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LABORATORY AND MODELING STUDIES OF NEPTUNIUM UPTAKE ON CALCITE

Prepared for

U.S. Nuclear Regulatory Commission
Contract NRC–02–97–009

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ABSTRACT

The U.S. Department of Energy (DOE) is currently investigating Yucca Mountain, Nevada, as a potential site for geologic disposal of high-level waste. The potential for radionuclides to be transported in groundwater from the proposed repository to the accessible environment is a key technical issue for the U.S. Nuclear Regulatory Commission (NRC), and the potential delay of the transport of radionuclides in groundwater has been identified as a principal factor in the DOE safety case. The widespread occurrence of calcite, including an uncertain abundance in the alluvium, the variation in the calcite saturation index of Yucca Mountain groundwater, and a lack of data regarding Np-237 sorption on calcite indicate a need to investigate and understand Np-237 uptake on calcite. Previous DOE studies noted the relatively strong sorption of Np-237 onto calcite and included the presence of calcite in assumptions for sorption values within the saturated zone. An understanding of the mechanisms and magnitude of calcite uptake of Np-237 from solution will be of benefit to NRC staff in their review of the DOE licensing case, if submitted, especially for ascertaining the potential transport of Np-237 through the saturated zone. Information on Np-237 and calcite interaction can be used in conjunction with previous studies of Np-237 sorption on minerals to develop more representative abstractions for radionuclide transport in the saturated alluvium. This report discusses experimental and modeling efforts to investigate Np-237 sorption on calcite and provides a preliminary review of recent results.

A second series of batch experiments was conducted using calcite substrate in solutions at or near saturation with respect to calcite for a pH range of 7.25 to 9. The solutions were at equilibrium with atmospheric partial pressures of $CO_2(g)$, and the initial concentration of Np-237 was ~1.6×10^{-6} M. The results of the experiments confirm the pH dependence of Np-237 sorption on calcite. Calcite is an effective sorber of Np-237 for the pH range studied, and the sorption magnitude observed is similar to or greater than the sorption of Np-237 by montmorillonite for the same pH range. The experimental results also indicate that previous experimental difficulties, perhaps induced by insufficient mixing during the sorption phase, have not been fully resolved. Nevertheless, an adequate amount of data has been collected to initiate efforts to model the Np-237 and calcite system.

Preliminary modeling results show that a nonelectrostatic surface complexation approach is ineffective at reproducing experimental data. The experimental data are fit reasonably using a simple ion exchange model and a constant capacitance surface complexation model. Model results indicate Np-237 uptake is reduced by the sorption of Ca^{2+} onto the calcite surface and by the formation of neptunyl carbonate complexes in solution; however, constant capacitance model results indicate some neptunyl carbonate sorption on calcite also occurs at high pH. A better understanding of Np-237 sorption on calcite will depend on a continuation of work to resolve experimental uncertainties and to expand the conditions of the experiments to include a range of Np-237 concentrations and varying partial pressures of $CO_2(g)$.

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QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT

DATA: CNWRA-generated original data contained in this report meet quality assurance requirements described in the CNWRA Quality Assurance manual. Sources for other data should be consulted for determining the level of quality for those data.

ANALYSES AND CODES: The EQ3NR Version 7.2b, MINTEQA2 Version 4, and FITEQL Version 3.1 computer codes were used for analyses contained in this report. These computer codes are controlled under CNWRA Software Configuration Procedures. The spreadsheet software Microsoft™ Excel 97 was used in calculations, and the graphical plotting software SigmaPlot Version 5 (SPSS Scientific) was used for some figures. These are commercial software packages, and only the object codes are available to the CNWRA.

1 REGULATORY BASES

The Nuclear Waste Policy Act of 1982, as amended in 1987 (Nuclear Waste Policy Act, 1982), directs the U.S. Department of Energy (DOE) to characterize and determine the suitability of Yucca Mountain, Nevada, as a geologic repository for high-level wastes. In February 2002, the Secretary of Energy determined that the Yucca Mountain site was suitable and recommended to the President that Yucca Mountain be developed as a long-term geologic repository. Pending approval of the suitability recommendation by Congress, the DOE will also be responsible for preparing an application to receive a license from the U.S. Nuclear Regulatory Commission (NRC) to construct and operate the repository. In preparing to review a possible license application, the NRC is directing activities toward resolving several key technical issues that the NRC considers most important to repository performance. The performance measure of a high-level waste geologic repository is its ability to limit radiological exposures to the public, and as such, one of these key technical issues is concerned with assessing the potential for radionuclide transport from the repository through the subsurface to the accessible environment.

The potential transport of radionuclides dissolved in groundwater is important to repository performance because the public can receive a radioactive dose exposure if radionuclides migrate from the repository through the geologic setting. The estimated or calculated radiological exposures to the public are directly related to the concentration of radionuclides in the groundwater. The U.S. Environmental Protection Agency (EPA) has defined the limits for public exposure from the proposed repository in its rule, Public Health and Environmental Radiation Protection Standards for Yucca Mountain, Nevada (40 CFR Part 197). The EPA rule notes that the reasonable maximally exposed individual to radionuclides released from the proposed repository within 10,000 years after closure is located approximately 18-km [approximately 11.2 mi] from Yucca Mountain along the expected transport path. The NRC rule, Disposal of High-Level Radioactive Wastes in a Proposed Repository at Yucca Mountain, Nevada (10 CFR Part 63), directs the license applicant (DOE) to adequately characterize the Yucca Mountain system and to develop a performance assessment that has a sufficient technical basis to reasonably estimate the performance of the proposed repository for the regulatory timeframe of 10,000 years. This rule requires that the DOE develop an adequate model to assess the transport of radionuclide from Yucca Mountain.

DOE identified the retardation of radionuclides in the unsaturated and saturated zones at Yucca Mountain as principal factors of the current postclosure safety (licensing) case (CRWMS M&O, 2000a). Retardation can result from various processes that lead to the effective removal of radionuclides as potential contributors to dose. These processes include sorption, precipitation, and matrix diffusion of radionuclides from the advecting groundwater. Radionuclide retardation is dependent on the hydrochemistry and mineralogy along the groundwater flow paths from the repository to the reasonable maximally exposed individual (NRC, 2000), and a clear understanding of the relative effects of chemical processes on retardation is a key aspect of evaluating the DOE safety case. Better understanding of geochemical processes that influence radionuclide transport may also be used to improve hydrologic models of the Yucca Mountain system.

The Radionuclide Transport Key Technical Issue addresses the main issue that radionuclide concentrations may be reduced during transport in groundwater. Radionuclide Transport Key

Technical Issue subissues, which examine transport through porous rock, fractured rock, and alluvium, have been the focus of previous review and study by NRC staff and form the basis for agreements reached during a series of DOE and NRC technical exchanges held during 2000[1] and 2001. These agreements represent a commitment by DOE to provide information that NRC staff require for a complete, high-quality license application with respect to a given subissue and form the basis for the issue resolution process.

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[1] Reamer, C.W. "U.S. Nuclear Regulatory Commission/U.S. Department of Energy Technical Exchange and Management Meeting on Radionuclide Transport (December 5–7, 2000)." Letter (December 12) to S.J. Brocoum, DOE. Washington, DC: NRC. 2000.

2 RADIONUCLIDE TRANSPORT IN PERFORMANCE ASSESSMENT

As part of its demonstration of the performance of the proposed Yucca Mountain repository following permanent closure, DOE must use a performance assessment (NRC, 1999), which consists of a number of linked system model abstractions designed to estimate doses from the repository to the public for the 10,000-year regulatory period. In the current DOE performance assessment model for Yucca Mountain, the Total System Performance Assessment–Site Recommendation, radionuclides are assumed to interact with the geologic setting during transport in groundwater through the unsaturated and saturated zones (CRWMS M&O, 2000b). In the Total System Performance Assessment–Site Recommendation model, retardation of radionuclides occurs through matrix diffusion from advecting groundwater into the relatively stagnant rock matrix and through sorption of radionuclides onto matrix rock surfaces and grains within the saturated alluvium. Sorption processes are not included in the Total System Performance Assessment–Site Recommendation model for radionuclide transport through fractures, although it is possible that fracture lining materials may play a role in retarding radionuclides. Total System Performance Assessment–Site Recommendation model sorption processes are represented using the distribution coefficient (K_D) as given by the equation:

$$K_D = \frac{[\mathrm{RN}]_{\mathrm{solid}}}{[\mathrm{RN}]_{\mathrm{aqueous}}} = \frac{\text{equilibrium mass RN on solid}}{\text{equilibrium mass RN in solution}} \times \frac{V}{M} \qquad \text{(2-1)}$$

where $[\mathrm{RN}]_{\mathrm{solid}}$ and $[\mathrm{RN}]_{\mathrm{aqueous}}$ are the concentrations of radionuclide on the solid and in the groundwater, M is the mass of the solid, and V is the solution volume (CRWMS M&O, 2000a,b,c). For saturated flow, radionuclide retardation is related to K_D by the equation:

$$R_f = 1 + \frac{\rho_b}{n} K_D \qquad \text{(2-2)}$$

where R_f is the retardation factor, ρ_b is the bulk density, and n is the porosity. For unsaturated flow, the moisture content, θ, is substituted for n (CRWMS M&O, 2000b,c). Inherent in the use of Eq. (2-2) is the assumption that sorption isotherms for radionuclides are linear (Freeze and Cherry, 1979). It is implicit in the current modeling approach that various processes, such as ion exchange and surface complexation, often combined under the term sorption, are not mechanistically or individually represented by the model. In fact, these processes are lumped together as one linear term. In the DOE Total System Performance Assessment–Site Recommendation model, as in previous efforts, sorption coefficients in the tuff matrix were assigned values and probability distributions based on expert elicitation. Specific constraints on the transport parameters have been modified, particularly for uranium, neptunium, and plutonium (Wilson, et al., 1994; Triay, et al., 1997; CRWMS M&O, 2000b). Sorption parameters and probability distribution functions were constrained assuming waters from saturated volcanic tuff (J-13 Well) and the Paleozoic (UE-25p#1 Well) aquifers bound the chemistry of the groundwaters at Yucca Mountain (Triay, et al., 1997). The basis for the values used for alluvium sorption parameters (CRWMS M&O, 1998) was the compilation of Thibault, et al. (1990).

K_D values for Np-237, which has been identified as a radionuclide important to performance, have been of particular concern. There has been little formal investigation of Np-237 K_Ds in alluvium materials (CRWMS M&O, 2000c). Because of a lack of experimental data, Np-237 sorption coefficients used for alluvium in the Total System Performance Assessment–Viability Assessment were assigned values greater than Np-237 K_Ds used for the saturated tuffs (CRWMS M&O, 1998). The K_Ds used were based on an assumption that the alluvium materials consisted of at least 5 percent calcite and on experimental indications that calcite was a possible strong sorber of Np-237 in Yucca Mountain waters (CRWMS M&O, 1998; Triay, et al., 1996, 1997). DOE performed sensitivity analyses using the Total System Performance Assessment–Viability Assessment code to investigate the effects of uncertainty in sorption parameters on performance (CRWMS M&O, 1998). The effects of uncertainty on sorption of Np-237 in the saturated zone volcanic rocks were investigated during the analyses, but the K_D for neptunium sorption in the alluvium was held constant at 10 mL/g [17.3 in^3/oz] (CRWMS M&O, 1998).

More recently, sensitivity analyses conducted for the DOE Total System Performance Assessment–Site Recommendation have shown that the saturated zone transport model is particularly sensitive to Np-237 K_Ds, with the variance in K_Ds producing two orders of magnitude variance in transport times for Np-237 through the saturated zone (CRWMS M&O, 2000b). The Total System Performance Assessment–Site Recommendation model sorption coefficients for neptunium in the saturated alluvium were modified to reflect recent experiments conducted on alluvial materials (CRWMS M&O, 2000b). These materials included drilling cuttings from wells in the Nye County Early Warning Drilling Program (Conca, et al., 2000; CRWMS M&O, 2000b,c). Based on the preliminary results of these batch sorption studies, the probability distribution function (which represents K_D range and magnitude) for Np-237 sorption on alluvium was adjusted. The preliminary batch results, however, may be influenced by sample artifacts (such as surface area changes during material preparation and specific mineral content of the sampled horizon), and further studies are under way (Conca, et al., 2000; Bechtel SAIC Company, 2001).

The known occurrence of calcite in tuffs and calcareous zones within the alluvium downgradient from Yucca Mountain and the known sensitivity of saturated zone transport models to K_D values used for Np-237, combined with the uncertainties in alluvium characterization and a poor understanding and body of information regarding Np-237 sorption on calcite, make it imperative that Np-237 interaction with calcite be more clearly understood prior to a potential license application. Other considerations include a need to understand the retention and redistribution of Np-237 near the surface, where Np-237 might be introduced in irrigation water pumped from a plume emanating from the proposed Yucca Mountain repository (NRC, 2000). Moreover, DOE has extensive plans to conduct further alluvium characterization that should help them better define parameter uncertainties, but results of these studies may not be available until very near the planned date for a potential license application.[2]

A linear sorption radionuclide transport model similar to that used by DOE is also employed for the saturated alluvium in the NRC independent performance assessment code,

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[2] Reamer, C.W. "U.S. Nuclear Regulatory Commission/U.S. Department of Energy Technical Exchange and Management Meeting on Radionuclide Transport (December 5–7, 2000)." Letter (December 12) to S.J. Brocoum, DOE. Washington, DC: NRC. 2000.

TPA Version 4.0 code (Mohanty, et al., 2001). The NRC TPA Version 4.0 code currently includes K_D probability distribution functions that are based, in part, on variations in system chemistry rather than mineralogy and have been informed through surface complexation modeling of minerals that occur in the Yucca Mountain region (Mohanty, et al., 2001; Turner, et al., 1999). Proposed revisions to the TPA code will provide a direct connection between modeled K_Ds and the probability distribution functions resulting from variations in groundwater chemistry. The experimental and modeling studies described in this report should aid in a more realistic representation of the retardation characteristics of the saturated zone.

3 EXPERIMENTAL BACKGROUND

Calcite is an important mineral for consideration in analyzing the DOE safety case because of its relatively widespread occurrence in the Yucca Mountain region (Bish, et al., 1996; Carlos, et al., 1995; Vaniman, 1994). Calcite deposits are found within the unsaturated and saturated zones, in tuff matrix, and as fracture lining material in both open and filled fractures, as well as in linings of lithophysal cavities (Carlos, et al., 1995; Vaniman, 1994). In some areas, however, calcite has been noted to occur less frequently in the first few hundred feet immediately below the water table in volcanic tuffs (Vaniman, 1994). Calcite deposits provide indications of forming from both precipitation from upwelling groundwater and precipitation associated with percolation of rainfall into the unsaturated zone (Carlos, et al., 1995; Vaniman, 1994). There is limited information on subsurface alluvium mineralogy, but calcareous units are identified in the lithologic logs for several of the Nye County Early Warning Drilling Program wells (Nye County, 2002). Recent analyses of cuttings from well NC–EWDP–02D reveal the presence of calcite and dolomite (Figure 3-1) (Bertetti, et al., 2001). Based on limited study, calcite appears to occur more commonly in water-producing zones ~300 M [1,000 ft] below the surface (Bertetti, et al., 2001). Thus, calcite occurs along all groundwater flow paths in the Yucca Mountain region.

Np-237 has been identified as a radionuclide of concern in the Yucca Mountain program (NRC, 2000). Np-237 exhibits a low sorption affinity for most minerals, and modeling results suggest that it sorbs to silicates through a surface complexation mechanism (e.g., Triay, et al., 1997; Turner, et al., 1999; Del Nero, et al., 1998). DOE batch sorption experiments with crushed tuff indicate the presence of calcite may enhance neptunium retardation (Triay, et al., 1996, 1997), and Allard (1984) reported Np-235, 237 sorption onto calcite from solutions very similar to J-13 Well water. Triay, et al. (1996) found that natural and synthetic calcite sorbed significantly greater quantities of neptunium than did silicate minerals and proposed Np-237 was effectively removed from solution by calcite through a coprecipitation mechanism. Triay, et al. (1996) also noted that steady-state neptunium uptake by calcite was not reached in 30 days of contact. The magnitude of removal of Np-237 from solution, however, was highly variable and was dependent on sample preparation, time of reaction, and differences in experimental solutions (Triay, et al., 1996). Though recommended by Triay, et al. (1996), no further DOE studies were made to determine mechanisms of Np-237 uptake or to better quantify the amount of Np-237 uptake on calcite substrates.

A recent Center for Nuclear Waste Regulatory Analyses (CNWRA) study investigated Np-237 uptake through coprecipitation with calcite (Nugent and Turner, 2000). Results showed that Np-237 was readily removed from solution during calcite precipitation. Calcite precipitated in a solution containing 28 parts per billion Np-237 produced a solid (coprecipitate) containing 500–1,000+ parts per million Np-237, suggesting neptunium is compatible with the calcite structure in some way. A comparison of neptunium-calcite and uranium-calcite coprecipitation demonstrated that uranium-calcite partition values are approximately two orders magnitude smaller (Nugent and Reeder, 1999; Nugent and Turner, 2000; Reeder, et al., 2000). This large discrepancy is surprising because research on neptunium and uranium adsorption behaviors on silicates and aluminosilicates indicates that they behave quite similarly (Nugent and Turner, 2000).

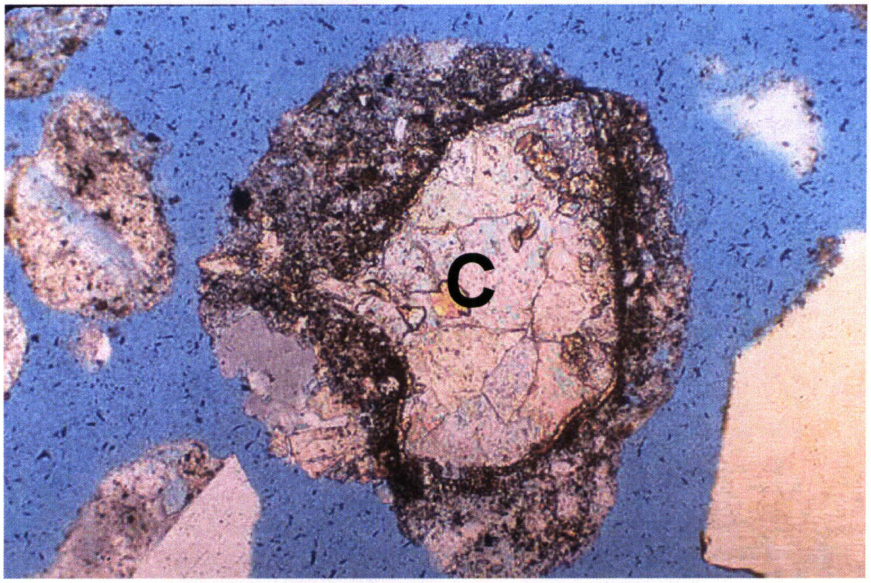

Figure 3-1. Photomicrograph of Cuttings Sample Taken from Nye County Well NC-EWDP-02D at a Depth of ~1,195 feet. Sparry Calcite (C) is Replacing a Feldspar Phenocryst Within a Volcanic Rock Fragment. Calcite and Dolomite Commonly Occur in Water Producing Zones at Depth in Well 02D.

Geochemical data indicate the groundwater along the expected flow path from Yucca Mountain to the reasonable maximally exposed individual is undersaturated with respect to calcite. Calcite saturations in the saturated zone in the Yucca Mountain region are represented in Figure 3-2, which is based on modified data from the Perfect, et al. (1995) database (Turner and Pabalan, 1999). Figure 3-2 has been updated from the previous letter report (Bertetti, 2001) to include geochemical data from Early Warning Drilling Program wells sampled in 1999 (Bertetti, et al., 2001). As indicated by the saturation index for calcite, which is <1.0 for undersaturation and >1.0 for oversaturation, calcite would not be expected to precipitate along the expected flow path from Yucca Mountain. Thus, Np-237 sorption processes that do not include coprecipitation may be more important for the Yucca Mountain region.

There have been a number of investigations of divalent metal (including transition metals and alkaline earths) sorption onto calcite (e.g., Davis, et al., 1987; Zachara, et al., 1988, 1991; Miyake, et al., 1988; Brady, et al., 1999; Stipp, et al., 1992). Results of these studies have shown that metals (such as zinc and cobalt) readily sorb to calcite surfaces. In general, the sorption of metals increases with increasing pH (from approximately 7 to 9.5). The mechanisms of metal sorption onto calcite are not well understood, and various explanations have been forwarded. These explanations include surface exchange between Ca^{2+} and the metal in solution (e.g., Zachara, et al., 1988, 1991), surface adsorption and chemisorption (McBride, 1980), adsorption on surface exchange sites followed by lattice incorporation (e.g., LaHann and Siebert, 1982; Davis, et al., 1987), and solid-state diffusion (e.g., Stipp, et al., 1992). Typically, fast uptake is interpreted as adsorption, while slow processes are interpreted to be coprecipitation, diffusion, or recrystallization (Davis, et al., 1987; Stipp, et al., 1992). In some cases, investigators have noted partial irreversibility of sorption (e.g., Zachara, et al.,

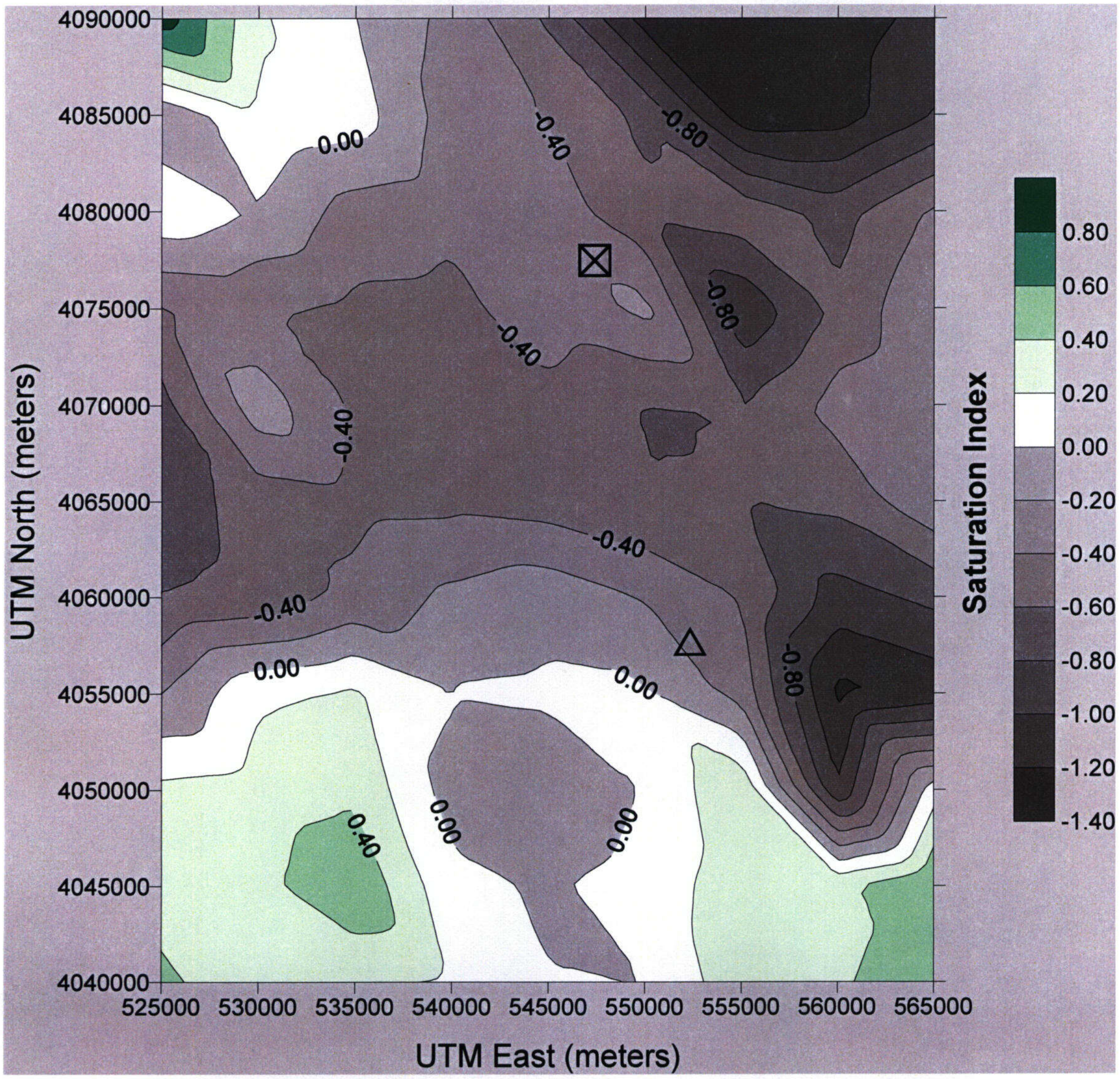

Figure 3-2. Contour Map of the Saturation Index for Calcite in Groundwater for the Yucca Mountain Region. The Approximate Location of the Proposed Repository is Shown by the Crossed-Box, While the Approximate Location of the Reasonably Maximally Exposed Individual (Compliance Point) is Shown by the Triangle. Figure Based on Turner and Pabalan (1999) and Updated for Recent Nye County Well Data.

1991). Miyake, et al. (1988) observed dissolution and recrystallization within 40 hours. Solution conditions play an important role, and a majority of the studies have been intentionally conducted under conditions that are at saturation with respect to calcite. As has been observed in previous studies (e.g., Bertetti, et al., 1998), solution chemistry and complexation reactions appear to be more important than surface charge when describing sorption onto the calcite surface (Zachara, et al., 1988). Another important component of studies on calcite surface reactions is the difficulty of conducting experiments with calcite as the sorbent. Dissolution and precipitation reactions are fast and occur on the order of the experiment duration. Similarly, speciation and surface reactions are sensitive to methods of pH adjustment, and varying carbonate values make assessment and interpretation of the sorption mechanisms difficult (Van Cappellen, et al., 1993).

Np-237 sorption onto calcite has been studied by Allard (1984) and Triay, et al. (1996, 1997). Brady, et al. (1999) examined actinide sorption onto dolomite [$CaMg(CO_3)_2(s)$]. Brady, et al. (1999) observed little or no sorption of Np-237 onto dolomite at pH values of less than 8 and an increase in sorption as pH was increased to more than 8 (although limited data are available and total measurement uncertainty was high). The Brady, et al. (1999) observations for Np-237 seemed inconsistent with their observations for uranium, which showed a pH-dependent sorption behavior consistent with that observed in studies using silicate sorbents (e.g., Pabalan, et al., 1998). Data from Allard (1984), however, also indicate an increase in Np-237 sorption onto calcite with increasing pH from approximately 7 to 9. Triay, et al. (1996, 1997) conducted experiments investigating Np-237 sorption onto natural calcite, synthetic calcite, and calcite-bearing volcanic tuffs in J-13 Well and UE25-p#1 Well waters (pH ~8.5 and 8.9). Results indicated that tuffs containing calcite exhibited significantly more Np-237 uptake from solution than did tuffs without calcite and showed that slightly less Np-237 was sorbed in J-13 Well water as compared to UE25-p#1 Well water (Triay, et al., 1996). It should be noted that the UE25-p#1 Well water used in DOE experiments exhibited precipitation of calcite after pumping and subsequent storage in the lab (Triay, et al., 1997). This precipitation was caused by loss of dissolved $CO_2(g)$ as the water equilibrated with the atmosphere. Similarly, the high pH of J-13 Well and UE25-p#1 Well waters is also caused by loss of $CO_2(g)$. The *in situ* pH value for both well waters is approximately 7. Importantly, the maximum Np-237 K_Ds reported in Triay, et al. (1996, 1997) were obtained only after rather long reaction times (greater than 14 days). Np-237 K_Ds typically increased an order of magnitude or more over the course of the experimental sampling period (Triay, et al., 1996). This increase is indicative of solutions that equilibrate with calcite and undergo a recrystallization process as suggested by Davis, et al. (1987).

One of the primary mechanisms for retardation of radionuclides is through sorption of the radionuclide onto rock and mineral surfaces. Np-237 sorption processes, such as surface complexation and ion exchange, have been investigated previously for silicates and some oxides (e.g., Pabalan, et al., 1998; Turner, 1995, and references therein), but only minimally for carbonate minerals, especially calcite. Zachara, et al. (1991) modeled divalent sorption onto calcite as an ion exchange reaction between Ca^{2+} loaded on surface and the divalent metal in solution. The Zachara, et al. (1991) proposed reaction

$$\text{X-Ca} + \text{Me}^{2+}(\text{aq}) \rightleftharpoons \text{X-Me} + \text{Ca}^{2+}(\text{aq}) \tag{3-1}$$

does not include assumptions regarding the nature of the surface species or surface sites, nor does it include any activity corrections for surface charge effects (Zachara, et al., 1991). The model is implemented by proposing two half-reactions, each with an assigned stability constant (K). The model was successful at reproducing divalent sorption behavior for a range of metal concentrations (Zachara, et al., 1991). This generic ion exchange model has similarities to the nonelectrostatic modeling approach described in Davis, et al. (1998). The nonelectrostatic modeling approach is implemented like a typical surface complexation model except that modeling components representing surface charge effects are not included. Protonation and deprotonation reactions for the modeled surface can be included, if desired (Del Nero, et al., 1998), but may not be necessary depending on the range of solution conditions modeled (Davis, et al., 1998). A limitation of these approaches is that the resulting apparent stability constants and reaction stoichiometries may not be realistic and are not transferrable to other mineral assemblages (Davis, et al., 1998). These generic approaches can effectively model retardation coefficients for a wide range of conditions within the originally defined system and, as such, are more advantageous than the linear K_D approach, which does not generally account for changes in solution chemistry.

Van Cappellen, et al. (1993) developed a surface complexation model for the calcite-solution interface. Van Cappellen, et al. (1993) postulated the formation of the hydration species $>CO_3H^0$ and $>MeOH^0$ at the surface of a divalent metal carbonate and invoked a series of reactions to govern surface speciation. Stability constants were developed for carbonate surfaces using a constant capacitance model. The stability constants for calcite were estimated because rapid dissolution and precipitation kinetics prevent adequate acid/base titrations of the surface; however, the proposed model was used to effectively examine the dissolution kinetics of calcite (Van Cappellen, et al., 1993).

The constant capacitance model proposed by Van Cappellen, et al. (1993) and the ion exchange model proposed by Zachara, et al. (1991) are used to evaluate the Np-237 and calcite sorption experimental data in this report.

4 EXPERIMENTAL AND MODELING OBJECTIVES

The ubiquitous occurrence of calcite in the Yucca Mountain region and the importance of Np-237 as a potential contributor to dose suggest that the role of calcite in the retardation of Np-237 needs further investigation. This study investigates the sorption of Np-237 on calcite and the geochemical factors that may influence sorption magnitude. Controlled experiments are conducted in which Np-237 sorption on calcite is studied for a range of chemical conditions relevant to the environment at Yucca Mountain. The results will help to provide an independent means to test DOE assumptions regarding radionuclide transport, to critically examine DOE incorporation of site characterization data into performance assessment, and to support NRC performance assessment analyses.

As noted in Figure 3-2, Yucca Mountain groundwater is undersaturated with respect to calcite, with saturation index values generally between 0.2 and 0.4 along the expected downgradient flow path. The pH of groundwater varies throughout the Yucca Mountain region, but the majority of waters exhibit a pH within the range of 7 to 9 (Turner and Pabalan, 1999). The partial pressure (*P*) of CO_2(g) within the groundwater also varies, with the majority of waters in the range of $10^{-2.5}$ to $10^{-3.5}$ atm PCO_2 (Turner and Pabalan, 1999). Calcite saturation, PCO_2, and pH are interrelated as exemplified by the idealized reaction

$$\mathrm{CaCO_3(s) + CO_2(g) + H_2O \rightleftharpoons H^+ + HCO^{3-} + Ca^{2+} + CO_3^{2-}} \tag{4-1}$$

The pH of experimental solutions can be adjusted by the addition of acid or base (while PCO_2 is held constant) or by varying PCO_2 of the atmosphere with which the solution is allowed to equilibrate. Investigations of the calcite-aqueous solution interface, however, have demonstrated that solution and surface (calcite) speciation can vary significantly depending on the method used to adjust solution pH (Van Cappellen, et al., 1993). For instance, PCO_2 control of pH results in lower carbonate and bicarbonate solution concentrations and higher Ca^{2+} concentrations at alkaline pH when compared to solutions adjusted using additions of acid and base. Both methods of pH adjustment have been used in calcite sorption studies (e.g., Davis, et al., 1987; Zachara, et al., 1991). When accomplished DOE investigators have adjusted pH with PCO_2 manipulation (Triay et al., 1996). In Np-calcite sorption studies, however, pH was not adjusted (Triay, et al., 1996). The implications calcite sorption studies are the interpretations of surface complexation reactions and sorption processes may differ because of the influence of the pH adjustment method. As a result, experiments are planned using both methods of pH adjustment with the first series of experiments using acid and base additions.

Ideally, experiments can be designed to cover the full range of conditions expected for a given system. Unfortunately, because of experimental complexity, system complexity, system size, and the inability to fully characterize all the necessary variables to completely describe any system, only a subset of experiments is usually feasible. Geochemical modeling can extend experimental results over a large range of potential conditions and can assist in the interpretation of the mechanisms of geochemical reactions. Surface complexation models have been used successfully to complement and interpret results of radionuclide sorption experiments and to aid in the incorporation of those results into performance assessment models (Turner, et al., 1999; Mohanty, et al., 2001). An objective of these sorption studies is to model observed neptunium sorption behavior using approaches similar to those that have been applied for neptunium sorption on other mineral surfaces (Turner, et al., 1999). When coupled with previous efforts, the Np-237-calcite models may help to build a more representative distribution of Np-237 retention in the saturated alluvium.

In summary, the experimental objectives for this study and future work on Np-237 and calcite sorption include:

- An examination of Np-237 sorption onto calcite under conditions that mimic the variation in groundwater chemistry at Yucca Mountain
- An investigation of the effects of the pH adjustment method on sorption results
- A comparison of sorption to solution saturation conditions through time
- Development of models of neptunium sorption behavior on calcite

The previous letter report (Bertetti, 2001) describing preliminary results of the Np-237-calcite batch experiments noted general trends of the magnitude and pH dependence of Np-237 sorption on calcite. Some inconsistencies in the results of those experiments, however, suggested that similar experiments be repeated to develop data that might be more appropriate for the modeling effort. Therefore, additional batch experiments were conducted, and the results are included in this report. Like their predecessors, the series of experiments discussed in this report are conducted for a pH range of 7 to 9, at $10^{3.5}$ atm PCO_2 [atmospheric CO_2(g)], and with solutions that initially were at or near saturation equilibrium with respect to calcite. The solid mass to solution volume ratios and the rate and frequency of mixing were altered in an effort to eliminate problems potentially associated with inadequate mixing of the calcite.

Also included in this report are preliminary results of modeling Np-237 sorption onto calcite. Several approaches are presented with the results of two discussed in detail.

5 MATERIALS AND METHODS

All chemicals used in the experiments were reagent-grade and, except as noted, were used without further purification. Glassware (class A) and plasticware were cleaned, soaked in a 10-percent nitric acid bath overnight, and rinsed with doubly deionized reagent-grade water (17.5 MΩ, Barnstead Nanopure) prior to use. Mass measurements were determined using a Mettler AE240 electronic balance. The pH measurements were determined using an Orion 920A pH/ISE/mV multimeter and Ross combination pH electrode with automatic temperature compensation.

5.1 Calcite

Reagent-grade calcite [$CaCO_3(s)$, Fischer Scientific], aged, dried, and separated for storage, was used in the experiments. The calcite was chemically and mineralogically free of impurities. Details of calcite preparation and analyses are provided in Bertetti (2001). The calcite had a surface area of approximately 0.23 ± 0.02 m^2/g [10,200 ± 880 in^2/oz] as measured using multipoint N_2-BET analysis (Coulter SA 3100), which is consistent with results of similarly prepared calcite from several studies (e.g., Stipp, et al., 1992; Zachara, et al., 1991). A scanning electron micrograph (Figure 5-1) indicates the crystallites were rhombohedral in morphology and intergrown, with an average edge length of approximately 8 µm [3.1×10^{-4} in].

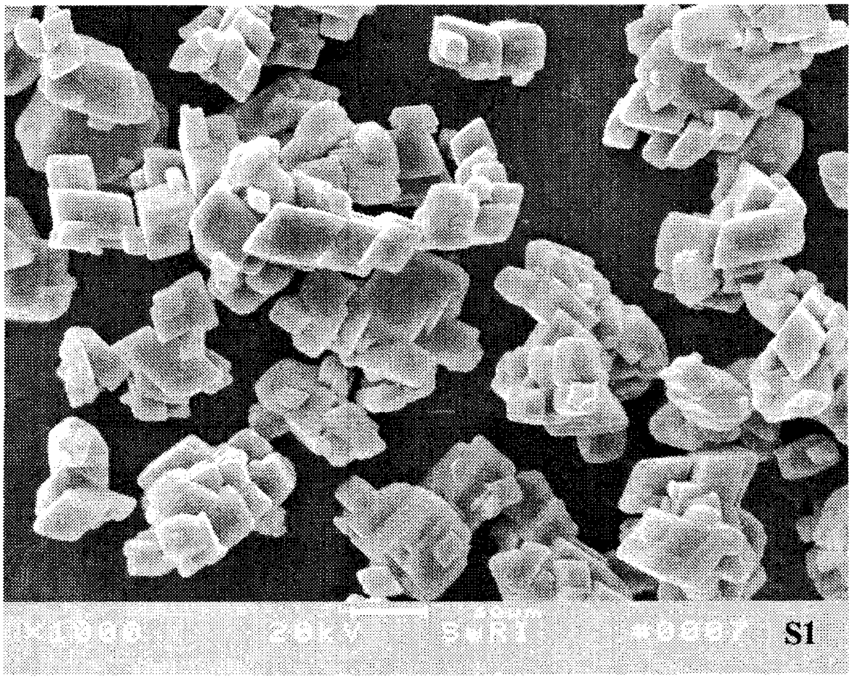

Figure 5-1. Scanning Electron Micrograph of Aged Calcite Prepared for Use in the Np-237 and Calcite Sorption Experiments. The S1 Batch Used in the Experiments Was Processed in 0.02 M $NaHCO_3$ for 30 days, Then Filtered, Freeze-Dried, and Stored for Eventual Use.

5.2 Np-237

The Np-237 used in the experiments was purchased as a standard solution from Isotope Product Laboratories (Burbank, California). The standard solution was composed of neptunyl nitrate in 4 M HNO_3 matrix and was carrier free. The standard solution had previously been diluted using doubly deionized water H_2O to make a stock solution containing ~118 ppm Np-237. Np-237 has been shown to exist in the 5+ oxidation state in similar stock solutions (Bertetti, et al., 1998; Nakayama and Sakamoto, 1991). The Np-237 stock solution was calculated to contain approximately 0.32 M HNO_3. Np-237 was added to experimental solutions using aliquots of the stock solution.

The Np-237 was analyzed by counting its alpha activity using a Packard 3100 TR/AB liquid scintillation analyzer. The Packard 3100 liquid scintillation analyzer is capable of discriminating between the alpha activity of Np-237 and the beta activity of its immediate daughter, Pa-233. All Np-237 samples were counted in 7-mL [0.43 in^3] glass scintillation vials using Ultima Gold AB (Packard) scintillation cocktail. Approximately 0.5 mL [0.03 in^3] of 0.1 M HNO_3 was added to each vial prior to the addition of Np-237/Pa-233 to minimize any potential radionuclide sorption onto the walls of the vial. Liquid scintillation analyzer performance and stock solution activity were confirmed during a series of preliminary tests to account for effects of ionic strength and acid content on the efficiency of counting. All Np-237 samples were counted for a period of time such that the total number of alpha counts collected resulted in a maximum 2σ error of 2 percent.

5.3 Experimental Solutions

Eight equilibrium $CaCO_3$(s)-$CaCO_3$(aq) solutions with pH ranging from 7.25 to 9 in ~0.25 increments were prepared for use in experiments. The solutions were prepared by adding varying quantities of $HClO_4$, $Ca(ClO_4)_2{\bullet}2H_2O$, $NaClO_4$, and NaOH to doubly deionized H_2O to make 2-L [122-in^3] solutions at the desired solution composition, pH, and a total ionic strength of 0.1 M (Note: Low pH solutions have a total ionic strength greater than 0.1 M at atmospheric PCO_2. For example, the solution of pH = 7.25 has a calculated ionic strength of 0.6 M while the pH = 7.5 solution has a calculated ionic strength of 0.14 M). Calculations were performed using EQ3NR Version 7.2b (Wolery, 1992) to determine the chemical composition of solutions, and hence, the amounts of reagents added, at equilibrium with calcite under atmospheric PCO_2. After preparation, approximately 25 g [0.88 oz] of reagent-grade calcite were added to each solution, and the solutions were allowed to equilibrate with the atmosphere, in contact with the $CaCO_3$(s), for approximately 2 weeks. A summary of the expected and measured chemistry for the equilibrium $CaCO_3$(s)-$CaCO_3$(aq) solutions is provided in Table 5-1. When used for experiments, ~30-mL [~1.8 in^3] aliquots of each solution were withdrawn and filtered through a 0.2-µm [7.9×10^{-6} in] membrane filter (polyethersulfone, Supor®-200, Gelman).

5.4 Sorption Experiments

Batch-type sorption experiments were conducted using 40-mL [2.4 in^3] polycarbonate test tubes. A hole {~5 mm [0.2 in]} was drilled in each tube cap prior to the start of the experiments to keep test tubes open to atmosphere during the course of the experiments. Experiments

Table 5-1. Summary of Chemistry of Experimental Solutions. The Saturation Index for Calcite is Well Bracketed by Calculated Value (Calculated Saturation Index), Based on Measured Amounts of Chemicals Added to Solutions, and Saturation Index (Measured Saturation Index) as Adjusted Based on Measured pH of the Solutions After a 2-Week Equilibration Period. Observed Sorption Behavior Appears to be Independent of the State of Saturation.

Experiment Solution	Target pH	Na^+ Added[A]	Ca^{2+} Added[A]	ClO_4^- Added[A]	Expected pH[B]	Calculated Saturation Index[C]	Measured pH	Measured Saturation Index[D]
A	7.25	0.01	0.2063	0.4224	7.20	-0.077	7.13	-0.125
B	7.50	0.01	0.04379	0.0973	7.51	0.054	7.41	-0.163
C	7.75	0.10	0.01388	0.1273	7.76	0.036	7.68	-0.123
D	8.00	0.10002	0.00414	0.1075	8.02	0.066	7.94	-0.102
E	8.25	0.10002	0.0013	0.1013	8.24	0.016	8.19	-0.097
F	8.50	0.1016	0.000475	0.1005	8.43	-0.051	8.47	0.020
G	8.75	0.1043	0.00014	0.09979	8.78	0.080	8.75	0.028
H	9.00	0.1087	4.55×10^{5}	0.09959	9.02	0.029	8.99	-0.032

Notes:
A: Calculated molarity based on actual amount added to each solution during preparation.
B: Calculated pH of solutions using EQ3NR Version 7.2b geochemical code and calculated concentrations.
C: Calculated saturation index of calcite given chemical additions.
D: Calculated saturation index of calcite in solutions based on measured pH. Na^+ or ClO_4 concentration adjusted to preserve charge balance and compensate for difference in measured versus calculated pH.

were conducted at each of the eight pH values established in the calcite equilibrium solutions. The mass of calcite added was varied between each experiment series. To initiate the sorption experiments, aged calcite was added to preweighed test tubes, after which, approximately 30 mL [1.8 in^3] of the appropriate filtered calcite equilibrium solution was added to each tube. The mass of each test tube was remeasured at each step to determine the amount of calcite and solution added {to the nearest 0.0001 g [3.5×10^{-6} oz]}. The calcite suspensions were agitated overnight using a gyratory shaker at 130 revolutions per minute. The following day, the test tubes were reweighed prior to adding the Np-237 spike, and a spot check of solution pH was conducted to confirm that conditions were similar to those expected. Np-237 was then added to each by transferring 100 µL [6.1×10^{-3} in^3] of the 118 ppm Np-237 stock solution to each tube. After weighing each tube to verify the mass of Np-237 spike added, an aliquot of 0.32 *N* NaOH was added to each tube to neutralize the acid added with the Np-237 spike. Tubes were reweighed to determine the total mass of solution in each tube. The concentration of Np-237 in the experiments, based on mass of transferred stock solution, was ~1.6×10^{6} M.

Following the addition of Np-237, all solutions were vortexed (Vortex Genie 2, Scientific Industries) to thoroughly mix and expose the calcite solid in each tube to the Np-237 bearing solution. Solutions were remixed (vortexed) each day for 4 days in an effort to improve mixing relative to the first series of experiments. A summary of initial conditions for the experiments is shown in Table 5-2.

Table 5-2. Summary of Initial Conditions for Second Series of Np-237 and Calcite Experiments

Experiment	Solution Volume (mL)	Mass Calcite (g)	M/V (g/L)	pH range	Initial Np-237 Concentration (M)
NpCA41	30	0.1	3.3	7.25–9.0	1.6×10^{-6}
NpCA42	30	0.1	3.3	7.25–9.0	1.6×10^{-6}
NpCA43	30	0.1	3.3	7.25–9.0	1.6×10^{-6}
NpCa51	30	0.2	6.6	7.25–9.0	1.6×10^{-6}
NpCA52	30	0.2	6.6	7.25–9.0	1.6×10^{-6}
NpCA53	30	0.2	6.6	7.25–9.0	1.6×10^{-6}
NpCA61	30	0.44	15	7.25–9.0	1.6×10^{-6}
NpCA62	30	0.44	15	7.25–9.0	1.6×10^{-6}
NpCA63	30	0.44	15	7.25–9.0	1.6×10^{-6}

After 4 days, and again after 7 days, the pH of each tube was measured and tubes were sampled for Np-237 by withdrawing duplicate 0.5-mL samples from each test tube. Tubes were weighed prior to and after sampling to account for losses from evaporation. Following removal of samples for Np-237 determination, several solutions were sampled for chemical analyses to help constrain solution conditions with respect to calcite saturation. Approximately 20-mL [1.2 in^3] aliquots were removed from the selected experimental solutions and transferred to polypropylene bottles. They were subsequently subsampled and analyzed for Ca^{2+}, Na^+, K^+, Mg^{2+}, Mn^{2+}, and Sr^{2+} using inductively coupled plasma atomic emission spectroscopy.

5.5 Calculations

The mass of Np-237 sorbed on calcite was determined by subtracting the Np-237 mass remaining in solution from the initial mass of Np-237 added (initial Np-237 was corrected for losses during intermediate sampling). The percent of Np-237 sorbed on calcite was calculated by dividing the calculated mass sorbed on calcite by the initial Np-237 mass and multiplying by 100. K_Ds were determined using Eq. (2-1). Mass Np-237 sorbed onto the polycarbonate tubes was assumed to be negligible as has been verified in previous experiments (Bertetti, et al., 1998)

6 EXPERIMENTAL RESULTS AND DISCUSSION

Results for the most recent series of experiments (series NpCA4, NpCA5, and NpCA6) are presented in Figures 6-1 and 6-2. The results follow the same general trend as observed in the previous experimental series (Bertetti, 2001). Np-237 uptake increases with increasing pH until reaching a maximum between pH 8 and 8.25, depending on the particular experiment. With further increase in pH, Np-237 uptake diminishes but does not reach zero or the low sorption values observed at the lowest pH values (Series NpCA4 solutions seem to be an exception because they have similar sorption values at pH 7 and 9).

With one notable exception, replicate experimental solutions exhibit similar magnitudes of Np-237 sorption. As would be expected, variation between replicates is greatest where sorption magnitude is most sensitive to change in pH (between pH of 7.5 and 8.5). Series NpCA43 results differ from to the results of other experiments with the same initial conditions (NpCA41 and NpCA42). The NpCA43 series results show significantly greater sorption of Np-237 for nearly all of the pH range examined. Reasons for these anomalous differences are unclear. An examination of experimental procedure, records, and data does not reveal any obvious cause. Further work will investigate the nature of the anomalous results for the NpCA43 experiments. The NpCA43 results are excluded from the summary data and modeling presentations discussed in the following sections.

A summary of results from the three experiment series in terms of percent Np-237 sorbed and K_D is provided in Figures 6-3 and 6-4, respectively. The data shown represent average measured values of experimental replicates, while error bars indicate the standard deviation ($\pm 1\sigma$) of the replicate measurements. Unfortunately, the data in Figures 6-3 and 6-4 reveal similar inconsistencies in the percent of Np-237 sorbed and K_D (normalization of mass and solution concentration) that were observed in the previous experiments (Bertetti, 2001). It appears that efforts to ensure adequate mixing during the sorption phase and representative sampling were not effective although some improvement is apparent.

Given the relatively small changes in the equilibrium concentration of Np-237 on both the solid and in solution between each experiment, it seems reasonable to assume that the sorption isotherm for the Np-237 and calcite system would be linear for the range of conditions studied. For instance, even if the true system behavior were nonlinear, over the less than one log unit changes in concentration in the experiments, the system sorption data would likely plot or appear to be linear. With that assumption in mind, one would anticipate that an experiment conducted at a similar initial concentration of Np-237, but with a larger initial mass of calcite (sorbent), would exhibit increased sorption proportional to the greater mass of sorbent. Inspection of Figure 6-3 reveals that series NpCA6, which contained the largest proportion of calcite mass to solution volume, did indeed sorb more Np-237 than NpCA4, for example, but did so proportionately only at the highest pH values. Likewise, a linear isotherm should produce overlapping sorption curves when the results are normalized using K_D. Inspection of Figure 6-4 shows, however, that all three experiments overlap only at the endpoints of the sorption versus pH curves. Where sorption is at a maximum near pH of 8, the curves exhibit their greatest differences in K_D.

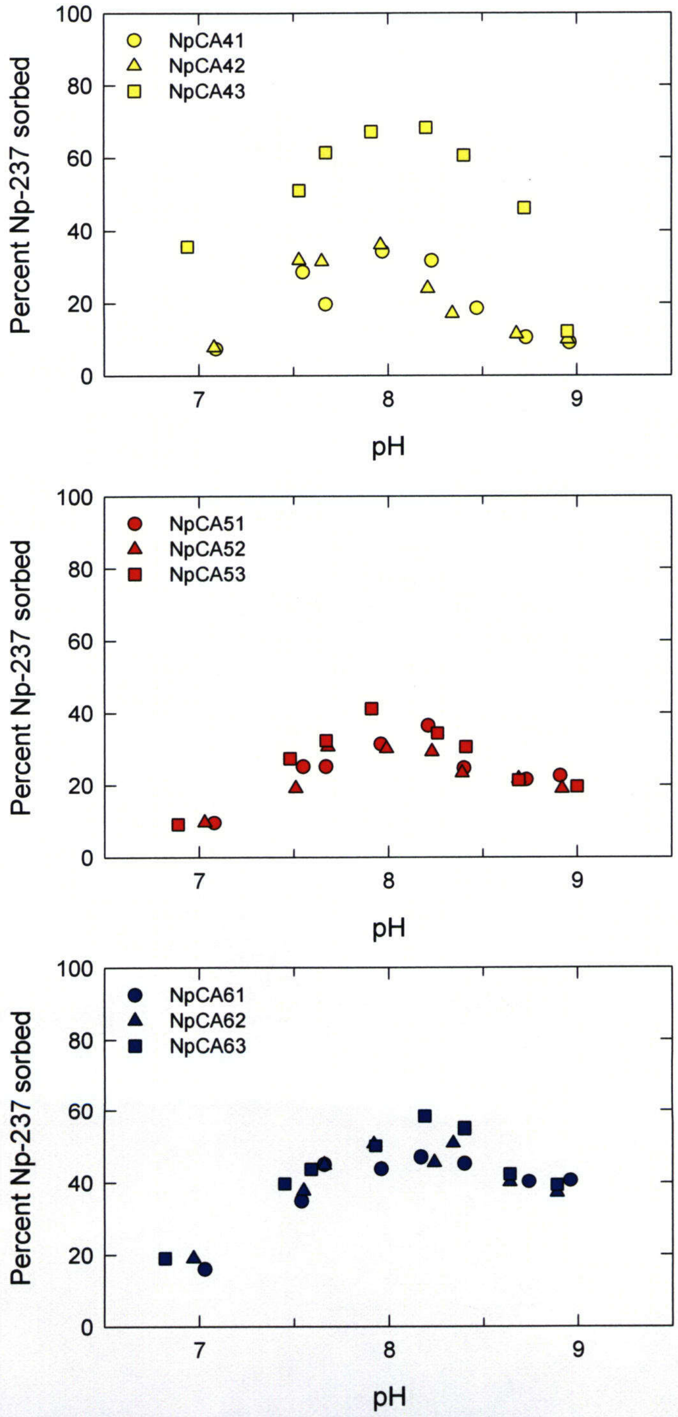

Figure 6-1. Results of NpCA4, NpCA5, and NpCA6 Experiments Plotted in Terms of Percent Np-237 Sorbed on Calcite

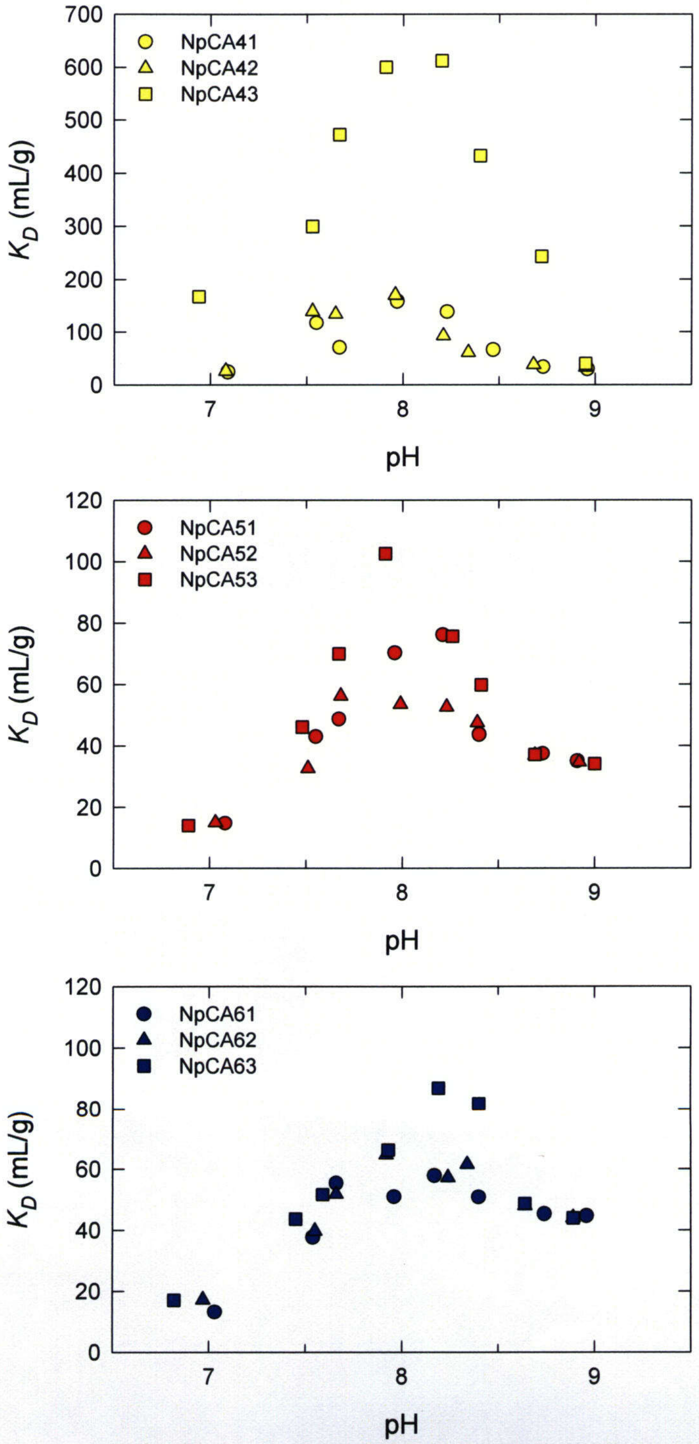

Figure 6-2. Results of NpCA4, NpCA5, and NpCA6 Experiments Plotted in Terms of K_D (mL/g)

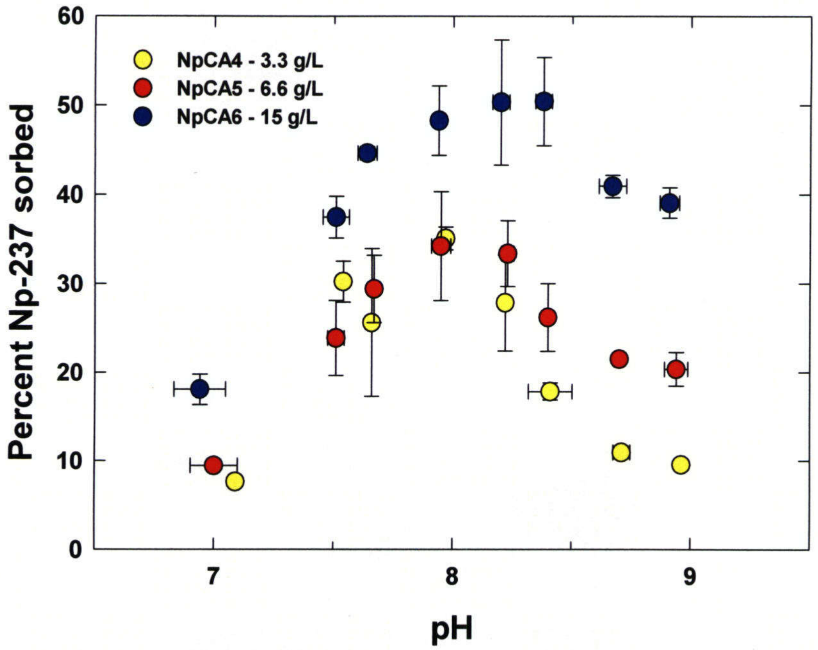

Figure 6-3. Results of NpCA4, NpCA5, and NpCA6 Experiments. Points Represent Averages of Replicate Solutions. Error Bars Represent Standard Deviation (±1σ) Between Replicate Values. Note Experiment NpCA43 Solutions are Excluded.

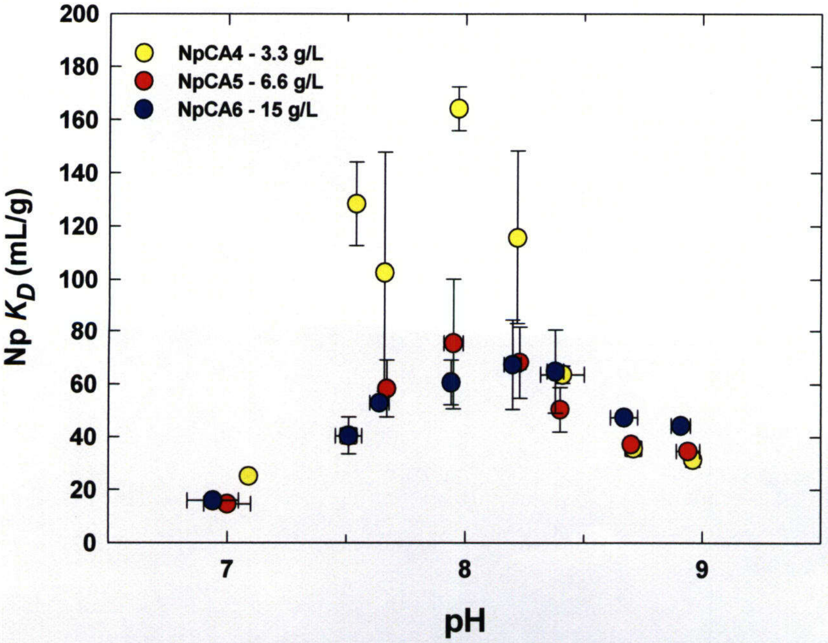

Figure 6-4. Results of NpCA4, NpCA5, and NpCA6 Experiments in Terms of K_D (mL/g). Points Represent Averages of Replicate Experimental Solutions. Error Bars Represent Standard Deviation (±1σ) Between Replicate Solutions. NpCA43 Solutions Are Excluded.

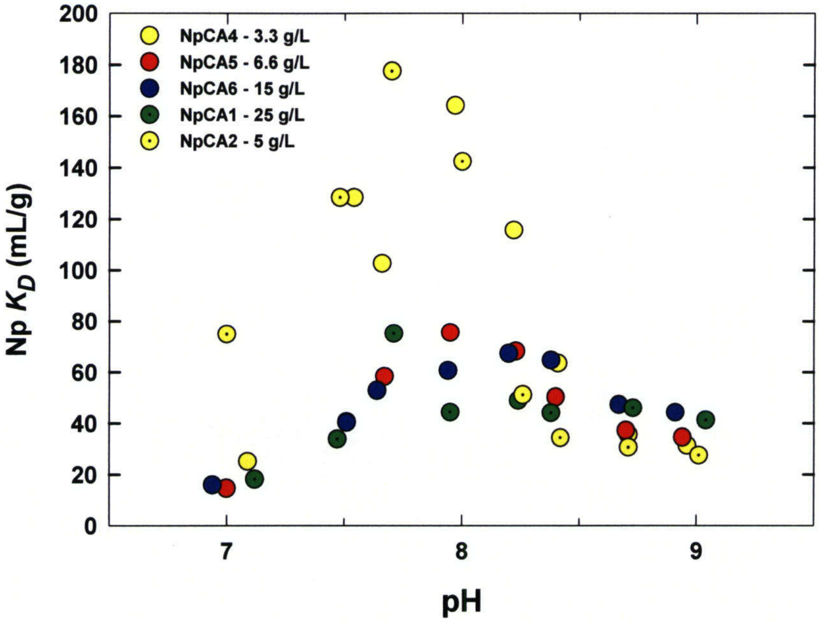

Figure 6-5. Results of All Np-237 and Calcite Batch Sorption Experiments Plotted in Terms of K_D

As postulated in the previous Np-237 and calcite report (Bertetti, 2001), these seemingly inconsistent results could be caused by insufficient mixing in the batch experiment tubes; poor mixing may prevent all of the potentially sorbing surfaces to be adequately exposed to the Np-237 bearing solution. Extra attention was paid to ensuring more complete mixing in the NpCA4–6 series of experiments, and tubes were vortexed daily during the sorption phase. As mentioned, the K_D data do show more overlap than in the previous experiments (Bertetti, 2001) but not under all conditions. Comparison of data from all the experiments completed to date (Figure 6-5) indicates a wide spread of K_D data rather than a set of overlapping curves. However, experiments NpCA4 and NpCA2, which were conducted with the same initial mass of calcite {and the smallest used in the experiments, 0.1 g [0.035 oz]}, show some overlap for the entire pH range.

Not filtering the samples counted for Np-237 activity is not likely to affect results because the calcite particle size used rapidly settles after mixing. Samples that contained particles from solution would tend to produce analyses that indicated low sorption, but it is unlikely that all replicates through the range of pH studied would contain entrained calcite particles. Examples of probable entrainment can be seen in the NpCA11 and NpCA21 results for samples at pH of ~7.9 (Bertetti, 2001). At the pH values studied, filtration would likely also result in the loss of aqueous Np-237 because of sorption on the filter media, which would generate additional uncertainty in the data. Other than experimental error, one possible explanation for the observed data trends is that the sorption isotherm is nonlinear for the concentration range of the experiments. The nonlinear behavior required would be equivalent to a Freundlich isotherm with the exponential coefficient, $n>1$, as shown in the equation

$$C_s = KC^n \tag{6-1}$$

where C_s is the mass of solute sorbed per unit of dry mass, C is the concentration of solute in solution in equilibrium with the mass of solute sorbed onto the solid, and K and n are constants (Fetter, 1993). An isotherm of this nature would reflect exponentially increasing sorption with increasing equilibrium solution concentration. The trend would not continue infinitely because the sorption sites would eventually become saturated, but it is possible for a limited concentration range. Zachara, et al. (1991) noted similar behavior for the sorption of Zn^{2+} onto calcite in their study of divalent metal sorption onto calcite but could not offer an explanation for the nature of the Zn^{2+} behavior. The small concentration range of the NpCA series experiments does not allow sufficient analysis of the isotherm trend to evaluate its linear or nonlinear nature. Additional controlled experiments will need to be conducted to fully evaluate the anomalous behavior observed, if indeed the data are anomalous.

The observed variation in sorption on calcite with pH is consistent with observed Np-237 sorption behavior on silicate and aluminosilicate minerals (e.g., Bertetti, et al., 1998) and is roughly similar to that observed for divalent metal sorption on calcite (Zachara, et al., 1988, 1991). Experience has shown the data may be successfully represented using surface complexation models or similar modeling approaches. Efforts to apply such approaches to the NpCA4–6 data are discussed in Section 7.

A review of Table 5-1 indicates the starting solutions for all experiments were at or near saturation with respect to calcite. Most solutions were calculated to be slightly undersaturated (SI<0), which was preferred compared to supersaturated conditions, for these experiments because measurements in the Yucca Mountain region indicate groundwater is undersaturated with respect to calcite. Table 6-1 presents results of analyses of the equilibrium chemistry for selected experimental solutions (NpCA41, NpCA52, and NpCA63).

As discussed in the previous report (Bertetti, 2001), precipitation of Np-237 as an explanation of the observed uptake on calcite seems unlikely. With the possible exception of the solutions near pH 7, which need further characterization because of high ionic strength, concentrations of Np-237 used in the experiments are below solubility limits for the conditions studied (Efurd, et al., 1998).

Table 6-1. Results of Chemical Analyses and Calculated Saturation Index [With Respect to $CaCO_3(s)$] for Selected Experimental Solutions. Major Cations Were Measured Using Inductively Coupled Plasma Atomic Emission Spectroscopy. Saturation Index Were Calculated Using the EQ3NR Version 7.2b Geochemical Code (Wolery, 1992).

Experiment Solution	Ca^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	Sr^{2+} (mg/L)	Solution Initial pH	pH at Sampling	Calculated Saturation Index
NpCA4A1	7583	292	29.7	0.755	7.13	6.92	-0.672
NpCA4B1	1608	275	17.2	0.177	7.44	7.48	-0.051
NpCA4C1	481	2391	25.0	0.067	7.68	7.67	-0.201
NpCA4D1	150	2363	29.0	0.027	7.93	7.94	-0.144
NpCA4E1	47.6	2253	20.7	0.016	8.17	8.16	-0.196
NpCA4F1	19.9	2334	19.6	0.012	8.39	8.34	-0.216
NpCA4G1	5.00	2430	31.4	0.009	8.70	8.63	-0.250
NpCA4H1	1.75	2469	25.4	0.007	9.00	8.87	-0.258
NpCA6A3	7544	285	18.7	0.763	7.13	6.85	-0.814
NpCA6B2	1572	265	21.6	0.198	7.44	7.41	-0.200
NpCA6C3	481	2269	17.9	0.070	7.68	7.55	-0.440
NpCA6D2	144	2308	20.9	0.027	7.93	7.86	-0.321
NpCA6E3	46.8	2327	22.0	0.017	8.17	8.10	-0.324
NpCA6F2	18.7	2332	23.7	0.013	8.39	8.40	-0.125
NpCA6G3	4.55	2406	25.8	0.009	8.70	8.58	-0.387
NpCA6H2	1.66	2486	20.0	0.008	9.00	8.90	-0.228

Wolery, T.J. "EQ3/6, A Software Package for Geochemical Modeling of Aqueous Systems: Package Overview and Installation Guide (Version 7.0)." UCRL–MA–110662–PT–I. Livermore, California: Lawrence Livermore National Laboratory. 1992.

7 MODELING RESULTS AND DISCUSSION

A qualitative comparison of Np-237 speciation in solution can be made with its observed sorption on calcite. Figure 7-1 depicts the speciation of 1.6 × 10^{-6} M Np-237 in a 0.1 M $NaClO_4$ electrolyte solution at equilibrium with atmospheric PCO_2. Equilibrium constants for neptunium species reactions (shown in Table 7-1) were derived from the recent NEA database (OECD Nuclear Energy Agency, 2001) and used along with the MINTEQA2 Version 4 geochemical code (Allison, et al., 1991) to calculate the speciation. Review of Figures 6-4 and 7-1 reveals that the sorption (desorption) edge at pH >8 is coincident with the pH range where Np-carbonate complexes become important in solution. Additionally, the net positive sorption observed between pH 8 and 9 in all experiments is coincident with the predicted $NpO_2(OH)^0$ species peak. These observations suggest that Np-237 sorption behavior on calcite may be successfully modeled using a surface complexation or Ca^{2+} exchange modeling approach that accounts for carbonate complexation.

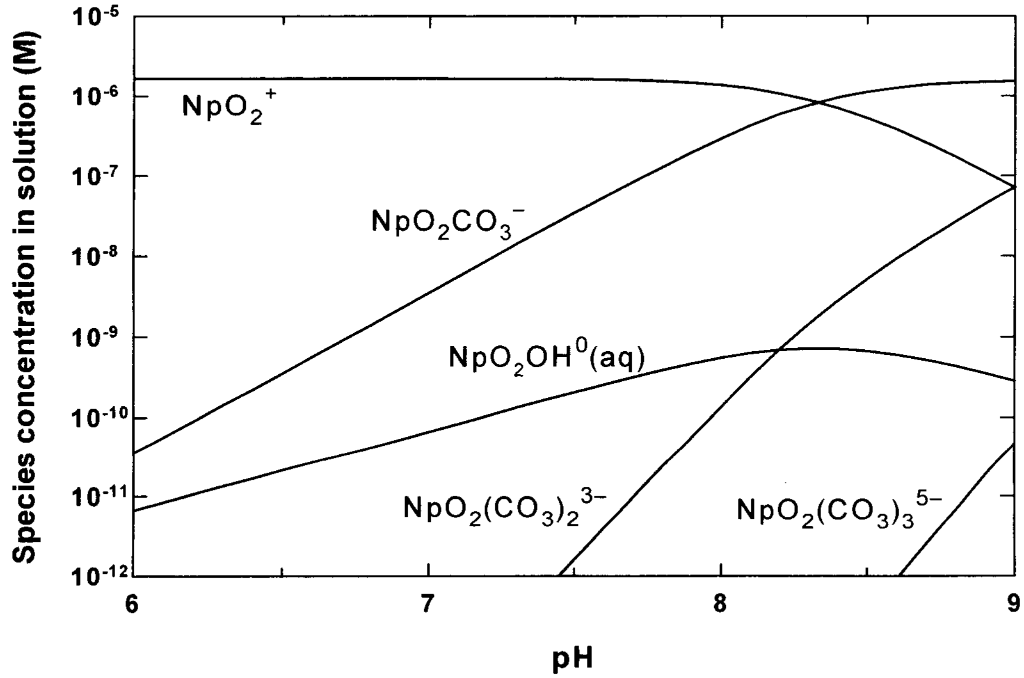

Figure 7-1. Calculated Speciation of Np(V) in a 0.1 M $NaClO_4$ Solution Containing 1.6 × 10^{-6} M Np at Equilibrium with Atmospheric PCO_2. Stability Constants Are Taken from the Nuclear Energy Agency Neptunium Database (OECD Nuclear Energy Agency, 2001).

Table 7-1. Thermodynamic Data Used in MINTEQA2 Version 4 Speciation Calculations Shown in Figure 7-1 Log *K*s from OECD Nuclear Energy Agency (2001).

Aqueous Speciation Reaction	Log *K*
$NpO_2^+ + H_2O \rightleftharpoons NpO_2OH^0 + H^+$	−11.30
$NpO_2^+ + 2H_2O \rightleftharpoons NpO_2OH_2 + 2H^+$	−23.60
$NpO_2^+ + CO_3^{2-} \rightleftharpoons NpO_2CO_3$	4.96
$NpO_2^+ + 2CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_2^{3}$	6.53
$NpO_2^+ + 3CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{5-}$	5.50

OECD Nuclear Energy Agency, eds. “Chemical Thermodynamics of Neptunium and Plutonium.” Amsterdam: Nuclear Energy Agency. Elsevier. 2001.

Surface complexation models assume that mineral surfaces form specific functional groups that react with dissolved solutes to form surface species in a manner that is analogous to species complexation reactions in solution (Davis, et al., 1998; Davis and Kent, 1990). Surface complexation models can be described using mass action equations and can make corrections for electrostatic interactions at the mineral surface (Davis and Kent, 1990). Several types of surface complexation models have been developed and used successfully to model sorption of metals, including Np, on mineral surfaces (e.g., Davis, et al., 1998; Turner, et al., 1998). There are numerous literature sources that provide detailed information about surface complexation model types and methods (e.g., Turner, 1995; Davis and Kent, 1990). As a result, a general description is not provided in this report. The specific reactions and parameters used to develop the models used in this study are presented.

Van Cappellen, et al. (1993) developed a surface complexation model to describe the surface speciation of carbonate minerals, including calcite. Their model proposes that hydration of a metal (in this case, Ca^{2+}) carbonate mineral surface produces two types of surface sites $>CaOH^0$ and $>CO_3H^0$. Using information from spectroscopic studies and an understanding of complex formation in solution, Van Cappellen, et al. (1993) developed several surface complexation reactions and associated stability constants (log *K*s) (Table 7-2). Because titration of the calcite surface is experimentally impracticable, stability constants were estimated using values that were consistent with aqueous complexation reactions and produced a calculated $pH_{pzc} = 8.2$ for the calcite surface (Van Cappellen, et al., 1993). As with other surface complexation approaches, the values for the stability constants are model dependent (Turner, 1995). Van Cappellen, et al. (1993) selected a constant capacitance model for their study. The constant capacitance model is limited to a single ionic strength because the capacitance of the electric double layer is dependent on the ionic strength and can vary significantly with changes in ionic strength of the solution. Based on titration data and fitting of $FeCO_3$ and $MnCO_3$ surfaces, Van Cappellen, et al. (1993) selected a capacitance value of 100 F/m^2 for the electric double layer in solutions with ionic strength of 0.1 M. This value is high compared to that commonly used for oxides (~1.4 F/m^2), but is justified on the basis of previous studies and differences in carbonate mineral surface structure (Van Cappellen, et al., 1993). Using guidelines from Davis and Kent (1990), Van Cappellen, et al. (1993) selected a surface site density of 5 sites/nm^2 for calcite. The selected site density (equivalent to 1.9×10^{-6} mol sites/g)

Table 7-2. Stability Constants and Model Parameters for Calcite Surface Speciation Calculations. Log *K* Values from Van Cappellen, et al. (1993).

Reaction	Log *K*
$>CO_3H^0 \rightleftharpoons >CO_3^- + H^+$	−4.9
$>CO_3H^0 + Ca^{2+} \rightleftharpoons >CO_3Ca^+ + H^+$	−2.8
$>CaOH^0 + H^+ \rightleftharpoons CaOH_2^+$	12.2
$>CaOH^0 \rightleftharpoons CaO^- + H^+$	−17.0
$>CaOH^0 + CO_3^{2-} + H^+ \rightleftharpoons CaCO_3^- + H_2O$	15.55
$>CaOH^0 + CO_3^{2-} + 2H^+ \rightleftharpoons CaCO_3 + H_2O$	24.15

Other Parameters:

EDL Capacitance: 100F/m^2	Calcite Surface Area: 0.23 m^2/g [1.02 × 10^4 in^2/oz]
Site Concentration: 5 sites/nm^2	Calcite Concentration in Solution: 3.3 g/L [1.9 × 10 ^{3}oz/in^3]
$PCO_2 = 10^{-3.5}$ atm	Solution at Equilibrium with CaCO$_3$(s)

Van Cappellen, P., L. Charlet, W. Stumm, and P. Wersin. "A Surface Complexation Model of the Carbonate Mineral-Aqueous Solution Interface." *Geochimica et Cosmochimica Acta*. Vol. 57. pp. 3,505–3,518. 1993.

corresponds well to other values used for calcite site density (2–3.6 μmol/g) that were determined from Ca-45 exchange reactions (Davis, et al, 1987; Zachara, et al., 1991). Figure 7-2 shows the calculated surface speciation of calcite in water at equilibrium with atmospheric PCO_2. Stability constants taken directly from Van Cappellen, et al. (1993) and solution conditions representing the NpCA4 experiment series were used with the constant capacitance model in MINTEQA2 Version 4 to determine the speciation. Noteworthy is the interaction of Ca^{2+} with the $>CO_3H^0$ surface site and its deprotonated complex $>CO_3$. The $>CO_3H^0$ species containing calcite diminished with diminishing calcite concentration in solution as pH increased (in solutions equilibrated with calcite), while the $>CaCO_3^-$ species increased significantly above pH ~8.4. The surface species in Figure 7-2 may provide some guidance to the selection of NpO_2^+ surface species in modeling Np-237 calcite sorption.

Zachara, et al. (1988, 1991) proposed that divalent metal sorption on calcite was controlled by the exchange of the metal with Ca^{2+} at the calcite surface and noted that the increase in sorption paralleled the decrease in aqueous Ca^{2+} concentration maintained by calcite solubility. Zachara, et al. (1991) proposed two ion exchange half-reactions

$$\mathrm{Ca^{2+}(aq)} + \mathrm{X} \rightleftharpoons \mathrm{X\text{-}Ca} \qquad K_{\mathrm{Ca}} \qquad (7\text{-}1)$$

$$\mathrm{Me^{2+}(aq)} + \mathrm{X} \rightleftharpoons \mathrm{X\text{-}Me} \qquad K_{\mathrm{Me}} \qquad (7\text{-}2)$$

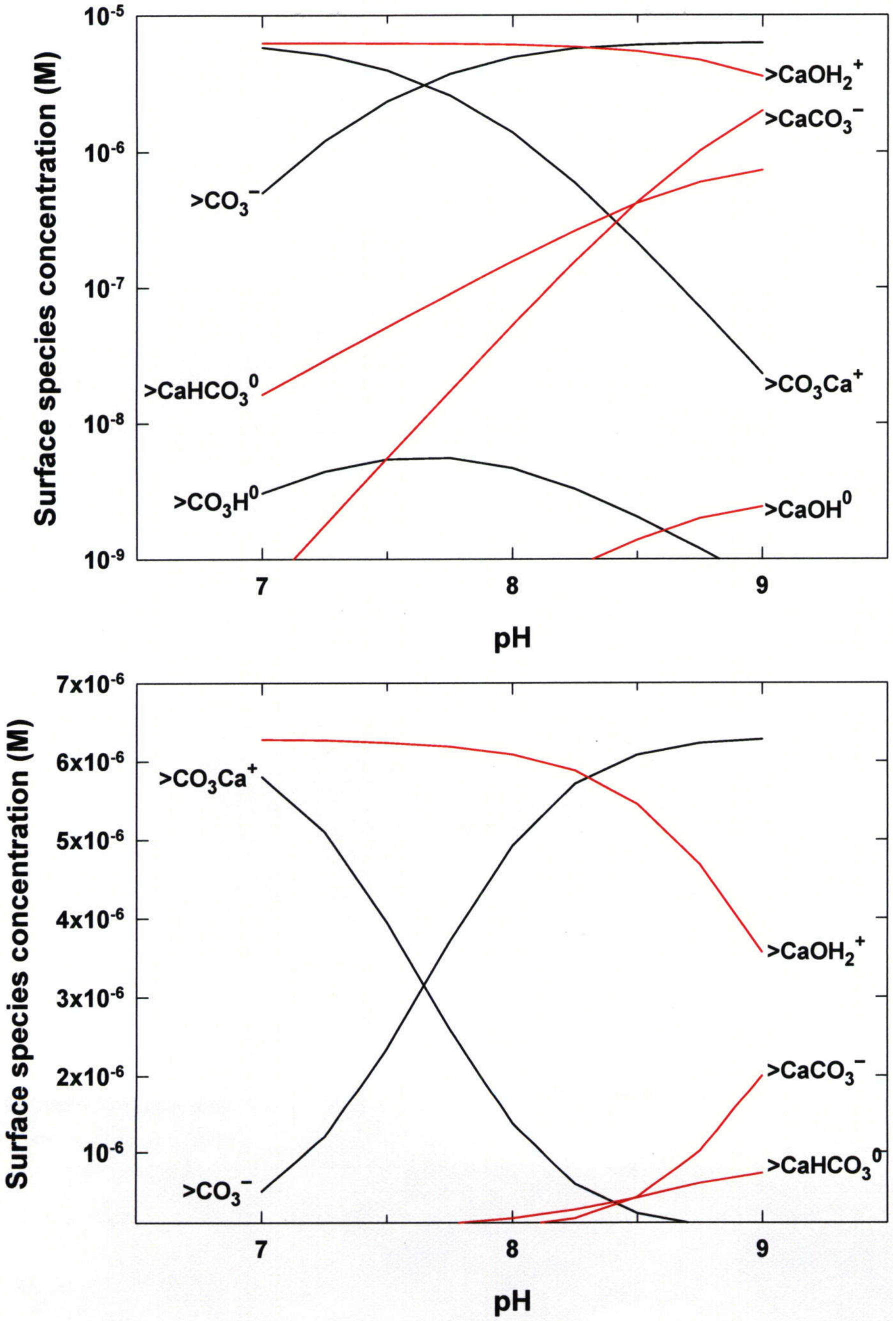

Figure 7-2. Calculated Speciation of the Surface of Calcite in a 0.1-M NaClO$_4$ Solution at Equilibrium with Atmospheric *P*CO$_2$ and CaCO$_3$(s). Model Calculations Based on the Stability Constants of Van Cappellen, et al. (1993) (Table 7-2) and the Experimental Conditions of NpCA4 Series Solutions. Speciation is Presented at Both Log and Linear Scales for Comparison.

The overall surface exchange constant [(Eq. (3-1)] is determined from the difference in the half-reaction constants (Zachara, et al., 1991). As noted in Section 3, the generic exchange reaction includes no assumptions regarding the nature of the surface complex (Zachara, et al., 1991). The ion exchange model assumes that the magnitude of the sorption of divalent metal from solution is influenced by competition from Ca^{2+}, which diminishes with increasing pH, and potentially, by formation of carbonate species in solution. Zachara, et al. (1991) found that a decrease in sorption of Co^{2+} on calcite at higher pH could be effectively modeled by including a Co-carbonate species (not originally in their solution speciation model) in solution to compete for the $Co^{2+}(aq)$. Similar competition between sorption of Np-237 and formation of neptunyl carbonate species in solution has been modeled in previous studies of Np-237 sorption on aluminosilicate minerals (Turner, et al, 1998). Davis, et al. (1998) suggested that metal sorption onto mineral surfaces, especially complex mineral surfaces difficult to characterize, can be effectively modeled using a nonelectrostatic version of the surface complexation modeling approach. In the nonelectrostatic modeling approach, surface sites and reactions are postulated in a fashion similar to electrostatic models except that activity correction for surface charge is not included in the model. Additionally, Davis, et al. (1998) suggest that protonation and deprotonation reactions (acidity constants) may not need to be included in the surface model because surface species are dominated by the neutral hydrolyzed $>XOH^0$ sites under most conditions. The nonelectrostatic approach is attractive for minerals, such as calcite, whose surfaces and acidity constants are difficult to measure. A limitation of the nonelectrostatic model is that the stability constants and other derived parameters are likely to be appropriate only for the system on which they were derived (Davis, et al., 1998).

Each of the models described in the preceding paragraphs was used with the averaged data and solution conditions from the experimental series NpCA4 (NpCA43 excluded) in an attempt to model Np-237 sorption on calcite. The NpCA4 series was selected because it was accompanied by solution chemistry data, and the series was consistent with data from the NpCA2 series conducted previously using the same initial calcite mass. Thus, the NpCA4 series had reasonable chemical control for Np-237, pH, and major cations and exhibited repeatable sorption data between experiments, making it a candidate for the most representative data set for Np-237 sorption on calcite. Initial stability or binding constants for the postulated surface reactions were determined by fitting the NpCA4 sorption data using FITEQL Version 3.1 (Herbelin and Westall, 1994). Depending on the complexity of the proposed model, the FITEQL Version 3.1 results were used only as starting points for a trial-and-error method of narrowing of the stability constants using MINTEQA2 Version 4 and the NpCA4 data. A summary of parameters and surface reactions used in the modeling exercises is provided in Table 7-3.

7.1 Nonelectrostatic Surface Complexation Model

The nonelectrostatic modeling approach did not produce a satisfactory fit to the data even after a variety of postulated model reactions were evaluated (not plotted). Surface species that included NpO_2^+, $NpOH^0$, and $NpO_2CO_3^-$ in various combinations and with various surface site types as well as competing surface reactions that included Ca^{2+}, were evaluated. In each case, the pH at which maximum model sorption occurred was significantly different (typically between 8.4 and 8.5, or greater) from the observed value. Likewise, the slope and magnitude of both sorption edges could not be reproduced while maintaining a reasonable sorption maximum.

Table 7-3. Stability Constant and Model Parameters for Sorption of Np-237 on the Calcite Surface

Reactions	*Log *K*
Ion Exchange Model	
$Ca^{2+} + X \rightleftharpoons XCa^{2+}$	2.4
$X + 2NpO_2^+ \rightleftharpoons X(NpO_2^+)_2$	12.05
Constant Capacitance Model	
$>CO_3H^0 + NpO_2^+ \rightleftharpoons >CO_3HNpO_2^+$	8.6
$>CO_3H^0 + Ca^{2+} \rightleftharpoons >CO_3Ca^+ + H^+$	−1.9
Constant Capacitance Model with NpO_2OH^0 Added to Model	
$>CaOH^0 + NpO_2^+ + H_2O \rightleftharpoons >CaONpO_2OH^- + 2H^+$	−9.6
Constant Capacitance Model with $NpO_2CO_3^-$ Added to Model	
$>CaOH^0 + NpO_2+ + CO_3^2 \rightleftharpoons >CaOHNpO_2CO_3^-$	12.4

Other Parameters:
*Log *K*s Determined Using FITEQL Version 3.1 and MINTEQA2 Version 4
Electric Double Layer Capacitance: 100 F/m^2 Calcite Surface Area: 0.23 m^2/g [1.02 × 10^4 in^2/oz]
Site Density: 5 sites/nm^2 Calcite Concentration in Solution: 3.3 g/L [1.09 × 10^3 in^3/oz]
$PCO_2 = 10^{-3.5}$ atm $[Np]_{TOT}=1.6 \times 10^{-6}$ M Solution at Equilibrium with $CaCO_3(s)$

7.2 Ion Exchange Model

The ion exchange model appears to provide a reasonable fit to the NpCA4 data (Figure 7-3). Stability constants for the half-reactions and the overall exchange reaction are provided in Table 7-3. The ion exchange model reproduces the sorption maximum well but slightly overestimates the magnitude of sorption along the sorption edges. The slightly elevated but constant sorption at high pH (8.75 to 9), observed in other data sets is not predicted by the ion exchange model. Adding a surface complex that included NpO_2CO_3 ($>X\text{-}NpO_2CO_3^-$) did not produce an improved fit of the data. To assess the model against another data set, the model was used to predict neptunium sorption on calcite under the conditions of the NpCA6 (average) experiment (essentially, increased surface sites from increased mass calcite). The ion exchange model prediction for NpCA6 tends to underestimate the observed sorption for the pH range. However, the sorption envelope is broader, similar to the broader sorption envelope for NpCA6.

7.3 Constant Capacitance Model

The constant capacitance model of Van Cappellen, et al. (1993) was used to fit the NpCA4 data rather than the diffuse layer approach, used in most previous sorption modeling studies conducted at the CNWRA, because the stability constants used in surface complexation models are not generally transferrable between model types (Turner, 1995) and the surface acidity constants for calcite estimated by Van Cappellen, et al. (1993) are not available for other model types. Constant capacitance model fits are shown in Figure 7-4, and stability constants for the surface reactions used in the model are shown in Table 7-3. The constant capacitance model reproduced the experimental data reasonably well by postulating one surface species for NpO_2^+ and by adjusting the log *K* for the $>CO_3Ca^+$ surface species proposed by Van Cappellen, et al. (1993) from 2.8 to 1.9. The model matched the sorption data for the range of pH and adequately reproduced the sorption maximum. The single NpO_2^+ species model did, however, underestimate sorption at the highest pH value (~9). The model's ability to predict sorption with a different calcite concentration was tested using the calcite mass and experimental data for the NpCA6 series. The single NpO_2^+ species model overestimated sorption for NpCA6 for most of the pH range and underestimated sorption at high pH.

Differences in prediction by both the constant capacitance surface complexation model and the ion exchange model highlight the potential problems with the NpCA6 data set. The potential nonlinear exponential nature of the sorption data is suggested by the ion exchange model under prediction. Inadequate mixing of the experimental system and the resulting artificially low sorption observed, are indicated by the constant capacitance model overprediction of sorption.

In an effort to better reproduce the Np-237 sorption behavior for the entire range of pH, an additional surface species for NpO_2^+ was postulated in the constant capacitance model. A review of predicted solution speciation for neptunium (Figure 7-1) and surface speciation on calcite (Figure 7-2) suggests that surface species containing $NpOH^0$, which increases in solution at higher pH values, or $NpO_2CO_3^-$, which also increases at high pH along with $>CaCO_3$ species on the calcite surface, could improve the model fit. To maintain consistency, stability constants derived from the single NpO_2^+ surface species model were held constant while species that included $NpOH^0$ and $NpO_2CO_3^-$ were evaluated.

Constant capacitance model fits for a two-species model that included the $>CaO\text{-}NpO_2OH^-$ species are shown in Figure 7-5. The model accurately reproduces the NpCA4 data and slightly improves the fit at high pH. The model prediction for NpCA6 overestimates the Np-237 sorption behavior but slightly broadens the sorption envelope as observed in the NpCA6 data relative to the NpCA4 data.

Constant capacitance model fits for a two-species model that included the $>CaOH\ NpO_2CO_3$ surface species are shown in Figure 7-6. The model does an excellent job of reproducing the fit to NpCA4 data for the entire pH range although there is a slight overprediction of sorption on the high pH edge of the sorption envelope. The model prediction of the NpCA6 experiment again overestimates Np-237 sorption for most of the pH range but accurately mimics the shape of the sorption envelope and reproduces the enhanced sorption at high pH (relative to the sorption at low pH). It is noteworthy that the model prediction for NpCA6 data is very good at higher pH values where the percent sorbed and K_D behavior between the NpCA4 and NpCA6 data was consistent or as expected.

Results from both the ion exchange and constant capacitance models suggest that Np-237 sorption on calcite is controlled by sorption of NpO_2^+ species on the calcite surface at pH values where NpO_2^+ dominates in solution and by competitive effects of Ca^{2+} sorption and neptunyl carbonate complex formation in solution. The results from the constant capacitance modeling effort suggest that sorption of Np-237 on calcite at higher pH is enhanced by sorption of neptunyl carbonate species.

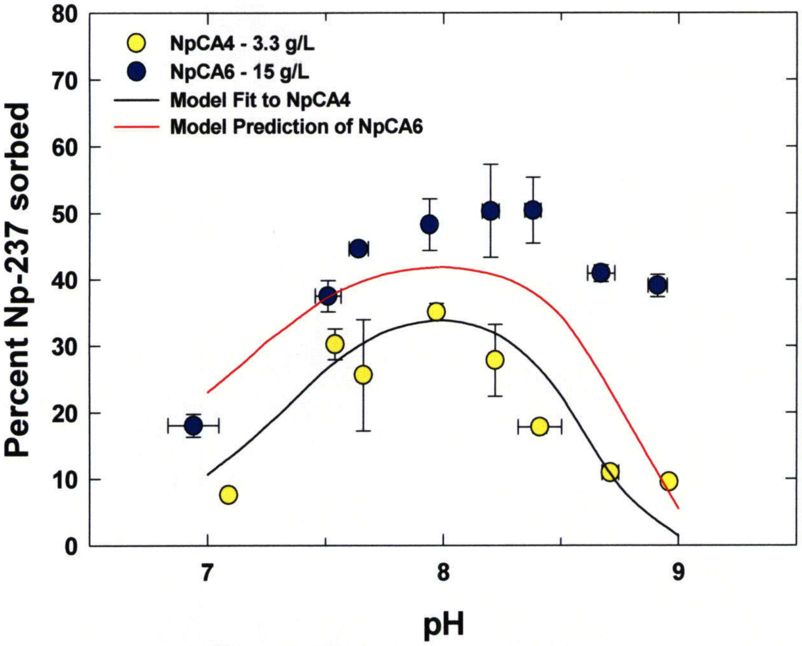

Figure 7-3. Results of Ion Exchange Model Fit and Prediction of NpCA4 and NpCA6 Experiments. Ion Exchange Model Reactions and Parameters Listed in Table 7-3.

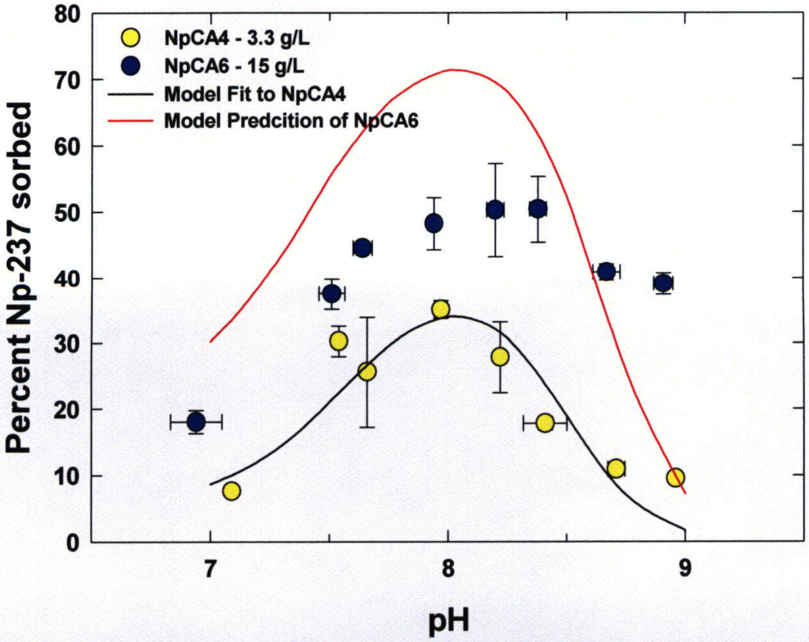

Figure 7-4. Results of Constant Capacitance Model Fit and Prediction for NpCA4 and NpCA6 Experiments. Model Assumes A Single NpO_2^+ Surface Species $>CO_3H\text{-}NpO_2^+$. Model Reactions and Parameters Are Listed in Table 7-3.

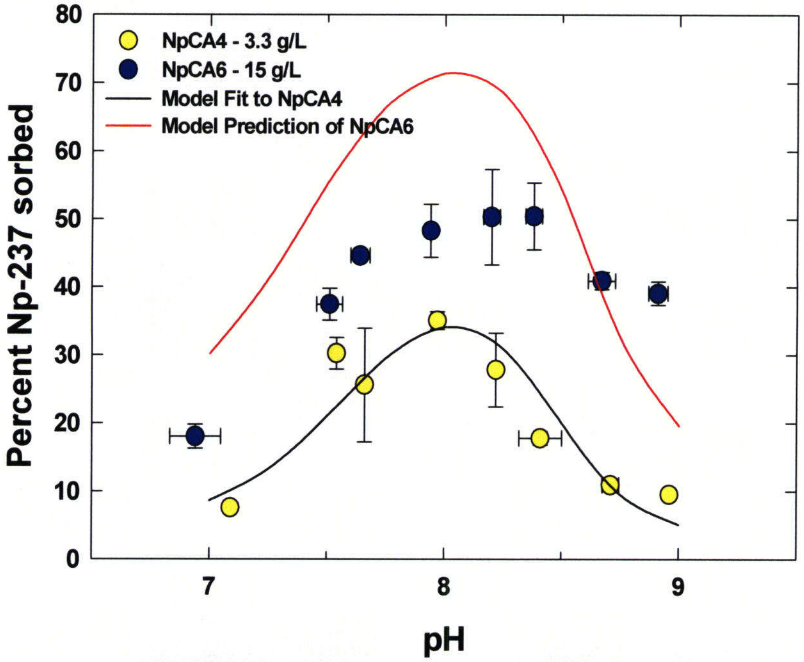

Figure 7-5. Results of Constant Capacitance Model Fit and Prediction for NpCA4 and NpCA6 Experiments. Model Assumes Two NpO_2^+ Surface Species, $>CO_3H\text{-}NpO_2^+$ and $>CaO\text{-}NpO_2OH^-$. Model Reactions and Parameters Are Listed in Table 7-3.

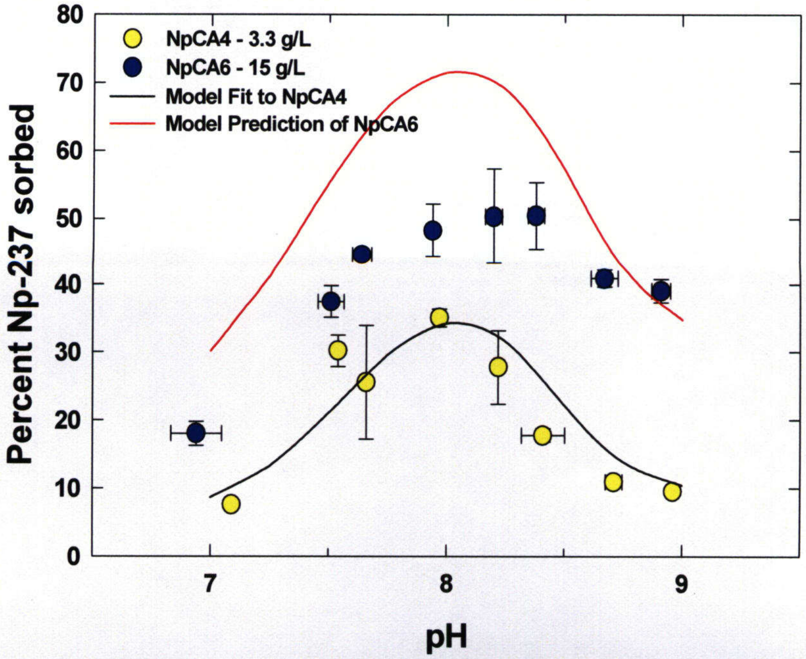

Figure 7-6. Results of Constant Capacitance Model Fit and Prediction for NpCA4 and NpCA6 Experiments. Model Assumes Two NpO_2^+ Surface Species, $>CO_3H\text{-}NpO_2^+$ and $>CaOH\text{-}NpO_2CO_3^-$. Model Reactions and Parameters Are Listed in Table 7-3.

8 SUMMARY AND CONCLUSIONS

Np-237 has been identified as a radionuclide of concern in performance assessment models for Yucca Mountain, and the retardation of Np-237 in the unsaturated and the saturated zones had been identified as a principal factor in the DOE site recommendation safety case for Yucca Mountain (CRWMS M&O, 2000a,b). The widespread occurrence of calcite, including an uncertain abundance in the alluvium, the variation in calcite saturation index of Yucca Mountain groundwater, and a lack of data regarding Np-237 sorption on calcite indicate a need to investigate and understand Np-237 uptake on calcite. An understanding of the mechanisms and magnitude of calcite uptake of Np-237 from solution will be of benefit to NRC staff in their review of the DOE licensing case, if submitted, especially for ascertaining the potential transport of Np-237 through the saturated zone. Information on Np-237 and calcite interaction can be used in conjunction with previous studies of Np-237 sorption on minerals to develop more representative abstractions for radionuclide transport in the saturated alluvium.

This report discusses recent and active experimental efforts to investigate Np-237 sorption on calcite, provides a review of recent results, and describes preliminary efforts to model the sorption behavior using a number of alternative modeling approaches.

Results of a second series of Np-237 and calcite sorption experiments conducted at ~1.6×10^{-6} M Np-237 for a range of pH from 7.25 to 9, at equilibrium with atmospheric $P\text{CO}_2$ and at or near equilibrium with calcite in solution, confirm the pH dependence of Np-237 sorption on calcite. Calcite is an effective sorber of Np-237 for the pH range studied, and the sorption magnitude observed is similar to or greater than the sorption of Np-237 by montmorillonite for the same pH range. The experiments also indicate that previous experimental difficulties, perhaps induced by insufficient mixing during the sorption phase, have not been fully resolved. Nevertheless, an adequate amount of data has been collected to initiate efforts to model the Np-237 and calcite system.

Preliminary modeling results show that a nonelectrostatic surface complexation approach is ineffective at reproducing experimental data. The data are reasonably fit using a simple ion exchange model and are superbly fit with a constant capacitance surface complexation model. Model results indicate that Np-237 uptake was reduced by sorption of Ca^{2+} onto the calcite surface and by formation of neptunyl carbonate complexes in solution; however, constant capacitance model results indicate that some neptunyl carbonate sorption on calcite also occurs at high pH.

A successful understanding of Np-237 sorption on calcite will depend on a continuation of work to resolve experimental uncertainties and to expand the conditions of the experiments. Solution chemistry must continue to be thoroughly analyzed to aid in the calculation of speciation and saturation indices for calcite. Additional experimental data must be collected to provide confidence in the modeling input data. The conditions of experiments must also be varied to include a larger range of equilibrium solution concentrations to evaluate the nature of the Np-237 and calcite sorption isotherm.

Additionally, experiments should be conducted at differing levels of PCO_2. Current experimental efforts include establishing calcite solutions at equilibrium with atmospheres of differing partial pressures of $CO_2(g)$. These experiments will commence following a reevaluation of the mixing protocol to ensure all calcite is contacted by Np-237 bearing solutions during the experiments. The model of Van Cappellen, et al. (1993) predicts differences in speciation and surface charge depending on if the pH is controlled by adding acid-base or by CO_2 overpressuring. Differences in speciation may affect sorption behavior and, as such, may help to guide the modeling effort.

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