Rationale for the Study of Colloid Formation, Characterization, and Stability (Activity 8.3.1.3.5.2.1)

##### 2.2.1 Rationale and Justification for the Selection of Properties of Radiocolloids

Several radionuclides that are expected to be found in the waste emplaced in the repository are known to form natural colloids under chemical conditions similar to those found in the ground water at the Yucca Mountain site. These colloids could form in the emplacement area or along flow paths to the accessible environment, and thus radionuclides could be transported as colloids or

dissolved species, or both. In addition, the colloids may disintegrate into other soluble ionic species. Therefore, a thorough characterization of these colloids under relevant conditions is essential to permit assessment of the concentration limits and transport mechanisms for the radionuclides at the site. Substances other than radionuclides form small particles that can be suspended in solution. Radionuclides may be adsorbed on these solids, forming complex colloids that could be transported in ground water. Complex colloids are considered in detail in Study 8.3.1.3.4.1 (Batch Sorption) under Activity 8.3.1.3.4.1.4 (Sorption on Particulates and Colloids). The transport properties of these complex colloids are also considered in Study 8.3.1.3.6.1 (Dynamic Transport) under Activity 8.3.1.3.6.1.5 (Filtration). This study will attempt to characterize the radiocolloids by collecting data and other existing information pertinent to the following questions.

- Which radionuclides can form colloids?
- What chemical and environmental conditions favor the formation of these colloids?
- What are the chemical and physical properties of these colloids?
- What factors influence the stability of these colloids?

The first question has been investigated in detail (Hobart et al., 1987; Newton et al., 1986b; Nitsche, 1987; Olofsson et al., 1982; Kim, 1986; Allard, 1982; Thiyagarajan et al., 1990). At present, only plutonium and americium have been identified definitely as colloid-forming radionuclides. In the initial stages of the investigation, we will emphasize the study of plutonium colloids because it is expected to be an important form of plutonium in the far-field. In subsequent stages of this study, we will focus on colloidal americium. If the solubility studies identify colloidal neptunium as an important species, this species will also be incorporated into the latter stages of the colloid study. No other colloidal radionuclides of consequence are anticipated.

The remaining three questions all pertain to the fundamental properties of the natural radiocolloids but in a very broad sense. To focus this investigation, it is first necessary to enumerate the specific colloidal properties that will be studied and to indicate the importance of these properties to YMP issues and information needs. The emphasis of the research in this activity will be to elucidate these specific colloid properties. All fundamental colloid properties fall into one of two categories: those that can be classified as physical characteristics and those that can be classified as chemical characteristics. This distinction is convenient primarily for organizing the discussion of this activity. The specific experimental details of this investigation will be presented later in this section and in Section 3.4.

The most important physical characteristics of the natural colloids are particle size, density, and bulk charge. All three of these are expected to be especially important in determining the transport characteristics of the natural colloids because these parameters govern such important properties as filtration, adsorption, and sedimentation. Knowledge of these physical characteristics is also crucial to the investigation of the chemical properties of the colloids because the chemical interactions will be predominantly heterogeneous [i.e., colloidal suspensions (sols) interacting with species dissolved in solution]. Thus, it will generally be desirable to be able to specify colloidal surface areas (which can be estimated from particle size data) and bulk charges for experiments designed to elucidate the chemical properties of the colloids.

The most important chemical characteristics of the natural colloids are chemical reactivity and colloidal structure. Reactivity refers to the rates and mechanisms of all chemical processes (including self-radiolysis) affecting colloid formation and stability, as well as to chemical equilibria. Thus, both equilibrium (thermodynamic) and non-equilibrium (kinetic) conditions are important to this study. We will study chemical reactivity to determine the influence of solution conditions on

colloid formation and stability. In particular, fundamental processes, such as the hydration of the aquated  $\text{Pu}^{4+}$  ion and the subsequent formation of  $\text{Pu}(\text{IV})$  colloid or the dissolution of colloidal suspensions, are all manifestations of the thermodynamic and/or kinetic properties of the colloids. Colloidal structure refers to the specification of colloid stoichiometry, the description of chemical bonding at the molecular level, and a specification of the disposition of the various atoms in the colloidal matrix. There are several important reasons for characterizing the structure of colloids. One of these is to obtain chemical bonding data (e.g., metal-to-oxygen bond strengths) to aid in interpreting observed reactivity data. Another is that a valid structural description of the disposition of the atoms in the colloid will aid in understanding and modeling colloid formation and dissolution and in understanding physical properties, such as bulk charge distributions and adsorptive interactions.

## 2.2.2 Rationale and Justification for the Tests and Analyses Selected to Investigate the Properties of Radiocolloids

We are currently developing the various tests and analyses to be performed for this activity. Surprisingly little is currently known about either the physical or the chemical characteristics of even the best-characterized radiocolloid, the  $\text{Pu}(\text{IV})$  colloid. Thus, it is impossible to determine at this point which of several possible test methods will provide the best route to a desired piece of information. For this reason, no preference for any particular method has been established. Instead, a reasonable and prudent course of experimentation has been devised to provide data on all of the aforementioned colloidal properties. Certain procedures and techniques that will form the basis of the initial phase of this investigation are outlined below. However, as data are collected and analyzed, new experimental approaches and techniques for acquiring additional information necessary for thorough characterization of the colloids will be suggested. These new approaches will be incorporated in this activity, as necessary.

Before describing the specific test methods to be implemented in the initial phase of the investigation, several general remarks are in order. The first concerns the specification of the experimental conditions that will be used in this activity to characterize colloidal properties. Because so little is currently known about the properties and behavior of the radiocolloids and because the best experimental approaches have not yet been identified, we will not initially emphasize experimental conditions that duplicate those expected at the proposed repository. Rather, most of the initial work will be carried out under conditions (such as dilute mineral acid solutions at room temperature) that have been used in earlier efforts to study actinide colloids, which is the most direct approach to assessing the various test methods. Subsequent experimental work in this study will be more Project-specific and will be carried out under a wide range of experimental conditions, including variations in the chemical composition of the water, temperature, and intensity of the radiation field. This experimental range will bracket the actual range of conditions expected at the repository and along the flow paths to the accessible environment. However, for completeness, we will rigorously simulate certain anticipated repository conditions e.g., by duplicating the chemical composition of water from Wells J-13 and UE-25p#1 for part of the experimental work.

At this time, it is expected that all of the proposed experimental work will be carried out at LANL and that site-specific data on colloid properties can be obtained by simulating anticipated repository conditions. Thus, this activity should have no direct impact on the proposed Yucca Mountain site, with the exception of a possible need for ground water samples from the site. Although the results from this activity are needed by several other activities and information needs (Section 1), it is not necessary that the results be available for these activities to begin. For this reason, there are no specific time constraints on this activity. Finally, the required levels of accuracy, where meaningful and appropriate, and precision for most of the chemical and physical properties of the colloids are conservatively estimated at ~5%. Many of these data will still be valid and significant to the issues and information needs at even lower levels of accuracy and/or

precision. Despite this, we will endeavor to obtain results with the highest possible levels of statistical significance.

#### 2.2.2.1 Rationale for the Tests Selected to Elucidate the Physical Characteristics of Radiocolloids

The physical characteristics of the radiocolloids to be investigated are particle size, particle density, and bulk particle charge. A logical working assumption in this investigation is that these physical properties may vary as a function of the chemical composition and temperature of the solutions in which the colloid forms and as a function of time. To assess the effects of these variations, we plan to conduct experiments in which pH, ionic strength, ionic composition, and temperature are varied. The investigation of the time dependence in the physical properties of the colloids is particularly important because the degree of time dependence will indicate the stability of the colloidal particles. Experiments will be conducted as a function of time to (1) determine the rate of aggregation and disaggregation of the particle, (2) establish whether there are upper limits to particle size and/or density, and (3) determine whether these properties reach steady-state values. We will conduct the experiments with different isotopes, at least for the plutonium colloid investigation, to examine the influence of alpha radiation fields on the physical properties of the colloids.

##### 2.2.2.1.1 Particle Size Determination of Colloids

The initial efforts to determine colloid particle size will rely on a technique known as autocorrelated photon spectroscopy (APS, Triay et al., 1991). This work will be done in collaboration with the LANL Dynamic Transport Task (Study 8.3.1.3.6). This method is based on the quasi-elastic scattering of incident laser light by particles suspended in solution and undergoing random diffusion (i.e., Brownian motion). The scattered light is collected and analyzed for intensity as a function of time. The result is an autocorrelation function, which is deconvolved for the diffusivity of the colloid particle. From the diffusivity, we can calculate the hydrodynamic radius (i.e., the particle size in solution) by the well-known Stokes-Einstein relationship (see below). In addition, by studying the angular dependence of the scattered light intensity, it is possible to determine the degree of sphericity of the colloid particles. The degree of sphericity is not a high priority in this investigation, but some samples may be examined for this property.

This technique has many advantages over other possible particle-sizing methods, such as electron microscopy and ultrafiltration. Foremost among these advantages is that APS provides absolute size information on colloid particles suspended in the solution in their natural hydrated state. Further, the size information includes both the mean particle size and the distribution of particle sizes about the mean. It is also possible to detect bimodal size distributions and degrees of sphericity as discussed above. In contrast, electron microscopy can provide specific size information but requires that the particles be dried. Thus, the data provided by this method may not adequately reflect colloid properties. Ultrafiltration using submicron-sized filters can be used on colloid samples suspended in solution, but the result is only upper and lower limits of particle size. The limits are set by the availability of commercial filters of sufficiently uniform pore size, and, at present, this availability is inadequate. In addition, colloidal particles adsorbed on the filters can interfere with this filtration method.

APS is not easily applied if there is a high degree of polydispersity in the colloid particle size. In addition, extreme care must be taken to remove or exclude dust particles and gas bubbles from the test solutions. Based on some preliminary results, the former limitation is not expected to cause problems in the radiocolloid study, and the latter limitation can be overcome with attention to experimental technique. The accuracy of the APS method is expected to be  $\pm 5\%$ , which is adequate for this investigation. The level of precision is comparable and is also adequate for this study.

#### 2.2.2.1.2 Determination of Colloid Particle Density

We will determine the density of the radiocolloid particles by an ultracentrifugation technique (Rundberg et al. 1988). Solutions of the suspended colloid are centrifuged at very high centripetal force to effect a separation of the colloid and the resulting stratified solution is analyzed for colloid concentration as a function of depth in the centrifuge tube. We can then calculate the colloid density from the laws of sedimentation (see below). However, a critical component in this calculation is particle size. Thus, it will be necessary to determine the particle size to determine the density. All other factors involved in the density calculation are either experimental constants or well-known physical constants. In principle, it is possible to get some information about the density-dependent distribution of colloids by analyzing sufficiently small depth increments in the centrifuge tube.

There are few, if any, other methods for determining colloid particle density. It may be possible to use simple pycnometric techniques to get some indication of colloid density, but because this approach is certain to be cumbersome and likely to be inaccurate, it is not currently under consideration. The accuracy and precision of the ultracentrifugation method for determining colloid particle density will be comparable to that obtained in the published report (Rundberg et al., 1988). These levels of accuracy and precision are expected to be adequate for this investigation. Finally, although adsorption of colloid particles on the centrifuge tube walls may alter the results produced by the ultracentrifugation method, it should be possible to mitigate this problem by proper treatment of the walls of the tubes or by correcting for this effect in the calculations.

#### 2.2.2.1.3 Determination of Colloid Bulk Charge

No specific decisions regarding the method(s) for determining the bulk charge on the colloidal particles have yet been made, but two approaches are currently under consideration. The first approach is to use electrophoresis, in which the charged particles of interest are suspended in an appropriate support medium and a high electric potential is imposed across a pair of electrodes in the medium. The charged particles then migrate in response to the electric potential. The extent of migration of the particles as a function of the applied potential and time can be used to calculate the charge-to-mass ratio of the particles. Then, having determined the average mass of the colloid particles from size and density data, we will be able to ascertain the average bulk charge on the colloid particles. A commercial instrument (ZetaSizer) is available for these determinations.

A second possible approach to determining bulk charge on the colloids is to use the proven ability of certain simple inorganic anions, such as nitrate ion ( $\text{NO}_3^-$ ), to precipitate the colloid as a "salt" of the anion (Bell et al., 1973). This method is used to study the variations in the concentration of the unprecipitated colloid as a function of the concentration of the simple anion. Mathematical expressions similar to solubility product expressions are then used to determine the particle charge. Although this approach appears to be straightforward from an experimental point of view, it is unclear at this time whether such a technique would be generally applicable to the study of all radiocolloids and under all the relevant chemical conditions.

It is impossible at present to assess the accuracy or precision of either of these techniques for determining bulk charge on the colloids. However, the most important piece of information concerning bulk charge is the sign of the charge (i.e., cationic or anionic). This will be determined with high accuracy by either method. For the absolute magnitude of the charge, uncertainties of 10-20 % are probably acceptable. The anion precipitation technique is inherently less accurate than the electrophoresis method because the data analysis required in the precipitation method involves construction of logarithmic concentration plots ("log/log" plots), which tend to be somewhat insensitive. However, even this assessment is tentative because it is still unclear what the magnitude of the bulk charge values will be. Large values for the bulk charge would reduce

the amount of uncertainty in the precipitation method. Clearly, the precipitation method offers the advantage of experimental simplicity. Thus, a definite choice of techniques for determining the bulk charge parameter will likely have to await testing of both methods.

#### 2.2.2.2 Rationale for the Tests Selected to Elucidate the Chemical Characteristics of Radiocolloids

The principal chemical characteristics of the radiocolloids to be addressed in this activity are reactivity and structure. It is expected that the chemical characteristics of the colloids will be influenced by the chemical composition and temperature of the solutions containing the colloids and will perhaps vary as a function of time. In fact, variation in the chemical composition and temperature of the solutions containing the colloids will be one of the primary methods used to elucidate the chemical reactivity properties of the colloids. The structure of the colloids may also be strongly dependent on the composition of the solutions, particularly with respect to the identities and concentrations of the electrolytes. Thus, variations in solution pH, ionic strength, electrolyte composition, and temperature will be integral parts of this investigation. The effects of intense radiation fields may also strongly affect the chemical characteristics of the colloids, especially with respect to attainment of chemical equilibrium (Newton et al., 1986b). Thus, investigations that use isotopes with differing specific activities are planned, at least in the case of the plutonium colloid.

Before we discuss specific tests, an important point should be emphasized: the approach to discerning the chemical properties of the radiocolloids differs distinctly from the approach to evaluating the physical characteristics of the colloids. The physical properties of the colloids are well-defined quantities that could, in principle, be investigated using a single technique with reasonable assurance that a specific value for the quantity of interest would result. For this reason, it is legitimate to compare the various techniques that could be used to solve a specific problem (e.g., determining particle size by APS versus ultrafiltration) and to select the probable best technique. In contrast, although a host of possible techniques and procedures can be used to determine chemical properties (e.g., colloid structure), the various methods provide complementary results, which, taken together, lead to a description of the chemical property of interest. For this reason, rather than focus on which of several methods is best for a particular characterization, and why, this study plan describes all of the tests that are currently planned. The lists described here are not exhaustive lists but will be supplemented as new techniques become available during this investigation.

##### 2.2.2.2.1 Chemical Reactivity of Colloids

The study of colloid reactivity will be concerned primarily with elucidating the rates and mechanisms (i.e., the kinetic properties) of colloid formation and dissolution under a variety of conditions, particularly those conditions expected at the proposed repository site. In addition, the possible existence of chemical equilibrium (i.e., the thermodynamic properties) in the colloid systems will be explored.

The principal technique for these investigations will be ultraviolet, visible, and near-infrared electronic absorption spectroscopy (Hobart et al., 1989). Kinetic data will be acquired as a function of time. This technique is based on the measurement of the characteristic electronic transitions in species that are either suspended in solution (colloids) or dissolved in solution (reactants and dissolution products in the colloid formation and dissolution processes). Because every species possesses a characteristic electronic spectrum whose spectral band intensities are proportional to the concentration of that species, it is possible, under optimum conditions, to use these electronic spectral data both to identify and quantify the various species present in the colloid containing solutions. The accuracy of this technique is typically quite good, even for weakly absorbing species at moderately high concentrations. For example, mineral acid solutions of

Pu(IV) can be detected routinely at  $10^{-4}$  M with an accuracy of ~5%. This level of accuracy is adequate to obtain meaningful kinetic rate data and equilibrium constants. However, it may prove necessary to use even lower concentration levels in this study to properly simulate expected site-specific conditions. If this is the case, it is still possible to obtain these same electronic spectral data, but PAS or related methods would be necessary.

Another general approach to characterizing reactivity is to apply electrochemical methods to study the redox properties of the colloids (Hobart et al., 1989). The principal emphases in these investigations will be to determine the potentials at which reduction and oxidation of the colloids take place and to investigate the kinetics of the redox transformations. These redox properties are of fundamental importance to colloid characterization because they are a viable mechanism for colloid degradation and radionuclide dissolution. These experiments will primarily use modern instrumental techniques, such as linear potential sweep voltammetry, controlled-potential coulometry, and standard three-electrode electrochemical cell designs. These designs will generally use either solid (platinum, gold, silver, carbon) or liquid (mercury) working electrodes. Using these instrumental methods, we can vary the potential of the system in a continuous manner while confining the redox transformations to the immediate vicinity of the working electrode. Additional experiments are planned using homogeneous redox reagents, such as the cerium(IV/III) redox couple, and heterogeneous reducing reagents, such as zinc amalgam. In this way, it will be possible to assess the differences in the redox reactivity of the colloids and to ascertain whether the reactivity is significant in the presence of dissolved redox reagents or surface-active redox reagents. The accuracy of the data to be collected in this activity is conservatively estimated to be 5 to 10 mV, which is entirely adequate. It is expected that the accuracy of any rate data collected in this study will be 5%, which is also quite adequate.

#### 2.2.2.2.2 Structure of Colloids

The emphasis in this activity will be on obtaining chemical bonding information for the colloids and on attempting to specify the disposition of the atoms in the smallest repeating structural entity ("unit cell") of the colloids. An absolute specification of the stoichiometry of the colloids would also be extremely valuable, but such information is not obtainable using currently available techniques. Thus, stoichiometric information must come from inferences drawn from other structural data. The principal techniques to be used in this characterization are x-ray diffractometry and Raman vibrational spectroscopy. Small-angle neutron scattering (SANS) has also been used recently to determine plutonium colloid structure and morphology (Thiyagarajan et al., 1990). Los Alamos has a neutron-scattering facility at which such work can be performed. However, these are protracted experiments from the perspective of both data acquisition and data reduction and analysis, and the results can be ambiguous. Thus, our efforts will focus first on the more tractable x-ray diffraction and vibrational spectroscopy work to attempt to obtain the desired structural data. If SANS experiments are warranted following the initial efforts they will be pursued.

We will use standard x-ray diffraction methods similar to those used to characterize the crystal symmetry and unit cell parameters in powdered solid samples for both dried colloid samples and concentrated suspensions of the colloid in solution. If well-defined x-ray patterns are obtained, the spacings of the lines in the pattern will be used to calculate the simple structural parameters, such as unit cell dimensions, according to well-established formulae. The application of x-ray diffraction methods to concentrated, undried suspensions is by no means straightforward, but this technology has been successfully demonstrated in our laboratories. It should be emphasized that this technique in general provides information on the average microscopic structural parameters for the samples under investigation. Thus, if the colloidal particles contain differing structural units, or if samples contain defect sites attributable to different nucleation processes or mechanisms, it may not be possible to discern these differences.

Raman vibrational spectroscopy is a very powerful tool for obtaining both crystal structure data to

complement the above x-ray diffraction results and molecular structure data from which chemical bonding information can be deduced. This technique is based on the inelastic scattering of incident laser light. The wavelength dependence of this scattered light is analyzed relative to the wavelength of the incident laser light to provide the Raman vibrational spectrum of the analyte. The crystal structure data are inferred from the vibrational spectrum of the lattice vibrational modes (i.e., those modes with energies typically below  $\sim 200 \text{ cm}^{-1}$ ). The energies and intensities of these lattice modes provide information on crystallinity and long-range order in crystalline environments. The data on molecular structure are inferred from the vibrational spectrum of the internal vibrational modes (those modes deriving from the stretching, bending, etc., of chemical bonds). The bond strength data can be calculated from the energies of these internal vibrational modes according to existing vibrational spectroscopic theory. As for the x-ray diffraction method, if the colloids possess differing structural units or significant populations of defect sites, these can mask or destroy the Raman lattice modes making the data interpretation related to long-range order more complicated.

Electronic spectroscopy will also be used to characterize colloid structure to obtain information that complements the data obtained using the other more incisive techniques. This technique is essentially the same as that for the characterization of chemical reactivity. Namely, the characteristic transitions between the electronic energy levels in the colloid will be measured. However, more attention will be focused on the theoretical basis for the energies and intensities of the electronic transitions. Theory predicts that both the energies and intensities of the electronic transitions are strongly influenced by the crystal and molecular structural properties of the analyte. Extracting this structural information from the electronic spectra is complicated. However, it is plausible to deduce this information by comparing the electronic spectra of the colloids with those obtained for other species, such as binary oxides, that are well characterized. Furthermore, these data are easily obtained using existing, conventional instrumentation.

We will also use well-characterized, model radionuclide compounds for the other techniques being implemented in this structural characterization. This approach will greatly assist in interpreting the often complex structural data and will save considerable time by eliminating the need for detailed theoretical calculations. In fact, a semi-quantitative description of colloid structure (e.g., identity of coordinating atoms, number of coordinating atoms, site symmetry) will be of great value in understanding and modeling the chemical reactivity of the colloids. For this reason, even though instrumental methods typically have a high level of accuracy, neither accuracy nor precision need be overwhelming concerns in this structural characterization.

It should be emphasized that the best approach that can be taken for the structural characterization of colloids is a combined one, in which many different sources of data are considered in deriving the best possible description of the microscopic structure of the colloid species. Even if this approach falls short of an unique, explicit description, the effort is valuable. For example, the data might still be used to eliminate categories of potential structures from consideration, thereby enabling us to make better inferences concerning the sorptive properties of these species.

### 3.0 DESCRIPTION OF TESTS AND ANALYSES

#### 3.1 Tests and Analyses for Measuring Radionuclide Solubility (Activity 8.3.1.3.5.1.1)

##### 3.1.1 General Approach

Equilibrium solubility conditions for a given radionuclide can exist when a solid containing that radionuclide is in contact with the solution for a sufficient time. The lowest aqueous solution concentrations of the radionuclide are controlled by the most stable solid that is in equilibrium with aqueous species of that radionuclide. Other more soluble solids containing the element should dissolve because they are less stable than the solid that controls solubility. This assumes a closed system at equilibrium.

##### 3.1.1.1 Oversaturation and Undersaturation

Ideally, solubility experiments should approach solution equilibrium from both oversaturation and undersaturation. The approach from oversaturation requires adding an excess amount of the element in soluble form to the aqueous solution and then monitoring the precipitation of insoluble material until equilibrium is reached. The solid formed must then be isolated and characterized. The approach from undersaturation requires a prepared, well-defined solid, which is allowed to dissolve in an aqueous solution until equilibrium is reached. In both cases, the solution concentration is measured as a function of time until equilibrium conditions are reached. This is the most reliable method for steady-state solubility determinations, and the one we will employ. First, we will perform experiments approaching steady-state concentrations from oversaturation and will characterize the solids that form. This procedure has the advantage of not specifying the solid that controls solubility but of allowing the system under investigation to determine the solid that will precipitate. We will then prepare these solids for use in experiments that approach steady state from undersaturation.

Solution kinetics will control the equilibration speed in a solubility experiment. Some solutions equilibrate rapidly, others more slowly. It must be demonstrated that equilibrium is reached, which is experimentally determined (for both oversaturation and undersaturation experiments) by measuring the solution concentration as a function of time. When the concentration stays constant for several weeks, it is assumed that equilibrium has been established. Because this assumption is based on judgment, the term "steady state" instead of "equilibrium" is more precise. The NRC defines "steady state" as "the condition where measurable changes in concentrations are not occurring over practical experimental times" (NRC, 1984). The change may be controlled by kinetics and may therefore be very slow and may not show in the experiment even after several years. These infinitesimal changes may require infinite experimental times. The steady-state solids formed in the experiments may therefore not represent the thermodynamically most stable solids with the lowest possible solubilities, but metastable solids having higher solubilities than the thermodynamically defined solids. The term "steady state" implies this condition.

Despite this constraint, time-limited laboratory solubility experiments can supply valuable information. They provide good estimates on the upper limit of radionuclide concentrations in solution because the experimentally determined steady-state concentrations are higher than the equilibrium concentrations.

##### 3.1.1.2 Phase Separation

Phase separations must be as complete as possible for these experiments. The separation of the solid from the solution often represents a significant practical problem in measuring solubility. Apparently higher or lower solubilities, compared with the steady-state values, can result from

incomplete phase separation or from sorption of solute during and after the separation. Incomplete phase separations (leaving some of the solid with the solution phase) lead to higher apparent radionuclide solubilities. Lower apparent solubilities are measured if constituents of the steady-state solution have been sorbed on filters during a filtration and on container walls after the separation.

Experimentally, the solids and solutions are separated based on differences in size (via filtration) or density (via sedimentation or centrifugation). Filtration is the more commonly applied technique because it physically partitions the solute and solids. Ultrafiltration (i.e., filtration using membranes <0.1  $\mu\text{m}$ ) can effectively remove colloidal particles from aqueous solution. Colloids are solids of an element under investigation that may not participate in the solubility equilibrium because reprecipitation or dissolution kinetics may be too slow. A potential problem with ultrafiltration is adsorption of soluble species on ultrafiltration membranes. Effective filters for solubility studies must pass soluble species through the filter quantitatively; that is, the filter either has no active sorption sites or any such sites on the membrane must be irreversibly blocked.

We will verify the most effective filtration methods for each nuclide studied. Filters will be judged to be adequate if they have a small enough pore size to retain the solids and colloids and if they also show no or only minimal sorption during multiple filtrations. These tests do not attempt to determine the filter sorption equilibrium but are made only to find filters that do not disturb the solution equilibrium during filtration.

#### 3.1.1.3 Identification of Solids

Thermodynamically meaningful results require the existence of a well-defined solid phase, which generally consists of crystalline material. The solids formed from oversaturation in solubility tests must be clearly identified by physical or chemical characterization methods. Only when identified unambiguously can the solid be synthesized for use in undersaturation solubility tests. We will attempt to conclusively identify the solids by x-ray powder diffraction analysis, Fourier transform infrared spectroscopy (FTIR), and neutron activation analysis (NAA). If we suspect that the solid formed contains more than one individual solid, FTIR can be used to identify the individual components of the mixture even when their weight is only 1% of the bulk solid's weight. We are currently developing the use of advanced techniques using synchrotron-based x-ray radiation. These techniques utilize x-ray absorption spectroscopy to give information on the composition of the solid and on the oxidation states of the metal ions being present in the solid. The most advanced technique that can be used is Near Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS, Stöhr 1992).

#### 3.1.1.4 Determination of Oxidation States and Speciation

This study is closely related to Activity 8.3.1.3.5.1.2, Speciation Measurements, which identifies complexes that may form between radionuclides and complex ions present in the ground water near the repository. The related activity provides important thermodynamic data. We will use the information to interpret results from oxidation state determinations in solubility test solutions. For example, if the radionuclide speciation activity shows that plutonium forms strong carbonate complexes, we can perform calculations to determine whether these complexes also form under the conditions of the solubility experiment. The knowledge that plutonium carbonate complexes are present under solubility conditions will help us to interpret results from oxidation state determinations in steady-state solubility solutions.

The oxidation state in solution describes the charge of soluble species, and speciation describes their nature. Radionuclides can have a single or several different oxidation states in solution. They can be present as simple ions or as complexes. When the ions react with one or several other solution components, they can form soluble complexes. Information on oxidation states and

speciation is important for transport models that simulate migration and sorption along the flow path. The charge and speciation of radionuclides will control their adsorption and transport in the geologic host.

Oxidation states and speciation in solution are commonly determined by (1) absorption spectrophotometry, (2) ion exchange chromatography, (3) solvent extraction, (4) coprecipitation, and (5) electrochemistry. Of these methods, only absorption spectrophotometry can provide information on speciation, while the others identify only the oxidation state in solution.

Absorption spectrophotometry has a detection limit of about  $10^{-5}$  M. This relatively high concentration limits the application of spectrophotometry for speciation determination in solutions from radionuclide solubility studies because the solubilities can be several orders of magnitude below  $10^{-5}$  M. PAS and PDS techniques described previously provide much greater sensitivity, approaching  $10^{-8}$  to  $10^{-9}$  M.

The methods listed above as 2 through 5 determine only the oxidation state in solution, and most do so indirectly. These indirect methods, however, detect very small concentrations ( $10^{-10}$  M and below), which is useful for radionuclide solubility studies. Solvent extraction and coprecipitation are often used successfully to determine the oxidation states of ions in very dilute solutions. Ion exchange chromatography is less reliable for this purpose because the exchange resin often electrochemically reduces the solution ions, which gives wrong results for the oxidation state distribution. Electrochemical detection reduces or oxidizes the solution ions and measures the potentials of the reduction and oxidation reactions, respectively. The potential then identifies the individual ion. Electrochemistry needs fast kinetics and reversible thermodynamics for the reduction or oxidation step. These criteria greatly limit the method because many radionuclide ion reactions are irreversible and slow (e.g., the reactions of  $\text{NpO}_2^+ / \text{Np}^{4+}$ ,  $\text{PuO}_2^+ / \text{Pu}^{4+}$ ).

The oxidation state of species in solution will be determined by a solvent extraction and coprecipitation technique. We will also attempt to determine the nature of the solution species by spectrophotometry when the solution concentration is greater than  $10^{-6}$  M.

The sensitivity of the available analytical methods limits this study. PAS is needed to determine directly the species in the supernatant solutions of the solubility experiments at submicromolar concentrations. Activity 8.3.1.3.5.1.2, Speciation Measurements, addresses this capability.

### 3.1.1.5 Radiation

Radiation can affect the solubility of radionuclides by altering the composition of the water and/or by altering the crystallinity of the solids that form. The primary effects of alpha radiation are a change in pH and a trend toward more oxidizing conditions in the water. Solids of alpha-emitting elements tend to show self-irradiation damage to their crystal structure. The effects of alpha radiation on solubility will be investigated by using actinide isotopes that are present in high-level waste. Two isotopes of the same element that are significantly different in their specific alpha activity will be used for selected solubility experiments. For example,  $^{239}\text{Pu}$  has 15.6 times the specific activity of  $^{242}\text{Pu}$ , and  $^{241}\text{Am}$  is 17.1 times more radioactive than  $^{243}\text{Am}$ . Because the spatial range of alpha particles is very short, the effects of alpha radiation on the solubility of coexistent radionuclides that are not alpha emitters will not be studied. The effect of alpha radiation on water composition will be considered in defining the ranges of water composition to be used for solubility measurements.

We will not consider the effects of gamma radiation on solubility because gamma radiation levels will be reduced considerably by the end of the containment period. Possible influences of the remaining gamma radiation levels on water composition are included in water compositions already considered.

### 3.1.2 Parameters and Materials Needed for the Solubility Study

#### 3.1.2.1 Radionuclides in the Waste to Be Emplaced at Yucca Mountain

Solubility determinations will be made for the following groups of radionuclides:

- neptunium, plutonium, and americium;
- thorium and uranium;
- radium, nickel, tin, and zirconium; and
- other radionuclides.

The category of other radionuclides will be specified in the future and will include radionuclides being identified as important to solubility as knowledge progresses.

#### 3.1.2.2 Parameters to Be Measured

The key parameters to be measured and / or controlled in the solubility study are the

- concentrations of the solution as a function of time,
- pH,
- temperature,
- redox potential (Eh),
- oxidation state of the soluble ions and complexes at steady state, and
- nature and identity of the solids formed at steady state.

The solution concentration is measured as a function of time; when consecutive measurements give the same concentration over a period of several weeks, the solubility test has reached steady-state conditions.

During a solubility test, the control of constant hydrogen activity (pH) is important because solubility is hydrogen ion activity-dependent. The solubilities of individual radionuclides will be measured over a pH range that brackets the natural pH value of the ground water. The bracket covers a change in hydrogen activity that does not exceed two orders of magnitude below or above the natural pH value. This pH range covers the possibility that shifts in pH might occur. Shifts in pH can be caused by alpha radiation and also by chemical changes when the radionuclides react with ground water. Furthermore, testing solubility over a pH range instead of a single pH provides a better understanding of the influence of pH on solubility.

The redox potential (Eh) of the steady-state solutions are measured to supply chemical modeling efforts with a reference value. Without modeling, however, the redox measurements are only of limited value because they may represent a combination of different reduction-oxidation reactions for each solubility measurement. These measurements are not comparable with Eh measurements in natural waters where many different redox reactions can occur.

The oxidation state determinations of soluble ions and solution complexes provide information on the charge of the soluble species. This information is vital as input for transport and retardation models.

The identification of the solids formed at steady state is very important. Solubility tests are complete and valid only when the solubility-controlling solid(s) is (are) clearly identified.

### 3.1.2.3 Experimental Conditions for the Solubility Tests

#### 3.1.2.3.1 Control of pH and Total Dissolved Carbonate

Shifts in pH from nominal well water pH values can be caused by alpha radiolysis and by chemical reactions between ground water and the constituents of the waste package. The nominal pH values of water from Wells J-13 and UE-25p#1 are 7 and 6.7, respectively. Therefore, solubilities will be measured at pH values of 6, 7, and 8.5.

The ground water from both wells contains carbonate. Changing the pH to values different from the natural pH will change the carbonate and bicarbonate concentrations. The total carbonate concentration, however, will remain constant in a closed system. During the solubility experiments, the total carbonate content of the solutions will be maintained at the amount the water has in its natural state; i.e., the water used for solubility measurements at pHs 6, 7, or 8.5 will contain the same amount of total carbonate. These levels will be maintained by controlling the carbon dioxide partial pressure with carbon dioxide/argon mixtures of defined carbon dioxide content. The carbon dioxide content needed for each pH at the given temperature is calculated using the thermodynamic constants for the carbonate/bicarbonate/carbon dioxide equilibrium. The calculated mixture is purchased from a commercial supplier and is used to equilibrate the appropriate ground water. If, after a pH adjustment has been made to reach the target pH of the ground water and after several days of equilibration time have passed, the ground water remains steady at the target pH, the validity of the thermodynamic calculations that led to the carbon dioxide concentration in the gas mixture is verified.

The following example illustrates the method of calculating the partial carbon dioxide pressure for a system of given ionic strength, pH, and temperature. The thermodynamic equilibrium constants for an open carbonate system are (Stumm and Morgan, 1985):

$$[\text{H}_2\text{CO}_3]/p\text{CO}_2 = K_H \quad (1)$$

$$[\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] = K_1 \quad (2)$$

$$[\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] = K_2 \quad (3)$$

where  $K_H$  is the Henry's constant, and  $K_1$  and  $K_2$  are the first and second dissociation constants of carbonic acid, respectively.

The total carbonate concentration is then

$$C_T = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (4)$$

Rearrangement and substitution of Equations 1, 2, and 3 in Equation 4 gives

$$C_T = p\text{CO}_2 K_H \{1 + (K_1/[\text{H}^+]) + (K_1 K_2/[\text{H}^+]^2)\} \quad (5)$$

Well J-13 ground water has the following specifications at 25°C:

- pH = 7, i.e.,  $[\text{H}^+] = 10^{-7}$  M;
- Alkalinity:  $[\text{Alk}] = 2.34 \times 10^{-3}$  equiv./L; and
- $I = 3.6 \times 10^{-3}$  M (ionic strength).

The carbonate alkalinity (Stumm and Morgan, 1985) is defined as

$$[Alk] = [HCO_3^-] + 2[CO_3^{2-}] \quad (6)$$

Because the YMP groundwaters have near-neutral pH, the carbonate alkalinity approximates the total alkalinity. Combining and rearranging Equations 1, 2, 3, and 6 leads to the expression for the carbon dioxide partial pressure

$$pCO_2 = \frac{[Alk][H^+]/K_H K_1}{\{1 + 2K_2/[H^+]\}} \quad (7)$$

It is now necessary to determine the partial pressure of carbon dioxide required to maintain the Well J-13 water at pH 8.5 and 60°C while keeping the total carbonate concentration ( $C_T$ ) unchanged.

The constants  $K_H$ ,  $K_1$ , and  $K_2$  are obtained from the literature (e.g., Phillips et al., 1985). They are however, only available for 50 and 75°C and for ionic strengths of 0 and 0.1 M. Because the ionic strength of the J-13 water is very small, the values for 0 ionic strength have been chosen. Then, linear interpolation to 60°C between the 50 and 75°C values gives  $K_H = 10^{-1.77}$ ,  $K_1 = 10^{-6.29}$ , and  $K_2 = 10^{-10.15}$ .

First the  $pCO_2$  at pH 7 (the natural pH of J-13 ground water) must be calculated using Equation 7. The result of  $pCO_2 = 2.683 \times 10^{-2}$  atm or 2.683%  $CO_2$  is then used to calculate the total carbonate concentration ( $C_T$ ) using Equation 5. The result is  $C_T = 2.794 \times 10^{-3}$  M; this total carbonate concentration is to remain constant at any given pH of J-13 water. Rearranging Equation 5 leads to the expression

$$pCO_2 = \frac{C_T/K_H}{\{1 + \{K_1/[H^+]\} + \{K_1 K_2/[H^+]^2\}} \quad (8)$$

which can be used to calculate the  $CO_2$  partial pressure of J-13 ground water at pH 8.5 as  $pCO_2 = 9.863 \times 10^{-4}$  atm or 0.09863%.

The commercial gas mixture sometimes contains a slightly different carbon dioxide content than was originally ordered, which will be indicated on the analysis certificate. In these cases, Equation 8 can be rearranged to

$$[H^+] = K_1 + \{K_1^2 + 4K_1 K_2 \{(C_T/K_H pCO_2) - 1\}\}^{1/2} / 2\{(C_T/K_H pCO_2) - 1\} \quad (9)$$

and the equilibrium pH can be determined for that mixture. For example, if the supplier shipped an argon/carbon dioxide mixture of 910 ppm carbon dioxide instead of 850 ppm, the equilibrium pH would be 8.46 instead of 8.50. Then, the solubility test would be conducted at pH 8.46.

The test solutions will be kept in cells with sealed ports at the top. The cells are made of chemically inert and relatively radiation-resistant materials such as teflon or polypropylene. Their volume is about 90 mL. The ports at the top accommodate the permanent emplacement of a pH electrode, a sealable opening through which to draw samples, and three 1/16-in. diameter teflon lines for addition of acid, base, and the carbon dioxide mixture (Tucker et al., 1988). The addition of acid or base is necessary to control the pH at the targeted value when the solution pH changes because of chemical reactions in the solution or because of radiolytic effects. This addition is done by a computer-operated control system (pH stat). The pH stat records and adjusts the pH values of the test solutions at the target values in accordance with standard deviations selected by the user.

The pH stat uses small amounts (usually between 5 and 50  $\mu$ L) of dilute (0.05 to 0.1 M) perchloric acid or carbonate-free sodium hydroxide solution to adjust the pH. When the pH fluctuates over

long times, possibly caused by a high alpha-radiation field or complex chemical reactions, these additions can increase the ionic strength of the test solution. This reaction is unavoidable, and there is no method to prevent it when simultaneous control of pH and total carbonate concentration is necessary. The pH adjustments, however, should not substantially change the water chemistry of the test solution.

Standard deviations in pH of 0.1 to 0.2 pH unit should be satisfactory for the solutions at near-neutral pH values. If the solubility tests show a stronger pH dependence, the pH will be controlled more stringently. pH electrodes require standardization with NIST-certified buffer solutions to get accurate pH measurements. The accuracy of the measured pH is controlled by (1) the accuracy of the certified standard buffer used for the standardization and (2) the degradation of the pH electrode after the calibration. The accuracy of a newly standardized pH electrode should be accurate to within 0.01 pH unit. Semiweekly restandardization will limit the degradation error to between 0.05 at 25°C and 0.1 pH units at 90°C.

#### 3.1.2.3.2 Temperature Control

To study the effect of temperature change on solubility and to provide orientation data for extrapolation to temperatures above the boiling point of water, solubilities will also be measured over a range of temperature. For Well J-13 water, solubility tests will be done at 25, 60, and 90°C. For Well UE-25p#1 water, tests will be done at 25 and 60°C. Solubility tests in the neutral electrolyte (sodium perchlorate) will also be done at 25 and 60°C.

The test cells are kept in an aluminum heater block to control their temperature. Several standardized thermocouples measure the temperature of the block during the test, and the pH stat records the temperature periodically. Because solubilities depend on temperature, the solution temperature will be controlled with an accuracy and precision of less than 1.5°C. The electric heater is mounted on an orbital shaker that shakes the solutions continuously.

#### 3.1.2.3.3 Determination of Oxidation State

At steady state, the solid and the supernatant solution will be analyzed separately. The oxidation state, and possibly the speciation of the supernatant solution, will be determined, providing information on the charge of the solution species. The charge of species in solution determines their sorption characteristics and thus the migration behavior of the soluble radionuclide. For a steady-state solution with relatively high radionuclide concentrations ( $>10^{-6}$  to  $10^{-5}$  M), ultraviolet, visible, and near-infrared absorption spectrophotometry will be used. Ions of a specific oxidation state have one or more spectral absorption bands at specific wavelengths. The wavelength of the absorption band is determined by the oxidation state of the solution ion or species. When the oxidation state changes, new absorption band(s) are detectable at different wavelengths. The characteristic absorption bands of many radionuclides are known, and changes in oxidation state during the experiment can be determined by comparing a spectrum of the radionuclide taken at the beginning of the solubility test with a spectrum taken at the end of the test.

Steady-state solutions with low concentrations ( $< 10^{-5}$  to  $10^{-6}$  M) cannot be analyzed by spectrophotometry. A combination of several solvent extractions and coprecipitation methods will be used to determine quantitatively the oxidation state in solution. This method was successfully tested for plutonium (Nitsche et al., 1987) using solutions of known oxidation states. The method uses the organic extractants thenoyl-trifluoro-acetone (TTA), methyl-isobutyl-ketone, and di(2-ethylhexyl) phosphoric acid (HDEHP) and lanthanum fluoride as coprecipitant. The extraction characteristics of TTA and HDEHP are pH-dependent; the dependence is used to separate different oxidation states. Table 3 lists the methods used and indicates their selectivity for the specific oxidation states.

Extraction and coprecipitation are performed in parallel. More reproducible results can be obtained when only a single extraction step is performed at a time on several separate solutions in parallel instead of performing several sequential extractions on a single solution. Individual oxidation states can be calculated as the difference between two or more different separations [e.g., HDEHP (pH 0) - TTA (pH 0) = PuO<sub>2</sub><sup>2+</sup>; LaF<sub>3</sub> (supernatant) - PuO<sub>2</sub><sup>2+</sup> = PuO<sub>2</sub><sup>+</sup>]. The accuracy for determining a single oxidation state is between 2 and 10%, depending on the initial concentration of the supernatant solubility solution. An oxidation state determination of a 10<sup>-9</sup> M <sup>239</sup>Pu solution with an accuracy of 10% for each oxidation state is satisfactory.

**TABLE 3**  
**METHODS OF DETERMINING THE OXIDATION STATE**  
**IN PLUTONIUM SOLUTIONS**

Method	Oxidation State Distribution	
	Organic Phase	Aqueous Phase
TTA extraction at pH 0	+4	+3, +5, +6, poly <sup>a</sup>
TTA extraction at pH 4	+3, +4, +6	+5, poly
HDEHP extraction at pH 0	+4, +6	+3, +5, poly
HDEHP extraction at pH 1	+3, +4, +6	+5, poly
Hexone extraction	+4, +6	+3, +5, poly
LaF <sub>3</sub> precipitation <sup>b</sup>	+3, +4, poly in precipitate	+5, +6 in supernatant

a Poly is Pu(IV) colloid  
 b Method with "holding oxidant."

**3.1.2.3.4 Analysis of Solid Phase**

The steady-state solids will be analyzed by x-ray powder diffraction measurements. A few micrograms of each radionuclide precipitate are placed in a quartz capillary tube. The tube is sealed and mounted in a Debye-Scherrer camera and irradiated with nickel-filtered copper K $\alpha$  x-rays. The compound is identified by comparing its powder pattern with patterns of known compounds listed in the literature. When the solids do not produce any pattern or when the pattern cannot be assigned to any known compounds, other methods will be used to determine the composition and stoichiometry of the unknown solids. FTIR will give information on the presence and bonding of hydroxide and carbonates. NAA will give information on the elemental composition and stoichiometry of the unknown solids.

**3.1.2.4 Materials Needed**

Samples of ground water are needed in sufficient amounts to run solubility measurements. Approximately 10 L of water from Wells J-13 and UE-25p#1 are needed. Supplies of radionuclides of sufficient purity are needed for solubility measurements.

### 3.1.2.5 List of Equipment

Radionuclide solubility studies require facilities equipped to handle elements that are highly radioactive and/or highly toxic. The control on the atmosphere above the experimental solutions necessitates performing the experiments in controlled atmosphere glove boxes. In addition to standard laboratory equipment, the following equipment will be used for this study:

- counting equipment with associated electronics:
  - intrinsic Ge detector (LBL design) for x-ray and low-energy gamma spectroscopy,
  - NaI (Beckmann, Gamma 4000),
  - liquid scintillation counter (Packard A460) for alpha and beta counting,
  - alpha gross counters (LBL design),
  - low-level alpha/beta gross counters (Tennelec, LB1000),
  - Si surface barrier detector (LBL design) for alpha spectroscopy;
- electrochemistry equipment:
  - potentiostat (EG&G, PAR Mod. 264A),
- atomic emission spectrometer dedicated for actinide purity analysis at trace levels (Baird Eagle Mount);
- x-ray powder diffraction analyzer (Phillips Electronic Instruments, Norelco Model 111);
- spectrophotometers:
  - ultraviolet near infrared with remote capability through fiber optics, computer-controlled (Guided Wave, Inc., Model 260), and
  - ultraviolet near infrared, double-beam recording (Cary 17H);
- computer-controlled data acquisition and feedback control system for pH control of solubility experiments (LBL design, TWS-INC-DP-76, Data Acquisition and Feedback Control System for Solubility Studies);
- electrical block heater for temperature control of solubility experiments inside the glove box; temperature range 25 to 90°C, tolerance to +0.5°C, maximum surface temperature not to exceed 30°C;
- manostats for carbon dioxide control above the experimental surfaces (LBL- design);
- containers for the solubility experiments: about 90-mL, leak- and gas-tight up to 100°C, resealable top openings for sampling, pH electrode insertion ports, acid and base injection lines, carbon dioxide/argon gas inlet line (design of commercial stock modified by LBL);
- shaker table to agitate the solubility samples (Lab Line Instr. Inc., Mod. Junior Orbit);
- high-speed centrifuge with temperature-controlling capability up to 80°C (Savant Instruments, Inc., Model HSC 1000); and
- high-speed microcentrifuge, capability 15,000 g (Eppendorf, Model 5412).

### 3.1.2.6 Expected Results of Experiments

The experiments in this activity will provide the following:

- Steady-state concentrations of radionuclides in water from Wells J-13 and UE-25p#1 and in noncomplexing perchlorate solution at the temperatures indicated will be reported. The expected concentration range for the solubilities is from about  $10^{-2}$  to  $10^{-10}$  M, depending on the radionuclide. Because there are no studies that report solubilities in aqueous solutions or groundwaters similar to the YMP groundwaters, it is difficult to estimate these values. However, using data for the actinides from solubility and complexation studies with individual complexing agents (Allard 1982, Nitsche 1986), we estimate the expected concentration for a) neptunium between  $10^{-3}$  and  $10^{-4}$  M, b) plutonium between  $10^{-6}$  and  $10^{-4}$  M, and c) americium between  $10^{-5}$  and  $10^{-10}$  M. The large variation in concentration reflects solubility dependence on the pH range studied. First results of this study are confirming the validity of our estimates (Nitsche 1991a, Nitsche 1991b, Nitsche et al. 1992c).
- Where possible, the oxidation states of the dissolved radionuclide species at steady state will be determined.
- Redox potentials (Eh) of the solubility solutions at steady state will be measured.
- The solids that control solubility in each water composition will be characterized. This characterization will include composition with a phase identification, if possible. Efficiencies of phase separation techniques will be reported based on multiple-filtration and centrifugation experiments.
- Results from periodic checks of water composition after solubility experiments will be given.

A complete characterization of the solids formed in the solubility experiments may require analytical methods other than x-ray powder diffraction, atomic emission spectroscopy, and NAA. If necessary, mass spectrometry, electron microprobe, scanning electron microscopy (SEM), FTIR, x-ray fluorescence analysis, and other methods will be considered to further identify the solids.

### 3.1.3 Examples of Results for the Solubility Study

The plutonium solubility measurements in Well J-13 water at pH 7 and temperatures of 25 and 60°C provide results typical for this study (Nitsche 1991a, Nitsche 1991b, Nitsche et al. 1992a). The solubility was studied from oversaturation by addition of  $\text{Pu}^{4+}$  to the groundwater. The J-13 groundwater was sampled at the site by Los Alamos and an Eh of 700 mV was measured. It was filtered through 0.05 mm polycarbonate membrane filters at Los Alamos before it was shipped to the Lawrence Berkeley Laboratory where the solubility experiments are performed. The water's natural carbon dioxide partial pressure ( $\text{pCO}_2$ ) could not be preserved during filtration and shipping. The natural state was induced for these experiments by re-equilibrating the water with mixtures of  $\text{CO}_2$  in argon to preserve the water's total dissolved carbonate content ( $2.81 \times 10^{-3}$  M) at each temperature. Mixtures with 1.57% and 2.35% carbon dioxide gas were used for the 25° and 60°C experiment, respectively. The initial plutonium (IV) concentration was  $5.1 \times 10^{-4}$  M and  $9.2 \times 10^{-4}$  M for the 25° and 60°C, experiment, respectively.

Because the solubilities are highly sensitive to pH and temperature changes, close control of these parameters is necessary. We used a computer-operated control system (pH-stat) to maintain the aqueous actinide solutions at constant temperatures and pH values for the solubility experiments (Nitsche et al., 1992a). The pH-stat records and adjusts the pH values of the experimental solutions (J-13 water) at the target values with standard deviations not exceeding 0.1 pH unit. It uses small amounts (usually between 5 to 50 microliters) of dilute (0.05–0.1 M)

HClO<sub>4</sub> or NaOH solution for the pH adjustments. The water chemistry was not substantially affected by this adjustment. Temperatures were controlled within less than 1°C.

After efficient phase separation by ultra-filtration, periodic samples of the aqueous phase were counted for plutonium concentration by L x-ray spectroscopy (Nitsche et al., 1992b) and liquid scintillation counting. For the 25°C experiment, a steady state concentration of  $(2.3 \pm 1.4) \times 10^{-7}$  M was reached after approximately 18 days, but the solution was monitored for an additional 70 days to confirm steady state. In a plutonium experiment of 127 days at 60°C, steady-state concentrations were  $(3.8 \pm 0.8) \times 10^{-8}$  M.

Plutonium oxidation state analyses for these steady-state solutions determined the effects of temperature on the oxidation state distribution. As shown in Table 4, both solutions contained predominantly Pu(V) and Pu(VI). The solubility was six times smaller when the temperature was increased from 25 to 60°C,

TABLE 4  
 TEMPERATURE EFFECT ON PLUTONIUM OXIDATION STATE  
 DISTRIBUTION IN WELL J-13 GROUND WATER AT pH 7

Temp (°C)	Oxidation States (%)			
	Pu(IV)	Pu(V)	Pu(VI)	Pu(III + poly)
25	6 ± 1	73 ± 7	18 ± 2	5 ± 1
60	2 ± 1	44 ± 9	52 ± 4	3 ± 1

The solids from both experiments were subjected to x-ray powder diffraction analyses. The results showed that the solid formed at 25 °C was amorphous and the solid formed at 60°C was crystalline. The x-ray diffraction of the crystalline material could not be related to the reference pattern for any known compound. When treated with acid, the 60°C solid partially dissolved and gas evolution occurred. The evolving gas was most likely carbon dioxide. Further analysis of the dissolved solid by spectrophotometry showed characteristic absorption bands for Pu(IV) polymer. Based on these observations, we concluded that it is likely that a mixture of plutonium carbonate and Pu(IV) polymer was formed. Further characterization of the solids (i.e., by neutron activation analysis) will identify their composition.

In summary, this study shows that the solubility of plutonium in Well J-13 ground water is decreased by a factor of 6 when the temperature changes from 25 to 60°C. The plutonium, although it was tetravalent at the beginning, was oxidized to the penta- and hexavalent states at steady-state conditions. Penta- and hexavalent plutonium likely adsorb on geologic materials in a manner that differs from that of tetravalent plutonium. The solids formed at the lower temperature are likely plutonium colloids. With increasing temperature, the solids become crystalline and therefore thermodynamically more stable.

The solubility values supply an upper limit on the plutonium concentration. When compared with the solubility limits specified by 10 CFR 60 (NRC, 1988) for each radionuclide, the experimental solubility limits will provide the conformance criterion for the repository. If the experimental values are above the values specified by 10 CFR 60, other mechanisms of nuclide retardation along the

flow path must be considered.

### 3.2 Tests and Analyses for the Study of Radionuclide Speciation (Activity 8.3.1.3.5.1.2)

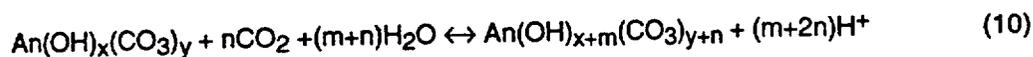
#### 3.2.1 General Approach to Determining Speciation

Because most commonly used techniques for speciation determinations are applicable at much higher concentration levels and at lower pH values, the study of speciation of the subject radionuclides in near-neutral ground water will involve tests and analyses that are in the developmental stages. Consequently, much of this activity is operating under the quality assurance (QA) guidelines set forth in TWS-QAS-QP-03.5, Procedure for Documenting Scientific Investigations. For many of the experimental procedures, the specific details have not been worked out, and implementation of these procedures will involve Edisonian methods. Furthermore, alternative approaches may be suggested in the course of these studies that are better suited or more expedient for characterizing speciation. These will be evaluated as they arise.

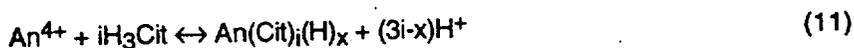
As discussed in Section 2.1.2.1 of this study plan, the principal approaches to determining speciation include the competitive complexation method; PAS, PDS, and LIF spectroscopic methods; and x-ray absorption and nuclear magnetic resonance spectroscopic methods.

##### 3.2.1.1 Competitive Complexation Method for Determining Speciation

In the first stage of these experiments, we will investigate the equilibrium in solutions of fixed carbon dioxide partial pressures and will measure pH values. These experiments will give relative equilibrium quotients and stoichiometric coefficients for reactions such as



where  $\text{An}(\text{OH})_x(\text{CO}_3)_y$  represents the least complexed species. (The charge on the complexes has been omitted here for clarity.) In the second stage, equilibria for reactions such as



will be examined. [Cit is the tri-anion of citric acid, and (H) signifies either protonation on the Cit or coordinated  $\text{OH}^-$ .] Finally, in the third stage, the competitive complexation equilibria, such as



will be examined. It will also be necessary to consider equilibria involving mixed carbonate and citrate complexes, such as  $\text{An}(\text{Cit})_{k-i}(\text{CO}_3)_{n-j}$ .

The experimental probe currently in use for the study of these equilibria is electronic absorption spectroscopy. Typically, the equilibrated solutions contain numerous species that absorb light in the ultraviolet, visible, and near infrared spectral regions. A specimen spectrum for Pu(IV) species is shown in Figure 1. In general, it is not possible to obtain the absorption spectrum of any of these species as isolated entities in solution. Thus, neither the identities of species in the equilibrated solutions nor their individual molar absorptivities are known. It is only possible to obtain the absorption spectrum of the equilibrated solutions, which will consist of the summation of the spectra of the individual species weighted by their concentrations in the solutions. At any given wavelength,  $\lambda$ , the measured absorbance can be expressed as

$$A_{\text{meas}}(\lambda) = \sum_i A_i(\lambda) = [\sum_i \epsilon_i(\lambda) C_i] l \quad (13)$$

where  $A_i(\lambda)$  = absorbance of component  $i$  at wavelength  $\lambda$   
 $\epsilon_i(\lambda)$  = molar absorptivity of component  $i$  at wavelength  $\lambda$  ( $M^{-1}cm^{-1}$ )  
 $C_i$  = concentration of component  $i$  ( $M$ )  
 and  $l$  = cell path length (cm)

and the summation runs over all  $i$  species in the solution. The procedure for determining the formation constants for the various species involves a nonlinear least-squares fitting of the absorbance data at the selected wavelengths as a function of the ligand (carbonate and/or citrate)

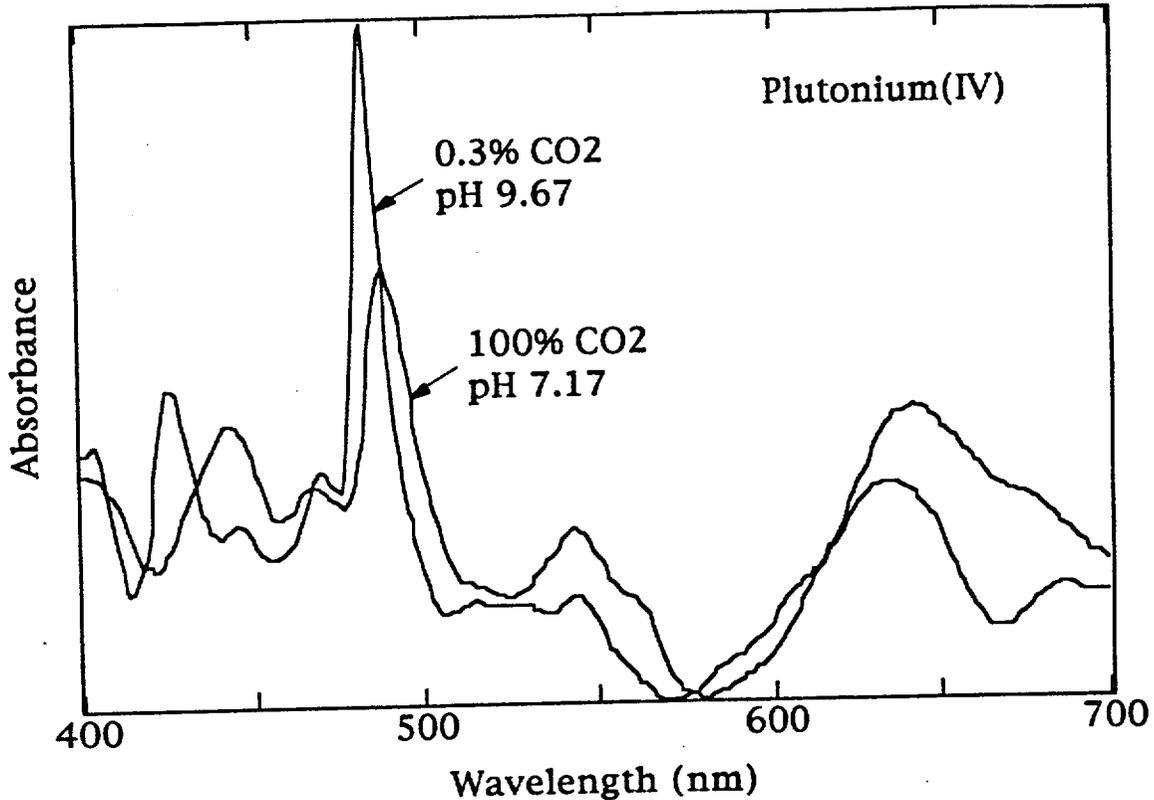


Figure 1. Spectra of Pu(IV) in different Carbonate Solutions.

and metal ion concentrations and solution pH. Trial values for the stoichiometric coefficients (e.g.,  $x$ ,  $y$ ,  $n$ , and  $m$  in Equation 10) and the formation constants are input, and the fitting routine iterates by varying the values of the formation constants to a statistical best fit to the absorbance data. An example is provided in Section 3.2.4. In principle, a unique fit to the absorbance data can be obtained that will specify the stoichiometries of the species in solution and their formation constants. However, in practice, several plausible fits may result. Several criteria are available for choosing the most reliable fit(s). These criteria include the statistical quality of the fit and the requirement that any mathematical solution be chemically reasonable based on existing knowledge of radionuclide speciation.

### 3.2.1.2 Photoacoustic and Related Spectroscopies

A pulsed laser PAS and PDS facility has been established at LANL. The heart of the system is the tunable, pulsed excitation source with a repetition rate of 10 Hz and a 9 ns pulse length based on a pulsed Neodymium: Yttrium Aluminum Garnet (Nd:YAG) amplifier/oscillator laser (Spectra

Physics Model DCR-3G-10) with the full complement of harmonic generating crystals; a pulsed dye laser (Spectra Physics Model PDL-2), and a wavelength extender unit with mixing and doubling crystals (Spectra Physics Model WEX-1b). This excitation source is capable of covering the wavelength range from the ultraviolet (~210 nm) to the mid infrared region (~4,500 nm) with no significant gaps. Thus, virtually all electronic transitions of all radionuclides of interest can be probed. The short pulses of this excitation source, besides providing a large density of photons to excite the sample, shift the PAS and PDS measurements from low-frequency (essentially dc) range to a much higher (GHz) frequency range. Use of the gigahertz frequency range enables the application of frequency filtering and selective amplification of the signal, as well as gating of the detector outputs with a boxcar averager or digital oscilloscope. Thus, much of the lower-frequency background noise can be readily eliminated. This approach has been demonstrated to be very effective in dramatically increasing sensitivity and, consequently, analytical detection limits. The LIF capability is provided by the same instrumentation as the PAS / PDS system, and requires only a photon detector (e.g., a photomultiplier tube) for implementation. This technique will be used as needed in this YMP task.

The specific tests and analyses for the PAS, PDS, and LIF techniques are exactly analogous to those used in the competitive complexation method described above. The only difference between the two methods is that the PAS, PDS, and LIF studies will focus directly on radionuclide solutions with characteristics specific to those expected of the ground water at the repository site. Detailed procedures for the operation and calibration of the instrumentation will be provided in 1992.

### 3.2.1.3 X-Ray Absorption Spectroscopy

The theory and experimental details of x-ray absorption spectroscopy are summarized in Koningsberger and Prins (1988). Experiments will be conducted on the Los Alamos beamlines at the National Synchrotron Light Source at Brookhaven National Laboratory and / or at the Stanford Synchrotron Radiation Laboratory. In general, the region of the L-adsorption edges of the actinides (~ 16 - 18 keV) will be used. The incident white x-ray beam will be monochromatized using a Si(220) monochromator. X-ray absorption will be detected in either the transmission mode using ionization detectors or in the fluorescence mode using either a Lytle detector or a Ge array detector. Absolute energy calibrations for the edge positions will be done using either metallic foils or well characterized actinide complexes (e.g., the oxides). Data analysis will be done using available software. Additional details can be found in a recent article on x-ray absorption studies of neptunium speciation (Combes et al., 1992).

### 3.2.2 Data, Parameters, and Materials Needed for the Speciation Study

Existing literature data concerning the aqueous complexation chemistry of the radionuclides and similar species will be surveyed. The existing data on complex formation constants and the identities of the radionuclide species will be evaluated and incorporated in the present study where appropriate. A proper assessment of the literature data may also indicate that the experimental work should be repeated to verify the reported results. If appropriate, the methodologies used in the reported studies will be used to design and perform experiments for the present study.

In selecting the radionuclide complexes for the speciation study, we will need input from Activities 8.3.1.3.5.1.1, Solubility Measurements, and 8.3.1.3.5.1.3, Solubility Modeling. Guidance in choosing the appropriate experimental conditions (ranges in radionuclide concentrations, complexing agent concentrations, pH, Eh, and temperatures) will also come from these two activities; however, the speciation studies may have to adhere to other experimental conditions to be tractable.

The only specific materials needed for the speciation studies are supplies of the germane radionuclides of sufficient purity to carry out the necessary experiments. Both isotopic and chemical purity, when possible, are advantageous because significant amounts of time are consumed in purifying samples. Work in progress requires plutonium, americium, and neptunium. It should be emphasized that the speciation determination is a basic thermodynamic study that involves wide variations in experimental parameters to obtain reliable results. For this reason, samples of water from the proposed repository site (e.g., water from Wells J-13 and UE-25p#1) are not prerequisites for this study; rather, the compositions and conditions of these site-specific water samples will be simulated when appropriate in the speciation studies.

### 3.2.3 Additional Technical Details for the Speciation Study

Inasmuch as the development of the DPs for the speciation study is an ongoing process (documented in accordance with TWS-QAS-QP-03.5, Procedure for Documenting Scientific Investigations), it is not possible to generate a specific list of DPs. However, several analytical procedures will be routinely performed in the course of this study and are outlined below. A list of the equipment used for these procedures is given below.

#### 3.2.3.1 Preparation of Pure Oxidation State Solutions of Actinides

The availability of solutions of the radionuclides having high purity with respect to both chemical constituents and oxidation state is vital to this study. The DP currently in use for preparing such solutions is TWS-INC-DP-78, Preparation of Solutions of Pure Oxidation States of Neptunium, Plutonium, and Americium, and the stability of these solutions has been documented recently (Newton et al., 1986a).

A typical procedure for preparation of a Pu(IV) stock solution is presented as an example. Pu(IV) is conveniently prepared from either plutonium metal or oxide. Upon dissolution of metal or oxide in 6 M HClO<sub>4</sub> or HCl, a pure Pu(III) solution is formed. This solution can be oxidized electrochemically by a platinum screen electrode at a potential of ~1.2 V. At this potential, Pu(V) and Pu(VI) could form, but the rate of formation for such irreversible reactions is small. These reactions are called irreversible because the products, PuO<sub>2</sub><sup>+</sup> and PuO<sub>2</sub><sup>2+</sup>, require a significant chemical rearrangement of the inner coordination sphere of Pu<sup>3+</sup> during the electrochemical exchange of electrons. This rearrangement requires a long time compared with the rate of the reversible reaction of Pu<sup>3+</sup> to Pu<sup>4+</sup>. The resultant electrochemically prepared Pu(IV) is further purified from other oxidation states and possible contamination from <sup>241</sup>Am by ion exchange purification. An equal volume of concentrated nitric acid is added to the Pu(IV) solution to form the anionic hexanitratoplutonium(IV). This complex is loaded on an anion exchange resin such as Biorex-9. The Pu(IV) complex is sorbed onto the resin, and all other contaminants are washed through the resin by multiple additions of 8 M nitric acid. The purified Pu(IV) is eluted and concentrated by stripping the anion exchange column with 1 M hydrochloric acid, which changes the anionic complex to cationic Pu(IV)<sub>aq</sub>. The resulting Pu(IV) stock solution in hydrochloric acid has a reasonably long shelf life.

Pure actinide solutions in other oxidation states are prepared using analytical methods similar to those outlined by Newton et al. (1986a).

#### 3.2.3.2 Determination of the pH of Solutions

The Detailed Technical Procedure for pH measurements is TWS-INC-DP-35, pH Measurements.

#### 3.2.3.3 Recording of Ultraviolet, Visible, and Near-Infrared Absorption Spectra

This procedure is outlined in the procedure for recording reflectance and absorption spectra.

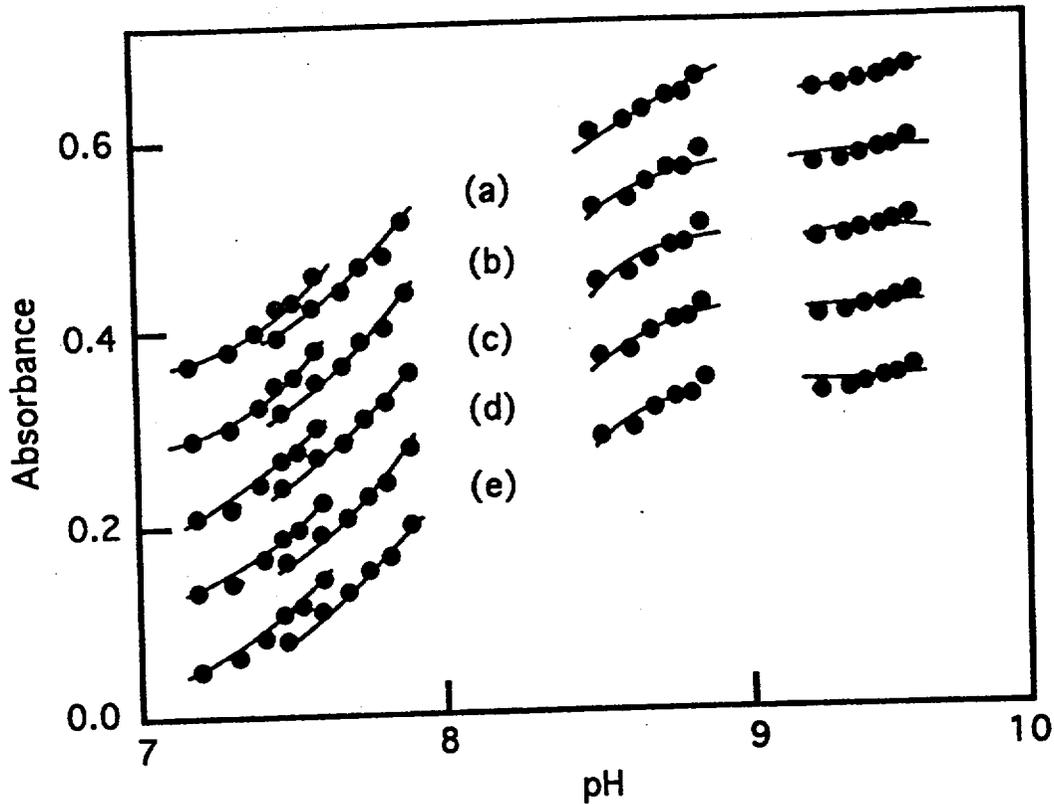


Figure 2. Results from fitting routine for Pu(IV) carbonate spectra showing the observed (circles) and calculated (lines) absorbance values for various speciation models in which two reactions of the type  $\text{Pu}^{4+} + m_1\text{HCO}_3^- + n_1\text{H}_2\text{O} = \text{Pu}(\text{OH})_{n_1}(\text{CO}_3)_{m_1} + (n_1+m_1)\text{H}^+$  are assumed. Models are  $(m_1, n_1, m_2, n_2)$ : (a) (1,0,0,1); (b) (1,1,0,1); (c) (1,2,0,1); (d) (2,0,0,1); and (e) (2,1,0,1). The curves for the different models have been offset on the absorbance scale for clarity. Numerical results are presented in Table 5.

TABLE 5  
 RESULTS OF LEAST-SQUARES CALCULATIONS  
 FOR THE Pu(IV) CARBONATE SYSTEM

Model <sup>a</sup> ( $m_1, n_1, m_2, n_2$ )	Data Set	$\text{p}Q_1^b$	$\text{p}Q_2^b$	$\text{RMS}^c$
1,0,0,1	2	8.00	15.73	5.10
1,0,0,1	3	8.14	15.72	4.84
1,1,0,1	2	22.34	14.48	5.77
1,1,0,1	3	23.49	15.27	5.56
1,1,0,1	2	37.30	13.78	6.49
1,2,0,1	3	38.65	14.79	5.51
1,2,0,1	2	16.62	15.34	6.44
2,0,0,1	3	16.90	15.42	5.49
2,0,0,1	2	31.87	15.00	6.77
2,1,0,1	3	32.07	15.09	5.58

a The model assumes two equilibria of the type  $\text{Pu}^{4+} + m_1\text{HCO}_3^- + n_1\text{H}_2\text{O} = \text{Pu}(\text{OH})_{n_1}(\text{CO}_3)_{m_1} + (n_1+m_1)\text{H}^+$ .

b The negative logarithm of the indicated equilibrium quotient.

c Root-mean-square deviation between the observed and calculated absorbance values  $\times 10^3$

Typically, a standard 1-cm or 10-cm cell is filled with distilled water and placed in the sample compartment of the spectrophotometer, and a baseline is recorded by scanning the monochromator through some predetermined wavelength region. The cell is then emptied and dried in an oven. The cell is removed from the oven, allowed to cool to room temperature, and then filled with the analyte solution. A spectrum is recorded over the same spectral region as that of the baseline. For quantitative determinations, the baseline value is subtracted from the analyte absorbance value to determine, for example, the concentration of an analyte by invoking Beer's law.

### 3.2.4 Examples of Results for the Speciation Study

The details of the method of competitive complexation for the study of speciation are outlined in Section 3.2.1.1. An example of the results from the nonlinear least-squares fitting routine for the absorbance data is shown in Figure 2. These results are from the study of Pu(IV) complexation by carbonate ion (Stage 1 experiments, Hobart et al., 1986a). The results in Figure 2 illustrate the observed absorbance data (dots) compared with the calculated fit to these data (solid lines) as a function of pH for several speciation models. The numerical results from this work are given in Table 5. At present, the best indication of the precision of these results is the degree of reproducibility of the data. As shown in Table 5, replicate determinations of the formation constants (equilibrium quotients) give values that differ by less than 0.5 log unit for the better models.

The net result of this study is the determination of the identity of the various species present and the equilibrium quotients for the various complexation reactions observed. These equilibrium quotient values are then used in the EQ3/6 modeling program to determine what the overall solubility is in ground water at near-neutral pH values for the radionuclide of interest. The overall solubility, in turn, provides a criterion by which to evaluate the conformance or non conformance to those solubility limits established for each radionuclide and specified in 10 CFR 60.

### 3.3 Tests and Analyses for Solubility Modeling (Activity 8.3.1.3.5.1.3)

All tests that provide information for the analyses described for this activity will be performed as part of the solubility and speciation measurements activities (Activities 8.3.1.3.5.1.1 and 8.3.1.3.5.1.2). In addition, this activity is critically dependent on the availability of an accurate and complete data base to use as input for the calculations. There are several noteworthy efforts outside the aegis of this task that are contributing to the availability of a robust data base. The first is an international effort under the auspices of the OECD / NEA to produce peer-reviewed compilations of thermodynamic data for uranium, neptunium, plutonium, americium, and technetium. The uranium data base has recently been completed, and the data bases for the other elements will be completed in time to benefit our activity. In addition, as noted previously, there has been a significant amount of work undertaken at Lawrence Livermore National Laboratory to improve the quality of the data base associated with the EQ3 / 6 code.

Using the best available data base, and all new data generated in the solubility and speciation activities, the analyses in the modeling activity will produce calculated solubilities of radionuclides under the conditions expected to exist at Yucca Mountain and an assessment of the sensitivity of the solubilities to variations in ground water chemistry, temperature, radiation, and any other parameters found to be important during experimental activities.

3.4 Description of the Specific Tests and Analyses for the Study of Radiocolloid Formation, Characterization, and Stability (Activity 8.3.1.3.5.2.1)

3.4.1 Preparation of Radiocolloids

All the experiments in this activity need samples of radiocolloids prepared under controlled and well-defined conditions. These samples will primarily be solutions of the suspended colloids (sols). However, dried colloid samples will also be used in some work. In the initial stages of this investigation, the experimental conditions used in the preparation of colloid samples will be limited to ambient temperatures and dilute mineral acid solutions such as hydrochloric or perchloric acid solutions at pH ~4 to 5. An example of such a preparation is given below for Pu(IV) colloid. After these initial investigations, the experimental conditions used for colloid preparation will be varied to reflect the conditions expected for the site and the flow paths to the accessible environment. These variations will include variations in temperature from 25 to 90°C, variations in pH from 4 to 7, variations in the carbonate and bicarbonate concentrations over a range that simulates the differences between water from Well J-13 and Well UE-25p#1 and a neutral pH electrolyte solution, and variations in the composition and concentrations of the electrolytes other than carbonate and bicarbonate, which are known to be present in ground water at the site (e.g., F<sup>-</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>). Not all of these variables can be varied independently. For example, the concentrations of carbonate and bicarbonate ions will determine the pH of the solutions. In addition, to assess the influence of alpha radiation fields on the colloid properties, we will prepare colloids using two isotopes of plutonium that have significantly different specific alpha activities, <sup>242</sup>Pu and <sup>239</sup>Pu. The latter has approximately 16 times greater activity than the former.

Much more is known about the preparation and properties of the Pu(IV) colloid than about any of the other potential colloid-forming radionuclides. For this reason, the initial phase of this activity will focus only on Pu(IV) colloid, and all of the properties of this species outlined in Section 2.2 will be explored. After satisfactory progress has been made in characterizing the plutonium colloid, we will turn our attention to the study of the Am(III) colloid. At this point, input from Activity 8.3.1.3.5.1.1, Solubility Measurements, will be sought for guidance in identifying the most appropriate solution conditions for the study of the Am(III) colloid and to ascertain whether any other potential colloid-forming radionuclides should be investigated.

The following description of the preparation of the <sup>239</sup>Pu(IV) colloid in hydrochloric acid solution is an example of a typical preparation of a radiocolloid. A pure metallic sample of <sup>239</sup>Pu is dissolved in 6 M HCl to make a stock solution of ~ 1.0 M Pu(III). Portions of this stock solution are then diluted with more dilute hydrochloric acid solutions, usually ~1 M HCl, and are electrochemically oxidized to Pu(IV) at a platinum grid anode. An aliquot of this Pu(IV) stock solution is then added dropwise to ~100 mL of deionized, distilled water. The resulting diluted solution is typically 0.01 M in Pu(IV) and ~0.04 M in HCl. This solution is allowed to stand at room temperature to enable the formation of the Pu(IV) colloid. The presence of a colloid sol is detectable to the eye as a characteristic green coloration within 10 days. In certain experiments, it is necessary to remove all other (ionic) forms of plutonium from these sol solutions. Removal is typically achieved by passing the sol solutions through a cation exchange column (Bio-Rad AG 50, X-8, for example). The sols can be assayed for purity by examining the visible electronic absorption spectrum using the characteristic absorbances of the colloid at 580, 615, and 740 nm.

3.4.2 Autocorrelated Photon Spectroscopy (APS) for the Determination of Colloid Particle Size

Elings and Nicole (1984) provide a detailed theoretical description of this method. The colloid samples are normally contained in cylindrical glass vials. The vials are immersed in a thermostat-controlled bath of an index-of-refraction matching fluid. Incident laser light impinges on the

solution in the vial, and the randomly diffusing colloid particles cause some of this light to be scattered. The scattered light is collected at some angle with respect to the incident light, usually 90°, and is focused on a photomultiplier tube. The output signal from the photomultiplier is proportional to the intensity of the scattered light. This intensity is electronically autocorrelated in real time to produce an exponential decay function referred to as the autocorrelation function. The autocorrelation function is then analyzed numerically to determine the decay constant proportional to the diffusivity,  $D$ , of the particle. From the diffusivity of the colloid particles, one can calculate the hydrodynamic radius,  $R_h$ , according to the Stokes-Einstein relation,  $R_h = kT/6\pi\eta D$ , where  $k$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $\eta$  is the shear viscosity of the colloid solution. In actual practice, a continuous sum of exponential decays in the autocorrelation function results from a distribution in colloid particle sizes. Thus, the numerical analysis of the function provides both an average particle size and a measure of the dispersion in sizes. We will use this same procedure to study the variations in the particle sizes of the radiocolloids as functions of chemical conditions, temperature, etc.

The autocorrelated photon spectroscopy apparatus currently in use consists of

- a Spectra Physics, Model 165, 2-W argon ion laser, which is typically tuned to the 514.4-nm lasing transition;
- a Brookhaven Instruments Corp. B1-200 automatic goniometer with temperature-controlled sample holder; and
- a Brookhaven Instruments Corp. B1-2030 autocorrelator.

Specific details on the operation of these instruments can be found in the operating manuals.

Several preliminary experiments have been conducted with APS (Triay et al., 1991) to determine the feasibility of using it in this activity. In these experiments, the particle size of the Pu(IV) colloid in dilute mineral acid solutions was determined. A freshly prepared sample of  $^{242}\text{Pu(IV)}$  colloid had a size of 5 nm with dispersion of < 1 nm. In contrast, a sample of  $^{239}\text{Pu(IV)}$  colloid that had been monitored for 2 yr had a reproducible size of 180 nm. In addition, commercially obtained polystyrene beads, whose size has been calibrated using electron microscope techniques, have been analyzed as suspensions in solutions using APS. The particle size of these beads as determined by APS is in excellent agreement with the size quoted by the manufacturers.

The single most important source of interference in these determinations is dust particles and/or gas bubbles in the solutions of the colloids. These substances tend to scatter incident laser light in much the same way as colloid particles do, thus complicating the analysis of the autocorrelation function. To circumvent these difficulties, several experimental approaches are plausible. The simplest is to use "clean room" conditions when preparing the colloids, which involves ultrafiltration of the solutions before the onset of colloid formation and taking care to ensure that the solutions are not subsequently subjected to any dust-containing environments. It is also possible, if the dust particles are sufficiently larger than the colloids, to filter the colloid solutions before beginning the APS experiments. The interference from gas bubbles can be circumvented simply by allowing the colloid solutions to degas adequately.

### 3.4.3 Ultracentrifugation for Determination of Colloid Density

The ultracentrifugation procedure we expect to use to determine colloid density has been demonstrated previously by Rundberg et al. (1988). It involves transferring suspensions of the colloidal sols (typically ~5 mL) to centrifuge tubes. The samples will then be centrifuged at speeds up to 50,000 rpm for periods lasting from several minutes to several hours. Following centrifugation, the stratified solution of the colloid will be divided into layered aliquots, usually of 0.5 mL, by careful pipetting from the top of the centrifuge tube. We will assay these aliquots using standard radiation counting techniques; thus, a profile of the concentration of the colloid as a

function of depth in the tube will be obtained. Using the concentration profile data at a given rotation speed and time, we will be able to calculate the average density of the colloid according to the following sedimentation law (Ichikawa and Sato, 1984):

$$\ln(R_2/R_1) = (2r^2\omega^2/9\eta)(d_p-d)(t_2-t_1) \quad (14)$$

where

- R<sub>1</sub> = radial position (in centimeters) from the center of the rotor at time t<sub>1</sub> (in seconds),
- R<sub>2</sub> = radial position at time t<sub>2</sub>,
- r = hydrodynamic radius of the particle (in centimeters),
- ω = angular velocity of the rotor (in radians/second),
- d<sub>p</sub> = particle density (in grams per cubic centimeter),
- d = density of solution (in grams per cubic centimeter), and
- η = shear viscosity of the solution (in poise).

The particle size, r, must be known before calculating the density. All other parameters in this expression are either known or are easily measured. Experiments in which the density is determined as a function of solution conditions, etc., will follow this same basic procedure. However, it will probably be impractical to maintain colloid solutions at elevated temperatures for this density determination. For this reason, the density determinations for colloids prepared at elevated temperatures will probably have to be carried out rapidly at reduced temperatures so as to perturb the colloid as little as possible.

No ultracentrifuge has yet been identified for this work. The instrument selected must meet two prerequisites: (1) it must possess a swinging bucket rotor so that the sedimentation law cited above can be used for the density determination, and (2) it must be capable of extremely high rotation rates (i.e., on the order of 50,000 to 75,000 rpm). These rates are necessary because the colloid particle densities may not be much different from those of the solutions in which the colloids are suspended. Thus, to facilitate stratification of colloids in reasonable time periods, a high rotation rate is needed.

There are several possible sources of error in this density determination. The first is adsorption of the colloids onto the walls of the centrifuge tubes. The magnitude of this problem cannot be estimated easily before initiating experiments on a specific radiocolloid. However, standard techniques exist for coating the walls of centrifuge tubes to minimize adsorption (using silanizing agents, for example). Alternatively, it may be possible to use centrifuge tubes constructed of different materials to mitigate this problem. Finally, it may be possible to correct for adsorption in the density calculation if the degree of adsorption is reproducible and can be quantified. Error could also be introduced while pipetting aliquots of the centrifuged solution from the tubes. Additional work is planned in the initial phase of this investigation to determine the optimal methods for obtaining these aliquots.

#### 3.4.4 Determination of Colloid Bulk Charge

No specific procedures have been established for either the electrophoresis technique or the precipitation method. However, commercial instrumentation for measuring electrophoretic mobility is available, and acquisition of this instrumentation is planned.

#### 3.4.5 Ultraviolet, Visible, and Near-Infrared Absorption Spectroscopy for the Determination of Colloid Reactivity

The experimental details of ultraviolet, visible, and near-infrared absorption spectroscopy and the

theoretical discussion of the relationship between the absorption intensity and species concentration are presented in Section 3.2.1. These considerations apply equally to the study of radiocolloid reactivity. For this activity, the absorption spectroscopy technique will be used predominantly to monitor the concentrations of the radionuclide species that are the precursors of the colloids and/or the products of colloid dissolution or degradation. We will measure the concentrations in colloid-containing solutions as a function of time to determine the rates of formation, aggregation, and degradation and to establish whether the colloid solutions reach steady-state or equilibrium conditions. We expect to monitor these properties for periods ranging from several hours to several hundred days. In addition, all rate studies will be conducted under a variety of solution conditions at selected temperatures above ambient levels. The exact details of the variations in solution conditions and temperatures have not yet been determined.

We will not rely strictly on absorption spectroscopy to quantify the amount of colloid suspended in the solutions. Although most of the radiocolloids are either known to yield or suspected of yielding a distinctive electronic absorption spectrum, it has not been conclusively established that the absorptivity of the colloids at any particular wavelength is independent of colloid properties such as particle size or density. In general, the amount of colloid can be determined from mass balance by first determining the concentrations of the other radionuclide species in the solutions. This approach has been demonstrated successfully in an earlier study (Newton et al., 1986b) and will be used in this investigation whenever possible. If it proves critical to quantify the colloid concentration using absorption spectroscopy, detailed studies of the dependence of absorptivity on the physical and chemical state of the colloid can be undertaken.

We will specify the rates of appearance or disappearance of the radionuclide species for each set of experimental conditions, based on the variations over time of the concentrations of the colloids and the other soluble ionic radionuclide species. Where sufficient data exist, attempts will be made to determine the rate laws for the time dependence of the concentration of the species. If there appears to be an equilibrium in a colloidal system for any particular set of experimental conditions, the measured concentrations of the various species will be used to calculate equilibrium constants for the solution processes. If the existence of true thermodynamic equilibrium cannot be established but steady-state conditions are observed, experimental concentration quotients (which approximate the equilibrium constants) will be reported.

The absorption spectra will be obtained on a Varian CARY Model 17D spectrophotometer equipped with standard accessories. The specific details of operation can be found in the manufacturer's operations manual (Varian, no date). The assays for some radionuclide species may require that other species not be present in the solution during the spectral acquisition. For these experiments, colloids will be removed by centrifugation or filtration, and other soluble species will be removed or masked using standard chemical methods. The concentrations of the analytes will be calculated from the spectral absorbance of one or more spectral bands according to Beer's law (Section 3.2.1.1). There are no serious sources of interference or uncertainty in the spectroscopic technique. Some problems may be encountered because of the lack of sensitivity in this method. These problems can be largely overcome by using PAS.

#### 3.4.6 Electrochemical Techniques for the Determination of Colloid Reactivity

The electrochemical investigation of redox reactivity of radiocolloids will use both instrumental and wet chemical methods. The primary instrumental techniques will be linear sweep voltametry (LSV) and controlled potential coulometry (CPC). All electrochemical methods involving instruments will use potentiostats equipped with working, counter, and reference electrodes. In LSV, the potential between the working and reference electrodes is varied in a linear fashion, and the current flowing between the working and counter electrodes in response to the electrochemical activity at the working electrode is monitored. In CPC, a constant potential is applied between the working and reference electrodes, and the current flowing between the working and counter

electrodes, in response to the electrochemical activity at the working electrode, is monitored. For these colloid reactivity studies, the electrochemical activity of interest is the oxidation or reduction of the colloid at the working electrode surface. Typically, this electrochemical activity is monitored by measuring the current flow; however, as an alternative to monitoring the current flow in CPC, the progress of the redox reaction can be monitored by absorption spectroscopic methods. This approach requires the use of an electrochemical cell constructed to fit in the sample compartment of the spectrophotometer. Both current monitoring and spectroscopic monitoring of colloid redox reactivity will be used in this study.

The theories of both LSV and CPC for dissolved species in solution are well established. However, for this investigation, the analyte of interest is a suspended colloid. The electrochemical response functions for suspended colloidal species are not well investigated, and true thermodynamic potential data will probably not be obtainable. Nonetheless, the measured electrochemical responses will provide valuable data on the rates and potentials of the colloidal redox processes at the working electrode. For example, it has already been determined by CPC with spectroscopic monitoring that a fresh solution of Pu(IV) colloid in 0.01 M HCl can be electrochemically reduced to aquated Pu(III) at a mercury cathode. However, the rate of this reduction is insignificant at potentials below about -0.4 V (compared with a normal hydrogen electrode) and reaches a maximum limiting rate at potentials of about -0.9 V (Hobart et al., 1989). We will use these instrumental electrochemical methods primarily to investigate colloid redox reactivity as a function of particle size to ascertain whether the potentials and rates of the redox processes are influenced by the size of the colloid particles. We will also study the effects on redox reactivity of variations in the chemical and physical conditions of the colloid solutions using these instrumental electrochemical methods.

Two state-of-the-art electrochemical instrumentation systems are available for these studies. The first is an EG&G Princeton Applied Research Model 273 digital potentiostat/galvanostat, which is a stand-alone unit capable of controlling both the LSV and CPC experiments. The second is an EG&G Princeton Applied Research Model 173 potentiostat/galvanostat equipped with a Model 179 digital coulometer and a Model 175 universal programmer. This latter system can also control both the LSV and CPC experiments. The specific details on the operation of these instrumental systems can be found in the respective reference manuals (EG&G Princeton Applied Research, 1985, and 1981a, b, and c). The spectroscopic monitoring of the CPC experiments will be performed on a Varian CARY 17D spectrophotometer. A standard electrochemical electrolysis cell design will be used for these experiments.

The main compartment of the cell will contain the analyte solution and the working electrode. Two auxiliary compartments, one for the counter electrode and the other for the reference electrode, will be isolated from the main compartment by glass frits. The reference electrode will normally be a Beckman Semimicro Saturated Calomel Electrode. Freshly prepared silver/silver chloride reference electrodes may also be used. The counter electrode will be either a platinum wire or a platinum grid. The material used for the working electrode will depend on the experiment and on the potential range of interest. The materials currently being considered include platinum wire, platinum grid, mercury, and glassy carbon. In general, large surface area working electrodes will be used for the CPC studies and small surface area electrodes for the LSV studies. Mercury, which has a severely limited positive potential range in aqueous solutions, will be used only for studies of colloid reduction processes.

The investigation of the colloid redox reactivity using wet chemical methods will use both homogeneous redox reagents (i.e., those dissolved in solution) and heterogeneous reagents (i.e., reactive metals and metal amalgams). For these studies, we will monitor the extent and rate of the redox reaction, primarily using absorption spectroscopy to measure the concentrations of the radionuclide species and/or redox reagents in the colloid solutions over the course of the redox reaction. Here, too, we will carry out the experiments as a function of time, emphasizing the

influence of colloid particle size and varying the chemical and physical states of the colloid solutions. The absorption spectroscopy will be performed on the Varian CARY 17D spectrophotometer, using the procedures described above. An exhaustive list of potential redox reagents has not been compiled; however, candidate reagents include the homogeneous oxidizing agent, cerium(IV/III), and the heterogeneous reducing agent, zinc (mercury) amalgam.

#### 3.4.7 X-Ray Diffraction for the Determination of Colloid Structure

X-ray diffraction methods will be used to investigate concentrated, undried colloid samples, dried colloid samples, and appropriate model compounds (YMP-LBL-DP-03, X-Ray Powder Diffraction Analysis for the Yucca Mountain Waste Element Solubility Study). The theory of x-ray diffraction from crystalline materials is well established. A brief discussion of this theory can be found in any standard text on physical chemistry (e.g., Barrow, 1973). In the first stage of these investigations, we will establish whether the colloids possess any crystallinity by inspecting an x-ray diffraction photograph of the colloid sample. If the x-ray diffraction photograph possesses a distinct line pattern, crystallinity is indicated. The position of the lines with respect to a  $0^\circ$  diffraction angle will be used to calculate the d-spacings according to the Bragg diffraction law,  $n\lambda = 2d\sin\theta$ , where  $n$  is an integer value, usually unity;  $\lambda$  is the x-ray wavelength;  $\theta$  is the measured diffraction angle; and  $d$  is the calculated d-spacing. The relative intensities of the diffraction lines will also be noted. If the space group symmetry of the crystal is known or can be estimated reasonably, we can use the d-spacings to determine the unit cell dimensions according to well-established mathematical relationships. The unit cell of the crystal is the smallest repeated structural entity. The calculation of these unit cell dimensions is the ultimate goal of the x-ray diffraction studies.

Typically, the crystal class of the sample is not known beforehand. However, there are only 32 such classes and each possesses a characteristic line spacing and intensity pattern. An x-ray diffraction pattern data base has been established by the Joint Committee on Powder Diffraction Standards (JCPDS) of the International Center for Diffraction Data, in Swarthmore, Pennsylvania. We will consult this data base to find the best match between any colloid x-ray data and the diffraction pattern of existing well-characterized crystalline materials. Normally, such a match enables the specification of the symmetry of the unknown sample so that the unit cell dimensions can be calculated as outlined above. If there are other radionuclide compounds or other pertinent materials (i.e., model compounds) that are not currently listed in this x-ray data base but that are expected to be structurally similar to colloids, consideration will be given to obtaining the x-ray diffraction patterns for these species.

No specific x-ray diffraction apparatus has been identified for these studies. We expect to use a standard x-ray method that employs a Debye-Scherrer camera and either a copper or molybdenum  $K\alpha$  x-ray source. If the resulting x-ray films are of sufficiently high quality, it is possible to extract the line spacings with a calibrated rule. A densitometric film reader will be used for films of lesser quality. In all cases, the colloid or model compound samples will be sealed in quartz capillary tubes for the analysis. We will attempt to obtain x-ray diffraction data for colloid samples prepared under a variety of conditions to determine how the varying conditions influence the structure.

#### 3.4.8 Raman Spectroscopy for the Determination of Colloid Structure

Raman spectroscopy will be used to obtain the vibrational spectra of colloid samples and other model compounds. The theory of Raman vibrational spectroscopy and details on the basic experimental aspects of laser Raman spectroscopy are discussed by a number of sources (e.g., Long, 1977). The samples can be either in solution, as for the suspended colloid, or in isolated solids, as for dried colloids. The samples are irradiated with laser light, usually in the visible or ultraviolet region of the spectrum. A portion of this light is inelastically scattered by the analyte. This inelastically scattered light is shifted in energy from the incident light by an amount equal to

the vibrational energy of one of the vibrational modes of the analyte. The scattered light is collected and focused in a light-dispersive detection system, such as a monochromator equipped with a sensitive light detector (e.g., a photomultiplier tube or diode array detector). The resulting spectrum is a plot of scattered light intensity versus the shift in energy (in  $\text{cm}^{-1}$ ) from that of the incident laser light and corresponds to the vibrational spectrum of the analyte. The primary advantage of using Raman spectroscopy instead of infrared spectroscopy to obtain the vibrational spectra of the colloid samples is that the sample constraints in the Raman technique are far less restrictive. For example, it is straightforward to obtain a Raman spectrum of an aqueous solution.

For the purpose of characterizing the structure of the colloids, the most important Raman data are the energies of the vibrational modes. Two distinct types of vibrational modes are important. The first are referred to as a "lattice" or "phonon" mode, which are usually very low energy modes that arise from the bulk motion of atoms or groups of atoms in the crystal lattice. For the colloids, data related to this type of vibrational mode will be used only in a qualitative sense. In particular, the presence of such modes implies that there is some degree of crystallinity in the colloid sample. The number and energies of these modes will be compared with those observed in structurally well-characterized model compounds to permit inferences on the structure of the colloids.

The second type of vibrational mode are referred to as "internal" modes. These modes arise from the displacements of the atoms in the molecular unit from their equilibrium positions caused by stretching and bending motions of the chemical bonds. Because these modes result from motions such as the elongation or compression of chemical bonds, the energies are directly related to the strengths of the bonds. Thus, the numbers and energies of the internal vibrational modes provide direct structural information on the types of bonds [e.g., Pu(IV) to hydroxide oxygen] and strengths of the bonds within the colloids. A detailed analysis of the vibrational data to obtain specific bond strengths is a prodigious undertaking requiring a full group theoretical treatment of the molecular vibration problem and isotopic substitution data. We will not perform such an analysis in this investigation; rather, we will assume simple harmonic oscillation to obtain estimates of the important bond strengths and/or distances between the colloid atoms. Here, too, we will need data for model compounds to assist in the interpretation of the colloid data.

A laser Raman instrumental system has been constructed as part of the calibration system for the PAS / PDS system. It is based on standard components including a scanning double monochromator with a data station. We will attempt to obtain these Raman spectral data for colloids prepared under the various experimental conditions cited for the other studies. In addition, we will emphasize the acquisition of these data as a function of colloid size.

#### 3.4.9 Ultraviolet, Visible, and Near-Infrared Spectroscopy for the Determination of Colloid Structure

We will use this technique only in a qualitative sense to deduce structural information for the colloids, emphasizing the number of spectral bands and their wavelengths. We will not attempt to quantify spectral intensities and will rely heavily on model compounds for comparison of the spectroscopic data to those obtained for the colloids. Spectroscopic data will be collected in one of two ways. The first way, which will be used for solutions of colloidal suspensions and for soluble model compounds, is identical to the absorption spectroscopic methods discussed previously. The second method will use diffuse reflectance spectroscopy on solid samples to obtain electronic spectra. This method is necessary because numerous model compounds are either insoluble or change chemical form on dissolution, and the solid forms are too opaque to permit the use of transmission spectroscopy. A discussion of the theory of diffuse reflectance spectroscopy can be found elsewhere (Wesley and Hecht, 1966; Frei and MacNeil, 1973). For the purpose of this investigation, a diffuse reflectance spectrum provides the same information as an absorption spectrum in terms of the number and positions of the spectral bands for any given analyte. The only difference between the two techniques is that the band intensities differ.

These spectroscopic probes can be used to deduce structural information on the colloids because the number of bands in the electronic spectrum of an actinide species and the wavelength of the band maxima depend to a large extent on the structural environment of the actinide ion. Here the structural environment refers to both the symmetry about the actinide ion and the identity of the ligands coordinated with the actinide ion. To make structural inferences about the colloids, we will compare the spectra of the colloids to those for structurally well-characterized compounds. A very strong correlation in the number and position of the spectral bands between the colloid and model compound spectra indicates that both species have the same symmetry and similar coordination spheres. For example, we have found that the electronic absorption spectrum of the Pu(IV) colloid suspended in solution very closely resembles the diffuse reflectance spectrum of a solid sample of highly fired plutonium dioxide, which suggests that these two species are structurally very similar and agrees with data obtained by x-ray diffraction methods (Hobart et al., 1989).

The experimental technique used to obtain the absorption spectra for the colloid samples and the soluble model compounds will be identical to that used in the reactivity studies described earlier. These studies will be carried out on the Varian CARY 17D spectrophotometer. This instrument will also be used to obtain the diffuse reflectance spectra; however, it will be modified to contain a diffuse reflectance apparatus in the sample compartment. The diffuse reflectance apparatus is a simple device consisting of two parabolic mirrors--one to deliver the monochromatic excitation source light to the sample and the other to collect the diffuse reflected light and focus it on the entrance slit of the spectrophotometer detector. Neutral density filters are used to attenuate the reference beam so that the instrumental response is kept within operating limits. The solid samples for the diffuse reflectance studies will be contained in glass vials with a flat bottom surface to optimize the reflected light. These structural studies will be carried out over a range of experimental conditions; however, the range will likely be more limited than those in the other characterizations because this technique is not as sensitive as either x-ray diffraction or Raman spectroscopic techniques.

#### 3.4.10 Other Routine Techniques

We will conduct several other routine procedures in conjunction with the tests and analyses described above. Because most of these are common analytical methods, such as the preparation of standard solutions, they are not discussed in detail here. However, we will rely heavily on measurement of solution pH and the control of temperature for the experiments conducted at temperatures above ambient. The pH of the solutions will be measured in accordance with TWS-INC-DP-35, pH Measurement. To control the temperatures of the various test solutions at levels above ambient, we will use liquid baths (most commonly water baths) controlled by thermostat. Several different units of local design and construction are available, which are always calibrated against mercury thermometers or thermocouples during operation.

#### 3.5 Quality Assurance Requirements

The activities in this study plan have been assigned as Quality Assurance Level I in accordance with LANL QA procedure TWS-QP-03.3, R0. Data from this study will be used for analysis of long-term radiological safety in the repository license application. The applicable criteria from NQA-I that apply to this study are shown in Appendix A, along with the procedures that will satisfy these criteria. The approved Quality Assurance Level Assignment sheets are also included in Appendix A.

Technical procedures for the work in this study are given throughout Section 3.0 and in Table 6, below. All procedures will be available 30 to 60 days before the test begin.

TABLE 6

TECHNICAL PROCEDURES FOR STUDY PLAN 8.3.1.3.5.1 AND 8.3.1.3.5.2

Technical Procedure	Type	Anticipated Date of Availability
Data Acquisition and Feedback Control Standard System for Solubility Studies (YMP-LBL-DP-O I)	Standard	8/21/89
Preparation of Actinide Solutions Containing Only One Oxidation State		TBD <sup>a</sup>
Phase Separation Techniques for Solubility Studies		TBD <sup>a</sup>
Neutron Activation Analysis		TBD <sup>a</sup>
Trace Metal Characterization by Atomic Emission Spectroscopy for the Yucca Mountain Waste Element Solubility Study (YMP-LBL-DP-04)	Standard	5/29/89
Trace Level Determination of Oxidation State of Soluble Species from Solubility Measurements		TBD <sup>a</sup>
Determination of Plutonium Oxidation States of Soluble Species from Solubility Measurements at Concentrations Below $10^{-5}$ M for the Yucca Mountain Waste Element Solubility Study (TWS-LBL-DP-10)	Standard	6/5/90
Determination of Plutonium at Trace Levels by Gamma and L X-ray Spectroscopy		TBD <sup>a</sup>
Quality Control in Counting Radioactive Nuclides		TBD <sup>a</sup>
Partial CO <sub>2</sub> Atmospheric Control of Ground water Chemistry		TBD <sup>a</sup>
pH Measurements (TWS-INC-DP-35)	Standard	3/13/89
X-Ray Powder Diffraction Analysis for the Yucca Mountain Waste Element Solubility Study (YMP-LBL-DP-03)	Standard	3/23/89
Preparation of Solutions of Pure Oxidation States of Neptunium, Plutonium, and Americium (TWS-INC-DP-78)	Standard	8/21/89
Recording Reflectance and Absorption Spectra		TBD <sup>a</sup>

**TABLE 6**

**TECHNICAL PROCEDURES FOR STUDY PLAN 8.3.1.3.5.1 AND 8.3.1.3.5.2  
 (concluded)**

Technical Procedure	Type	Anticipated Date of Availability
Calibration of Low-Energy Gamma Counters for the Yucca Mountain Waste Element Solubility Study (TWS-LBL-DP-02)	Standard	8/21/89
Sodium Concentration Determination Procedure for the Yucca Mountain Waste Element Solubility Study (TWS-LBL-DP-05)	Standard	2/23/90
Eh (Redox Potential) Measurements for the Yucca Mountain Waste Element Solubility Study (TWS-LBL-DP-06)	Standard	8/21/89
Sample Identification and Handling Procedure for the Yucca Mountain Waste Element Solubility Study (YMP-LBL-DP-07)	Standard	8/21/89
Measurement of Photoacoustic Spectra	Standard	1/7/93

<sup>a</sup> TBD = to be determined. Procedures will be ready 30 to 60 days before tests.

#### 4.0 APPLICATION OF THE RESULTS FROM THE STUDIES OF DISSOLVED SPECIES CONCENTRATION LIMITS (STUDY 8.3.1.3.5.1) AND COLLOID BEHAVIOR (STUDY 8.3.1.3.5.2)

The information derived from the studies and activities described in this study plan will be used to calculate concentration limits of dissolved radionuclides, speciation of radionuclides, and concentration of radiocolloids in water passing through the emplacement area and along flow paths to the accessible environment. These data will be used in a number of analyses and assessments concerning radionuclide release to the accessible environment [Issues 1.1, Total System Performance; 1.2, Individual Protection; and 1.3, Groundwater Protection (SCP Sections 8.3.5.13 through 8.3.5.15)], higher-level findings involving geochemistry [(Issue 1.9, Higher-Level Findings--Postclosure System and Technical Guidelines (SCP Section 8.3.5.18)], and Issue 1.8, NRC Siting Criteria (SCP Section 8.3.5.17). These data will also be used by Issue 1.1 in the formulation of transport phenomenology.

Radionuclide concentration limits and, possibly, radiocolloid concentrations will be used as input to calculate releases from the engineered barrier system [Information Need 1.5.4, Determination of the Release Rates of Radionuclides from the Waste Package and Engineered Barrier System for Anticipated and Unanticipated Events (SCP Section 8.3.5.10.4)] and cumulative releases to the accessible environment along the water pathway [Information Needs 1.1.4 and 1.1.5, Determination of the Radionuclide Releases to the Accessible Environment Associated with Realizations of Potentially Significant Release Scenario Classes (SCP Section 8.3.5.13.4) and Probabilistic Estimates of the Radionuclide Releases to the Accessible Environment Considering All Significant Release Scenarios (SCP Section 8.3.5.13.5)]. Speciation of radionuclides will be used in assessing retardation by sorption (Investigation 8.3.1.3.4, Studies to Provide the Information Required on Radionuclide Retardation by Sorption Processes along Flow Paths to the Accessible Environment) and in studying retardation by dispersive, diffusive, and advection processes (Investigation 8.3.1.3.6, Studies to Provide Information Required on Radionuclide Retardation by Diffusive, Dispersive, and Advective Processes along Flow Paths to the Accessible Environment). Speciation data will also be important input to assess the effectiveness of the geochemical barrier by Investigation 8.3.1.3.7, Studies to Provide Information Required on Radionuclide Retardation by All Processes along Flow Paths to the Accessible Environment.

Evaluation of favorable and potentially adverse conditions requires knowledge of (1) solubility limits of radionuclide concentrations, (2) the speciation of radionuclides in local water, and (3) whether radiocolloids will form and be stable. This information will be used to evaluate Issue 1.8, NRC Siting Criteria, and to support certain higher-level findings (qualifying and disqualifying conditions) in Issue 1.9, Higher-Level Findings--Postclosure System and Technical Guidelines. Solubility limits on radionuclides are critical for realistically calculating the cumulative releases to the accessible environment required by 10 CFR 960.3-1-5 (Issue 1.9).

## 5.0 SCHEDULE AND MILESTONES

Because of the importance and potential impact of water composition in the unsaturated zone on the solubility limits of radionuclides, there is a strong link between the solubility determination work in this Study and the determination of unsaturated-zone water composition in Study 8.3.1.2.2.7. The results from Study 8.3.1.2.2.7 should be available by the time the solubility determinations in the waters from Wells J-13 and UE-25p#1 are complete so that any additional solubility determinations can be scheduled and completed on time. This link is indicated in Figure 3. The timeliness with which the Solubility Modeling activity is initiated is also an issue to insure adequate progress in the Solubility and Speciation activities. The necessary start date for modeling to mitigate a negative impact is indicated in Figure 3. The data generated by the Solubility, Speciation, Modeling, or Colloid activities will be supplied to other Studies, most notably Sorption (8.3.1.3.4) and Dynamic Transport (8.3.1.3.6), as it becomes available. The vehicle for the information exchange will be reports and formal submissions to the Project's Technical Data Base.

Table 7 shows the milestones for these studies, which are depicted graphically in Figure 3.

TABLE 7  
 MILESTONES FOR DISSOLVED SPECIES CONCENTRATION LIMITS  
 AND COLLOID BEHAVIOR

Milestone Designation	Level	Title
3329	M3	Report on the Solubility of Np, Pu, and Am from Oversaturation
3031	M3	Speciation Measurements
3330	M3	Development of Photothermal Spectroscopies
3029	M3	Progress Report on EQ3/6 Data Base
3117	M3	Progress Report on Pu(IV) Colloid Stability and Characterization
3328	M3	Report on the Solubility of Np, Pu, and Am from Undersaturation
3007	M3	Final Report on Thermodynamic Code Development
3095	M3	Progress Report on Colloid Formation for Other Radionuclides
T539	M3	Interim Report on Solubility Calculations using EQ3/6
T518	M3	Final Report on Pu(IV) Colloid
3230	M3	Final Report on the Solubility of Np, Pu, and Am
3274	M3	Summary Report on Colloid Formation from Other Radionuclides

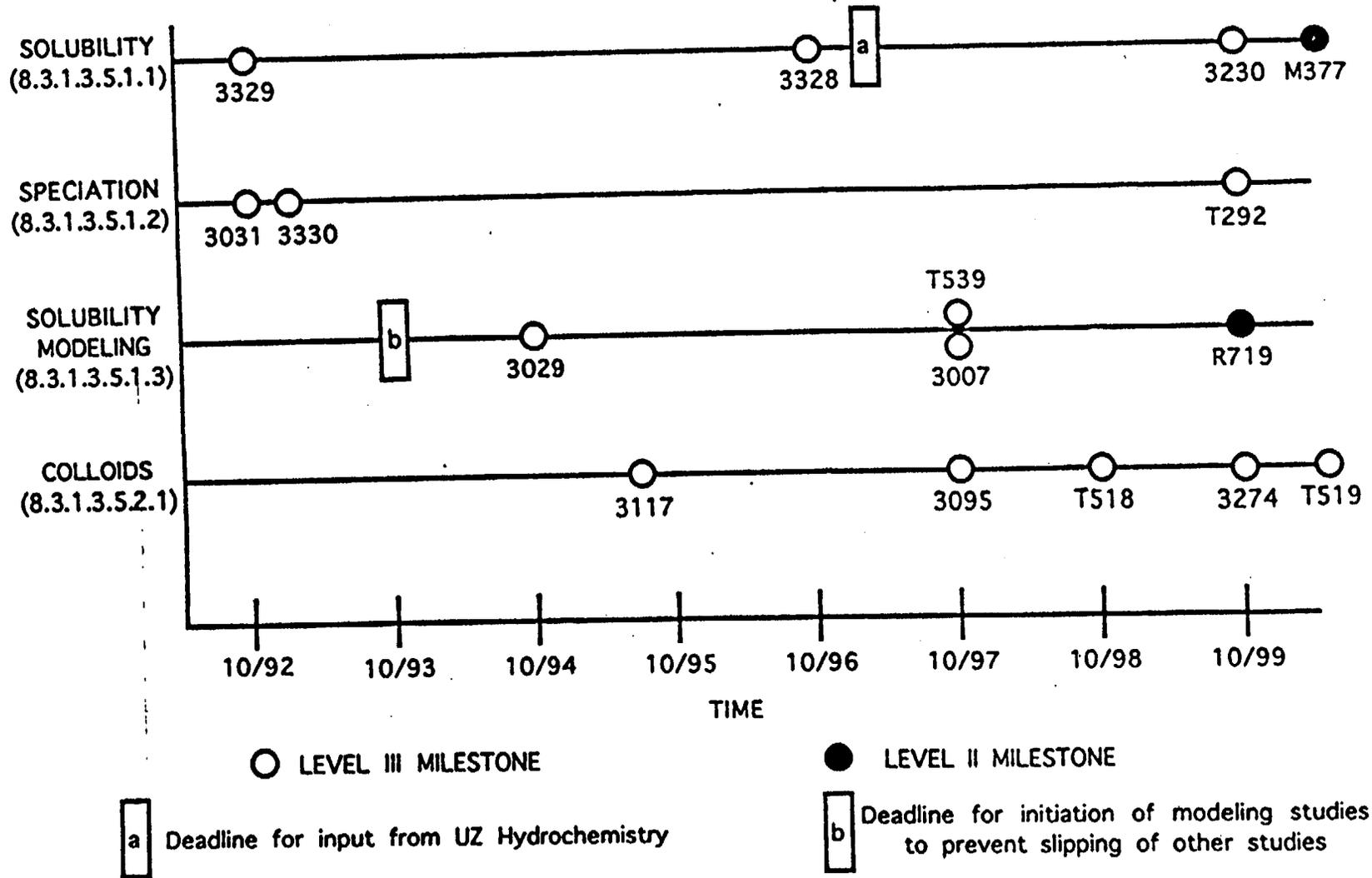


Figure 3. Schedule and Milestones for Dissolved Species Concentration Limits and Colloid Behavior

R719	M2	Solubility Calculations for Elements on the EPA Critical List
T292	M3	Final Report on Speciation Measurements
T519	M3	Final Report on Colloid Formation, Characterization, and Stability
M377	M2	Final Report : Solubility of Radionuclides in Yucca Mountain Waters

## 6.0 REFERENCES

- Åberg, M., Ferri, D., Glaser, J., and Grenthe, I. (1983a). "Studies of Metal Carbonate Equilibria. 8. Structure of the Hexakis(carbonato)tris[dioxouranate(VI)] Ion in Aqueous Solution. An X-ray Diffraction and  $^{13}\text{C}$  NMR Study," Inorganic Chemistry, Vol. 22, pp. 3981-3985.
- Åberg, M., Ferri, D., Glaser, J., and Grenthe, I. (1983b). "Structure of the Hydrated Dioxouranium(VI) Ion in Aqueous Solution. An X-ray Diffraction and  $^1\text{H}$  NMR Study," Inorganic Chemistry, Vol. 22, pp. 3986-3989.
- Allard, B. (1982). "Solubilities of Actinides in Neutral or Basic Solutions," in Actinides in Perspective, N. Edelstein, ed., Pergamon Press, New York, pp. 553-580.
- Barrow, G. M. (1973). Physical Chemistry, Third Edition, McGraw-Hill Book Co., New York, New York.
- Bell, J. T., Coleman, C. F., Costanzo, D. A., and Biggers, R. E. (1973). "Plutonium Polymerization-III. The Nitrate Precipitation of Pu(IV) Polymer," The Journal of Inorganic and Nuclear Chemistry, Vol. 35, p. 629.
- Bennett, D. A., Hoffman, D., Nitsche, H. Russo, R. E., Torres, R. A. Baisden, P. A. Andrews, J. E. Palmer, C. E. A., and Silva, R. J. (1992). "Hydrolysis and Carbonate Complexation of Dioxoplutonium(V)," Radiochimica Acta, Vol. 56, pp. 15-19.
- Berg, J. M., Morris, D. E., Clark, D. L., Tait, C. D., Woodruff, W. H., and VanDer Sluys, W. G. (1991a). "Pulsed Photothermal Spectroscopy Applied to Lanthanide and Actinide Speciation," Proceedings of the SPIE, Vol. 1435, p. 331.
- Berg, J. M., Tait, C. D., Morris, D. E., and Woodruff, W. H. (1991b). "Actinide Speciation by Photothermal Spectroscopies: Instrumentation Development," Materials Research Society Symposium Proceedings, Vol. 212, p. 531.
- Cotton, F.A. and Wilkinson, G. (1988). Advanced Inorganic Chemistry, Fifth Edition, John Wiley and Sons, New York, New York, p. 486.
- Combes, J. M., Chisholm-Brause, C. J., Brown, Jr., G. E., Parks, G. A., Conradson, S. D., Eller, P. G., Triay, I. R., Hobart, D. E., and Meijer, A. (1992). "EXAFS Spectroscopic Study of Neptunium(V) Sorption at the  $\alpha\text{-FeOOH}$  / Water Interface," Environmental Science and Technology, Vol. 26, pp. 376-382.
- DOE (U.S. Department of Energy) (1988). "General Guidelines for the Recommendation of Sites for Nuclear Waste Repositories," Code of Federal Regulations, Energy, Title 10, Part 960, Washington, DC.
- DOE (U.S. Department of Energy) (1988). "Site Characterization Plan, Yucca Mountain Site, Nevada Research and Development Area, Nevada," DOE/RW-199 Office of Civilian Radioactive Waste Management, Washington, DC.
- EG&G Princeton Applied Research (1985). Model 273 Potentiostat/Galvanostat Operating Manual, EG&G Princeton Applied Research, Princeton, NJ.
- EG&G Princeton Applied Research (1981a). Model 173 Potentiostat/Galvanostat Operating and Service Manual, EG&G Princeton Applied Research, Princeton, NJ.

EG&G Princeton Applied Research (1981b). Model 179 Digital Coulometer Operating and Service Manual, EG&G Princeton Applied Research, Princeton, NJ.

EG&G Princeton Applied Research (1981c). Model 175 Universal Programmer Operating and Service Manual, EG&G Princeton Applied Research, Princeton, NJ.

Eiswirth, M., Kim, J. I., and Lierse, C. (1985). "Optical Absorption Spectra of Pu(IV) Carbonate / Bicarbonate Media," Radichimica Acta, Vol 38, pp. 197-201.

Elings, V. B., and Nicoli, D. F. (1984). "A Recent Advance in Submicron Particle Sizing by Dynamic Light Scattering," American Laboratory, June, pp. 34-39.

EPA (U.S. Environmental Protection Agency) (1987). "Environmental Radiation Protection Standards for Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Wastes," Code of Federal Regulations, Protection of Environment, Title 40, Part 191, Washington, DC.

Eppendorf. Eppendorf Digital Pipette Instruction Manual, Brinkmann Instruments, Inc., Westbury, NY, p. 9.

Ferri, D., Glaser, J. and Grenthe, I. (1988). "Confirmation of the Structure of  $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$  by  $^{17}\text{O}$  NMR," Inorganica Chimica Acta, Vol. 148, pp. 133-134.

Freeman, A.J., and Keller, C. (1991). Handbook on the Physics and Chemistry of the Actinides, Volume 6, North-Holland, Amsterdam, Netherlands, pp. 471-510.

Frei, R. W., and MacNeil, J. D. (1973). Diffuse Reflectance Spectroscopy in Environmental Problem-Solving, CRC Press, Cleveland.

Hartley, F.R., Burgess, C., and Alcock, R. (1980). Solution Equilibria. John Wiley and Sons, New York, New York, p. 27.

Hobart, D. E., P. D. Palmer, and T. W. Newton (1986a). "The Carbonate Complexation of Plutonium(IV)," Los Alamos National Laboratory Report No. LA-UR-86-968, Los Alamos, New Mexico.

Hobart, D. E., T. W. Newton, and P. D. Palmer (1986b). "The Carbonate Complexation of Americium(III)," Los Alamos National Laboratory Report No. LA-UR-86-966, Los Alamos, New Mexico.

Hobart, D. E., Morris, D. E., and Palmer, P. D. (1987). "Formation, Characterization, and Stability of Plutonium(IV)-Colloid," Nevada Nuclear Waste Storage Investigations Report No. R718, Los Alamos National Laboratory Report LA-UR-87-3505.

Hobart, D. E., Morris, D. E., Palmer, P. D., and Newton, T. W. (1989). "Formation, Characterization, and Stability of Plutonium(IV) Colloid: A Progress Report," Proceedings of the Topical Meeting on Nuclear Waste Isolation in the Unsaturated Zone: FOCUS '89, p.118.

Ichikawa, F. and Sato, T. (1984). "On the Particle Size Distribution of Hydrolyzed Plutonium(IV) Polymer," Journal of Radioanalytical and Nuclear Chemistry, Vol. 84, p. 269.

Johnstone, J. K., Peters, R. R. and Gnirk, P. F. (1984). "Unit Evaluation of Yucca Mountain, Nevada Test Site: summary Report and Recommendations," Sandia National Laboratories Report SAND83-0372, Albuquerque, New Mexico.

Kerrisk, J. F. (1987). "Groundwater Chemistry at Yucca Mountain, Nevada, and Vicinity," Los Alamos National Laboratory Report 10929-MS, Los Alamos, New Mexico.

Kerrisk, J. F. (1985). "Solubility Experiments for the Nevada Nuclear Waste Storage Investigations Project," Los Alamos National Laboratory Report LA-10560-MS, Los Alamos, New Mexico.

Kim, J. I. (1986). "Chemical Behavior of Transuranic Elements in Natural Aquatic Systems," in Handbook on the Physics and Chemistry of the Actinides, A. J. Freeman and C. Keller, eds., Elsevier Science Publishers, New York, Chapter 8.

Koningsberger, D. C. and Prins, R., Eds. (1988). X-ray Absorption. Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES, John Wiley and Sons, New York.

Levine, I. N. (1978). Physical Chemistry, McGraw-Hill, New York.

Long, D. A. (1977). Raman Spectroscopy, McGraw-Hill, London, U.K.

Martell, A. E. and Smith R. M. (1982). Critical Stability Constants, Volumes 1-5, Plenum Press, New York.

Newton, T. W., Hobart, D. E. and Palmer, P. D. (1986a). "The Preparation and Stability of Pure Oxidation States of Neptunium, Plutonium, and Americium," Los Alamos National Laboratory Report No. LA-UR-86-967, Los Alamos, New Mexico.

Newton, T. W., Hobart, D. E. and Palmer, P. D. (1986b). "The Formation of Pu(IV)-Colloid by the Alpha-Reduction of Pu(V) and Pu(VI) in Aqueous Solutions," Radiochimica Acta, Vol. 39, p. 139.

Newton, T. W., and Sullivan, J. C. (1985). "Actinide Carbonate Complexes in Aqueous Solution," Handbook on the Physics and Chemistry of the Actinides, A. J. Freeman and C. Keller, eds., Elsevier Science Publishers, New York Vol. 3, Ch. 10, p. 387.

Nitsche, H., and Edelstein, N. M. (1985). "Determination of the Solubilities and Complexation of Waste Radionuclides Pertinent to Geologic Disposal at the Nevada Test Site," Radiochimica Acta, Vol. 39, pp. 22-33.

Nitsche, H. (1986). "Temperature Effects on the Solubility and Speciation of Selected Actinides," U.S. Nuclear Regulatory Commission, report NUREG/CR-4582, Washington, D.C.

Nitsche, H., Lee, S. C. and Gatti, R. C. (1987). "Determination of Plutonium Oxidation States at Trace Levels Pertinent to Nuclear Waste Disposal," J. Radioanal. and Nucl. Chem., Vol. 124, No. 1, pp. 171-185.

Nitsche, H. (1987). "Effects of Temperature on the Solubility and Speciation of Selected Actinides in Near-neutral Solution," Inorg. Chim. Acta, Vol. 127, pp. 121-128.

Nitsche, H. (1991a). "Solubility Studies of Transuranium Elements for Nuclear Waste Disposal: Principles and Overview," Radiochim. Acta, 52/53, pp. 3-8.

Nitsche, H. (1991b). "Basic Research for Assessment of Geologic Nuclear Waste Repositories: What Solubility and Speciation Studies of Transuranium Elements Can Tell Us," Mat. Res. Soc. Sym. Proc., Vol. 212, pp. 517-529.

Nitsche, H., Müller, A., Standifer, E.M., Deinhammer, R.S., Becraft, K., Prussin, T., Gatti, R.C.

- (1992a). "Dependence of Actinide Solubility and Speciation on Carbonate Concentration and Ionic Strength in Groundwater," Radiochim. Acta, in press.
- Nitsche, H., Gatti, R.C., and Lee, S.C. (1992b). "Low Level Determination of Plutonium by Gamma and to X-Ray Spectroscopy," Lawrence Berkeley Report, LBL-30617, J. Radioanal. Nucl. Chem., Vol 160, No. 2.
- Nitsche, H., Gatti, R.C., Standifer, E.M., Lee, S.C., Müller, A., Prussin, T., Deinhammer, R.S., Maurer, H., Becraft, K., Leung, S., and Carpenter, S.A. (1992c). "Measured Solubilities and Speciations of Neptunium, Plutonium, and Americium in a Typical Groundwater (J-13) from the Yucca Mountain Region," Report Lawrence Berkeley Laboratory, LBL-30958, in review.
- NRC (Nuclear Regulatory Commission) (1988). "Disposal of High-Level Radioactive Wastes in Geologic Repositories," Code of Federal Regulations, Energy, Title 10, Part 60, Washington, DC.
- NRC (Nuclear Regulatory Commission) (1984). "Determination of Radionuclide Solubility in Ground Water for Assessment of High-Level Waste Isolation."
- Ogard, A. E., and Kerrisk, J. F. (1984). "Review of the Groundwater Chemistry along Flow Paths Between a Proposed Repository Site and the Accessible Environment," Los Alamos National Laboratory Report No. LA-10188-MS, Los Alamos, New Mexico.
- Olofsson, U. Allard, B., Torstenfelt, B. and Andersson, K. (1982). "Properties and Mobilities of Actinide Colloids in Geologic Systems," in Scientific Basis for Radioactive Waste Management V, W. Lutze, ed., Elsevier Science Publishing Co., Paris, pp. 755-764.
- Oversby, V. M. (1985). Lawrence Livermore National Laboratory Letter WP:65-85/6026N to J. F. Kerrisk, Los Alamos National Laboratory, May 7, 1985, Livermore, California.
- Phillips, S. L., Phillips, C. A. and Sheen, J. (1985). "Hydrolysis and Ionization Constants at 25°C and at High Temperature/High Ionic Strength," Lawrence Berkeley Laboratory Report LBL-14996, Berkeley, California.
- Rundberg, R. S., Mitchell, A. S., Triay, I. R., and Torstenfelt, N. B. (1988). "Size and Density of a  $^{242}\text{Pu}$  Colloid," Materials Research Society Symposium Proc, Vol. 112, p.243-248.
- Shugar, G.J., and Dean, J.A. (1990). The Chemist's Ready Reference Handbook, McGraw-Hill, New York, NY, p. 294.
- Strom, E. T., Woessner, D. E., and Smith, W. B. (1981). " $^{13}\text{C}$  NMR Spectra of the Uranyl Tricarbonate-Bicarbonate System," Journal of the American Chemical Society, Vol. 103, pp. 1255-1256.
- Stöhr, J. (1992). NEXAFS Spectroscopy, Springer-Verlag, New York, NY.
- Stumm, W., and Morgan, J. J. (1985). Aquatic Chemistry, 2nd Edition, John Wiley & Sons, New York, New York, pp. 171-229.
- Stumpe, R., Kim, J. I., Schrepp, W. and Walther, H. (1984). "Speciation of Actinide Ions in Aqueous Solution by Laser-Induced Pulsed Photoacoustic Spectroscopy," Applied Physics, B, Vol. 34, p. 203.
- Tait, C. D., Morris, D. E., Berg, J. M., Ekberg, S. A., and Woodruff, W. H. (1993). "Evaluation of

Alternative Detection Schemes for Actinide Speciation Using Photoacoustic Spectroscopy," Yucca Mountain Site Characterization Program Milestone Report 3330, Los Alamos National Laboratory.

Thiyagarajan, P., Diamond, H., Soderholm, L., Horwitz, E. P., Toth, L. M., and Felker, L. K. (1990). "Plutonium(IV) Polymers in Aqueous and Organic Media," Inorg. Chem., Vol. 29, pp 1902-1907.

Triay, I. R., Hobart, D. E., Mitchell, A. J., Newton, T. W., Ott, M. A., Palmer, P. D., Rundberg, R. S., and Thompson, J. L. (1991). "Size Determination of Plutonium Colloid Using Autocorrelation Photon Spectroscopy," Radiochimica Acta, Vols. 52/53, pp. 127-131.

Tucker, D. B., Standifer, E. M., Nitsche, H. and Silva, R. J. (1988). "Data Acquisition and Feedback Control System for Solubility Studies of the Nuclear Waste Elements Neptunium and Plutonium," Lanthanide and Actinide Res., 2(4), p. 279.

Varian Instrument Division "CARY Model 17D Spectrophotometer System," Instruction Manual 17D-015, A370.

Wendlandt, W. W., and Hecht, H. G. (1966). Reflectance Spectroscopy, Interscience Publishers, New York.

Wolery, T. J. (1983). EQ3NR, A Computer Program for Geochemical Aqueous Speciation Solubility Calculations: User's Guide and Documentation, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53414.

Wolery, T. J., Jackson, K. T., Boureier, W. L., Bruton, C. J., Viani, B. E., Knauss, K. G., and Delany, J. M. (1989). "The EQ3/6 Software Package for Geochemical Modeling: Current Status," Am. Chem. Soc. Symposium Volume, Chemical Modeling in Aqueous Systems II, pp. 105-116.

Yang, I. C., Turner, A. K., Sayre, T. M., and Montazer, P. (1988). "Triaxial-Compression Extraction of Pore Water from Unsaturated Tuff, Yucca Mountain, Nevada," Water-Resource Investigations Report 88-1489, U. S. Geological Survey.

SP 8.3.1.3.5.1, R0  
SP 8.3.1.3.5.2, R0

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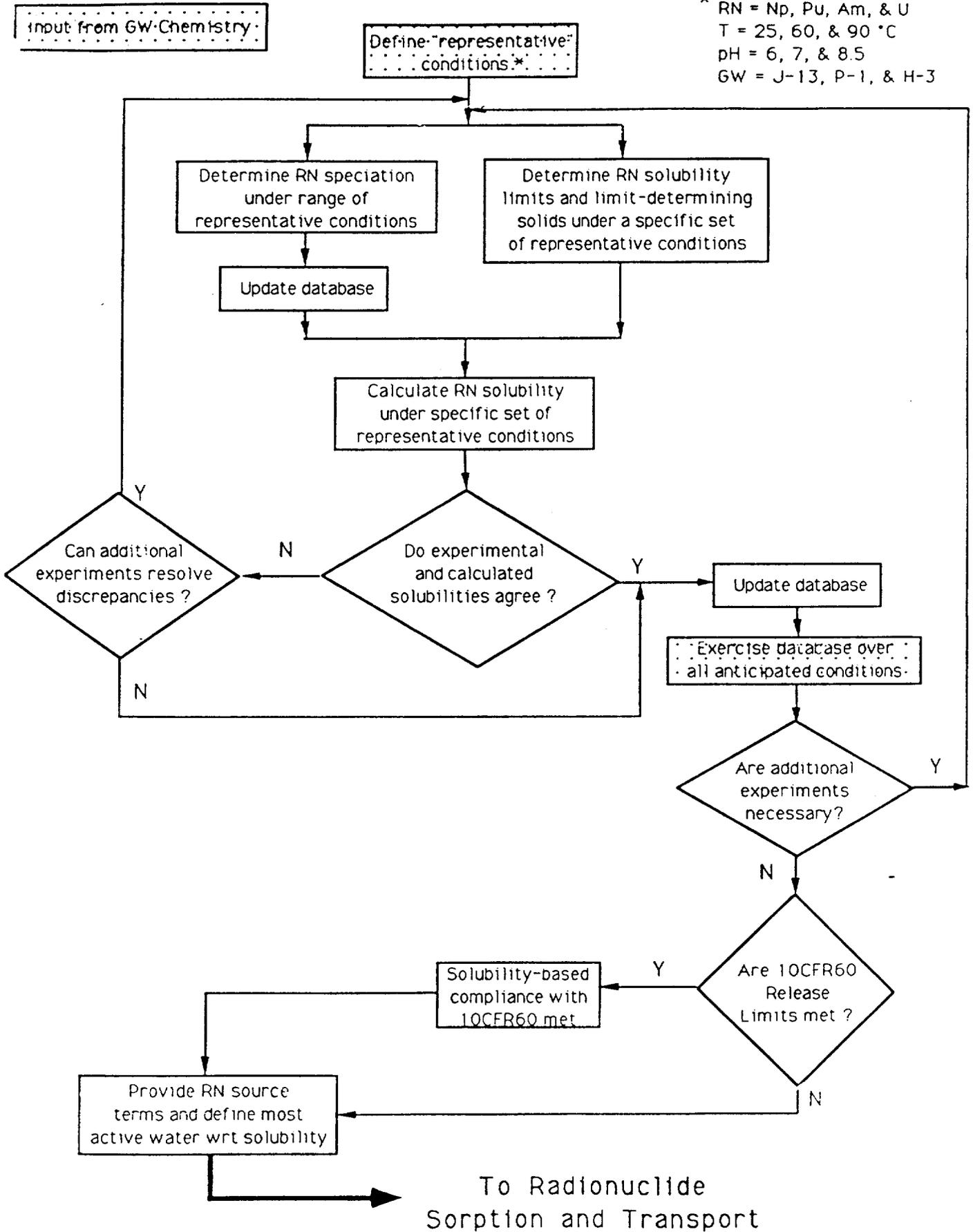
TECHNICAL PROCEDURES FOR STUDY PLAN 8.3.1.3.5.1  
AND 8.3.1.3.5.2, "DISSOLVED SPECIES  
AND CONCENTRATION LIMITS AND COLLOID BEHAVIOR"

<u>Title of Detailed Technical Procedure</u>	<u>Reference</u>
Data Acquisition and Feedback Control Standard System for Solubility Studies	YMP-LBL-DP-01
Preparation of Actinide Solutions Containing Only One Oxidation State	in preparation
Phase Separation Techniques for Solubility Studies	in preparation
Neutron Activation Analysis	in preparation
Trace Metal Characterization by Atomic Emission Spectroscopy for the Yucca Mountain Waste Element Solubility Study	YMP-LBL-DP-04
Trace Level Determination of Oxidation State of Soluble Species from Solubility Measurements	in preparation
Determination of Plutonium Oxidation States of Soluble Species from Solubility Measurements at Concentrations Below $10^{-5}$ M for the Yucca Mountain Waste Element Solubility Study	TWS-LBL-DP-10
Determination of Plutonium at Trace Levels by Gamma and L X-Ray Spectroscopy	in preparation
Quality Control in Counting Radioactive Nuclides	in preparation
Partial CO <sub>2</sub> Atmospheric Control of Ground Water Chemistry	in preparation
pH Measurements	TWS-INC-DP-35
X-Ray Powder Diffraction Analysis for the Yucca Mountain Waste Element Solubility Study	YMP-LBL-DP-03
Preparation of Solutions of Pure Oxidation States of Neptunium, Plutonium, and Americium	TWS-INC-DP-78
Recording Reflectance and Absorption Spectra	in preparation
Calibration of Low-Energy Gamma Counters for the Yucca Mountain Waste Element Solubility Study	TWS-LBL-DP-02
Sodium Concentration Determination Procedure for the Yucca Mountain Waste Element Solubility Study	TWS-LBL-DP-05
Eh (Redox Potential) Measurements for the Yucca Mountain Waste Element Solubility Study	TWS-LBL-DP-06
Sample Identification and Handling Procedure for the Yucca Mountain Waste Element Solubility Study	YMP-LBL-DP-07
Measurement of Photoacoustic Spectra	in preparation

procedures may be found in Table 6, pages 52-53, in study plan

# STRATEGY FOR DISSOLVED SPECIES CONCENTRATION LIMIT STUDIES

\* RN = Np, Pu, Am, & U  
 T = 25, 60, & 90 °C  
 pH = 6, 7, & 8.5  
 GW = J-13, P-1, & H-3



## DISCUSSION ON SITE CHARACTERIZATION ANALYSIS (SCA) OPEN COMMENT 96

The U.S. Nuclear Regulatory Commission (NRC) SCA has identified a concern regarding the investigations to characterize the retardation of radionuclides by sorption processes (Comment 96). Study Plan 8.3.1.3.5.1 and 8.3.1.3.5.2, "Dissolved Species Concentration Limits and Colloid Behavior," is explicitly cited in the discussion of this concern because: (1) precipitation could potentially act as an alias for sorption leading to uncertainty and ambiguity in the way sorptive retardation is incorporated into total system performance modeling, and (2) Study 8.3.1.3.5.1 states that credit will be taken for precipitation as a retardation mechanism.

Study 8.3.1.3.5.1 specifically addresses the issue of the solubility limit for key radionuclides under conditions anticipated at the proposed repository. We note that credit is taken for retardation by precipitation processes, but only for retardation of the transport of dissolved species. We acknowledge that the precipitated radionuclides could undergo transport as colloidal species. This possibility was considered in detail at the recent Yucca Mountain Site Characterization Project Colloid Workshop, and the conclusions and recommendations regarding colloid transport are described in the meeting report, "Colloid Facilitated Radionuclide Transport at Yucca Mountain (LA-UR-93-1265)," that will be transmitted to the NRC when it becomes available to the U.S. Department of Energy.

With regard to the potential ambiguity between sorption and precipitation, we agree with this concern and have outlined a course of experimentation and modeling in our study plan to address this potential problem. Specifically, empirical solubility determinations are being undertaken for key radionuclides using water compositions chosen to bracket the anticipated conditions at the proposed repository. These experiments will provide upper limits to radionuclide solubility that can then be used in the proper design and interpretation of batch and column sorption experiments. We acknowledge that these solubility experiments cannot be conducted for all radionuclides under all foreseeable groundwater chemistry scenarios. For this reason we are simultaneously conducting more fundamental speciation studies to provide thermodynamic data that can be used to model solubility under a broader range of conditions.

We have also developed a strategy for dissolved species concentration limit studies that provides the experimental flexibility to undertake additional solubility determinations as warranted to resolve discrepancies or minimize uncertainty under crucial groundwater scenarios. The logic diagram for this strategy is attached and the strategy will be discussed in detail with the NRC in the forthcoming Technical Exchange on Radionuclide Migration at Yucca Mountain (October 13-15, 1993 in Los Alamos, New Mexico).