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6220 Culebra Road • San Antonio, Texas, U.S.A. 78228-5166
(210) 522-5160 • Fax (210) 522-5155

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U.S. Nuclear Regulatory Commission
ATTN: Dr. John W. Bradbury
Division of Waste Management
Two White Flint North
Mail Stop TD–13
Washington, DC 20555

Subject: Transmittal of the deliverable "Laboratory Experiments of Neptunium Uptake—Letter Report" (IM 01402.871.110).

The enclosed paper is identified as IM 1402.871.110 in the CNWRA Operations plans for the Key Technical Issue (KTI) on Radionuclide Transport. The title of the deliverable was changed in the period 7 Program Manager's Periodic Report to reflect the focus of the work on neptunium (Np).

This work is part of ongoing efforts to evaluate changing U.S. Department of Energy (DOE) reliance on the alluvial portion of the potential radionuclide transport paths for a significant portion of repository performance. Batch experiments were conducted using calcite substrate in solutions at or near saturation with respect to calcite over a pH range of 7 to 9. The solutions were at equilibrium with atmospheric $PCO_2$, and the initial concentration of $^{237}Np$ was $2.5 \times 10^{-6}$ *M*. The results of the first experiments indicate that sorption of $^{237}Np$ is significant below pH of ~8.2. The sorption behavior, which is dependent on solution pH, suggests that the solution speciation of $^{237}Np$ plays a large role in the magnitude of $^{237}Np$ sorption. Distinct differences in sorption were observed when calcite was added to solutions previously spiked with $^{237}Np$ as compared to solutions in which calcite was allowed to equilibrate prior to adding $^{237}Np$. A comparison of results is made to previous results from DOE studies. This comparison indicates that the limited chemical range used in DOE studies may not adequately represent Np uptake by calcite from groundwater down-gradient from Yucca Mountain.

If you have any questions regarding this submittal, please contact me (210-522-5540) or Mr. Paul Bertetti (210 522-5228).

Sincerely,

English C. Pearcy
Element Manager
Geohydrology and Geochemistry

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|---|---|---|---|
| cc: | J. Linehan | J. Ciocco | CNWRA Directors |
| | D. DeMarco | B. Leslie | CNWRA Element Mgrs |
| | E. Whitt | D. Brooks | T. Nagy (SwRI Contracts) |
| | B. Meehan | K. Stablein | |
| | J. Piccone | W. Dam | |
| | W. Reamer | W. Patrick | |

Washington Office • Twinbrook Metro Plaza #210
12300 Twinbrook Parkway • Rockville, Maryland 20852-1606

# LABORATORY EXPERIMENTS OF NEPTUNIUM UPTAKE ON CALCITE

*Prepared for*

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

*Prepared by*

**F. Paul Bertetti**

**Center for Nuclear Waste Regulatory Analyses**
**San Antonio, Texas**

**June 2001**

# ABSTRACT

The U.S. Department of Energy (DOE) is currently investigating Yucca Mountain, Nevada (YM) as a potential site for geologic disposal of high-level nuclear waste (HLW). A HLW repository would be evaluated for its ability to limit radiological exposures to the public. The potential for radionuclides to be transported in groundwater from the proposed repository to the accessible environment is a key technical issue (KTI) 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. $^{237}$Np has been identified as a radionuclide of concern in analyses of the performance of the proposed YM repository because of its relatively high solubility, reported low retardation factors, and the known sensitivity of performance assessment models to retardation factors used for $^{237}$Np. DOE studies have suggested that $^{237}$Np sorption on calcite, which has a widespread occurrence at YM, is enhanced relative to sorption on other common mineral phases. Nevertheless, little is known regarding the mechanism and potential for sorption of $^{237}$Np on calcite. This report discusses experimental efforts to investigate $^{237}$Np sorption on calcite and provides a preliminary review of recent results.

Batch experiments were conducted using calcite substrate in solutions at or near saturation with respect to calcite over a pH range of 7 to 9. The solutions were at equilibrium with atmospheric $PCO_2$, and the initial concentration of $^{237}$Np was $2.5 \times 10^{-6}$ *M*. The results of the first experiments indicate that sorption of $^{237}$Np is significant below pH of ~8.2. The sorption behavior, which is dependent on solution pH, suggests that the solution speciation of $^{237}$Np plays a large role in the magnitude of $^{237}$Np sorption. Distinct differences in sorption were observed when calcite was added to solutions previously spiked with $^{237}$Np as compared to solutions in which calcite was allowed to equilibrate prior to adding $^{237}$Np. A comparison of results is made to previous results from DOE studies. Discussions of future work and considerations for modeling of the $^{237}$Np-calcite system are also included.

# CONTENTS


Section Page

FIGURES ..... vii
TABLES ..... ix
ACKNOWLEDGMENTS ..... xi

1 LABORATORY STUDIES OF NEPTUNIUM UPTAKE ..... 1-1
1.1 REGULATORY BASES ..... 1-1

2 RADIONUCLIDE TRANSPORT IN PERFORMANCE ASSESSMENT ..... 2-1

3 EXPERIMENTAL BACKGROUND ..... 3-1

4 EXPERIMENTAL OBJECTIVES ..... 4-1

5 MATERIALS AND METHODS ..... 5-1
5.1 CALCITE ..... 5-1
5.2 $^{237}$NEPTUNIUM ..... 5-1
5.3 EXPERIMENTAL SOLUTIONS ..... 5-2
5.4 SORPTION EXPERIMENTS ..... 5-2
5.5 CALCULATIONS ..... 5-5

6 RESULTS ..... 6-1

7 DISCUSSION ..... 7-1

8 SUMMARY AND CONCLUSIONS ..... 8-1

9 REFERENCES ..... 9-1

# FIGURES


Figure Page

4-1 Calculated saturation index (SI) for groundwaters in the Yucca Mountain (YM) region (see text for discussion). . . . . 4-2

5-1 X-ray diffraction pattern for aged calcite sample S1 shown with peaks for synthetic calcite . . . . . 5-3

5-2 Scanning electron micrographs of "aged" calcite prepared for use in the Np-calcite sorption experiments.. . . . . 5-4

6-1 Percentages of initial $^{237}$Np sorbed on calcite after 11 days. NpCA1 series (a) experiments utilized an M/V ratio of 25 g/L, NpCA2 series (b) experiments utilized an M/V of 5 g/L, while NpCA3 series (c) experiments utilized an M/V of 10 g/L. . . . . 6-2

6-2 $K_D$ values for $^{237}$Np sorption on calcite after 11 days. NpCA1 series (a) experiments utilized an M/V ratio of 25 g/L, NpCA2 series (b) experiments utilized an M/V of 5 g/L, while NpCA3 series (c) experiments utilized an M/V of 10 g/L. . . . . 6-3

6-3 Comparison of measured $^{237}$Np $K_D$ values for two experiments that were sampled after 3 days and again at 11 days. . . . . 6-4

6-4 Comparison of measured $^{237}$Np $K_D$ values for all experiments. Solid lines are added as an aid to the eye in grouping experimental series. . . . . 6-4

7-1 Calculated speciation of Np(V) in 0.1 *M* $NaClO_4$ at equilibrium with atmospheric $PCO_2$. . . . 7-2

7-2 Comparison of representative data from Triay et al. (1996), shown by the filled circles, to results of experiments from this study. . . . . 7-4

# TABLES


Table | Page

4-1 Calculated saturation index (SI) of calcite, and chemical data used in the calculations, for waters collected from selected EWDP wells. . . . . 4-3

5-1 Chemical analyses of calcite used in experiments. . . . . 5-2
5-2 Summary of initial conditions for $^{237}$Np-calcite experiments . . . . . 5-6

7-1 Thermodynamic data used in MINTEQA2 speciation calculations shown in figure 7-1 . . . . . 7-2

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# QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT

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

**ANALYSES AND CODES**: The EQ3/6 Version 7.2b (Wolery, 1992) and MINTEQA2 Version 3.11 (Allison, 1991) 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 LABORATORY STUDIES OF NEPTUNIUM UPTAKE

## 1.1 REGULATORY BASES

As prescribed by the U.S. Nuclear Waste Policy Act of 1982, as amended (U.S. Nuclear Waste Policy Act, 1982), Yucca Mountain (YM), Nevada, is currently under consideration as a geologic repository for high-level radioactive wastes (HLW). A HLW repository would be evaluated for its ability to limit radiological exposures to the public. In preparing to review any U.S. Department of Energy (DOE) license application (LA) to construct and operate a proposed HLW repository at YM, the U.S. Nuclear Regulatory Commission (NRC) is directing activities toward resolving key technical issues (KTIs) it considers most important to repository performance. One of these KTIs is concerned with assessing the potential for radionuclide transport (RT) from the repository through the subsurface to the accessible environment.

As defined in Environmental Protection Agency rule, "Public Health and Environmental Radiation Protection Standards for Yucca Mountain, Nevada " (40 CFR Part 197), the reasonable maximally exposed individual (RMEI) for radionuclides released from the YM repository within 10,000 yr after disposal is expected to be located approximately 18 km from YM. 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 RMEI are related directly to the concentration of radionuclides in the groundwater.

The delay of radionuclide transport through the unsaturated zone (UZ) and saturated zone (SZ) at YM is identified by DOE as a principal factor of the current postclosure safety case (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000a). Retardation can result from 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 RMEI (U.S. Nuclear Regulatory Commission, 2000), and a clear understanding of the relative effects of chemical processes on retardation is a key aspect of evaluating the DOE safety case. Understanding of geochemical processes that influence RT may also be used to improve hydrologic models of the YM system.

The RT KTI addresses the main issue that radionuclide concentrations may be reduced during transport in groundwater. RT KTI subissues, which include transport through porous rock, fractured rock, and alluvium, have been the focus of previous review and form the basis for agreements reached during a series of DOE/NRC technical exchanges held during 2000 and 2001[1]. These agreements are commitments by DOE to provide information that NRC staff require for a complete, high-quality LA with respect to a given subissue, and form the basis for the issue resolution process.

[1]For example, Reamer, W. *Summary Highlights of NRC/DOE Technical Exchange and Management Meeting on Radionuclide Transport.* Letter (December 5–7, 2000) to D.R. Williams, U.S. Department of Energy. Washington, DC: U.S. Nuclear Regulatory Commission. 2000.

# 2 RADIONUCLIDE TRANSPORT IN PERFORMANCE ASSESSMENT

As part of its demonstration of the performance of the proposed YM repository following permanent closure, DOE must use a performance assessment (PA) (U.S. Nuclear Regulatory Commission, 1999), which consists of a number of linked system model abstractions designed to estimate doses from the repository to the public during the 10,000-yr regulatory period. In the current DOE YM PA model, the *Total System Performance Assessment—Site Recommendation* (TSPA-SR), radionuclides are assumed to interact with the geologic setting during transport in groundwater through the UZ and SZ (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000b). In the TSPA-SR, 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 TSPA-SR model for RT through fractures, although it is possible that fracture-lining materials may play a role in retarding radionuclides. TSPA-SR sorption processes are represented using the distribution coefficient ($K_D$) as given by the equation:

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

where $[\mathrm{RN}]_{\mathrm{solid}}$ and $[\mathrm{RN}]_{\mathrm{aqueous}}$ are the concentrations of radionuclide on the solid and in the groundwater, respectively, M is the mass of the solid, and V is the solution volume (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000a,b,c). For flow in the SZ, radionuclide retardation is related to $K_D$ by the equation:

$$R_f = 1 + \frac{\rho_b}{n} K_D \tag{2-2}$$

where $R_f$ is the retardation factor, $\rho_b$ is the bulk density, and $n$ is the porosity. For flow in the UZ, the moisture content, $\theta$ is substituted for $n$ (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000b,c). Inherent in the use of Eq. (2-2) is the assumption that sorption isotherms for radionuclides are linear (Freeze and Cherry, 1979). In the DOE TSPA-SR, as in previous efforts, sorption coefficients in the tuff matrix were assigned values and probability distributions based on expert elicitation, although the specific constraints on the transport parameters have been modified, particularly for uranium (U), neptunium (Np), and plutonium (Wilson et al., 1994; Triay et al., 1997; Civilian Radioactive Waste Management System Management and Operating Contractor, 2000b). Sorption parameters and probability distribution functions (PDFs) were constrained assuming that waters from saturated volcanic tuff (Well J–13) and the Paleozoic (UE–25p#1) aquifers bound the chemistry of the groundwaters at YM (Triay et al., 1997).

Probability distributions and $K_D$ values for Np ($^{237}$Np), which has been identified as a radionuclide important to performance, have been of particular concern (U.S. Nuclear Regulatory Commission, 2000). The DOE performed sensitivity analyses using the *Total System Performance Assessment—Viability Assessment* (TSPA-VA) code to investigate the effects of uncertainty in sorption parameters on performance (Civilian Radioactive Waste Management System Management and Operating Contractor, 1998). The effects of uncertainty on sorption of $^{237}$Np in the SZ volcanic rocks were investigated during the analyses, but the $K_D$ for Np sorption in the alluvium was held constant at 10 mL/g (Civilian Radioactive Waste Management System Management and Operating Contractor, 1998). There has been little formal investigation of $^{237}$Np

$K_D$s in alluvium materials (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000c). Because of a lack of experimental data, $^{237}$Np sorption coefficients used for alluvium in the TSPA-VA were assigned values greater than $^{237}$Np $K_D$s used for the saturated tuffs (Civilian Radioactive Waste Management System Management and Operating Contractor, 1998). The $K_D$s 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 $^{237}$Np in YM waters (Civilian Radioactive Waste Management System Management and Operating Contractor, 1998; Triay et al., 1996, 1997).

More recently, sensitivity analyses conducted for TSPA-SR have shown that the SZ transport model is particularly sensitive to $^{237}$Np $K_D$s, with the variance in $K_D$s used for TSPA-SR producing a two order of magnitude variance in transport times for $^{237}$Np through the SZ (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000b). In the DOE TSPA-SR, sorption coefficients for Np in the saturated alluvium were modified to reflect recent experiments conducted on alluvial materials (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000b). These materials included drilling cuttings from wells in the Nye County Early Warning Drilling Program (EWDP) (Conca et al., 2000; Civilian Radioactive Waste Management System Management and Operating Contractor, 2000b,c). Several of the EWDP wells are located within the predicted flow path down-gradient of YM. Based on the preliminary results of these batch sorption studies, both Np $K_D$s and PDFs were adjusted. However, the preliminary batch results 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 underway (Conca et al., 2000)[1].

[1]Reamer, W. *Summary Highlights of NRC/DOE Technical Exchange and Management Meeting on Radionuclide Transport.* Letter (December 5–7, 2000) to D.R. Williams, U.S. Department of Energy. Washington, DC: U.S. Nuclear Regulatory Commission. 2000.

# 3 EXPERIMENTAL BACKGROUND

Calcite is an important mineral for consideration in analyzing the DOE safety case because of its relatively widespread occurrence in the YM region (Bish et al., 1996; Carlos et al., 1995; Vaniman, 1994). Calcite deposits are found within the UZ and SZ, 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, 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 having been formed from precipitation from upwelling groundwater and from precipitation associated with percolation of rainfall into the UZ (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 EWDP wells (Nye County, 2001). Thus, calcite occurs along all groundwater flow paths in the YM region.

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

A recent CNWRA study investigated $^{237}$Np uptake through coprecipitation with calcite (Nugent and Turner, 2000). Results showed that $^{237}$Np was readily removed from solution during calcite precipitation. Calcite precipitated in the presence of 28 ppb of $^{237}$Np contained 500 to 1,000+ ppm $^{237}$Np, suggesting Np is compatible with the calcite structure. A comparison of Np-calcite and U-calcite coprecipitation demonstrated that U-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 Np and U adsorption behaviors on silicates and aluminosilicates indicates that they behave quite similarly (Nugent and Turner, 2000).

Although coprecipitation of $^{237}$Np with calcite was the proposed mechanism suggested by DOE investigators (Triay et al., 1996, 1997), one of the primary mechanisms for retardation of radionuclides is through sorption of the radionuclide onto rock and mineral surfaces. Sorption often occurs through a surface complexation mechanism or through ion exchange, processes that have been, in the case of $^{237}$Np, investigated previously for silicates and some oxides (e.g., Pabalan et al., 1998; Bertetti et al., 1998), but only minimally for carbonate minerals, especially calcite.

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 on calcite 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 possible 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., 1991). Miyake et al. (1988) observed dissolution and recrystallization within 40 hr. 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 surface complexation 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). Investigators have successfully modeled observed changes in the sorption of $Co^{2+}$ with respect to pH by explicitly incorporating carbonate complexation with $Co^{2+}$ (Zachara et al., 1991). 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 the method of pH adjustment, and varying carbonate values make assessment and interpretation of the sorption mechanisms difficult (Van Cappellen et al., 1993).

As mentioned previously, $^{237}Np$ sorption onto calcite has been studied by Allard (1984) and Triay et al. (1996, 1997). Brady et al. (1999) examined actinide sorption onto dolomite [$CaMg(CO_3)_2(s)$] and observed little or no sorption of $^{237}Np$ onto dolomite at pH values below 8, along with an observed increase in sorption as pH was increased above 8 (although limited data are available, and total uncertainty in measurements was high). Brady et al. (1999) observations for $^{237}Np$ seemed inconsistent with their observations for U, 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 $^{237}Np$ sorption onto calcite with increasing pH from approximately 7 to 9. Triay et al. (1996, 1997) conducted experiments investigating $^{237}Np$ sorption onto natural calcite, synthetic calcite, and calcite-bearing volcanic tuffs in Well J–13 and UE25–p#1 waters (pH ~8.5 and 8.9, respectively). Results indicated that tuffs containing calcite exhibited significantly more $^{237}Np$ uptake from solution than did tuffs without calcite and showed that slightly less $^{237}Np$ was sorbed in Well J–13 water as compared to UE25–p#1water (Triay et al., 1996). It should be noted that the UE25–p#1 water used in DOE experiments exhibited precipitation of calcite after pumping and subsequent storage in the lab (Triay et al., 1997). This precipitation was due to the loss of dissolved $CO_2(g)$ as the water equilibrated with atmosphere. Importantly, the maximum $^{237}Np$ $K_D$s reported in Triay et al. (1996, 1997) were obtained only after rather long reaction times (greater than 14 days). $^{237}Np$ $K_D$s typically increased an order of magnitude or more during 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.

# 4 EXPERIMENTAL OBJECTIVES

The known occurrence of calcite in tuffs and calcareous zones within the alluvium down-gradient from YM and the known sensitivity of SZ transport models to $K_D$ values used for $^{237}$Np, combined with the uncertainties in alluvium characterization and a poor understanding and body of information regarding $^{237}$Np sorption on calcite, make it important that $^{237}$Np interaction with calcite be more clearly understood prior to a potential LA. Other considerations might include a need to understand the retention and redistribution of $^{237}$Np near the surface, where $^{237}$Np might be introduced in irrigation water pumped from a plume emanating from the proposed YM repository. Moreover, DOE has plans to carry out further alluvium characterization that should help reduce parameter uncertainties, but results of these studies may not be available until very near the planned date for a potential LA (U.S. Nuclear Regulatory Commission, 2000)[1].

Thus, for NRC to evaluate the technical basis for the DOE treatment of Np transport in a timely manner relative to review of a potential LA, the role of calcite in the retardation of $^{237}$Np needs further investigation. This study investigates the sorption of $^{237}$Np on calcite and the geochemical factors that may influence its magnitude. The experiments are conducted using a range in chemical conditions relevant to the environment at YM. The results will help provide an independent means to support NRC total performance assessment analyses and test DOE assumptions.

As discussed previously, experiments have been conducted with $^{237}$Np and calcite in solutions that were supersaturated with respect to calcite (coprecipitation). However, groundwater down-gradient and in the expected flow path from YM is undersaturated with respect to calcite. Calcite saturations in the SZ in the YM vicinity are represented in figure 4-1, which is based on a screened subset of data from the database of Perfect et al. (1994) (Turner et al., 1999). The saturation index (SI) of a mineral can be defined by

$$\mathrm{SI} = \log\left(\frac{\mathrm{IAP}}{K_{sp}}\right) \tag{4-1}$$

where IAP is the ion activity product and $K_{sp}$ is the solubility product constant. A system is undersaturated with respect to a mineral if the calculated SI for that mineral is < 0, whereas SI values > 0 indicate supersaturation. As indicated in the figure, calcite would not be expected to precipitate along the expected flow path from YM. Calculations using groundwater collected from EWDP wells within the Fortymile Wash region confirm the predominantly undersaturated conditions (table 4-1). Although well EWDP–3S is not within Fortymile Wash, it is included in the table for comparison because it has been used as a water source in recent DOE alluvium $K_D$ experiments (Conca et al., 2000). Saturation levels do vary across the region, however, so one long-term goal of the studies described here is to conduct experiments over a range of saturation levels similar to those found at YM.

Experiments will also be conducted over a range of pH from approximately 7 to 9, which reflects the variation in pH of groundwater in the YM region. Solution pH can be adjusted by the addition of acid or base (while $PCO_2$ is held constant) or by the variance of $PCO_2$ in the atmosphere with which the solution is

[1]Reamer, W. *Summary Highlights of NRC/DOE Technical Exchange and Management Meeting on Radionuclide Transport.* Letter (December 5–7, 2000) to D.R. Williams, U.S. Department of Energy. Washington, DC: U.S. Nuclear Regulatory Commission. 2000.

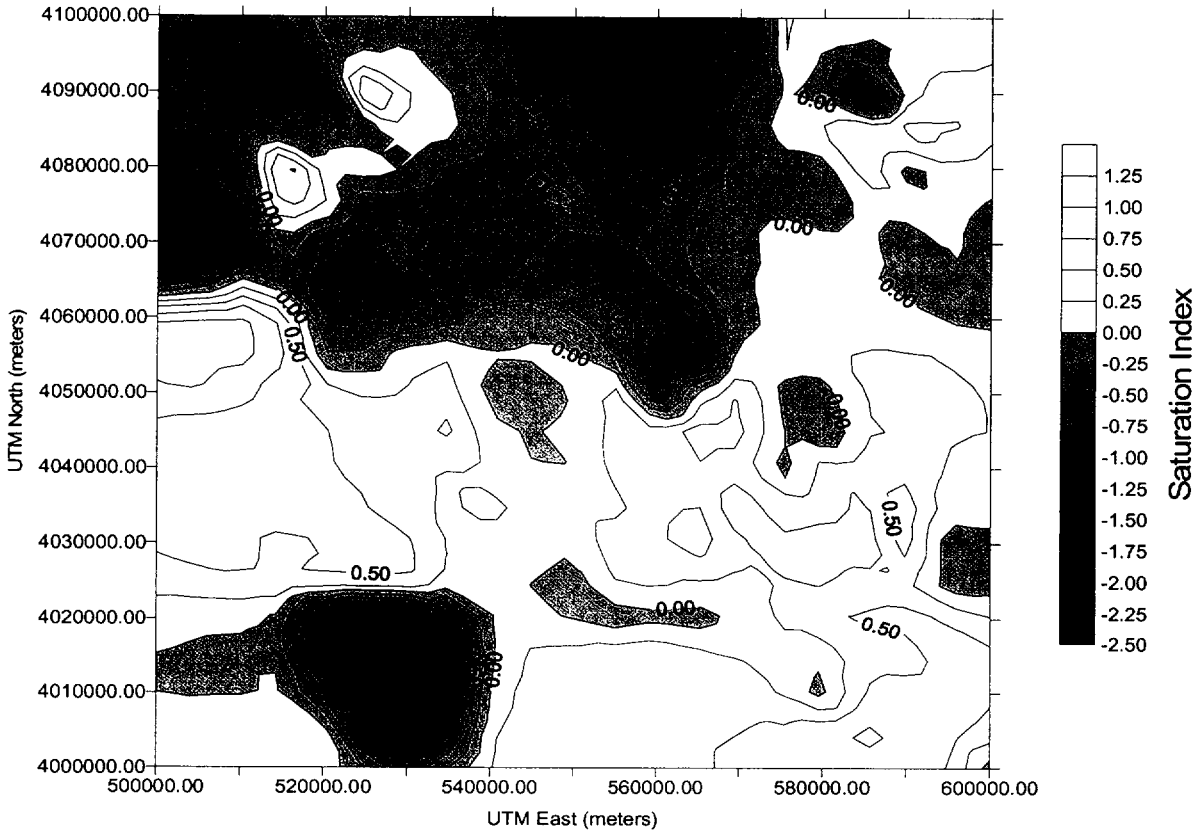


**Figure 4-1. Calculated saturation index (SI) for groundwaters in the Yucca Mountain (YM) region (see text for discussion). Approximate location of YM is given by the diamond symbol in upper center of map. Approximate location of the reasonably maximally exposed individual along the expected flow path from YM is given by the crossed box. Water is undersaturated with respect to calcite for SI values less than zero.**

allowed to equilibrate. However, investigations of the calcite-aqueous solution interface have demonstrated that solution and surface (calcite) speciation can vary significantly, depending on the method used to vary solution pH (Van Cappellen et al., 1993). For example, $PCO_2$ 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 acid and base. Both methods of pH adjustment have been used in calcite sorption studies. For example, Zachara et al. (1991) used acid-base addition while Davis et al. (1987) used $PCO_2$. DOE investigators have adjusted pH with $PCO_2$ manipulation, although in Np-calcite sorption studies, pH was not adjusted (Triay et al., 1996). The implications for $^{237}$Np-calcite sorption studies are that the interpretations of surface complexation reactions and sorption processes may differ due to the influence of the pH adjustment method. As a result, experiments in this study will be conducted using both methods of pH adjustment, with the first series of experiments utilizing acid and base additions.

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

- An examination of $^{237}$Np sorption onto calcite under conditions that mimic the variation in groundwater chemistry at YM including the pH range of 7 to 9 and variable solution saturation with respect to calcite

**Table 4-1. Calculated saturation index (SI) of calcite, and chemical data used in the calculations, for waters collected from selected EWDP wells. Generally, groundwater in the saturated alluvium is slightly undersaturated or near saturation with respect to calcite. Calculated log $PCO_2$ values in equilibrium with the well waters are also shown (Note: Atmospheric log $PCO_2$ is approximately –3.5). With the exception of data for NC–EWDP–19D, chemistry data represent average values from multiple sampling events.**

| | NC-EWDP-15P[A] | NC-EWDP-19D[A] | NC-EWDP-19P[A] | NC-EWDP-03S Zone 3[B] |
|---|---|---|---|---|
| pH | 8.1 | 8.6 | 8.1 | 8.8 |
| $SiO_2$ (aq) (mg/L) | 45.5 | 65.0 | 56.1 | 48.0 |
| $HCO_3^-$ (mg/L) | 163 | 228 | 132 | 254 |
| $CO_3^{2-}$ (mg/L) | — | 8.3 | — | 24.0 |
| $Cl^-$ (mg/L) | 8.5 | 6.5 | 8.05 | 10.1 |
| $SO_4^{2-}$ (mg/L) | 48.5 | 29.0 | 28.8 | 47.3 |
| $NO_3^-$ (mg/L) | 5.8 | 2.3 | 5.5 | — |
| $Na^+$ (mg/L) | 72.8 | 111 | 46.6 | 135 |
| $K^+$ (mg/L) | 3.6 | 3.90 | 4.75 | 3.0 |
| $Ca^{2+}$ (mg/L) | 11.6 | 1.87 | 17.3 | 0.82 |
| $Mg^{2+}$ (mg/L) | 1.9 | 0.10 | 1.48 | 0.10 |
| **Calculated SI** | –0.063 | –0.233 | 0.041 | –0.376 |
| **Calculated log $PCO_2$** | –2.9 | –3.24 | –2.99 | –3.39 |

Note: A. Data collected by Nye County personnel February–October 2000 (R. Downing, personal communication)
B. Data collected by United States Geological Survey May–November 1999 (DTN: GS0103083123322.002)

- An investigation of the effects of pH adjustment method on sorption results
- A comparison of sorption to solution saturation conditions over time and
- When enough data are accumulated, an effort to model Np sorption behavior on calcite.

The experiments and results discussed in this report include preliminary examinations of $^{237}Np$ sorption on calcite over a range of pH, which has been adjusted using additions of acid and base, in solutions that initially were at or near saturation equilibrium with respect to calcite.

# 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 ($ddH_2O$) (17.5 MΩ, Barnstead Nanopure) prior to use. Mass measurements were determined using a Mettler AE240 electronic balance. pH measurements were determined using an Orion 920A pH/ISE/mV multimeter and Ross combination pH electrode with automatic temperature compensation.

## 5.1 CALCITE

Prior to its use in sorption experiments, purchased reagent-grade calcite [$CaCO_3$(s), Fisher Scientific] was aged according to the procedure of Reddy and Nancollas (1971) by mixing two 125-g aliquots each in 4 L of 0.02 *M* $NaHCO_3$. The calcite aliquots were contacted with the bicarbonate solutions under atmospheric $PCO_2$ for 30 days and were mixed daily during this period. The aging procedure establishes calcite crystallites with a more uniform particle diameter than reagent-grade calcite through recrystallization (Zachara et al., 1991). Recrystallization refers to a process in which smaller crystallites and surfaces with defects dissolve and reprecipitate as energetically more stable forms (Davis et al., 1987; Zachara et al., 1991). Following the aging period, the $CaCO_3$ solid was separated from the storage solution by filtration, air dried at 50 °C, and stored in a desiccator flask under vacuum.

Chemical (table 5-1) and mineralogical (figure 5-1) analyses of the aged calcite indicated that no significant impurities were present. The calcite had a surface area of approximately 0.23 ± 0.02 $m^2/g$ as measured using multipoint $N_2$-BET analysis (Coulter SA 3100), which is consistent with results from several studies (e.g., Stipp et al., 1992; Zachara et al., 1991). Scanning electron micrographs (figure 5-2) indicate that the crystallites were rhombohedral in morphology and intergrown, with an average edge length (for both samples) of approximately 8 μm. Only the S1 calcite batch was used in the experiments discussed in this report.

## 5.2 $^{237}$NEPTUNIUM

$^{237}$Np 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 $ddH_2O$ to make a stock solution containing ~118 ppm $^{237}$Np. $^{237}$Np has been shown to exist in the 5+ oxidation state in similar stock solutions (Bertetti et al., 1998; Nakayama and Sakamoto, 1991). The $^{237}$Np stock solution was calculated to contain approximately 0.32 *M* $HNO_3$. $^{237}$Np was added to experimental solutions using aliquots of the stock solution.

$^{237}$Np was analyzed by counting its alpha activity using a Packard 3100 TR/AB liquid scintillation analyzer (LSA). The Packard 3100 LSA is capable of discriminating between the alpha activity of $^{237}$Np and the beta activity of its immediate daughter, $^{233}$Pa. All $^{237}$Np samples were counted in 7-mL glass scintillation vials using Ultima Gold AB (Packard) scintillation cocktail. Approximately 0.5 mL of 0.1 *M* $HNO_3$ was added to each vial prior to addition of $^{237}$Np/$^{233}$Pa to minimize any potential radionuclide sorption on the walls of the vial. LSA performance and stock solution activity were confirmed during a series of preliminary tests to account for effects of ionic strength and acid content on efficiency of counting. All $^{237}$Np 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.

**Table 5-1. Chemical analyses of calcite used in experiments**

| Element | Reagent $CaCO_3$ (ppm) | S1–aged $CaCO_3$ (ppm) | S2–aged $CaCO_3$ (ppm) |
|---|---|---|---|
| Aluminum | 5.3 | 5.8 | 5.0 |
| Barium | 6.9 | 6.8 | 6.8 |
| Copper | 6.7 | 3.9 | 6.7 |
| Iron | 10.0 | 9.9 | 9.3 |
| Lead | 0.9 | 1.0 | 0.9 |
| Magnesium | 5.0 | 5.9 | 5.4 |
| Phosphorous | 12.3 | 15.8 | 15.2 |
| Silicon | 6.3 | 5.6 | 5.1 |
| Sodium | 35.6 | 34.6 | 35.7 |
| Strontium | 109.0 | 106.1 | 106.3 |
| Sulfur | 39.5 | 49.1 | 44.9 |
| Zinc | 0.6 | 1.0 | 0.9 |

## 5.3 EXPERIMENTAL SOLUTIONS

Eight equilibrium $CaCO_3(s)$-$CaCO_3(aq)$ solutions with pH ranging from 7.25 to 9.0 in ~0.25 increments were prepared for use in experiments. The solutions were prepared in a series of steps. First, a series of EQ3NR (Wolery, 1992) calculations were performed to determine the chemical composition of solutions at equilibrium with calcite under atmospheric $PCO_2$. Then varying quantities of $HClO_4$, $Ca(ClO_4)_2 \cdot 4H_2O$, $NaClO_4$, and NaOH were mixed with ddH2O to make 2-L solutions at the desired solution composition, pH, and a total ionic strength of 0.1 *M* (Note: low pH solutions, 7.25 and 7.5, have a total ionic strength greater than 0.1 *M* at atmospheric $PCO_2$). Approximately 30 g of reagent-grade calcite were then added to each solution. Finally, the solutions were allowed to equilibrate with atmosphere, in contact with the $CaCO_3(s)$ for approximately 2 wk. Measurements confirmed that pH of each solution was within 0.1 unit of the equilibrium pH calculated by EQ3NR code. When used for experiments, ~20-mL aliquots of each solution were withdrawn and filtered through a 0.2-μm membrane filter (polyethersulfone, Supor®-200, Gelman).

## 5.4 SORPTION EXPERIMENTS

Batch-type sorption experiments were conducted using 40-mL polycarbonate test tubes. The experiments were performed on the bench-top at 22 ± 2 °C. A hole (~5 mm) 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 were conducted at each of the eight pH values established in the calcite

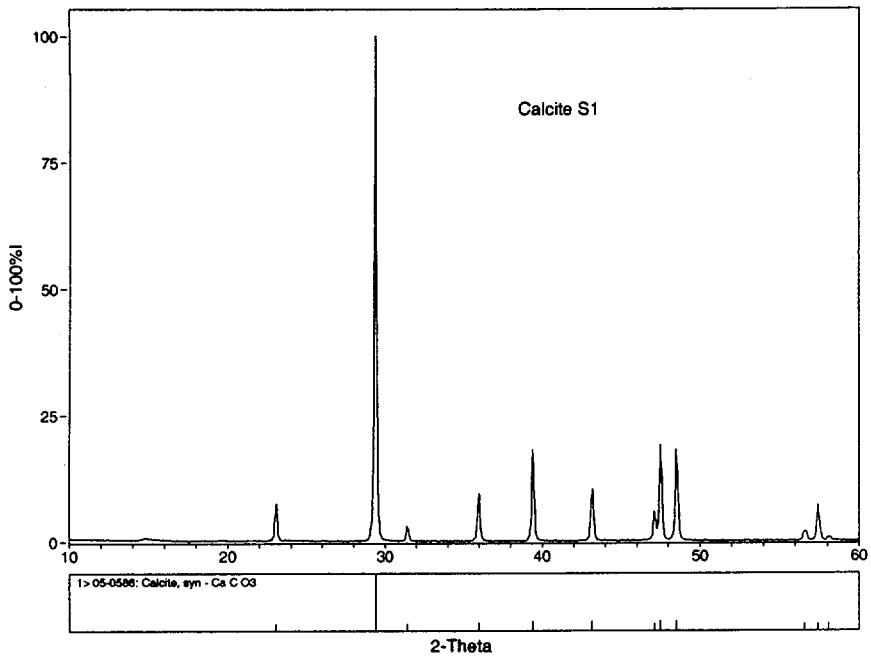


**Figure 5-1. X-ray diffraction pattern for aged calcite sample S1 shown with peaks for synthetic calcite**

equilibrium solutions. The mass of calcite added was varied between each experiment series. Replicate experiments were conducted at each M/V ratio. For example, NpCA11, NpCA12, and NpCA13 represent replicate experiments, all of which were conducted using an M/V ratio of 25 g/L. Two general experimental protocols were followed. In the first protocol, calcite and solutions were added and allowed to reequilibrate overnight prior to addition of $^{237}$Np. In the second protocol, experimental solutions were spiked with $^{237}$Np prior to the addition of calcite.

For experiments in which the first protocol was used, aged calcite was added to preweighed test tubes, after which approximately 20 mL of the appropriate filtered calcite equilibrium solution were added to each tube. The mass of test tubes was remeasured at each step to determine the amount of calcite and solution added (to the nearest 0.0001 g). The calcite suspensions were agitated overnight using a gyratory shaker at 130 rpm. The following day, the test tubes were reweighed prior to adding the $^{237}$Np spike, and a spot check of solution pH was conducted to ensure that conditions were similar to those expected. $^{237}$Np was then added to each by transferring 100 μL of the 118 ppm $^{237}$Np stock solution to each tube. After weighing each tube to verify the mass of $^{237}$Np spike added, an aliquot of 0.32 *N* NaOH was added to each tube to neutralize the acid added with the $^{237}$Np spike. Tubes were reweighed to determine the total mass of solution added.

A second experimental protocol was followed to test the effects of not allowing the aged calcite to equilibrate with the experimental solutions prior to adding the $^{237}$Np spike. For these experiments, approximately 20 mL of the appropriate filtered calcite equilibrium solutions were added to 40-mL polycarbonate tubes. Each tube was then spiked with 100 μL of $^{237}$Np followed by addition of equivalent

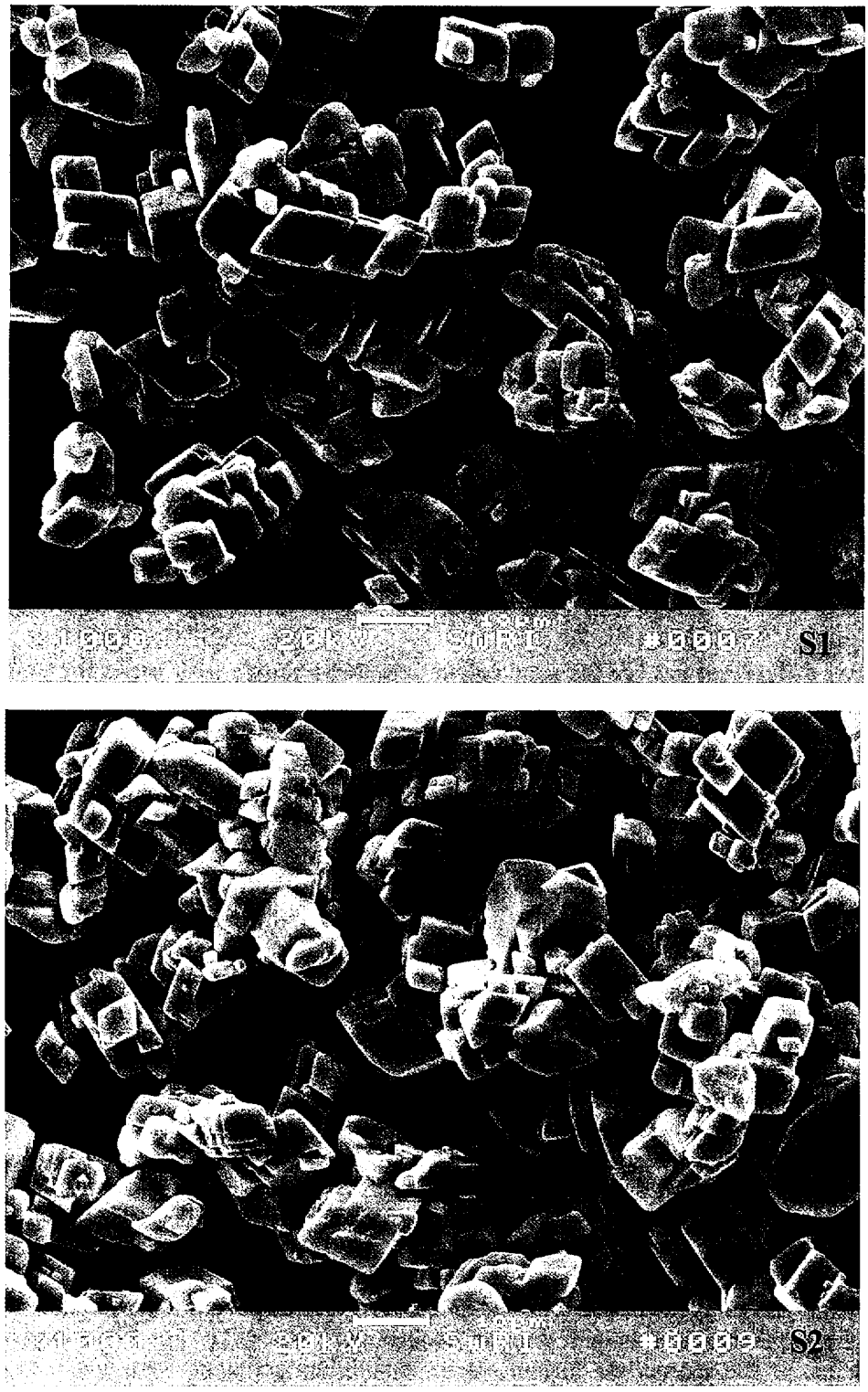


**Figure 5-2. Scanning electron micrographs of "aged" calcite prepared for use in the Np-calcite sorption experiments. Two separate batches S1 and S2 were processed in 0.02 *M* $NaHCO_3$ for 30 days. Only the S1 batch was used in the experiments reported in this study.**

amount of 0.32N NaOH as before. The mass of each tube was recorded at each step. The $^{237}$Np-bearing solutions were then sampled to verify the initial amount of $^{237}$Np added. The solutions were agitated overnight at 130 rpm using a gyratory shaker. The following day, aged calcite was added to each solution. The tubes were weighed before and after addition of the calcite. The concentration of $^{237}$Np in each experiment, calculated based on mass of transferred stock solution and verified by initial sampling of the NpCA3 series, was $2.5 \times 10^{-6}$ *M* (~930 cpm/g).

Following the addition of calcite and $^{237}$Np, all solutions were vortexed (Vortex Genie 2, Scientific Industries) to mix thoroughly and expose the calcite solid in each tube to the $^{237}$Np-bearing solution. Solutions were then allowed to react with the calcite for 11 days while agitating on gyratory shakers. Initial conditions for the experiments are summarized in table 5-2.

After 11 days, the pH of each tube was measured, and tubes were sampled for $^{237}$Np by withdrawing duplicate 0.5-mL samples from each test tube. In addition, pH was measured, and samples were withdrawn from two experiments after 3 days to examine intermediate values of $^{237}$Np uptake. Tubes were weighed prior to and after sampling to account for sampling and evaporation losses.

Following removal of samples for $^{237}$Np determination, several solutions were sampled for chemical analyses to help constrain solution conditions with respect to calcite saturation. Depending on the dilution factor required, 3- or 8-mL aliquots were removed from experimental solutions and transferred to polypropylene bottles. They were subsequently subsampled, diluted as needed, and analyzed for $Ca^{2+}$ using a Perkin-Elmer 3100 flame atomic absorption spectrophotometer.

## 5.5 CALCULATIONS

The mass of $^{237}$Np sorbed on calcite was determined by subtracting the $^{237}$Np mass remaining in solution from the initial mass of $^{237}$Np added (initial $^{237}$Np was corrected for losses during intermediate sampling). The percent $^{237}$Np sorbed on calcite was calculated by dividing the calculated mass sorbed on calcite by the initial $^{237}$Np mass and multiplying by 100. $K_D$s were determined using Eq. (2-1). Mass $^{237}$Np sorbed onto the polycarbonate tubes was assumed to be negligible as has been verified in previous experiments (Nugent and Turner, 2000; Bertetti et al., 1998)

**Table 5-2. Summary of initial conditions for $^{237}$Np-calcite experiments**

| Experiment | Solution Volume (V) (mL) | Mass Calcite (M) (g) | M/V (g/L) | pH range | Initial $^{237}$Np Concentration (*M*) |
|---|---|---|---|---|---|
| NpCA11 | 20 | 0.5 | 25 | 7–9 | $2.5 \times 10^{-6}$ |
| NpCA12 | 20 | 0.5 | 25 | 7–9 | $2.5 \times 10^{-6}$ |
| NpCA13 | 20 | 0.5 | 25 | 7–9 | $2.5 \times 10^{-6}$ |
| NpCA21 | 20 | 0.1 | 5 | 7–9 | $2.5 \times 10^{-6}$ |
| NpCA22 | 20 | 0.1 | 5 | 7–9 | $2.5 \times 10^{-6}$ |
| NpCA23 | 20 | 0.1 | 5 | 7–9 | $2.5 \times 10^{-6}$ |
| NpCA31 | 20 | 0.2 | 10 | 7–9 | $2.5 \times 10^{-6}$ |
| NpCA32 | 20 | 0.2 | 10 | 7–9 | $2.5 \times 10^{-6}$ |

# 6 RESULTS

Figure 6-1 shows percent $^{237}$Np sorbed as a function of pH for all experiments, while figure 6-2 shows values of $K_D$ as a function of pH for the same experiments. Results indicate that for experiments in which calcite was added prior to addition of $^{237}$Np (NpCA1 and NpCA2 series), $^{237}$Np uptake by calcite varies significantly with pH (figures 6-1a,b, 6-2a,b). $^{237}$Np uptake increases with increasing pH until approximately 8.2. With further increase in pH, $^{237}$Np uptake diminishes, in some cases very rapidly. Above pH of 8.25 the uptake seems to stabilize at some net positive value. Note that each experiment series was comprised of two (NpCA31 and NpCA32) or three (e.g., NpCA11, 12, and 13) separate replicate experiments, which were grouped based on similar starting conditions as shown in table 5-2.

Experiments in which calcite was added after the addition of $^{237}$Np show low sorption throughout the pH range tested, with a slight increase in sorption above pH 8 (figures 6-1c and 6-2c). Figure 6-3 compares results from intermediate sampling (3 days) of the NpCA12 and NpCA22 experiments with results from final sampling (11 days) of those experiments. There was little net change in $^{237}$Np sorption between the 3- and 11- day sampling times, although some change in pH is evident.

Inspection of figure 6-4, which displays $K_D$ values for all experiments, reveals that, unlike the expected trend of percent $^{237}$Np sorbed (figure 6-1), normalization of results for mass and solution concentration does not produce an overlap between the NpCA1 and NpCA2 series results. This overlap might be expected given that calculation of $K_D$ normalizes results for differences in M/V ratio, which is the only significant difference between experiments in these two series (Bertetti et al., 1998). Also of note are results from two solutions, one in the NpCA11 experiment and one in the NpCA21, both at pH ~7.86. These two solutions do not fit the trend of increasing sorption with increasing pH demonstrated by solutions at similar pH from the other NpCA1 and NpCA2 series experiments.

Table 6-1 displays the calculated calcite SI for all experimental solutions based on the measured quantities of reagents added to the solutions and on pH measurements after equilibration.

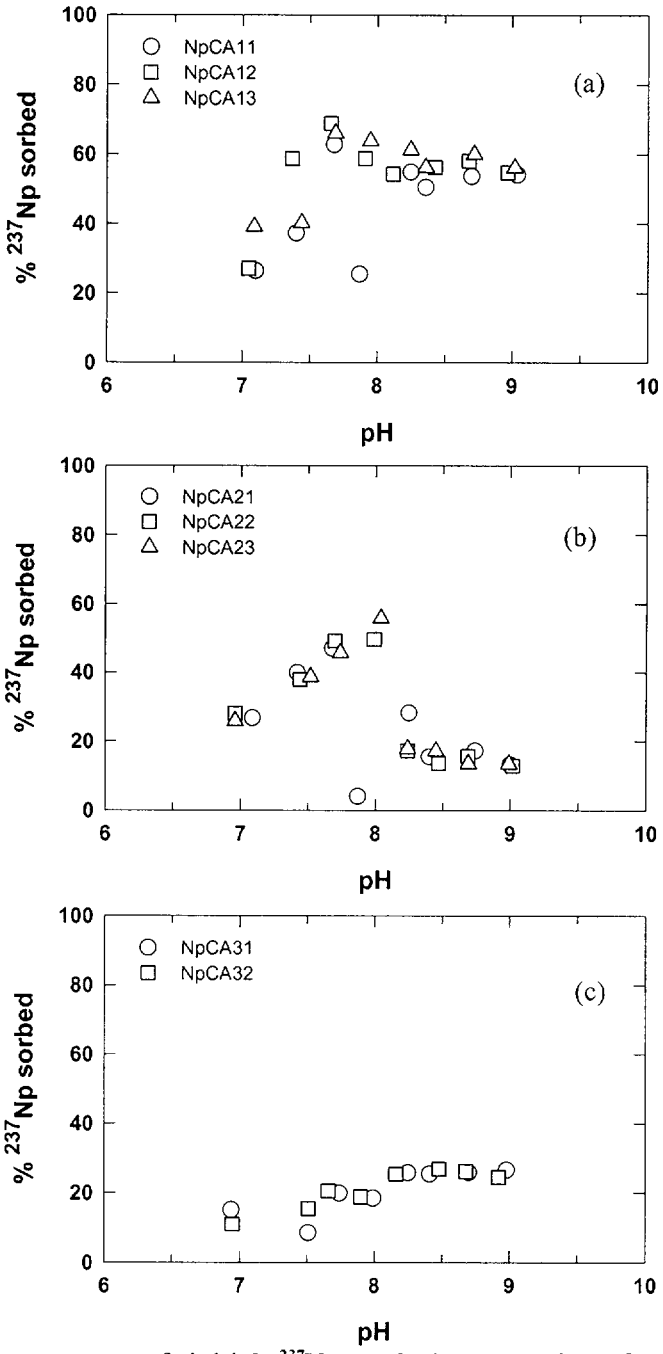


**Figure 6-1. Percentages of initial $^{237}$Np sorbed on calcite after 11 days. NpCA1 series (a) experiments utilized an M/V ratio of 25 g/L, NpCA2 series (b) experiments utilized an M/V of 5 g/L, while NpCA3 series (c) experiments utilized an M/V of 10 g/L. All experiments had an initial $^{237}$Np concentration of ~$2.5 \times 10^{-6}$ *M*. Calcite was added *prior* to spiking with $^{237}$Np in the NpCA1 and NpCA2 series, while calcite was added *after* $^{237}$Np in the NpCA3 series.**

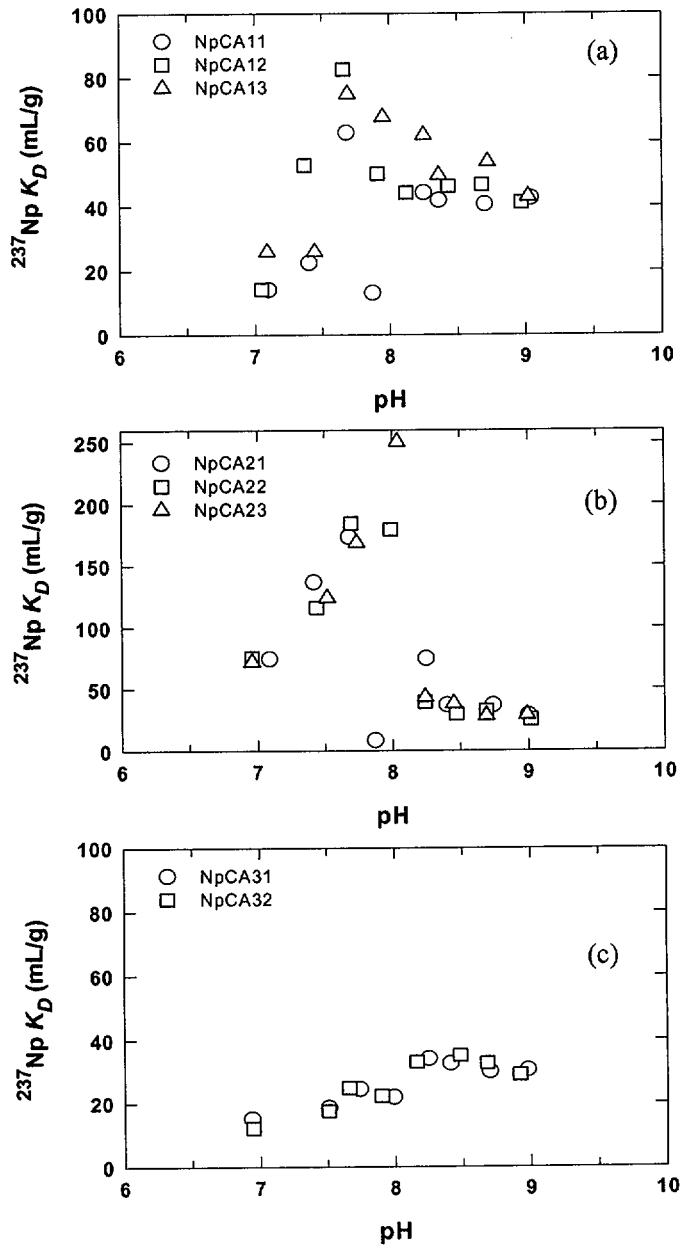


**Figure 6-2. $K_D$ values for $^{237}$Np sorption on calcite after 11 days. NpCA1 series (a) experiments utilized an M/V ratio of 25 g/L, NpCA2 series (b) experiments utilized an M/V of 5 g/L, while NpCA3 series (c) experiments utilized an M/V of 10 g/L. All experiments had an initial $^{237}$Np concentration of ~2.5 × $10^{-6}$ *M*. Calcite was added *prior* to spiking with $^{237}$Np in the NpCA1 and NpCA2 series, while calcite was added *after* $^{237}$Np in the NpCA3 series. Note the scale change for 6-2(b).**

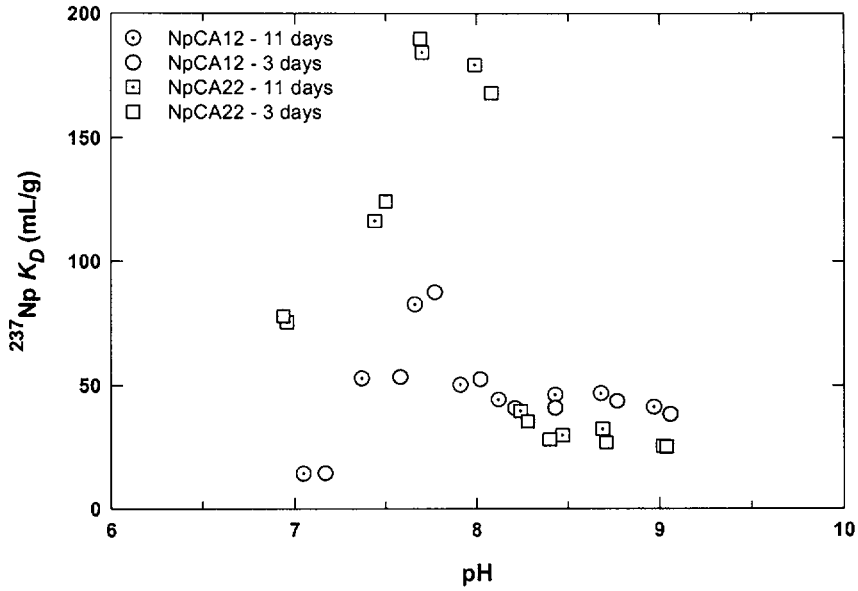


**Figure 6-3. Comparison of measured $^{237}$Np $K_D$ values for two experiments that were sampled after 3 days and again at 11 days. The magnitude of $^{237}$Np sorption on calcite does not change appreciably after 3 days, although some solution pH changes are notable.**

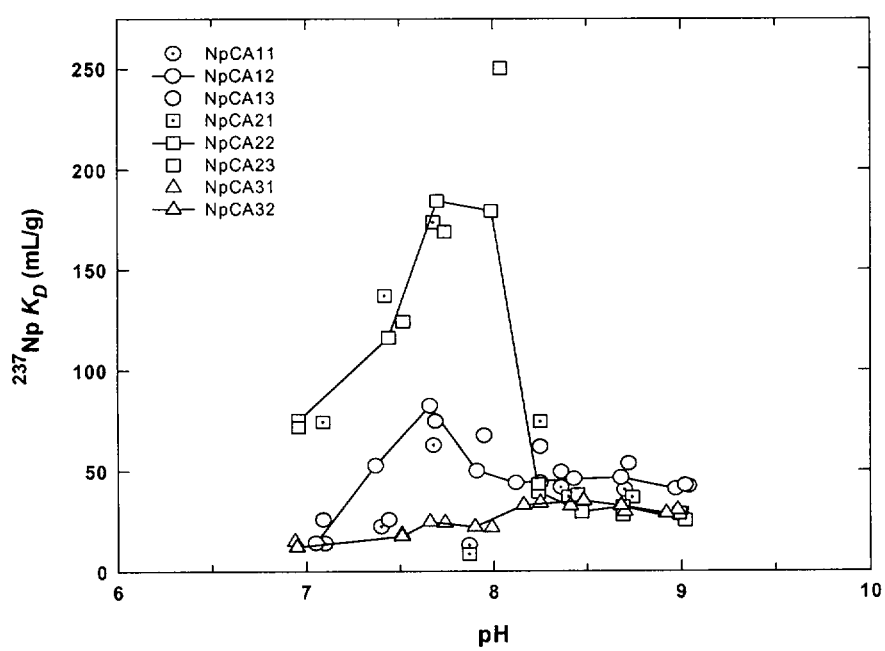


**Figure 6-4. Comparison of measured $^{237}$Np $K_D$ values for all experiments. Solid lines are added as an aid to the eye in grouping experimental series.**

# 7 DISCUSSION

As noted previously, figure 6-4 reveals that experiments with 0.1-g calcite added (NpCA2 series) sorbed a significantly higher quantity of $^{237}Np$ per gram than the experiments with 0.5 g of added calcite (NpCA1 series). The reason for this change is not clear as other investigators have used similar M/V ratios without adverse effects (Zachara et al., 1991; Triay et al., 1996). Both sets of experiments were processed in the same manner using the same starting solutions. Calculation of $K_D$ should normalize sorption results for differences in mass to solution volume ratio and $^{237}Np$ concentration (Bertetti et al., 1998). It may be that the 0.5-g solutions were not adequately mixed by the gyratory shaker; however, following addition of the $^{237}Np$ spike, the solutions were thoroughly mixed by vortexing, and the sorption reaction should have been fast for the small amounts of calcite used in the experiments.

A review of table 6-1 indicates that the starting solutions for all experiments were at or near to 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. The quantities of reagent needed to achieve a desired pH at saturation with calcite were successfully estimated by the EQ3NR code.

The observed sorption behavior, with respect to change in pH, of $^{237}Np$ on calcite is roughly similar to that observed for divalent metal sorption on calcite (Zachara et al., 1988, 1991). Zachara et al. (1988, 1991) proposed that the metal sorption was controlled by 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. However, the observed $^{237}Np$ behavior is also consistent with a surface complexation reaction similar to that observed for $^{237}Np$ sorption on silicate minerals. Of note is the sorption of $Co^{2+}$ on calcite (Zachara et al., 1991). In their experiments, Zachara et al. (1991) observed a decrease in $Co^{2+}$ sorption with an increase in pH above 8.5, after an initial $Co^{2+}$ sorption peak. Subsequent modeling efforts were able to simulate this behavior only by including a Co-carbonate complex, which effectively competed with the $Co^{2+}$ sorption reaction (Zachara et al., 1991). Similarly, aqueous carbonate complexes have been used to describe and predict successfully the sorption decreases observed for actinides, including $^{237}Np$, with further increase in pH following a sorption maximum (e.g., Pabalan et al., 1998; Turner et al., 1998).

A qualitative comparison of $^{237}Np$ speciation can be made with its observed sorption on calcite. Figure 7-1 depicts the speciation of $2.5 \times 10^{-6}$ $M$ $^{237}Np$ in a 0.1 $M$ $NaClO_4$ electrolyte solution at equilibrium with atmospheric $PCO_2$. The equilibrium constants shown in table 7-1 were used along with the MINTEQA2 geochemical code (Allison et al., 1991) to calculate the speciation. Review of figures 6-4 and 7-1 reveals that the strong (desorption) edge above pH 8 is coincident with an initial predicted appearance and increase of Np-carbonate complexes 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. Also consistent with these observations are the results of Brady et al. (1999) for U sorption on dolomite. The trends in U sorption with pH mimic the sorption behavior of noncarbonate minerals, sorption behavior that has been consistently modeled using a surface complexation approach (Brady et al., 1999; Pabalan et al., 1998). Careful observation of figure 6-3 reveals additional support for a surface exchange or complexation mechanism. Note that, for the sorption peak below pH 8.2, the small changes in pH over time also show appropriate increases or decreases in sorption magnitude consistent with a reversible sorption mechanism. These observations suggest that $^{237}Np$ sorption behavior on calcite may be successfully modeled using a surface complexation or $Ca^{2+}$ exchange approach that accounts for carbonate complexation.

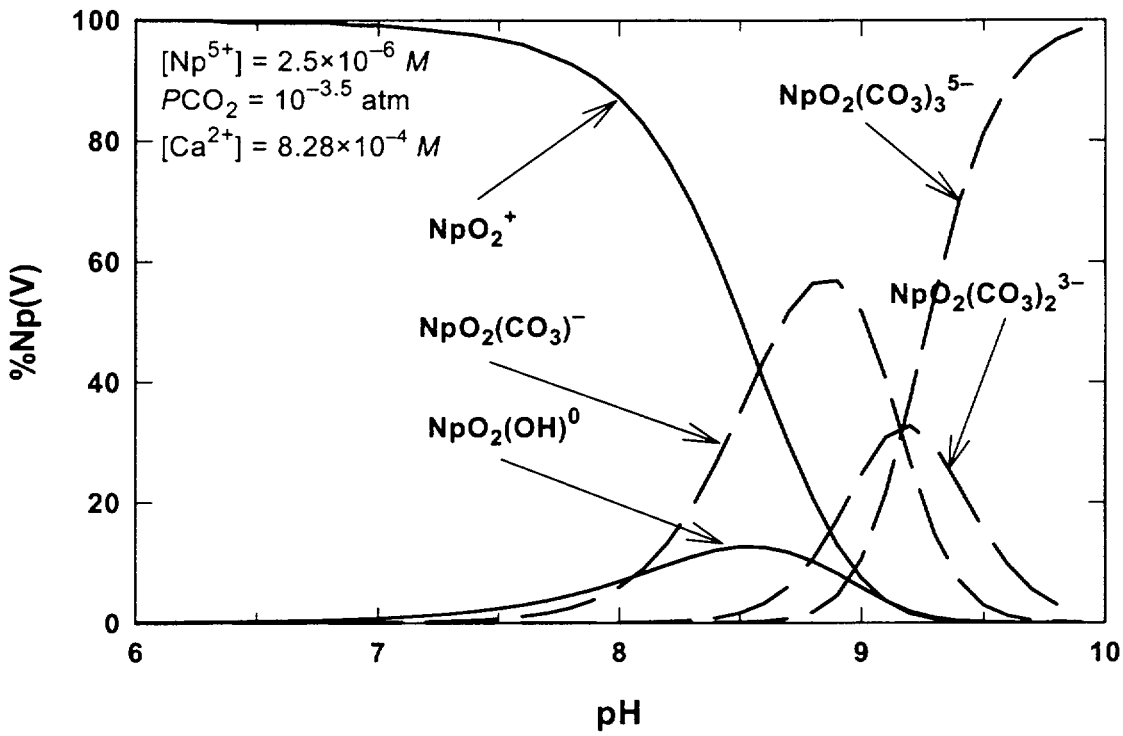


**Figure 7-1. Calculated speciation of Np(V) in 0.1 *M* $NaClO_4$ at equilibrium with atmospheric $PCO_2$. $Ca^{2+}$ concentration determined by equilibrium conditions with calcite at pH 8.37. Thermodynamic data used in the MINTEQA2 calculations are shown in table 7-1.**

**Table 7-1. Thermodynamic data used in MINTEQA2 speciation calculations shown in figure 7-1**

| Aqueous Speciation Reaction | Log *K* |
|---|---|
| $NpO_2^+ + H2O \rightleftharpoons NpO_2OH^0 + H^+$ | $-8.9^A$ |
| $NpO_2^+ + CO_3^{2-} \rightleftharpoons NpO_2CO_3^-$ | $4.6^A$ |
| $NpO_2^+ + 2CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_2^{3-}$ | $7.0^A$ |
| $NpO_2^+ + 3CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{5-}$ | $8.5^A$ |
| $NpO_2^+ + NO_3^- \rightleftharpoons NpO_2NO_3^0$ | $-0.5^B$ |

A: Lemire, R.J. *An Assessment of the Thermodynamic Behavior of Neptunium in Water and Model Groundwaters from 25 °C to 150 °C.* AECL–7817. Pinawa, Manitoba: Atomic Energy of Canada Limited. 1984.
B: Danesi, P.R., R. Chiarizia, G. Scibona, and G.J. D'Alesandro. Stability constants of nitrate and chloride complexes of Np(IV), Np(V), and Np(VI) ions. *Inorganic Nuclear of Chemistry* 33: 3,503–3,510. 1971.

Precipitation of $^{237}Np$ as an explanation of the observed uptake on calcite seems less likely. With the possible exception of the solutions near pH 7, which need further characterization because of high ionic strength, concentrations of $^{237}Np$ used in the experiments are below solubility limits for the conditions studied (Efurd et al., 1998). The low pH solutions show the least amount of removal of $^{237}Np$, however, so it is not expected that Np precipitation occurred even in those solutions. Uptake of $^{237}Np$ by coprecipitation has been proposed as a mechanism to explain high $K_D$s observed in other studies (Triay et al., 1996, 1997). A plot of representative results of $^{237}Np$ sorption on calcite from the data of Triay et al. (1996), in comparison with data from this study, is shown in figure 7-2. Recall that waters from Well J–13 are undersaturated with respect to calcite, but that when equilibrating with atmosphere (and $PCO_2$ of atmosphere), waters from UE25–p#1 precipitate calcite, which implies that the resulting UE25–p#1 composition is at or very near to saturation with respect to calcite. Inspection of figure 7-2 reveals that the results of Triay et al. (1996) are very similar to the results observed in this study with the exception of experiments conducted in UE25–p#1 water that were allowed to continue for several weeks. It might be expected that calcite surfaces in the UE25–p#1 solutions would undergo recrystallization through a process similar to that used to age the calcite substrate used in the experiments for this study. Because $^{237}Np$ is readily incorporated into calcite through coprecipitation (Nugent and Turner, 2000), it would be expected that $^{237}Np$ $K_D$s would increase over time in these solutions, and that is what is observed. Moreover, precipitation of calcite would be expected to produce a slight decrease in pH as the reaction progressed (Nugent and Turner, 2000); a small drop in pH with time is also observed in the Triay et al. (1996) data. For experiments conducted in J–13 water, $^{237}Np$ sorption did not increase significantly with time (Triay et al., 1996). As a rough comparison of the magnitude of $^{237}Np$ removal through sorption and precipitation, calculated $^{237}Np$ $K_D$s [as defined in Eq. (2-1)] for coprecipitation with calcite (with initial Np concentrations of $\sim 10^{-7}$ $M$, and precipitation rate of $3 \times 10^{-4}$ mol/m$^2$/hr) are on the order of $10^4$ mL/g (based on results of Nugent and Turner, 2000).

More difficult to explain is the difference in sorption behavior presented by the NpCA3 series experiments in which calcite was added after the solutions were spiked with $^{237}Np$. Brady et al. (1999) observed a similar pattern of $^{237}Np$ sorption on dolomite, that is, low sorption over the range of pH studied with slight increases at higher pH, but results were somewhat obscured by large uncertainties. Overall, the final chemistry of the NpCA3 series experiments was very similar to the experimental solutions of the NpCA1 and NpCA2 series, and no significant changes in pH or $Ca^{2+}$ concentration in solution were noted for equivalent starting solutions between experiments. One possibility is that the surface of the calcite when added did not have the proper hydration layer established to promote surface adsorption of $^{237}Np$. This lack of a proper layer would seem to have affected the kinetics of sorption, but not the overall sorption magnitude after a relatively long experimental period of 11 days. Another possibility is that the addition of $^{237}Np$ prior to addition of calcite caused the solutions to be further from equilibrium during the initial stages of sorption, thus limiting the maximum sorption observed. Additional characterization and experimentation are needed before the differences in sorption due to the timing of the addition of calcite can be explained; however, an implication of the differences is evident. One might suggest the experiments in which calcite was added prior to $^{237}Np$ and the experiments in which calcite was added after are analogous to conditions of transport in the SZ and UZ, respectively. Calcite along flow paths in the SZ will have equilibrated with water prior to arrival of $^{237}Np$ transported in the groundwater, and, given the preliminary results of this study, sorption would occur of a magnitude indicated by pH and Np-complexation in solution. In the UZ, the calcite would be exposed to the $^{237}Np$-carrying plume without prior exposure or equilibration with the groundwater. Using the results obtained in this study, one would predict a much lower magnitude of sorption for similar solution conditions. Differences in the sorption behavior of $^{237}Np$ as a result of prior equilibration of mineral surfaces with water have not been observed in experiments with silicate or aluminosilicate minerals (e.g., Bertetti et al., 1998; Triay et al., 1997), and, if the preliminary results of this study are confirmed, RT models may need to account for additional uncertainties. Other explanations for the differences in behavior between experiments might include competition between the solution speciation of $NpO_2^+$ and its sorption on the calcite surface, or the existence of two distinct sorption mechanisms, which are differently expressed in the two protocols used.

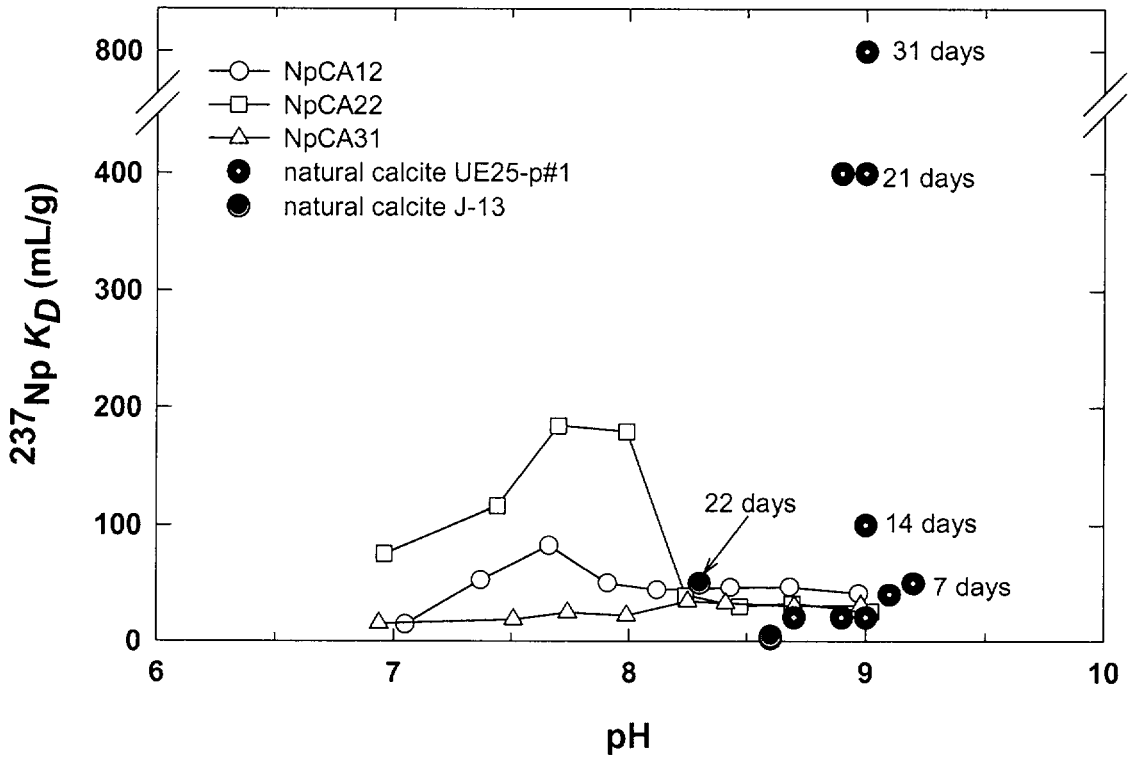


**Figure 7-2. Comparison of representative data from Triay et al. (1996), shown by the filled circles, to results of experiments from this study. Labels indicate length of time before sampling in some experiments. Results of Triay et al. (1996) experiments using synthetic calcite are not shown but are consistent with those for natural calcite.**

# 8 SUMMARY AND CONCLUSIONS

$^{237}$Np has been identified as a radionuclide of concern in PA models for YM, and the retardation of $^{237}$Np in the UZ and the SZ has been identified as a principal factor in the DOE site recommendation safety case for YM (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000a,b). However, uncertainties regarding transport parameters for $^{237}$Np, such as $K_D$, remain (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000c). Similarly, characterization of the mineralogy and transport characteristics of the saturated alluvium down-gradient of YM is not yet complete (U.S. Nuclear Regulatory Commission, 2000). The widespread occurrence of calcite, including an uncertain abundance in the alluvium, the variation in calcite saturation index of YM groundwaters, and a lack of data regarding $^{237}$Np sorption on calcite indicate a need to investigate and understand $^{237}$Np uptake on calcite. An understanding of the mechanisms and magnitude of calcite uptake of $^{237}$Np from solution will be of benefit to NRC staff in their review of the DOE licensing case, if submitted. Such information is needed soon, as the schedule for characterization and LA preparation preclude a lengthy review period.

$^{237}$Np uptake on calcite has been proposed to be governed by coprecipitation and exchange with $Ca^{2+}$ at the surface-water interface (Triay et al., 1996; Brady et al., 1999). Coprecipitation as a mechanism of uptake is significant, but may be limited in importance and extent by the location of the RMEI and calcite-saturated waters at YM (Nugent and Turner, 2000). The sorption of $^{237}$Np by calcite has not been extensively investigated. Because waters in the near vicinity of YM are generally undersaturated with respect to calcite and the RMEI and predicted flow path are located in that vicinity, $^{237}$Np-calcite experiments in solutions slightly undersaturated with respect to calcite are warranted. This report discusses recent and active experimental efforts to investigate $^{237}$Np sorption on calcite, and a preliminary review of recent results has been provided.

The results of the first $^{237}$Np-calcite experiments indicate that sorption of $^{237}$Np is significant below pH of ~8.2. The sorption behavior, which is dependent on solution pH, suggests that the solution speciation of Np plays a large role in the magnitude of Np sorption. Distinct differences in sorption were observed when calcite was added to solutions previously spiked with $^{237}$Np as compared to solutions in which calcite was allowed to equilibrate prior to adding $^{237}$Np. These differences may be important in characterizing sorption of $^{237}$Np on calcite in the UZ and SZ at YM. A net positive but constant sorption of $^{237}$Np was observed above pH of 8.2 in all experiments. This positive sorption may be associated with Np speciation or with a slow uptake of $^{237}$Np by coprecipitation as the calcite surface recrystallizes at near calcite-saturation conditions over time. There were some inconsistencies in the magnitude of sorption for experiments with different M/V ratios, although these differences may be due to inadequate mixing of calcite-solution suspension. The experiments suggest that sorption of $^{237}$Np on calcite may be significant even at lower pH values (e.g., pH 7–8) and in solutions that are undersaturated with respect to calcite. There is some evidence to indicate that the sorption reaction is reversible in this pH range.

A successful understanding of $^{237}$Np sorption on calcite will depend on a continuation of work to resolve experimental uncertainties and expand the conditions of the experiments. Solution chemistry should be thoroughly analyzed to aid in the calculation of speciation and saturation indices for calcite. Kinetics and reversibility need to be evaluated, which will assist in the selection of modeling approach. Additional experimental data must be collected to provide confidence in the modeling input data. The conditions of experiments should also be varied as planned. Conducting experiments further from saturation with respect to calcite may help in understanding if active dissolution of the calcite surface strongly influences sorption.

Additionally, experiments should be conducted at differing levels of $PCO_2$. This regimen is important because DOE has used $CO_2$ overpressuring to adjust pH in previous sorption experiments (although pH was not adjusted for sorption experiments involving calcite) (Triay et al., 1996, 1997) and because speciation in solution is sensitive to $PCO_2$. Van Cappellen et al. (1993) proposed a surface complexation model for the carbonate-water interface. Their model predicts differences in speciation and surface charge that are dependent on the method of pH control. Differences in speciation may impact sorption behavior and, as such, affect interpretation during the modeling effort. For instance, with $PCO_2$ adjustment of pH, the concentrations of $HCO_3^-$ and $CO_3^{2-}$ in solution in equilibrium with calcite at pH 7 are at least an order of magnitude greater than in a calcite-equilibrated solution that has been adjusted by means of acid or base addition (Van Cappellen et al., 1993). This increased concentration implies a shift in the observed desorption edge of $^{237}Np$ to lower pH and a possible overall reduction in magnitude of sorption due to $^{237}Np$-carbonate complexation. Confirmation of this kind of sorption behavior change due to $PCO_2$ influence would suggest that a mechanistic sorption model or, at least, a sorption model capable of accounting for solution chemistry be used to support the RT in abstraction PA modeling.

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