Understanding the Thermodynamics of Actinide Speciation at Solid and Water Interfaces through Self-Consistent Surface Complexation Modeling (SCM)

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UNDERSTANDING THE THERMODYNAMICS OF ACTINIDE SPECIATION
AT SOLID AND WATER INTERFACES THROUGH SELF-CONSISTENT
SURFACE COMPLEXATION MODELING (SCM)

A Dissertation
Presented to
the Graduate School of
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Doctor of Philosophy
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by
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ABSTRACT

This study focused on understanding the energetics and thermodynamics of actinide interactions at different solid and water interfaces. Interactions at three model interfaces were studied: goethite (an Fe hydroxide; FeOOH), kaolinite (a clay mineral; \( \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \)) and graphene oxide (a synthetic sorbent). Batch sorption experiments under variable conditions (i.e., temperature, aerobic/anaerobic, ionic strength and actinide concentrations) were conducted and the experimental results were simulated by an electrostatic surface complexation model (SCM) based on thermodynamics.

For the goethite and kaolinite system, the redox complicated Pu interactions at these two systems were studied under variable temperatures and aerobic/anaerobic conditions, respectively. An overall endothermic process for Pu(IV) sorption to goethite was observed by the batch sorption experiment at variable temperatures. Positive enthalpy and entropy (27.9 ± 11.8 kJ/mol and 173.4 ± 28.4 J/K/mol) for Pu(IV) sorption to goethite were extrapolated through a van’t Hoff plot, indicating an entropy driven inner sphere complexation of Pu to goethite. Similar batch sorption of Th(IV), with stable oxidation state, to goethite at variable temperature was conducted as a comparison. Positive enthalpy and entropy (57.8 ± 18.4 kJ/mol and 249.6 ± 68.5 J/K/mol) were also extrapolated through a van’t Hoff plot, meaning a similar entropy driven inner sphere complexation of Th(IV) to goethite. For the Pu-kaolinite system, different sorption patterns were observed for Pu sorption under aerobic and anaerobic conditions, caused by the Pu oxidation state transformations. The oxidation of Pu(IV) to Pu(V) in the aqueous phase was observed at
bench-top in both Pu-goethite and Pu-kaolinite systems; while a reduction of Pu(IV) to Pu(III) in the aqueous phase was observed during the batch experiment of Pu(IV) sorption to kaolinite under anaerobic condition. The batch sorption results involving Pu at room temperature were all modeled through a redox-coupled SCM, which simulated both the sorption as a function of pH and the Pu oxidation state distribution in the aqueous phase. Ion exchange process was also observed for Pu sorption to kaolinite by batch sorption experiment under variable ionic strength, this process was also modeled by coupling an ion exchange model to the SCM based on Vanselow convention.

For the graphene oxide (GO), the sorption of actinide/its analog in all four oxidation states (Eu(III), Th(IV), Np(V), U(VI)) was studied through batch sorption experiments and SCM. The protonation and deprotonation of GO were characterized through a series of acid/base titrations of GO with variable concentrations, and the primary sorption sites (carboxylic and sulfonate) of GO were identified and quantified by SCM of the titration data. The overall strong and high sorption capacities of actinides and Eu(III) to GO were observed during the batch sorption experiments as a function of pH and analyte concentration as well as modeled based on the same SCM. In addition, a linear free energy relationship was observed between the stability constants of these actinides and Eu(III) complexation to the carboxylic sites on GO and their complexation to carbonate in the aqueous phase. Furthermore, the enthalpies for Eu(III) and U(VI) complexation to GO were calculated directly based on the heat release measurements obtained from isothermal titration calorimetry (ITC) and the SCM of Eu(III)/U(VI) speciation at the GO surface.
Overall, SCM of actinide interactions developed based on batch sorption experiments is capable of modeling the interfacial reactions under variable conditions and sheds light on the mechanism and energetics for sorption. Therefore, SCM based on batch sorption experiment is a robust approach to understand the interactions at solid and water interfaces. Specifically, the redox-coupled SCM, capable of modeling redox reactive elements, will improve the understanding of redox reactive elements partitioning at the interface.
DEDICATION

To all the people I love.

To people who suffered from environmental hazards related diseases.

To a better home.
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CHAPTER 1

INTRODUCTION

Significant amounts of actinides (mostly Pu, and smaller amounts of Np, Am, and Cm) were produced from nuclear weapon production since the start of Manhattan Project in 1939. In addition, the generation of commercial nuclear power produces spent nuclear fuel (SNF) in which a range of transuranic elements, including metric ton quantities of Pu, have been produced and must be safely stored. The global inventory of Pu was ~1,900 tons by 2010 and growing by 70 to 90 tons per year, retained in both SNF and nuclear weapon stockpiles.\(^1\) Although large amounts of other fission products (e.g., \(^{137}\text{Cs},^{90}\text{Sr}\)) are present in the legacy weapon waste and SNF, most of them are short-lived and will decay to stable isotopes within 100 years. Conversely, actinides within the waste have long half-lives (e.g., \(t_{1/2} (^{239}\text{Pu}) = 2.4 \times 10^4\) years, \(t_{1/2} (^{237}\text{Np}) = 2.1 \times 10^6\) years), which account for the primary long term radio-toxicity and require extra caution for proper containment and waste management. Even trace quantities of actinide elements must be carefully monitored and controlled to ensure the protection of human and environmental health. For examples, the United States Environmental Protection Agency (US EPA) has regulated the gross alpha particles in drinking water at less than 15 pCi/L (0.56 Bq/L), for \(^{239}\text{Pu}\), that is \(10^{-12}\) M. Overall, the fate of actinides in the environment determines whether nuclear power is viewed as an environmental “friendly” source of energy.\(^1\)

For permanent disposal of nuclear wastes, the plan is to contain them in engineered barriers and store them in deep geological repositories as a secondary barrier.\(^2\) It is an
international consensus that deep geological burial is the best option to sequester radionuclides and protect the human population and biosphere. However, the engineered barriers will inevitably breach after a long period of time, and actinide transport in the subsurface is predicted to be the primary contributor of radio-toxicity.

In the United States, the commercial nuclear waste and the legacy nuclear waste produced from weapon production are treated separately. Therefore, separate treatment and disposal option for each waste stream is under consideration. Yucca Mountain, NV, was selected as a potential permanent geological repository for the SNF from commercial nuclear power production. However, it is no longer under consideration due to unsolved scientific and technology issues. The SNF is currently stored onsite at over 100 locations in either spent fuel pools or dry cask storage. A permanent repository site for the SNF is still under investigation. The Waste Isolation Pilot Plant (WIPP) in Carlsbad, NM was built as the permanent geological repository to accept the transuranium waste (TRU) and the low level waste (LLW) from nuclear weapon production. With a capacity of over 170,000 m³ for the TRU, WIPP has been successfully operated for 15 years except for an accident releasing radionuclides to the atmosphere after a chemical explosion in February 2014. Currently, there is no operating facility to accept the large volumes of HLW produced from weapon production (approximately 340,000 m³ of liquid waste), which are temporarily stored in underground tanks at the Hanford Site in Washington and the Savannah River Site in South Carolina. At the Hanford Site, 67 out of 117 underground tanks are suspected to be leaking approximately 5700 m³ of HLW, resulting in more than a million curies of radionuclides exposed to the subsurface. At the Savannah River Site,
nine out of 48 tanks have leaked waste into their secondary containments; one of them overflowed the secondary containment resulting in tens of liters of HLW released to the subsurface. These subsurface contaminations and the potential of additional subsurface releases of actinides make the understanding of the subsurface migration of actinides a vital undertaking.

Actinide interactions at the solid (such as sediments, rock, and colloids) and water interfaces are the primary controls for the mobilization of actinides in the subsurface, particularly for actinides at environmental concentrations ($10^{-8}$ to $10^{-15}$ M), which are below their solubility limits. The term “interactions” is an overall term to capture many potential reactions at the solid and water interfaces including aqueous complexation, sorption (surface complexation), surface-mediated redox reactions, electrostatic attraction and repulsion, surface precipitation, and counter-ion competition. Each of these potential reactions may affect actinide transport in the subsurface. However, understanding these reactions for actinides is complicated because of the fact that light actinides can present in four different oxidation states (III, IV, V, and VI) under environmental conditions and these oxidation states exhibit different mobilities in the environment owing to their different affinities to ligands and minerals. Moreover, some light actinides such as Np, U, and Pu can present in more than one oxidation states in the environment and are subject to change depending on the environment conditions. In addition, the heterogeneity of the subsurface environments (e.g., differences in mineralogy and petrology, percentage of natural organic matter and redox condition) increases the difficulty in understanding the transport of actinides in the subsurface. Last but not least, the radioactive decay of fission products in
the HLW elevates the temperature in the subsurface, which also affects the actinide partitioning at the solid and water interface. Because of all the complications stated above, empirical approaches are not capable of providing valid predictions of actinides transport in the subsurface. Instead, a detailed and thermodynamically-based understanding of the actinide speciation at the solid and water interfaces is a key research need to predict the subsurface transport of actinides, to provide scientific insight for the selection of geological repositories, as well as to design better plans for nuclear waste remediation, separation, and management.

The complexity of actinide geochemical speciation discussed above is clearly illustrated by plutonium behavior. Plutonium was generally considered to be immobile in the subsurface due to the predominance of Pu(IV) in the environment that exhibits a low solubility and high affinities for mineral surfaces. However, far-field transport events of Pu were observed both at the Nevada Test Site, USA and the Mayak site, Russia\textsuperscript{8-10}, where significant amounts of Pu have migrated several kilometers from their source over decades. At both sites, the strong sorption of Pu(IV) to mineral colloids was proposed to facilitate the enhanced transport. The observed far-field transport requires scientists to reevaluate the geochemical behaviors of Pu and develop a more accurate prediction of its subsurface transport. A reactive transport model that accounts for the chemical and physical changes of the actinides and geochemical heterogeneity in the subsurface could provide a better understanding of radionuclide fate and transport.\textsuperscript{11}

In order to predict the transport of actinides, the key chemical processes for their subsurface transport need to be understood and quantified. However, the distribution
coefficient ($K_D$) and retardation factor ($R$) approach that is traditionally used in transport modeling are not sufficient to give an accurate prediction of the transport for elements with complex chemistry such as Pu in the subsurface primarily because the $K_D$ value is a subject to change as environmental parameters such as the pH, dissolved ion concentrations, the redox potential ($E_H$), and the concentrations of organic matter change. The $K_D$ values measured from experiments conducted in the lab are only appropriate for the experimental conditions under which they were measured. However, as all natural systems are subject to change (e.g., the level of the water table, temperature, $E_H$, and pH), a single $K_D$ value is not able to capture these potential variations under environmental conditions that further influence the partitioning of element as it moves in the subsurface. Rather, a semi-empirical surface complexation modeling (SCM) approach, which is capable of quantifying actinide interfacial reactions at the solid and water interface through thermodynamically-based stability constants ($K_s$), has the potential to provide a better simulation of the actinide reactions at interfaces under variable environmental conditions. The stability constants for actinide sorption to surfaces are commonly simulated by curve fitting of a batch experiment of its sorption to pure mineral/synthetic material under variable conditions (e.g., pH, $E_H$, temperatures and background electrolyte). As noted above, many crucial factors, such as the aqueous hydrolysis and complexation, the changes of pH, and the presence of competing ions can influence the actinide interactions at the interface. These factors can all be taken into account by using the SCM approach. Therefore, the SCM is a more suitable approach to interpret the actinide interactions at the solid and water interface than the traditional approach using $K_D$. 
The objective of this work is to understand the energetics and mechanisms of actinide interfacial reactions with different types of model surfaces (Fe-hydroxide, clay, and synthetic graphene oxide) via surface complexation modeling (SCM) of macroscopic batch sorption data, spectroscopic studies, and isothermal titration calorimetry (ITC). The macroscopic experimental data was simulated using SCMs to quantify the underlying Gibbs free energy ($\Delta G$), enthalpy ($\Delta H$), and entropy ($\Delta S$) that control the interfacial reactions. SCM is a geochemical modeling approach based on the thermodynamics that simulates the target actinide speciation at the solid and water interfaces under variable conditions (e.g., different pH, $E_H$, and ionic strength). This study also incorporated the Pu redox reactions into SCM to improve the modeling of the redox speciation and interfacial interactions of Pu. Stability constants calculated from these SCMs for the interfacial reactions can be further applied for transport model to provide an improved prediction on the transport of actinide. The knowledge gained from this work can be used to evaluate actinide behavior in natural systems as well as to help design novel sorbents for separation/remediation of high-level actinide waste.
CHAPTER 2

BACKGROUND

2.1 General Actinide Chemistry

The actinides (An) are a group of elements ranging from actinium (N=89) to lawrencium (N=103), located at the bottom of a periodic table representing elements possessing 5f orbitals. The 5f orbitals extend far from the nucleus allowing them to participate in bonding and giving rise to a range of possible oxidation states of the “light” actinides (up to Americium (Am), N=95) ranging from III to VI in the environment. Beyond Am, the contraction of the ionic radii and shielding of the 5f orbitals makes the “heavy” actinides predominantly exist as trivalent ions similar to the 4f lanthanide series. The complex chemistry of the “light actinide” will be the major subject in this study. The possible oxidation states of the light actinides are listed in Table 1 and the dominant oxidation state(s) in the environment are indicated with bold characters. Thorium, neptunium, and uranium primarily exist as tetravalent, pentavalent, and hexavalent oxidation states, respectively, in aqueous systems. Both neptunium and uranium can persist as tetravalent species as well under reducing conditions. Plutonium is anomalous and unique on the periodic table because it can simultaneously exist in four oxidation states in solution. The variability in Pu oxidation states and sensitivity to redox transformations are a manifestation of the shift from itinerant to localized electron behavior, which is the transition between the light and heavy actinide elements.
The high positive nuclear charge and large ionic radii of the actinides lead to high coordination numbers and a strongly bound hydration sphere of waters around aqueous ions. Actinides in different oxidation states in general possess a different number of coordinating water molecules. In aqueous systems, the hydration coordination numbers are 9 – 10 for An\(^{3+}\), 9 – 12 for An\(^{4+}\), 4 – 5 for AnO\(_2^+\) and 5 – 6 for AnO\(_2^{2+}\).\(^{12}\) Figure 1 presents examples of the coordination water model for An(III/IV) and An(V/VI). The number of coordination water molecules influences the interaction of actinides with both aqueous species and surface species, because some or all of the coordination waters around actinides need to be removed in order to form inner sphere complexes between actinides and other compounds.

Table 1 Oxidation states of light actinides\(^{12}\) (The dominant environmental oxidation states are bolded.)

<table>
<thead>
<tr>
<th></th>
<th>Th</th>
<th>Pa</th>
<th>U</th>
<th>Np</th>
<th>Pu</th>
<th>Am</th>
<th>Cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>III</td>
<td>III</td>
<td>III</td>
<td>III</td>
<td>III</td>
<td>III</td>
<td>III</td>
<td>III</td>
</tr>
<tr>
<td>IV</td>
<td>IV</td>
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<td>IV</td>
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<td>IV</td>
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<td>V</td>
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<td>V</td>
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<tr>
<td>VI</td>
<td>VI</td>
<td>VI</td>
<td>VI</td>
<td>VI</td>
<td>VI</td>
<td>VI</td>
<td>VI</td>
</tr>
<tr>
<td>VII</td>
<td>VII</td>
<td>VII</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1: Possible molecular geometries for actinide and coordinating waters. Left: An(III/IV), right: An(V/VI) (Figure adapted from Clark, 2000\(^{13}\)). Green ball represents actinide atom, red ball represents oxygen, and white ball represents hydrogen.
The oxidation states further affect the molecular structure of actinides in the aqueous phase. Actinides in trivalent and tetravalent states are present as simple hydrated ions (An$^{3+}$ and An$^{4+}$) in the aqueous environment. While the actinide in pentavalent and hexavalent states, possessing higher positive nuclear charges, readily strip oxygen atoms from water molecules and form a unique structure with linear double bonds to two oxygen atoms (O=An=O) above and below the equatorial plane of the ion. Therefore, actinides in pentavalent and hexavalent states persist as AnO$_2^+$ and AnO$_2^{2+}$, respectively. These species are referred to as actinyl ions.

The different molecular configurations of each oxidation state further dictates the complexation strength and mobility of actinides in the environment. Because of the axial oxygen atoms, the effective charges for An(V)O$_2^+$ and An(VI)O$_2^{2+}$ are lowered from +5 and +6 to ~+2.2 and ~+3.3, respectively. The higher effective charge relative to the formal charges of 1 and 2 for the An(V) and An(VI) ions is due to the exposure of the strong nuclear charge about the equatorial plane. Therefore, the complexation strength of actinides for both aqueous compounds and sorption follows the effective charge instead of the formal charge, which yields the general trend:

\[ \text{An(IV)} > \text{An(VI)} \approx \text{An(III)} > \text{An (V)} \].

Actinides in the tetravalent state possess the strongest affinity for sorption and complexation in the aqueous phase. Hexavalent actinides and trivalent actinides exhibit similar complexation affinities and the pentavalent state has the least affinity for complexation. Following this trend, thorium is the least mobile actinide since it is stable only in the tetravalent state. It readily forms the hydrolyzed species, exhibits strong
sorption to mineral surfaces and can precipitate as insoluble ThO$_2$ or Th(OH)$_4$. Np(V) is generally more mobile than other actinides due to its stability in the pentavalent state which has the weakest affinity for complexation and sorption. The mobility of U, Np and Pu is more complicated mainly due to the fact that they can exist in more than one oxidation state under environment conditions. Thus the mobility of U, Np, and Pu is highly dependent on the redox conditions and the oxidation state of the actinide. The case for Pu is extremely complicated and unique, because of the similarity in reduction potentials, Pu often coexists in more than one oxidation states and is highly sensitive to changes in the environment.

Because of the high positive charge, actinides readily interact with inorganic and organic ligands as well as minerals. In general, actinides form multiple hydrolysis products in water even at very low pH. For example, Pu can form multiple hydrolysis products in all four oxidation states (Table 2). Besides hydrolysis, actinides form aqueous complexes with various common anionic ligands present in natural systems such as carbonate, sulfate, phosphate, chloride, fluoride, nitrate and silicate. The general trend in strength of complexation for these ligands is shown below:

$$\text{OH}^-, \text{CO}_3^{2-} > \text{F}^-, \text{HPO}_4^{2-}, \text{SO}_4^{2-} > \text{Cl}^- \text{ NO}_3^-.$$  

<table>
<thead>
<tr>
<th>Reaction stoichiometry</th>
<th>log $\beta^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu (III)</td>
<td></td>
</tr>
<tr>
<td>$\text{Pu}^{3+} + \text{H}_2\text{O} \rightarrow \text{Pu(OH)}^{2+} + \text{H}^+$</td>
<td>-6.9</td>
</tr>
<tr>
<td>$\text{Pu}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{Pu(OH)}^{2+} + 2\text{H}^+$</td>
<td>-15</td>
</tr>
<tr>
<td>$\text{Pu}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Pu(OH)}^{3+} + 3\text{H}^+$</td>
<td>-26.5</td>
</tr>
<tr>
<td>Pu (IV)</td>
<td></td>
</tr>
<tr>
<td>$\text{Pu}^{4+} + \text{H}_2\text{O} \rightarrow \text{Pu(OH)}^{3+} + \text{H}^+$</td>
<td>0.6</td>
</tr>
<tr>
<td>$\text{Pu}^{4+} + 2\text{H}_2\text{O} \rightarrow \text{Pu(OH)}^{2+} + 2\text{H}^+$</td>
<td>0.6</td>
</tr>
</tbody>
</table>
PuO$^{2+}$ + H$_2$O $\rightarrow$ PuO$_2$(OH)(aq) + H$^+$ $<$-11.3

PuO$_2$$^{2+}$ + 2H$_2$O $\rightarrow$ (PuO$_2$)$_2$O$^{2+}$ + 2H$^+$ -7.5

*The log β is corrected to zero ionic strength using specific ion interaction theory (SIT).

2.2 Plutonium Redox Chemistry

Plutonium can present in the aqueous environment with four oxidation states: Pu(III), Pu(IV), Pu(V), and Pu(VI). Because of the similarity in the reduction potentials (Table 3), two or three Pu oxidation states can exist simultaneously in different proportions in the same solution. Generally speaking, aqueous Pu(III) is only stable under acidic/reducing conditions; as pH and E$_H$ of the environment increase, the more oxidized Pu(IV), Pu(V), and Pu(VI) become stable and dominant species in the aqueous phase. The redox half reactions for all environmentally relevant Pu oxidation states are tabulated in Table 3. It can be seen that both pH and E$_H$ of the environment have profound influence on plutonium oxidation state in the aqueous phase. The redox reactions for Pu(IV)/Pu(III) and Pu(VI)/Pu(V) are only dependent on the E$_H$ of the environment; while for Pu(V)/Pu(VI) and Pu(VI)/Pu(IV), pH also has a strong influence. A pH-E$_H$ diagram of Pu speciation in water at 25°C is presented in Figure 2. The Pu oxidation state changes significantly as a function of pH and E$_H$. Coexistence of two oxidation states is common and at certain pH and E$_H$ values, Pu can exist in three oxidation states. The influence of pH on the hydrolysis
reactions for each oxidation state is seen as reducing the charge of the ion as pH increases, which generally leads to the formation of insoluble hydrolysis products.

<table>
<thead>
<tr>
<th>Redox Pair</th>
<th>Redox Half Reaction</th>
<th>pH 0</th>
<th>pH 8</th>
<th>pH 14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu(IV)/Pu(III)</td>
<td>Pu^{++} + e^- = Pu^{3+}</td>
<td>0.98</td>
<td>-0.39</td>
<td>-1.04</td>
</tr>
<tr>
<td>Pu(V)/Pu(IV)</td>
<td>4H^+ + PuO_2^{2+} + e^- = Pu^{4+} + 2H_2O</td>
<td>1.17</td>
<td>0.7</td>
<td>0.52</td>
</tr>
<tr>
<td>Pu(VI)/Pu(V)</td>
<td>PuO_2^{2+} + e^- = PuO_2^{+}</td>
<td>0.92</td>
<td>0.60</td>
<td>0.16</td>
</tr>
<tr>
<td>Pu(VI)/Pu(IV)</td>
<td>4H^+ + PuO_2^{2+} + 2e^- = Pu^{4+} + 2H_2O</td>
<td>1.04</td>
<td>0.65</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Data are from Choppin\textsuperscript{16}; the unit is in volt.

Figure 2: $E_{H}$ – pH diagram for plutonium. Plot based on LLNL thermochemical database created in Geochemist Workbench v8. (T = 25 °C, P = 1.013 bars, [Na\textsuperscript{+}] = 0.01 M, [Cl\textsuperscript{-}] = 0.01M)
Besides the profound influence from pH and E$_H$, some factors such as the presence of complexing inorganic anions, dissolved organic matter, and mineral surfaces can influence the Pu oxidation state. Pu(V) is measured as the dominant Pu oxidation state in the ocean due to the high redox potential and high carbonate concentration in the seawater as well as Pu(IV) generally has a stronger affinity for mineral surfaces. Dardenne et al. observed that Pu(IV) is the predominant species in groundwater with high humic content, regardless if Pu(III), Pu(IV), or Pu(VI) is the initial oxidation state added to the experiment. The reduction of Pu(V) to Pu(IV) facilitated by humic acid was also observed by Andre and Choppin, their study also showed that the presence of divalent cations and exposure to light increased the rate of Pu(V) reduction.

Mineral surfaces and soils have also been shown to alter Pu oxidation state. Many studies indicated that Pu(IV) is the dominant sorbed species on mineral surfaces which is facilitated by surface-mediated Pu(V) reduction. Reduction of Pu(V) to Pu(IV) has been frequently observed on many “non-reducing” minerals such as hematite and quartz. However, the underlying mechanism is still unknown. Some studies also observed Pu(III) associated with a solid phase. Kaplan et al. detected 37% Pu(III) along with 67% Pu(IV) in a lysimeter study with SRS sediment using X-ray absorption near-edge spectroscopy (XANES) analysis. Lujaniene et al. also measured over 10% Pu(III) associated with clay and goethite with initial trace concentration of Pu(IV) and Pu(V) ($10^{-10}$ – $10^{-11}$ M) by solvent extraction technique.

A variety of techniques have been developed to determine the Pu oxidation states at different concentrations in the aqueous phase (Table 4). Solvent extraction and
lanthanum fluoride co-precipitation techniques are capable of separating Pu oxidation states at ultra-trace level (\(<10^{-10} \text{ M}\)).^{30-32} However, these methods may shift the Pu chemical and redox equilibrium during the experiment.\(^\text{16}\) In contrast, spectroscopic and spectrophotometric techniques measure the oxidation states directly but usually require much higher concentration.\(^\text{33}\) Recently developed capillary electrophoresis with inductively coupled plasma mass spectrometry (CE-ICP-MS) reported a lower detection limit for Pu oxidation state measurement.\(^\text{34}\)

| Table 4 Selected techniques for Pu oxidation state measurements and their detection limits |
|---------------------------------|----------------------------------|
| Technique                       | Approximate Detection Limits     |
| X-ray absorption spectroscopy   | \(10^{-1}–10^{-8} \text{ M}\)    |
| ultra-violet- visible light absorption spectroscopy | \(10^{-5}–10^{-6} \text{ M}\) |
| Laser-Induced Photoacoustic Spectroscopy | \(10^{-5}–10^{-9} \text{ M}\) |
| CE-ICP-MS                       | \(10^{-8}–10^{-10} \text{ M}\)   |

Information assembled from Choppin\(^\text{16}\) and Burger et al.\(^\text{34}\)

2.3 Observations of Actinide Subsurface Transport

Four major chemical processes play important roles in actinide transport in the subsurface: precipitation, complexation, sorption, and colloid formation.\(^\text{14,16}\) Precipitation can occur if the concentration of actinide in the solution exceeds its solubility. Precipitation will limit the actinide concentration in the aqueous phase, and limit the overall mobility of actinides in the subsurface. Actinides form aqueous complexes with dissolved organic/inorganic ligands as discussed above. Of particular note are actinide complexes with natural organic matter such as humic acid which can drastically alter subsurface transport.\(^\text{9,35-38}\) Formation of actinide complexes with inorganic and organic ligands can increase the solubility of actinides as well as alter the sorption affinity. For example, complexation of \(\text{UO}_2^{2+}\) with
carbonate can enhance uranium solubility in the aqueous phase and cause desorption of uranium at high pH values.\textsuperscript{39} Sorption to mineral surfaces is one of the most important factors that retard actinide subsurface transport. Actinides can sorb to common metal (hydr)oxide and silicate minerals such as goethite (FeOOH), hematite (Fe_{2}O_{3}), kaolinite (Al_{2}Si_{2}O_{5}(OH)_{4}) and quartz (SiO_{2}), and be removed from the aqueous phase that will limit transport.\textsuperscript{40-42} During the past 20 years, concern and attention was raised by colloidal facilitated transport of actinides prompted by observations of far-field transport of Pu at the Nevada Test Site, USA, and Mayak Site, Russia.\textsuperscript{8,10} Colloids can be defined as organic/inorganic solids in the size ranges from 1 nm to 1000 nm that remain suspended in water.\textsuperscript{43} Although the mass percentage of mobile colloids in the subsurface may not be high, actinide complexes with colloids may move further in the subsurface depending on the physical and chemical property of the colloid. Actinides may also form intrinsic colloids, such as PuO_{2}, that could be mobile in the subsurface.\textsuperscript{44,45} Studies of Pu transport in the vadose zone with SRS sediments using mid-term (2–11 years) field lysimeters and laboratory column studies\textsuperscript{46-48} indicated that the transport of Pu varied with different Pu source oxidation states. These studies indicated that the redox reactions of Pu affect its transport in the subsurface. To better model the Pu transport in the subsurface, the Pu redox reactions need to be taken into account.

\textbf{2.4 Mineral Surface Chemistry}

The interaction of water with mineral surfaces produces large, reactive, and possibly catalytic surface sites (Figure 3).\textsuperscript{49} Although different minerals have different lattice structures, the surfaces are generally covered with hydroxyl groups in the presence
of water as illustrated in Figure 3c. The surface hydroxyl groups are highly reactive and form coordinative bonds with ions that are similar to ligand complexation in the aqueous phase (illustrated in Equations 1 and 2). As shown in Equation 2, the hydrolyzed surface site is generalized as $\equiv$SOH species; the coordinative bonding of an ion to a surface hydroxyl group is then written in a reaction that is similar to an aqueous complexation and named as a surface complexation.

$$\text{R} - \text{COOH} + \text{Pu}^{4+} = \text{R} - \text{COOPu}^{3+} + \text{H}^+ \quad \text{(Aqueous complexation)}$$  \hspace{2cm} \text{Equation 1}

$$\equiv \text{SOH} + \text{Pu}^{4+} = \equiv \text{SOPu}^{3+} + \text{H}^+ \quad \text{(Surface complexation)}$$  \hspace{2cm} \text{Equation 2}

Surface complexation is based on the generalization of the mineral surface as an amphoteric surface $\equiv$SOH, which goes through protonation and deprotonation reactions (shown in Equations 3 and 4) as a function of pH of the solution. The log $K^+$ and log $K^-$ are referred to as surface acidity constants and can be determined from acid/base titrations of mineral suspensions. Different minerals have different acidity constants, which fundamentally dictates their surface charge and ability to attract or repel ions. For example, actinide sorption to various metal oxides generally decreases in the series iron $>$ aluminum $>$ titanium $>$ silica oxide.\textsuperscript{49} The surface speciation can be calculated from Equations 3 and 4, where at pH values lower than log $K^+$, the mineral surface will be dominated by protonated
surface species \([\equiv \text{SOH}^+]\) and at pH values higher than \(\log K^+\), the mineral surface will be dominated by deprotonated surface species \([\equiv \text{SO}^-]\). Another important reference value for surface protonation is the pH value where the net surface charge is zero (pH\(_{\text{PZC}}\)). This is the pH measured in an acid/base titration where the net acid-base added is zero. In general, minerals with lower pH\(_{\text{PZC}}\) will be deprotonated at lower pH and the surface will become more negative which facilitates cation sorption. Conversely, minerals with higher pH\(_{\text{PZC}}\) values will remain positively or neutrally charged until the deprotonated surface sites develop at pH > pH\(_{\text{pzc}}\). Writing the surface complexation reactions (including \(\equiv \text{SOH}\) as an approximation of the surface site) into typical chemical reactions, mineral surface protonation and actinide sorption can be simultaneously modeled and coupled to the relevant aqueous complexation reactions.

\[
\begin{align*}
\equiv \text{SOH} + H^+ &= \equiv \text{SOH}^2+ & \log K^+ & \text{Equation 3} \\
\equiv \text{SOH} &= \equiv \text{SO}^- + H^+ & \log K^- & \text{Equation 4}
\end{align*}
\]

The chemistry of actinides as discussed in previous sections also affects the surface complexation. The positive charges of actinides lead to an overall increase in actinide surface complexation to minerals with increasing pH as more negative-charged surface sites are available. Another overall trait is that actinide sorption affinity, similar to its aqueous complexation or hydrolysis, follows the effective charge as: An(IV) > An(VI) \(\approx\) An(III) > An(V) discussed previously. Figure 4 shows the sorption of actinides with different oxidation states to hematite as an example of the trend due to the effective charge.
In addition to surface complexation to the hydrolyzed mineral surface, actinides can also sorb to minerals via the permanent negative-charged site caused by isomorphic substitution of higher valent cation by lower valent cation in the mineral structure. For example, the substitution of Si(IV) by Al(III) in many clay minerals such as montmorillonite, kaolinite, and illite. This sorption process is named as ion exchange, and is independent of pH but affected by ionic strength of the solution. It is common for actinide sorption to clay mineral to occur through both surface complexation and ion exchange process.

2.5 Surface Complexation Modeling

Surface complexation modeling (SCM) is a thermodynamically-based chemical modeling approach developed in the 1970s for the purpose of modeling interfacial reactions in a manner that accounts for changing chemical environments. Several different types of models based on different assumptions have been developed, such as the constant
capacitance model, triple layer model, and diffuse layer model. Essentially the SCMs incorporate surficial reactions into typical speciation modeling programs that allow the user to simultaneously model the aqueous and surface speciation. The reactions described by the SCM are quantified using thermodynamically-based stability constants for reactions at the surface (log $K_s$). A generic surface complexation reaction and associated equilibrium constant describing cation sorption is shown Equation 5:

$$
\equiv \text{SOH} + M^{m+} \rightleftharpoons \equiv \text{SOM}^{m-1} + H^+ \quad \text{with} \quad K_s = \frac{[\equiv \text{SOM}^{m-1}]}{[\equiv \text{SOH}][M^{m+}]} e^{(m-1)\Psi R T} \quad \text{Equation 5}
$$

where $\equiv \text{SOH}$ is a generalized amphoteric sorption site on an oxide surface and M is a sorbed cation. The exponential term in the equilibrium constant contains an electrical potential term ($\Psi$), which accounts for electrostatic interactions between the charged surface and the sorbed ion. R is the universal gas constant of 8.314 J•K^{-1}•mol^{-1}, T is temperature in kelvin.

The SCM quantifies the reactions at the solid and water interface by approximating both the chemical free energy of forming the surface complex as well as the electrostatic free energy of the attraction of the ion to the surface. To quantify the electrostatic interaction, the potential is approximated using a variety of assumptions regarding the modes of ion interaction with the surfaces and the rate of change of the electrostatic potential as a function of distance from the surface. For example, the diffuse layer model assumes a constant potential near the surface and a layer of exponentially decreasing potential as it approaches the bulk liquid (Figure 5B). Furthermore, all the surface complexes are inner sphere complexes; and usually there is no interaction of the background electrolyte ions with the surface. The triple layer model (TLM) assumes an
extra layer between the bulk surface and bulk aqueous phases, and decreasing potentials in all three layers. In the TLM, ions can form inner sphere or outer sphere complexes (Figure 5C). Similar to speciation calculations for aqueous complexes, the SCM can calculate the speciation and concentration for both surface and aqueous species based on the chemical reactions and their stability constants for variable chemical conditions (e.g., changing concentration, pH, P_{CO_2}, E_H).

Figure 5: Schematics depicting the solid–solution interface for the surface complexation models: (A) constant capacitance model (CCM), (B) diffuse layer model (DLM), (C) triple layer model (TLM).

2.6 Rationale for Coupling Redox Reaction to SCM

The complex Pu redox reactions in environmental systems and the different mobility of each oxidation state requires a redox-coupled speciation model to predict the Pu aqueous and surface speciation across a range of conditions. It is theoretically possible to incorporate the redox half reactions to the chemical speciation model by converting the redox potential to stability constants through the Nernst equation (Equation 6).

\[
\ln K = \frac{nFE^0}{RT}
\]

Equation 6

where \( \ln K \) represents the stability constant (in natural logarithmic form), \( n \) is the number of electrons transferred in the redox half reaction, \( F \) is the Faraday’s constant (\( F = 9.648 \times 10^4 \) C/mol), \( E^0 \) is the redox potential (volt) at a given temperature, \( R \) is the universal

20
gas constant (R = 8.314 J/K/mol), and T is the temperature in kelvin. By converting the redox potentials for Pu half reactions to stability constants, they can be coupled to existing Pu aqueous and surficial reactions.

Furthermore, the redox reactions of Pu are profoundly controlled by the pH and E\textsubscript{H} (as shown in Table 3); and these two parameters can be controlled and monitored in the laboratory. The measured pH and E\textsubscript{H} can be used as input parameters to constrain the redox reactions. Moreover, Pu oxidation state can be well controlled and characterized in the laboratory, which makes it possible to input Pu in the form of a single oxidation state and observe its transformation to multiple oxidation states in equilibrium both in the aqueous phase and at a surface under given pH and E\textsubscript{H} condition.

Specifically, Pu initially present in a single oxidation state will be used for the batch sorption experiments. For example most of this work initially started with Pu(IV). The pH and E\textsubscript{H} of the suspension were measured, and used as input parameters to constrain both SCM and the redox reactions. The Pu oxidation states in the aqueous phase and at the solid phase in equilibrium at the given pH and E\textsubscript{H} values can be measured using a solvent extraction technique. Therefore, batch sorption under variable pH and E\textsubscript{H} conditions was designed to test the sensitivity of the redox-coupled speciation model. A good redox-coupled SCM should not only simulate the Pu partitioning at the solid and water interface, but also calculate the Pu oxidation states as measured in experiments.

The incorporation of Pu redox reactions into SCM requires both database modification and additional input parameters that are not required for non-redox coupled surface complexation models. The following is an example of coupling a Pu redox reaction
for incorporation into the thermodynamic database. Equation 7 shows hydrolysis of Pu(III); Equation 8 is the Pu(IV)/Pu(III) redox half reaction; and Equation 9 is the combination of equation 7 and 8, which couples the Pu(IV)/Pu(III) redox reaction to Pu(III) hydrolysis. All aqueous, surfacial, and cation exchange reactions that involve Pu(III/V/VI) can be coupled with Pu(IV) redox half reactions to utilize Pu(IV) as the basis species in the database. The redox-coupled model captures the sensitivity of the redox reactions and is theoretically be more accurate and realistic than models that assume only one Pu oxidation state. A novel aspect of this work is the fitting of sorption data using the redox-coupled SCM. This effort effectively determined the free energy of the surface species. These calculations can be used as evidence that the free energy of the aqueous ions is different from the surface complexes.

\[
\begin{align*}
\text{Pu}^{3+} + \text{H}_2\text{O} &= \text{Pu(OH)}^{2+} + \text{H}^+ & \log K &= -6.8 & \text{Equation 7} \\
\text{Pu}^{4+} + e^- &= \text{Pu}^{3+} & \log K &= 17.69 & \text{Equation 8} \\
\text{Pu}^{4+} + \text{H}_2\text{O} + e^- &= \text{Pu(OH)}^{2+} + \text{H}^+ & \log K &= 10.89 & \text{Equation 9}
\end{align*}
\]

2.7 Knowledge Gap

A geochemical database that allows the calculation of actinide partitioning at the solid and water interfaces under variable geochemical conditions is necessary for reactive modeling of actinide transport in the subsurface. Developing databases for actinide sorption in binary systems that contain reliable, and thermodynamically-based K_s values as well as the fundamental thermodynamic values (\Delta H, \Delta S, and \Delta G) will provide solid foundations for modeling actinide interactions in more complicated systems, such as ternary systems and systems at elevated temperatures. However, the geochemical databases
currently in use are incomplete and require 1) further understanding of the underlying reaction mechanisms at solid and water interfaces and 2) development of a modeling approach to better simulate actinide reactions and speciation at solid and water interfaces.

Some of the underlying mechanisms of the complex redox behavior of Pu at solid and water interface are still unclear. Many studies have observed the surface-mediated reduction of Pu(V) to Pu(IV) on both redox active and inactive mineral surface.\textsuperscript{21, 24, 25} The underlying mechanism of this surface mediated reduction has never been shown and multiple hypotheses are being currently tested. Some crucial questions such as what components in the aqueous/on the solid serve as reductants for Pu(V/VI) reduction to Pu(IV) at the solid and water interface remain unanswered. The underlying mechanism and thermodynamic driver for the favorability of Pu(IV) on surfaces observed in previous studies need to be addressed. In addition, Pu(III) was previously considered less environmentally relevant but clearly has importance under reducing conditions.\textsuperscript{47} Pu(IV) reduction to Pu(III) and the subsequent impact on sorption behavior of Pu under reducing conditions has not been studied previously.

Moreover, the complex redox behavior of Pu poses a challenge to applications of surface complexation models that can quantitatively predict Pu partitioning between aqueous and solid phases. Thus, there are very few surface complexation models for Pu interactions at mineral and water interfaces in peer-reviewed literature.\textsuperscript{56, 57 58-60} Of those, only two coupled the Pu oxidation states in the sorption reactions.\textsuperscript{57, 60} The absence of surface complexation stability constants (K\textsubscript{s}) for Pu in different oxidation states is one of the major deficiencies within actinide geochemical reaction databases. The approach for
the incorporation of Pu redox reactions into surface complexation reactions needs to be further studied for self-consistency.

Furthermore, reliable enthalpy ($\Delta H$) and entropy ($\Delta S$) values for actinide interfacial reactions are lacking. Most published $\Delta H$ and $\Delta S$ values for actinide sorption to minerals were extrapolated through a van’t Hoff plot based on the empirical $K_D$ values at variable temperatures. However, $K_D$ is only valid at the given experimental condition, and is subject to change under variable conditions. For example the $\Delta H$ and $\Delta S$ extrapolated from $K_D$ from one pH value may be different from another at a different pH value. Furthermore, $K_D$ values capture the overall partitioning of actinides at solid and water interfaces, which may include multiple reactions (surface deprotonation, water formation, actinide sorption). Therefore, the extrapolated apparent $\Delta H$ and $\Delta S$ values are not reliable $\Delta H$ and $\Delta S$ for the specific sorption reactions. Approaches for direct measurement of the thermodynamic values for actinide interfacial reactions need to be developed.

Above all, the replacement of conventionally used partition coefficients ($K_D$) by thermodynamic based stability constants ($K_S$) calculated through SCM has the potential to provide a more accurate transport model. There are several advantages of this replacement:

- $K_S$ is essentially a constant that account for both aqueous and surface speciation of a target contaminant. For a single target contaminant, $K_S$ represents each surface species which will be combined in a transport model, and therefore, captures the partition under variable chemical conditions such as pH, E_H, ionic strength, and existence of competition ions.
• Instead of searching for a retardation factor for a similar geologic environment, a SCM model only requires basic geologic/environmental parameters such as pH, \( E_H \), and mineralogy, and can provide a reliable prediction of partitioning between aqueous and solid phases.

• Utilizing the SCM, one can simulate/predict the speciation and partitioning of multiple contaminants simultaneously such as for the case of mobilizing one contaminant while remediating the other. For example, the model could have predicted the unintended mobilization of iodine at the SRS F-area due to base neutralization of the groundwater that was done to minimize the migration of Np and other cationic radionuclides.\(^{61}\)

• Analysis of surface species in terms of free energies (\( i.e., \) achievable through determination of \( K_s \)) can be used to examine the energetic favorability of particular oxidation states of surface species, such as the preferential formation of Pu(IV) surface complexes.
CHAPTER 3

HYPOTHESES AND RESEARCH PLAN

The hypotheses to be tested in this study are listed in section 3.1. The solid phases to be studied in this work are described in section 3.2 along with the rationale for selecting these phases. Both experiments and geochemical modeling that are designed to test the hypotheses are listed in section 3.3.

3.1 Hypotheses

1. The energetic favorability of the actinide surface complexes is strongly driven by positive sorption entropy, which is mechanistically achieved by displacement of coordinating water molecules from the actinide and mineral surface during sorption.

2. In a binary system, the pH and $E_H$ of the system have profound influence on Pu speciation and control the extent of sorption reactions. Specifically, under oxic conditions, Pu(IV) and Pu(V) are the dominant species in the aqueous phase; Pu(V) becomes more favorable at high pH under the same $E_H$ condition. Under anoxic conditions, Pu(III) is stable under acidic conditions and at higher pH ranges, Pu(IV) becomes dominant.

3. The thermodynamic favorability of Pu(IV) surface complexes could drive Pu(V) reduction and Pu(III) oxidation at the solid and water interface. This is due to an increase in the reduction potential of Pu(V) and a decrease in the reduction potential
of Pu(III) at the surface, which leads to a more favorable Pu(IV) surface complex. The reaction could be sufficiently energetically favorable for the oxidation or reduction of water to complete the redox half reactions. This hypothesis is further illustrated by Equation 10 and 11, which showing the hypothesized change of redox potentials for Pu(IV) at the surface and its relationship to the redox potential for water oxidation.

\[ E_{\text{Surface}}[\text{Pu(IV)}] > E_{[O_2/H_2O]} > E_{\text{Aqueous}}[\text{Pu(IV)}] \] (Aerobic) \hspace{1cm} \text{Equation 10}

\[ E_{\text{Surface}}[\text{Pu(IV)}] < E_{\text{Aqueous}}[\text{Pu(IV)}] \] (Anaerobic) \hspace{1cm} \text{Equation 11}

4. Inner sphere complexes of actinides and GO are formed for all four actinide oxidation states and the complexation strength follows the effective charges of actinides.

5. Actinides in all oxidation states preferentially bind to carboxylate functional groups on the GO surface. Such behavior can be quantified and predicted using a double layer SCM. Thus, a linear free energy relationship should exist between the stability constants for actinide-GO sorption and actinide-carboxylate aqueous complexes.

### 3.2 Selection of Solid Phases and Actinides to Examine in This Work

Three solid phases were selected to for sorption studies: goethite (α-FeOOH), kaolinite (Al₂Si₂O₅(OH)₄), and graphene oxide (GO). Because of the complex redox chemistry of Pu, it was chosen as the major actinide of interest for this study to demonstrate the need and advantage of the redox-coupled models to be developed in this work. However, due to the sensitivity of Pu to redox transformations, actinides in more stable oxidation
states were frequently used as analogs for the various Pu oxidation states. Specifically, this study used Th(IV) as an analog for Pu(IV), Np(V) for Pu(V), U(VI) for Pu(VI), and Eu(III) for Pu(III).

Goethite and kaolinite represent naturally occurring solid phases present in many environments, particularly as a major sorbent at F-area, Savannah River Site. Both goethite and kaolinite are minerals formed via chemical weathering, which makes them ubiquitously coated on soil and sediments. Goethite is the second most common iron (hydr)oxide in the natural environment next to hematite (Fe₂O₃) and is derived from chemical weathering of iron-bearing minerals under oxygenated environments. All the iron in goethite is in the form of Fe(III) making it non-reducing. The prevalence of goethite and its known structure makes it a common model iron (hydr)oxide for sorption studies. Kaolinite is formed from chemical weathering of aluminum silicates such as feldspar. It is a phyllosilicate mineral that can be visualized as a gibbsite (Al(OH)₃) and silica sheets in 1:1 ratio. Kaolinite has a thin interlayer and does not expand or contract to the same extent as 2:1 clay minerals. It also has a low cation exchange capacity (2 meq/100g for the kaolinite used in this study). The chemically-weathered minerals are better representatives for the solid and water interface than those minerals formed at higher temperature and pressure simply because they are more likely to be abundant and stable at solid and water interface in near surface environments. At the same time both goethite and kaolinite possess simple mineral structure comparing to other common minerals such as biotite (K(Mg, Fe)₃(AlSi₃O₁₀)(OH)₂) and hornblende (Ca₂(Mg,Fe,Al)₅ (Al,Si)₈O₂₂(OH)₂), which are conducive to the simplified assumptions made in surface complexation models.
Actinide complexation with graphene oxide (GO), a synthetic two-dimensional carbon-based material, was also studied. There are several reasons to study actinide complexation with GO and comparing the results to studies with actinide metal-oxide mineral interactions. First, several recent studies have shown GO to be an efficient sorbent for actinides making it a potential sorbent for actinide separations. However, many aspects of actinide complexation to GO such as determination of sorption capacities, understanding sorption mechanisms, and reaction reversibility need to be addressed before further application. Similar studies of actinide sorption to metal-oxide mineral surface may provide some insight to these reactions and also provide a basis for comparison to this novel sorbent.

GO is essentially a sheet of aromatic carbon rings that contains multiple functional groups (e.g., carboxyl, hydroxyl, and epoxide). The complexation of actinide to GO maybe different from mineral since GO does not contain a bulk lattice structure as a crystalized mineral and will have C-OH functional groups at the surface instead of M-OH groups (with M = Fe, Al, or Si). However, the same SCM method may be applicable to understand actinide complexation to GO by treating the GO functional groups as surface sites. Actinide binding to these surface functional groups may be more similar to ligand complexation in the aqueous phase. However the influence of an electrostatic double layer, particularly for a surface such as GO that can become highly charged must be taken into account. Finally, GO may allow for greater control over the surface reactivity than metal-oxides. For examples, in many cases the density of metal oxide surface functional groups may have to be assumed and the range of functional site geometries is not known. For GO, the surface
density, the types and quantities of functional groups on GO, and possible specific interactions between actinides and functional groups could possibly be measured through advanced lab techniques (FTIR, XAS, NMR).

3.3 General Task Descriptions

My work consisted of material/surface characterization (Phase 1), macroscopic batch sorption experiments under various conditions (Phase 2), Pu oxidation state analysis (Phase 2), modeling of the batch sorption data and Pu redox reactions (Phase 3), and direct quantification of enthalpy for sorption reaction using isothermal titration calorimetry (ITC) (Phase 4). The workflow for the study and their inter-relationships are shown in Figure 6. The workflow represents the general approaches taken for each of the three solids examined in this work although different experiments were designed for each solid. After characterizing each material, batch sorption experiments were conducted. Where necessary additional spectroscopic or indirect oxidation state analysis techniques were applied. Each batch experiment included variables such as temperature, redox conditions, pH or analyte concentration. The rationale for altering each of these values was guided by the hypotheses above. SCM of the batch sorption data (phase 3) was achieved for all solids. ITC titrations (Phase 4) were only conducted for the GO systems to probe the method for direct measurement of enthalpy value for actinide surface complexation. The specific experimental project related to each solid, hypotheses tested and results for each of project are listed below in Table 5.
Figure 6: Workflow for the study.

Table 5 List of projects and expected results

<table>
<thead>
<tr>
<th>Project</th>
<th>Hypothesis</th>
<th>Expected results</th>
</tr>
</thead>
</table>
| 1. Pu(IV)/Th(IV) sorption to goethite at variable temperatures (15 °C – 65 °C) coupled with SCM. | 1, 2       | 1. Test for the entropy-driven hypothesis;  
2. Calculation of empirical ΔH and ΔS for Pu(IV)-goethite and Th(IV)-goethite system;  
3. Observation of Pu(IV) oxidized to Pu(V) in the aqueous phase and redox-coupled SCM of Pu(IV) sorption to goethite. |
| 2. Pu(IV/V) sorption to kaolinite under aerobic/anaerobic condition and Pu redox coupled SCM. | 2, 3       | 1. Observation of pH and E_H influence on Pu redox speciation;  
2. Redox-coupled SCM of Pu(IV) sorption to kaolinite under aerobic/anaerobic condition;  
3. Provide insights on thermodynamic favorability of surficial Pu(IV) by comparing |
| 3. Sorption isotherm of Eu(III), Th(IV), Np(V), and U(VI) on graphene oxide and SCM modeling of actinide sorption to GO as function of analyte concentration and pH. | 3, 4, 5 | 1. Identification of carboxylate functional group on GO the dominant sorption site for actinide in all four oxidation states;  
2. Calculation of Ks for actinides in all four oxidation states through SCM;  
3. Identification of the LFER between actinide-carboxylate complexation on GO and actinide-carbonate complexation in the aqueous phase; |
|---|---|---|
| 4. Quantification of the sorption enthalpy of Eu(III) complexation to GO through ITC. | 1, 4 | 1. Direct measurement of enthalpy (ΔH) for GO protonation/deprotonation;  
2. Direct measurement of enthalpy (ΔH) for Eu(III) sorption to GO. |
CHAPTER 4

Pu(IV)/Th(IV) SORPTION TO GEOTHITE AT VARIABLE TEMPERATURES (15 °C – 65 °C) AND SCM MODELING

Abstract

Due to the elevated temperature expected in nuclear waste repositories, there is need for a better understanding the behavior of radionuclides at the elevated temperatures. In this work, sorption of Pu(IV) and Th(IV) to goethite was monitored at variable temperatures (15 °C to 65 °C) across the pH range 1 to 6. Both Pu(IV) and Th(IV) showed an increased sorption to goethite with increasing temperature. Van’t Hoff plots were used to estimate the formation enthalpies and entropies for both Pu-goethite and Th-goethite complex. For Pu-goethite complex, the average entropy and enthalpy values were 173.4 ± 28.4 J/K/mol and 27.9 ± 11.8 kJ/mol. The entropy and enthalpy for the Th-goethite complex increased with increasing pH value, and have average values of 249.6 ± 68.5 J/K/mol and 57.8 ± 18.4 kJ/mol. The changes in enthalpy and entropy values with increasing pH are hypothesized to be due to changes in the thorium and plutonium speciation. These data also indicate that Pu(IV) and Th(IV) sorption on goethite are both endothermic, and the surface complexes are strongly driven by the positive sorption entropies. This reaction is hypothesized to be mechanistically driven by displacement of solvating water molecules from the actinides and mineral surface during sorption.
4.1 Introduction

It is crucial to understand the geochemical processes of plutonium (Pu) in the subsurface because large amounts of nuclear waste containing Pu were generated from weapons manufacturing and nuclear power production, eventually to be stored in geological repositories. In the United States, most of the nuclear waste containing Pu were either temporarily stored at the Department of Energy facilities (the Hanford Site, WA and the Savannah River Site, SC) or sit on-site at over 100 nuclear power plants because permanent geological repositories for high level nuclear waste (HLW) are still under investigation as of 2016. The release of nuclear wastes containing Pu has been reported both at the Hanford Site, WA, and the Savannah River Site, SC, resulting in rivers, soils and sediment under remediation and monitoring. Far-field migration of Pu in groundwater was also observed at the Nevada Test Site, where underground nuclear tests were conducted between 1956 and 1992 resulting in a large amount of radioactive material deposited in the area. Most Pu isotopes are alpha emitters and some of them have long half-lives (e.g., $t_{1/2}^{(239\text{Pu})} = 2.14 \times 10^4$ years), which will pose long term radio-toxicity to the biosphere if exposed. Although the short half-lived radionuclides (e.g., $^{90}\text{Sr}$ and $^{137}\text{Cs}$) account for the majority of the current radio-toxicity, modeling the eventual release of radionuclides from the repository indicates that the actinides (including Pu) are predicted to be the primary sources of radio-toxicity. Furthermore, the residual heat load and heat from radioactive decay may cause temperatures within the repository to be as high as $120 \degree \text{C}$. The elevated temperature has the potential to affect the geochemical behavior of radionuclides such as the aqueous speciation, surface complexation, and subsurface
transport. Therefore, a thorough understanding of the geochemistry of radionuclides under elevated temperatures is required. Some research has been done to understand actinide aqueous complexation at elevated temperatures\textsuperscript{60-71}, but overall data examining actinide geochemical behavior under elevated temperatures are still limited.

The geochemistry of Pu is particularly complex primarily because of its complicated redox chemistry. Pu can coexist in four oxidation states (III, IV, V, and VI) under environmental conditions, and the mobility of each oxidation state in the environment depends on the effective charge with the trend as: Pu(IV)< Pu(VI) ≈ Pu(III) < Pu(V) (from least to highest mobility). Tetravalent and pentavalent are considered the most relevant species as Pu transport in the subsurface under aerobic condition. Pu(IV), with the strongest affinity to the mineral surfaces, is the least mobile species. Conversely, Pu(V), with the least sorption affinity and, therefore, the most mobile Pu oxidation state, is considered the dominant in the oxic aqueous phase.

Here we studied Pu(IV) sorption to goethite as a function of pH with temperature ranging from 15°C – 50°C. Similar batch sorption experiment using Th(IV) as a stable tetravalent oxidation state was conducted as a comparison. Sorption of Pu(IV) and Th(IV), increased with increasing temperature, indicating an endothermic processes. The enthalpy (ΔH) and entropy (ΔS) for Pu(IV) and Th(IV) sorption to goethite were extrapolated from van’t Hoff plots of the data. The positive sorption entropies are proposed to be a manifestation of the removal of coordinating water from the actinides or mineral surfaces upon sorption. Pu(IV) was initially added to the goethite suspension, and the redistribution of Pu oxidation states after sample equilibration was measured using solvent extraction.
These data show that despite initially adding Pu(IV), Pu(V) was presented in the aqueous phase after equilibration. Thus the data were modeled using a redox coupled surface complexation model.

### 4.2 Materials and Methods

#### 4.2.1 Chemical

A 10 μCi mL⁻¹ solution of ²³⁸Pu in 4M HNO₃ was used as the starting stock solution for this work. To obtain the ²³⁸Pu(IV) working solution, a small aliquot of the ²³⁸Pu stock was evaporated to dryness and re-dissolved using 0.1 M HCl in a Teflon vial. A few crystals of solid NaNO₂ was added to fix the aqueous Pu in the tetravalent state. The oxidation states of the ²³⁸Pu solution were confirmed using solvent extraction³⁰-³², ⁷² and lanthanum fluoride co-precipitation⁷³. The concentration of the ²³⁸Pu working solution was 3.80×10⁻⁸ ± 4.29 × 10⁻¹⁰ mol/L (5.74 × 10⁶ ± 4.29 × 10⁴ Bq/L), determined using liquid scintillation counting (LSC, PerkinElmer TriCarb).

The Th(IV) working solution used in this study was diluted from a NIST traceable 1000 ppm Th(IV) stock solution (in 2% HNO₃, High Purity Standards) and characterized using an inductively coupled plasma mass spectrometry (ICP-MS, Thermo Scientific X-Series II).

All chemicals used in this experiment were analytical grade. All solutions were prepared with distilled deionized water with a resistivity greater than 18 MΩ·cm and less than 1 ppb total organic carbon obtained from a Millipore SuperQ water filtration system. The ionic strength of all solutions in the work was fixed at 0.1 M using NaCl.
4.2.2 Goethite Characterization

Goethite used in this study was synthesized using the method described in Schwertmann and Cornell\textsuperscript{74}, and characterized using X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The specific surface area (SSA) of the goethite was measured via BET-N\textsubscript{2} (g) sorption. The details for the goethite characterization are shown in Appendix A.

The surface protonation/deprotonation of goethite at variable temperatures was measured using an acid/base addition method conducted in the anaerobic chamber (filled with 98\% N\textsubscript{2} and 2\% H\textsubscript{2}, Coy Laboratory Products) to eliminate the interference from atmospheric carbon dioxide. All the samples were prepared using degassed water to eliminate dissolved CO\textsubscript{2}(g); the pH was measured using an automatic temperature compensated electrode (Thermo 9157BNMD). Specifically, 15 samples, containing 15 g/L goethite, 4mM initial HCl and fixed ionic strength of 0.01 M in each, were prepared in 7 mL glass vials with screwed caps in the anaerobic chamber. A 0.005 M NaOH was added to each sample by 0.05 mL increments to reach the desired initial pH. A known amount of 0.01 M NaCl solution was added to each sample to make the total volume fixed at 5 mL. The samples were placed in a heating block with temperature controlled at 25 °C and shaken on a horizontal shaker for more than 6 hours to reach equilibrium. The pH of each sample was measured and re-measured after several hours of continued shaking. The temperature of the samples was raised to 50 °C when the pH of the samples at 25 °C become stable. The equilibrium pH values of each sample at 50 °C and 80 °C were determined follow the same procedures described above. However, the equilibrium periods for the 50
°C and 80 °C events were less than 1 hour to minimize the evaporation of samples at these elevated temperatures. These data were used to calculate the acidity constants (K⁺ and K⁻) of goethite at variable temperatures.

4.2.3 Batch Sorption of Pu(IV) and Th(IV) at Variable Temperatures

Batch experiments of ultra-trace level of Pu(IV) and trace level of Th(IV) (initial input concentrations are 1.1×10⁻¹⁰ M and 1.3×10⁻⁷ M, respectively) sorption to goethite as a function of pH and temperature were prepared in 50 mL polypropylene centrifuge tubes. Each tube initially contained 0.5 g/L of goethite in 0.1 M NaCl. The pH of the suspension in each tube was adjusted to pH ranging from 1 to 6 using 0.1M/0.01M NaOH or HCl, by 0.5 pH unit increments. No additional pH adjustment was made after the initial pH adjustment. The batch samples were shaken horizontally in a temperature-controlled orbital shaker (VWR) to reach equilibrium. Samples were monitored and measured at a 5-day interval. The pH of each sample was measured using an Ag/AgCl electrode with automatic temperature compensation (Thermo 9157BNMD). The E_H of each sample was measured using an ORP electrode (Thermo Scientific Orion 9778BNWP). The sorption percentage in each sample was quantified by the difference between the initial Pu/Th concentration and its concentration remaining in the aqueous phase after sorption. Specifically, a 1.5 mL homogeneous suspension was removed from each sample, centrifuged at 8000 rpm for 30 minutes for solid and liquid separation and a 1 mL aliquot of the supernatant was collected for quantification. The Pu concentration in the aqueous phase in each sample was quantified using LSC, and the Th concentration in the aqueous phase in each sample was measured using ICP-MS with ²⁴²Pu as an internal standard.
percentage of Pu or Th that sorbed to goethite in each sample was calculated using Equation 12, where \( C_0 \) is the initial aqueous concentration of Pu or Th, and \( C_{aq} \) is the aqueous concentration of Pu or Th measured after equilibrium.

\[
\text{Sorption Percentage} (\%) = \frac{C_0 - C_{aq}}{C_0} \times 100\%
\]  
Equation 12

After 2 to 5 additional days of mixing, the concentrations of Pu/Th were measured again, using the same procedure described above, to determine if sorption equilibrium has been reached. Temperature of the batch samples was raised when the results from two sampling events showed no significant difference. Batch sorption of Pu(IV) to goethite was examined at 15 °C, 25 °C, 35 °C, and 50 °C and Th(IV)-goethite sorption experiments were conducted at 25 °C, 35 °C, 55 °C, and 65 °C.

4.2.4 Entropy and Enthalpy Extrapolation via van’t Hoff plot

The distribution coefficients (\( K_D \)) for Pu and Th sorption to goethite were calculated using Equation 13:

\[
K_D = \frac{\text{Concentration of the element associated with the solid} \left( \frac{\text{g}}{\text{kg}} \right)}{\text{Concentration of the element in the aqueous} \left( \frac{\text{g}}{\text{L}} \right)}
\]  
Equation 13

A van’t Hoff plot of \( \ln K_D \) as a function of the inverse temperature (1/T) was used to determine the enthalpy (\( \Delta H \)) and entropy (\( \Delta S \)) of the sorption process based on Equation 14:

\[
\ln K_D = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}
\]  
Equation 14

Because \( K_D \) values are empirical sorption coefficients and do not represent a specific reaction, the \( \Delta H \) and the \( \Delta S \) extrapolated in this study are for the overall sorption process, which may include more than one reaction.
4.2.5 Surface Complexation Modeling

The acidity constants (log $K_+$ and log $K_-$) of goethite at variable temperatures were calculated from modeling of the results of acid/base addition of goethite at variable temperatures using FITEQL 4.0. An electrostatic triple layer model (TLM) was used to account for the electrostatic effects at the goethite and water interface. The TLM assumes sodium and chloride sorb as outer sphere complexes and thorium and plutonium form inner sphere complexes. Thus the impact of the background electrolyte and sorbing species on surface protonation/deprotonation can be approximated. An amphoteric, 2-pKa goethite surface site [$\equiv$FeOH] was considered using the following protonation and deprotonation reactions.

**Protonation:** $\equiv$FeOH + $H^+$ = $\equiv$FeOH$_2^+$ \hspace{1cm} $\log K_+ \hspace{1cm} pH < pK_a$

**Deprotonation:** $\equiv$FeOH = $\equiv$FeO$^-$ + $H^+$ \hspace{1cm} $\log K_- \hspace{1cm} pH > pK_a$

The surface site density of [$\equiv$SOH] for surface complexation was calculated using Equation 15:

$$Surface\ site\ density\ (mol/L) = C \left(\frac{g}{L}\right) \times SSA \left(\frac{m^2}{g}\right) \times \frac{10^{10} nm^2}{m^2} \times 2.3 \left(\frac{site}{nm^2}\right) \times \frac{1}{N_A}$$

in which the surface site density was calculated in the unit of molarity (mol/L), C represents the concentration of goethite in the suspension (in g/L), SSA represents the specific surface area of the goethite, 2.3 site/nm$^2$ was assumed as the average site density, and $N_A$ represents Avogadro’s number of $6.022 \times 10^{23}$. The measured pH and the known total [$H^+$] concentration of each sample were used as input parameters to constrain the model when determining the acidity constants ($K_+$ and $K_-$) for the goethite surface. The
temperature dependence of water dissociation was also taken into consideration by modifying the water dissociation constant (log $K_W$) in the FITEQL interface.

The results of the batch sorption of Pu(IV) and Th(IV) as a function of pH were modeled using FIT4FD (a modified version of FITEQL 4.0). FIT4FD has the full capabilities of FITEQL but has been modified for incorporation of activity corrections and database usage.\textsuperscript{77} The stability constants of Pu in different oxidation states and Th(IV) aqueous complexation from the LLNL Thermochemical database\textsuperscript{78} were used to predict aqueous speciation, including the formation of carbonate, chloride, and hydroxide complexes. For the modeling of Pu sorption to goethite, Pu redox changes were taken into consideration by re-writing all Pu reactions in the database in terms of a Pu(IV) basis species based on transformation of the reduction potentials to equilibrium constants using the Nernst Equation. The details of the redox coupling theory and procedures are discussed in detail in the Experimental Methods section of Chapter 5. The results of Pu sorption to goethite at elevated temperature were not modeled because Pu hydrolysis constants at elevated temperatures are not available. For the modeling of Th(IV) to goethite at variable temperature, hydrolysis constants for Th(IV) at elevated temperatures were extrapolated from the reaction enthalpies based on the van’t Hoff relationship (assuming a constant heat capacity).

4.3 Results and Discussions

4.3.1 Goethite Surface Characterization

The results of acid/base addition experiment of goethite at variable temperatures are shown in Figure 7 where the measured pH is plotted as a function of total [H+] in the
Because the total added [H+] is a constant for each sample, the y-axis values remain constant and pH shift shown on the x-axis demonstrate the influence of temperature. The measured pH increased with the increasing temperature across the pH range 4 to 8.5 and decreased with increasing temperature at pH above 8.5. The pH_{PZC} of the goethite is around pH 8.5; therefore, the experimental results indicated the protonation of goethite is promoted by increased temperature.

Goethite surface acidity constants (log K_+ and log K_-) at 25 °C, 50 °C and 80 °C were determined through triple layer modeling (TLM) of the goethite protonation/deprotonation measurement at variable temperatures (represented by the lines in Figure 7) and listed in Table 6. The log K_+ increased while the log K_- decreased with increasing temperature indicating that the protonation of goethite surface (aka: the formation of [≡FeOH_2^+]) increased while the deprotonation of the goethite surface (aka: the formation of [≡FeO^-]) decreased with increasing temperatures. This modeling results are consistent with the observation of pH shifting with temperature in the experiment. The modeling results of the outer-sphere complexation of Na^+ and Cl^- to goethite indicated decreased complexation with increasing temperatures (Table 6). The changing K_+ and K_- values may be the result of the changing water properties at elevated temperatures (i.e., the concentration of [OH^-] increased and dielectric constants of water decreased with increasing temperature). Van’t Hoff plots of the goethite protonation and deprotonation constants were used to determine the protonation and deprotonation enthalpies of 31.56 kJ/mol and -30.82 kJ/mol, respectively (See Appendix A for details).
Figure 7: Experimental results and modeling of goethite protonation/deprotonation at variable temperatures.

Table 6 Goethite surface acidity constants at variable temperatures modeled using a TLM-SCM

<table>
<thead>
<tr>
<th>Reaction</th>
<th>T °C</th>
<th>log K</th>
</tr>
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<tbody>
<tr>
<td>$K_W$ $H_2O \leftrightarrow H^+ + OH^-$</td>
<td>25</td>
<td>-14</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-13.05</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>-12.41</td>
</tr>
<tr>
<td>$K_+ \equiv FeOH + H^+ \leftrightarrow \equiv FeOH_2^+$</td>
<td>25</td>
<td>7.01</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>7.17</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>7.87</td>
</tr>
<tr>
<td>$K_\equiv FeOH \leftrightarrow \equiv FeO^- + H^+$</td>
<td>25</td>
<td>-9.43</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-9.65</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>-10.27</td>
</tr>
<tr>
<td>$K_{Na^+} \equiv FeO^- + Na^+ \leftrightarrow \equiv FeONa$</td>
<td>25</td>
<td>-7.55</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-7.54</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>-7.92</td>
</tr>
<tr>
<td>$K_{Cl^-} \equiv FeOH_2^+ + Cl^- \leftrightarrow \equiv FeOH_2Cl$</td>
<td>25</td>
<td>5.97</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>4.93</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>4.38</td>
</tr>
</tbody>
</table>
4.3.2 Pu(IV) and Th(IV) Sorption to Goethite at Variable Temperatures

Results of Pu(IV) and Th(IV) sorption to goethite as a function of pH at temperatures from 15 °C to 65 °C are shown in Figure 8. For both Pu(IV) and Th(IV), the sorption increased as a function of pH, and almost 100% sorption was reached at approximately pH 4 to 4.5. A similar pattern of Pu(IV) sorption to goethite was found by Sanchez et al.40 Also as shown in Figure 8, both the sorption of Pu(IV) and Th(IV) increased with increasing temperature; however, Th(IV) exhibited a more obvious increase compared to Pu(IV). The partition coefficients (K_D) for Pu and Th at the goethite and water interface at variable pH and temperatures were calculated and plotted as a function of the inverse temperature (1/T, in Kelvin) in Figure 9. Both showed slightly negative linear trends as a function of 1/T, indicating an endothermic sorption process for both Pu and Th sorption to goethite. For the Pu-goethite complex, the average entropy and enthalpy values were extrapolated to be 173.4 ± 28.4 J/K/mol and 27.9 ± 11.8 kJ/mol. The entropy and enthalpy for the Th-goethite complex increased with increasing pH value, with average values of 249.6 ± 68.5 J/K/mol and 57.8 ± 18.4 kJ/mol. Because the data indicated an endothermic process for both Pu(IV) and Th(IV) sorption to goethite, the formation of surface complexes were likely to be driven by the positive sorption entropies. This reaction was hypothesized to be mechanistically driven by displacement of solvating water molecules from the actinides and mineral surface during sorption. It was noted that the enthalpy for Pu sorption to goethite was similar to that of goethite protonation, which may explain the less obvious increase of sorption with increasing temperatures for Pu. As the temperature increased, more [FeOH₂⁺] formed, which offset the endothermic process of Pu
sorption to goethite. In contrast, the enthalpy for Th(IV) sorption to goethite was higher, corresponding to the observed more obvious influence by temperature. The less obvious Pu(IV) sorption to goethite with elevated temperature compared to that of Th(IV) may also be related to their different hydrolysis behavior in the aqueous phase. Pu\(^{4+}\) hydrolysis products start forming as low as < pH 1, resulting in a small amount of unhydrolyzed Pu\(^{4+}\) in the aqueous phase. While the Th\(^{4+}\) hydrolysis products start forming at higher pH (~ pH 2.5), therefore, there was still a significant amount of unhydrolyzed Th\(^{4+}\) in the aqueous phase. Since the hydrolysis of Pu/Th was also affected by the elevated temperature, the effect of Pu sorption at the goethite and water interface may be offset by its strong hydrolysis reactions in the aqueous phase. For Th(IV) with less hydrolysis reactions at the lower pH range, its sorption was more severely affected by temperature.

The Pu oxidation state redistribution in the aqueous phase and associated with the goethite were measured at the end of the batch sorption experiment via solvent extraction techniques. Pu(IV) remained the predominant oxidation state associated with the goethite surface (99% Pu(IV) of total Pu associated with goethite). However, measureable amounts of Pu(V) were observed in the aqueous phase and the fraction of Pu(V) relative to the total aqueous Pu increased with increasing pH (Figure 10). Approximately 50% of the total Pu was Pu(V) in the aqueous phase at pH 4. This behavior is consistent with stabilization of Pu(V) at circumneutral pH values as well as the lack of Pu(V) stability under acidic conditions due to disproportionation and stability of Pu(IV) and Pu(VI). At pH >4, almost all Pu was sorbed to the goethite and the aqueous Pu concentrations were below detection limit for reliable oxidation state analysis.
Figure 8: A. Pu(IV) sorption to goethite at variable temperature; B. Th(IV) sorption to goethite at variable temperature.

Figure 9: A. van’t Hoff plot for Pu(IV) sorption to goethite; B. van’t Hoff plot for Th(IV) sorption to goethite.
4.3.3 SCM of Pu(IV) Sorption to Goethite

Pu(IV) sorption to goethite as a function of pH at 25 °C was modeled using a Pu redox-coupled SCM (Figure 11A). The Pu redox reactions were coupled to all Pu aqueous and surface reactions based on the Nernst equation and the coupling procedures described in the Material and Methods section in Chapter 5. The measured pH, $E_H$ (converted to pe) and the percentage of Pu sorption were used as input parameters to constrain the model. According to the SCM, Pu(OH)$_3^+$ is the predominant species sorbed to the goethite. This SCM simulated Pu(IV) as the primary sorbed species as well as the generation of Pu(V) at pH 3 to 4 in the aqueous phase, which is consistent with the Pu oxidation state measurements (Figure 12). As shown in Figure 12, the SCM calculated Pu oxidation state distribution predicted >99% Pu(V) in the aqueous phase above pH 4, which is higher than the measurement. While at the lower pH 1 to 2, both the experiment and model indicate Pu(IV) as the stable aqueous phase oxidation state.

A non-redox coupled SCM was also capable of modeling the sorption process (Figure 11B). As shown in Figure 11B, Pu(OH)$_2^{2+}$ and Pu(OH)$_3^+$ are the two dominant
species sorbed to goethite in the non-redox coupled model. However, without the redox coupled database in the SCM, the model was not able to predict the Pu oxidation states distributions. The two SCMs calculated slightly different stability constants for Pu(IV) sorption to goethite (The stability constants were listed in Table A1 in Appendix A). However, our current understanding on actinide chemistry cannot determine which model is more representative because no current method can determine the speciation of Pu associated with solid at such low concentration. Results of Pu(IV) sorption to goethite at elevated temperatures were not modeled because of missing Pu hydrolysis constants at those temperatures.
4.3.4 SCM of Th(IV) Sorption to Goethite at variable temperatures

Th(IV) sorption to goethite as a function of pH from 25 °C to 65 °C was modeled via SCMs (Figure 13). The Th(IV) hydrolysis constants at these elevated temperatures are extrapolated from the corresponding constants at 25 °C using the van’t Hoff Equation and their reaction enthalpies (Appendix A). It is noted that only the first and second hydrolysis
constants for Th were adjusted for the temperature change but these species span the pH conditions of interest to this work. Th\(^{4+}\) sorption to [≡FeO\(^{-}\)] and [≡FeOH\(_2^+\)] was used to model the sorption process. The modeled stability constants for Th sorption to goethite at variable temperature are listed in Table A2 in Appendix A. A van’t Hoff plot using these modeled stability constants versus the inverse temperature showed extremely high \(\Delta H\) and \(\Delta S\) values for Th\(^{4+}\) sorption to goethite, which were considered not reliable values. This huge discrepancy from the empirical values from van’t Hoff plot of the \(K_D\) may be due to several reasons. The error from modeling the goethite acidity constants at variable temperatures may have been carried over into the Th(IV)-goethite sorption model. Also, the Th hydrolysis constants at elevated temperatures were extrapolated using an empirical approach and were not applied to all the Th hydrolysis constants. This may also lead to the uncertainties in the following modeling of Th sorption to goethite at elevated temperature. These modeling results indicated that caution needs to be taken when using the stability constants of surface complexation modeled from SCM for thermodynamic value calculation.
4.4 Conclusions

Here we studied the Pu(IV) sorption to goethite from 15 °C to 50 °C using a batch sorption experiment; a similar batch sorption experiment was conducted using Th(IV), Pu(IV)'s analog with a stable oxidation state, as comparison. Positive enthalpy and entropy values were calculated using van’t Hoff plot of the sorption data at variable temperature for both Pu(IV) and Th(IV), indicating endothermic and entropy driven processes for both Pu(IV) and Th(IV) sorption to goethite. The positive entropy further indicated a mechanism that involved removal of coordination water molecules of Pu/Th or at the goethite interfaces as the sorption occurred. However, the exact geometry of the sorption such as the number of coordination water lost needs to be probed by advanced spectroscopic approaches. The transformation of Pu(IV) to Pu(V) in the aqueous phase was observed at an intermediate pH range. A redox coupled SCM simulated the sorption of Pu(IV) to goethite as well as the Pu oxidation state distribution.
This study indicated complicated interactions occurring at the solid and water interface as temperature elevated. The macroscopic experiment method used here revealed the overall sorption trend and energetics with increased temperature. However, to understand the influence of temperature on actinide behavior at the interface, a thorough understanding of the thermodynamics of actinide speciation in the aqueous phase and the thermodynamics of the mineral surface itself is needed.
CHAPTER 5

REDOX-COUPLED SURFACE COMPLEXATION/ION EXCHANGE MODELING OF Pu(IV) SORPTION TO KAOLINITE

Abstract

The complex redox chemistry of plutonium (Pu) is a major factor that hinders the understanding of Pu partitioning at the solid and water interface, because Pu often coexists in multiple oxidation states in the aqueous phase that are subject to change under varying environmental conditions such as pH and E_H. In addition, each Pu oxidation state possesses different aqueous speciations and different affinity for the surface, making the modeling of Pu partitioning at the solid and water interface a challenge. Here we studied Pu(IV) sorption to kaolinite at pH 2 to 8 under both aerobic and anaerobic conditions and it exhibited different sorption patterns. The redistributions of Pu oxidation state after sorption experiments were measured via solvent extraction techniques, showing the initially spiked Pu(IV) partially oxidized to Pu(V/VI) under the aerobic condition while partially reduced to Pu(III) under the anaerobic condition. SCMs based on the electrostatic double layer model (DLM) and component additivity approach (CA), with coupled Pu(III), Pu(IV), Pu(V), and Pu(VI) redox reactions modeled Pu(IV) sorption to kaolinite under both conditions and confirmed the redox influence on sorption. The SCMs also showed the influence of cation exchange process on sorption: the cation exchange process dominated Pu sorption to kaolinite at pH<4; surface complexation of Pu dominated the sorption at pH
4 to 8. The cation exchange process was further confirmed by batch sorption experiment of Pu(IV) sorption to kaolinite under variable ionic strengths. Lacking the stability constants of Pu(III) complexation to kaolinite, Am(III) sorption to alumina and silica gel was modeled as an analog for Pu(III) sorption to aluminol and silanol surface sites on kaolinite. The modeled log Ks of Am(III) complexation to alumina and silica gel, coupled with Pu(III)/Pu(IV) redox potential were used directly to model the Pu(IV) sorption to kaolinite under anaerobic condition. The redox-coupled SCM not only predicted the Pu partition at kaolinite/water interface, but also predicted the Pu oxidation state distribution in the aqueous phase.

5.1 Introduction

The fate and transport of plutonium (Pu) is a concern for the permanent storage of nuclear waste because large amounts of this element are present in both legacy waste from weapon production and used nuclear fuel.\(^1,3,4\) It has been reported that more than a hundred tons of weapon-graded Pu has been produced by the US military since the start of the Manhattan Project in 1939.\(^3\) By 2010, the global inventory of Pu was ~1900 tons, increasing by 70 to 90 tons per year, primarily from used nuclear fuel\(^1\). Moreover, Pu is an alpha emitter and, \(^{239}\)Pu, the most abundant Pu isotope in nuclear waste, has a long half-life of \(2.41 \times 10^4\) years, posing long-term radio-toxicity to the biosphere if exposed. For example, leakage of nuclear waste containing Pu has occurred both at the Hanford Site, WA, and the Savannah River Site, SC, resulting in rivers, sediments and soil requiring long-term monitoring and remediation.\(^47,79,80\) In addition, far-field transport of Pu also has been observed both at the Nevada Test Site, USA, and the Mayak site, Russia,\(^8,10\) where
significant amounts were transported several kilometers from the source, possibly facilitated by mineral colloids in the subsurface and Pu intrinsic colloids. To protect the public health from the alpha emitters like Pu, the US EPA regulates the gross alpha particles in drinking water to under 15 pCi/L (0.56 Bq/L), for $^{239}$Pu that is at the level of $10^{-12}$ M. As the transport of Pu at such low concentrations is primarily controlled by its sorption to the sediments and bedrock it encounters in the subsurface, it is crucial to understand Pu chemistry at the solid and water interface in order to predict its transport in the subsurface.

However, the complex redox chemistry of Pu is a major factor limiting the understanding of its behavior at the solid and water interface because it usually coexists in four oxidation states, Pu(III), Pu(IV), Pu(V), and Pu(VI) in different proportions depending on the environmental conditions (e.g., pH and $E_H$), and each of these oxidation state exhibits a different affinity for aqueous complexation and sorption depending on its effective charge, which follows Pu(IV) > Pu(VI)$O_2^{2+}$ $\approx$ Pu(III) > Pu(V)$O_2^{+}$.\textsuperscript{81} Generally speaking, aqueous Pu(III) is stable only under acidic/anoxic conditions; as the pH and $E_H$ in the environment increases, oxidized Pu(IV), Pu(V), and Pu(VI) become stable and dominant in the aqueous phase. Pu(IV) usually possesses 2 to 3 magnitudes higher partition coefficients ($K_D$) than Pu(V), meaning that Pu(V) is the dominant aqueous species in oxic waters and Pu(IV) is the dominant species associated with mineral/sediment.\textsuperscript{21, 25} Several studies have demonstrated the importance of incorporating these Pu redox reactions in transport modeling. For example, Fjeld et al.\textsuperscript{82} incorporated Pu(V) reduction to Pu(IV) into the 1D modeling of its transport in a column study, finding that the Pu(V) to Pu(IV) reduction rate is crucial for transport modeling, while Kaplan et al.\textsuperscript{47} examined Pu transport
in a lysimeter exposed to the natural environment for 11 years, also finding the importance of incorporating the Pu(V)/Pu(IV) reduction/reoxidation cycle into the Pu transport modeling. Although Pu(III) was considered less stable and, therefore, less relevant for transport modeling under environmental conditions, Kaplan et al.\textsuperscript{28} directly measured 37\% of Pu(III) out of the total Pu associated with SRS sediment via x-ray absorption near-edge spectroscopy analysis (XANES), further supporting the importance of taking it into consideration in transport modeling. Recent studies have also observed surface-mediated Pu(V) reduction to Pu(IV) on several minerals\textsuperscript{21, 25}, making the understanding and modeling of its behavior and transport at the solid and water interface even more challenging. As these results suggest, further research on Pu redox reactions at the mineral and water interface to understand the redox reaction mechanisms as well as to improve the modeling of Pu at the solid and water interface under the influence of redox reactions is needed.

The partition coefficients (K\textsubscript{D}) that have been traditionally used in transport models are not reliable because they are affected by changes in the environment (\textit{e.g.}, pH, E\textsubscript{H}, and dissolved ions) and, therefore, do not provide a good model for elements with complex chemistry such as Pu. Rather, surface complexation modeling (SCM) describing the interfacial reactions based on thermodynamics provides a better prediction of the partition of elements of interest at the solid and water interface under variable environmental conditions. Over the past two decades, SCMs have been successfully applied to model radionuclide (U, Np, Am and etc.) sorption to pure minerals and sediments.\textsuperscript{41, 83-86} Moreover, the component additivity approach that models the partition of radionuclides to
natural sediment by summing the sorption of these elements to each coating mineral provides an approach for applying the stability constants calculated through SCM modeling of the lab results of their sorption to pure minerals directly to the field samples. However, SCM for Pu is limited primarily because of the difficulty in modeling its complex redox reactions.

To address this limitation, a modeling approach that incorporated the Pu redox reactions into SCM was developed using kaolinite (Al₂Si₂O₅) for batch sorption experiments and modeling. Kaolinite was chosen in this study for two reasons. First, it is a ubiquitous clay mineral having a low ion exchange capacity compared to other clay minerals such as montmorillonite and illite, therefore, minimizing the influence of ion exchange process for the study. Second, no redox reactive elements (such as Fe and Mn) presents as the major composition of kaolinite; therefore, the influence of Pu redox reaction mediated by redox reactive mineral surface is also neglected in this study. Thirdly, kaolinite was determined to be a crucial sorbent coated on sediments at the Savannah River Site, SC (SRS), where kilograms of Pu plume were accidentally disposed into the vadose zone in the subsurface. A previous study has modeled U(VI) sorption to SRS sediments by summing its sorption to its major coating minerals (kaolinite and goethite) using SCM. To predict the Pu partition at SRS sediments using the same approach, SCMs describing this element partitioning to kaolinite and goethite are needed.

In this study, batch experiments of initially input Pu as Pu(IV) sorption to kaolinite with the pH ranging from 2 to 8 were conducted under both aerobic and anaerobic conditions. Additional batch sorption experiments at variable ionic strengths were
conducted under aerobic conditions to assess the influence of the ion exchange process. Different sorption patterns under aerobic and anaerobic conditions were observed throughout the experiment because of the influence of Pu redox reactions. The redistribution of Pu oxidation states in the aqueous phase and at the kaolinite surface after sorption was measured using solvent extraction techniques. SCMs coupled with Pu redox reactions based on the Nernst equation, which transforms redox potential to stability constant, were applied to model the results of Pu sorption to kaolinite under both conditions. Both the experiments and the modeling indicated that the Pu(IV) reduction to Pu(III) under anaerobic condition could significantly affect its sorption to kaolinite. The SCMs incorporated Pu redox reactions in this study exhibited a good prediction of the Pu sorption pattern under both aerobic and anaerobic conditions as well as the redistribution of Pu oxidation states in the aqueous phase.

5.2 Materials and Methods

5.2.1 Pu(IV) Preparation

$^{238}\text{Pu}$ (Isotope Products, WA) was used for the experiment. To obtain Pu(IV) working solutions, a small aliquot of the $^{238}\text{Pu}$ stock solution was evaporated to dryness and re-dissolved in 0.1 M HCl in a Teflon vial. A small amount of NaNO$_2$ was added to reduce possible Pu(V/VI) to Pu(IV) in the solution. The concentrations of $^{238}\text{Pu}$ in the working solutions were determined using a liquid scintillation counter (LSC). The oxidation states of the $^{238}\text{Pu}$ working solutions were confirmed using the solvent extraction technique$^{30-32, 72, 87}$ prior to each batch experiment. More than 93% of Pu as Pu(IV) was
achieved prior to the batch sorption experiments. (Table B1 in Appendix B lists the concentrations and the oxidation state distributions of Pu in the working solutions).

5.2.2 Kaolinite and Other Chemicals

The purchased kaolinite standard KGa-1b (Washington County, Georgia, USA) was used for this study. The specific surface area of 10.05 ± 0.02 m²/g and the cation exchange capacity (CEC) of 0.02 meq/g from Data Handbook for Clay Minerals and Other Non-metallic Minerals for KGa-1b were used for the SCM modeling. The chemical composition of KGa-1b has been characterized in a previous study. As seen in the chemical composition of the kaolinite that is listed in Table B2 in Appendix B, a trace amount of TiO₂ is present.

All chemicals used in the experiment were analytical grade. All the solutions were prepared using distilled deionized water with a resistivity greater than 18 MΩ cm and less than 1 ppb total organic carbon. The distilled deionized water used for the experiment under anaerobic condition was degassed through a vacuum and then transferred to a vinyl anaerobic chamber (filled with N₂, and ~2% H₂, COY Laboratory Products). All the chemicals used for the experiment under anaerobic conditions were prepared in the anaerobic chamber. The oxygen content in the chamber is monitored using an oxygen monitor (COY Laboratory Products).

5.2.3 Liquid Scintillation Counting (LSC)

The ²³⁸Pu concentrations in the aqueous phase were determined via LSC (Hidex 300SL, Finland). Specifically, 0.5 mL – 1 mL of the aqueous sample was mixed with 5 mL of an optiphase HiSafe scintillation cocktail (PerkinElmer, MA) in a 7 mL plastic
scintillation vial. The alpha particles in each sample were counted in the range of 400 to 800 MeV for 30 minutes. A plastic scintillation vial containing only the scintillation cocktail was prepared and the alpha particles in it were counted for 30 minutes as the background prior to each counting event. The concentration of $^{238}$Pu in the aqueous phase ($C_{Pu-238}$, dpm/L) in each sample was calculated using Equation 16:

$$C_{Pu-238} \left( \frac{dpm}{L} \right) = \frac{CR_{Pu-238} - CR_{bkgd}}{V}$$

Equation 16

where $CR_{Pu-238}$ represents the count rate of alpha particles in each sample, $CR_{bkgd}$, the count rate of alpha particles of the background sample, and $V$, the volume of the aqueous sample measured.

5.2.4 Batch Sorption Experiment

Batch experiments of Pu(IV) sorption to kaolinite (1 g/L) with the pH ranging from 2 to 8 and the ionic strength fixed at 0.1 M (adjusted using NaCl) were conducted under both atmospheric CO$_2$(g) ($P_{CO2}$= $10^{-3.5}$ atm) and anaerobic conditions (conducted in a vinyl anaerobic chamber filled with N$_2$ and ~ 2% H$_2$). Additional batch experiments of Pu(IV) sorption to kaolinite from a pH ranging from 2 to 8 with ionic strengths of 0.05 M and 0.5 M were conducted under atmospheric conditions. The pH of the suspension solutions was adjusted by 1 pH unit increment using 0.1 M or 0.01M NaOH or HCl solutions. All samples were prepared in 15 mL polypropylene centrifuge tubes sealed with screw caps. The samples were mixed in an end-over-end tumbler until they reached equilibrium. For the purpose of quality control, duplicate samples were prepared at pH 2, 4, 6, and 8; samples free of kaolinite but spiked with $^{238}$Pu (IV) were also prepared at pH 2, 3, 4, and 8.
Pu concentration in the aqueous phase was measured via LSC every 5 days until the sorption equilibrium was reached. Specifically, 1.3 mL of suspension from each sample was transferred to a 1.5 mL centrifuge tube, and centrifuged at 8000 rpm for 30 min (Beckman Coulter Allegra X-22R Centrifuge). This setup was calculated to leave particles < 100 nm in the supernatant. Subsequently, 1 mL of supernatant was sampled for $^{238}$Pu measurement via LSC. For the anaerobic samples, all the sampling and oxidation state separation procedures were conducted in the anaerobic chamber, while the centrifuge for solid/liquid separation as well as the LSC analysis were conducted under atmospheric condition. The sorbed fraction was calculated by subtracting the Pu aqueous concentration $[Pu_{aq}]$ from the initial Pu concentration $[Pu_{initial}]$. The percentage of Pu sorbed to kaolinite $[Pu_{sorbed}]$ was calculated using Equation 17.

$$[Pu_{sorbed}] (\%) = \frac{[Pu_{initial}] - [Pu_{aq}]}{[Pu_{initial}]} \times 100$$  \hspace{1cm} \text{Equation 17}

5.2.5 pH and $E_H$ measurements

The pH and $E_H$ of each sample suspension were measured prior to each sampling event. The pH electrode (Thermo Scientific) was calibrated at room temperature using certified commercial buffers (Thermo Scientific) with pH = 4.01, pH = 7.00, and pH = 10.01. The $E_H$ was measured by a glass body ORP redox electrode (9778BNWP, Thermo Scientific), which was calibrated using an ORP Standard (Thermo Scientific) of 220 mV for Ag/AgCl the reference electrodes. The measured $E_H$ values were converted to the standard reduction potential ($E_H^\circ$) at room temperature by adding 200 mV. Because the modeling software constrain the redox potential of the system using electron activity (-
log_{ae} - or pe), the $E_{H^0}$ values were converted to pe values for modeling using the relationship of $pe=16.9E_{H^0}$ at 25 °C.

5.2.6 Determination of Aqueous and Solid Plutonium Oxidation States

Because the concentration of $^{238}$Pu used in this study was at trace level ($10^{-10}$ M), spectroscopic technique cannot be used for the direct Pu oxidation state measurement. Instead, the distribution of Pu oxidation state in the aqueous phase as well as that associated with the solid phase was determined after the sorption reaching equilibrium using solvent extraction techniques.\(^{30-32, 72, 87}\)

Specifically for Pu oxidation states analysis in the aqueous phase, the procedure was as follows. First, each sample in the 15 mL polypropylene tube was centrifuged at 8000 rpm for 30 minutes. The supernatant was then passed through a 3k MWCO filter for ultrafiltration in two fractions, with the first fraction used to equilibrate the filter with the filtrate being discarded; the second fraction of filtrate was used for the oxidation state analysis in the aqueous phase. Next, 0.025 M 4-benzyol-3-methyl-1-phenyl-2-pyrazolin-5-one (PMBP) dissolved in hexane and 0.5 M bis-(ethylhexyl)-phosphoric acid (HDEHP) dissolved in hexane were used for the Pu oxidation state analysis. Specifically, 0.8 mL of aqueous sample were mixed vigorously with 0.2 mL of 5 M HCl and 0.5 mL of PMBP for 3 minutes and centrifuged at 8000 rpm for 3 minutes for phase separation; the aqueous phase and the organic phase were then sampled separately for Pu quantification using LSC. The PMBP organic phase selectively extracts Pu(IV) at pH 0, leaving Pu(V) and Pu(VI) in the aqueous phase, which quantified the Pu(IV) in the sample. The same procedure was conducted using HDEHP for Pu(V) quantification because the 0.5 M HDEHP organic
solution selectively extracts Pu(IV) and Pu(VI) at pH 0, leaving Pu(V) in the aqueous phase.

To determine the concentration of Pu(III) in the anaerobic samples, an additional PMBP solvent extraction was conducted in combination with 4 mM potassium dichromate (K₂Cr₂O₇) (Cr-PMBP). This Cr-PMBP procedure extracts both Pu(III) and Pu(IV) to the organic phase. The concentration of Pu(III) was then determined based on the difference between the Pu concentration in the Cr-PMBP and the PMBP organic phases.

The Pu oxidation state associated with the solid phase was analyzed using the following procedure. After decanting the aqueous phase of the original sample, the wet sediment was resuspended in 0.3M HCl and mixed for 15 minute to leach the sorbed Pu into the acidic aqueous phase. The mixture was then centrifuged, and the supernatant was passed through a 3k MWCO centrifugal filter in the same manner described in the previous procedure. This acid leaching step was assumed to remove all the Pu(V) and Pu(VI) associated with the sediment surface, and any unleachable plutonium was assumed to be Pu(IV). The oxidation states of Pu in the filtrate of the acid leachate were determined using the solvent extraction described previously.

5.2.7 Modeling

A FORTRAN-based computer code FIT4FD⁷⁷ (a version adapted from FITEQL 4.0⁷⁵) was used for the non-linear fitting of the experimental data and determining the stability constants for Pu cation exchange constants at the kaolinite and water interface. The hydrolysis reactions of Pu(III/IV/V/VI) were considered in the modeling, while Pu (bi)carbonate complexation was neglected for the pH range studied here. The Pu
interactions at the kaolinite and water interface were modeled through both surface complexation and cation exchange reactions via a double layer model (DLM) to account for the electrostatic effect at the interface as well as to maintain the fewest modeling parameters. The mineral structure of kaolinite (Al$_2$Si$_2$O$_5$) was visualized as a gibbsite layer (Al(OH)$_3$) overlying a siloxane layer (SiO$_2$) at a 1:1 ratio. Here a component additivity method was used to model the kaolinite surface complexation by assuming two surface complexation sites [=AlOH] and [=SiOH] at a 1:1 ratio corresponding to the kaolinite structure. The stability constants for Pu(IV) and Pu(V) surface complexation to [=AlOH] and [=SiOH] calculated from the SCMs of Pu complexation to other aluminosilicate minerals were used to calculate the Pu surface complexation to kaolinite in this study. The total surface site density for surface complexation was calculated using the following equation:

$$\text{Surface site density (mol/L)} = C \left( \frac{g}{L} \right) \times SSA \left( \frac{m^2}{g} \right) \times 10^{18} \frac{nm^2}{m^2} \times 2.3 \left( \frac{\text{site}}{nm^2} \right) \times \frac{1}{N_A}$$

in which the surface site density was calculated in the unit of molarity (mol/L), C represents the concentration of kaolinite in the suspension (in g/L), SSA represents the specific surface area of the kaolinite, 2.3 site/nm$^2$ is the average site density assumed in many SCMs, and $N_A$ represents the Avogadro’s number of $6.022 \times 10^{23}$. Specifically in this model, it is assumed that the [=AlOH] and the [=SiOH] each account for half of the total surface site density based on the 1:1 ratio structure of kaolinite. Stumm and Coppin et al. provided thorough descriptions of the origin of the surface sites on kaolinite, finding three types of surface sites are available for the surface complexation: the edge surfaces of the gibbsite layer and the siloxane layer as well as the gibbsite basal plane. Some previous
studies modeled the surface complexation of actinide to clay mineral using only 20% of the total surface site density, based on an assumption that the surface complexation process only occurs at the edge sites of clay minerals. However, in this study, it is assumed that the surface complexation occurs both at the interlayer and the basal plane of the kaolinite.

The cation exchange sites on kaolinite originate from the isomorphic substitution of Si by Al. The primary difference between the cation exchange site and the surface complexation site is that the former is a permanent site not affected by the pH of the solution, while the later experiences protonation and deprotonation depending on the pH of the solution. The cation exchange process was modeled in this study using the Vanselow convention. The CEC of kaolinite was used to calculate the concentration of the total cation exchange sites. Because the background electrolyte is monovalent NaCl, the cation exchange site for 1 g/L of kaolinite suspension is calculated to be $2 \times 10^{-5}$ M.

All the aqueous and surface reactions involving Pu(III), Pu(V), and Pu(VI) in the database for SCM were coupled with Pu redox reactions with Pu(IV), resulting in all the Pu reactions in the modified database using Pu(IV) as a reactant. The standard electrode potentials ($E^0$) for Pu redox half reactions at zero ionic strength were converted to stability constants based on the Nernst equation:

$$\ln K = \frac{nFE^0}{RT}$$

And the stability constants for Pu redox half reactions were coupled to reactions with Pu(III/V/VI) as reactants. An example of the redox coupling is shown below:

$$\begin{align*}
\text{Pu}^{3+} + \text{H}_2\text{O} &= \text{Pu(OH)}^{2+} + \text{H}^+ \\
\text{Pu}^{4+} + e^- &= \text{Pu}^{3+}
\end{align*}$$

\begin{align*}
\log K &= -6.8 \quad \text{Equation 18} \\
\log K &= 17.69 \quad \text{Equation 19}
\end{align*}
Equation 20

\[
\text{Pu}^{4+} + \text{H}_2\text{O} + e^- = \text{Pu(OH)}^{2+} + \text{H}^+ \quad \log K = 10.89
\]

Equation 18 exhibits Pu(III) hydrolysis reaction and its stability constant, Equation 19 exhibits the Pu(III)/Pu(IV) redox half reaction and the stability constant associated with it, and Equation 20 results from summing Equation 18 and Equation 19 (both the reactions and the stability constants), which coupled the Pu(IV)/Pu(III) redox reaction to the Pu(III) hydrolysis reaction and made Pu\(^{4+}\) the reactant in the modified reaction instead of the Pu\(^{3+}\) appearing in the original uncoupled reaction. All the aqueous, surface complexation, and cation exchange reactions involving Pu(III), Pu(V), and Pu(VI) were coupled with Pu redox half reactions in this manner. This modified database simulated the situation of initial Pu as Pu(IV), and the energy required for the transformation of the oxidation state from Pu(IV) to Pu(III/V/VI) was, therefore, incorporated into the modeling of the Pu interactions at the solid and water interface.

The pH, \([\text{Pu}_{\text{initial}}]\), and \([\text{Pu}_{\text{aq}}]\) measured from the batch sorption experiments were used as the input parameters to constrain the Pu speciation at the kaolinite and water interface. The pe values, which is a crucial parameter for modeling the redox potential of the system, were calculated from the pH + pe = 16.2 relationship used in Marsac et al.\(^{57}\) for modeling Pu sorption to kaolinite under the aerobic condition, mainly because the measured ones did not converge to consistent stability constants for the cation exchange process for Pu sorption to kaolinite at different ionic strengths. However, the measured pe values were used for modeling the Pu sorption to kaolinite under the anaerobic condition. The pH and pe values together govern the Pu redox reactions, and the speciation of Pu in the aqueous phase as well as the surface complexation reaction.
5.3 Results and Discussions

5.3.1 Pu(IV) Sorption to Kaolinite under Aerobic/Anaerobic Conditions

The sorption of Pu(IV) to kaolinite as a function of pH showed different patterns under aerobic and anaerobic conditions (Figure 14). For the aerobic condition, strong sorption began at a low pH of 2 to 3, followed by a zone of decrease at an intermediate pH of 4 to 6, with the highest sorption being achieved at approximately pH 7.5 (Figure 14). Similar sorption pattern was observed for the Pu-kaolinite system at higher initial Pu(IV) concentration by Buda et al.\(^93\) However, for Pu sorption to kaolinite under the anaerobic condition, the elevated sorption at pH 2 to 3 was not seen; instead the sorption increased as a function of pH with almost 100% sorption appearing at ~ pH 6.

This difference in the sorption patterns under these two conditions is probably a result of the different transformations of the Pu oxidation state under oxidizing and reducing conditions, a hypothesis confirmed by the Pu oxidation state analysis shown in Figure 2. Under the aerobic condition, significant ingrowth of Pu(V) in the aqueous phase was measured in the samples at a pH ranging from 3 to 7.7 (Figure 15A). This ingrowth is probably the cause of the decrease in sorption at pH 4 to 6 because Pu(V) has a weaker affinity for the surface than Pu(IV). A batch sorption experiment of Th(IV), an actinide stable in the tetravalent state, to kaolinite as a function of pH showed no decrease of sorption at this intermediate pH region\(^93\), further indicating the pattern of Pu(IV) sorption to kaolinite under the aerobic condition is affected by the change in its oxidation state.

On the contrary, the oxidation state analysis of Pu in the aqueous phase under the anaerobic condition measured a significant ingrowth of Pu(III) in the samples at a pH
ranging from 1 to 4 (Figure 15B). This ingrowth probably shifted the Pu sorption edge towards a higher pH range. The sorption of Pu(IV) to kaolinite under the anaerobic condition showed a pattern similar to that of Pu(III) and Am(III) sorption to kaolinite found by Buda et al.94 The results of Pu oxidation state analysis above pH 4 are not shown in Figure 15B, because the majority of Pu was sorbed to kaolinite at pH 4 and above, resulting in Pu concentration in the aqueous samples close to the background, meaning the measurement was no longer reliable. The oxidation state analysis for Pu associated with the kaolinite measured more than 99% Pu(IV) for the aerobic samples and 95% Pu(IV) for the anaerobic samples (See Appendix B).

The high sorption of Pu(IV) at the low pH ranges is probably the result of cation exchange, because the kaolinite complexation sites are protonated at these low pH values (pKₐ of kaolinite is approximately 4.2). The effect of cation exchange was further examined by comparing Pu(IV) sorption to kaolinite at the different ionic strengths of 0.05 M and 0.5 M under the aerobic condition in Figure 16, exhibiting that higher sorption of Pu to kaolinite at the ionic strength of 0.05 M than that of 0.5 M. The differences are particularly significant in the low pH ranges, indicating the influence of cation exchange. Previous studies have also observed this cation exchange process at the kaolinite and water interface.42, 95-98
Figure 14 Sorption of Pu (IV) on kaolinite (1 g/L) as a function of pH at I = 0.1M (NaCl) and room temperature under aerobic (red) and anaerobic conditions (blue). Samples were collected at the 5th day and 10th day; both experiments showed equilibrium within 5 days.
Figure 15: Pu oxidation state distribution in the aqueous phase as a function of pH under aerobic condition (A) and anaerobic condition (B).

Figure 16: Pu sorption to kaolinite with ionic strength of 0.05 M and 0.5 M adjusted using NaCl. Errors are propagated from counting statistics.
5.3.2 SCM of Pu Sorption to Kaolinite under the Aerobic Condition

Pu(IV) sorption to kaolinite under the aerobic conditions at ionic strengths of 0.05 M, 0.1 M, and 0.5 M was modeled using the redox-coupled SCMs (Figure 17). Cation exchange constants for Pu(OH)$^{3+}$ and Pu(OH)$_2$$^{2+}$ were calculated through simultaneously modeling the sorption data at three variable ionic strengths. The surface complexation and cation exchange reactions and their stability constants used for the modeling are also listed in Table 7. Two types of interactions were used to model the Pu sorption to kaolinite. As shown in Figure 17, the cation exchange of Pu(IV) dominated the sorption from pH 2 to 4, while Pu complexation to [$≡$AlOH] and [$≡$SiOH] dominated the sorption from pH 4 to 8. These results are consistent with Dong et al. 42, who modeled UO$_2$$^{2+}$ sorption to SRS soil primarily coated with kaolinite and goethite. Their study indicated that at pH < 4.0, UO$_2$$^{2+}$ sorbed to the SRS soil dominantly via the exchange sites on kaolinite, while at pH > 4.0, UO$_2$$^{2+}$ complexation to the goethite and kaolinite edge sites dominated the sorption. In addition, models in my study showed that the cation exchange process weakened with increasing ionic strength; in particular at the ionic strength of 0.5 M, only a very small portion of the cation exchange process contributed to the overall sorption (Figure 17C), which is consistent with the observation and previous understanding of the cation exchange process that the exchange site is preferentially taken by the background electrolyte. Moreover, this model indicated a larger portion of Pu sorbed to [$≡$AlOH] than [$≡$SiOH], findings consistent with previous results that complexation to aluminol sites are stronger than silanol sites. 90,91 This model used 100% of the surface sites, indicating that the surface
complexation occurred not only at the edge site, but also at the basal plane, probably because the kaolinite structure exposed the \([\equiv \text{AlOH}]\) basal surface for complexation.

The calculated pe values instead of the measured ones were used for this modeling because the latter did not converge to consistent stability constants across variable ionic strengths. Several reasons may explain these unrepresentative pe measurements: 1. The dissolution of trace Ti\(^{4+}\) from kaolinite at the low pH ranges may interfere with the functionality of the platinum electrode; and 2. The redox potential at the interface may differ from that measured in the aqueous phase as surface mediated Pu redox reactions were observed on both redox reactive and non-redox reactive mineral surfaces in previous studies.\(^{21,25}\)

Here essentially two criteria were applied to evaluate the goodness of the SCM/CE modeling for Pu(IV) sorption to kaolinite: 1. Whether the model predicted the partition of Pu at the kaolinite and water interface; and 2. Whether the model predicted the Pu aqueous oxidation state speciation. Figure 17D plotted the distribution of Pu oxidation states calculated from this SCM, which is consistent with the measurements of the Pu oxidation states in this study. Despite the ingrowth of Pu(V), the SCM also predicted predominant Pu(IV) (>99%) as the sorption species, which is also consistent with the measurements of the Pu oxidation state associated with kaolinite.

Marsac et al.\(^{57}\) modeled the Pu(IV) sorption to kaolinite under aerobic conditions using a similar Nernst formalism to couple the Pu redox reactions to the surface complexation modeling. However, a generic surface species \([\equiv \text{SOH}]\) and a non-electrostatic assumption were used for their modeling. Because of the differences in their
surface species and modeling assumptions compared to the models in this study, it is difficult to directly compare their modeled stability constants with ours. However, both models predicted the evolving of Pu(V) at ~ pH 3 under the aerobic condition.

Figure 17: Modeling of Pu(IV) sorption to kaolinite under aerobic condition with ionic strength of 0.05 M (A), 0.1 M (B), and 0.5 M (C). For Figure 17 A – C, the dots represent experimental data, solid black line represents the total modeling outcome. Blue dash line represents ion exchange process, green and red dash lines represent Pu complexation to the aluminol and the silanol site, respectively. Model predicted Pu oxidation state distribution in the aqueous phase with ionic strength of 0.1 M (D).
Table 7 Selected Surface Reactions and Constants for Kaolinite

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>≡AlOH = ≡AlO(^-) + H(^+)</td>
<td>-9.73</td>
</tr>
<tr>
<td>≡AlOH + H(^+) = ≡AlO(^2+)</td>
<td>8.33</td>
</tr>
<tr>
<td>≡AlOH + Pu(^{4+}) + H(_2)O = ≡AlOPu(OH)(^{2+}) + 2H(^+)</td>
<td>13.87</td>
</tr>
<tr>
<td>≡AlOH + Pu(^{4+}) + 2H(_2)O = ≡AlOPu(OH)(^{2+}) + 3H(^+)</td>
<td>5.46</td>
</tr>
<tr>
<td>≡AlOH + Pu(^{4+}) 3H(_2)O = ≡AlOPu(OH)(^{3+}) + 4H(^+)</td>
<td>-2.92</td>
</tr>
<tr>
<td>≡AlOH + Pu(^{4+}) + 2H(_2)O = AlOPuO(_2) + 5H(^+) + e(^-)</td>
<td>-23.7</td>
</tr>
<tr>
<td>≡AlOH + Pu(^{4+}) + e(^-) = ≡AlOPu(^{2+}) + H(^+)</td>
<td>22.61 (anaerobic)</td>
</tr>
<tr>
<td>≡SiOH = ≡SiO(^-) + H(^+)</td>
<td>-7.2</td>
</tr>
<tr>
<td>≡SiOH + Pu(^{4+}) + 2H(_2)O = ≡SiOPu(OH)(^{2+}) + 3H(^+)</td>
<td>2.202</td>
</tr>
<tr>
<td>≡SiOH + Pu(^{4+}) + 3H(_2)O = ≡SiOPu(OH)(^3) + 4H(^+)</td>
<td>-2.189</td>
</tr>
<tr>
<td>≡SiOH + Pu(^{4+}) + 2H(_2)O = ≡SiOPuO(_2)(^+) + 4H(^+) + e(^-)</td>
<td>-15.58</td>
</tr>
<tr>
<td>≡SiOH + Pu(^{4+}) + e(^-) = ≡SiOPu(^{2+}) + H(^+)</td>
<td>21.41 (anaerobic)</td>
</tr>
<tr>
<td>≡SiOH + Na(^+) = ≡SiONa + H(^+)</td>
<td>-5.5</td>
</tr>
</tbody>
</table>

Ion Exchange

X\(^-\) + H\(^+\) = XH | 1.224 |
3X\(^-\) + Pu\(^{4+}\) + 3X\(^-\) = X3Pu | 20.17  |
4X\(^-\) + Pu\(^{4+}\) + H\(_2\)O = X2PuOH + H\(^+\) | 6.3    |
4X\(^-\) + Pu\(^{4+}\) + 2H\(_2\)O = X2Pu(OH)\(_2\) + 2H\(^+\) | 3.226  |

5.3.3 Modeling of Pu(IV) sorption to kaolinite under the anaerobic condition

The significant ingrowth of Pu(III) under the anaerobic condition requires the incorporation of the Pu(IV)/Pu(III) redox reaction as well as the Pu(III) interactions with kaolinite in order to model the sorption under this condition. Stability constants for Pu(III) sorption to kaolinite were not available from previous studies, but stable trivalent actinides are often used as surrogates.\(^{57,62}\) The experimental results of Am(III) sorption to alumina
in Righetto et al.\textsuperscript{99} and Am(III) sorption to silica gel in Moulin et al.\textsuperscript{100} were modeled via non-redox coupled SCMs (Figure 18A and 18B). The stability constants calculated from the SCMs are shown in Appendix B. Figure 18 shows that the surface complexation dominated the Am(III) sorption to both alumina and silica gel and the effect of cation exchange is very weak because there is no isomorphic element substitution for either alumina or silica gel.

![Figure 18: A) SCM of Am(III) sorption on alumina, 0.1 M; B) SCM of Am(III) sorption on silica gel, 0.1M.](image)

The stability constants determined from the SCMs of Am(III) sorption to silica gel and alumina were coupled with the Pu(III)/Pu(IV) redox reaction for the purpose of incorporating the energy required for Pu(IV) reduction to Pu(III) into the modeling of
Pu(IV) sorption to kaolinite. Essentially all the stability constants for Am(III) sorption were increased by 17.69 to model the Pu(IV) sorption to kaolinite under the anaerobic condition with Figure 19 showing the results. Similar to the SCMs under the aerobic condition, the cation exchange process dominated at the pH < 4 under the anaerobic condition, and Pu complexation to \([≡\text{AlOH}]\) and \([≡\text{SiOH}]\) dominated at the pH 4 to 8 (Figure 19). Pu complexation to \([≡\text{AlOH}]\) is also stronger than its complexation to \([≡\text{SiOH}]\). However, unlike modeling under the aerobic condition, both measured pH and pe values were used as constraints for the model under the anaerobic condition, which predicted a significant ingrowth of Pu(III) in the aqueous phase, findings consistent with our measurements of the Pu oxidation states in the experiment. The modeled Pu aqueous oxidation state speciations are shown in Appendix B. However, the model also predicted Pu(III) as the dominant species sorbed to kaolinite, which is not consistent with the measurements of the Pu oxidation states on kaolinite with dominant Pu(IV). Contradicting results regarding the Pu oxidation states associated with the solid were shown in previous research. The predominance of Pu(IV) associated with mineral surfaces has been observed in many previous studies.\textsuperscript{21, 25} Moreover, some studies have found that Pu(III) is not stable on the surface because it oxidizes to Pu(IV) there. However, recent Pu oxidation states measured using a spectroscopic approach observed a significant amount of Pu(III) associated with the solid phase.\textsuperscript{28} Currently, research on Pu(III) redox reactions on the surface is limited, with the mechanism of the sorption and redox reactions of Pu(III) at the solid and water interface remaining unclear. Although the experimental results indicated a possible process
of Pu(III) oxidizing to Pu(IV) at the kaolinite surface under the anaerobic condition, the current model could not predict redox reactions occurring at the surface.

![Figure 19: Redox coupled SCM of Pu sorption on kaolinite under anaerobic condition.](image)

### 5.4 Conclusions

The batch experiment of Pu(IV) sorption to kaolinite under aerobic condition and anaerobic condition exhibited different sorption pattern, and the oxidation state analysis of Pu indicated the difference resulting from the different Pu oxidation state transformation under different environments. Pu(V) evolved at an intermediate pH range under aerobic condition during the sorption, while Pu(III) evolved in the acidic samples under anaerobic condition. In order to model the Pu sorption to kaolinite with the influence of Pu oxidation state transformation, redox coupled SCMs were applied to incorporate the Pu(IV) to Pu(V), Pu(III) and Pu(VI) transformation into the Pu aqueous and surface speciation modeling. The redox coupled SCMs were capable of modeling the Pu sorption to kaolinite under both conditions. In addition, ion exchange process at low pH range was observed and the process
was needed to model the Pu sorption to kaolinite at that pH range. However, the modeling of Pu sorption to kaolinite at variable ionic strength required the use of empirical $E_H$ values instead of experimentally measured ones indicating the challenge of modeling a complex system under variable conditions. Above all, both the experimental results and the modeling indicated the influence of Pu redox transformation on its sorption to kaolinite as well as the importance of incorporating the Pu redox reactions to modeling. A SCM coupled with Pu redox reactions and ionic strength process provides a more accurate modeling approach for the partitioning of Pu at the clay and water interface. The component additivity approach is capable of modeling Pu sorption to kaolinite, however, modeling of other actinides/heavy metals using this approach is needed.
CHAPTER 6

SURFACE COMPLEXATION MODELING OF Eu(III) AND U(VI) INTERACTIONS WITH GRAPHENE OXIDE

Abstract

Graphene oxide (GO) has great potential for actinide removal due to its extremely high sorption capacity, but the mechanism of sorption remains unclear. In this study, the carboxylic functional group and an unexpected sulfonate functional group on GO were characterized as the reactive surface sites and quantified via diffuse layer modeling of the GO acid/base titrations. The presence of sulfonate functional group on GO was confirmed using elemental analysis and x-ray photoelectron spectroscopy. Batch experiments of Eu(III) and U(VI) sorption to GO as a function of pH (1 – 8) and as a function of analyte concentration (10 – 100, 000 ppb) at a constant pH ≈ 5 were conducted; the batch sorption results were modeled simultaneously using surface complexation modeling (SCM). The SCM indicated that Eu(III) and U(VI) complexation to carboxylate functional group is the main mechanism for their sorption to GO; their complexation to the sulfonate site occurred at the lower pH range and the complexation of Eu(III) to sulfonate site are more significant than that of U(VI). Eu(III) and U(VI) facilitated GO aggregation was observed with high Eu(III) and U(VI) concentration and may be caused by surface charge neutralization of GO after sorption.
6.1 Introduction

Radionuclide immobilization and removal from aqueous solutions is crucial for efficient radioactive waste management and environmental remediation. Particularly for actinides with long half-life, even small amounts of radioactivity can pose a long-term radiation hazard for drinking water (EPA Maximum Contaminant Level for alpha emitters is 15 picocuries per liter). Sorption is one of the most efficient approaches for actinide removal from aqueous solutions; many studies have been conducted of radionuclide sorption onto natural materials (e.g., Fe-oxides and clay minerals) with an interest in developing linear free energy relationships between surface complexes and comparable aqueous complexes.\textsuperscript{41, 50} These minerals are ubiquitous in the environment and play an important role for radionuclide retardation and immobilization. However, the minerals have a low capacity and efficiency for radionuclide removal\textsuperscript{68, 101} relative to the GO studied in this work.

Recent studies have shown that GO has greater actinide sorption capacity and faster actinide sorption kinetics than most natural materials and commonly used synthetic sorbents, like activated carbon or carbon nanotubes.\textsuperscript{64, 66-68, 101-103} For example, the reported maximum U(VI) sorption onto GO ranges from ~100 – 300 mg/g at pH 4 – 5, which is one to two orders of magnitude higher than that for natural materials.\textsuperscript{64, 101, 102} Other work has demonstrated remarkably fast kinetics of actinide sorption to GO reaching equilibrium within 5 min to an hour.\textsuperscript{67, 68, 103} Of these studies, only one observed weak sorption
hysteresis after the fast sorption in the first hour.\textsuperscript{101} The sorption of actinides to GO is pH dependent, but independent of ionic strength up to 1 M.\textsuperscript{64, 68, 102} Thus actinides can clearly outcompete background electrolyte ions for sorption sites and likely form inner sphere complexes with functional groups on the GO surface, similar to analogous aqueous complexation studies with similar functionalized ligands. Thermodynamic values extrapolated from van’t Hoff plots and extended x-ray absorption fine structure (EXAFS) data have demonstrated that inner sphere complexes form.\textsuperscript{64, 66, 68, 101-103}

The abundant oxygen-containing functional groups on GO are believed to be crucial for actinide sorption via binding with hard-acid carboxylate groups. However, no studies have identified specific functional groups controlling actinide sorption. Moreover, the type and amount of functional groups on GO varies depending on the GO preparation method and conditions\textsuperscript{104}, leading to different sorption capacities for different GO materials. Variations in GO morphology and particle size (single sheet vs. multi-layered, nano vs micron size) may also affect the sorption capacity.

Surface complexation modeling (SCM) has been applied to simulate actinide interactions at solid-water interfaces.\textsuperscript{41, 83, 105} The stability constant (log $K_S$) modeled from SCMs can be used to account for many environment-related factors like pH, ionic-strength, aqueous speciation, etc., and is considered to be more robust than the traditionally-used empirical partition coefficient ($K_d$) for sorption modeling and prediction. The surface complexation equilibrium constants developed from SCMs have the potential to achieve more accurate models of solid-water partitioning and can be used to more accurately represent waste treatment process and actinide environmental transport modeling. SCMs
have not been applied to model the interfacial interaction between actinides and GO, and possible interactions between actinides and GO functional groups have only been deducted. Although the exact quantity of surface functional groups is unknown on GO due to its differences in production methods and inherently complex physical structures, the reactive surface sites on GO can be characterized and quantified by SCM of the protonation/deprotonation from acid/base titration of GO. A few SCM models have been applied to understand the surface properties of GO and heavy metal binding to GO.\textsuperscript{66, 106} Sun et al.\textsuperscript{66} simulated Eu(III) sorption on graphene oxide nanosheets using a diffuse double layer model (DLM) with the assumption that the GO surface is amphoteric ($\equiv$SOH\textsubscript{2}\textsuperscript{+} at lower pH range and $\equiv$SO\textsuperscript{−} at basic condition). Their model showed that Eu(III) was the dominant sorbed species at pH 2-6, and the Eu\textsubscript{2}(OH)\textsubscript{4}\textsuperscript{4+} bidentate complex with GO was dominant at pH 7 - 11. However, their model could not explain the high degree of sorption at pH < pHzc.

In the present study, batch sorption experiments and SCM modeling were combined to evaluate Eu(III) (as an analog for trivalent actinides\textsuperscript{62, 105}) and U(VI) sorption onto GO. The GO surface deprotonation was characterized through acid/base titration and subsequent DLM modeling in order to characterize the reactive surface sites and corresponding surface acidity constants (log K\textsubscript{S}). Batch sorption experiments of Eu(III) and U(VI) sorption onto GO using variable pH (1-8) and variable sorbate concentrations (at a constant pH ≈ 5) were conducted. Both sets of batch sorption results were modeled simultaneously using a DLM-SCM. Aggregation facilitated by high concentrations of Eu(III) and U(VI) were observed during isotherm studies and further studied using SCM.
6.2 Materials and Methods

6.2.1 Graphene Oxide

A 4 g/L GO dispersion (in H₂O) stock solution (Sigma Aldrich) prepared by the method of Hummers and Offeman was used for this study. The GO was characterized using field emission scanning electron microscopic (SEM), Fourier transformed infrared spectroscopy (FT-IR), and powder x-ray diffraction (XRD). The specific surface area (SSA) of GO was obtained using BET-N₂ (g) sorption. In order to confirm the existence of sulfonate group on GO, the GO dispersion solutions were washed by 1 M NaCl, 0.1 M HCl, and DDI water to eliminate any possible sulfate and other residues in the purchased sample (see Appendix C for the detailed wash steps). Both unwashed GO (used for acid/base titration and batch sorption experiments) and washed GO were further characterized using CHNS elemental analysis and x-ray photoelectron spectroscopy (XPS) for bulk carbon and sulfur content as well as surficial carbon and sulfur quantification. A detailed description of the GO characterization can be found in Appendix C.

6.2.2 Other Chemicals

Eu(III) and U(VI) used in this study were diluted from 1000 ppm stock solution in 2% HNO₃ (High Purity Standards) and characterized using inductively coupled plasma mass spectrometry (ICP-MS, Thermo Scientific X Series II). All chemicals used in this experiment were analytical grade. All the solutions were prepared with distilled deionized water with a resistivity greater than 18 MΩcm and less than 1 ppb total organic carbon. The ionic strength of all the solutions used in the work was fixed at 0.01 M NaCl.
6.2.3 Acid/base Titration

The surface protonation/deprotonation of GO was characterized using potentiometric titrations. The titrations were conducted using a Metrohm 836 Titrando autotitrator controlled by Windows-based software TIAMO (Metrohm, Switzerland). Four sets of titrations with different GO concentrations (0.02 g/L, 0.1 g/L, 0.5 g/L, and 1 g/L) were conducted in 0.01 M NaCl from pH 2.5 to 10.5. Approximately 40 mL of the GO suspension was stirred in a 75 mL glass titration cell at room temperature. To prevent CO₂ interference, during the titration the headspace of the titration cell was purged with high purity N₂ gas which had bubbled through 1 M NaOH then water. Prior to base titration, a known amount of 0.1 M HCl was added to the suspension in order to lower the pH to ~2.5, and the suspension was purged with high purity N₂ for 30 min for dissolved CO₂ elimination. The base titrations were performed by incremental addition of 0.05 mL of 0.1 M NaOH until the pH of the suspension reached 10.5. Acid titration was then performed by incremental addition of 0.05 mL of 0.1 M HCl until the pH of the suspension was lowered to 3. Each incremental addition was added after the pH drift became less than 0.1 mV/min, or after an equilibrium time of 10 min. The total [H⁺] (ca, mol) added, total [OH⁻] (cb, mol) added, and total volume of suspension (V_total) after titration was recorded. The net proton concentration (Net [H⁺]) in the suspension was calculated using Equation 21.

\[
\text{Net } [\text{H}^+] = \frac{(c_a - c_b)}{V_{\text{total}}}
\]

Equation 21

6.2.4 Eu(III) and U(VI) Sorption Experiment

Batch experiments of 10 ppb Eu(III) or U(VI) (6.6 × 10⁻⁸ M and 4.2 × 10⁻⁸ M, respectively) sorption to 0.1 g/L of GO as a function of pH (1-8) with ionic strength of 0.01
M were prepared at room temperature. Duplicate samples were made at pH 2, 4, and 6 for quality assurance. Constant pH sorption isotherms examining Eu(III) and U(VI) sorption to GO were conducted under room temperature with 0.1 g/L GO at pH 5.0 ± 0.1 in 0.01 M NaCl. For the isotherms, the initial input of Eu(III) or U(VI) ranged from 10 to 100,000 ppb. The batch samples were shaken for two days to achieve sorption equilibrium which has been shown in previous studies to be adequate.\textsuperscript{67, 101, 103} After 48 hours 1.3 mL of suspension from each sample was transferred to a 1.5 mL centrifuge tube, and centrifuged at 8000 rpm for 60 min for solid and aqueous phase separation (Beckman Coulter Allegra X-22R Centrifuge). The concentration of Eu(III) or U(VI) in the aqueous phase ($C_{aq}$) was measured using ICP-MS. The percentage of Eu(III) or U(VI) that sorbed to GO ($C_{sorbed}$) was calculated using Equation 22, where $C_0$ is the initial input concentration of Eu(III) or U(VI). The concentration of Eu(III) or U(VI) associated with GO ($C_{sorbed}$, mol/g) was calculated using Equation 23, where $V$ is the total volume of the sample and $m$ is the mass of GO in the sample.

\[
Sorption\ Percentage(\%) = \frac{C_0 - C_{aq}}{C_0} \times 100\% \quad \text{Equation 22}
\]

\[
C_{sorbed} = \frac{(C_0 - C_{aq})V}{m} \quad \text{Equation 23}
\]

### 6.2.5 Surface Complexation Modeling

GO surface acidity constants ($\log K_+\alpha$ and $\log K_\alpha$), U(VI)/Eu(III) sorption as a function of pH, and the respective sorption isotherms were modeled using a modified version of FITEQ 4.0 to use b-dot activity corrections and database usage\textsuperscript{75}. U(VI) and Eu(III) stability constants from the LLNL V6 R6 database were used to model U(VI) and
Eu(III) aqueous speciation, including formation of carbonate, chloride, and hydroxide complexes. The diffuse double layer model (DLM) was chosen to account for electrostatic interactions among GO sheets in a simplified manner, requiring minimal modeling parameters. Typical SCMs of a mineral surface approximates the amphoteric behavior of surfaces using the generic site \( \equiv \text{SOH} \) which can become protonated (\( \equiv \text{SOH}^+ \)) at \( \text{pH} < \text{pH}_{\text{pzc}} \) and deprotonated (\( \equiv \text{SO}^- \)) at \( \text{pH} > \text{pH}_{\text{pzc}} \). Rather than modeling an amphoteric surface, in this study the GO surface was approximated using carboxylic [\( \equiv \text{COOH} \)] and total sulfur [\( \equiv \text{SOH} \)] sites which deprotonated based on pK\(_a\) values of 4 and -1.7\(^{108}\). These pK\(_a\) values were fixed and the only fitting parameters used to model the potentiometric titration data were the site densities of carboxylic and total sulfur sites. These pK\(_a\) values and surface site densities were then fixed when modeling Eu(III) and U(VI) sorption.

6.3 Results and Discussions

6.3.1 Acid/base Titration and Surface Site Modeling

Base titrations of GO with GO concentrations ranging from 0.02 g/L to 1 g/L in 0.01 M NaCl are shown in Figure 20A. Acid and base titration patterns are similar; only weak hysteresis was seen in the neutral pH range (See Figure C3 in Appendix C). Figure 20A showed the titration curves shifted towards more negative net [H\(^+\)] as the concentration of GO in suspension increased from 0.02 g/L to 1 g/L, indicating that as the GO concentration is increased, more hydroxide is needed to reach the same pH value (i.e., additional surface deprotonation occurs with increasing GO concentration). In addition, the apparent pH\(_{\text{pzc}}\) decreased from 5.04 to 2.8 as the GO concentration increased from 0.02
g/L to 1 g/L. The change in apparent pH_{PZC} is due to the buffering capacity of the GO and thus the lower value likely represents the true pH_{PZC} of this GO sample. The low pH_{PZC} indicates the existence of acidic functional group(s) that readily dissociate and buffer the GO suspension at low pH. The acidic nature of GO has also been observed by previous studies\textsuperscript{66, 102, 106, 109, 110}, which saw pH_{PZC} values ranging from ~2.8 to 4.2. Duster et al.\textsuperscript{106} measured a similar pH_{PZC} by the acid/base titration of 1 g/L GO, and also showed that the deprotonation of GO is not affected by ionic strength.

DLM-SCMs were applied to simulate the titration curves for varying concentrations of GO (Figure 20A). Both reactive surface sites and total surface site concentrations (in molarity) were optimized. Although multiple functional groups have been identified on GO, the SCM used two surface sites to approximate the titration curves (log K\textsubscript{1} = -4 and log K\textsubscript{2} = 1.7) (Table 9). The agreement between the model and data were acceptable though there was some deviation at circumneutral pH values. The deviation was likely due to the heterogeneous nature of GO which would be more accurately represented by a multiple sites with a distribution of pK\textsubscript{a} values. However, a more practical approach has been taken here to approximate the surface with only two sites. Log K\textsubscript{1} corresponds to the deprotonation of carboxylic surface site (\equiv\text{COOH}) on GO. The pK\textsubscript{a} for a carboxylic functional group varies depending on its position. The pK\textsubscript{a} values for carboxylic group on aromatic rings range from 3.65 to 4.2\textsuperscript{108}, which is consistent with the modeled value. The extremely acidic log K\textsubscript{2} was unlike to be from any carbon related functional groups, but most likely to result from the deprotonation of residual sulfur related functional group(s) from the production of GO using the Hummers and Offeman method. Previous evidence
of the existence of sulfur related functional groups on GO are limited\textsuperscript{111} though the use of hot sulfuric acid to produce sulfonate groups on polystyrene for the production of cation exchange resins is well known\textsuperscript{112}. However, residual sulfate ions entrained within the GO may also be a source of sulfur in GO. Due to the potentially similar pK\textsubscript{a} values, it is not possible to differentiate the protonation/deprotonation of aqueous sulfate and that of sulfonate functional groups on the GO surface. Thus, the SCM modeled logK\textsubscript{2} corresponds to the total sulfur including residual sulfate and sulfonate functional groups on GO.

For both carboxylic and total sulfur (sulfonate/sulfate) sites, linear relationships were seen between modeled total sites and GO mass concentration (Figure 20B). Note that the titrations were run on unwashed GO and thus contain both free sulfate and sulfonate functional groups on GO. The slope of the linear relationship yielded an average 2 mmol/g\textsubscript{GO} of carboxylic functional group on GO and an average 2.2 mmol/g\textsubscript{GO} of total sulfur site. The deprotonation of hydroxyl functional group occurs at much higher pH (similar to phenol, pK\textsubscript{a} \approx 10). Therefore its contribution to the surface acidity of GO under these experimental conditions was negligible.
Figure 20: A: Base titration of GO (dots) and SCM modeling fitted for different GO concentration (lines) (0.02 g/L to 1 g/L). B: Linear relationship of GO mass concentration with modeled total surface site density. Note that the units of the y-axis in Figure 20B are in moles of sites per liter of solution which is the output of the FITEQL program.

6.3.2 Elemental Analysis and XPS

Elemental analysis (CHNS) and XPS measurement for both washed and unwashed GO provided further evidence for the existence of sulfonate functional groups on GO. Elemental analysis yielded an average of 3.2% total sulfur by dry weight for the unwashed
GO and an average of 0.8% of total sulfur for the washed GO (See Table C1 and C2 in Appendix C for details). According to the CHNS measurements, the remaining sulfur on the washed GO accounts for 25% of the original total sulfur content. The C1s, and S2p XPS spectra and their deconvoluted peaks (using Gaussian function) for unwashed and washed GO are shown in Figure 21. The detailed deconvoluted peak energies and the ratio of the functional group over total carbon/sulfur spectra for C1s and S2p spectra are listed in Table 8. The S2p spectra at ~168 eV for both unwashed GO and washed GO (Figure 21 C and D) demonstrate that sulfonate group\textsuperscript{113,114} remained on the GO surface; the decrease of S2p intensity for the washed GO is consistent with the elemental analysis results. The S2p XPS spectra for unwashed GO were deconvoluted to peaks at ~168 eV and ~169 eV that correspond to sulfonate functional groups (C-SO\textsubscript{3}H) and inorganic sulfate (Figure 21 C and D) according to previous studies\textsuperscript{113-115}. Based on the XPS measurement, the sulfonate functional group accounted for 33% percent of total sulfur, that was consistent with the CHNS estimation of 25% remaining sulfur after wash step. C1s XPS spectra for both unwashed and washed GO were deconvoluted based on previous studies\textsuperscript{116-118} to peaks at ~284.5 eV, ~285.7 eV, ~286.6 eV, 287.54 eV, 288.94 eV, and ~292 eV corresponding to the planar C-C bonding, C-O bonding possibly from attached hydroxyl functional group, C-O-C bonding from epoxide group, >C-O from carbonyl functional group, carboxylic functional group, and π-π* transition from graphite substrate (Figure 21 A and B). The ratio of carboxylic over total carbon spectra were 8% for the unwashed GO and 5% for washed GO (Table 8). Based on the CHNS measurements of 46% and 60.5% carbon by weight for unwashed and washed GO (See Table C1 and C2 in Appendix C), we can assume that the
50\% of carbon by weight for GO. Then the amount of carboxylic functional groups on GO estimated from XPS measurements will be between 2 mmol/g\textsubscript{GO} and 3 mmol/g\textsubscript{GO}. This estimation of carboxylic functional group based on XPS is consistent with value calculated from acid/base titration.

Based on the elemental analysis and XPS, it was assumed that sulfonate functional groups on GO account for 25\% of the modeled total sulfur sites from potentiometric titrations. This assumption was used to define the total sulfonate sites available for Eu(III) and U(VI) SCM in the following section.

Figure 21: Deconvoluted peaks for (upper left) C1s spectra of unwashed GO, (upper right) C1s spectra of washed GO, (lower left) S 2p spectra of unwashed GO, and (lower right) S2p spectra of washed GO.
### Table 8 Deconvoluted XPS peaks and area ratio

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Peaks</th>
<th>Unwashed GO</th>
<th>Washed GO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>BE (eV)</td>
<td>Area</td>
</tr>
<tr>
<td>0</td>
<td>C-C</td>
<td>284.60</td>
<td>8673</td>
</tr>
<tr>
<td>1</td>
<td>C-O</td>
<td>285.70</td>
<td>1329</td>
</tr>
<tr>
<td>2</td>
<td>C-O-C</td>
<td>286.73</td>
<td>2906</td>
</tr>
<tr>
<td>3</td>
<td>&gt;C-O</td>
<td>287.54</td>
<td>1722</td>
</tr>
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<td>COOH</td>
<td>288.94</td>
<td>1395</td>
</tr>
<tr>
<td>5</td>
<td>π-π transition</td>
<td>292.08</td>
<td>2378</td>
</tr>
<tr>
<td>0</td>
<td>Sulfonate</td>
<td>168</td>
<td>1294</td>
</tr>
<tr>
<td>1</td>
<td>Sulfate</td>
<td>169</td>
<td>2609</td>
</tr>
</tbody>
</table>

### 6.3.3 Batch Sorption Experiments and Surface Complexation Modeling

Batch experiments were performed for Eu(III) and U(VI) sorption to GO as a function of pH (Figure 22 A and B). For both Eu(III) and U(VI), sorption was observed to increase with increasing pH. The Eu(III) sorption edge occurred at pH 2.7 and over 97% sorption was achieved between pH 2.74 and 7.25. The U(VI) sorption edge occurred at pH 3.8 and over 95% of sorption was achieved between pH 3.8 and 7.25. For both Eu(III) and U(VI), the greatest sorption was achieved above pH 2.7, which is consistent with the expectation of high sorption above the pH\(_{pzc}\) where surface sites are deprotonated. For U(VI), the decrease in sorption seen above pH 7 is likely due to the formation of aqueous uranyl-carbonate complexes which hinder U(VI) sorption. This behavior has been previously observed for numerous metal oxide surfaces\(^{119-125}\). The complexation of U(VI) to GO is also confirmed by FTIR spectra of GO+U at pH 5 (Figure C10) showing the uranyl asymmetric stretch peak at 912 cm\(^{-1}\), which indicates a redshift of ~50 cm\(^{-1}\) relative
to the 961-962 cm\(^{-1}\) peaks previously reported\(^{126-128}\) for UO\(_2^{2+}\) in solution. For U(VI), the decrease in sorption seen above pH 7 is likely due to the formation of aqueous uranyl-carbonate complexes which hinder U(VI) sorption. This behavior has been previously observed for numerous metal oxide surfaces.\(^{119-125}\) The lower sorption observed at lower pH for U(VI) relative to Eu(III) may be due to competition from U(VI) hydrolysis which will begin around pH 5 compared with pH \(~6\) for Eu(III)\(^{105}\).

Variable concentration sorption isotherms for Eu(III) and U(VI) were conducted at pH 5 and both isotherms indicated that sorption became non-linear above a solid phase loading near 10 mg\(_{U/Eu}\) per gram of GO (Figure 22). The Eu(III) sorption isotherm plateaued with a maximum sorption load of 78 mg/g (Figure 22C). Even at the maximum aqueous uranium concentration in this study, which yielded a solid phase concentration of 298 mg\(_U/g_{GO}\), the GO surface was not appeared to be fully saturated (Figure 22D).

Data from variable pH and variable concentration batch experiments was simultaneously modeled using the DLM-SCM assuming Eu(III) and U(VI) sorption to both carboxylate ([\(\equiv\text{COO}^-\)]) and sulfonate sites ([\(\equiv\text{SO}_3^-\)]) (Figure 22). The stability constants simulated from SCM are shown in Table 9. For both Eu(III) and U(VI), sorption to [\(\equiv\text{SO}_3^-\)] occurs at lower pH and sorption to [\(\equiv\text{COO}^-\)] dominates after pH is increased. For Eu(III), [\(\equiv\text{SO}_3\text{Eu}^{2+}\)] accounts for the high sorption at low pH 1 – 3; at higher pH, [\(\equiv\text{COO}\text{Eu}^{2+}\)] becomes the dominant sorbed species (Figure 22A). For U(VI), small percentage of U(VI) sorbs to the sulfonate site at pH 1 – 2; [\(\equiv\text{COO}\text{UO}_2^{+}\)] is the dominant sorbed species through the whole pH range (Figure 22B). The log K values for U(VI) sorption to GO are about 1-2 orders of magnitude higher than Eu(III), which is consistent with the greater sorption of
U(VI) in the variable concentration isotherm data. Models of both Eu(III) and U(VI) isotherms showed greater complexation to carboxylate site over sulfonate site (see Table C4 in Appendix C). The SCM model demonstrates U(VI) sorption to GO occurs mostly through complexation with carboxylate sites except at very low pH (1-2) where sorption is dominated by U(VI) binding to sulfonate groups. On the contrary, Eu(III) sorption to GO via sulfonate group dominates from pH 1 - 4. Based on the surface complexation stability constants, U(VI) showed very strong affinity for carboxylate functional group and comparative weak affinity for sulfonate group, thus carboxylate sites are the major site for U(VI) sorption. This behavior is consistent with the well-known fact that U(VI) has strong affinity for dissolved carbonate. The modeled surface complexation constant for Eu-carboxylate sites is about 2 orders magnitude lower than that of U(VI). Therefore, though a weaker sorption site, the sulfonate sites are able to compete with carboxylate sites for Eu(III) sorption at low pH.

Consideration of the ratio of sorbed ions to available surface sites can yield some information regarding the stoichiometry of the surface sites. At maximum Eu(III) loading, the model calculated the ratio of sorbed Eu to total carboxylate sites ([≡COOEu²⁺]/[≡COOH]) was 0.26; at maximum U(VI) loading, the ratio of (≡COOOUO₂⁺)/(≡COOH) is 0.45 (See Table C4 in Appendix C). Thus, it appears that all of the available surface sites were not saturated with Eu(III) or U(VI). The observed aggregation of GO in these samples is likely a manifestation of this significant site occupancy. It may be circumstantial but the site occupancy ratios of 0.26 and 0.45 for Eu(III) and U(VI), respectively, would be close to maximum theoretical sorption capacities.
assuming 3 and 2 carboxylate sites are needed for charge neutralization of Eu$^{3+}$ and UO$_2^{2+}$, respectively. However, these species with higher stoichiometry (i.e., (=COO)$_3$Eu$^0$ and (=COO)$_2$UO$_2^0$) were not required to approximate the batch sorption data.

SEM and visual images of the Eu(III) and U(VI) loaded from the highest concentration isotherm samples are shown in Figure 23. Aggregation of the GO was visually observed in these samples and can be seen in the aggregated particles shown in Figure 23. Similar aggregation of GO in high ionic strength waters was observed by Romanchuck et al.$^{67}$ indicating that neutralization of the GO surface charge will result in formation of large aggregates which will not remain suspended. EDS mapping of these samples with highest Eu(III) and U(VI) loading showed no precipitation occurred (See Figure C4 and C5 in Appendix C).
Figure 22: Experimental data (dots) and SCM fit (lines) of (A) Eu(III) sorption to GO as a function of pH and (B) U(VI) sorption to GO as function of pH. Sorption isotherms and SCM fit for (C) Eu(III) and (D) U(VI) at a constant pH of 5. All experiments were performed using 0.1 g/L GO in a 10 mM NaCl electrolyte solution.

Table 9 Surface reactions and complexation constants describing U(VI) and E(III) sorption to GO

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log $K_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\equiv$COOH $\rightarrow\equiv$COO$^- + H^+$</td>
<td>-4$^a$</td>
</tr>
<tr>
<td>$\equiv$SO$_3$H $\rightarrow\equiv$SO$_3^- + H^+$</td>
<td>1.7$^a$</td>
</tr>
<tr>
<td>$\equiv$COO$^- +$ Eu$^{3+}$ $\rightarrow\equiv$COOEu$^{2+}$</td>
<td>0.2 $\pm$ 0.02$^b$</td>
</tr>
<tr>
<td>$\equiv$SO$_3^- +$ Eu$^{3+}$ $\rightarrow\equiv$SO$_3$Eu$^{2+}$</td>
<td>-1.95 $\pm$ 0.02$^b$</td>
</tr>
<tr>
<td>$\equiv$COO$^- +$ UO$_2^{2+}$ $\rightarrow\equiv$COOOUO$_2^+$</td>
<td>2.78 $\pm$ 0.01$^b$</td>
</tr>
<tr>
<td>$\equiv$SO$_3^- +$ UO$_2^{2+}$ $\rightarrow\equiv$SO$_3$UO$_2^+$</td>
<td>-0.833 $\pm$ 0.09$^b$</td>
</tr>
</tbody>
</table>
aconstants fixed when modeling surface site densities and Eu(III) or U(VI) sorption
buncertainty reported at a 95% confidence level based on FITEQL output

Figure 23: SEM and visual images demonstrating aggregation of GO after sorption. (Left) SEM image of GO isolated from 100 ppm Eu(III), (middle) SEM image of GO isolated from 100 ppm U(VI), and (right) visual image of GO suspensions containing no added U(VI) and 100 ppm U(VI) on the left and right tubes, respectively. The precipitate phases observed in the middle SEM image were identified as NaCl salts using EDS and the uranium distribution was homogeneous, not directly associated with the precipitates.

The observation and quantification of both carboxylate and sulfonate functional groups on GO surfaces in this work highlights the importance of detailed characterization of GO materials produced using various techniques to allow consistent comparisons of literature data. SCM of Eu(III) and U(VI) indicates the sulfonate sites are important at low pH values and may explain the strong sorption of many cations to GO under relatively acidic conditions. However, at circumneutral pH values where both Eu(III) and U(VI) are strongly sorbed, the experimental data and SCM indicate that carboxylate groups are the dominant sorption sites.
6.4 Conclusions

Batch experiments of Eu(III) and U(VI) sorption to GO as a function of pH (1 – 8) and as a function of analyte concentration (10 – 100, 000 ppb) at a constant pH ≈ 5 were conducted in this study and the batch sorption results were modeled simultaneously using surface complexation modeling (SCM). A carboxylic functional group and an unexpected sulfonate functional group on GO made via Hummers and Offeman method were characterized as the reactive surface sites and quantified via diffuse layer modeling of the GO acid/base titrations. The presence of the sulfonate functional group on GO was confirmed using elemental analysis and XPS. The SCM indicated that Eu(III) and U(VI) complexation to carboxylate functional group is the main mechanism for their sorption to GO and their complexation to the sulfonate site occurred at the lower pH range. Eu(III) and U(VI) facilitated GO aggregation was observed with high Eu(III) and U(VI) concentration and may be caused by surface charge neutralization of GO after sorption.
CHAPTER 7

SURFACE COMPLEXATION MODELING OF Th(IV) AND Np(V)O$_2^+$ SORPTION TO GRAPHENE OXIDE AND A LINEAR RELATIONSHIP FOR ACTINIDE SORPTION TO GO

Abstract

Here we studied Th(IV) and Np(V) sorption to graphene oxide (GO) as a function of pH and the Th(IV) and Np(V) concentrations. Almost 100% Th(IV) sorption began at pH 1, and 191 milligrams Th(IV) per gram of GO sorbed was achieved at pH 3 with an initial 100,000 ppb Th(IV) input. Np(V) showed weaker sorption to GO compared to Th(IV). Surface complexation modeling (SCM) using an electrostatic double layer model (DLM) simultaneously modeled Th(IV) and Np(V) sorption to GO over the pH and the analyte concentration ranges. The SCM indicated Th(IV) complexation to sulfonate sites dominated at a low pH (1 to 2) and its complexation to carboxylate sites dominated at a higher pH (3 to 8). In contrast, Np(V) showed a stronger affinity for sulfonate sites than carboxylate sites over the pH and concentration ranges we studied. Combining the results from a previous study on Eu(III)/U(VI) sorption to GO with results from this study, it is observed that the affinities of actinide sorption to GO depends on their effective charges, which is similar to their sorption to metal oxide minerals. Moreover, a linear relationship was observed between the stability constants for actinides and Eu(III) (with oxidation state
from III to VI) complexation to carboxylate sites on GO and the stability constants for their complexation to carbonate.

7.1 Introduction

Light actinides (Atomic numbers 90 – 94), which occur naturally (e.g., U and Th) or are generated from nuclear power production and weapon manufacture (e.g., Pu and Am) pose environmental concerns due to their long half-lives, radio-toxicity, and multiple oxidation states in the natural environment. Exhibiting different affinities for complexation (in the aqueous phase and to the surface of solids), these oxidation states impact the transport and fate of the actinides in the environment. Specifically, these actinides occur in the natural environment in four oxidation states, III, IV, V, and VI, some of which are not stable (e.g., U, Np, and Pu), and undergo further transformation under changing conditions (e.g., pH, EH, or carbonate concentration). In general, the complexation strength of actinides in different oxidation states depends on their effective charges, with the higher the charge, the stronger the affinity for complexation as shown in the following sequence: An (IV) > An (VI) ≈ An (III) > An (V). For instance, tetravalent species such as Pu(IV) and Th(IV), with the highest effective charge, and therefore, the highest affinity for complexation among the actinides. These tetravalent species readily hydrolyze at low pH values and form multiple hydrolysis products, exhibit strong sorption to mineral surfaces and are sparingly soluble. Np(V)O2+, which exhibits the weakest effective charge, has been observed to transport faster and further than actinides in other oxidation states due to the low complexation and sorption affinity of pentavalent species. Moreover, because of their long half-lives, actinides and their daughter products account for the majority of the
long-term radio-toxicity in nuclear waste ($10^3 – 10^6$ years). This property emphasizes the need for their long-term immobilization in deep geological repositories for nuclear waste as well as an accurate model of their transport in the subsurface if these engineered barriers fail. Strong or selective sorbents capable of removing actinides from the mobile aqueous phase are currently under investigation in order to achieve better nuclear waste strategies (e.g., decrease the waste volume and immobilize the waste in solid phases) as well as to design reliable remediation plans for currently contaminated sites.

One such sorbent, graphene oxide (GO), has shown great potential for radionuclide removal from the aqueous phase. Its application has several advantages over using natural minerals. First, GO is more stable than many natural minerals which undergo chemical/physical changes (e.g., dissolution, corrosion, and recrystallization), while the properties of synthetic materials can be controlled and designed to adapt to specific environmental needs. Secondly, actinide sorption to GO reaches equilibrium faster than its sorption to natural minerals, within 10 minutes to 1 hour. In contrast, actinide sorption to natural minerals commonly reaches equilibrium within 2 to 7 days. Finally, GO exhibits a 1 to 2 magnitude higher sorption capacity for actinides than natural minerals. In addition, functional groups on the graphene sheets can be modified. Therefore, understanding the mechanism of actinide sorption to GO has the potential to lead to further enhancement of these materials, resulting in an even higher sorption capacity.

Previous research has characterized two primary reactive functional groups on GO, the carboxylic functional groups ([$\equiv$COOH]) and the unexpected sulfonate functional
groups ([≡SO$_3$H]), by surface complexation modeling (SCM) of the acid/base titration of GO and by XPS analysis of the GO synthesized using the method of Hummers and Offeman.$^{107}$ Furthermore, the batch sorption results from Eu(III) and U(VI) sorption to GO as a function of the pH and their concentrations have also been modeled through their complexation to these two functional groups.$^{137}$ The thermodynamic-based stability constants (log $K_s$) calculated for Eu (III) and U(VI) sorption to GO via SCM can be further applied to predict their sorption to GO under variable conditions. This SCM approach has a major advantage over the empirical Freundlich or Langmuir modeling approaches, which have been widely used to study sorption processes, because it approximates sorption using a chemical thermodynamic model and the stability constants generated from it can be used to predict sorption in a more complicated environment than experimental conditions (e.g; in the presence of other competition cations or sorbents). Therefore, SCM has the potential to enhance the understanding of the mechanism of radionuclide/heavy metal sorption to graphene-based materials.

Extending the previous research on trivalent and hexavalent actinides, this study investigated tetravalent Th(IV) and pentavalent Np(V) sorption to GO as a function of pH and as a function of their concentrations. SCMs were applied to understand the mechanism of Th(IV) and Np(V) sorption to GO, the results indicating that Th(IV) sorbed to GO primarily via [≡COOH], while Np(V) sorbed to GO via [≡SO$_3$H]. The stability constants (log $K_S$) for Th(IV) and Np(V) complexation to GO were also obtained through SCM. Analyzing these results with those from the previous research on Eu(III) and U(VI) sorption to GO$^{137}$, it was observed that the affinity of actinide sorption to GO follows the
expected trend with respect to effective charge. Moreover, a linear relationship was observed between the stability constants of actinide complexation to the carboxylate functional group on GO and those of actinide complexation to carbonate.

7.2 Materials and Methods

7.2.1 Graphene Oxide

A 4 g/L GO dispersion (in H₂O) stock solution (Sigma Aldrich) prepared by the method of Hummers and Offeman was used for this study.¹⁰⁷ The GO was characterized using field emission scanning electron microscopy (SEM), Fourier transformed infrared spectroscopy (FT-IR), powdered x-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and CHNS elemental analyzer. The specific surface area of GO was obtained through BET measurement. Although various functional groups (e.g., carboxylic, hydroxyl, and epoxide) were detected on the GO, carboxylic functional groups and residue sulfonate functional groups were characterized as the two reactive surface sites and quantified via SCM of the GO acid/base titrations based on a diffuse double layer model (DLM). For more details on the characterization of GO, see the previous research in Xie et al.¹³⁷

7.2.2 Other Chemicals

The Th(IV) used in this study was diluted from 1000 ppm stock solution in 2% HNO₃ (High Purity Standards) and characterized using inductively coupled plasma mass spectrometry (ICP-MS, Thermo Scientific X-Series II). The Np(V) used was diluted from a 1.5 mM Np(V) stock solution in 1M HNO₃ from the Clemson University radionuclide
source supply (originally obtained as a 10 μCi source in 4M HNO$_3$ from Eckert and Zeigler (Atlanta, GA) and purified using ion exchange). The dominant pentavalent Np state was verified spectrophotometrically using a Cary 300 UV-Vis. All chemicals used in this experiment were ACS analytical grade or higher. All solutions were prepared with distilled deionized water with a resistivity greater than 18 MΩ•cm and less than 1 ppb total organic carbon. The ionic strength of all solutions used in the work was fixed at 0.01 M using NaCl.

### 7.2.3 Np(V) and Th(IV) Sorption Experiment

Batch experiments of trace level Th(IV) or Np(V) ($7.64 \times 10^{-8}$ M and $4.2 \times 10^{-8}$ M, respectively) sorption to 0.1 g/L GO as a function of pH with an ionic strength of 0.01 M were prepared at room temperature. The pH for Th(IV) sorption to GO ranged from 1 to 8, and the pH for Np(V) sorption to GO ranged from 1 to 6. Duplicate samples were prepared at pH 2, 4, and 6 for quality assurance. Constant pH sorption isotherms measuring Th(IV) and Np(V) sorption to GO as a function of their analyte concentrations were conducted at pH $3.12 \pm 0.04$ and $7.00 \pm 0.10$, respectively, in 0.01 M NaCl, with initial input Th(IV) ranging from $4.3 \times 10^{-8}$ M to $4.3 \times 10^{-4}$ M (10 ppb to 100,000 ppb) and initial input of Np(V) ranging from $4.2 \times 10^{-8}$ M to $4.2 \times 10^{-6}$ M (10 ppb to 1000 ppb). The sorption isotherm for Th(IV) was conducted at a comparatively low pH in order to prevent precipitation. The batch samples were shaken in an orbital shaker for two days to reach sorption equilibrium, a time period which has been shown adequate in previous studies.$^{67,101,103}$ After two days, a 1.3 mL of a homogenous suspension from each sample was transferred to a 1.5 mL centrifuge tube, and centrifuged at 8000 rpm for 60 min to achieve solid and aqueous phase separation (Beckman Coulter Allegra X-22R Centrifuge). The
concentration of Th(IV) and Np(V) in the aqueous phase \((C_{\text{aq}})\) was measured using ICP-MS using \(^{242}\)Pu as an internal standard. The percentage of Th(IV) or Np(V) that sorbed to GO was calculated using Equation 24, where \(C_0\) is the initial input concentration of Th(IV) or Np(V).

\[
\text{Sorption Percentage} \, (\%) = \frac{C_0 - C_{\text{aq}}}{C_0} \times 100\% \tag{Equation 24}
\]

The concentration of Th(IV) and Np(V) associated with GO \((C_{\text{sorbed}}, \text{mol/g})\) was calculated using Equation 25, where \(V\) is the total volume of the sample and \(m\) is the mass of GO in the sample.

\[
C_{\text{sorbed}} = \frac{(C_0 - C_{\text{aq}})V}{m} \tag{Equation 25}
\]

### 7.2.4 Surface Complexation Modeling

Th(IV) and Np(V) sorption as a function of pH and their sorption isotherms were modeled using a modified version of FITEQL 4.0 for b-dot activity corrections and database usage.\(^{75}\) The two reactive functional groups on GO, carboxylic (\(\log K_{\text{[\equiv COOH]}} = -4\)) and sulfonate (\(\log K_{\text{[\equiv SO3H]}} = 1.7\)), as well as their quantities (2 mmol\[\equiv COOH]/g[GO] and 0.55 mmol\[\equiv SO3H]/g[GO]) were determined in Xie et al.\(^{137}\) A double layer (DLM) SCM was used to model the surface acidity and sorption data as previously described.\(^{137}\) The stability constants of Th(IV) and Np(V) aqueous complexation from the LLNL Thermochemical Database\(^{78}\) were used to model Th(IV) and Np(V) aqueous speciation, including the formation of carbonate, chloride, hydroxide and sulfate complexes. The DLM was used to account for the electrostatic interactions at GO and water interface.
7.3 Results and Discussions

7.3.1 Th(IV) Sorption to GO

The experimental results of Th(IV) sorption to GO as a function of pH (1 to 8) and its sorption isotherm at pH 3 with initial Th(IV) concentrations ranged from $4.3 \times 10^{-8}$ M to $4.3 \times 10^{-4}$ M (10 ppb to 100,000 ppb) as shown in Figure 24 (represented by the black dots). More than 97% of Th(IV) sorption was achieved from pH 1 to 8 (Figure 24A), similar to previously published results. However, studies of the sorption with higher initial Th(IV) concentrations at 18 mg/L ($7.8 \times 10^{-5}$ M) and at 120 mg/L ($5.2 \times 10^{-4}$ M) did not show the same result; rather approximately 100% Th(IV) sorption began at pH 2.5 and pH 4, respectively. This difference indicates different sorption mechanisms for Th(IV) sorption to GO at the lower pH (1 to 4) than at the higher. Figure 24B shows Th(IV) sorption to GO at pH 3 with initial Th(IV) concentrations ranging from 10 ppb to 100,000 ppb. The isotherm reaches a plateau at higher Th(IV) concentration ranges indicating Th(IV) saturated or was close to saturation of the sorption sites on GO at the highest Th(IV) spike. At pH 3, 191 mg $\frac{[\text{Th(IV)}]}{[\text{GO}]}$ Th(IV) sorption was achieved at the highest Th(IV) spiked sample of 100,000 ppb. SEM images did not reveal any discrete Th precipitates ($i.e.$, ThO$_2$), therefore, this high Th solid phase concentration may be primarily monomeric sorbed complexes because only 32% of the total available carboxylate and sulfonate sites are occupied at this loading level.

Figure 24 also shows the result of the SCM modeling of Th(IV) sorption to GO as a function of pH and its concentrations (as represented by the solid and dashed lines in Figure 24). Because thorium hydrolysis products start forming at pH 1 and become the
dominant thorium species at pH 3, Th(IV) sorption to GO was modeled assuming multiple hydrolyzed species form surface complexes on GO. SCM modeled Th(IV) sorption to GO using Th$^{4+}$ sorption to [$\equiv$SO$_3^-$] and the complexation of four other Th(IV) hydrolysis products to [$\equiv$COO$^-$]. This model shows that different Th(IV) hydrolysis products dominate the sorption as the pH increases (Figure 24A). Th$^{4+}$ complexation to sulfonate sites dominates the sorption at pH 1 to 2, while Th(IV) hydrolysis product complexation to carboxylate sites dominates from pH 2 to 8. The reactions and stability constants used to model the sorption are listed in Table 1. The stability constant of [$\equiv$SO$_3^-$Th$^{3+}$] is much lower than those for thorium hydrolysis product complexation to [$\equiv$COO$^-$], indicating that Th(IV) complexation to carboxylate is stronger than to sulfonate. This modeling result is consistent with those of Eu(III) and U(VI) complexation to GO. It also explains the lower sorption percentages at the lower pH range observed in other studies with much higher input Th(IV) concentrations: the total quantity of [$\equiv$SO$_3$H] is one fourth of that of [$\equiv$COOH] on GO; therefore, with higher Th(IV) concentrations, the sulfonate sites are saturated with Th(IV) and the carboxylic sites are not deprotonated for sorption at these lower pH ranges.

As shown in Figure 24B, the SCM overpredicts Th(IV) sorption to GO in the range of 4.3 × 10$^{-8}$ M to 4.3 × 10$^{-6}$ M (10 ppb to 1000 ppb) initial Th(IV) concentration; however, it gives a better prediction of the experimental results at higher initial Th(IV) concentrations. At lower Th(IV) concentrations, the model predicts almost 100% sorption, but the experimental data showed approximately 90% sorption. The measurement of aqueous Th(IV) concentrations after sorption for samples with lower initial Th(IV) is close
to the detection limit of the ICPMS, leading to higher uncertainties in these measurements. Overall, the model predicts the same level of Th(IV) sorbed to GO as the experimental data over all concentration ranges.

Previous research has determined the stability constants for thorium hydrolysis, which were compared with the modeled stability constants for the complexation of thorium hydrolysis products to the carboxylate sites in this study. A linear relationship is observed between these two sets of stability constants (Figure 25). This result indicates the dependence of the complexation of Th(IV) to carboxylate sites on GO on the hydrolysis of Th(IV).

Aggregation of GO facilitated by $4.3 \times 10^{-4}$ M (100,000 ppb) of Th(IV) was observed during the batch sorption experiment and further studied using SEM (Figure 26). The SCM of Th(IV) sorption provides a possible explanation for the aggregation observed. The SCM calculated that the ratio of Th(IV) sorbed to GO to the total deprotonated site (sum of carboxylate and sulfonate site) as 0.53 at the highest Th(IV) concentration (see Appendix D). This is close to the theoretical charge balance ratio of 0.5 for Th(OH)$_2^{2+}$ complexation to GO, a hydrolysis product used here because SCM calculated it to be the primary species sorbed to GO at pH 3. Therefore, the mechanism of aggregation is probably a result of the sorption-induced neutralization of the abundant negative charges on GO that maintain its dispersion in solution.
Figure 24: Th(IV) sorption onto GO. A: Th(IV) sorption onto GO as a function of pH (black dots), SCM modeling (red solid line), and sorbed species used for modeling (dash lines); B: Th(IV) sorption onto GO isotherm at ~pH 3 with initial Th(IV) from 10 ppb to 100,000 ppb, and SCM modeling of the sorption isotherm (red solid line).
7.3.2 Np(V)O₂⁺ Sorption to GO

Figure 27 shows the experimental results of Np(V)O₂⁺ sorption to GO as a function of pH and its concentrations at pH 6.81 ± 0.13 with initial Np(V) ranging from 5 ppb to 1000 ppb (as represented by the black dots in Figure 27). As shown in Figure 27A, the sorption of Np(V) to GO increased slightly with increasing pH, but the sorption showed more fluctuation over the pH range than the sorption of actinides in other oxidation states.
to GO. Approximately 20% to 40% of Np(V) sorption was achieved at ~ pH 4. Similar low Np(V) sorption results were also found by Romanchuk et al. Figure 27B shows that the concentration of sorbed Np(V) increased almost linearly with increasing Np(V) concentration, indicating Np(V) has not saturated the GO surface at 1000 ppb of Np(V) (Figure 27B). Overall, the Np(V) sorption to GO is not as high as the sorption of actinides in other oxidation states.

Simultaneous SCM modeling of Np(V) sorption to GO as a function of pH and its analyte concentrations was conducted (Figure 27). Different from Eu(III), Th(IV) and U(VI) sorption to GO, Np (V) complexation to the sulfonate sites on GO dominated both across the pH range and its concentration range, while the NpO$_2^+$ complexation to carboxylate sites exhibited no significance. There is no current research on the SCM of Np sorption to GO for comparison; however, a DFT computational modeling study of Np(V) complexation to GO also indicated limited complexation of Np(V) to the carboxylic sites on GO.$^{138}$

Figure 27: Np(V)O$_2^+$ sorption onto GO. A: Np(V)O$_2^+$ sorption onto GO as a function of pH (black dots), SCM modeling (red solid line), and sorbed species used for modeling (dash lines); B: Np(V)O$_2^+$ sorption onto GO isotherm at ~ pH 6.8 with initial Th(IV) from 4.2 × 10$^{-8}$ M to 4.2 × 10$^{-6}$ M (10 ppb to 1000 ppb), and SCM modeling of the sorption isotherm (red solid line).
Table 10 SCM modeled reactions and stability constants (log K values)

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>≡COOH = ≡COO⁻ + H⁺</td>
<td>-4</td>
</tr>
<tr>
<td>≡SO₃H = ≡SO₃⁻ + H⁺</td>
<td>1.7</td>
</tr>
<tr>
<td>≡COO⁻ + NpO₂⁺ = ≡COONpO₂</td>
<td>-1.5</td>
</tr>
<tr>
<td>≡XO⁻ + NpO₂⁺ = ≡XONpO₂</td>
<td>0.84</td>
</tr>
<tr>
<td>≡XO⁻ + NpO₂Cl (aq) = ≡XONpO₂Cl⁻</td>
<td>5.4</td>
</tr>
<tr>
<td>≡COO⁻ + ThOH³⁺ = ≡COOThOH²⁺</td>
<td>2.8</td>
</tr>
<tr>
<td>≡COO⁻ + Th(OH)₂²⁺ = ≡COOTh(OH)₂⁺</td>
<td>5.5</td>
</tr>
<tr>
<td>≡COO⁻ + Th(OH)₃⁺ = ≡COOTh(OH)₃</td>
<td>6</td>
</tr>
<tr>
<td>≡COO⁻ + Th(OH)₄⁻ = ≡COOTh(OH)₄⁻</td>
<td>8.5</td>
</tr>
<tr>
<td>≡XO⁻ + Th⁴⁺ = ≡XOTh¹⁺</td>
<td>-2.35</td>
</tr>
</tbody>
</table>

Note: Total sites of [≡COOH] is 2.14×10⁻⁴ M and total sites of [≡SO₃H] is 1.49×10⁻⁵ M.

7.3.3 Linear Free Energy Relationship

Linear free energy relationship (LFER) is an empirical plotting method that has been widely used to compare the stability constants or reaction rate constants of one set of reactions with another. The linear relationship between two sets of reactions gives an indication of similarity in the reaction mechanism and, therefore, can be used to enhance the understanding of the set of reactions with uncertain mechanisms based on the well-understood ones. The LFERs can also be applied to predict the stability constants or rate constants for similar reactions that have not yet been quantified through experiments. Over the last decade, it has also been applied to improve the understanding of the chemistry of heavy metal and actinide sorption mechanisms at mineral and water interfaces. LFERs have been observed between the hydrolysis constants of actinides and heavy metals.
and the stability constants for their complexation to minerals (such as hematite, illite and montmorillonite), further suggesting that the complexation of heavy metals and actinides to mineral surfaces is through the surficial hydroxyl functional groups formed at the mineral and water interfaces. Recent research has also observed LFERs between the sorption of multiple metals to GO and their complexation to acetate and hydroxide.\(^{140}\) Because the LFER is capable of enhancing the understanding of sorption mechanisms, it was applied in this study to further understand the actinide chemistry at the GO: water interface. The experimental and SCM modeling results for Eu(III) and U(VI) from previous research\(^ {137}\) were combined with the results from this study to better understand the influence of oxidation states on actinide sorption to GO as well as the sorption mechanism.

The results of the sorption of actinides in different oxidation states (III, IV, V, and VI) to GO as a function of pH are shown in Figure 28A and indicate that almost 100% Th(IV) sorption begins at pH 1, and that U(VI) and Eu(III) sorption to GO is comparable with almost 100% sorption beginning at pH 3, while Np(V) sorption to GO is the weakest. Similar to their sorption to minerals, the sorption strengths of actinides in different oxidation states sorption to GO also follow their effective charges, that is: An(IV) > An(VI) \(\approx\) An(III) > An(V).\(^ {14,50}\) This result indicates that, similar to sorption of actinides to metal oxide minerals, the oxidation state remains the primary factor influencing actinide sorption to synthetic materials such as GO across the pH range.

Although the sorption of Eu(III) and U(VI) to GO was comparable across the pH range, the maximum U(VI) sorption to GO (287 mg\([\text{U(VI)}/\text{g(GO)}]\)) was almost four times higher than that of Eu(III) (74 mg\([\text{Eu(III)}/\text{g(GO)}]\)). This extremely high U(VI) sorption to GO
was likely due to the favorability of U(VI) carbonate complexation, which leads to a free energy relationship between the actinides complexation to the carboxylate sites on GO and their complexation with carbonate. A linear relationship was observed between the log $K_S$ for actinide complexation to $[≡COO^-]$ on GO and the log $K$ for actinide complexation to carbonate ($R^2 = 0.95$) (Figure 28B). The stability constants used in this linear relationship are listed in Table D2 in Appendix D. The linear relationship indicates a similarity between actinide complexation to the carboxylate ($[≡COO^-]$) site on GO and actinide-carbonate ion complexation. The binding of actinide to carboxylate may be similar to that of carbonate because they both possess one carbon and conjugated oxygen atoms. In addition, as shown in Figure 28B, the stability constants of actinide complexation to the carboxylate sites on GO also follows their effective charges, i.e., Th(IV) has the highest log $K_S$, followed by U(VI) and Eu(III), while Np(V) has the lowest log $K_S$. Because the carboxylate site on GO is identified as the primary reactive surface site for actinide sorption, this correlation may be further used to predict other actinide/lanthanide/heavy metal complexation to GO from the log $K$ of their complexation to carbonate in the aqueous phase. However, since the current LFER plots only four data point for actinides, future research should be conducted to validate this result for lanthanide and other metals. Because this study used a different modeling approach than the research conducted by Gu et al.\textsuperscript{140}, the stability constants for metal sorption to GO determined in their study cannot be directly compared with the current work. The linear relationship observed between actinide complexation to the carboxylate sites on GO and actinide complexation to carbonate may also indicate that GO is capable of loading large amounts of metals with strong affinities to carbonate.
Figure 28: A) Comparison of actinides in different oxidation states sorption to GO as a function of pH. B) Linear relationship between logK of actinides complexation to carboxylate site on GO and log K of actinide carbonate complexation.

7.4 Conclusions

Batch sorption and SCM were applied in this study to understand the mechanism of Th(IV) and Np(V) sorption to GO. In addition, by combining and comparing the results from previous research\textsuperscript{137}, a LFER was applied to understand the influence of actinides in different oxidation states on their sorption to GO, and to explain the comparatively high loading of U(VI) to GO observed in previous studies compared to other actinides. Both the results from batch sorption and the stability constants for actinide sorption to GO calculated from the modeling indicated a correlation between sorption affinity and effective charge of the actinide. These results are consistent with previous research on actinide aqueous complexation and their sorption to minerals, which indicated the similarity between actinide sorption to synthetic materials like GO and their sorption to minerals. Previous research has already identified GO as a robust sorbent for actinides and other metals, but its nonstoichiometric property makes it difficult to study the mechanism of this sorption.
The results from this study identified the importance of carboxylic functional groups on GO for actinide sorption using experimental and modeling method, improving the understanding of the sorption mechanism, which may help material engineers enhance the sorption capacity of graphene-based materials. Furthermore, results from this study provide data to estimate the quantity of GO needed as a sorbent for certain amount of actinides; the stability constants for actinide sorption to GO calculated from SCM can be used directly in geochemical modeling with the same DLM assumption to model the actinide interfacial behavior under different conditions. Therefore, the results from this study further support the application of GO for the remediation of actinide contamination in the environment as well as for effective nuclear waste management. Lastly, the thermodynamically based approach used in this study provides a better understanding of the actinide sorption to GO than other empirical modeling approaches, indicating its potential to be applied to other sorption processes in the future research.
CHAPTER 8

QUANTIFICATION OF THE ENTHALPY OF Eu(III) AND U(VI) COMPLEXATION TO GRAPHENE OXIDE USING MICROCALORIMETRY

Abstract

Here we calculated the enthalpies for Eu(III) and U(VI) complexation to graphene oxide (GO) based on isothermal titration calorimetry experiment (ITC) and surface complexation modeling (SCM) of the Eu(III)/U(VI) sorption to GO. The enthalpies for the deprotonation of carboxylate and sulfonate on GO (14.7 kJ/mol and -22 kJ/mol, respectively) were obtained by base titrations of GO with variable concentrations using the ITC. Calorimetric measurement of approximately 3 mM of EuCl₃/UO₂(NO₃)₂ sorption to 2 g/L GO were obtained using ITC. The enthalpies for Eu(III)/U(VI) complexation to the carboxylate functional group on GO are calculated to be 13 kJ/mol and 17.5 kJ/mol, respectively; the enthalpies for their complexation to the sulfonate functional group on GO are calculated to be 10 kJ/mol and 8 kJ/mol, respectively. The positive enthalpies indicated that the Eu(III)/U(VI) sorption to GO are both endothermic processes, and the spontaneous sorption reactions are driven by positive entropies. These two sorption reactions are hypothesized to be mechanistically driven by displacement of solvating water molecules from the actinides and GO surface during sorption. Base titrations of GO with background electrolyte ranging from 0.01 M to 1 M NaCl using ITC showed no significant difference on heat release, indicating an outer-sphere binding of Na⁺/Cl⁻ to GO.
8.1 Introduction

Graphene oxide (GO) has been found to be a strong and efficient synthetic sorbent for heavy metals and radionuclides and has great potential for applications in environmental remediation of radionuclides and heavy metals, and waste water treatment. The low-toxicity, low density, and hydrophilicity also give GO some advantages over other mineral sorbent. It is commonly believed that the sorption of heavy metal and radionuclides to GO is due to complexation with carboxylate and sulfonate functional groups on the GO surface (see Chapter 6 and 7 in this dissertation). However, the exact mechanism is still under investigation. Some studies have applied batch sorption and surface complexation modeling (SCM) to understand the mechanism of actinide to GO. For instance, Duster et al. and Gu et al. modeled a series of +2 valent cations sorption to GO using a nonelectrostatic 4 site model, Gu et al. also found a linear free energy relationship between those cations sorption to one site on GO and their complexation to acetate (CH₃COOH), with one carboxylic functional group attached to it. Xie et al. modeled Eu(III) and U(VI) sorption to GO via an electrostatic double layer model, indicating that both elements sorbed to GO primarily through their complexation to the carboxylic functional groups on GO, as well as their complexation to an unexpected residue SO₃H functional group on GO made by Hummers and Offeman method.

For application of GO to permanent nuclear waste management, interactions at elevated temperatures need to be taken into consideration, because the disintegration of radioactive waste is estimated to raise the ambient temperature to 90 °C – 120 °C in a repository. The interaction of radioactive elements at the solid and water interface at
elevated temperature is usually studied using batch sorption experiment at these temperatures, and their empirical enthalpy and entropy value will be extrapolated by using van’t Hoff plot.

Isothermal titration calorimetry (ITC) directly measuring heat release of reactions in solution, was applied to study the energetics for ligand and protein binding in modern molecular biology.\textsuperscript{141, 142} Very few studies have directly measured the enthalpy for protonation/deprotonation or sorption at solid and water interfaces.\textsuperscript{143, 144} Here we applied ITC to measure the heat release during base titrations of GO with different suspension concentrations and ionic strengths, as well as during Eu(III)/U(VI) sorption to GO. Enthalpies for GO deprotonation and Eu(III)/U(VI) complexation to GO were calculated from the heat release data based on a surface complexation modeling (SCM) for GO in a previous study.\textsuperscript{137} The enthalpy values calculated in this study are consistent with those extrapolated using van’t Hoff plots conducted in previous studies.

8.2 Materials and Method

8.2.1 Graphene Oxide

A 4 g/L GO dispersion (in H\textsubscript{2}O) stock solution (Sigma Aldrich) prepared by Hummers and Offeman method was used for this study. The GO was characterized using field emission scanning electron microscopy (SEM), Fourier transformed infrared spectroscopy (FT-IR), powdered x-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and CHNS elemental analyzer. The specific surface area of GO was obtained through BET measurement. Despite multiple functional groups (e.g., carboxylic, hydroxyl, and epoxide) were detected on GO and commonly considered nonstoichiometric,
a carboxylic functional group ([≡COOH]) and a sulfonate functional group ([≡SO₂H]) were characterized as the two reactive surface sites on GO, and quantified via surface complexation modeling (SCM) of the GO acid/base titrations based on a diffuse double layer model (DLM). Details of the characterization of GO can be found in Xie et al.\textsuperscript{137}

8.2.2 Other Chemicals

Eu(III) and U(VI) working solutions used in this study were prepared by dissolving EuCl\textsubscript{3}•xH\textsubscript{2}O (Alfa Aesar) and UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}•6H\textsubscript{2}O (Electron Microscopy Sciences) in 0.01 M NaCl solution, and the pH of the working solutions were adjusted using 0.01 M NaOH or HCl. The concentrations of Eu(III) and U(VI) working solution were characterized using inductively coupled plasma mass spectrometry (ICP-MS, Thermo Scientific X Series II). All chemicals used in this experiment were analytical grade. All the solutions were prepared using distilled deionized water with a resistivity greater than 18 MΩ cm and less than 1 ppb total organic carbon. The ionic strength of all the solutions used in the work was adjusted using NaCl.

8.2.3 Titration Calorimetry

The calorimetric titrations were conducted at 25 °C using an isothermal titration microcalorimeter (TAM III, TA Instruments), which continuously measures the heat flow during titration by the heat difference between a reaction cell and a reference cell loaded in an adiabatic chamber. The adiabatic chamber maintained a temperature stability at 25 °C ± 0.0002 °C, and was capable of detecting the heat as low as 0.1 μJ. All titrations were conducted in a 2 mL cell made of the corrosion-resistant HASTELLOY\textsuperscript{®} alloy to prevent any reactions between the cell and the sample solution at an extremely low or high pH. The
initial solutions were prepared identically (concentration, volume, ionic strength, and pH) for the reaction cell and the reference cell. All the titrants were loaded in a 250 μL glass body syringe (Hamilton) and titrated into the reaction cell regulated using 3810 Syringe Pump (TA Instruments). The suspension in the reaction cell was stirred by an 18 K gold propeller at 180 rpm during the experiment to prevent diffusion heat during titration. The reaction cell and the reference cell loaded with GO suspension were placed in adiabatic chamber for more than 8 hours before the start of titration to allow the temperature of the system to reach equilibrium.

Three sets of calorimetric titrations were conducted. 1. Base titration of 0.01 M NaOH to GO in different concentrations (0.1 g/L, 0.5 g/L and 1 g/L) in order to measure the enthalpy of GO deprotonation; the ionic strength of all titrations was fixed at 0.01 M using NaCl; the initial pH of the suspensions was approximately pH 3. 2. Base titration of 0.01 M NaOH to 0.5 g/L GO suspension adjusted to different ionic strengths (I = 0.01 M, 0.1M, and 1M) to quantify the influence of Na⁺ binding to GO. During these titrations, both the solution in the cells and the titrant solutions were adjusted to the same ionic strength using NaCl to prevent the heat from NaCl dilution; the initial pH of the suspensions was approximately at pH 3. 3. Incremental titration of ~3 mM of Eu(III) or U(VI) solution to 2 g/L GO suspension at a constant pH of 3 or 5. Specifically, ~750 μL of 2 g/L GO suspensions were prepared in both the reaction cell and the reference cell, 250 μL of titrant solution containing either Eu(III) or U(VI) was prepared in the glass syringe. To the reaction cell 12 μL titrant a time was introduced, with 17 incremental steps, limiting the total volume in the reaction cell to less than 1000 μL. A period of 15 minutes between
each titration step was set to allow the temperature stabilization to baseline. The pH values of the suspension before and after titration were measured.

For the GO base titration the following reactions are expected.

\[
\text{COOH} = \text{COO}^- + H^+ \text{ (Major)} \\
\text{SO}_3H = \text{SO}_3^- + H^+ \\
H^+ + OH^- = H_2O \text{ (Major)} \\
\text{COO}^- + Na^+ = \text{COONa}
\]

For the U(VI) or Eu(III) titration to GO the following reactions are expected.

\[
\text{COO}^- + \text{UO}_2^{2+} = \text{COO}UO_2^+ \\
\text{SO}_3^- + \text{UO}_2^{2+} = \text{SO}_3UO_2^+ \\
\text{COO}^- + \text{Eu}^{3+} = \text{COOEu}^{2+} \\
\text{SO}_3^- + \text{Eu}^{3+} = \text{SO}_3Eu^{2+}
\]

8.2.4 Modeling

The enthalpies of the GO deprotonation as well as Eu(III) and U(VI) complexation to GO were calculated based on the stability constants for GO deprotonation and Eu(III)/U(VI) complexation to GO calculated in Xie et al. The aqueous and surface speciations at each titration step were modeled using a Windows-based geochemical modeling program FIT4FD (modified from FITEQL 4.0 for better database usage). The concentration of GO in the suspension, the initial pH of the suspension, and the total [H\(^+\)] added to the system at each titration step were used as input parameters to model the speciation during titration. The enthalpies for the deprotonation of \([\equiv\text{COOH}]\) and \([\equiv\text{SO}_3\text{H}]\) on the GO were calculated by least square fitting the heat release of the base titrations of
GO. The enthalpies of the Eu(III) and U(VI) complexation to GO were calculated by least square fitting the heat release the Eu(III) and U(VI) titration to GO.

8.3 Results and Discussions

8.3.1 Enthalpy for GO Deprotonation

Exothermic peaks were observed during the ITC base titrations of GO (all the ITC heat flow results for base titration were plotted in Appendix E). These exothermic peaks were primarily resulted from the formation of water ($\Delta H_{\text{H}_2\text{O}} = 55.81 \text{ kJ/mol}$) by the protons released from the $[\equiv\text{COOH}]$ sites on GO and the titrated hydroxide. Figure 29 exhibits the experimental results and modeling of the accumulative heat released as a function of accumulative NaOH titrated to the reaction cell with variable GO concentrations. As shown in Figure 29, with 0.1 g/L GO present in the reaction cell, the accumulative released heat reached a plateau in the middle of the titration, meaning the water formation process was completed. This is likely caused by the full deprotonation of $[\equiv\text{COOH}]$ sites on GO with approximately 0.1 mL of 0.01 M NaOH in the system. As fewer and fewer protons were released from the GO surface to the aqueous phase to neutralize the NaOH titrant, water formation; and therefore, the released heat became smaller and smaller. In contrast, the accumulative heat during NaOH titrating of 0.5 g/L and 1 g/L GO suspension increased steadily, meaning the neutralization and water formation process occurred during the entire ITC titrations. The amounts of $[\equiv\text{COOH}]$ in these two systems were 5 and 10 times more than that in the 0.1 g/L GO system, meaning 5 to 10 times more free $[\text{OH}^-]$ is needed to deprotonate all the $[\equiv\text{COOH}]$ to $[\equiv\text{COO}^-]$ in these two systems. Therefore, it is reasonable that there were remaining $[\equiv\text{COOH}]$ at the end of ITC titrations for these two systems. The
pH measured at the end of these three titrations are consistent with the interpretation of heat release. For 0.1 g/L GO system the pH reached to 11.33 at the end of titration, while for 0.5 g/L and 1 g/L GO system, the pH values were 6.97 and 6.67, respectively. Comparing to the titration to 0.5 g/L and 1 g/L GO system, the 0.1 g/L GO system did not provide as many deprotonated $[\text{H}^+]$ from the $[\equiv\text{COOH}]$ sites to neutralize the titrated $[\text{OH}^-]$, therefore several magnitude higher concentrations of free $[\text{OH}^-]$ was presented in the 0.1 g/L GO system than the other two systems at the end of titration.

The modeling of the heat release based on GO speciation calculations is also shown in Figure 29 (represented by solid lines) and the enthalpy for the deprotonation of GO was calculated based on this modeling. The measured initial pH prior to the ITC titration was used to determine the initial free proton concentration as well as the GO speciation at the beginning of the ITC titration in the model. Because the volume and concentration of input NaOH at each titration step are known, the titrated proton concentration at each titration step is known and used as the other input parameter (the titrated proton concentration is the negative of the input concentration NaOH). The amounts of total $[\equiv\text{COOH}]$ and $[\equiv\text{SO}_3\text{H}]$ sites in the suspension were also used as input parameters for modeling and the dilution of these sites during titration was also calculated. The deprotonation of $[\equiv\text{COOH}]$ and $[\equiv\text{SO}_3\text{H}]$ sites as well as the concentrations of free $[\text{H}^+]$ and $[\text{OH}^-]$ during the titration were simulated. The difference between the total input $[\text{OH}^-]$ and the modeled free $[\text{OH}^-]$ is assumed to be the amount of water formed at each step. The enthalpies for the deprotonation of $[\equiv\text{COOH}]$ and $[\equiv\text{SO}_3\text{H}]$ sites on GO were calculated by the least square fitting of the accumulative heat using the sum of heat release from water formation,
deprotonation of \([\equiv\text{COOH}]\) and deprotonation of \([\equiv\text{SO}_3\text{H}]\) for the three titration systems simultaneously. The calculated enthalpy for \([\equiv\text{COOH}]\) and \([\equiv\text{SO}_3\text{H}]\) deprotonation were 14.7 kJ/mol and -22 kJ/mol, respectively (Table 12). The enthalpy of \([\equiv\text{COOH}]\) deprotonation was comparable to that of bicarbonate (\(\text{HCO}_3^-\)), its structural analogue, disassociation in the aqueous phase.

The goodness of the modeling fit is determined by two criteria. First, whether the model produced a reliable simulation of the accumulative heat released as a function of accumulative NaOH titrated to the system; second, whether the model predicted the final pH measured at the end of the ITC titration. The comparison of the measured and model predicted pH with different GO concentration were shown in Table 11.

Figure 29: Experimental results (dots) and modeling of the accumulated heat released (J) as a function of the accumulative NaOH volume (mL) titrated to the system with variable GO concentrations in the suspension.
Table 11 Comparison of the measured and modeled pH values

<table>
<thead>
<tr>
<th>GO conc. (g/L)</th>
<th>Stage</th>
<th>Experimental</th>
<th>Model</th>
<th>RSD%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 g/L</td>
<td>Initial</td>
<td>2.97</td>
<td>3.01</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td>Final</td>
<td>11.33</td>
<td>11.01</td>
<td>2.82</td>
</tr>
<tr>
<td>0.5 g/L</td>
<td>Initial</td>
<td>2.54</td>
<td>2.55</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>Final</td>
<td>6.97</td>
<td>7.33</td>
<td>5.16</td>
</tr>
<tr>
<td>1 g/L</td>
<td>Initial</td>
<td>2.66</td>
<td>2.74</td>
<td>3.01</td>
</tr>
<tr>
<td></td>
<td>Final</td>
<td>6.67</td>
<td>7.91</td>
<td>18.6</td>
</tr>
</tbody>
</table>

Note: RSD% represents the relative error, calculated by the absolute value of the difference between the measured pH and the modeled one divided by the measured pH.

GO aggregation facilitated by high ionic strength was observed in a previous study\textsuperscript{67}; therefore, the influence of ionic strength on the enthalpy for GO deprotonation was also studied. Figure 30 shows the accumulative heat released as a function of accumulative 0.01 M NaOH titrated into the 0.5 g/L GO suspended in solution with different ionic strengths. No significant differences were shown as the ionic strength of the suspension and titrants changed from 0.01 M to 1M. Although the background Na\textsuperscript{+} and Cl\textsuperscript{-} concentration does affect the morphology of the GO, it does not have significant influence on the thermodynamics of GO in the aqueous phase; and therefore, was neglected in this study.
Figure 30: Experimental results of the accumulated heat released (J) as a function of the accumulative 0.01 M NaOH volume (mL) titrated into 0.5 g/L GO suspension with variable ionic strengths.

8.3.2 Enthalpies for Eu(III) and U(VI) Complexation to GO

The plots of heat flow for EuCl₃ and UO₂(NO₃)₂ titration to GO at pH 5 are exhibited in Figure 31, which shows endothermic peaks during the EuCl₃ titration while exothermic peaks during the UO₂(NO₃)₂ titration. ICP-MS measured 96% Eu(III) and 88% U(VI) sorption, while the model predicted 90% Eu(III) sorption and 96% of U(VI) sorption. Triplicate experiments for both ITC titrations were conducted and the heat flow plots are shown in Appendix E. The heat flow results indicated that Eu(III) sorption to GO was likely an endothermic process, but the exothermic peaks shown during U(VI) titrating to GO do not necessarily mean U(VI) complexation to GO was an exothermic process. The exothermic heat flow during the U(VI) titration was likely due to the redistributions between U(VI) hydrolysis products (e.g., (UO₂)₂(OH)₂²⁺, (UO₂)₃(OH)₅⁺ (UO₂)₄(OH)₇⁺) and the free UO₂²⁺ after UO₂²⁺ sorption to GO. The titrant U(VI) solution contained a high
concentration of U(VI) ($3 \times 10^{-3}$ M), leading to the formation of significant amounts of uranyl hydrolysis products (e.g., (UO$_2$)$_2$(OH)$_2^{2+}$, (UO$_2$)$_3$(OH)$_3^+$, (UO$_2$)$_4$(OH)$_4^{2+}$) at pH 5 (The speciation of uranyl at $10^{-3}$ M were shown in Appendix E). As UO$_2^{2+}$ sorbed to GO during titration, these uranyl hydrolysis products will disassociate to reach aqueous re-equilibrium within the titration system; the [OH$^-$] they released during disassociation will then neutralize the [H$^+$] deprotonated from the [$\equiv$COOH] site after sorption. The heat released from the neutralization process (water formation) exceeds the heat absorption during UO$_2^{2+}$ sorption to GO, lead to a total exothermic peak at each titration step of U(VI) to GO. In contrast, Eu(III) remains as free Eu$^{3+}$ in the aqueous phase at pH 5 (Eu$^{3+}$ does not form significant hydrolysis products until pH 6) meaning no aqueous reaction that has significant heat exchange occurred during Eu titrating to GO. Therefore, most of the heat during Eu titrating to GO resulted from Eu(III) complexation to GO.

The pH measurements before and after the titrations were also consistent with this hypothesis. The pH value decreased from 4.97 to 3.99 after the Eu(III) titration to GO, while it increased slightly from pH 4.56 to pH 4.71 after the U(VI) titration (The initial and end pH for Eu(III) and U(VI) titrations were shown in Appendix E). The decease of pH after the Eu(III) titration can be explained by the deprotonation of [$\equiv$COOH] after Eu(III) sorption. While the slight change in pH after the U(VI) titration likely resulted from the neutralization of the free [H$^+$] deprotonated from [COOH] by the free [OH$^-$] released from the disassociation of uranyl hydrolysis products.
The experimental (dots) and modeled (lines) accumulated heat release as a function of the accumulative titrated volume of Eu(III)/U(VI) are shown in Figure 32. The total titrated Eu(III)/U(VI) concentration, and total \([\equiv\text{COOH}]\) and \([\equiv\text{SO}_3\text{H}]\) sites at each titration step were used as modeling parameters. The initial free proton concentration for the modeling was determined based on the initial measured pH value. For the Eu(III) titration to GO, the model predicted both the pH and the amount of Eu sorption to GO. The
model predicted an initial pH of 4.96 and an end pH of 3.97, which were consistent with the pH measurements. The model predicted 86% Eu(III) sorption to GO which was also consistent with the experimental measurement of 90% sorption. The modeled enthalpy for GO deprotonation and the enthalpy for water formation were known values and the enthalpies for Eu$^{3+}$ complexation to GO through [$≡$COOH] and [$≡$SO$_3$H] sites were calculated by least square fitting of the experimental data. The enthalpies for Eu$^{3+}$ complexation to [$≡$COOH] and [$≡$SO$_3$H] were calculated to be 13 kJ/mol and 10 kJ/mol, respectively.

Some assumptions were made for modeling the U(VI) titration to GO, because the model simulated all input U(VI) as UO$_2$$^{2+}$, but the titrant U(VI) formed significant amounts of uranyl hydrolysis products prior to its titration. However, the modeling of U(VI) sorption to GO did not simulate the re-equilibrium of uranyl hydrolysis products after the UO$_2$$^{2+}$ sorption that was proposed to happen during the titration; therefore, this process was estimated based on some assumptions. The model does simulate the [H$^+$] released from UO$_2$$^{2+}$ sorption to GO under the condition of UO$_2$$^{2+}$ the only input U(VI) species; and the pH of the suspension after titration is predicted to be 3.51. It was assumed that the modeled final free [H$^+$] concentration subtracting the measured free [H$^+$] concentration was the total concentration of [H$^+$] neutralized by the [OH$^-$] released from the diassociation of uranyl hydrolysis products after UO$_2$$^{2+}$ sorption. The enthalpy values for UO$_2$$^{2+}$ complexation to [$≡$COOH] and [$≡$SO$_3$H] on GO were calculated to be 17.5 kJ/mol and 8 kJ/mol, respectively.
Figure 32: The measured (dots) and modeled (lines) accumulative heat release for Eu(III) and U(VI) titrating to GO in ITC.

Table 12 Calculated enthalpy values for GO deprotonation, Eu$^{3+}$ and UO$_2^{2+}$ complexation to GO.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\equiv COOH = \equiv COO^- + H^+$</td>
<td>14.7</td>
</tr>
<tr>
<td>$\equiv SO_3H = \equiv SO_3^- + H^+$</td>
<td>-22</td>
</tr>
<tr>
<td>$\equiv COOH + Eu^{3+} = \equiv COOEu^{2+} + H^+$</td>
<td>13</td>
</tr>
<tr>
<td>$\equiv SO_3H + Eu^{3+} = \equiv SO_3Eu^{2+} + H^+$</td>
<td>10</td>
</tr>
<tr>
<td>$\equiv COOH + UO_2^{2+} = \equiv COOUO_2^{+} + H^+$</td>
<td>17.5</td>
</tr>
<tr>
<td>$\equiv SO_3H + UO_2^{2+} = \equiv SO_3UO_2^{+} + H^+$</td>
<td>8</td>
</tr>
</tbody>
</table>
8.4 Conclusions

This study directly measured the heat releases for Eu(III)/U(VI) sorption to GO using the ITC and calculated the enthalpies for their complexation to GO based on the SCM of the sorption reactions developed in a previous study. The enthalpies for the deprotonation of the carboxylic and sulfonate functional groups on GO were also calculated based on the base titrations of GO with variable concentrations using ITC and the SCM. Slightly positive enthalpies were measured for both Eu(III) and U(VI) complexation to the carboxylic and sulfonate functional groups on GO, meaning these spontaneous sorption reactions are endothermic and are likely driven by positive entropies. Similar to the hypothesized sorption mechanism for actinide sorption to mineral, their sorption to GO are also likely to be driven by displacement of solvating water molecules from the actinides and GO surface during sorption.
CHAPTER 9

CONCLUSIONS

In this study, SCMs were used to model actinides (including Pu) sorption to goethite, kaolinite and graphene oxide as a function of pH, indicating the capability of modeling the actinide partitioning at different types of solid and water interfaces based on thermodynamics. These materials were selected to represent a range of surfaces including a metal hydroxide, clay mineral, and synthetic functionalized carbon based sorbent. By coupling Pu redox reactions to SCMs based on the Nernst equation, a more robust modeling of Pu sorption to kaolinite and goethite and its redox transformation in the aqueous phase was developed. In addition, this study showed the importance of incorporating an ion exchange process into the modeling of Pu sorption to a clay mineral at a lower pH range. Furthermore, the SCM was also applied to characterize the protonation/deprotonation behavior and site densities of reactive surface functional groups. In the study of actinide sorption to GO, the reactive functional groups on GO were characterized using potentiometric titrations. Based on the characterization, a representative model which indicated the mechanism of actinide sorption to GO via carboxylate and sulfonate functional groups was developed, and the enthalpy of actinide complexation to GO was obtained from microcalorimetry. Overall, this study demonstrated the utility of applying the SCMs to approximate actinide interactions at multiple solid and water interfaces as well as using the SCM to quantify the thermodynamics of actinide sorption to different surfaces. More importantly, experiences gained from this work could lead to better experimental
practice and modeling to develop a more complete understanding of actinide speciation at the solid and water interfaces.

A critical component of this modeling approach is good characterization of the solid phase used in batch sorption experiments. Impurities or minor components in the solid sample may affect the interpretation of experimental results and the subsequent modeling assumptions. For example, in this study, the purchased kaolinite was of high quality. However, natural kaolinite may contain a small amount of impurities such as TiO$_2$, Fe$_2$O$_3$, and organic matter. The potential effects of these impurities were not included in this modeling effort. Particularly for redox active ions, the presence of impurities may influence the pE measurement in the experiment. Another example is that the purchased GO suspension contained a trace amount of sulfonic acid impurity (~0.0003 M) that affected the modeling assumption and stability constant calculation. While this additional functional group was identified in and incorporated into the model, it was done so after many unsuccessful attempts to model the data. Therefore, it is preferable to fully characterize the surface earlier to avoid wasted time. However, it is also noteworthy that the unsuccessful model fits provided an indication that some information was missing and lead me down the path of identifying a previously uncharacterized and unquantified functional group on GO. Identifying all potential surface reactive sites is vital because given the trace to ultra-trace actinide concentration used in this study, even a small percentage of impurities may affect the result of the experiment.

Moreover, to study mechanisms of actinide sorption at the solid and water interfaces, it is crucial to accurately characterize the protonation and deprotonation
behavior of the solid at interface, in order to describe the influence of pH on sorption reactions. It is important to obtain a reliable point of zero charge (pzc) measurement during acid/base titration for comparison and normalization with the results obtained from previous studies. It is also important to examine the possible factors that may affect the surface behaviors during acid/base titration, such as ionic strength, carbonate infiltration and the presence of impurities.

In addition, the dissolution and stability of the solid phase in solution, especially with experiments at acidic or basic conditions and elevated temperatures, need to be taken into consideration.

SCMs were extensively used in this study to quantify actinide interactions at multiple solid and water interfaces; therefore, the limitation and future direction of SCM are also summarized below. The ultimate goal of applying SCMs to describe the interactions at the interface is to provide a better approach to incorporate these interactions into a reactive transport model. Although the study showed that SCMs are capable of modeling actinide sorption to different types of surfaces accommodated to changing conditions, and it has been studied and under continuous development over the past two decades, it is still challenging to construct a database to apply all the stability constants calculated from SCMs to model the transport. First of all, different sorption assumptions were used in different models making the stability constants calculated from one study not compatible with those from another study. This was done to take the most accurate and simplest model for each surface. However, there is no consistent approach to compare constants developed from different modeling constructs. For instance, some models ignore
the electrostatic effect at the solid and water interface, while other models use different assumptions to model the electrostatic effect such as the double layer model, triple layer model or Stern model. In this study, I did not compare the difference by using different modeling assumption. In addition, different assumptions on the surface site density were made among different studies, making the assembling of the stability constants generated in various studies to one database challenging. In this study, an empirical surface site density of 2.3 site/nm² was used to model the actinide complexation to minerals, while the surface site density of GO was obtained by modeling the potentiometric titration of GO. Moreover, some studies tend to use a universal \([≡SOH]\) to model a heterogeneous surface, while other studies used component additivity approach to study the interaction at each surface and modeling the heterogeneous surface by summation. The existence of these different modeling assumptions and approaches is one of the challenges to assembling a comprehensive and consistent database for solid and water interface.

In some cases, non-unique sets of SCM stability constants were capable of modeling one set of experimental results. The modeling practice through this study indicated that by modeling one set of experimental data may not give the optimal stability constants, rather stability constants calculated from modeling multiple dataset under varied conditions yields more robust and reliable stability constants. For example, in the study of actinide sorption to GO, the SCM simultaneously modeled sorption as a function of pH and sorbate concentration. Therefore, SCM conducted by modeling data with variable pH, sorbate concentrations, and ionic strengths may provide more reliable stability constants.
SCMs may provide a more robust prediction of radionuclide partition and speciation at the solid and water interfaces when compared with empirical sorption models. However, analytical techniques that are capable of measuring this speciation at the solid and water interface such as x-ray absorption spectroscopy and electron microscopy are encouraged to help define the interaction and speciation at molecular level. Quantum mechanical modeling of the interaction at the solid and water interface may also shed light on the speciation and complexation.

Below is a summary of insight for each specific study conducted for the dissertation work:

- The interactions at the solid and water interface under elevated temperature are extremely complicated and require more research. This is primarily due to the changing properties of water and the sorbing surfaces at elevated temperatures. The changing properties will affect actinide speciation both in the aqueous and solid phases. It is still unclear which are the major factors impacting actinide sorption at elevated temperature.

- Significant amounts of Pu(III) evolved in the aqueous phase during the study of Pu(IV) sorption to kaolinite under anaerobic conditions. Although the redox coupled SCM simulated the transformation of Pu(IV) to Pu(III) under anaerobic condition, previous research on Pu(IV) reduction to Pu(III) at the solid and water interface is limited. The reduction rate of Pu(IV) to Pu(III), and the possibility of Pu(III) oxidation to Pu(IV) mediated by the surface under anaerobic condition, as well as the stability constants for
Pu(III) sorption to different surfaces are not known and require additional work.

- From studies of actinide-GO interactions, many advantage of GO such as the strong and fast sorption kinetics and, the light weight and dispensability of the material compared to minerals was exhibited. However, in order to promote the possible future application of GO for nuclear waste management, further research including characterization of the reversibility of actinide sorption to GO, the efficiency and loading of radionuclides to GO and the long term stability of GO under variable conditions is needed.

- Direct quantification of the enthalpy for actinide complexation at the solid and water interface using ITC is challenging, primarily due to the fact that multiple reactions are occurring during actinide titration into the suspension and all processes yield a change in the system heat due to actinide sorption difficult to obtain. Therefore, it is recommended its application on a comparatively well understood system or more sophisticated modeling approach are needed to interpret calorimetric titration data at the solid and water interfaces. From the direct measurement of the enthalpy of Eu(III) and U(VI) sorption to GO in this study, some experience and recommendation are listed below:

1) The titration calibration syringe needs to be calibrated periodically. It is important to know an accurate titration volume since very little difference at each step can accumulate to a large error after 15 to 20
titration steps. Changes in the volume of titrant added could occur due to blockages in the syringe after repeated uses. Therefore, it is important to conduct periodical thorough cleaning and calibration of the syringe. Taking the syringe apart, sonicating in DDI water for ~ 5 minutes and wiping it clean would be adequate. To calibrate the syringe, titrate DDI water and weigh each titrant. The uncertainty in volume can be calculated from the difference between the measured and target weights.

2. The pH is a crucial value for interactions at the solid and water interface (actinide sorption changes as a function of pH, the surface deprotonation resulting from actinide sorption can change the pH of the solution, as well as the redistribution of actinide aqueous species after sorption may also change the pH). However only the initial and end pH can be measured for the ITC experiment, and the reactions during ITC titration are simulated based on using SCM. Therefore, it is important to have the modeled initial pH and end pH consistent with measured ones. If the SCM cannot provide a valid estimation of the end pH for the ITC titration, it may not have an appropriate assumption for the system it modeled. In addition, the concentration of input and sorbed actinide at the end of ITC titration can be quantified through analytical approach. Therefore an accurate estimation of the actinide sorption is another validation of the model.
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APPENDICES
Appendix A  Supporting Information for Chapter 4

A1  Goethite Characterization

The synthesized goethite was characterized using powder x-ray diffraction and field emission scanning electron microscopic (SEM) (Figure A1 and A2). The XRD pattern of the synthesized goethite used in this study matches that of natural goethite standard (Colorado, USA), which confirmed the mineralogy.

![Figure A1: A) XRD spectrum of the synthesized goethite used in this study. B) XRD spectrum of natural goethite standard from Colorado, USA](image)

A2  Van’t Hoff Plot for Potentiometric Measurements at Variable Temperatures

Figure A2 shows the van’t Hoff plot of the SCM modeled acidity constants of goethite at variable temperatures. The linear relationships between the ln K and inverse temperature were developed for both goethite protonation and deprotonation process. The
linear relationship exhibit that the protonation of goethite (formation of $\equiv\text{FeOH}_2^+$) is an endothermic process while the deprotonation of goethite (formation of $\equiv\text{FeO}^-$) is an exothermic process.

Figure A3 shows the van’t Hoff plot of the SCM modeled stability constants of Na$^+$ and Cl$^-$ outer-sphere complexation to goethite at variable temperatures. The positive slope for both Na$^+$ and Cl$^-$ complexation to goethite versus inverse temperature meaning both reactions are exothermic process.

![Figure A2: van’t Hoff plot for goethite protonation and deprotonation at variable temperatures.](image)

\[
y = -3796x + 28.667 \\
R^2 = 0.8862
\]

\[
y = 3706.5x - 33.993 \\
R^2 = 0.9316
\]
Table A1: Stability constants for Pu(IV) complexation to goethite modeled by redox coupled SCM and the non-redox coupled SCM.

<table>
<thead>
<tr>
<th>Pu Surface Reactions</th>
<th>Stability Constant (log Ks)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Redox Coupled</td>
</tr>
<tr>
<td>≡FeOH + Pu^{4+} + H_2O = ≡FeOPuOH^{2+} + 2H^+</td>
<td>12.82</td>
</tr>
<tr>
<td>≡FeOH + Pu^{4+} + 2H_2O = ≡FeOPu(OH)_{2}^{+} + 3H^+</td>
<td>6.917</td>
</tr>
<tr>
<td>≡FeOH + Pu^{4+} + 3H_2O = ≡FeOPu(OH)_3^{+} + 4H^+</td>
<td>1.216</td>
</tr>
</tbody>
</table>

Figure A3: van’t Hoff plot for Na^+ and Cl^- complexation to goethite surface.
A4  Th(IV) Hydrolysis Constants at Elevated Temperatures

Table A2: Water dissociation constants and thorium hydrolysis constants at the elevated temperatures used in modeling.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>T (°C)</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_w$</td>
<td>25</td>
<td>-13.99</td>
</tr>
<tr>
<td>$H_2O = H^+ + OH^-$</td>
<td>35</td>
<td>-13.68</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-13.26</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>-12.91</td>
</tr>
<tr>
<td>$*\beta_{1.1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Th^{4+} + H_2O = ThOH^{3+} + H^+$</td>
<td>25</td>
<td>-2.50</td>
</tr>
<tr>
<td>$\Delta_r H^\circ = 44.20 \text{ kJ} \cdot \text{mol}^{-1}$</td>
<td>35</td>
<td>-2.25</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-1.90</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>-1.58</td>
</tr>
<tr>
<td>$*\beta_{2.1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Th^{4+} + 2H_2O = Th(OH)_2^{2+} + 2H^+$</td>
<td>25</td>
<td>-6.20</td>
</tr>
<tr>
<td>$\Delta_r H^\circ = 85.70 \text{ kJ} \cdot \text{mol}^{-1}$</td>
<td>35</td>
<td>-5.71</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-5.04</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>-4.42</td>
</tr>
</tbody>
</table>

Table A3: SCM calculated stability constants for Th sorption to goethite at variable temperatures

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Log K $[\equiv \text{FeOTh}^{3+}]$</th>
<th>Log K $[\equiv \text{FeOH}_2\text{Th}^{5+}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>21.64</td>
<td>17.71</td>
</tr>
<tr>
<td>35</td>
<td>23.5061</td>
<td>18.9145</td>
</tr>
<tr>
<td>50</td>
<td>25.54</td>
<td>20.48</td>
</tr>
<tr>
<td>65</td>
<td>27.8061</td>
<td>21.8675</td>
</tr>
</tbody>
</table>
Figure A4: van’t Hoff plot of SCM modeled Th sorption to goethite.

Table A4: $\Delta H$ and $\Delta S$ extrapolated from van’t Hoff plot in Figure A4

<table>
<thead>
<tr>
<th></th>
<th>$\text{FeOTh}^{3+}$</th>
<th>$\text{FeOH}_2\text{Th}^{5+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H$ (kJ/mol)</td>
<td>225</td>
<td>266</td>
</tr>
<tr>
<td>$\Delta S$ (J/mol/K)</td>
<td>1228</td>
<td>1128</td>
</tr>
</tbody>
</table>
Appendix B  Supporting Information for Chapter 5

B1  Pu(IV) Working Solution Characterization

Three $^{238}$Pu(IV) working solutions were prepared for this study; their oxidation states were characterized using solvent extract techniques and their total Pu concentration was quantified using LSC (Table B1). It can be seen from Table B1 that the input Pu is primarily in the tetravalent oxidation state.

<table>
<thead>
<tr>
<th>Batch Experiments</th>
<th>0.1 M aerobic</th>
<th>0.1 M anaerobic</th>
<th>0.05 M/0.5 M aerobic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu(IV)</td>
<td>98% ± 0.7</td>
<td>93% ± 0.5</td>
<td>97% ± 0.4</td>
</tr>
<tr>
<td>Pu(V)</td>
<td>1% ± 0.05</td>
<td>3% ± 0.06</td>
<td>2% ± 0.03</td>
</tr>
<tr>
<td>Pu(VI)</td>
<td>1% ± 0.75</td>
<td>3% ± 0.56</td>
<td>1% ± 0.43</td>
</tr>
<tr>
<td>Total Pu Conc. (M)</td>
<td>$1.4 \times 10^{-8}$</td>
<td>$1.7 \times 10^{-8}$</td>
<td>$1.9 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

B2  Chemical Composition of Kaolinite (KGa-1)

The chemical composition of the kaolinite (KGa-1) used in this study were characterized in previous studies and the results are listed in Table B2. As shown in Table B2, SiO$_2$ and Al$_2$O$_3$ are the predominant composition in the kaolinite. Trace amount of TiO$_2$ also present in the sample.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>KGa-1B</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>45.4%</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>39.2%</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.54%</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.22%</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>-------</td>
</tr>
<tr>
<td>MgO</td>
<td>0.02%</td>
</tr>
<tr>
<td>CaO</td>
<td>0.01%</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.02%</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.04%</td>
</tr>
<tr>
<td>Loss on Ignition at 1025 °C</td>
<td>13.7%</td>
</tr>
</tbody>
</table>

**B3 Acid/Base Titration**

Potentiometric titrations of K-Ga1 were conducted using TIAO automatic titration system with background electrolyte with different ionic strengths. Acid and base titrations were conducted at pH ranging from 3 to 9. Figure B1 plotted the results of base titrations of kaolinite at different ionic strengths adjusted using NaCl. Because the acid and base titrations exhibit the same pattern, only the results of base titrations were shown here. The pH$_{PZC}$ of kaolinite is measured from the titrations at approximately pH 4.2, which is consistent with previous studies. It can be seen from Figure B1, the titration patterns for KGa-1 at different ionic strengths overlapped at pH > 5, while slight differences were shown for the titration with 0.5 M background electrolyte, which is probably caused by the weak cation exchange process at kaolinite.
B4 Pu Oxidation State Analysis Associated with the Solid Phase

Table B3 and B4 present the results of Pu oxidation state analysis associated with the solid phase after the batch sorption experiments under aerobic condition and anaerobic condition, respectively. As shown in Table B3, Pu(IV) is the predominant sorbed species on kaolinite; small amount of Pu(VI) were measured at the kaolinite surface in the higher pH samples. For the Pu oxidation state analysis associated with the kaolinite under anaerobic condition, over 90% of Pu(IV) was measured at most samples, except for one sample measured only 85% of Pu(IV) associated with kaolinite. As the pH increased, some Pu(VI) and 1-2% percentage of Pu(V) were also measured at the kaolinite surface.

Table B3: Oxidation state analysis of the Pu associated with kaolinite under the aerobic condition

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Pu(IV)</th>
<th>Pu(V)</th>
<th>Pu(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KaopH1_oxic_solid</td>
<td>100%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>KaopH2_oxic_solid</td>
<td>100%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>KaopH2DUP_oxic_solid</td>
<td>100%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>KaopH3_oxic_solid</td>
<td>100%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>KaopH4_oxic_solid</td>
<td>98%</td>
<td>0%</td>
<td>2%</td>
</tr>
<tr>
<td>KaopH4DUP_oxic_solid</td>
<td>98%</td>
<td>0%</td>
<td>2%</td>
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<tr>
<td>KaopH5_oxic_solid</td>
<td>97%</td>
<td>0%</td>
<td>3%</td>
</tr>
</tbody>
</table>
Table B4: Oxidation state analysis of the Pu associated with kaolinite under the anaerobic condition

<table>
<thead>
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<th>Sample ID</th>
<th>Pu(IV)</th>
<th>Pu(V)</th>
<th>Pu(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KaopH1_anoxic_solid</td>
<td>99.06%</td>
<td>0.03%</td>
<td>0.91%</td>
</tr>
<tr>
<td>KaopH2_anoxic_solid</td>
<td>99.09%</td>
<td>-0.13%</td>
<td>1.04%</td>
</tr>
<tr>
<td>KaopH3_anoxic_solid</td>
<td>98.80%</td>
<td>0.14%</td>
<td>1.06%</td>
</tr>
<tr>
<td>KaopH4_anoxic_solid</td>
<td>97.13%</td>
<td>0.32%</td>
<td>2.55%</td>
</tr>
<tr>
<td>KaopH5_anoxic_solid</td>
<td>85.45%</td>
<td>2.35%</td>
<td>12.20%</td>
</tr>
<tr>
<td>KaopH6_anoxic_solid</td>
<td>93.52%</td>
<td>2.03%</td>
<td>4.45%</td>
</tr>
<tr>
<td>KaopH7_anoxic_solid</td>
<td>95.88%</td>
<td>1.38%</td>
<td>2.74%</td>
</tr>
<tr>
<td>KaopH8_anoxic_solid</td>
<td>91.82%</td>
<td>1.98%</td>
<td>6.20%</td>
</tr>
</tbody>
</table>

B5 SCM of Am(III) Sorption to Silica Gel and Alumina

The stability constants calculated from the SCM of Am(III) sorption to silica gel and alumina are listed in Table B5.

Table B5: Stability Constants for Am(III) sorption to silica gel and alumina calculated from SCM

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\equiv\text{SiOH} + \text{Am}^{3+} = \equiv\text{SiOAm}^{2+} + \text{H}^+$</td>
<td>3.72</td>
</tr>
<tr>
<td>$\equiv\text{SiOH} + \text{Am}^{3+} = \equiv\text{SiOAm}^{2+} + \text{H}^+$</td>
<td>-0.31</td>
</tr>
<tr>
<td>$\equiv\text{SiOH} + \text{Am}^{3+} = \equiv\text{SiOAm}^{2+} + \text{H}^+$</td>
<td>4.92</td>
</tr>
<tr>
<td>$\equiv\text{SiOH} + \text{Am}^{3+} = \equiv\text{SiOAm}^{2+} + \text{H}^+$</td>
<td>2.8</td>
</tr>
</tbody>
</table>
Appendix C  Supporting Information for Chapter 6

C1  Graphene Oxide Characterization

A 4 g/L graphene oxide (GO) suspension in water purchased from Sigma Aldrich was used in this study. We have used the term graphene oxide throughout this manuscript thought the material may be more appropriately called graphite oxide based on the observation of an easily identifiable peak in the XRD pattern and strong aggregation of the particles. However, to remain consistent with the manufacturer’s label of graphene oxide, we have continued using that term. Based on our characterization of the sample, it appears the material was prepared by oxidation of graphite using Hummers method. The GO was characterized using field emission scanning electron microscopic (SEM), Fourier transformed infrared spectroscopy (FT-IR), powdered x-ray diffraction (XRD). The specific surface area (SSA) of GO was obtained through N₂(g) sorption BET analysis of a dried GO sample. The weight percentage of carbon, hydrogen and sulfur of GO was quantified via CHNS elemental analyzer. For the SEM imaging, an aliquot of GO suspension (pH≈5, adjusted using 0.01M NaOH) was pipetted on a copper strip and slowly air-dried in the hood with a cover on it for dust prevention. The SEM image was obtained using SU-6600 high-resolution analytical field emission SEM (Hitachi). FT-IR spectroscopy measurements were made on a Thermo Nicolet 6700 spectrometer (Thermo Scientific) using a single bound diamond attenuated total reflectance cell (Smart iTR) at room temperature. An aliquot of GO suspension (pH≈5, adjusted using 0.01M NaOH) was deposit to the diamond platform and dried by air prior to measurement. For the
measurement of the uranium bearing sample also at pH 5, the wet GO paste following centrifugation was deposited on the crystal and allowed to air dry prior to the measurements. The XRD pattern was measured using a Miniflex x-ray diffractometer (Rigaku, Japan). For BET specific surface area measurement and CHNS elemental analysis, 6 mL of GO stock solution was transferred to a biker and evaporated with moderate heat (<80 ºC); the dried GO samples were then vacuumed at < 100 ºC in a vacuum oven overnight to remove moisture and impurities in the samples. The BET surface area measurement was performed with a physisorption analyzer (Micromeritics ASAP 2020). The CHNS elemental analysis was conducted with FlashEA 1112 elemental analyzer. BBOT (C_{26}H_{26}N_{2}O_{2}S) was used as a standard for CHNS quantification.

The SEM image of GO showed that the GO used in this study was in the size of several microns and no aggregation was observed (Figure C1, C). The FTIR spectrum of GO at pH 5 showed peaks at 1730 cm\(^{-1}\), 1620 cm\(^{-1}\), 1370 cm\(^{-1}\), 1220 cm\(^{-1}\), and 1040 cm\(^{-1}\) (Figure S1, A); this is consistent with previous GO characterization. Previous studies has attributed these vibrations to carbon-based functional groups; however there is an overlap region for carbon-based and sulfonate group at ~1200 cm\(^{-1}\) to 1000 cm\(^{-1}\) region, it is difficult to identify the existence of sulfonate using FTIR. On the XRD pattern, a single peak at ~10 degrees was seen for GO (Figure C1, B), which reflects the layering of the GO sheets and is also consistent with previous GO characterization. The BET measured surface area of GO is 307 m\(^2\)/g. On average 3.2% of total sulfur on the GO used for this study was quantified through CHNS elemental analysis (Table C1).
Figure C1: Characterization of GO. A: FTIR pattern at pH 5; B: XRD pattern at pH 5; C: SEM image of GO at pH 5.

Table C1: CHNS elemental analysis of unwashed GO (in weight percentage w/w%)

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Element</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>BBOT_STND</td>
<td></td>
<td>72.6</td>
<td>6.3</td>
<td>6.4</td>
<td>7.5</td>
</tr>
<tr>
<td>GO</td>
<td></td>
<td>46.6</td>
<td>1.8</td>
<td>0.0</td>
<td>3.7</td>
</tr>
<tr>
<td>GO_DUP_1</td>
<td></td>
<td>46.5</td>
<td>2.0</td>
<td>0.0</td>
<td>3.6</td>
</tr>
<tr>
<td>GO_DUP_2</td>
<td></td>
<td>45.0</td>
<td>2.1</td>
<td>0.0</td>
<td>4.5</td>
</tr>
<tr>
<td>GO_DUP_3</td>
<td></td>
<td>59.0</td>
<td>2.8</td>
<td>0.0</td>
<td>1.4</td>
</tr>
<tr>
<td>GO_DUP_4</td>
<td></td>
<td>56.2</td>
<td>2.6</td>
<td>0.0</td>
<td>2.9</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>46.0</td>
<td>2.0</td>
<td>0.0</td>
<td>3.2</td>
</tr>
</tbody>
</table>

In order to confirm the existence of sulfonate group and discriminate the possible residue sulfate in the purchased GO suspension, the purchased GO was washed and characterized using x-ray photoelectron spectroscopy (XPS) and CHNS elemental analysis.
Specifically, the wash steps are as following: 1. 1 M NaCl: 12 mL of 4 g/L GO suspension was mixed with 40 mL of 1 M NaCl, sonicated for 30 min for mixing and centrifuged at 8000 rpm for 1 hr for GO/solution separation, decant the supernatant, and repeat the wash procedure with 1 M NaCl for 3 times; 2. 0.1 M HCl: same wash procedures were conducted for 3 times using 0.1 M NaCl to eliminate the residue NaCl on GO; 3. DDI water: same wash procedures were conducted using DDI water to eliminate HCl residue until the pH of the washed GO unchanged. The washed GO paste was dried at ~ 80 C till dryness for XPS and CHNS measurement.

XPS measurements were performed using a Kratos AXIS Ultra DLD XPS system equipped with a hemispherical energy analyzer and a monochromatic Al K\(_\alpha\) source. The monochromatic Al K\(_\alpha\) source was operated at 15 keV and 150 W; pass energy was fixed at 40 eV for the detailed scans. All samples were prepared as pressed powders supported on a gold-plated stainless steel stub for the XPS measurements. A C 1s, O 1s, and S 2p XPS spectra for the washed and unwashed GO were shown on Figure C2. All the spectra were calibrated using the 284.6 eV C-C peak. The intensity of C 1s and O 1s peaks remained the same which indicates the washing steps did not alter the carbon bearing functional groups on GO. The different C 1s XPS spectra may result from the nonstoichiometric property of GO. Significant peak intensity changes were observed for S2p spectra. The unwashed GO showed a clear sulfonate/sulfate peak at ~168 eV. The intensity of the sulfonate peak is much weaker for the washed GO sample, but the peak position is unchanged at ~ 168 eV. The S 2p XPS spectra indicated the peak at 168 eV is partially from the deposition of residue sulfate in the aqueous phase, but after the intensive wash steps, the peak at 168 eV
persists indicating the existence of sulfonate functional groups associated with GO. The CHNS elemental analysis for total sulfur weight percentage lowered to 0.8 % after wash step (Table C2). Thus, both elemental analysis and XPS analysis confirm that sulfonate functional groups persist on the GO surface which are likely produced during production of the GO. These functional groups appear to play an important role in the sorption of Eu(III) and U(VI) at low pH.

Figure C2: C1s, O1s and S2p XPS spectra of GO (black line) and washed GO (red line).

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Element</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>BBOT_STND</td>
<td></td>
<td>72.53</td>
<td>6.09</td>
<td>6.51</td>
<td>7.44</td>
</tr>
<tr>
<td>Washed_GO_1</td>
<td></td>
<td>60.5</td>
<td>2.4</td>
<td>0</td>
<td>0.7</td>
</tr>
<tr>
<td>Washed_GO_2</td>
<td></td>
<td>59.7</td>
<td>2.3</td>
<td>0</td>
<td>0.7</td>
</tr>
<tr>
<td>Washed_GO_3</td>
<td></td>
<td>63.4</td>
<td>2</td>
<td>0.1</td>
<td>0.8</td>
</tr>
</tbody>
</table>
C2 Full results of acid/base titrations and modeling

The results of acid and base titrations for GO at variable concentrations are shown in Figure S3. Both acid and base titrations showed similar patterns indicating the reactions were reversible over the timeframe of the titration. Surface complexation modeling (SCM) via diffuse layer model was applied to simulate the protonation/deprotonation reactions for GO. Two sites (≡COOH and ≡SOH) were used to approximate the titration data. The modeled total sites (mol/L) for GO with variable concentrations were listed in Table C3. Note that the unit on this axis are mol/L of sites in the suspension. The slope of a plot of the site concentrations (mol\text{sites}/L) versus GO suspension concentration (g\text{GO}/L) yields a slope representing the site density in mol\text{sites}/g\text{GO}. These simulated total sites were further used in the paper for SCM of Eu(III)/U(VI) complexation to GO.

<table>
<thead>
<tr>
<th>Washed_GO_4</th>
<th>58.4</th>
<th>2.1</th>
<th>0</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>60.5</td>
<td>2.2</td>
<td>0</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Figure C3: Result of GO acid/base titration. AT = acid titration, BT = base titration.
Table C3: SCM determined total reactive sites for GO from potentiometric titrations

<table>
<thead>
<tr>
<th>GO Conc. (g/L)</th>
<th>Total sites[\equiv\text{COOH}] (mol\text{sites/L})</th>
<th>Total sites[\equiv\text{SOH}] (mol\text{sites/L})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>1.49E-05</td>
<td>8.54E-06</td>
</tr>
<tr>
<td>0.1</td>
<td>2.13E-04</td>
<td>1.49E-04</td>
</tr>
<tr>
<td>0.5</td>
<td>1.18E-03</td>
<td>9.49E-04</td>
</tr>
<tr>
<td>1</td>
<td>1.93E-03</td>
<td>2.28E-03</td>
</tr>
</tbody>
</table>

C3  EDS Mapping of GO loaded with 100 ppm Eu/U

EDS mapping for C, O, and Eu or U were performed to detect possible precipitation of Eu or U at high concentration (Figure C4 and C5). The EDS mapping indicated that Eu and U were dispersed throughout the GO but formation of nanoprecipitates could not be ruled out.
Figure C4: EDS mapping of GO aggregation facilitated by 100ppm Eu.
Figure C 5: EDS mapping of GO aggregation facilitated by 100ppm U. The precipitate phases observed in the SEM image were identified as NaCl salts using EDS. The uranium distribution was not directly associated with the precipitates.

C4 Eu(III) and U(VI) Facilitated Aggregation

GO aggregation was observed in samples with the higher spiked Eu(III) and U(VI) concentrations (Figure C6). To confirm the aggregation, the particle size of the GO suspension was determined as a function of Eu(III)/U(VI) concentration dynamic light scattering (90Plus with ZetaPALS, Brookhaven Instruments Corporation) (Figure C7 and C8). Figure C7 shows that the GO particle size increased a function of Eu(III) concentration and a similar result was found for U(VI) in Figure C8.
Figure C6: Photos of GO aggregation facilitated by Eu(III) and U(VI). A: The left tube contains 0.1 g/L GO suspension, the right tube contains 0.1 g/L GO suspension spiked with 100,000 ppb Eu(III); B: The left tube contains 0.1 g/L GO suspension, the right tube contains 0.1 g/L GO suspension spiked with 100,000 ppb U(VI).
Figure C7: Particle size measurement of GO suspensions with varying spiked Eu(III) concentration from (10 ppb – 100,000 ppb). The pH of all suspensions are adjusted to ~ pH 5.

Figure C8: Particle size measurement of GO suspensions with varying spiked U(VI) concentration from (10 ppb – 100,000 ppb). The pH of all suspensions are adjusted to ~ pH 5.

C5 Models of Eu(III) and U(VI) Surface Speciation

Modeled Eu(III) and U(VI) surface speciation on GO are shown in Table C4. The far right columns show the ratio of sorbed Eu(III) or U(VI) to [≡COO⁻] and [SO₃⁻]. For both Eu(III) and U(VI), the model showed that carboxylate groups are the dominant
sorption site for Eu(III) or U(VI) and the ratio of metal-carboxylate sites to metal-sulfonate sites increased with increasing total Eu(III) and U(VI) concentration. The ratio of $[\equiv\text{COOEu}^{2+}]$ or $[\equiv\text{COOUO}_2^{2+}]$ to total $[\equiv\text{COOH}]$ sites was also calculated. The total $[\equiv\text{COOH}]$ site is fixed at 2.14E-4 mol/L (based on 2.0 mmol $\equiv\text{COOH}$ per g$_{\text{GO}}$) modeled from acid/base titration data. The ratio at highest Eu or U concentrations indicate saturation of the GO was achieved which could lead to surface charge neutralization and the observed aggregation.

Table C4: Selected Eu(III) and U(VI) surficial speciations

<table>
<thead>
<tr>
<th>Aq Eu(III)</th>
<th>FIT4FD calculated speciation (mol/L)</th>
<th>Ratio</th>
<th>Aq U(VI)</th>
<th>FIT4FD calculated speciation (mol/L)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$[\equiv\text{COOH}]$</td>
<td>$[\equiv\text{SO}_3^{2-}]$</td>
<td>$[\equiv\text{COO}^-]$</td>
<td>$[\equiv\text{SO}_4^{2-}]$</td>
<td>$[\equiv\text{COOEu}^{2+}]$</td>
</tr>
<tr>
<td>1.60E-10</td>
<td>2.09E-04</td>
<td>2.85E-09</td>
<td>5.45E-06</td>
<td>3.73E-05</td>
<td>7.31E-08</td>
</tr>
<tr>
<td>1.71E-09</td>
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<td>5.59E-06</td>
<td>3.73E-05</td>
<td>6.77E-07</td>
</tr>
<tr>
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<td>9.67E-06</td>
<td>3.72E-05</td>
<td>6.64E-06</td>
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<td>4.27E-05</td>
<td>1.32E-04</td>
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<td>4.56E-05</td>
<td>3.72E-05</td>
<td>3.61E-05</td>
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<td>6.34E-04</td>
<td>7.72E-05</td>
<td>7.05E-11</td>
<td>8.12E-05</td>
<td>3.72E-05</td>
<td>5.55E-05</td>
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<td>1.93E-10</td>
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<td>3.14E-09</td>
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<td>3.73E-05</td>
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<td>6.51E-06</td>
<td>3.73E-05</td>
<td>6.96E-09</td>
</tr>
<tr>
<td>3.28E-07</td>
<td>1.83E-04</td>
<td>1.51E-09</td>
<td>9.03E-06</td>
<td>3.73E-05</td>
<td>2.20E-08</td>
</tr>
<tr>
<td>2.12E-06</td>
<td>1.53E-04</td>
<td>5.89E-10</td>
<td>1.93E-05</td>
<td>3.73E-05</td>
<td>1.98E-08</td>
</tr>
<tr>
<td>3.46E-04</td>
<td>5.53E-05</td>
<td>6.45E-11</td>
<td>6.37E-05</td>
<td>3.73E-05</td>
<td>1.36E-08</td>
</tr>
</tbody>
</table>

C6 K$_D$ Plots

Figure C9 and C10 showed SCM modeled K$_D$ versus experimental K$_D$ as a function of pH for Eu(III) and U(VI), respectively. The detection limits of ICPMS at 0.01 ppb Eu(III)/U(VI) were also shown on the figures. It is noted that big differences were seen between the modeling and the experimental data for those close to/above detection limit.
Basically at above pH 4, the majority of Eu(III) were sorbed to GO, leaving Eu(III) concentration lower than the ICPMS detection limit. These Eu(III) aqueous measurements were based on the extrapolation of the calibration curves, which can lead to big uncertainties. Moreover, at close to 100% sorption, $K_D$ value tend to show huge difference as the numerator getting close to zero. For U(VI), highest sorption achieved at about pH 5, the aqueous U(VI) concentration were also lower than the ICPMS detection limit, and the modeling showed bigger different at pH 5 data, but at above pH 5, the complexation U(VI) to carbonate lowered the U(VI) sorption to GO, and the SCM predicted the trend.

![Figure C9: Experimental $K_D$ (black dots) and SCM modeled $K_D$ (red line) for Eu(III) sorption to GO as a function of pH. The detection limit of ICPMS for Eu(III) is shown in red dash line.](image-url)
Figure C10: Experimental $K_D$ (black dots) and SCM modeled $K_D$ (red line) for U(VI) sorption to GO as a function of pH. The detection limit of ICPMS for U(VI) is shown in red dash line.

C7 FTIR spectra

Figure C11: FTIR spectra for bulk GO and GO with 100 ppm U(VI).
Appendix D  Supporting Information for Chapter 7

Table D1: Ratio of the major sorbed species over total available sorption site

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$[≡\text{COOTh(OH)}_2]^+/[\equiv \text{COO}^- + \equiv \text{SO}_3^-] }$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ppb_Th</td>
<td>0.00</td>
</tr>
<tr>
<td>100 ppb_Th</td>
<td>0.01</td>
</tr>
<tr>
<td>1000 ppb_Th</td>
<td>0.12</td>
</tr>
<tr>
<td>5000 ppb_Th</td>
<td>0.36</td>
</tr>
<tr>
<td>10000 ppb_Th</td>
<td>0.46</td>
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<tr>
<td>50000 ppb_Th</td>
<td>0.50</td>
</tr>
<tr>
<td>100000 ppb_Th</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Table D2: Stability Constant ($\log K_S$) for linear relationship

<table>
<thead>
<tr>
<th>Surface Species</th>
<th>Log $K_{[\text{COO}^-]}$</th>
<th>Actinide-Carbonate complex</th>
<th>Log $K_{[\text{CO}_3^{2-}]}$</th>
<th>I</th>
<th>Reference</th>
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<tr>
<td>$≡\text{COOEu}^{2+}$</td>
<td>0.2</td>
<td>Eu$(\text{CO}_3)^+$</td>
<td>6.57</td>
<td>0.1</td>
<td>Kim et al., 1994</td>
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<tr>
<td>$≡\text{COONpO}_{2}$</td>
<td>-1.5</td>
<td>Np$2(\text{CO}_3)^-$</td>
<td>4.34</td>
<td>0.1</td>
<td>Clark et al., 1995</td>
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<tr>
<td>$≡\text{COOUO}_2^{+}$</td>
<td>2.78</td>
<td>U$2\text{CO}_3$</td>
<td>8.54</td>
<td>0.5</td>
<td>Clark et al., 1995</td>
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<tr>
<td>$≡\text{COOTh(OH)}_3$</td>
<td>6</td>
<td>Th$(\text{OH})_2(\text{CO}_3)^-$</td>
<td>15.28</td>
<td>3</td>
<td>Clark et al., 1995</td>
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Appendix E  Supporting Information for Chapter 8

E1  Heat Flow Results for Base Titrations

Figure E1: Heat flow for 0.01 M NaOH titrating to 0.1 g/L GO suspension. 10 µL of NaOH titrated at each step.

Figure E2: Heat flow for 0.01 M NaOH titrating to 0.5 g/L GO suspension. 10 µL of NaOH titrated at each step.
Figure E3: Heat flow for 0.01 M NaOH titrating to 1 g/L GO suspension. 10 µL of NaOH titrated at each step.

Figure E4: Heat flow for 0.01 M NaOH titrating to 0.5 g/L GO suspension. Ionic strength for both GO suspension and titrant are at 0.01 M adjusted using NaCl. 13 µL of NaOH titrated at each step.
Figure E5: Heat flow for 0.01 M NaOH titrating to 0.5 g/L GO suspension. Ionic strength for both GO suspension and titrant are at 0.1 M adjusted using NaCl. 12 µL of NaOH titrated at each step.

Figure E6: Heat flow for 0.01 M NaOH titrating to 0.5 g/L GO suspension. Ionic strength for both GO suspension and titrant are at 1 M adjusted using NaCl. 12 µL of NaOH titrated at each step.
Figure E7: Approximately 3 mM of EuCl$_3$ titrating to 2 g/L GO at pH 5. I = 0.01 M adjusted using NaCl. 10 µL of EuCl$_3$ titrated at each step.

Figure E8: Approximately 3 mM of EuCl$_3$ titrating to 2 g/L GO at pH 5. I = 0.01 M adjusted using NaCl. 12 µL of EuCl$_3$ titrated at each step.
Figure E9: Approximately 3 mM of UO$_2$(NO$_3$)$_2$ titrating to 2g/L GO at pH 5. I = 0.01 M adjusted using NaCl. 12 µL of UO$_2$(NO$_3$)$_2$ titrated at each step.

Table E1: Initial and end pH during ITC titrations of Eu(III) to GO

<table>
<thead>
<tr>
<th>Eu_Titrations</th>
<th>Initial pH</th>
<th>End pH</th>
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<tr>
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<td>3.99</td>
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<tr>
<td>Modeled_1/28/2016</td>
<td>4.94</td>
<td>3.97</td>
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<tr>
<td>4/23/2016_ITC_1</td>
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<td>4/23/2016_ITC_3</td>
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Table E2: Initial and end pH during ITC titrations of U(VI) to GO

<table>
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<tr>
<th>U_Titrations</th>
<th>Initial pH</th>
<th>End pH</th>
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<tbody>
<tr>
<td>1/28/2016</td>
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<td>4.71</td>
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<tr>
<td>4/25/2016_ITC_1</td>
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<tr>
<td>4/25/2016_ITC_3</td>
<td>5.05</td>
<td>5.4</td>
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</table>
E3 Uranyl Speciation in the Aqueous Phase

Figure E10: $\text{UO}_2^{2+}$ hydrolysis as a function of pH, $[\text{UO}_2^{2+}] = 1 \times 10^{-3}$ M.