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Evaluating actinide sorption to graphite with regards to TRISO repository performance

Corey Christopher Keith
University of Nevada, Las Vegas

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EVALUATING ACTINIDE SORPTION TO GRAPHITE WITH REGARDS TO TRISO
REPOSITORY PERFORMANCE

By

Corey Christopher Keith

B.S. Physics

University of Texas at El Paso

2010

A thesis submitted in partial fulfillment of
the Requirements for the

Master of Science in Health Physics

Department of Health Physics and Diagnostic Sciences

School of Allied Health Sciences

Graduate College

University of Nevada, Las Vegas

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THE GRADUATE COLLEGE

We recommend the thesis prepared under our supervision by

Corey Keith

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**Evaluating Actinide Sorption to Graphite with Regards to Triso
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Master of Science in Health Physics
Department of Health Physics and Diagnostic Sciences

Gary Cerefice, Committee Chair

Steen Madsen, Committee Member

Ralf Sudowe, Committee Member

Vernon Hodge, Graduate College Representative

Thomas Piechota, Interim Vice President for Research and Graduate Studies
and Dean of the Graduate College

August 2012

ABSTRACT

Evaluating Actinide Sorption to Graphite with Regards to TRISO Repository Performance

By

Corey Christopher Keith

Dr. Gary Cerefice, Examination Committee Chair
Professor of Health Physics
University of Nevada, Las Vegas

Graphite has the potential for inclusion in nuclear waste for disposal in waste repository settings. Implementation of High Temperature Gas-cooled Reactors contributes to this potential through use of TRISO fuel, if direct disposal of the graphite matrix surrounding the fuel is employed. The inclusion of the large mass and volume in the TRISO fuel waste form differs significantly from used light water reactor fuel waste forms, requiring new performance models to describe the behavior in a repository setting. The purpose of this study is to evaluate the potential for the graphite to improve actinide, specifically uranium and neptunium, retardation from the waste form.

A review of the literature exposed no specific data on neptunium interactions with graphite, so experimental study was employed. Uranium and neptunium sorption behavior was evaluated across a range of conditions through batch experiments. Solid/liquid ratios and temperature experiments were performed to evaluate possible effects on uranium sorption. Temperature was found to have a significant impact on measured sorption. Neptunium metal concentrations, pH range, counterion concentration experiments were performed for neptunium. Neptunium sorption appears to follow a

linear isotherm, at the concentration range used. The partitioning to graphite was weakly influenced by pH, with a maximum K_d of 4.6 (ml/g). The ionic behavior showed that both the specific counterion, when switched from Cl^- to ClO_4^- , and concentration inhibits sorption,

The desorption kinetics were evaluated for neptunium using batch experiments, revealing close to negligible desorption once sorbed. Based on the results, even though low sorption occurs for neptunium, the negligible desorption allows graphite to significantly impact neptunium transport with respect to graphite mass. Surface complexation models were evaluated. Although a Triple Layer (TL) model was suggested for use, more data is needed (counterion influence) before implementation can be accomplished.

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CHAPTER 1

INTRODUCTION

1.1 Problem and Research Objectives

Nuclear power continues to see interest whether in the United States or the rest of the world. China alone plans 40 GWe by 2020 according to the medium and long term nuclear power development plan [NDRCC 2007]. In view of the expansion of nuclear power, new reactor designs have had more interest, such as High Temperature Gas-Cooled Reactors (HTGR). The main interest in HTGRs is their capability of reaching thermal efficiencies in between 40% to 50%; which, when comparing to the 30% - 36% thermal efficiency of current light water reactors (LWR) makes a strong case for implementation [Herranz et al, 2009]. Another benefit of HTGRs is the possibility of production of hydrogen with the high heat supply [Ueta 2011]. Implementation of HTGRs has been demonstrated by such reactors as the High Temperature Engineering Test Reactor of 30MW_{th} [Saito et al, 1994] in Japan and the HTR-10 [Xu et al, 2002] in China, which both utilize TRISO particle fuel.

HTRs have many positive aspects, but before commercial deployment can be adopted, there are some areas of research lacking that need to be addressed. Specifically for this thesis, the differences for HTR fuel, which is composed of Tri-Isotropic or TRISO particles, compared to standard spent nuclear fuel (SNF) are significant that research remains to be done to evaluate new HTR repository models. The parameters of the TRISO particle, specific for Figure 1.1, consists of a microsphere with a diameter of close to 1.5 mm consisting of a fuel kernel (containing the fissile material) surrounded by a low density carbon buffer designed to relieve stress caused by fission products,

followed by a layer of silicon carbide (SiC) surrounded by two layers of pyrocarbon (PyC). The fuel particles are then placed in a graphite compact which is then drilled into a larger graphite matrix [Peterson et al, 2011].

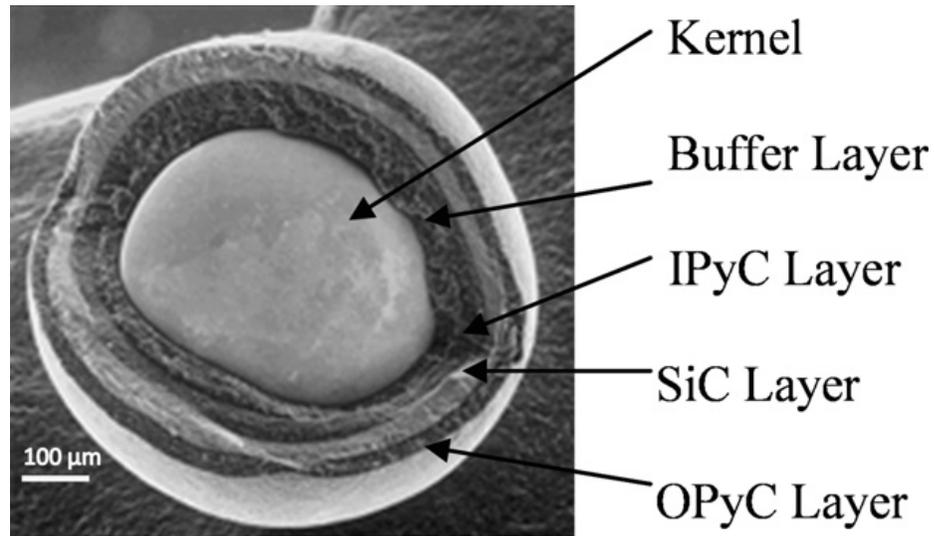


Figure 1.1: Cross-section of TRISO fuel coating layers [Peterson, 2010].

The TRISO particle failure model (figure 1.2) shows the different considerations that need to be made when comparing TRISO against typical PWR. The large differences, mainly the multiple carbon layers and the sizable graphite matrix, render current models for the release of radionuclides from SNF inappropriate to the calculation of radionuclide release from TRISO fuels. In order for new models to be reliable, studies need to be made on the TRISO fuel performance in a repository setting. Research on TRISO fuel failure models for transport to the near field, such as the study by Peterson and Dunzik-Gougar, seems to focus only on analyzing degradation rates, and does not consider the graphite matrix in repository designs [2011]. Some disposal plans, however, include the disposing the TRISO fuel while it is surrounded by graphite in either the prismatic or pebble form [Grambow et al., 2006]. If this were the case for disposal, the

large quantity of graphite needs to be evaluated to determine the impact it has on radionuclide transport for repository models.

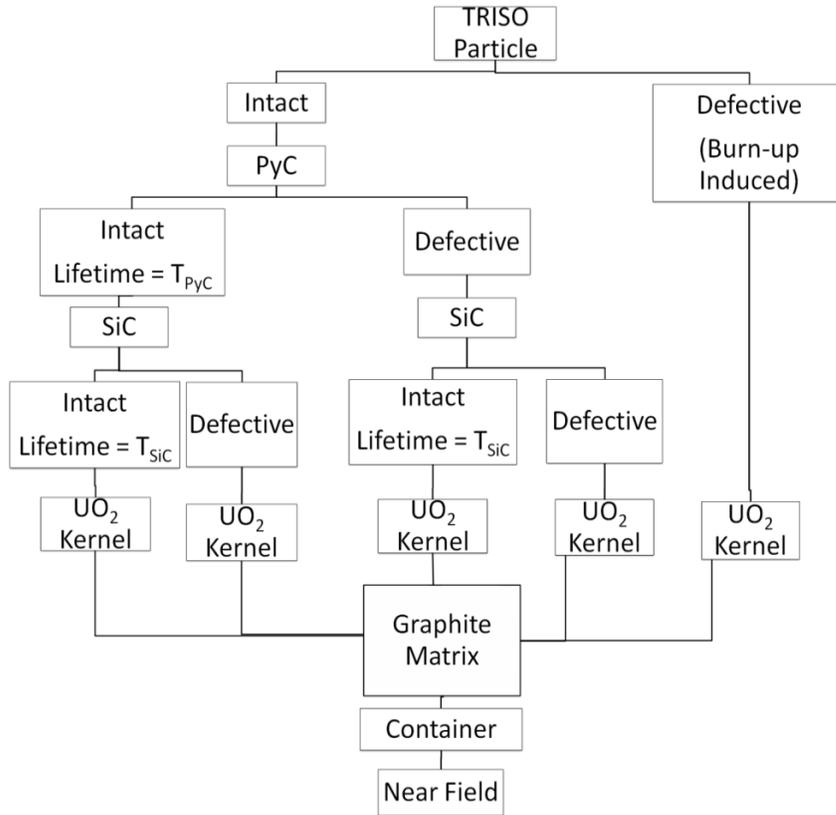


Figure 1.2: TRISO failure model [Schmidt 2010]

1.1.1 Research Goals

The approach of not including the surrounding graphite when modeling the transportation of radionuclides, or in using standard LWR models, can lead to inaccuracies. Literature searches revealed a lack of data on radionuclides of interest ability to sorb onto graphite. The proposed research therefore will focus on the potential retardation of radionuclides (specifically neptunium) due to sorption on the graphite matrix aspect of the TRISO failure model. The effects of the groundwater chemistry,

such as pH or carbonate concentration, on the sorption of the radionuclides will be explored. The end goal of the research is to use the data obtained to support modeling the performance of the spent fuel over time with graphite retardation considered.

1.2 Background

In order to improve existing models to incorporate the graphite matrix surrounding the TRISO fuels, it is important to understand the basics of sorption and the physical/chemical properties of the spent fuel. The physical and surface charge of the graphite needs to be better described to determine what surface reactions are contributing to sorption.

1.2.1 Sorption

Sorption is any process of removing a soluble compound from a solution phase and incorporates many retention mechanisms such as adsorption or precipitation [Essington 2003]. Adsorption is a surface process which results in a buildup of an adsorbate to the solution adsorbent junction. When focusing on trace heavy metal ions, such as neptunium, adsorption refers to surface complexes described by either outer-sphere or inner sphere. Outer-sphere and inner-sphere complexes are influenced by the waters of hydration that generally surround the ion of interest in an octahedral shape [Essington, 2003]. Even though these waters are usually strongly coordinated by the ion in solution, the ion in solution can have an influence that can extend out beyond the primary coordination sphere [Essington, 2003]. This attraction can result in an outer sphere complex, as it is controlled by electrostatic forces and, in the case of sorption, can result in an electrostatic attraction to the surface. An inner-sphere complex is without a water molecule between the adsorbed ion and surface ligand, which cause a more tightly

bound process than an outer-sphere complex. Inner-sphere complexes tend to be more stable, causing desorption kinetics to be very slow.

Outer-sphere adsorption for metal ions, such as neptunium, tends to rely on charge formation on the adsorbent surface [Essington 2003]. As will be discussed in section 1.2.2, surface charge can have some dependence on pH; as pH increases the surface charge becomes more negative and conversely as pH decreases the surface charge can become more positive. The influential pH range for outer-sphere adsorption tends to be broad and sorption is easily reversible compared to inner-sphere. Inner-sphere adsorption will tend to have a narrow influential pH range and is more irreversible than outer-sphere adsorption [Essington 2003].

Sorption due to surface complexation and electrostatic adsorption in solution can be quantitatively described by several models. These models include the Constant Capacitance (CC) Models, Diffuse Layer (DL) Models and Triple Layer (TL) Models. The previous three models will be described in more detail in section 1.2.6 and how it relates to the current work being done.

1.2.2 Graphite Sorption Properties

The reactivity of a surface sorbing medium primarily results from the combined influence of functional groups that can be charged or neutral and large specific surface area. Surfaces with charges are neutralized by counter ions or polar species that are near the surfaces seen as the diffuse ion swarm in figure 1.3. In order for outer-sphere sorption to occur, the local species needs to be displaced. In general, there are two types of charge that can develop on a surface: permanent charge that transpires when the mineral is developed which cannot be altered, and pH dependent [Essington 2003]. The

permanent charge is caused by isomorphous substitution and the associated charge density is represented by σ_o in figure 1.3. Permanent charge remains constant under the proposed experimental conditions and therefore only needs to be considered when finding the pH charge as compared to the total charge. Charge that is pH dependent results from protonation and deprotonation of the surface hydroxyl groups. The pH can therefore have an impact both on the surface charge and on the hydrolysis of the neptunium speciation (section 1.2.4).

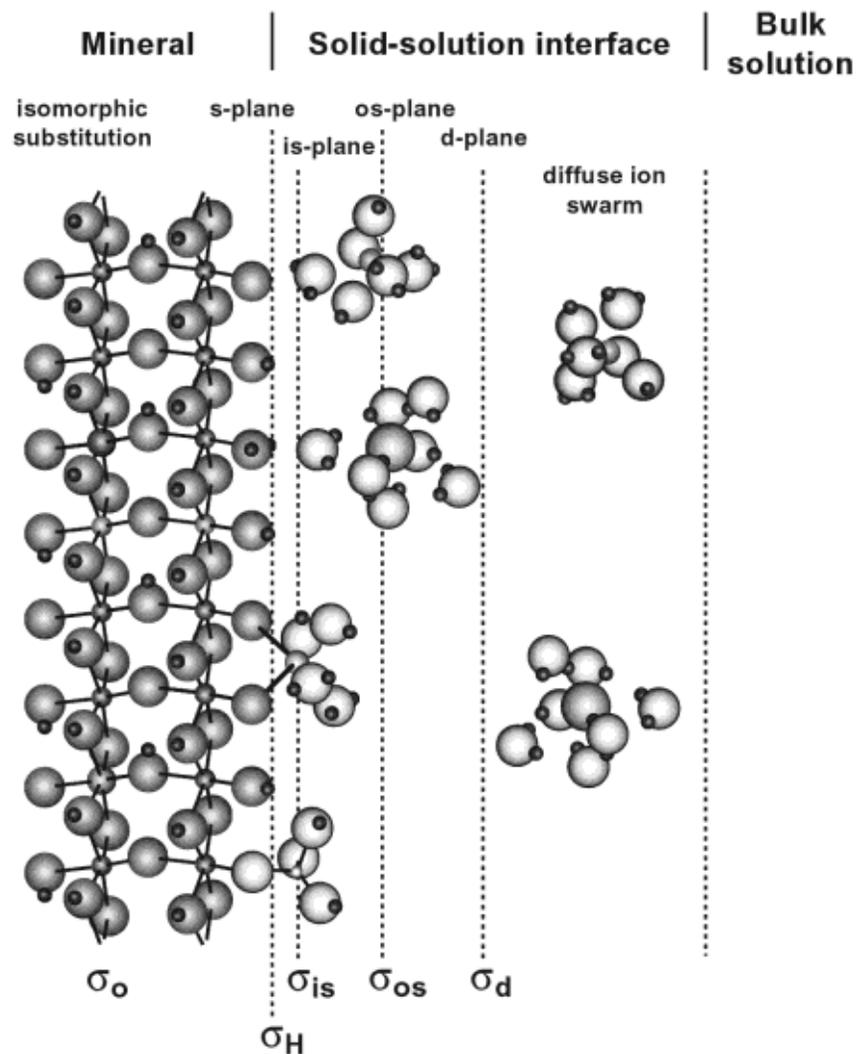


Figure 1.3: Schematic representation of the solid-solution interface illustrating the adsorption planes [Essington 2003].

The pH dependent charge, with an associated charge density is represented by σ_H , in figure 1.3, is charge that only results from the adsorption of the potential-determining ions, H^+ and OH^- , (occurring in the s-plane) and not any other specifically adsorbed ions or molecules. Therefore, the permanent structural charge and the pH dependent charge are intrinsically defined by the adsorbent characteristics (i.e. sorbing species will not affect the two charges). Adsorbed ions and molecules do contribute to the overall charge and are represented by charge densities σ_{is} and σ_{os} in figure 1.3. The difference between the two is that ions or molecules are specifically adsorbed in the is-plane (forms inner-sphere complexes), while ions and molecules in the os-plane are held by outer-sphere complexes.

A characterization of the pH dependent surface charge is needed to be able to successfully evaluate the impact the neptunium speciation has on sorption. The pH point of zero net proton charge (PZNPC), which is defined as the point where the net proton charge density disappears [Essington 2003], will be used to evaluate the sorption dependence on surface charge. Previous experiments evaluated the proton charge density for the experimental graphite and found a value such that $pH_{PZNPC} \approx 9.3$ [Schmidt 2010]. The value can be used to evaluate whether a sorption effect is due to the ion speciation or the sorbing surface charge.

Graphite Preparation	Measured PZC ^a	Graphite HNO ₃	Measured PZC ^b
0 day atm	9	0 M	10
1 day atm	8.9	0.2 M	7.8
7 day atm	9	0.4 M	6
20 day atm	8.6	1.0 M	5.5
30 day atm	8.4	2.0 M	3.5
3 hr @ 250°C	2.2		

Table 1.1: PZC of differently prepared graphite, where data is taken from [Menendez, 1995]^a and [Noh, 1990]^b.

Table 1.1 shows the variable values of PZC depending on graphite preparation and treatment. The 0-30 day atm refers to graphite exposed to atmosphere under environmental conditions for given time periods. The 3 hr @ 250°C term refers to graphite exposed to air at 250 °C for three hours. The data from Noh shows graphite treated by differing concentrations of HNO₃ to oxidize the graphite. The change in PZC seen in table 1.1 was accomplished through conditions that would not affect the experimental graphite. Regardless, it was reported that depending on the graphite, pretreatment can cause active sites which are oxidized as soon as exposed to oxygen at room temperature [Menendez, 1995].

1.2.3 Uranium Speciation and Sorption

Uranium is of great importance, in regards to repository performance, due to its representation of the majority of heavy metal in spent fuel. Studies have been done on uranium sorption on different materials because of its importance [Baik et al, 2003]. Prior to previous work by this research group [Schmidt, 2010] there is no information on uranium interactions with graphite under environmental conditions in the literature. The

work explored pH, CO₂ concentration, and ionic strength as factors that might affect uranium sorption, and continued work will explore other environmental factor dependence on uranium sorption onto graphite.

There are four oxidation states known for uranium ions in aqueous solutions (+III to +VI) which usually exist as U⁺³, U⁺⁴, UO₂⁺, and UO₂⁺² [Grindler, 1978]. Uranium (IV) tends to be stable in the absence of air, but is oxidized by oxygen. Uranium (V) is the most stable in the pH range of 2 to 4 as it tends to disproportionate to U(VI) and U(IV) [Grindler 1978]. Uranium (VI) tends to be the most stable oxidation state in oxidizing groundwater and is the focus of the previous work on uranium sorption to graphite [Schmidt, 2010]

The ability of uranium to form complexes needs to be considered when exploring sorption onto graphite. Complexation data is needed especially when considering the ionic species and acid media of the aqueous solutions as ideally no or very little complexation should occur. There seems to be some variation in the reported equilibrium constants for uranyl ion to chloride, but in general it is agreed that chloride forms a weak complexation [Grindler 1978]. The conditions used in the following experiments for uranium, using even a conservative estimate for the equilibrium constant would not result in a significant chloride complexation.

1.2.4 Neptunium Speciation and Sorption

Neptunium-237 can be generated by several pathways in UO₂ fuels such as by ²³⁸U (n,2n) ²³⁷U which then decays to ²³⁷Np. Although neptunium is initially present in small amounts in nuclear spent fuel (0.03%), the level will increase with time due to production from the decay of its parent (²⁴¹Am) and grandparent (²⁴¹Pu). Neptunium-237

is a radionuclide of some focus in nuclear waste repositories due to a number of factors. It has been estimated, based on radiotoxicity, that initially in the span of $10 - 10^4$ years ^{241}Am will be the most environmentally hazardous isotope in waste repositories storing spent nuclear fuel; and in the span of 10^4 to 10^5 years ^{239}Pu , ^{240}Pu , and ^{243}Am will be the primary isotopes [Nilsson et al, 1989]. After which, ^{237}Np is reported to be the primary environmental hazard in waste repositories [Tinnacher et al, 2010].

The neptunium concentration potentially released in groundwater will depend on multiple factors including fuel type (fuel cycle, waste type etc.) and repository design (location, barriers, etc.). Multiple experiments have been run to determine averaged concentrations of ^{237}Np released in groundwater under differing conditions which have led to a wide range $10^{-3} - 10^{-6}$ M ^{237}Np [Friese et al. 2003]. The neptunium concentration under most credible repository conditions is around the 10^{-5} M [Friese et al. 2003].

Neptunium has five reported oxidation states in aqueous solutions (+III to +VII) which usually exist as Np^{+3} , Np^{+4} , NpO_2^+ , NpO_2^{+2} , and NpO_2^{+3} ions [Dozol 1993]. The stability of the neptunium oxidation states can be strongly affected by such factors as the acidity of the solution, complex forming ligands, and the concentration of neptunium. Np^{3+} is quickly oxidized to Np^{4+} when exposed to air, while both can exist as hydrated ions. The pentavalent neptunium ion tends to be the most stable oxidation state in solution and behaves as strong lewis acids and forms dioxo species, NpO_2^+ similar to the hexavalent ion NpO_2^{2+} , in acidic solutions [Yoshida, 2006]. Compared to other pentavalent actinides, NpO_2^+ is stable due to it only hydrolyzing at $\text{pH} > 7$, disproportionating only at high acid concentrations, and forming no polynuclear complexes [Burney 1974]. The relatively high solubility under oxidizing conditions,

along with predicted low sorption, of the most stable pentavalent neptunium dioxo species, to minerals typically found in ground water [Wilson et al., 1994; Andrews et al., 1995], causes the sorption of neptunium on different surfaces and chemical environments an important focus for previous research, although relatively few studies have been conducted to investigate Np(V) sorption behavior.

The ability of neptunium to form complexes needs to be considered when exploring sorption as these potential complexes can encourage or inhibit the sorption. As differing ionic species (as it affects sorption for neptunium) will be explored in the following experiments, complexation needs to be considered. Np(IV) forms strong complexes with most anions compared to that of Np(V). Np(V), which exists primarily as the neptunyl ion, is a poor complexing agent because of its large size and low charge [Burney 1974].

Less information is available in the literature regarding the sorption behavior of neptunium than the other actinides, which could be caused by the fact that neptunium generally only is a focus in waste management in the fuel cycle. Regardless, there have been neptunium sorption studies completed in differing media such as montmorillonite and bentonite [Beall et al, 1981; Allard et al, 1984; Torstenfelt et al, 1988; Sakamoto et al, 1990; Triay et al, 1993; Ohe et al, 1993; Kozai, 1994].

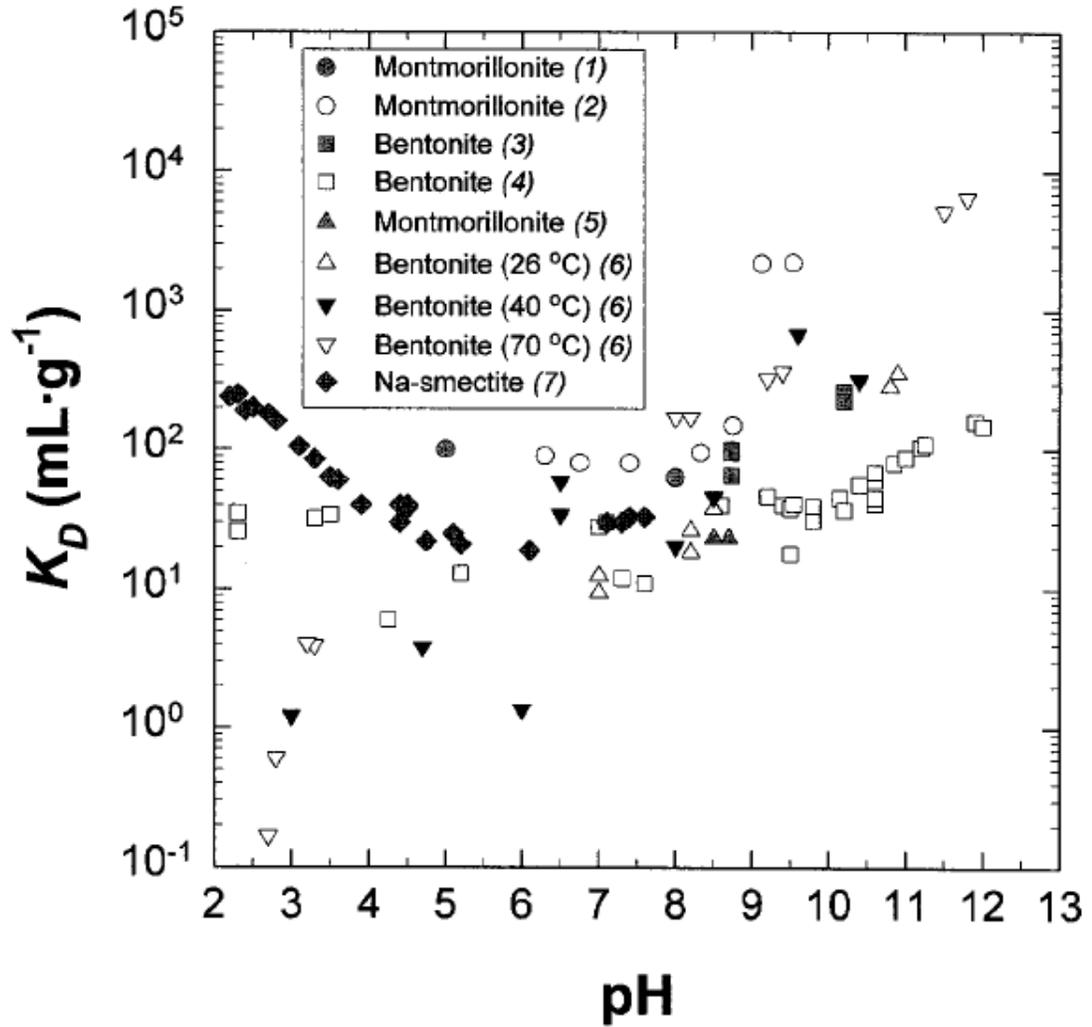


Figure 1.4: Comparison of Np(V) sorption data on montmorillonite and Bentonite from various studies, Data sources include: (1) Beall and Allard (1981); (2) Allard et al. (1984); (3) Torstenfelt et al. (1988); (4) Sakamoto et al. (1990); (5) Triay et al.(1993); (6) Ohe et al. (1993); (7) Kozai (1994).

Figure 1.4 shows a compilation of some of the previous sorption work for neptunium on clay as a function of pH, which is shown through K_d values and will be elaborated on in section 1.2.6. The variation in K_d values between studies is thought to be due to differences in experimental conditions (mass/graphite ratio, temperature, etc.) or material characterization. The wide range of K_d values is why it is important to look at other effects other than pH on sorption

Although there are studies of neptunium sorption on other media, such as montmorillonite as reported previously, no research could be found on neptunium sorption onto graphite. The complex processes of sorption as discussed in section 1.2.1 make any extrapolation using other surface studies impractical. As seen previously, the chemical properties are also varied for neptunium from that of uranium such that neptunium sorption cannot be extrapolated to that of uranium under similar conditions. Neptunium primarily exists in the +V oxidation state, whereas uranium exists in the +VI oxidation for the environmental conditions being explored in solution. The differences in solution speciation suggest that the sorption behavior of neptunium may be very different from uranium.

1.2.5 Environmental Effects on Sorption

Previous work has shown that neptunium sorption is strongly impacted by a number of parameters, including: neptunium concentration, carbonate concentration, and pH for neptunium sorption and pH [Tinnacher et al, 2011]. The speciation of uranium and neptunium are affected by the pH of the solution due to the change in concentrations of H^+ and OH^- ions and therefore includes positive, negative and neutral species. The differing species, due to pH, can therefore have dissimilar affinities for sorbing onto charged surface functional groups of the sorbent. Speciation curves were created for both neptunium and uranium under different conditions using the EQ3/6 geochemical modeling software with the database developed for the Yucca Mountain Project [Wolery et al, 1992]. Uranium can form many species with a wide range of charge, with the U (VI) oxidation state, including UO_2^{2+} and $UO_2(CO_3)_3^{4-}$ as shown in figure 1.5. As can be seen in figure 1.6, the speciation of neptunium is varied with pH and consists of both the

Np (V) and Np (VI) oxidation states. Data was collected for the pH points in the range (3 – 10) that represent the speciation seen in figure 1.6.

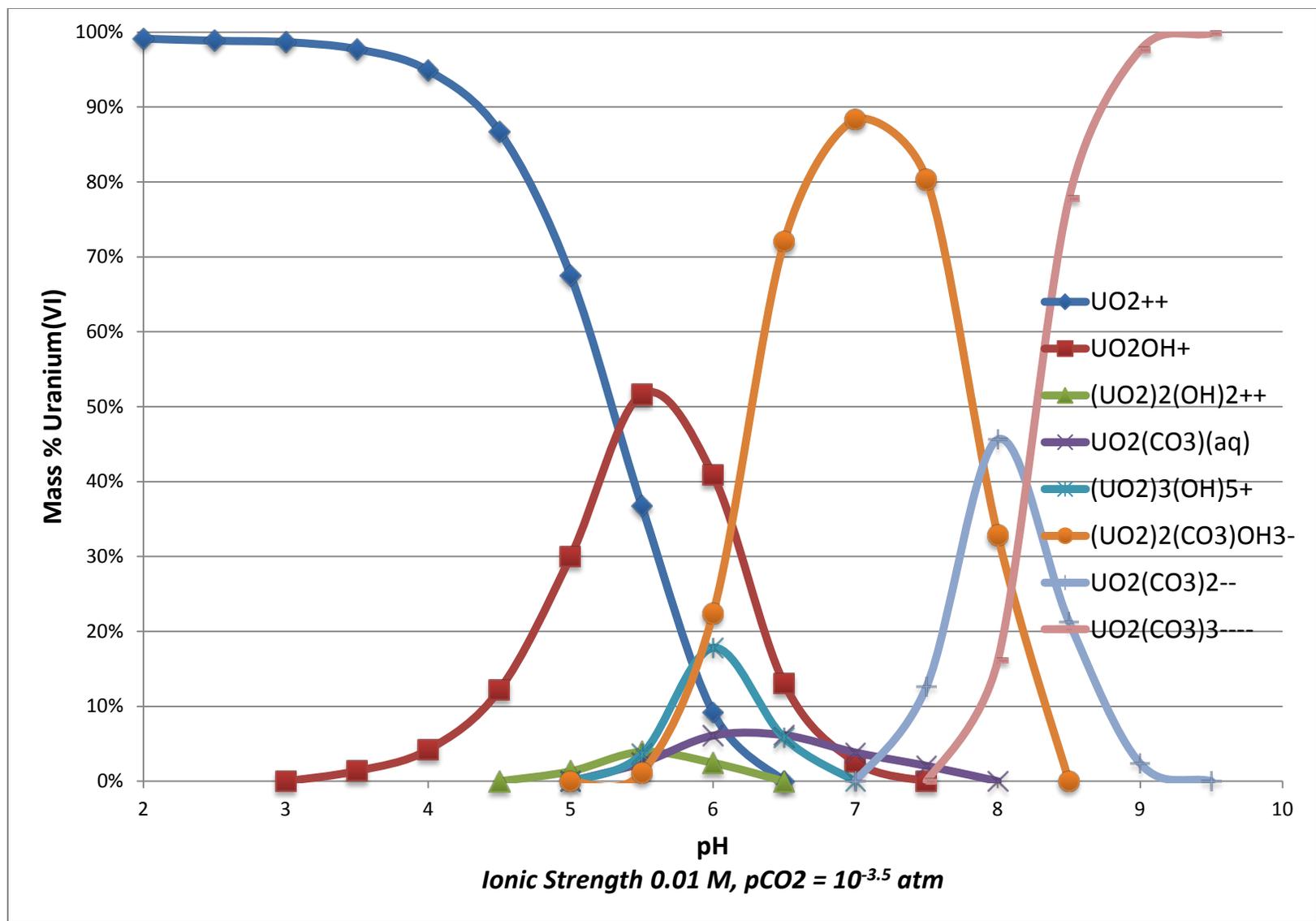


Figure 1.5: Uranium speciation under experimental batch sorption conditions $[\text{U}] = 500$ ppb

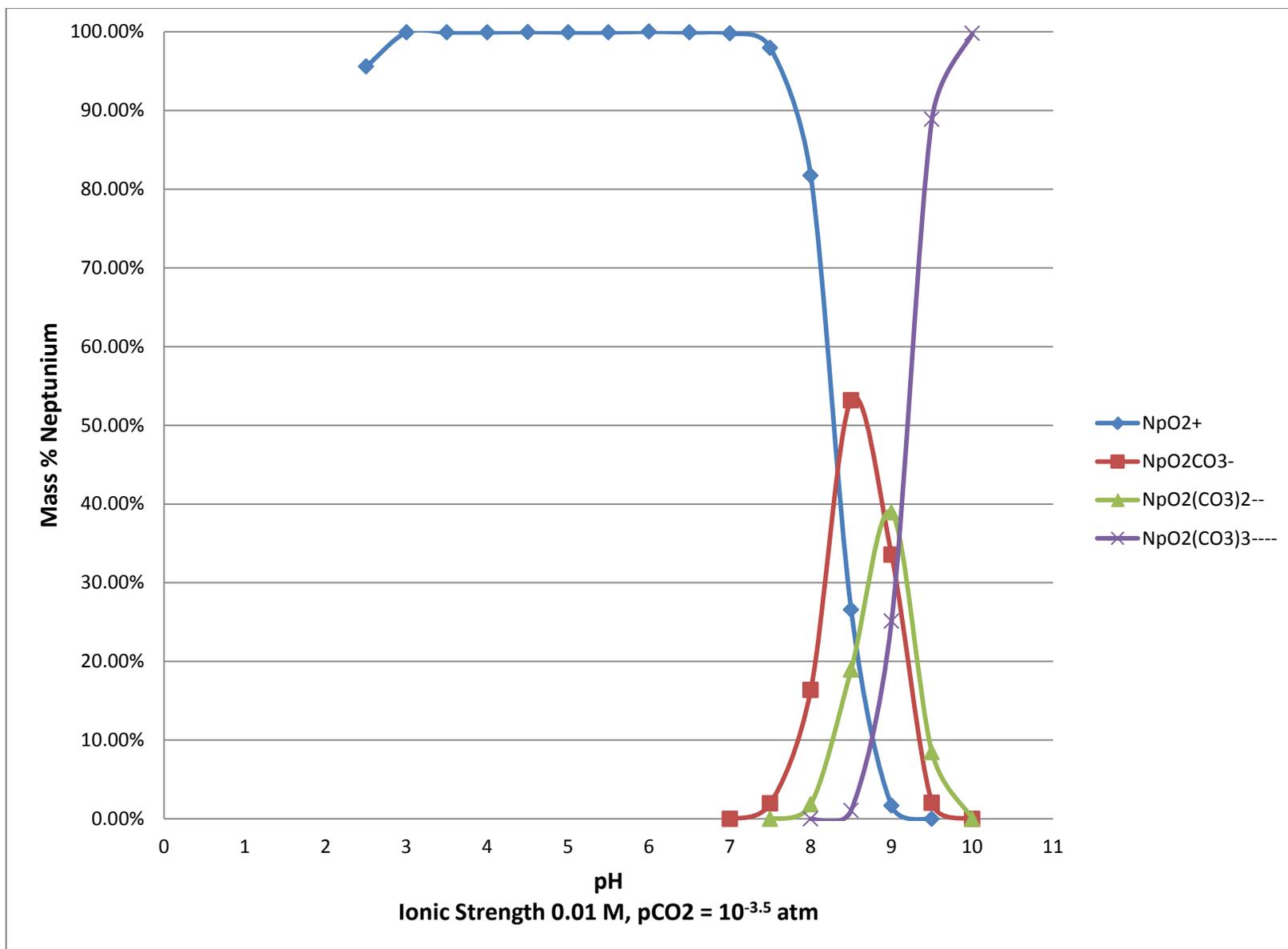


Figure 1.6: Neptunium speciation under experimental batch sorption conditions [Np] = 2.1E-06 M

The concentration of CO₂ in the environment also plays a role in the speciation chemistry as it affects the concentration of carbonate ions. If CO₂ is suppressed in the atmosphere, such as an inert argon atmosphere, the neptunium carbonate species become suppressed. The opposite is true for increasing the carbonate ion concentration; if the atmosphere is composed of pure CO₂, the carbonate species of neptunium will play a bigger role in lower pH values. An example of neptunium speciation with 100% Carbonate Atmosphere and a concentration: [Np] = 1.6E-06 M is shown in figure 1.7.

Temperature dependence is not considered a major factor in actinide sorption, as literature searches have found relatively little information. However, looking at general sorption studies [Chang, 2007], it has been found that temperature may have some influence depending on the dominating sorption process. Studies have shown that when a cation exchange process dominates the reaction (for these cases pH < 6), sorption is relatively independent of temperature; however, for surface complexation reactions the sorption can be dependent on temperature [Chang, 2007]. Uranium speciation for 50 °C under the experimental conditions being evaluated is shown in figure 1.8.

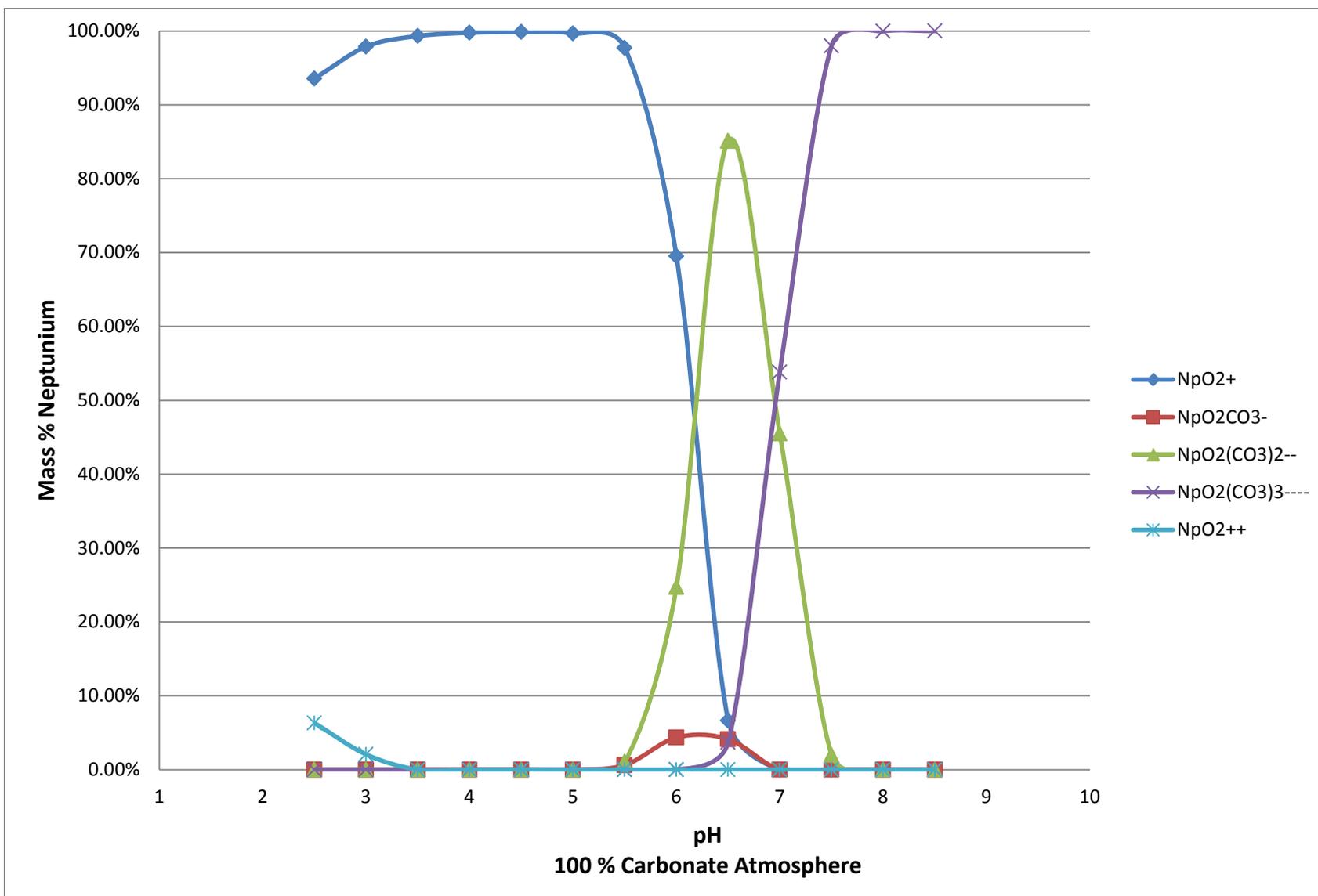


Figure 1.7: Neptunium speciation with 100% Carbonate Atmosphere $[Np] = 1.6E-06 M$

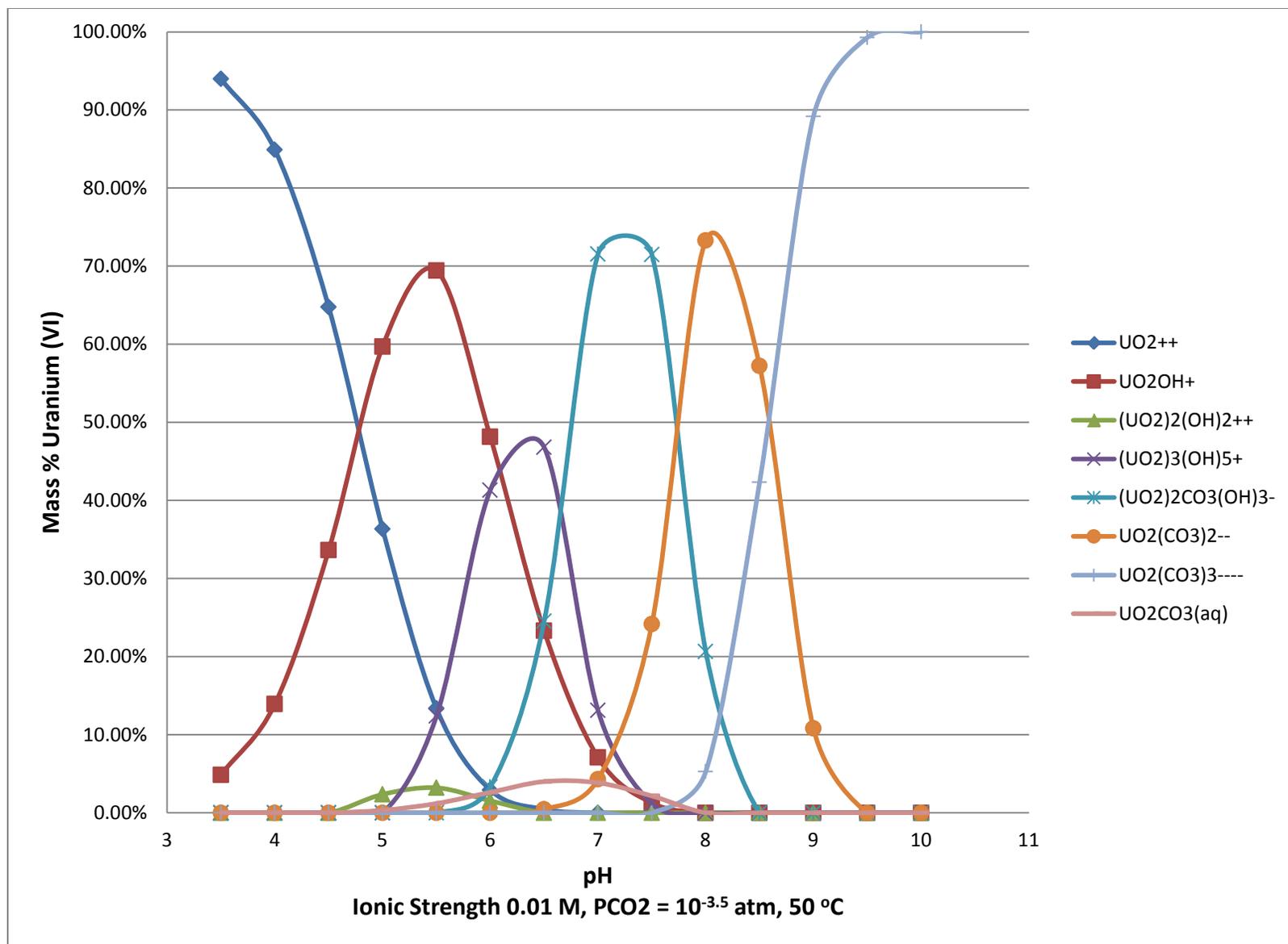


Figure 1.8: Uranium speciation under 50 degrees centigrade $[U] = 2E-06$ M

While other research has evaluated sorption using similar parameters such as the neptunium concentration or speciation [Frohlich et al, 2011; Nagasaki et al, 1999], the complexity of the many parameters and surface chemistry make extrapolation from previous work to actinide behavior with graphite unsuitable. Work on neptunium sorption onto UO_2 , for instance, has to include the fact that a change in pH can lead to a change in oxidation state and speciation of not only neptunium but the UO_2 surface. It was reported that the reduction to U(IV) resulted in a greater stabilization of Np(IV) than would be seen with neptunium by itself [Burney et al, 1974], which would need to be accounted for in the analysis of the sorption. Such considerations would not need to be made for graphite and shows the fundamental differences between varying adsorbents / environmental conditions that are evaluated.

1.2.6 Modeling

Quantitative Sorption

To model the mobility of the actinides of interest due to sorption processes, a device is needed to quantitatively measure the sorption. Batch experiments are a useful method to evaluate sorption that has been employed by numerous neptunium sorption studies [Frohlich et al, 2010; Nagasaki et al, 1999]. Batch studies, which will be used in this research, involves adding some known amount of an adsorbate in solution to an adsorbent and allowing contacting until equilibrium is achieved. The solid metal sorbed per gram graphite /equilibrium mass in solution distribution can then be described by some distribution coefficient described by equation 1:

$$K_d = q/C_{eq}$$

Equation 1.1

Where:

K_d = distribution coefficient (ml/g)

q = equilibrium mass of adsorbate sorbed to mass adsorbent (g/g)

C_{eq} = equilibrium mass of adsorbate in solution to volume of solution (ml/g)

The distribution coefficients are unique for each type of solution chemistry and are not transferable from one chemical environment to another. To be able to apply the information to any environment, distribution coefficients need to be determined as a function of the solution chemistry. An adsorption isotherm, which assesses the amount of adsorbate sorbed compared against the concentration of adsorbate, can still be evaluated however with a singular set of solution chemistry conditions. The two approaches (chemistry dependence and isotherm) will be looked at in this research to better model the actinide sorption.

The adsorption isotherm for a given adsorbate/adsorbent, as discussed previously, is just a plot of q with varying C_{eq} under the same conditions (i.e. temperature, pressure, solution chemistry). The shape of the curve of the isotherm is generally categorized as one of four types as shown in figure 1.9.

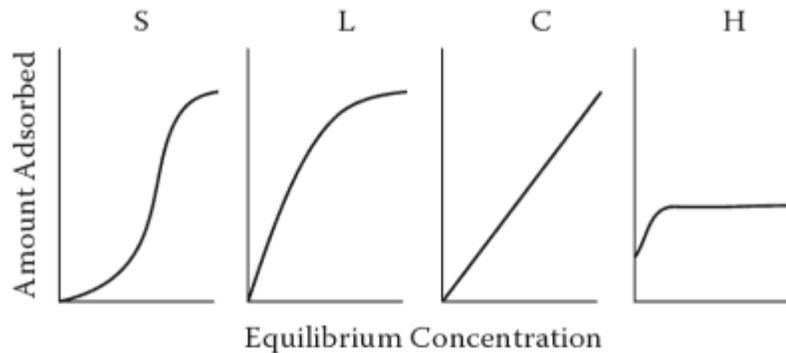


Figure 1.9: Four general types of isotherms

The two most common isotherms are the S and L curve; the L-curve is indicative of a sorbate with a higher affinity for the sorbing surface when surface coverage is incomplete whereas an S-curve would indicate a low affinity between sorbate and surface at low surface coverage [Essington 2003]. K_d can be used to correlate to a retardation factor:

$$R = 1 + \left(\frac{\rho}{\theta}\right) K_d \quad \text{Equation 1.2}$$

Where:

R = Retardation factor

ρ = dry bulk density of graphite in column

θ = porosity of graphite when fully saturated

K_d = distribution coefficient

The retardation factor is useful in that it is the ratio between the rate of groundwater movement and the rate of contaminant movement. Estimated retardation factors can then be computed for the experimental K_d values found under different conditions.

Surface Complexation Models

A surface complexation model (SCM) can be used to predict the distribution of the substance of interest between adsorbed and aqueous phases. The accuracy of the model is dependent on how well the model validates the real retention mechanisms and equilibrium constants [Essington 2003]. Three common SCMs are the constant capacitance (CC), triple layer (TL), and the diffuse layer (DL) models.

The CC model assumes adsorption occurs in a single surface plane, meaning that the surface functional groups are only allowed to form inner sphere (no outer sphere) surface complexes with the adsorbate. The surface charge is attributed to both the proton

and adsorbed species. The model does not require charge balance at the surface, meaning that the model ignores counter-ions balancing out the charge. The adsorbed species in the DL model is assumed to be specifically adsorbed to the zero plane similar to the CC model. The difference between the two models is that the DL model considers the counter-ions as a process for balancing the charge at the surface. The TL model, as the name suggests, includes a third layer of sorbing charge around the surface. The TL model then allows metal and ligand sorption to occur in both inner and outer sphere complexes.

More detailed explanation of the models can be found in Langmuir [1997] and Essington [2003]. The research into the mechanisms of the surface complexation used by the sorbed actinide species will allow a better choice in what model to implement. The experimental data will need to be compared with the sorption mechanics to lead to the best SCM chosen to have more reliable predictions.

1.2.7 TRISO Waste Management

Although no research, other than previous work done by Schmidt, has been done on actinide sorption onto graphite (the largest mass fraction of the HTGR fuel element), there exists some focus on the graphite fuel element in disposal considerations. Studies have looked into multiple disposal methods that vary from: disintegration of the graphite matrix by an electrochemical method [Tian, 2009] to mechanically separating most of the carbon from the fuel compacts [Del Cul, 2002]. The studies look into new methods for separating the graphite matrix from the SNF for the option to separately dispose of the resulting components, although direct disposal of fuel particles embedded in the graphite matrix has been demonstrated to be feasible [Abdelouas et al, 2006]. Most methods have

existing problems and costs associated with the separation, as well as the need to still dispose of the separated graphite, and in some cases in geological media [De Cul et al, 2002].

Any of the disposal options, whether direct disposal or separate disposal, will lead to significant changes in the proposed fuel cycle. For example the mechanical separation of graphite blocks from the fuel compacts requires specific fuel designs that allows for an easier separation method, yielding intricate adjustments between reactor design and cost [De Cul, 2002]. The costs and potential benefits associated with each option need to be analyzed and weighed against each other before deciding on a disposal plan for TRISO fuel. However, all the analysis that was found on the graphite matrix disposal has ignored any potential benefits that direct disposal of the graphite element with the SNF intact would have, other than ease of disposal. The impact of directly disposing of the graphite matrix with the TRISO kernels on reactive transport of SNF needs to be evaluated not only for a more accurate analysis between disposal options; but if direct disposal is chosen, repository models will need to be updated to more reliably assess the repository performance.

It is a primary goal of the current work to develop a better understanding of the mechanisms that influence sorption (in this case for uranium and neptunium) and transport through a graphite matrix under a variety of environmental conditions. Through this understanding, models can eventually be chosen that accurately reflect the potential role the graphite fuel element could play in retardation of SNF to the near field in a repository environment.

CHAPTER 2

MATERIALS AND METHODS

2.1 Approach

The primary experimental methodology used to investigate the interaction of uranium and neptunium with graphite was batch contact experiments, where the radionuclide in a simulated environmental matrix is allowed to interact with a fixed mass of graphite. Batch experiments were performed to examine the impact of a number of environmental factors, including pH, ionic strength, metal concentration, and temperature, on the sorption of neptunium to graphite. Expanding on previous work done with uranium, batch experiments were also used to examine the effect of temperature on uranium sorption as well. To examine the reaction kinetics and the desorption/release behavior, the general batch experiments were modified slightly. For the reaction kinetics experiments, samples were allowed to contact the graphite for differing time intervals. To examine the desorption behavior, graphite was contacted with neptunium and allowed to reach equilibrium. This was then followed by a multi-step batch desorption technique that will be described in more detail in section 2.4.2. The graphite characterization was previously analyzed more than a year previously. To verify that the data is still representative of the graphite used, additional graphite characterization was done to match up with the previous data.

2.2 Materials

2.2.1 Water

All experiments that were done used deionized water with a resistivity of 18 M Ω -cm, which was allowed to come to equilibrium with the atmosphere by static equilibrium

for at least 2 hours in an unsealed container. For most experiments, the ionic strength was adjusted to 0.01 M using sodium chloride (Spectrum Lot #: RF1546). The ionic strength was selected to minimize any effect that ionic strength had on speciation / sorption, and was large enough to make any differences in the variable amounts of HCl and NaOH in pH adjustment negligible. The ionic strength used (0.01 M NaCl) was described by the literature (Dozol, 1993) to represent typical groundwater chemistry.

2.2.2 Graphite

Graphite was obtained from Alfa Aesar Lot #A12U026 with a mesh size -20+100 (0.853 mm > diameter > 0.152 mm). Although graphite with a smaller particle ground flake diameter was available from Alfa Aesar, previous work by Schmidt on graphite (2010) has indicated the difficulty of use in aqueous experiments, based mainly on the severe hydrophobicity and difficulty in separation. The surface of the experimental graphite was characterized by Schmidt using BET surface analysis, measuring an average surface area of $0.5544 \pm 0.0274 \text{ m}^2/\text{g}$ [Schmidt, 2010]. The proton exchange capacity of the experimental graphite was found to be $0.25 \pm 0.15 \text{ millieq} / 100 \text{ g}$ of graphite, yielding a specific exchange of $451 \pm 91 \text{ } \mu\text{moles H}^+ / \text{m}^2$ of graphite surface [Schmidt, 2010]. The PZC of the experimental graphite was found to be 9.3.

2.2.3 Uranium

Uranium in solution was established by the addition of ^{233}U solution, which was previously prepared from a UO_2Cl_2 solid. The concentration of ^{233}U used for all experiments, unless indicated, was 150 Bq / ml (2E-6 M uranium). Activity concentration of ^{233}U was verified by liquid scintillation counting (LSC) comparison to a known NIST traceable standard from Eckert & Ziegler.

2.2.4 Neptunium

Neptunium in solution was established by the addition of ^{237}Np solution prepared from a ^{237}Np standard (Isotope Products Laboratories) with a density of 1.1296 g/mL (at 20 °C) and concentration of 0.1780 uCi / g plus or minus 3.1% (at the 99% confidence interval). The diluted concentration used for all experiments, except when exploring concentration dependence on sorption, was 10 Bq / ml. The concentration was chosen as a result of both neptunium availability and activity limit considerations and will be discussed more in section 3.3.3. The resulting concentration of 0.44 ug/ml ^{237}Np is below the solubility of any solid phase of the speciation observed [Neck, V. 1994].

2.2.5 Reagents

Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used for pH adjustment for all experiments except when differing ionic species was explored, (discussed in section 3.3.2). Solutions of 0.01 M, 0.1 M and 1 M of each were prepared and used to adjust solution pH.

Sodium perchlorate (NaClO_4) was used to create 0.01 M perchlorate solutions to evaluate the impact, if any, differing ionic species had on sorption. As a consequence, pH adjustments were accomplished using sodium hydroxide (NaOH) and perchloric acid (HClO_4).

Sodium tetraborate decahydrate (Borax) was used as a buffer for experiments with pH between 8 and 10 as the dissociation of dissolved bicarbonate resulted in changes in pH over the experimental equilibration time. The buffer was chosen as it's pKa is in the region needed (9.4) and has reported low complexing with both uranium

and neptunium. Possible influences on sorption by the buffer will be discussed in section 3.3.1.

2.3 Batch Sorption Experiments

The equilibrium sorption behavior of uranium and neptunium was examined through batch sorption experiments. Samples were prepared by contacting a fixed volume of solution with a known mass of graphite. These samples mixed continuously and allowed to equilibrate for an average of 5 days (time based on initial scoping kinetics experiments, described in 2.4). This methodology was used to examine the impact of solution pH, ionic strength, and temperature on the sorption behavior, and was modified to allow the investigation of the sorption kinetics (2.4.1) and desorption behavior (2.4.2). Each data point represents 10 samples, 7 samples fixed volume of solution contacting a known mass of graphite and three with just solution. The three samples with solution were used to evaluate sorption to container wall. Three 1 ml aliquots were taken of the solution to establish the initial concentration. The percent change in concentration was then established, accounting for sorption to the wall. The mass sorbed to graphite could then be found and by using equation 1.2, the K_d was also calculated. Error was propagated through use of the standard deviation measured between the samples.

2.3.1 Adsorption Isotherms

A large variation in the concentration of neptunium in solution was more difficult to achieve as compared with uranium without exceeding activity limits. Also a limiting factor for concentration was the amount of ^{237}Np available for use and resulted in only one data point evaluated at the largest concentration. The concentrations used were in the range of $3\text{E-}7\text{ M}$ to $3\text{E-}6\text{ M}$ neptunium initially in solution in both pH 4 and 10. Also one

additional point was evaluated with a neptunium concentration of around $1.0\text{E-}5$ M at pH 10. The graphite mass that was used was kept the same as the previous experiments as well as all other conditions.

2.3.2 pH Measurements and Controls

Sample solutions, pH-adjusted, containing neptunium were added to VWR polypropylene (PP) conical centrifuge tubes containing graphite in an approximately 10:1 solution/solid mass ratio. Fluorinated ethylene propylene (FEP) Oak Ridge centrifuge tubes were planned to be used for batch experiments with pH between 6 and 8 since sorption onto PP containers in that region for uranium has been found to be significant. Initial experiments found sorption to the PP container to be negligible for neptunium and therefore FEP tubes were not used since they require significant cleaning and decontamination before reuse. For each data point, ten replicate samples were used; seven with graphite and three without to correct for neptunium sorption onto the container. Initial kinetics experiments showed no significant increases in neptunium sorption to graphite after 1 day; therefore, samples were allowed to equilibrate on a hematology mixer for longer than four days (99.99 percentile).

2.3.3 Ionic Species Experiments

The effects of changing ionic species and concentration in neptunium and uranium solutions before contact of graphite occurred and the impact on the kinetics of equilibrium were evaluated. Experiments were done with two ionic species, NaCl and NaClO₄, and three ionic concentrations equal to 0.01 M, 0.05 M, and 0.1 M. The ionic strengths were chosen to limit the non-ideal effects in solutions which would make analysis of pH impossible using a standard non-equilibrated glass probe and pH meter.

The changes in ionic concentration had no additional steps needed from that of the previous pH study except for increasing the dissolved mass of NaCl or NaClO₄.

However, when changing the ionic species in solution from NaCl to NaClO₄ we needed to also change the acid used from HCl to HClO₄. The concentrations of both acids were kept the same. The change in acid also had an impact on disposal so attempts were made to limit the waste generated.

2.3.4 Solid to liquid

During the initial scoping experiments, it was observed that in some samples the graphite was not uniformly wetted by the solution (sticking to the containers or forming dry lumps that did not break down). The result is that some of the graphite surface area, and consequently the sorption sites, will not have equal exposure to the uranium ions. Solid to liquid studies were therefore performed to understand the dependence of the mass of graphite to the volume of solution. Solid to liquid studies were evaluated through uranium sorption to graphite as the data was missing from previous work. All conditions will be kept the same as stated above, except the graphite masses used will be: 1.6 g, 1.2 g, 0.8 g, 0.4 g, 0.08 g, 0.04g.

2.3.5 Temperature impact on sorption

The effects of changing the temperature during equilibration are planned to be examined by increasing the temperature of the samples during contacting with the graphite. As uranium sorption had a greater variance and temperature impact was not evaluated in previous work, it was used to assess temperature influence. Several pH points were chosen to represent the acid/alkaline regions and, for each pH point, a dual set of samples (one with elevated temperature and one at room temperature) were run

with identical mixing procedures and Np concentration and ionic strength (.01 M NaCl) to evaluate temperature dependence. The elevated temperature samples were placed in the oven and heated to 55 centigrade.

2.4 Neptunium Kinetic Studies

2.4.1 Batch Kinetic Study

A batch kinetic study was done to determine the appropriate contacting time for neptunium in solution to graphite and were evaluated at 1, 5, and 30 day contacting times. Another kinetic study was done with shorter time intervals to determine the linearity behavior of neptunium sorption to graphite at times from 1 minute to 36 hr.

2.4.2 Batch Desorption Studies

Desorption studies are planned to be performed to evaluate the release rate from neptunium sorbed graphite. The method of evaluating the desorption reactions are by exchanging a known amount of the neptunium dissolved contacting solution with the same volume of neptunium free solution of the same ionic strength and pH. The new sample would be allowed to re-equilibrate for a longer than a 4 day period and then the new solution activity would be measured by liquid scintillation counting (LSC) to determine desorbed neptunium mass. The process of exchanging the contacting solution with a fresh solution could be continued until the neptunium activity in solution could not be measured.

2.5 Analytical Methods

2.5.1 Liquid Scintillation Counting (LSC)

All sorption experiments will be analyzed by use of liquid scintillation counting. For this work, LSC counting was used for analyzing uranium and neptunium

concentrations in all liquid samples. LSC was selected due to the ease of sample preparation and high efficiency for alpha detection. The radionuclides in the samples were known, so it was not necessary to identify the radionuclides in the system and the additional energy resolution of alpha spectroscopy was not necessary. LSC measurements of sample solutions consist of a ratio of 1:10 solution to Ultima GOLD biodegradable organic scintillant from PerkinElmer. The protocol settings for uranium samples had standard settings (30 minute count time to obtain a 2% sigma), with a one minute settling time between vials.

2.5.2 Alpha/Beta discrimination by LSC

Neptunium samples have another obstacle to overcome. The decay chain for ^{237}Np involves decaying to ^{233}Pa via alpha decay, followed by the beta (minus) decay of ^{233}Pa , with a half-life of 26.967 days. To measure the ^{237}Np activity in the samples without any interference from the in-growth of the daughter, it is necessary to either design an experiment on a time scale where the in-growth is manageable, or to use an analytical technique that can resolve the ^{237}Np signal from the ^{233}Pa signal.

The LSC that is being used for analysis has pulse shape discrimination available, which allows us to discriminate between alpha and beta radiation and consequently ^{237}Np and ^{233}Pa . The protocol was then set to have alpha beta separation in our LSC samples. To set the pulse shape discriminator (PSD), pure alpha and beta LSC standards are used to measure the misclassification of alpha particles counted as betas and vice versa. Once the PSD value is determined, that value is used for any LSC measurements of our neptunium samples. A NIST traceable standard of ^{237}Np with known activity is used to verify the alpha beta discrimination.

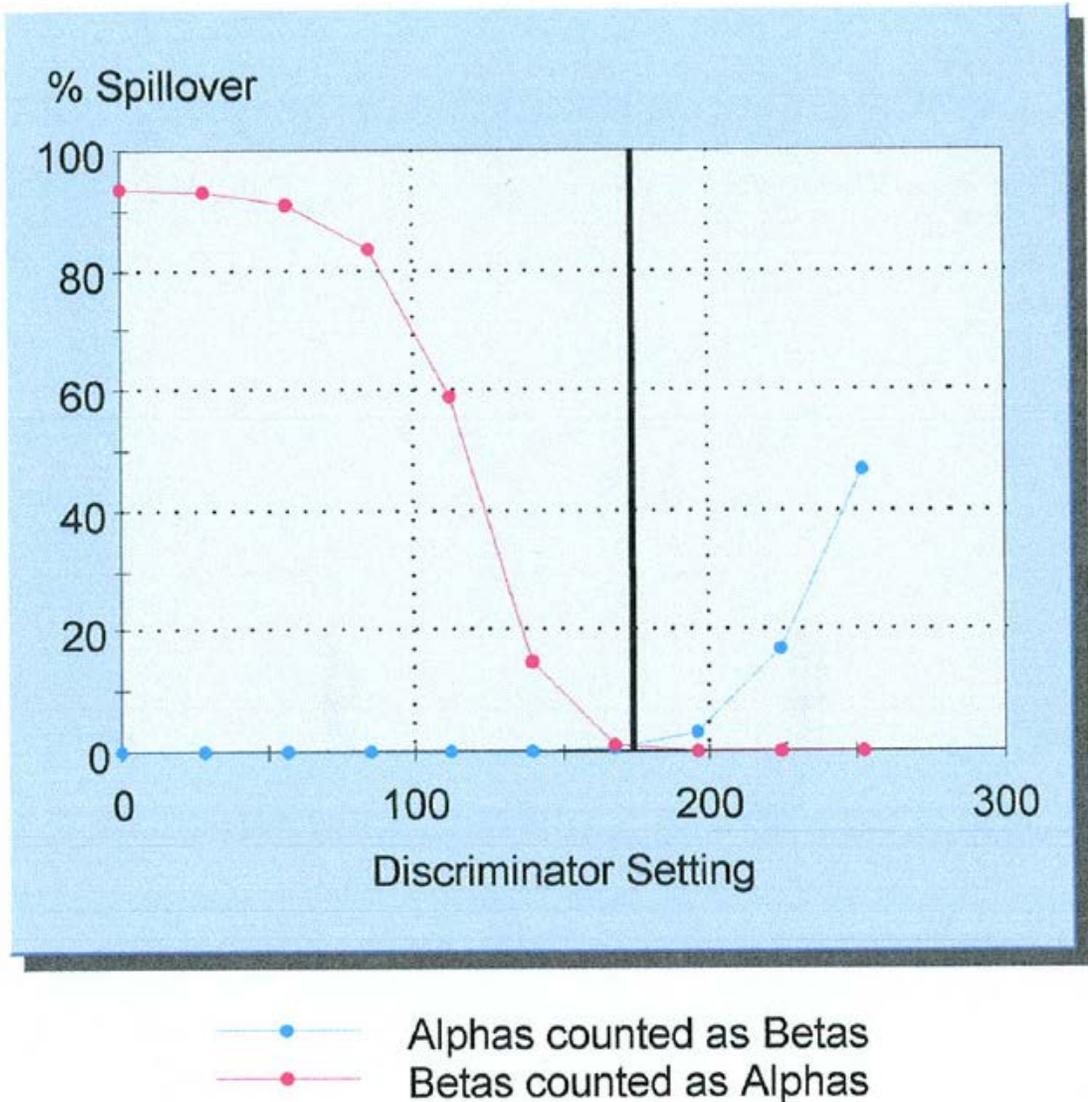


Figure 2.1: Alpha/Beta standard curve generated using standard set for LSC 3100.

The alpha/beta standard curve was generated to determine the ideal discriminator setting to run the LSC analysis with and is shown in figure 2.1. For the Tricarb 3100, it was determined that an ideal discriminator setting was 174, which had a 0.32 % alpha spillover and a 0.28 % beta spillover for the pure alpha and beta emitters respectively.

2.5.3 Graphite Characterization

The graphite used for all experiments had been analyzed previously (Schmidt 2010) and reported in section 1.3. The literature suggests that graphite oxide and other compounds formed by the functionalization of graphite are strongly sorbing species that could potentially dominate the effects of graphite sorption. Menendez, et. al. (1995) reported that graphite from the same batch exposed to the atmosphere at room temperature for varying amounts of time had differing degrees of oxidation through analysis of the PZC and IEP [Menendez, 1995]. The graphite used in that study, however, had a much higher surface area than the graphite used in our experiments, therefore it is thought that the atmosphere will not have as significant an impact but will still be evaluated.

The time spent between the initial analysis and the present experiments (~ 1 year) was sufficient to warrant additional characterization on the graphite to make sure no significant changes occurred. The graphite characteristics were re-evaluated to detect any change in surface charge distribution.

The point of zero charge (PZC) is the pH where the net particle charge density equals zero (1.2.2). The PZC of the experimental graphite was determined by performing a titration in a mixed DI solution containing graphite. The same titration system from Metrohm USA was used as the previous analysis done by Schmidt [2010] which consisted of a Titrino 799, a 685 Dosimat and an 801 Magnetic stirrer. The titration system was used to dose 50 μ l increments of 0.1 M NaOH and HCl into a graphite containing solution while measuring the change in pH. The measured PZC was evaluated by comparing the theoretical change in pH due to an addition of acid/base with that of the

real change in the presence of differing amounts of electrolyte concentrations. In the absence of metals and ligands forming inner-sphere complexes (just graphite in solution), we were able to determine the PZC using the zero salt effect. The zero salt effect is based on the fact that the pH surface charge densities observed in titrations are a function of ionic strength and pH. However the pH where the surface charge is zero is independent of ionic strength. Using this, two titrations of differing ionic strengths can be done, and the point each set shares should be where surface charge is zero. Titrations were done using 0.01 M NaOH and HCL solutions to both 0.01 M and 0.1 M NaCl graphite containing solutions. The initial volume of the solution was 30 ml and the mass of the graphite was 3 g, keeping the 10:1 ratio used in all batch experiments.

CHAPTER 3

RESULTS

3.1 Graphite Characterization

As described in section 1.3, adsorbent surfaces can convey electronic charge and metal and ligand complexation capabilities that influence the interfacial region [Essington 2003], or the region where the solid-solution interface occurs. Therefore, the structural and electrochemical characteristics of the bulk adsorbent (graphite) in solution can greatly influence the interfacial region and, by extension, the capacity to retain sorbing species (neptunium). In order to understand the mechanics of neptunium sorption in solution to graphite, a good understanding of the characteristics of the specific graphite used in all experiments is needed. Work done by Schmidt has already gone into characterizing the specific graphite (Alfa Aesar Lot #A12U026) used such as physical and electronic properties; although the graphite was tested more than two years before the current experiments. The literature reveals that graphite surface charge properties are greatly varied [Menendez, 1995] and it was not clear if age and atmosphere exposure contributed to the existing differences. As a consequence, (although no changes were expected) the electronic properties of the graphite were re-evaluated and compared with work done by other authors.

3.1.2 Point of Zero Charge

The results of variation in net proton charge as a function of pH for the two potentiometric acid-base titrations, with differing ionic concentrations used, are shown in figure 3.1.

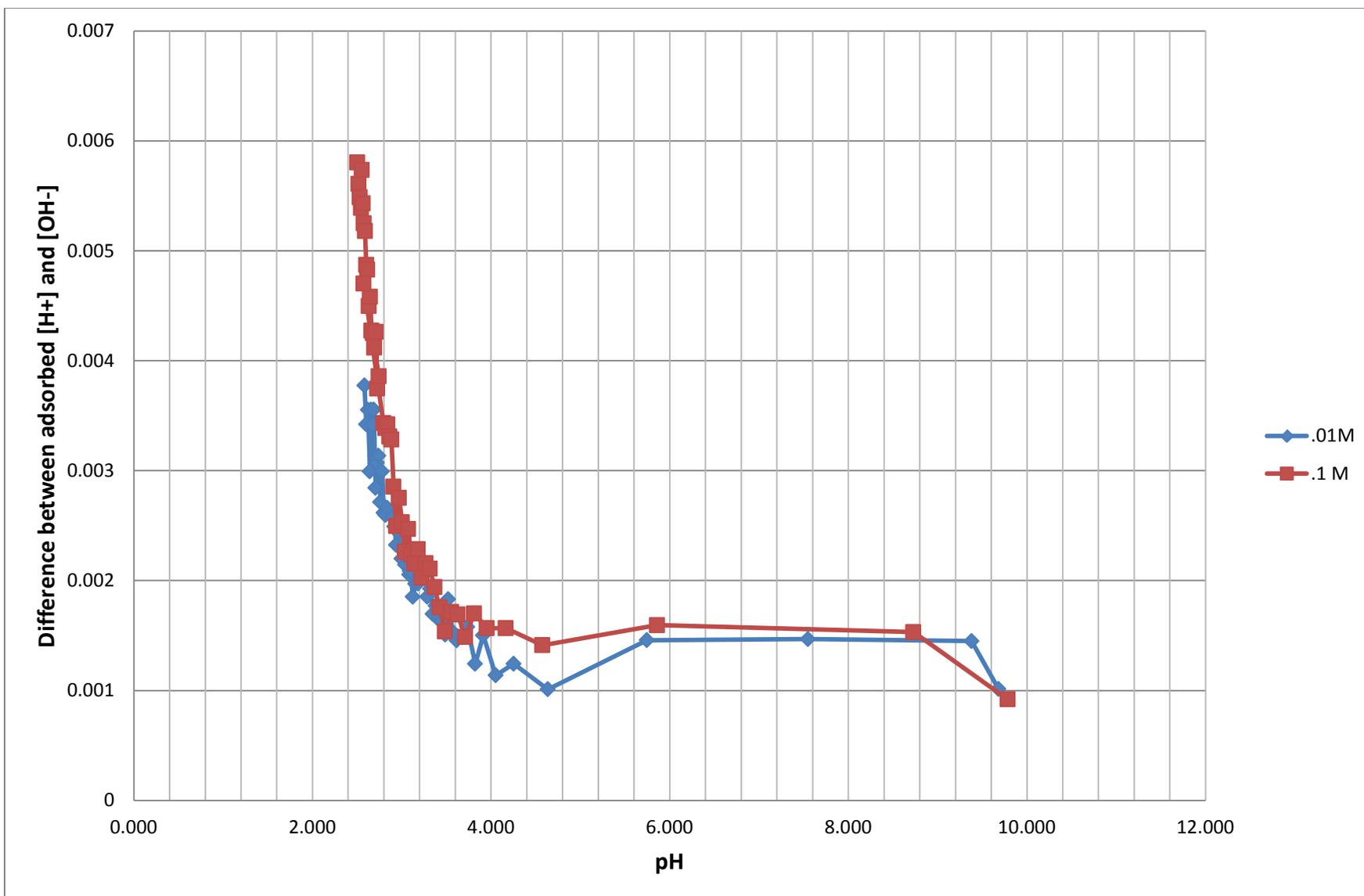


Figure 3.1: Two titrations of graphite under 0.01 and 0.1 M NaCl

We are able to evaluate the point of zero charge by employing two facts (section 1.2.2): pH dependent surface charge densities are a function of ionic strength, and the pH at which surface charge is zero is independent of ionic strength. Using this information, it is known that, regardless of ionic strength, the point of zero charge is shared by all titrations. The two titration curves cross at $\text{pH} \approx 8.8$; therefore, the measured PZC used for the experimental graphite is at pH 8.8. Previous analysis of the graphite performed by Schmidt [2010] indicated a PZC of $\text{pH} \approx 9.3$. The deviation between measured PZC is not necessarily a real deviation from the original measured PZC. Near the point of zero charge, the system is very sensitive to small additions in acid/base, increasing the uncertainty in the PZC determination which could result in measured PZC deviation. Regardless, the current measured PZC is close enough to the previously measured PZC, so that a reasonable assumption could be made that additional graphite oxidation has not occurred between measurements.

Both PZC graphs had the same general shape for the titrations. Even the deviation from the trend observed in the neutral region, noticed in Schmidt's work [2010], was found in the current PZC work. The experimental graphite behaves closely to both shape of titration curves and overall PZC to regard the previous characterization as reliable.

3.2 Uranium Equilibrium Sorption

3.2.1 Solid to Liquid Ratio

Table 3.1 shows the results of the solid/liquid ratio experiments performed at pH of 8.0 and 10.5. The pH points were chosen because little pH variance (due to the buffer) was observed, and ideally changes in sorption observed were a consequence of

solid/solution ratios. The ratios of solid mass to solution volume were chosen to represent a spectrum around the experimental ratio (1:10) used in all other batch experiments.

	<i>pH 8</i>		<i>pH 10.5</i>	
Solid-to-liquid ratio (g/L)	K_d(ml/g)	SD	K_d(ml/g)	SD
5.00	104.29	14.33	40.01	2.74
10.00	57.35	10.13	27.24	1.75
50.00	3.63	0.37	11.27	0.57
100.00	2.86	0.04	6.58	0.04
150.00	4.19	0.54	7.84	0.34
200.00	4.49	1.70	12.93	0.73

Table 3.1: Uranium sorption ($[U] = 1.6E-06 M$) to graphite as a function of Solid/Liquid Ratio: Ionic strength = 0.01 M, $pCO_2 = 390 ppm$

The solid-to-liquid experiments were run to confirm the choice of graphite to solution ratio used for the rest of the experiments. Ideal mixing procedures should have a relatively constant K_d for varying ratios as long as initial uranium concentration was kept constant. If K_d was a function of solid/solution ratio, we could not use the measurements from batch experiments to predict transport at a field-relevant scale [Phillippi, 2007]. Therefore, equation 1.1 can be manipulated to relate solid-to-liquid ratio to distribution ratio of uranium to graphite under given conditions. The manipulations give the resulting equation, which is shown as equation 3.1.

$$\frac{S}{L} = \left[\frac{C_{in}}{C_{fi}} - 1 \right] \frac{1}{K_d} \quad \text{Equation 3.1}$$

Where,

S/L = Graphite mass (g) divided by volume of uranium solution (ml)

C_{in} = Initial conc. of uranium solution, $\mu\text{g/ml}$

C_{fi} = Conc. of solution after equilibration, $\mu\text{g/ml}$

K_d = distribution coefficient

Since a constant initial concentration was used in all S/L studies done, it can be seen in equation 3.1 that S/L is inversely proportional to that of final concentration of uranium in solution. Therefore it can mathematically describe the distribution ratio as being constant, given no experimental error. The choice of solid-to-liquid ratio of 100 g/L was confirmed to be ideal, as there was very little variation in K_d for the data points around that value. An variations was seen in K_d for S/L ratios below that of 50 g/L. K_d values have sometimes been reported to vary, where usually a decrease in batch-measured K_D is shown for increased S/L ratios [Oscarson and Hume, 1998]. The increase was indeed observed for the data as seen in table 3.1, and attempts were made to determine whether the result was a true phenomenon or the result of experimental artifacts. Solid concentration effects (term referring to the effect where decreases in S/L yield increases in K_D) have been attributed to a variety of causes including: the presence of colloids, particle-particle interactions, kinetic effects, and heterogeneous media [Phillippi 2007].

During these experiments, observations of the system may begin to reveal the phenomena responsible for the non-ideal behavior of the system. As graphite has a hydrophobicity tendency in aqueous solutions, a fraction of the graphite mass was observed to float on the surface. A fraction of graphite mass, therefore, would not be

homogenously exposed to solution as the rest of the graphite and have a small effect of equilibrium sorption. At mass concentrations used for graphite in all batch experiments, the graphite mass fraction was small enough to have a more negligible effect. However, when the solid-to-liquid ratio was decreased, the fraction of graphite not fully exposed to solution also increased. The result was a large deviation from that of the S/L ratio used in all other batch experiments. Future work could look into possible colloid effects of graphite, as the importance not only pertains to batch experiment results (such as this), but on repository performance modeling in general if graphite disposal is chosen.

The real significance of solid concentration effects is when, for experimental considerations, a solid/liquid ratio is used where this effect occurs, which would lead to overestimation of the measured distribution ratio. The solid/liquid ratio that was chosen (100 g/L) is not influenced by solid concentration effects as evidenced by table 3.1. Since the solid/solution ratio results are more dependent on the graphite characteristics in solution and on the methodology for batch experiments used, it was thought to be unnecessary to run the same study for neptunium (since all parameters are kept equal).

3.2.2 Impact of Elevated Temperature on Sorption

Two temperatures were picked for the experiment, 20°C (room temperature) and 50°C. The results of the temperature experiments in regards to uranium sorption are shown in figure 3.2. Data points were obtained from both the acidic and alkaline regions to determine if temperature had any impact on sorption. As the pH of the solution was changed to 9.0 and greater we see some variation in sorption in the two temperatures. As borate buffer was needed to maintain pH at the data points that showed variance, additional work went into trying to determine if the change in sorption was real. The pKa

for the borax buffer was found to shift by 0.5 for the elevated 50°C. Attempts were made to eliminate the use of the buffer by daily adjusting the pH of the solution. The pH of the un-buffered alkaline solutions was found to drift to a great extent, so attempts to manually adjust the pH daily by additions of respective acid/base led to unreliable results. It was found that lower concentrations of the buffer could be used and still limit pH drift, so differing concentrations of borax buffer was explored in the alkaline region in regards to temperature variance on sorption. The uranium sorption at differing temperatures and borax concentrations is plotted as a function of pH (figure 3.2).

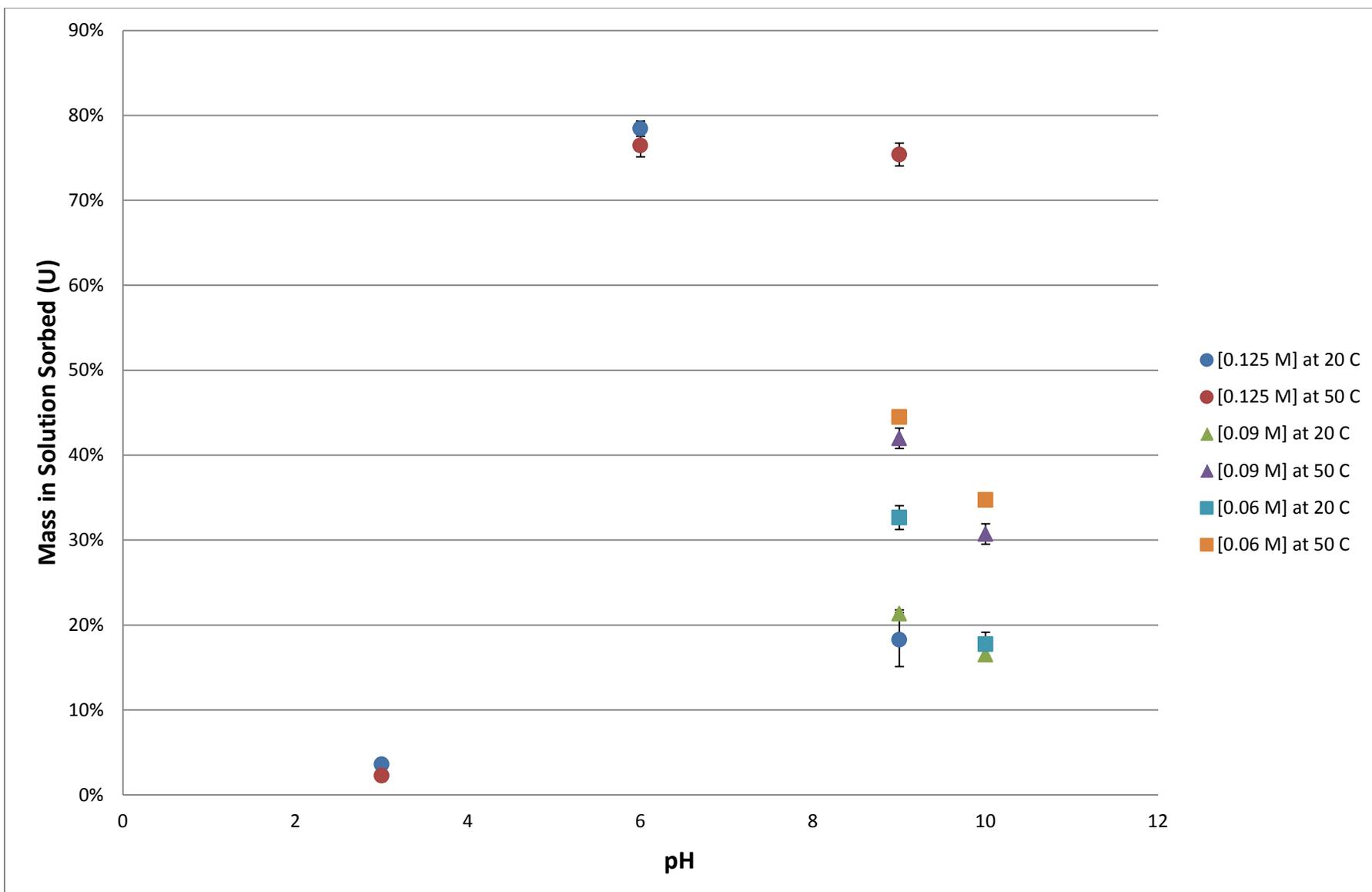


Figure 3.2: Uranium sorption to graphite as a function of pH for various buffer concentrations and temperatures

The differences in uranium mass sorbed only began to be significant above pH 8, where the acidic pH points had no variance (figure 3.2).

The buffer concentration was decreased to observe any possible impact it had on sorption with elevated temperatures. The buffer behavior in blank solutions (no neptunium) was also evaluated for the elevated temperature used. The pKa of the borax buffer in room temperature is around 9.3. As the temperature was elevated to 50° C, we found a shift in the pKa to around 8.8. To account for the shift in pH that occurred for all elevated temperature samples, the pH of the samples was adjusted while at the elevated temperature state.

Speciation also was thought to play a role in the differences in sorption, as differences were found through use of EQ3/6, shown in table 3.2. As some uranium species tended to have a greater affinity for sorption onto graphite, a change in the uranium species concentration for elevated temperatures at a given pH could have some impact on sorption.

	pH 8.5		pH 9	
	20°C	50°C	20°C	50°C
UO₂(CO₃)₂--	19.74%	57.23%	2.12%	10.80%
UO₂(CO₃)₃----	79.97%	42.32%	97.88%	89.19%
UO₂++	0.00%	0.00%	0.00%	0.00%
(UO₂)₂CO₃(OH)₃-	0.00%	0.00%	0.00%	0.00%
(UO₂)₂(OH)₂++	0.00%	0.00%	0.00%	0.00%

Table 3.2: Percentage of uranium species by mass for given pH and temperature

3.3 Neptunium Batch Studies

3.3.1 Sorption Dependence on pH

In regards to both neptunium availability and activity limit considerations, the concentration of neptunium was kept at the lower range for groundwater release (10^{-6} M) in all experiments evaluating neptunium sorption onto graphite dependence on pH. The concentration used allowed for the use of neptunium in a hood, when evaluating activity limits in the lab. An increase in neptunium activity would have required the use of a glove box, which would have complicated the methods. A graph of the mass in solution sorbed as a function of pH with an initial $[Np] = 1.6E-06$ M, ionic concentration = 0.01 M NaCl, and atmospheric CO₂ is shown in figure 3.3.

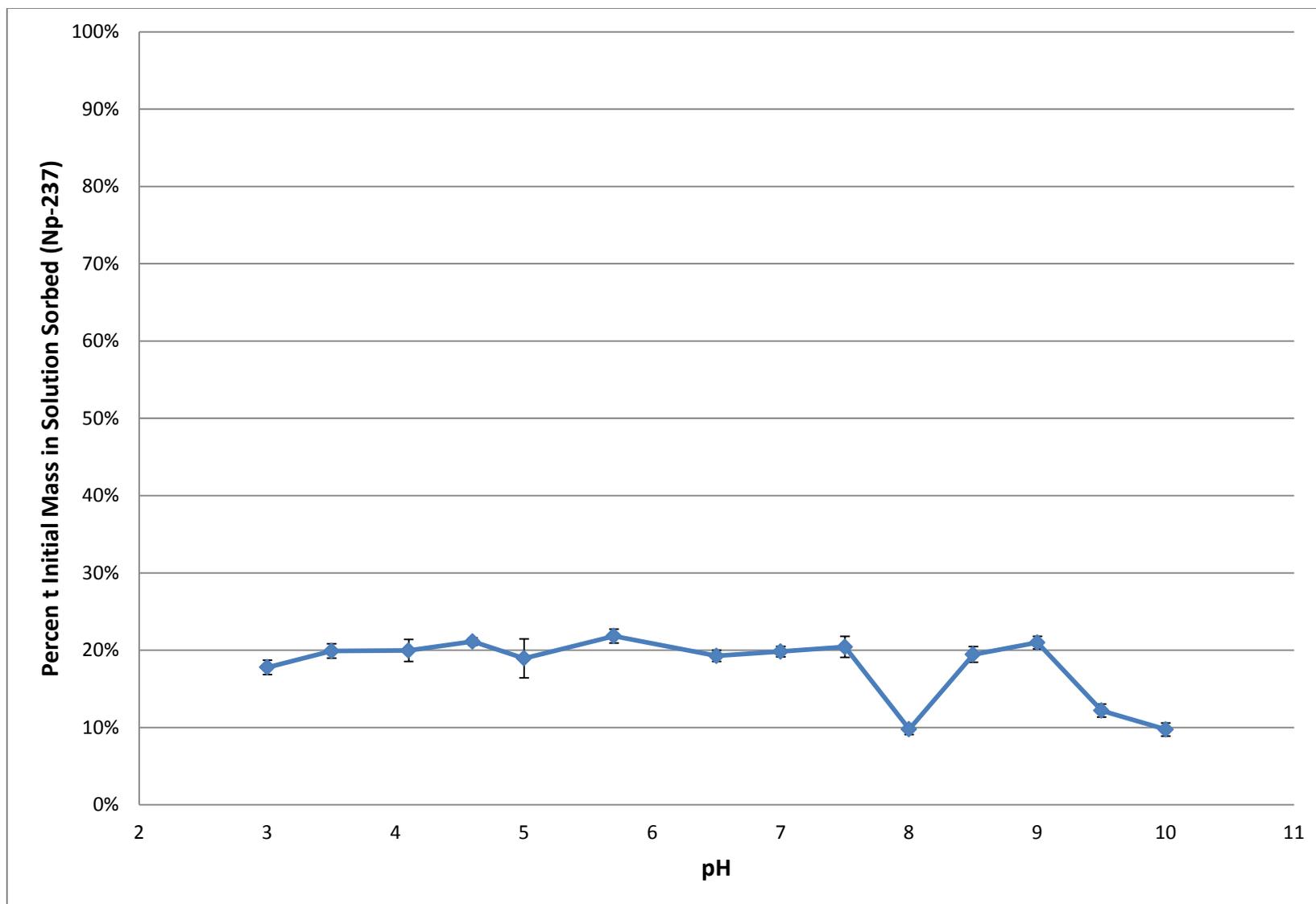


Figure 3.3: Percent of Neptunium mass sorbed to graphite as a function of pH
(Experimental conditions defined in section 2.3.2)

The error bars are representative of plus/minus one standard deviation.

Neptunium sorption was found not to vary significantly in the pH region between 3 and 7.5. The pH point 8 had a large decrease in sorption compared to the pH points around 8, which was where we started adding borax buffer. The peak sorption to graphite is observed at pH = 5.5 with $21.8\% \pm 0.89\%$ of the neptunium in solution sorbed. The region near the pH point is also within standard error of peak sorption, showing again the relative minimal variance in sorption. The pH points where the buffer was added (pH 8 – 10) seemed to have the most variance in mass sorption, and additional experiments were done to evaluate the cause. This data was used to estimate a K_d value for this system, which more clearly shows that the sorption appears to be relatively pH independent (table 3.3 and figure 3.4).

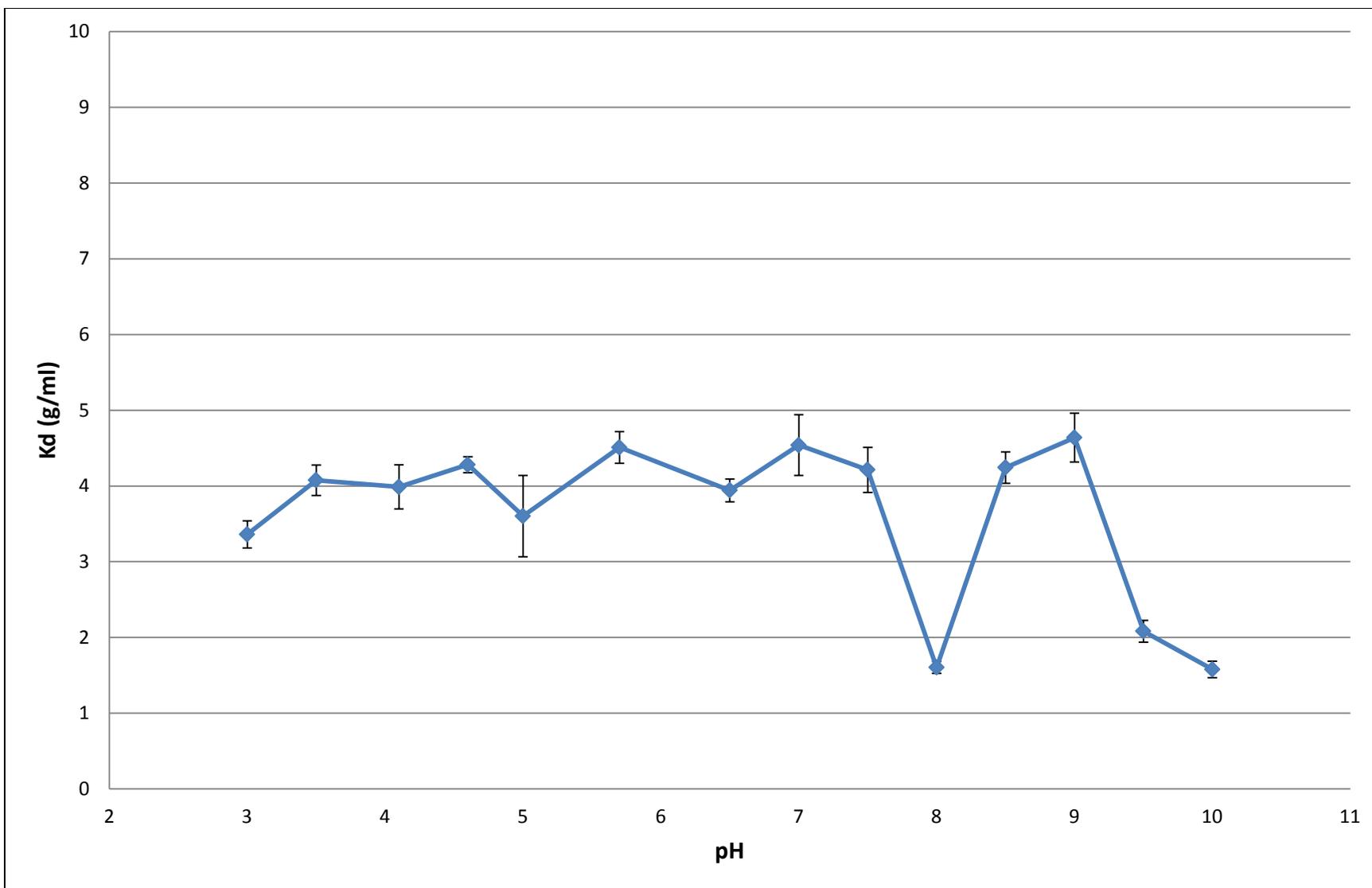


Figure 3.4: Neptunium K_d variation with regards to pH (initial $[Np] = 1.6E-06 M$)

pH	Kd (ml/g)	Retardation factor
3.00	3.36 ± 0.18	34.6 ± 2.05
4.00	3.99 ± 0.29	40.9 ± 3.06
5.00	3.60 ± 0.54	37.0 ± 5.46
6.00	3.94 ± 0.15	40.4 ± 1.81
7.00	4.54 ± 0.40	46.4 ± 4.13
8.00	1.60 ± 0.08	17.0 ± 1.27
9.00	4.64 ± 0.32	47.4 ± 3.38
10.00	1.58 ± 0.11	16.8 ± 1.48

Table 3.3: Sample retardation factors and distribution coefficients are calculated for neptunium in graphite as a function of pH

To attempt to understand the variations observed in the pH range from 8 to 10, work went (table 3.3) into evaluating whether the data from the pH region from 8-10 is a real effect from pH or whether the buffer is affecting the sorption behavior. One experiment was done to compare buffered and non buffered samples at the same pH points on the edges of the buffered region (pH 8 and pH 10), but the pH tended to still drift for the non buffered samples. The data from that experiment was therefore unreliable. The pKa of borax buffer is approximately 9.15 and the range of the buffering system is 8.0 – 10.7 [Robinson, 1968]. The buffered samples approaching the buffered range (i.e. pH 8 and 10) required a large addition of acid/base that possibly led to non-ideal results.

To address the potential for the buffer to complex with the neptunium, experiments were also performed varying the borax concentration. Neptunium sorption

was evaluated in the pH region of 8 – 10 for differing borax concentrations (0.06 M, 0.09 M, and 0.125 M borax buffer) and is shown in table 3.4.

	% Initial Np Sorbed		
pH	0.006 M Borax	0.009 M Borax	0.0125 M Borax
8.0	20.74% ± 0.54%	15.06% ± 1.17%	9.78% ± 0.68%
8.5	7.79% ± 1.41%	12.52% ± 2.17%	19.46% ± 1.02%
9.0	5.69% ± 0.80%	13.16% ± 0.32%	20.99% ± 0.8%
9.5	3.95% ± 0.82%	18.32% ± 1.10%	12.19% ± 0.85%

Table 3.4: % neptunium mass sorbed in pH region of 8-9.5 for differing borax concentrations.

Neptunium mass sorbed onto graphite in the pH region of 8-9.5 reaches a maximum value around the pKa of the borax buffer (9.14) for the 0.125 M borax buffered samples. As the concentration of borax buffer was decreased to 0.09 M borax, the peak sorption is still at pH 9.5 which is around the pKa of the borax buffer. However, the difference between the maximum (pH 9.5) mass sorption and the minimal mass sorption points (pH 8, 10) is lower for the 0.09 M borax buffered samples when compared to the 0.125 M borax buffered samples. The 0.06 M borax buffered samples deviated from the trend displayed by the previous two samples in that the maximum mass sorbed is at pH 8 with decreasing sorption as pH increases. It was noted that the 0.125 M and 0.09 M borax buffered samples started at pH 9.2 (around the maximum sorption point) before the incremental additions of acid/base. The concentration of the borax for the 0.06 M borax buffered samples was too low to overcome the acidity of the spike of

neptunium solution. As a consequence, the sample solutions pH started at pH 3 before the incremental additions of base, and required large amounts of base to reach the pH points around 9.5 and 10 (where the least sorption was seen) as compared to all the other sample sets. This will be discussed in more detail in section 4.3.1.

3.3.2 Impact of Ionic Strength on Sorption

The experimental conditions were kept the same as the initial neptunium equilibrium studies except for the concentration / counterion of the salt used in solution, which was varied to evaluate the effect on sorption as described in section 2.3.3. The results of the variation in counterions are shown in Table 3.5 for neptunium. The considerable change in sorption resulting from a change of counterions led to additional experiments in evaluating if a change in sorption kinetics was occurring. The data points in Table 3.5 were repeated except at a 15 day contacting time with no change in sorption above two standard deviations.

pH	Concentration (M)	Mass % Sorbed	Kd (ml/g)
4	0.01 M NaCl	17.23% ± 0.92%	2.40 ± 0.16
4	0.05 M NaCl	3.19% ± 1.60%	0.33 ± 0.17
4	0.1 M NaCl	3.23% ± 1.18%	0.34 ± 0.13
8	0.01 M NaCl	20.74% ± 1.54%	2.64 ± 0.19
8	0.05 M NaCl	14.16% ± 3.23%	2.16 ± 0.59
8	0.1 M NaCl	13.45% ± 1.80%	2.02 ± 0.33
4	0.01 M NaClO₄	1.63% ± 0.97%	0.17 ± 0.10
4	0.05 M NaClO₄	0.96% ± 0.73%	0.10 ± 0.08

4	0.1 M NaClO₄	0.92% ± 0.96%	0.09 ± 0.07
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Table 3.5: Neptunium [1.6E-06 M] Sorption and K_d variation with differing counterions and concentration

The large change in sorption with differing counterions for the neptunium study led to a re-evaluation of the effects of the ionic strength and counterion used for the uranium sorption work previously performed. The same conditions (pH, ionic strength, etc.) were repeated for the uranium study and are shown in Table 3.6.

pH	Concentration (M)	Mass % Sorbed	K_d (ml/g)
4	0.01 M NaCl	38.55% ± 0.84%	6.30 ± 0.19
4	0.1 M NaCl	27.83% ± 1.18%	3.88 ± 0.29
4	0.01 M NaClO₄	40.16% ± 1.59%	6.82 ± 0.47
4	0.1 M NaClO₄	32.94% ± 0.66%	4.93 ± 0.18

Table 3.6: Uranium [1.7E-06 M] Sorption and K_d variation with differing counterions and concentration

3.3.3 Np Concentration

To obtain specific adsorption parameters that quantitatively describe adsorption in a specific environment, we measured sorption isotherms at varying conditions. An adsorption isotherm is an ideal way to evaluate the behavior of varying neptunium mass in solution on sorption, and is shown as a graph of the amount of neptunium sorbed plotted against the equilibrium solution concentration at fixed solution chemistry (same ionic strength and pH). The behavior can then be classified under a general isotherm type (figure 1.9). Two adsorption isotherms for neptunium in contact with graphite are shown in figure 3.5.

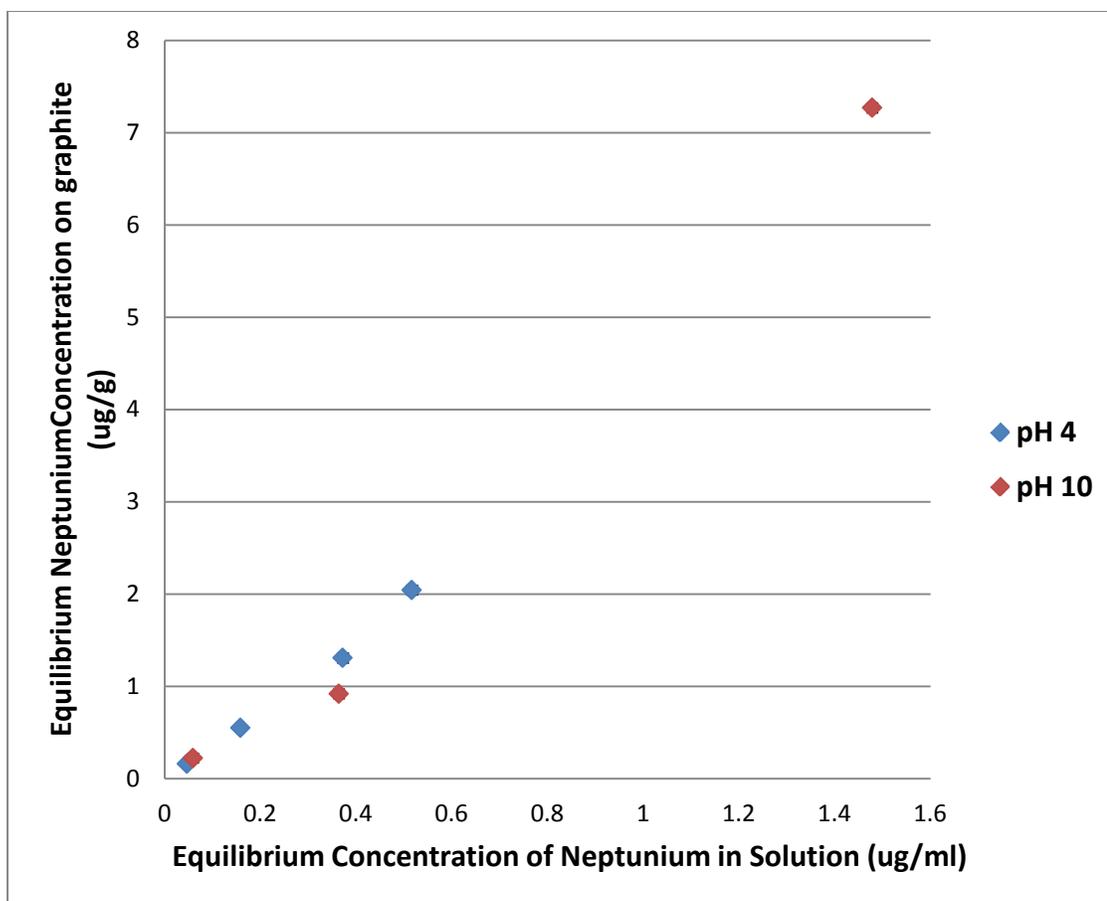


Figure 3.5: Adsorption isotherms for neptunium sorption to graphite

The pH points were chosen because there was little variation in the neptunium species around the points, and both a positive and negative neptunium species was represented. The mass values were chosen to represent a range of mass around that used in all other batch experiments (0.3 ug). The data, shown in figure 3.5, at first glance indicates a linear relationship between neptunium mass sorbed to that of equilibrium neptunium concentration in solution. Using particular models fitted to the data, the linearity of the relationship we can mathematically evaluated. Isotherms can be described by many types (figure 1.9). Even though there is a limited concentration range described by the neptunium isotherms, one of the main objectives of performing a sorption isotherm is to obtain parameters used to describe sorption in that specific

environment. Mathematical functions already exist that describe common adsorption isotherms, so ideally the neptunium isotherm data should be fitted to one.

3.4 Neptunium Kinetic Study

Batch equilibrium studies are useful in determining bulk behavior of sorption at equilibrium, through use of an effective K_D value, which describes many different reaction mechanisms occurring simultaneously. However, using equilibrium studies prevents distinguishing between different mechanisms of interactions that might be occurring at different rates, which is why kinetic studies are employed. In the case for uranium sorption to graphite, for example, kinetic sorption is seen to occur through both a fast acting sorption/desorption process combined with a slower/stronger sorption process.

3.4.1 Batch Kinetic Results

Long Term Study

Initial neptunium experiments were performed to determine if the contacting time used for the uranium studies was appropriate. The first kinetic experiment was performed at pH = 4 at the typical solution conditions ([10 bq/ml], I = .01 M NaCl), as at that pH point there was no significant change in speciation and buffer was not needed. Others were then repeated for inclusion of buffer and more alkaline pH. The samples were allowed to equilibrate after a period of 1, 5, 30 days. The results are shown in table 3.7.

	<i>Mass % Neptunium Sorbed</i>		
pH	1 Day	5 Day	30 Day
4	23.9% ± 0.9%	23.8% ± 1.32%	24.7% ± 1.79%
9	19.9% ± 1.99%	21.2% ± 2.21%	21.1% ± 1.86%

Table 3.7: Kinetic data for change in Neptunium sorbed onto graphite over time

All changes after the five day contacting period were within the margin of error, and sampling in between the two periods showed no deviation from that conclusion. Consequently, the contacting time for all batch experiments was chosen to be not less than 5 days. Even though one day would have been a sufficient time period, five days was chosen to limit variation. Five days was also short enough to be feasible for the experiments (i.e. one week experimental set).

Short Term Study

The initial kinetic experiment, shown in table 3.7, was done to determine the appropriate contacting time for neptunium in solution to graphite. As a consequence, the shorter kinetics was ignored for that experiment. Shorter time intervals were explored to determine the linearity behavior of neptunium sorption to graphite and are shown in figure 3.6.

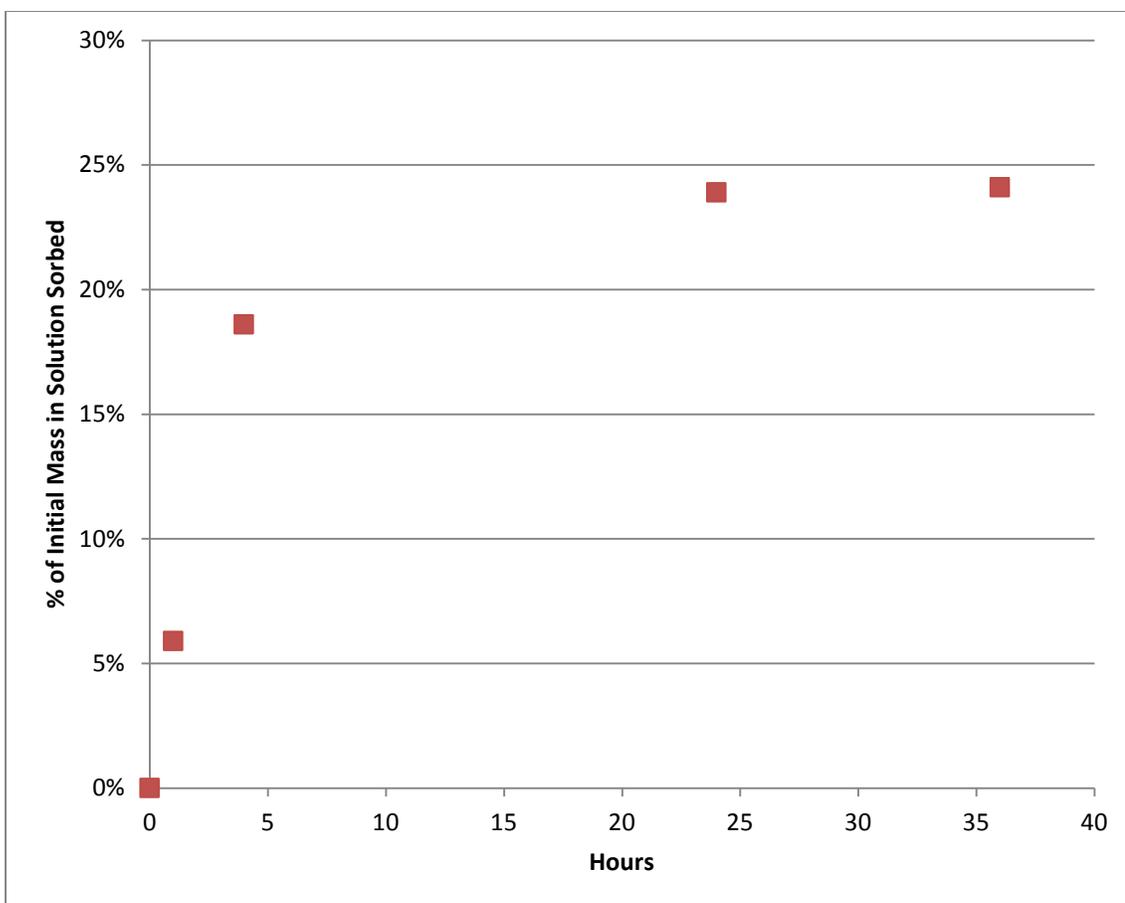


Figure 3.6: Percentage of initial mass sorbed with respect to contact time (hours)

Significant sorption was observed in the first hour of contact, so additional experiments were performed with sampling intervals within the first hour. The shorter contact time necessitated a different mixing procedure than used previously. Active mixing of the samples was done manually, with a contact time of one minute, before centrifuging occurred. All time periods do not factor in the 20 minute centrifuge time period for the kinetics. As a result, the data is not to be taken as an absolute since sorption/desorption possibly occurred during centrifuge time (although not necessarily homogeneously). The methods were kept the same for all samples, however, so the data is analyzed relative to each other.

3.4.2 Batch Desorption Results

Step-wise desorption experiments were carried out for samples with differing initial sorption conditions. Step-wise desorption was completed by replacing the solution in equilibrium neptunium sorbed samples with blank (no neptunium) solutions in same volume. This process is repeated in a distinct step-wise method which is described in detail in section 2.4.2. Desorption studies were carried out for samples in both the acidic and alkaline pH region, as well as for a range of initial Np sorption to the graphite. Desorption experiments were performed as three sequential five day contact periods. The pH adjusted blank solution was contacted with the loaded graphite and allowed to equilibrate for five days. At the end of this interval, the solution was removed for analysis, and the solution was replaced with pH adjusted blank solution prior to another 5 day contact interval. In addition, a single batch, 30 day desorption experiment was performed to evaluate long-term desorption kinetics. The resulting total percentage of neptunium desorbed after batch desorption is shown in table 3.8. The multiple step desorption, as well as the 30 day batch experiment, did not change significantly between steps; but is shown in figure 4.3.

The results of the desorption studies show relatively low desorption regardless of initial sorption conditions. Some desorption was observed in the first 5 day interval. However, this desorption was also observed in the no-graphite sorption blank, and appears to be desorption from the sample vessel surface. Accounting for this effect, the desorption from the graphite appears to be very low. Comparing the pH 4 and 10 data shows low desorption from the graphite under both conditions, with slightly elevated desorption at pH 10.

The long-term desorption kinetics (30 day interval) showed no change from that of the initial 5 day desorption time period. As the alkaline conditions were shown to have slightly elevated desorption, the long-term kinetics under those conditions would ideally be evaluated.

pH	Mass/Mass (ug/g)	% Np Desorbed	Mass Np Remaining Sorbed (ug)
4	0.16	0.00% ± 1.82%	0.13
4	0.55	0.81% ± 6.22%	0.44
4	1.31	0.00% ± 2.37%	1.05
4	2.04	0.00% ± 2.03%	1.64
8	0.74	1.32% ± 1.97%	0.59
8.5	0.70	2.74% ± 0.73%	0.54
9	0.57	4.57% ± 1.42%	0.44
9.5	1.05	10.19% ± 1.44%	0.76

Table 3.8: Desorption data for various pH and Mass Sorbed samples

CHAPTER 4

DISCUSSION

4.1 Graphite Surface Charge

PZC was reported in previous literature to be dependent on the preparation of the graphite. By changing surface oxidation of the graphite, the PZC also results in a significant change [Menendez, 1995; Noh, 1990]. As graphite is subjected to air oxidation, more acidic oxygen-containing surface groups are added to the graphite surface. The oxidation of graphite causes a decrease in PZC compared to similar prepared graphite without oxidation occurring, and an example of the effect is shown in table 1.1.

The PZC was used for a qualitative method to observe if the experimental graphite underwent any significant change in surface oxidation during exposure to the atmosphere. The PZC for the experimental graphite was measured at 8.8 for this work and measured at 9.3 by Schmidt [2010]. The sensitivities for the titrations in the PZC region led to changes in the measured PZC; as a result no meaningful change was seen for the experimental graphite between the measurements, as both had similar PZC with respect to the sensitivities seen in the titrations. Consequently, the experimental graphite characteristics have not been affected by exposure to the atmosphere.

4.2 Temperature Evaluation on Sorption

In figure 3.2, it can be seen that temperature, when elevated, had a measurable increase in uranium sorption to graphite at pH 9 and 10 and a negligible effect for the acidic pH samples. Distinguishing the mechanism that is affected by uranium sorption is, however, a difficult task. Multiple factors were evaluated that could potentially lead to

the temperature effect on observed sorption. These factors include buffer influence, shift in speciation, and the thermodynamics of complexation. Properties of water also vary for increases in temperature, such as the ionic product ($K_w = [H^+][OH^-]$) which increases by almost 3 orders of magnitude from 0 to 100 °C [Zanonato 2004]. Significant increases in the ionic product leads to adjusted calculations of the pH measured, so error can result in pH measurement. However, temperature corrections to pH were accomplished through use of Metrohm pH parameter adjustments.

The samples showing the largest temperature effects also contained the borax buffer for pH control. Borate buffer was used in other uranium sorption studies [Schmidt, 2010], and no evidence was found for borate ions complexing with uranium species under experimental conditions. In support of this observation, no information was available in the literature suggesting that uranium complexes with borate under any conditions used in the study. However, the pKa of the borate buffer was found to decrease by approximately 0.5 [Robinson, 1968], leading to changes in the pH of the solutions. To account for the shift, the experimental methodology was altered to heat the respective solutions to the elevated temperature initially and all pH measurements occurred at the elevated temperature.

To exclude the borate buffer from the alkaline samples, manual adjustment of the pH was attempted to offset pH drift. However, the pH drift for the samples (without buffer) in the alkaline region was too large to offset by pH measurements during the contact time. Instead, to further evaluate the potential impact of the borax buffer on uranium sorption, a second set of experiments was performed by fixing the pH and varying the borax concentration. Under all buffer concentrations, pH was found not to

drift to a significant degree. Sorption was measured the same for the 20 °C samples, regardless of a change in buffer concentrations. Only the elevated temperature samples showed a measurable change. At 50 °C, uranium sorption to graphite was observed to decrease for decreasing buffer concentration. However when analyzing further, it was found the decrease in sorption was a result of an increase in sorption to the container walls for the blank samples. Whether this is a competing process for sorption to graphite for the graphite-containing samples is unclear. Further studies need to be done using Teflon containers to observe whether sorption on the container is a competing process for graphite sorption for elevated temperatures.

Another possible factor is the change in speciation for uranium in solution at elevated temperatures. Using the Yucca Mountain database in EQ3/6, the speciation of uranium is observed to slightly suppress carbonate speciation seen in table 3.2. However, few studies have been conducted of uranium (VI) hydrolysis in aqueous solutions at elevated temperatures. The scarcity or lack of important thermodynamic parameters at elevated temperatures can lead to error in calculating speciation for uranium. It is unknown whether the Yucca Mountain database has good data for elevated temperatures and so exclusively comparing data at similar speciation concentrations for elevated and non-elevated temperatures, cannot be included until the issue is addressed. The speciation of uranium at pH 10 is relatively unchanged by temperature, so this point was chosen to evaluate the impact of temperature on the sorption process vs. the impact of speciation. At this pH, there was a decrease in sorption at 50 °C vs. room temperature, even though speciation was essentially the same according to EQ3/6 models using the Yucca Mountain database. For room temperature uranium samples, significant sorption

to the PP containers was observed in the pH 6-8 region [Schmidt, 2010]. However, significant sorption to the PP containers for the elevated temperature samples occurred at pH 9 and 10.

Surface complexation models have been examined for uranium sorption onto graphite, and, according to previous work [Schmidt 2010], a modified triple layer model fits the uranium data the best. We can qualitatively examine whether temperature should have an effect on the stability of the uranyl carbonate complex to the graphite surface by observing the model trend with respect to temperature. An example of the complexation reaction [Schmidt, 2010] thought to occur where temperature has an impact (pH 9-10) for the modified triple layer model is shown as equation 4.1.

$$K_{UO_2(CO_3)_2^{2-}}^{int} = \frac{[\equiv C - O - UO_2(CO_3)_2^{3-}]}{[\equiv C - (OH)][UO_2(CO_3)_2^{2-}]} \exp\left(\frac{F(\psi_{is} - \psi_0)}{RT}\right) \quad \text{Equation 4.1}$$

Where,

K^{int} is the intrinsic complexation constant for the particular sorbing species

Ψ_0 = Intrinsic potential for the adsorbent surface

Ψ_{is} = Potential at inner sphere surface

R = Ideal gas law constant

T = Temperature (K)

K^{int} is the intrinsic adsorption constant for a particular species sorbing onto a particular surface site. Since the intrinsic adsorption is constant, according to the model, the ratios (that of a particular uranyl carbonate species complexed to a graphite surface site to that of the initial uranium species and surface site concentration) is dependent on surface potential and on temperature. If assumptions are made that the potential at given surfaces are constant, then when temperature is increased the adsorption also increases until the intrinsic adsorption constant is reached. The same trend is seen with the

temperature data for the alkaline region but not in the acidic region, which could be explained based on the MTL model since adsorption is limited to the intrinsic adsorption constant. The temperature needed to reach the intrinsic adsorption constant (assuming surface potentials are constant over temperature range) is dependent on how large $F(\Psi_{is} - \Psi_0)$ is. Temperature impact on sorption is, based on the model, dependent on the sorbing mechanism (inner or outer-sphere) of the uranium species and therefore shows a difference in sorbing mechanisms for acidic and alkaline uranium species.

Although several possibilities have been explored, the exact mechanism behind temperature impacting the measured uranium sorption is unknown. Regardless of the true mechanisms behind the temperature impact on uranium sorption, the data has shown a significant response. Temperature will need to be considered more carefully in batch studies evaluating sorption as, like in this case, it can alter the expected results.

4.3 Adsorption under Environmental Conditions

To be able to understand the sorption mechanisms of neptunium on graphite and ultimately calculate stability constants for the neptunium ion – surface complex, ideally the sorbing species and surface sites need to be identified. Previous work by another group [Schmidt, 2010] examined the sorption of uranium (VI) to graphite as a function of pH, and was able to correlate the observed sorption behavior with the predicted chemical speciation. In this work, a similar approach was used to explore neptunium sorption as a function of pH (figure 3.3). Using the database in EQ3/6, the speciation of neptunium under these conditions is shown in figure 4.1, alongside the sorption data at the same pH range.

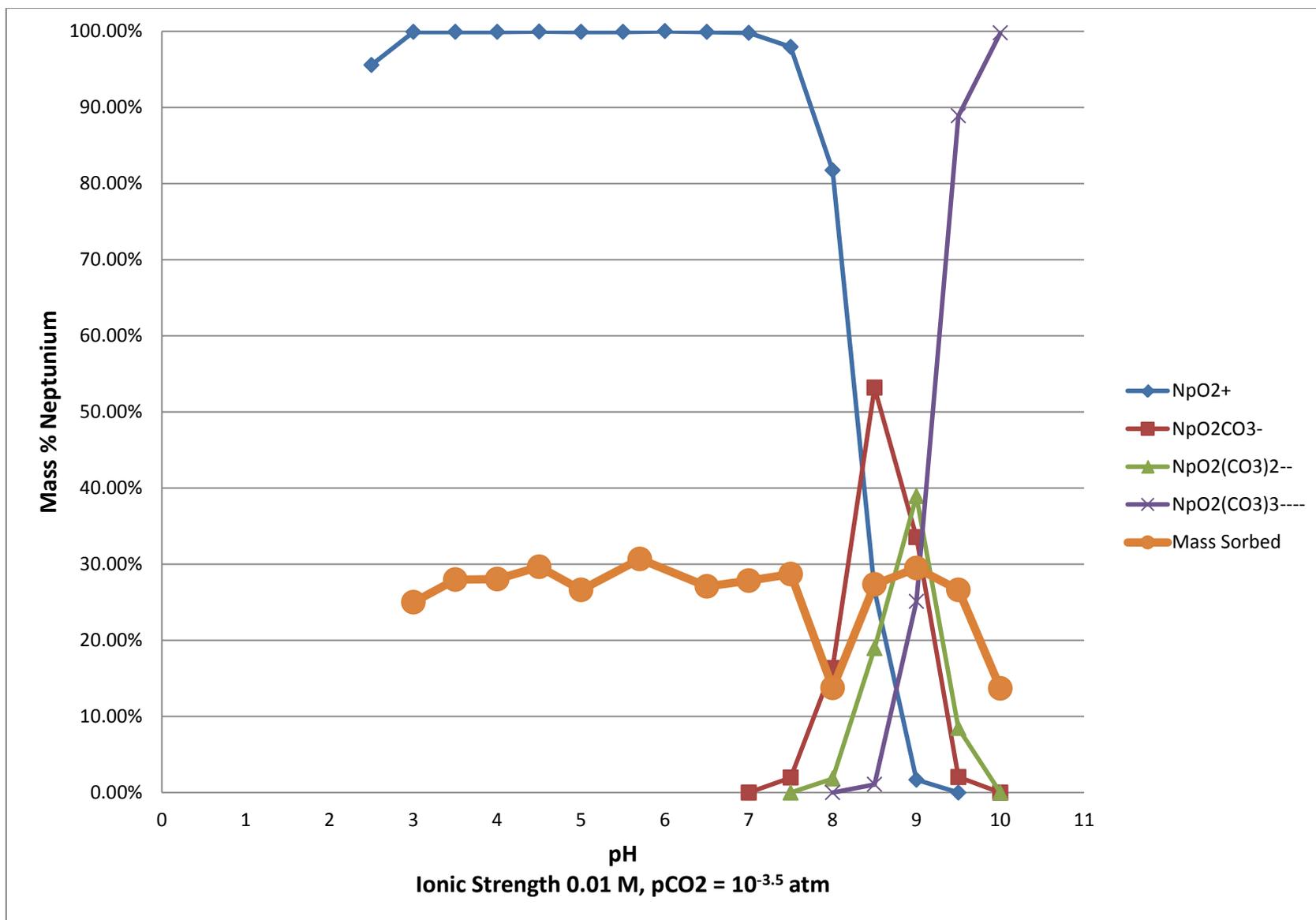


Figure 4.1: Neptunium Speciation with Mass Percentage Sorbed with respect to pH

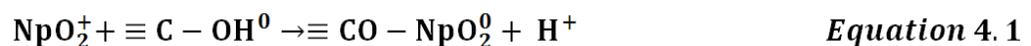
It can be seen that evaluating neptunium speciation on sorption to graphite is not easily done using figure 4.1. Neptunium sorption to graphite does not seem to be impacted by the pH of solution for the neptunyl ion, suggesting that an inner sphere sorption process is occurring. It can also be noted that the charge of the dominant Np species changes over the pH range, from the +1 NpO_2^+ to a -4 for the neptunyl carbonate species. However, the sorption to the graphite is relatively unchanged over this range, except for pH 8. Previous work on neptunium sorption to other adsorbents, such as hydrargilite, has shown that NpO_2^+ has relatively low sorption and the main species that contribute to sorption are the neptunyl carbonate complexes seen around pH 8 for the experimental conditions [Del Nero et al, 1997]. However no neptunium sorption data was found on graphite-like adsorbents. The low sorption of NpO_2^+ seen by Del Nero can be explained by the low charge relative to the mass for the ion described (section 1.2.4). In this work, however, the same trend was not observed. No appreciable increase in sorption was measured as the major species shifted from the neptunyl ion to a neptunyl carbonate species. In fact, the minimum sorption measured was seen where neptunyl carbonate speciation dominated in concentration. One explanation could be the fact that the neptunium concentration used in the previous experiments limited the mass sorbed onto graphite. Isotherms were evaluated to observe the impact the concentration of neptunium had on mass sorbed and, as indicated in figure 3.5, there was a linear relationship for the range used. As described in section 4.1, graphite has a relatively low exchange capacity and surface area compared to other adsorbents investigated at for neptunium sorption studies. This could result in the concentration having a larger influence on neptunium sorption than speciation. If different affinities for sorption exist

for the different species of neptunium, it is possible that a higher concentration would be needed.

Some observations on neptunium sorbing species on graphite can still be made by looking at particular pH data sets. From pH 3 – 7 the speciation of neptunium is dominated by the neptunyl ion, NpO_2^+ , at nearly 100% of the neptunium in solution. Across the same pH range, the neptunium sorption remains essentially constant, accounting for uncertainty. In this region, it may be assumed that the NpO_2^+ species plays a large role in neptunium sorption on graphite. However, based on the PZC measurements (section 3.1), the graphite surface should have a net positive ionic charge, which should not be favored by the NpO_2^+ species. One explanation would be that even though there exist a net positive intrinsic charge, there are still some deprotonated sites that could complex with NpO_2^+ .

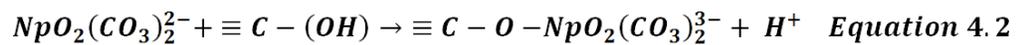
At higher pH values, the speciation becomes dominated by the NpCO_3^{4-} species and the neptunyl ion concentration becomes negligible. The sorption in the pH range remains essentially constant, suggesting that the neptunyl carbonate species is also sorbing onto graphite.

At a minimum, it is reasonable to conclude that both the NpO_2^+ species and some form of the neptunyl carbonate species are both sorbed onto graphite, as each species has a specific pH where essentially all neptunium mass is in the given form. A prospective reaction for the observed NpO_2^+ species seen is shown



A monodentate structure is proposed to achieve an overall electrical neutrality of the surface complex formed. The number of bonds a central metal cation forms with the surface complexing sites (bidentate or polydentate) influences the stability of the surface complex [Essington 2003]. So based on bonding number, neptunium with the proposed monodentate structure seen in equation 4.1 is not as stable as uranium which has a proposed bidentate structure due to electrical neutrality. However, this is not the only possible complex that could be formed on the surface for the particular neptunium species and more study will be needed to determine the right one.

At pH=9.27, the concentration of the free neptunyl in solution is approximately 2.5×10^{-19} M or approximately 0.00000000012% of the total neptunium mass in solution (EQ3/6) at a point where 21.0% of the mass in solution sorbs. As discussed above, a surface complex between some neptunyl carbonate species and the graphite surface is proposed. Another potential reaction that would give an explanation of the data is listed as equation 4.2.



It is hard to make assumptions about which neptunium species is preferentially sorbed onto graphite since, as stated previously, it is thought that sorption is inhibited by another process. An example is shown in table 4.1.

Mass % Concentration		
	pH 7.5	pH 8
NpO₂⁺	97.93%	81.72%
NpO₂CO₃⁻	1.96%	16.36%
NpO₂(CO₃)₂⁻⁻	0.00%	1.83%
Mass Sorbed	28.71%	13.74%

Table 4.1: Mass % Concentration of species and mass sorbed at pH 7.5 and 8.

As seen in table 4.1, from pH 7.5 to 8 there is a 16.56 % drop in NpO₂⁺ mass concentration, while the neptunium mass sorbed to graphite drops 52.14 %. Even if it is assumed that the only sorbing species onto graphite is the NpO₂⁺ species and neptunyl carbonate complex sorption is negligible (unlikely as sorption still occurs when NpO₂⁺ mass concentration approaches zero), there still is a 50 % drop in sorption with only a 16.56 % drop in initial neptunium concentration. A limiting factor is therefore thought to occur for neptunium sorption on graphite.

4.3.1 Borax buffer

The possibility of the buffer to inhibit sorption was evaluated, as the decreases in neptunium sorption was observed when buffer was first introduced to the samples (pH 8) as seen in figure 3.3. Additional experiments were run in that region to try to determine whether the change in mass sorbed was due to the buffer or neptunium speciation. With the original concentration of buffer used (0.0125 M), the pH was initially at 9.2, and required a large amount of acid/base to shift the pH to 8 and 10 respectively. Consequently, those points are where the largest decrease in sorption was seen, and the maximum sorption was observed where the least acid/base was used. Some of the borax

experiments looked at what influence changes in the buffer concentration had on sorption. At the 0.009 M borax concentration, a similar trend to the original buffer concentration was seen except the difference between the maximum and minimum sorption values was decreased. As the concentration of buffer was lowered, less acid/base was needed to overcome the buffer effect and maintain pH 8 and 10. The lowest concentration (0.006 M) of buffer still prevented pH drift, except the initial pH was around 2. The 0.006 M buffered samples required additions of NaOH to achieve the desired pH points (pH 8-10), with the least amount needed for pH 8 and the most base needed for pH 10. The Neptunium mass sorbed followed the trend of the most sorption being seen in pH 8 (least NaOH added) with a decreasing drift ending at the minimum sorption being seen in pH 10 (greatest NaOH added). One possible explanation of the results is that the associated increase in ion concentration with addition of acid/base is inhibiting neptunium sorption to graphite. Ionic species / concentration were evaluated, therefore, for any potential impact of neptunium sorption to graphite.

4.4 Impact of Counter-ions on Sorption

Changing the anion species and, to some extent, the concentration had a large impact on the ability of neptunium to sorb onto the graphite. The species and concentration used for all other experiments (0.01 M NaCl) had the maximum mass percentage sorbed regardless of pH. When the NaCl concentration was increased, the neptunium mass sorbed onto graphite dropped to negligible. When the counter-ion species was switched to ClO₄, the sorption of neptunium to the graphite decreased significantly. The results initially indicate that either perchlorate is inhibiting neptunium sorption or chloride (at concentrations of around 0.01M) is improving sorption. As the

sodium salts were used for both anions, the sodium itself was assumed not to play a significant role in this effect. To explain the chloride and perchlorate results, first the complexation constants for chloride were considered. For chloride complexation the following reactions shown in figure 4.2 can be assumed.

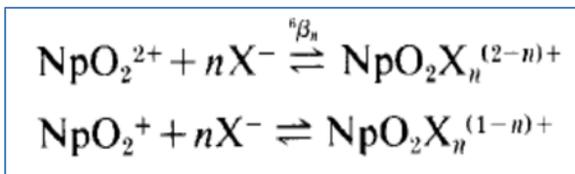


Figure 4.2: Possible Neptunium chloride complexation reactions

Where X is Cl, $n = 1, 2, 3, \dots$, and ${}^6\text{B}_n$ and ${}^5\text{B}_n$ are the stability constants of Np(VI) and Np(V) respectively. It has been reported that ${}^5\text{B}_1$ is not significant when compared with ${}^6\text{B}_1$ (Al-Niaimi et al., 1969) also there has been no indication of Np(V) complexing with more complexing anions such as fluoride and sulphate (Al-Niaimi et al., August 1969). Also, spectroscopic data in acidic 5M NaCl solutions showed a relatively small shift of from the characteristic NpO_2^+ absorption band observed in 0.1M NaCl solution (Runde et al., 1996). The shift observed does not seem to be sufficient to indicate any inner-sphere chloro complexes. Rather, any chloride interactions might better be described by ion association. Perchlorate complexation to neptunium is negligible in comparison to even low chloride complexation (Al-Niaimi et al., August 1969) so is treated as non-existent. Looking to the literature, no information on chloride or perchlorate interactions with graphite was found; as such, the possibility of a surface interaction with perchlorate on graphite may need to be pursued further before excluding it as a source of interference.

By comparing the influence of ionic concentration / anion for both neptunium and uranium sorption, several observations can be made. Both the neptunium and uranium concentration were kept at the same metal concentration in order for a more reliable and qualitative comparison of the two results. From the data in table 3.5, both the anion species and concentration play a significant role for neptunium sorption. For uranium sorption at similar mass concentrations, changes to sorption occurred for different anion conditions, although to a lesser degree. It has been reported that increases in ionic strength, decrease the affinity for outer-sphere sorption on a medium [Essington 2003]. Previous work done on uranium sorption to graphite has reported that the mechanisms consist of both inner and outer-sphere sorption [Schmidt 2010]. If uranium mass sorbed onto graphite was held partially by outer-sphere retention, it could explain why an increase in ionic strength decreases the mass sorbed only moderately. Outer-sphere adsorption could have a greater influence on neptunium sorption to graphite, and is why ionic species / concentration have a much bigger impact.

Regardless, it is clear that neptunium sorption onto graphite is significantly impacted on both ionic species and the concentration, which should be factored in when evaluating modeling the transport of neptunium to the near field.

4.5 Desorption

In many cases when evaluating sorption/desorption mechanisms, there exists an asymmetrical sorption behavior. In other words, sorption kinetics is dependent on initial conditions and is not purely reversible. Various sorption characteristics can have an influence on the sorption/desorption, including the stability of the surface complexation.

To be able to accurately model neptunium transport through a graphite medium in regards to neptunium sorption to graphite the desorption kinetics needs to be understood.

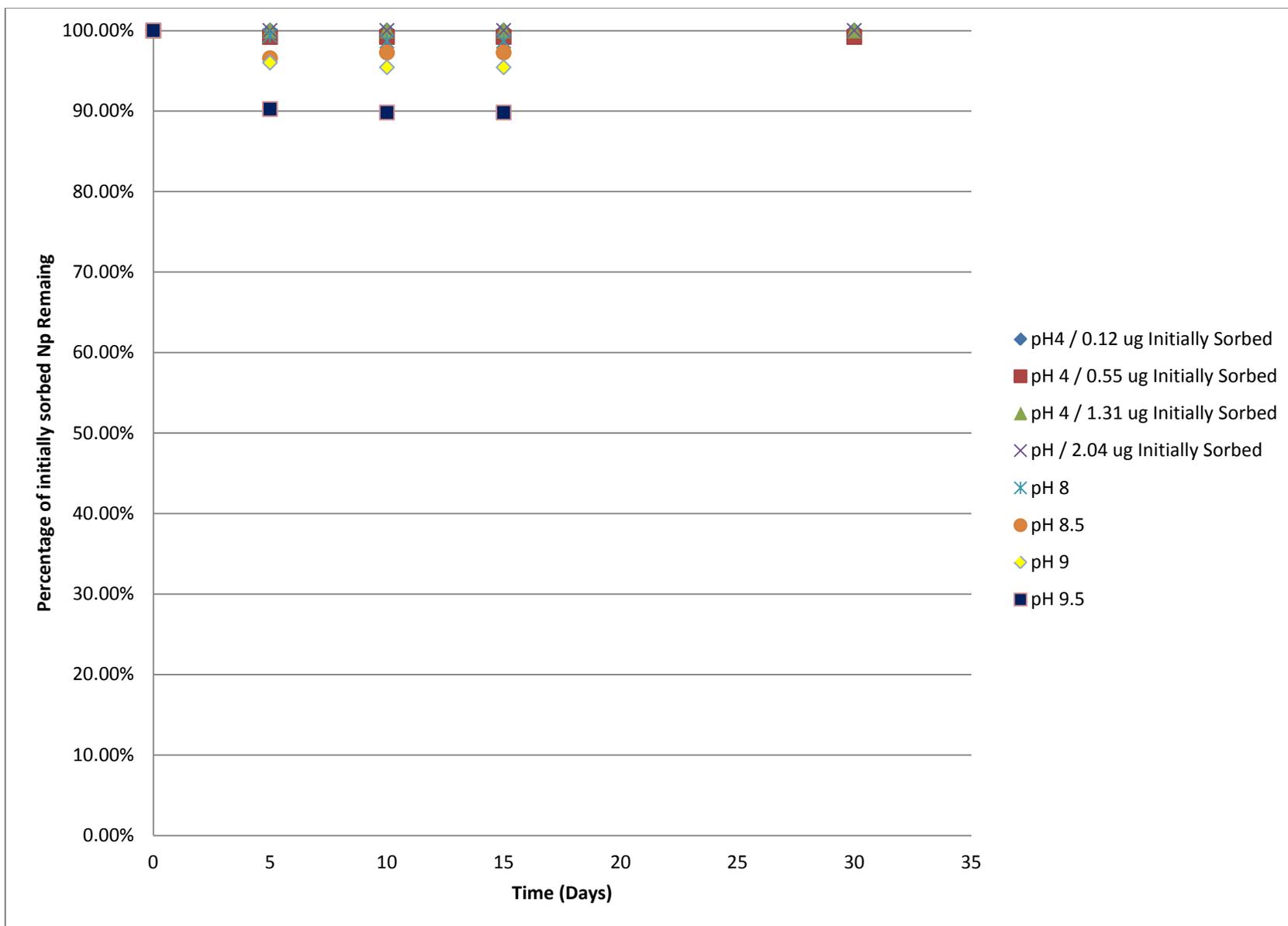


Figure 4.3: Percentage of initial sorbed Np remaining sorbed on graphite with respect to desorption time (differing pH and initial Np mass sorbed)

As seen in figure 4.3, desorption of neptunium from graphite appears to be minimal, even over 30 days. Although desorption of neptunium is low regardless of the initial sorbing conditions, a larger percentage of desorption region is observed for the more alkaline pH. Evaluating speciation in the pH region shows that the neptunyl carbonate species (at least one) is less strongly sorbed than that of the NpO_2^+ species. Even though ionic concentration greatly affected the neptunium mass sorbed onto graphite, it did not seem to have an impact on sorption kinetics. When a blank solution with increased NaCl was introduced to neptunium sorbed graphite, desorption did not change significantly, within experimental variance, from that of a blank solution with 0.01 M NaCl; which can be observed in table 4.2.

Mass/Mass (ug/g)	[NaCl] Blank Solution	% Np Desorbed
0.16	0.01 M	0.00% ± 1.82%
0.22	0.05 M	6.49% ± 4.86%
0.17	0.1 M	3.46% ± 5.56%

Table 4.2: Desorption data for samples under same sorption conditions (pH4, [NaCl]=0.01M) and different NaCl concentrated blank solutions

Difficulty in assessing the desorption data comes from the fact that the neptunium mass sorbed initially to the graphite is low compared to other studies that evaluate desorption kinetics. Uranium desorption studies on graphite have shown a relationship between initial uranium mass available for sorption and desorbed fraction after reaching equilibrium [Schmidt 2010]. As the initial uranium mass in solution during sorption (decrease in mass sorbed onto graphite) is decreased, the fraction of mass desorbed lowers significantly. The lowest desorption fraction for uranium that was evaluated was

at 12 %, where the initial mass sorbed was 5 ug. In comparison the highest initial neptunium sorbed was only 0.8 ug, so it is a reasonable assumption that desorption would be low regardless of the existing desorption characteristics. So neptunium desorption is not necessarily irreversible under any conditions, although for the concentrations examined neptunium has negligible desorption.

4.6 Adsorption Isotherms

Sorption Isotherms were evaluated for a small concentration range for both acidic and alkaline pH as shown in figure 3.5. The main objective of performing an adsorption isotherm study was to attempt to quantitatively describe adsorption under the specific conditions used. The neptunium data was modeled using both the Freundlich and Langmuir equations (4.3 and 4.4 respectively).

From the plotted data, the sorption isotherm appears to follow either an L/C – curved isotherm (figure 1.9). To distinguish between an L/C – curved isotherm, we tried fitting the data to the two most common adsorption isotherms used to describe the L-shaped isotherms, the Langmuir and Freundlich isotherm as described by equations 3.1 and 3.2 [Essington, 2003].

$$q = \frac{bK_L c_{eq}}{(1 + K_L c_{eq})} \quad \text{Equation 4.3}$$

Where,

q = Mass uranium sorbed per mass graphite, $\mu\text{g/g}$

c_{eq} = Conc. of solution after equilibration, $\mu\text{g/ml}$

K_L = Empirical parameter, ml/g

b = Empirical parameter, usually indicated as adsorption maxima, $\mu\text{g/g}$

$$q = K_F c_{eq}^N \quad \text{Equation 4.4}$$

Where,
 q = Mass uranium sorbed per mass graphite, $\mu\text{g/g}$
 c_{eq} = Conc. of solution after equilibration, $\mu\text{g/ml}$
 K_F = Empirical parameter, ml/g
 N = Empirical parameter, dimensionless

The data was fitted to both the Langmuir and Freundlich isotherms to see how well each isotherm describes the data using the coefficient of determination (R^2). The Langmuir isotherm, when fitted, had $R^2 = 0.7485$, which shows that the assumptions built into the Langmuir equation make it non-ideal to describe the neptunium sorption data. The results of the Langmuir fit were not plotted since it was clear that the description would lead to significant error in its assumptions.

A Freundlich isotherm equation was used next and the results of the fit are shown in figure 4.4, where the pH 4 data series is used as the representative sample. The fit was more successful than the Langmuir equation at describing the data with an R^2 value of 0.96. The parameters of the Freundlich isotherm were found by using figure 4.4 and equation 4.4. The resulting Freundlich fit is shown in equation 4.5 for the neptunium data.

$$q = K_F c_{eq}^N = 3.87 c_{eq}^1 \quad \text{Equation 4.5}$$

The data used for the fit as well as the resulting calculated q' and the residual between the observed and calculated q value is shown in table 4.3.

Ceq	q	log Ceq	log q	q'	residual
0.046809	0.159746	-1.32967	0.159746	0.15717	0.002577
0.158521	0.552471	-0.79991	0.552471	0.562978	-0.01051
0.372582	1.308268	-0.42878	1.308268	1.376253	-0.06799
0.516995	2.04467	-0.28651	2.04467	1.938684	0.105986

Table 4.3: Data used for the Freundlich fit and the calculated q' from the fit with resulting residual

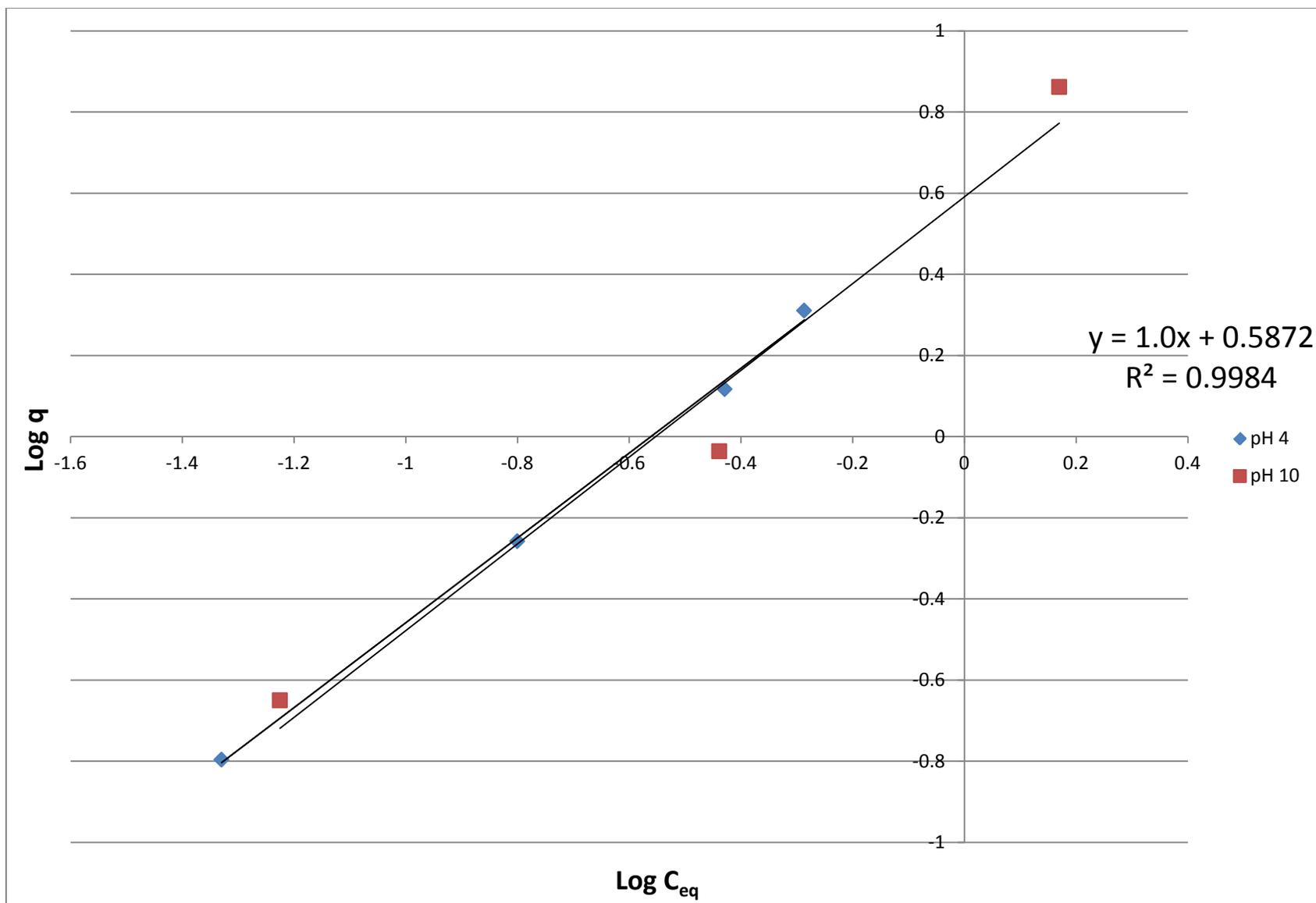


Figure 4,4: Freundlich fit to Neptunium sorption data with the slope = N and the intercept = $\log(K_F)$

The attempt to model the neptunium data to a Langmuir model led to large error in correlation between the data points. Therefore one or more of the built in assumptions for the model, such as a homogeneous surface (adsorption sites are identical) and sorbed species do not interact, was incorrect for neptunium sorption onto graphite. The Freundlich isotherm better fit the Np sorption data, due to the relaxation of a number of key assumptions from the Langmuir model, which allows it to model both linear and L-shaped isotherms. The resulting Freundlich fit is shown in equation 3.3 and some observations can be made from it. It has been shown that N is a measure of the heterogeneity of adsorption sites on the adsorbent surface [Essington 2003]. In the case for neptunium sorption onto graphite, N is equal to one, indicating that there is a high degree of surface homogeneity. Also, the neptunium sorption isotherm is indeed linear (C isotherm) as N describes the curvature of the isotherm for the given concentration range. The adsorption isotherm equation found in equation 3.3 is, however, empirical, and additional data will be needed to evaluate neptunium sorption mechanisms.

4.7 Surface Complexation Models

From the above discussion, an adsorption isotherm for specific solution conditions can be described that quantify sorption as a function of equilibrium neptunium mass in solution. However, the isotherm will not identify the mechanisms of retentions (inner/outer-sphere) or sorbing species. A surface complexation model needs to be evaluated to be able to better predict the distribution of neptunium between the adsorbed and aqueous phases under a variety of conditions.

4.7.1 Comparison of Models (CC, DL, TL)

The Constant Capacitance model assumes that adsorption only occurs through a single surface plane, combination of s and i s plane (figure 1.3). This leads to the model only considering inner-sphere sorption. Also because the model only considers a single surface plane, ionic species/strength is also ignored. The development of a CCM model is not believed to be able to describe the experimental results. Counterion and concentration does have an impact on neptunium sorption to graphite which is the main reason the model was not considered.

The Diffuse layer is more versatile in that it considers both weak outer-sphere adsorbed species as well as strong inner-sphere complexes. It also corrects adsorption for ionic strength using Gouy-Chapman theory [Langmuir, 1997]. However, both the DL and CC model do not explicitly consider electrolyte ions competing for adsorption to the neptunium. As previously noted, ionic species/concentration plays a complex role in neptunium sorption to graphite, and it is unclear how it affects sorption. Until the electrolyte mechanisms on sorption are further evaluated, a model that does not consider electrolyte sorption to graphite would not be ideal to model the experimental data.

The Triple Layer model, however, does account for the adsorption of electrolyte ions, but becomes more complex since it requires intrinsic constants for the electrolyte species. The TL model has the most parameter requirements, as mentioned previously, of all the models discussed but exhibits the most versatility. It is capable of modeling complex systems over a range of pH and solution conditions where all sorbate species (including electrolytes) compete for surface sites and have different sorptive affinities

[Langmuir, 1997]. The modified TLM describes the surface charge by Equation 4.6 below [Essington, 2003].

$$\sigma_{is} + \sigma_H + \sigma_{os} = -\sigma_d \quad \text{Equation 4.6}$$

Where,

σ_{is} = Surface charge contributed from inner-sphere complexes

σ_H = Surface charge from adsorbed hydrogen ions

σ_{os} = Surface charge from outer-sphere cation-anion complexation

σ_d = Charge density of counter-ions

The TL model is the most complex model considered, but is thought to have the required number of parameters to describe the neptunium-graphite system. A complete calculation of the parameters needed to model neptunium sorption to graphite is outside the goals of this thesis, although the Triple Layer Model is thought to have the complexity needed in order to model neptunium graphite interactions.

CHAPTER 5

CONCLUSIONS

High Temperature Gas-Cooled Reactors have benefits for implementation, such as higher thermal efficiency. If commercial deployment becomes wide spread, however, waste considerations need to be made on the new fuel type. One of the waste disposal options considered would include direct disposal of the fuel with the graphite matrix included. Evaluation of the impact of the graphite matrix inclusion on the performance of a geologic repository is therefore required. Specifically, the uranium/neptunium interactions with graphite under environmental conditions need to be determined in order to be incorporate it into a repository performance assessment.

This research has shown that uranium/neptunium sorption mechanisms to graphite are complex due to solution chemistry and the variability in the composition of graphite. However some general conclusions can still be made from the data presented. An increase in temperature was shown to increase sorption to graphite for the uranyl carbonate species, although the specific basis is still unknown. Still, whether speciation or stability constants are affected, temperature considerations need to be evaluated for sorption batch studies. Neptunium adsorption isotherms displayed linear tendencies and led to the hypothesis of a linear partition behavior. For the concentration range explored, the linear partition was confirmed by modeling data to a Freundlich fit, which showed no inflection of the curve and a narrow distribution of adsorption site types. So unlike uranium sorption, which is thought to have a fast acting and a slower sorption process [Schmidt, 2010], neptunium is predicted to have only one sorption process.

Sorption was also shown to be relatively independent of pH except for pH 8 and 9.5 - 10. The only changes in sorption were observed in data points that required large additions of acid/base. A possible explanation is that the large addition of acid/base is increasing the ionic strength to a point at which it inhibits sorption. When the buffer concentration was lowered, a change at pH points that require a large addition of base is seen that follows the decreases in sorption. The counterions are not thought to be directly complexing with the neptunium, however some type of ion association is hypothesized to be occurring that seems to be blocking the surface sites.

Compared to uranium sorption, neptunium sorption to graphite is shown to have less of an impact. The maximum K_d associated with neptunium sorption, at any condition, was measured to be less than 4 ml/g. However due to the little to no desorption measured once sorbed, graphite can still play an important role in neptunium transport. Neglecting neptunium retardation by graphite will therefore always be a conservative estimate, however in certain instances it can lead to large underestimates of repository performance.

5.1 Future Work (Near-Term)

The work done in this thesis has shown interesting phenomena in regards to both uranium and neptunium sorption on graphite. Speculation has been made on possible mechanisms that would explain the particular behavior, however further experimental data is needed before further analysis can be done.

The elevated temperature experiments were only done at two temperatures, and a large amount of sorption occurred on the centrifuge vials at low buffer concentrations. In order to evaluate temperature impact on sorption, both a new temperature data series (80

°C) is needed and the amount of sorption on the vial needs to be reduced by possibly using FEP vials.

More data is needed to evaluate the sorption inhibition at higher NaCl concentration and when switching the counterion from NaCl to NaClO₄. One proposed experiment is to use differing ratios of NaCl to NaClO₄ while keeping ionic strength equal to .01M and evaluate changes in sorption.

Considerations need to be made on new analysis techniques for use in column studies for neptunium. A transport model could be then developed and tested using the new analysis.

A direct investigation of complexed neptunium on graphite was not done in this study. A detailed analysis of neptunium-graphite complexes, possibly using extended X-ray absorption fine structure (EXAFS), would provide more information on the sorption mechanisms of neptunium.

5.2 Future Work (Long-Term)

Further work is also needed to increase our understanding of the behavior of spent fuel transport through a graphite matrix in a waste repository environment. New work is needed to update repository models for inclusion of a large graphite mass in the spent fuel.

Other radionuclides of interest in spent fuel, such as plutonium and technetium, need to have similar studies done to assess potential surface complexations or sorption mechanisms on graphite.

As the graphite properties are very dependent on the manufacturing, even among same procedures, experiments on the effect of different graphite on sorption needs to be

done. Assessing different ratios of graphite to graphite oxide using methods for oxidizing graphite can be used to examine what role graphite oxide functional groups play on sorption, for example.

As a specific waste repository is still in question, the environmental conditions are unknown. As a consequence, investigating reducing conditions on uranium and neptunium sorption on graphite for repository reducing groundwater is needed.

The TL model was proposed for both the neptunium and uranium sorption studies, however was left undeveloped. The completion of the model would allow the examination of the stability constants for specific complexations and an assessment on the ideal model for sorption to graphite could be accomplished.

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VITA

Graduate College
University of Nevada, Las Vegas

Corey Christopher Keith

Degrees:

Bachelor of Science, Physics, 2010

University of Texas at El Paso

Thesis Title: Evaluating Actinide Sorption to Graphite with Regards to TRISO

Repository Performance

Thesis Examination Committee:

Chairperson, Gary Cerefice, Ph. D.

Committee Member, Ralf Sudowe, Ph. D.

Committee Member, Steen Madsen, Ph. D.

Graduate faculty Representative, Vernon Hodge, Ph. D.