Thermodynamics of Metals Adsorption onto Uranium Dioxide

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THERMODYNAMICS OF METALS ADSORPTION ONTO URANIUM DIOXIDE

by

Koi Ling Lim

A Thesis
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Koi Ling Lim
Wastes and pollution containing uranium are released to the environment through mining, ore processing, industrial manufacture of nuclear fuel and weapons materials, and the disposal of spent nuclear fuel. There are a wide variety of processes that can affect UO$_2$ stability. This research focuses on the surface reactivity of UO$_2$ in reducing aqueous solutions, with an emphasis on assessment of the pH-dependent surface charge, reactive surface area, and the adsorption of dissolved lead (Pb), cadmium (Cd), lanthanum (La) onto UO$_2$ particles. A surface complexation model was used to explain the adsorption and titration phenomena of UO$_2$. Our results show that UO$_2$ has two major surface sites, an amphoteric site and an acidic site, which are responsible for the release and uptake of protons. The N$_2$-BET specific surface area of UO$_2$ was measured at 3.505 m$^2$/g. Pb exhibits strong adsorption onto UO$_2$, followed by La and Cd. Pb and La adsorptions are independent of ionic strength indicating that they probably form inner-sphere complexes at the surface. Cd adsorption decreases with increasing ionic strength, which is a typical phenomenon of outer-sphere complexes.
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CHAPTER I

INTRODUCTION

1.1 Sources of Uranium Contamination in the Environment

Uranium dioxide (UO$_2$) is the most abundant ore mineral for the element uranium (U) in the Earth’s crust. It is the principal form of spent fuel from nuclear fission reactors, and so-called ‘depleted’ UO$_2$, widely used in military munitions, is a major source of heavy metal contamination in regions of conflict. Anthropogenic wastes and pollution containing UO$_2$ are released to the environment throughout the entire nuclear fuel cycle, from activities including mining, ore processing, uranium enrichment, fuel fabrication, industrial manufacture of nuclear fuel and weapons materials, and most significantly, the disposal of spent nuclear fuel at the Earth’s surface or in the geologic subsurface. The increased amount of uranium in groundwater poses a serious threat to the environment and to human and ecosystem health. Uranium occurs naturally in the Earth’s crust at an average concentration of about 2 ppm. Uraninite (also called pitchblende) is the most common U ore (Finch and Murakami, 1999). Uranium can also be found in other minerals, including autunite, uranophane, torbernite, and coffinite (Finch and Murakami, 1999). Significant concentrations of uranium can occur in some rocks such as phosphate deposits, and minerals such as lignite, and monazite sands in uranium-rich ores (Finch and Murakami, 1999). This research examines the chemical properties of UO$_2$, primarily from the standpoint of how solid UO$_2$ in an aqueous setting interacts with dissolved charge solutes. A better understanding of such reactions can provide for
better control over anthropogenic U pollution, and a more detailed depiction of U ore formation and weathering processes.

1.1.1 Uranium Waste Disposal

1.1.1.1 High Level Waste

Enriched UO₂ is used primarily as nuclear fuel, in the form of UO₂ alone or as a mixture of UO₂ and PuO₂ (plutonium dioxide) called mixed oxide fuel (MOX fuel) for fuel rods in nuclear reactors. Nuclear reactors are utilized to generate electricity, to produce fissile material for nuclear weapons; and are used by military and civilian agencies in a number of industrialized and developing nations. One ton of natural uranium can generate over 40 million kilowatt-hours of electricity. Alternatively, 40 million kilowatt-hours of electricity can also be obtained by burning 16,000 tons of coal or 80,000 barrels of oil (DOE, 2006). Using nuclear fuel as a replacement of burning coal and gasoline has helped reduce carbon emissions by 90 percent in the United States energy division from 1981 to 1994 (DOE, 2006). To date in the United States, there are 103 operating nuclear power plants that offer more than 20 percent of the electricity throughout the whole country. Twenty three percent of the electricity used on Earth is provided by 442 nuclear power plants globally (DOE, 2006). Up to now, 45,000 tons of spent fuel from nuclear power plants is in storage (NUREG/BR-0216, Rev. 2, 2002). The intensive usage of nuclear reactors in the past twenty years has increased the amount of nuclear spent fuel waste in the United States by 25 fold (DOE, 2006).
The operation of nuclear reactors results in spent nuclear fuel (SNF) when the fissionable $^{235}\text{U}$ is exhausted in isotopically enriched-UO$_2$ fuel pellets. Spent nuclear fuel is temporarily stored in a water pool at the reactor site to allow the decay of highly radioactive, short-lived fission products until a permanent repository site or a choice of decontamination is selected. The spent fuel can also be reprocessed to recover unfissioned $^{235}\text{U}$ and fissionable $^{239}\text{Pu}$ produced by neutron activation of $^{238}\text{U}$, using chemical separation methods. Even after the fissionable uranium is exploited, the nuclear fuels remain highly radioactive and detrimental to human and ecosystem health (NRC, 2006), owing to the potentially wide range of unstable fission products generated by $^{235}\text{U}$ fragmentation into smaller nuclei. The United States Nuclear Regulatory Commission (US NRC) has categorized both unprocessed and reprocessed spent nuclear fuel as high-level radioactive waste (HLW) (NRC, 2006). Since the mid-1940s, HLW has accrued all over the US. To date, no permanent storage location is firmly established, although the US Department of Energy (US DOE) site in Yucca Mountain, Nevada is pending approval from the US NRC as a national permanent repository site, as stipulated in the Nuclear Waste Policy Act of 1982 (DOE, 2006). HLW is currently stored in underground storage tanks or stainless steel storage towers at some 125 sites in 39 states (DOE, 2006). Figure 1.1 shows the current location of temporary nuclear waste storage (DOE, 2006). HLW is also temporarily stored at US DOE reprocessing facilities in Savannah River, South Carolina, at Hanford, Washington and at the commercial Nuclear Fuel Services Plant in West Valley, New York (NRC, 2006). As a step before the final disposal at the
permanent storage repository, scientists at these facilities have initiated plans to solidify and stabilize the nuclear waste.

Elevated concentrations of uranium in soils and surface sediments have been documented at both facilities in Savannah River, South Carolina and Hanford, Washington. Radioactive waste is introduced to the soil, groundwater and surface water during handling, processing and storage. In Hanford, Washington, there are 53 million gallons of radioactive and chemically hazardous waste in 177 underground storage tanks, 2,300 tons of spent nuclear fuel, nine tons of plutonium in different forms, about 25 million cubic feet of buried or stored solid waste, and groundwater contaminated above drinking water standards, spread out over about 80 square miles, more than 1,700 waste sites, and about 500 contaminated facilities (DOE RL, 2006).
1.1.1.2 Low Level Waste

Low level wastes (LLW) are composed of any objects that have been contaminated by radioactive materials (NUREG/BR-0216, Rev. 2, 2002). They include protective clothing used in handling radioactive substances, cleaning tools used at nuclear sites, laboratory supplies used with any radioactive materials, water treatment residues, and nuclear reactors components. LLW are enclosed in containers that provide appropriate shielding for a certain period of time until the radioactivity decreases to a harmless level (NUREG/BR-0216, Rev. 2, 2002). In the US, LLW disposal is primarily concentrated at US NRC sites near Barnwell, South Carolina, in Richland, Washington and at Envirocare, Utah (NUREG/BR-0216, Rev. 2, 2002). Subsurface trenches overlain by geotextile liners were constructed to contain the LLW. Similar to any other landfill, contamination of nearby groundwater can occur when there is a substantial amount of leachate from the waste.

1.1.2 Uranium Mining and Milling

Uranium mining is performed at open pits or underground excavations. Typical ores contain about 0.14% of $\text{U}_3\text{O}_8$ (DOE, 2006). U can also be dissolved directly from the ore deposits by in-situ leaching and pumped to the surface. U ore is processed and treated at a mill to separate the uranium from the ore. The processed U is in the form of $\text{U}_3\text{O}_8$ concentrate, called the “yellow cake”. The yellow cake is then converted to gaseous uranium hexafluoride ($\text{UF}_6$), followed by an enrichment stage to increase the $^{235}\text{U}$ content from about 0.71% to 3%. The enriched U is ready to be fabricated and used as fuel or for weapon productions. Uranium mill tailings are the
residual solids produced through extraction of U from pitchblende ore; processing and enrichment of yellow cake, and the manufacture and finishing of U industrial and military products (Abdelouas et al, 1999). Uranium mill tailings contain a substantial amount of remnant U, and its daughter products such as thorium (Th), radium (Ra), radon (Rn) and other non-radioactive heavy metals such as lead (Pb) (Abdelouas et al, 1999). Mill tailings are usually piled near the mining or milling sites awaiting final disposal. In the US, a reported 230 million tons of tailing wastes are discarded at milling sites (Morrison and Spangler, 1992). Once disposed of, UO$_2$ can weather or degrade in a number of ways that can lead to U in groundwater. With atmospheric precipitation or contact with surrounding groundwater or surface water system, U and its associated heavy metals and daughter products can be leached into groundwater or surface water bodies while advection will help spread the contaminants, along with the flow of groundwater.

Sulfide minerals, such as pyrite, are commonly present in association with uranium ore and mill tailings. Singer and Stumm (1970) and Moses et al (1987) have shown that oxidation of pyrite by oxygen will increase acidity within tailing piles and thus boost the leaching of uranium as well as other hazardous elements such as Cd, Cr, and Zn (Abdelouas, 1999). When pyrite is exposed to oxygen in atmosphere, the ferrous ions (Fe$^{2+}$) will be oxidized to ferric ions (Fe$^{3+}$) and the sulfide (S$^{2-}$) will be oxidized to sulfate (SO$_4^{2-}$) (Luther, 1987, Singer and Stumm, 1970, Moses et al, 1987, Moses and Herman, 1991). Equations 1.1 show how the oxidation of sulfide mineral can increase the acidity of the water body.

Equation 1.1: Pyrite Oxidation

$$4\text{FeS}_2 + 14\text{H}_2\text{O} + 15\text{O}_2 \rightarrow 4\text{Fe(OH)}_3 (\text{aq}) + 8\text{SO}_4^{2-} + 16\text{H}^+$$
Microorganisms such as *Thiobacillus ferrooxidans* can increase the oxidation rate by 5 to 6 orders of magnitude (Abdelouas et al, 1999). The resulting strongly acidic water amplifies the leaching of U from tailings, mostly in the hydrolyzed uranyl form of $\text{UO}_2^{2+}$, as well as other associated heavy metals and daughter products. Dissolved U(VI) is transported by advection, dispersion and diffusion in the aquifer. At some distance away from the mill tailing site, groundwater pH will increase due to reactions such as dissolution of carbonate, silicate or oxide minerals or due to mixing/dilution with less acidic solutions (Finch and Murakami, 1999). At this point, dissolved uranium can be remineralized from solution in the form of U(IV) under reducing conditions, or a wide variety of U(VI) phases, depending on other compositional factors. Dissolved U, heavy metals and daughter products can also complex or chelate with carbonate, sulfate, or organic ligands such as humics, which will increase their concentrations in the aqueous phase.

Junghans and Helling (1998) found that the dissolved U concentration of a tailings-impacted groundwater in Germany is three orders of magnitude higher than the surrounding uncontaminated groundwater. U concentration in dry soil measured at 275 mg/kg at a tailing disposal site, as compared to 1 mg/kg for nearby uncontaminated soil (Abdelouas et al, 1999). Studies by Brookins (1993) at a mill tailing site in Maybell, CO revealed leaching of uranium by sulfuric acid. The pH at this site ranges from 2.87-3.26, with 8.1-11.1 g/L of sulfate (Abdelouas et al, 1999). Tailings pore waters show high concentrations of uranium at 0.44-1 mg/L, Se at 0.95-1.27 mg/L, Fe at 380-560 mg/L and Mn at 710-870 mg/L (Abdelouas et al, 1999).
Research regarding uraniferous sediments in the Caeson range of Nevada and California by Otton (1989) demonstrated that U ore minerals exposed near the surface can be eroded naturally by groundwater with high dissolved oxygen content. Uranium concentrations in groundwater that flows through the Caeson range can reach as high as 177 µg/L. Analogous to the mill tailings problem discussed above, oxidation of naturally-occurring UO₂ can lead to dissolution of U(VI) and soluble daughter elements such as Pb, Cd and La. *Thiobacillus ferrooxidans* can mediated oxidation of Fe(II) to Fe(III), and the resulting ferric iron can oxidize natural UO₂ to produce soluble U(VI) species (Abdelouas et al, 1999). During a rain event, water percolation through the deposit can flush solutes into neighboring groundwaters and form a contamination plume.

1.1.3 Reductive Precipitation of U(VI)

Several innovative remediation methods have been employed to reduce the uranium concentration in groundwater, including pump and treat, permeable reactive barriers with zero valent iron, bioreduction, biobarriers, ion exchange, and reverse osmosis. Pump and treat is a conventional but most widely used technique. Quinton et al. (1997) demonstrate that *in situ* bioremediation can be a cost effective remediation technique. Most of the *in situ* bioremediation techniques, such as permeable reactive barriers (PRB) with zero valent iron, *in situ* redox manipulation (ISRM) and bioremediation, share a mutual concept, which is to immobilize the soluble U(VI) by reduction to relatively insoluble UO₂. For example, in PRB, a trench filled with reactive materials is constructed so that it transects perpendicular to the groundwater
flow (Abdelouas, 1999). The reactive materials are capable of removing uranium from groundwater by adsorption or reductive precipitation when groundwater flows through the barrier. Zero valent iron is a highly effective reactive material that induces reductive precipitation of U(VI) to U(IV) oxide, so that the movement of a U contamination plume is restricted. Studies by Gu et al. (1998) demonstrate effective removal of uranium at an initial concentration up to 18g/L at the U.S. Department of Energy's Y-12 Plant located in Oak Ridge, TN. Metal reducing bacteria (MRB) such as *Geobacter* and *Shewanella* species, as well as sulfate reducing bacteria (SRB) such as *Desulfovibrio desulfuricans*, are able to use uranium as a electron acceptor to generate energy for growth while precipitating uranium dioxide (Lovley and Phillips, 1992, Luu and Ramsay, 2003). Pilot studies were implemented to evaluate microbial reduction of U(VI) to U(IV)O₂ in Area 3 of the U.S. DOE Natural and Accelerated Bioremediation Research Field Research Center, Oak Ridge. Dissolved carbonate was injected to the aquifer to induce desorption of U(VI) from the host rock because U(VI) highly complexes with carbonate (Wu et al., 2006). Once U(VI) is released to the aqueous phase, denitrifying, sulfate-reducing, and iron-reducing bacteria in groundwater start reducing U(VI). Analyses of the sediment samples in the injection, monitoring and extraction wells show precipitation of solid-phase U(IV)O₂ (Wu et al., 2006). However, the resulting fine-grained precipitates of UO₂ may not be persistently stable. Several potential chemical processes, including solute adsorption reactions, can affect the stability of solid UO₂ phases. One method of appraising the chemical stability of UO₂ is to quantify the properties of reactions occurring at the UO₂ mineral-water interface, because these reactions typically govern bulk rates of
1.1.4 Military Use of Depleted Uranium

Depleted uranium (DU) is the residue from uranium isotopic enrichment. Natural U contains less than 0.72% of fissionable $^{235}\text{U}$, the remainder being non-fissionable $^{238}\text{U}$. During industrial enrichment of U with respect to $^{235}\text{U}$, a corresponding $^{238}\text{U}$ enriched (or $^{235}\text{U}$ depleted) excess necessarily remains. In the form of $^{235}\text{U}$-depleted uranium dioxide, DU has been widely used in military industry to produce armor and armor-piercing munitions because U is 70% denser than lead and has a melting temperature that is substantially higher than steel. In 1994, 3.3 tons of DU munitions were fired at 12 locations during the Bosnia-Herzegovina war (US DOD, 2006). Approximately 10.2 tons of DU munitions were used in Kosovo in 1999 (US DOD, 2006). During the first Gulf war from 1990-1991, a total of 320 tons of DU rounds were fired, making it the most significant application of DU to date (US DOD, 2006). When DU rounds are fired, fragments and dust of $\text{UO}_2$ are dispersed throughout the air, and eventually settle into soil. The fragments may persist as solid $\text{UO}_2$, or may be oxidized and leached by water to form $\text{U(VI)}$, thus forming a $\text{U(VI)}$ groundwater plume. Several health problems have been associated with exposure to DU, including birth defects, Gulf War Syndrome and cancer (WHO, 2006).
1.2 Uranium and Adsorption

Weathering reactions and mineral alteration reactions (see also Chapter 2.1.3 Natural Alteration of Spent Fuel and Uraninite); as well as microbial interactions are mainly surface reactions, and they are important in determining the stability of UO$_2$ in spent fuel and uraninite. Some of the surface reactions may cause dissolution of U from uraninite or spent fuel, and some may cause precipitation of secondary UO$_2$ overgrowths. Solute adsorption, is also very important in affecting the stability of UO$_2$ as well as the mobility of adsorbing cations, especially the radiogenic products of U and heavy metals associated with nuclear spent fuel. However, at present there is very little data in the literature describing surface properties and adsorption reactions occurring on the UO$_2$ surface. This research is designed to examine the adsorption of a few important metals associated with U. Lead (Pb), cadmium (Cd) and lanthanum (La) are selected as the representative adsorbates due to their widespread pollution problem and connection with uranium. There are extensive reports on the contamination caused by Pb and Cd in the environment, and a number of them are associated with uranium mill tailings. Lanthanum is a fission product of uranium decay and can be found regularly in uranium leachates. Detailed discussion of each adsorbent, focusing on their contamination and association with U is presented in the following chapters.

1.2.1 Sources of Lead (Pb) Contamination

Lead (Pb) is chosen as one of the adsorbates in this research due to its widespread presence as a contaminant throughout the world. Most of the Pb
contaminant present in near surface environments today originates from extensive historical to modern use of Pb in paint and leaded gasoline. Tetraethyl lead (TEL) was used as an additive in gasoline in the US until the 1970s, and remains in use in many parts of the developing world. Lead from current and historical TEL use accounts for 80-90% of all existing environmental lead contamination (EPA, 2006). After recognizing the health impacts to the public and the environment, the US EPA commenced incremental cutback of TEL in gas in 1973 (EPA, 2006). In 1982, there was 1.25g of lead per gallon of gasoline, which accounted for 86% of the lead in the atmosphere (EPA, 2006). By 1986, the Pb content of gasoline went down to 0.1g /gal, but by then, lead used in U.S. gasoline since the 1920s summed up to 7 million metric tons (EPA, 2006). From January 1, 1996, the Clean Air Act banned the sale of leaded fuel for use in on-road vehicles (EPA, 2006). Leaking underground storage tanks (LUST) at gas stations have been the most significant and common contribution of groundwater contamination in the US. As gasoline contamination degrades under natural conditions, Pb is normally released in the form of dissolved cations. Dissolved Pb tends to strongly adsorb onto mineral and soil particle surfaces. Studies of soil lead contamination in major US cities by the US EPA (EPA 747-R-98-001a, 1998) revealed that one of the three major contributors to soil Pb contamination is Pb emissions from vehicle exhaust. In Honolulu, Hawaii, research by Fu (1989) noted that soil Pb concentrations from a boulevard strip next to a park was 1650 ppm. Yet, in the rural area of Mt. Pleasant, MI, the soil lead concentration averaged around 280ppm, with individual samples ranging from 100 to 840 ppm, relative to 200 ppm in background soil (EPA 747-R-98-001a, 1998).
Leaded paint is the next largest source of Pb contamination. Lead was used to shorten paint drying times, and improve paint durability. In 1978, the US Consumer Product Safety Commission banned the use of paint that contains over 0.06% of lead for residential purposes. However, it is still widely used in industrial and military applications. The shedding of Pb based paint from exterior walls during remodeling or painting is its main pathway to the soil (US EPA, 2006). A US Department of Housing and Urban Development national Pb survey reported an average of 72 ppm soil Pb concentration around housing areas, relative to 47 ppm in some distant areas (Weitz, 1990). Today, lead is primarily used in two industries: lead acid batteries and radiation shielding. New contamination may result from improper storage, transport and disposal in these industries.

Since Pb is the final daughter product of U decay series, high concentrations of radiogenic Pb can be found in some naturally U enriched rocks, such as in Newark Basin, NJ (Szabo and Zapecia, 1991) and Clarendon Springs Formation, VT (Witten, 1988, Kim and Becker, 2001, Ryan et al, 2002, Cowden, 2004). As high as 15-20 weight percent (wt %) has been reported in some uraninite, with most samples ranging from 7-10 wt% (Finch and Murakami, 1999). In most hydrothermal and sedimentary uranium deposits, Pb is the most abundant species after U (Finch and Murakami, 1999). The Clarendon Springs Formation in VT contains the primary U bearing minerals zircon, apatite, monazite, sphene and dolomite (Kim and Becker, 2001). Uranium concentrations in groundwaters associated with the Clarendon Springs Formation averaged around 41 ppm by Ryan et al. (2002) while Pb concentrations ranged from undetectable to 842 ppb. The values exceed MCL
(Maximum Contamination Level) upper limits of 0.015ppm for lead for drinking water, set by US EPA.

1.2.2 Sources of Cadmium (Cd) Contamination

Cadmium is widely used in several industries due to its bright yellow/orange/red color, wide temperature tolerance and high resistance to corrosion. About 70% of mined Cd is used in Ni-Cd batteries. Other uses include color pigments in painting, plastic, ceramic and glasses; stabilizers in polyvinylchloride (PVC), coatings on non-ferrous metal to prevent corrosion as well as cadmium alloys. Similar to Pb and U, Cd can be released to the environment naturally or anthropogenically. The average crustal abundance of Cd is 0.1-0.5 ppm. Cadmium concentrations may reach as high as 500 ppm in marine phosphates and phosphorites (Cook and Morrow, 1995). Approximately 16,530 tons of Cd is weathered and eroded naturally from rocks every year (WHO 1992, OECD 1994).

Anthropogenic sources of Cd contamination include the production, use and improper disposal of Cd products discussed above. Cadmium can also be released to the environment from fossil fuel, cement, phosphate fertilizers, and leakage from landfill and contaminated sites (OECD 1994, ERL 1990, Van Assche and Ciarletta 1992). Reported Cd concentrations in groundwaters range from 10 to 4000 ng/L (WHO 1992, OECD 1994). The fate of Cd in water strongly depends on the pH, Eh and soil composition. Cadmium has a preference to be adsorbed onto soil or sediment under typical aquifer environment (Van Assche and Ciarletta, 1992).
Heavy metals such as Cd, cobalt (Co), Fe, manganese (Mn), and some of the products of radioactive decay of U are associated with U mining and milling sites. Elevated Cd concentrations were reported at U mill tailings disposal sites in Gunnison, Colorado (DOE technical report DOE/AL/62350--57D, 1993) and Bear Creek, WY (Zhu et al., 2001). The Bear Creek mill is located in the Powder River Basin in Wyoming, and was operated from the 1970s through the mid 1980s (Zhu et al., 2001). Sulfuric acid and sodium perchlorate have been used to extract U from tailings, and the resulting acidic and metal-rich waste water was disposed at a pond nearby without appropriate isolation from the surrounding sediments (Zhu et al., 2001). An estimated 3.3 million tons of tailings and 880 million gallons of liquid effluent have occupied the tailings pond (Zhu et al., 2001). The pH of the tailings fluid is between 1.5 and 3.5, total dissolved solid (TDS) concentration measured at about 20 g/l, and high concentrations of Cd, arsenic (As), beryllium (Be), chromium (Cr), Pb, molybdenum (Mo), nickel (Ni), selenium (Se), radium ($^{226}$Ra, $^{228}$Ra), thorium ($^{230}$Th), and U (Zhu et al., 2001) are present.

1.2.3 Sources of Lanthanum (La) Contamination

Lanthanum occurs naturally in rare earth minerals such as cerite, monazite, allanite, and bastnasite. Monazite and bastnasite are the major ores for La, and contain about 25 % and 38 % of La by weight, respectively. Although La is categorized as a “rare earth element”, it occurs fairly abundantly in the earth’s crust, at an average concentration of 32 ppm. Lanthanum is also produced as a U fission product. Lanthanum is regularly used to delineate the amount of fissioned nuclear
fuel due to its high solubility in solution of nuclear fuel (Cummings et al, 1999). Lanthanum is often detected in U leachate at tailing sites along with other heavy metals and daughter products. At least half of the mill solutions examined in a survey by Petrow (1963) contained La, cerium (Ce), praseodymium (Pr), and neodymium (Nd). Lanthanum is a strongly adsorbing cation in water, owing to its trivalent charge. Adsorption of La has been reported in association with oxide minerals (Fendorf and Fendorf, 1996) such as goethite, rutile and birnessite; as well as microorganisms, such as *Pseudomonas* (Kazy et al., 2006). In this study La was examined both because of this property and its geochemical association with U.

1.3 Research Objectives

One method of appraising the chemical stability of UO₂ is to quantify the properties of reactions occurring at the UO₂ mineral-water interface, because these reactions typically govern bulk rates of mineral weathering and alteration in nature (Stumm and Morgan, 1996). At present there are few literature data quantifying the surface chemical properties of uraninite or synthetic UO₂. The primary goal of this research is to investigate the fundamental chemical properties of UO₂. This study will focus on the surface reactivity of UO₂, with an emphasis on measuring the pH-dependent surface charge, reactive surface area, and cation coordinative potential of UO₂, similar to nuclear fuel or depleted uranium. Experiments designed to achieve these goals include:

(1) Specific surface area measurement
(2) Titration experiments – Titration experiments results were used to delineate the number and densities of surface sites, which are responsible for the proton transfer.

(3) Adsorption experiments of Pb, Cd and La onto UO₂ – Adsorption results were used to quantify the pH- and ionic-strength independent equilibrium adsorption constants using Surface Complexation Models (SCMs).

The results of this study will fundamentally advance the field of uranium geochemistry by substantially augmenting the available database for the surface properties of UO₂. This study will provide new thermodynamic values for chemical reactions controlling the surface reactivity of UO₂. These values are directly relevant to efforts of the US DOE and others to develop improved methods of handling and disposing of uranium-bearing wastes.
CHAPTER II

BACKGROUND INFORMATION

2.1 Uranium Geochemistry

Uranium has atomic number 92 and atomic mass 238.02891 g/mol and is in the actinide series in periodic table. It was discovered in 1789 by Martin Klaproth, a German chemist, and was named after the planet Uranus. Uranium has very high density (19.1 g/cm$^3$), about 65% more dense than Pb. In air, uranium metal can easily be oxidized and coated with uranium oxide, which gives it a black appearance. Uranium occurs in three naturally-occurring isotopes: $^{238}$U, $^{235}$U and $^{234}$U. Natural uranium metal is comprised of 99.28% $^{238}$U, 0.71% $^{235}$U and 0.0054% $^{234}$U. The majority isotope, $^{238}$U, is non-fissionable, while $^{235}$U may be caused to undergo nuclear fission via interaction with an energetic neutron. To make use of U as a fuel for nuclear fission, U is enriched in $^{235}$U by industrial isotopic separation from 0.71% to at least 3%. The complementary product of isotopic enrichment, which contains 0.2%-0.4% of $^{235}$U is termed depleted uranium (DU).

2.1.1 Uranium Fission and Decay

Uranium is fissionable. When struck by an energetic neutron, the $^{235}$U nucleus can absorb the neutron to become U-236. The U-236 isotope is very unstable and will split into normally two fragments, called fission products or daughter nuclei, and will also yield two to three additional free neutrons with high kinetic energy. These free neutrons may strike nearby U-235 nuclei, which in turn fission and produce even...
more neutrons, resulting in a chain reaction that rapidly propagates fission events through a mass of U. For the chain reaction to be self-sustaining, that is for the reaction to continue at a steady-state rate that does not decay or accelerate, requires that a critical mass of $^{235}\text{U}$-enriched U be assembled. There are about 300 uranium fission products, including major pollutant isotopes such as iodine-131, strontium-90, cesium-137, and krypton-85, all of which are radioactive. Most fission products are radioactive because most randomly produced fragments of a $^{235}\text{U}$ nucleus will represent unstable nuclear configurations. Many other heavy metal and rare earth isotopes are produced by fission, including isotopes of the elements Cd and La which are examined in this project.

The natural radioactivity of U is well understood. Natural $^{238}\text{U}$ and $^{235}\text{U}$ decay spontaneously through a chain of unstable daughter products, ultimately arriving at $^{206}\text{Pb}$ and $^{207}\text{Pb}$, respectively. There are only a dozen or so natural daughter products of U compared to the 300 fission products. Figure 2.1 illustrates the decay series of $^{235}\text{U}$ and $^{238}\text{U}$. It should be noted that the final stable fission product of both the decay series is Pb. Therefore, radiogenic Pb is commonly associated with natural U, up to 20 wt% in some uraninite (Finch and Murakami, 1999). Pb/U radiometric dating is widely used to determine the formation ages of igneous and metamorphic minerals that can incorporate U into their crystal lattices.
2.1.2 Uranium Speciation

Uranium can stably exist under environmental conditions as either U(IV) (tetravalent U) or U(VI) (hexavalent U: \( \text{UO}_2^{2+} \) or uranyl), with U(III) found only as a trace substituent in some U(IV) phases such as uraninite (\( \text{UO}_2 \)), and U(V) which readily disproportionates to U(IV) and U(VI). Uranium(IV) is sparingly soluble in water, however U(VI) is highly soluble, mainly in the form of \( \text{UO}_2^{2+} \). In natural waters, U(VI) concentrations typically vary from less than 1 µg/l to 100 µg/l or more. In many countries groundwaters in uranium-rich areas have concentrations up to 1000...
μg/l, and in uranium polluted or ore-bearing regions up to 1 mg/l or more have been reported (Abdelouas et al. 1999; Meinrath et al., 2003).

Uranium(VI) can form solid compounds and stable aqueous complexes with a wide range of inorganic (i.e. phosphate, arsenate, carbonate) and organic ligands, resulting in the occurrence of over 200 different known U(VI) minerals (Finch and Murakami, 1999; Plant et al., 1999). Uranium(IV) forms far fewer minerals, the most important and most common being uraninite, which is the principal ore mineral for uranium. Natural uraninite is partially non-stoichiometric owing to lattice substitutions with U(VI) and other metals such as Pb, Ca, Mg and rare earth elements (Burns, 1999). Under reducing geochemical conditions uraninite is apparently stable over multi-megayear time scales. Under oxidizing conditions natural uraninite or UO₂ in nuclear spent fuel readily alters by oxidative dissolution or reaction with dissolved solutes to form a wide variety of U(VI) minerals, such as uranyl oxide hydrates like becquerelite and schoepite (Windt et al., 2003). If there is sufficient dissolved silicate in the system, formation of uranyl silicates (soddyite) and alkali-alkaline earth silicates (bolwoodite, uranophane) are possible (Windt et al., 2003). U(VI) can also form complexes with aqueous ligands such as carbonate, hydroxyl, phosphate, sulfate, and organic ligands (Windt et al., 2003). Studies have also shown that U(VI) strongly adsorbs onto clays, hydrous ferric oxides and insoluble humic substances (Windt et al., 2003). All chemical processes described above depend on aquifer physical and chemical conditions, including pH, Eh, and concentration of dissolved competing chemical species.
Figures 2.2 and 2.3 illustrate the calculated speciation of uranium as a function of Eh and pH at a concentration of $10^{-7}$ M in the absence and presence of dissolved inorganic ligands (chloride, nitrate, carbonate and sulfate). In the absence of inorganic ligands (Figure 2.2), U(IV) species are dominant under reducing conditions, while U(VI) prevails in oxidizing environments. $\text{UO}_2^{2+}$ is dominant below pH 5 under oxidizing conditions; $\text{UO}_2(\text{OH})_2^0$ between pH 5 and 9; and $\text{UO}_2(\text{OH})_3^-$ at pH 9 or higher (Krupka and Serne, 2002). Figure 2.3 shows a calculated uranium speciation as a function of pH and Eh in the presence of 22 mg/L chloride, 1.7 mg/L nitrate, 67.5 mg/L carbonate and 108 mg/L sulfate, as reported in groundwater of Hanford, Washington (See Chapter 1.1.1.1. High Level Waste) (Krupka and Serne, 2002). At low pH, neutral U(VI) sulfate complexes are the dominant species; at higher pH, neutral and anionic carbonate species become significant.

Figure 2.2: Eh-pH Diagram of uranium species at 25 °C in the absence of aqueous ligands, $[\text{U}^{6+}] = 10^{-7}$ M (modified from Krupka and Serne, 2002).
2.1.3 Natural Alteration of Spent Fuel and Uraninite

2.1.3.1 Oxidative Dissolution

The corrosion and dissolution of UO₂ in nuclear spent fuel has been correlated to the concentration of carbonate due to the preferred formation of uranyl carbonate species under oxidizing solution conditions, as shown in Figure 2.2 (Torrerro et al., 1996). Dissolution of UO₂ is also significantly affected by pH and Eh. Studies by Torrerro and workers (1996) show decreasing dissolution rate with increasing pH and increasing dissolution rate at higher Eh. The kinetic mechanism of synthetic UO₂ oxidative dissolution has been proposed by several workers (Aronson, 1957; Bruno, 1991; Casas, 1994; de Pablo, 1999). In contact with an oxidant such as O₂, U(IV) is easily oxidized to U(VI), especially at the mineral surface. Upon oxidation to U(VI),
U is easily coordinated with available aqueous ligands, such as bicarbonate (HCO$_3^-$). The U(VI) carbonate species are almost immediately dissolved and released to the bulk solution. The assumption of a fast detachment of the U(VI) carbonate surface complex is supported by results from X-Ray Photoelectron Spectroscopy analysis, where U(VI) species are not detectable at the mineral surface following oxidation (de Pablo, 1999). Uraninite and nuclear spent fuel subject to oxidation in dry air at temperatures below 150° C produce disordered cubic U$_4$O$_{9+x}$ (Finch and Murakami, 1999). In the case of uraninite in contact with groundwater, oxidation is unable to proceed beyond U$_4$O$_{9+x}$ because dissolution rates become faster than the rate of oxidation (Finch and Murakami, 1999). Uranium(VI) released to groundwater may be followed by the precipitation of uranyl oxyhydroxides such as ianthinite, schoepite, becquerelite, vandendriesscheiti, and fourmarieriete (Finch and Murakami, 1999). These phases may subsequently alter to more stable U(VI) phases, depending on the composition of the groundwater (Finch and Murakami, 1999).

2.1.3.2 Uraninite Paragenesis in the Presence of Pb

There are two methods by which the presence of Pb can cause uraninite paragenesis: destabilization of UO$_2$ structure and auto-oxidation (Finch and Murakami, 1999). Some ancient uraninite hosts as much as 20 wt% radiogenic Pb (Janeczek and Ewing, 1995). Under reducing conditions, uraninite may be subject to alteration due to the accumulation of radiogenic Pb (Finch and Murakami, 1999), which can weaken the UO$_2$ structure due to the difference in charge and ionic radius between Pb(II) and U(IV) (Finch and Murakami, 1999). Pb tends to fill in the
interstitial sites of UO₂, resulting in higher strain in UO₂ structure (Finch and Murakami, 1999). Since Pb is incompatible in UO₂ crystals, Pb is eventually released along with some U. Under reducing conditions, Pb released is likely to form galena (PbS) along with the recrystallization of UO₂ (Finch and Murakami, 1999).

Pb(IV) is the final product of the ²³⁵U and ²³⁸U decay series. Since Pb(IV) is a strong oxidizer, it oxidizes U(IV) to U(VI) while reducing to Pb(II) (Finch and Murakami, 1999). This process is called auto-oxidation, where the U(VI)/U(IV) ratio is elevated in uraninite. U(VI)/U(IV) ratio of uraninite in Cigar Lake, Saskatchewan, is reported to range from 0.02 to 0.75 although the ore is under anoxic conditions at a depth of about 400 m below the surface (Sunder et al., 1996). This process will also cause loss of U from uraninite since because U(VI) is highly soluble in water.

Remineralization of UO₂ can take place when groundwater containing dissolved U(VI) flows through a reducing porous medium. The types of U mineral formed are strongly dependent upon the groundwater composition. At Argonne National Laboratory, dissolution of spent fuel was examined by drip tests using groundwater as leachant, and was compared to Nopal I U deposit in at Pena Blanca, Mexico (Wronkiewicz and Buck, 1999). Results show that both natural U and spent fuel share a similar paragenetic sequence of mineral phase formation, from uraninite (UO₂⁺ₓ) to uranyl oxide hydrates, to uranyl silicates, followed by alkali or alkaline earth uranyl silicates (Wronkiewicz and Buck, 1999).

The stability of UO₂ in spent fuel and uraninite is greatly influenced by weathering reactions and mineral alteration reactions, as discussed above, and even by microbial interactions (see Chapter 1.1.3 Reductive precipitation of U(VI)). All of
these reactions are largely surface-reaction driven phenomena. Solute adsorption also plays an important role in determining the stability of UO₂ as well as the mobility of adsorbing cations, especially the radiogenic products of U and heavy metals associated with nuclear spent fuel. However, at present there is very little data in the literature describing adsorption reactions occurring on the UO₂ surface. This paucity of information is one motivation for the current study.

Uraninite has a “fluorite type” lattice structure, where one U(IV) bonds with eight O atoms in a cubic arrangement, while one O atom bonds with four U(IV) atoms (Burns, 1999). The predicted U(IV)-O bond lengths range from 2.25 to 2.36 Å (Burns, 1999). Due to the close structural similarities between uraninite and UO₂ nuclear fuel, they are both assumed to have comparable chemical behaviors in nature (Finch and Ewing, 1992). Minor disparities may arise due to the different impurities found in uraninite and spent fuel. At the surface of uraninite and nuclear fuel UO₂, because the bonds are not connected to any ions, they have partially unfulfilled charges. In contact with water, hydroxyl groups (OH⁻) can coordinate to exposed U(IV) atoms with unfulfilled charges by means of dissociative sorption (Dzombak and Morel, 1990). First, water molecules fill in the vacant coordination sites by chemisorption (Dzombak and Morel, 1990). This is followed by a process called hydroxylation where one of the protons from the sorbed water molecule is transferred and coordinated to the adjacent O (from UO₂) to reach a state of charge neutralization in the lattice (Dzombak and Morel, 1990). These processes result in a monolayer of hydroxyl groups at the surface of UO₂. Since the UO₂ surface can exhibit amphoteric properties, >UOH surface groups can deprotonate (release H⁺) or protonate (adsorb
H\(^+\)) depending on the pH of the solution. Protonation and deprotonation cause an electric potential field at the surface, which can attract ions of opposite charges to the surface, resulting in adsorption. In Section 2.2, a detailed discussion of adsorption is presented.

2.2 Adsorption

The mobility and bioavailability of dissolved cations are controlled by various geochemical processes, including formation of complexes with ligands, mineralization, and complexation reactions at the aqueous/solid interface (Koretsky, 2000). For example, when Pb\(^{2+}\) is solubilized, it may form complexes with e.g. hydroxyl, carbonate, silicate or humic ligands, depending on cation and ligand concentration; it may also remain in solution as the Pb\(^{2+}\) aquo ion. If solid surfaces (sediments/minerals) in a porous medium are negatively charged due to high pH (surplus of OH\(^-\)), surface complexation reactions may take place where Pb\(^{2+}\) or Pb complexes are adsorbed onto surface sites or functional groups. In this situation, the adsorbed Pb ions are immobilized. Adsorption has proven effective to immobilize and decrease the bioavailability of metals and organic species in groundwater (Davies et al, 2004, Fein et al, 2001a, Haas et al., 2001, Koretsky, 2000). However, adsorption reactions are affected by several conditions of the system, including pH, ionic strength, temperature, solution composition, and solute/sorbent ratio (Fein et al, 2001a, Koretsky, 2000). Changes in any of these parameters may result in desorption of the adsorbed species which thus regain their mobility and bioavailability in groundwater. In order to thoroughly understand the basis of surface complexation
reactions, it is necessary to learn about the speciation of dissolved chemical species in groundwater; as well as the surface structure of the minerals. Taking account of the speciation of dissolved ions can tell us about the abundance of individual species and their complexes, which might be adsorbed onto the mineral. Mineral surface structure gives us an idea on the densities of different functional sites that are responsible for adsorbing various aqueous species in groundwater. We can then describe each discrete adsorption of aqueous species at a specific functional site using thermodynamic mass law equations (Koretsky, 2000).

Surface complexation reactions between the water and sediment interface, also termed sorption, entail redistribution of chemical species from solution to mineral surfaces (Koretsky, 2000). Sorption happens when dissolved chemical species are electrostatically attracted by the unfulfilled charge on the mineral surface, and thus attach to the surface sites to minimize the mineral surface energy. The generalized term "sorption" includes at least three separate processes: adsorption, absorption and ion exchange (Figure 2.4). Adsorption is a process where dissolved species are chemically attached to the mineral surface to form a monolayer; while absorption occurs when the attracted species penetrate into the mineral crystal lattices (Figure 2.4) (Koretsky, 2000). Ion exchange is a process in which a chemical species, typically a cation, is substituted for another at a solid surface or clay mineral interlayer (Appelo and Postma, 1993; Drever, 1982). Adsorption is further broken down into physical adsorption and chemical adsorption based on the different types of bonds formed. When the dissolved species are weakly bonded to the mineral surface with Van der Waals forces as a result of electrostatic attraction, it is called physical
adsorption. The type of complex formed at the mineral surface is referred as an outer sphere complex as there remains a hydration sphere of water molecules separating the adsorbing ion and the charged solid surface (Figure 2.5). Chemical adsorption involves stronger bonds of a more covalent character between the adsorbing species and mineral surface (Koretsky, 2000). This stronger bond results in direct attachment of dissolved species to the surface functional group where one or more water molecule is removed, and the resulting species is referred to as an inner sphere complex (Figure 2.5).

Figure 2.4: Schematic illustration of adsorption and absorption of Pb\(^{2+}\) onto UO\(_2\) surface. Pb\(^{2+}\) remains at UO\(_2\) surface in adsorption while penetrates into UO\(_2\) lattices in absorption (modified from Koretsky, 2000).
Figure 2.5: Schematic illustration of physical and chemical adsorption. (Left) All H₂O molecules are retained as Cd²⁺ is adsorbed, forming an outer sphere complex. (Right) Pb²⁺ is directly adsorbed to UO₂ functional group (OH⁻) as one of the H₂O molecule is lost, forming an inner sphere complex (modified from Koretsky, 2000).

2.2.1 Models of Adsorption

There are several ways to quantitatively describe adsorption reactions, such as adsorption isotherms and surface complexation models (SCMs). Adsorption isotherms are functions that relate the ratio of adsorbate to adsorbent at constant temperature, while surface complexation models utilize thermodynamics to depict aqueous speciation and surface reactions. The most common adsorption isotherms include distribution coefficients, Langmuir and Freundlich isotherms. As an example, Pb²⁺ adsorption onto UO₂ surface hydroxyl group (UO₂–OH) is described using distribution coefficients (Kₐ), Langmuir (KₐL) and Freundlich (KₐF) isotherms in Equation 2.1-2.3, respectively.
Equation 2.1 Distribution coefficient ($K_d$)

\[ >\text{U-O-Pb}^+ \] = $K_d$ \{Pb$^{2+}$\}(aq)

Equation 2.2 Langmuir isotherm constant ($K_L$)

\[ K_L = \frac{>\text{U-O-Pb}^+}{>\text{U-OH}} \{\text{Pb}^{2+}\}(aq) \}

Equation 2.3 Freundlich isotherm constant ($K_F$)

\[ >\text{U-O-Pb}^+ \] = $K_F$ \{Pb$^{2+}$\}(aq)$^n$

where

[] Concentration

{} Activity

$>\text{U-O-Pb}^+$ Pb$^{2+}$ that has adsorbed onto UO$_2$

Pb$^{2+}$(aq) Aqueous dissolved Pb$^{2+}$

$>\text{U-OH}$ UO$_2$ surface site with functional group OH$^-$

n Constant between 0 and 1

Values of $K_d$ can be determined from experiments by measuring the remaining aqueous species after adsorption has taken place. The concentration of an adsorbed aqueous species can thus be calculated by subtracting the dissolved concentration from the total concentration. Distribution coefficients calculated in this way are only applicable to the system measured (Koretsky, 2000). Distribution coefficients assume that there is a linear relationship between the concentrations of adsorbed and dissolved aqueous species. Therefore, the use of a $K_d$ approach is only appropriate when applied to trace levels of an adsorbing ion in solution, where a solute’s dissolved concentration is far less than the concentration of available surface sites. When a mineral surface is fully saturated with adsorbed aqueous species, it will no longer follow the linear relationship as described in distribution coefficient theory, and consequently the distribution coefficient becomes invalid.
Langmuir isotherms have two major assumptions: (1) All surface sites are equally attractive and (2) adsorption occurs via a similar mechanism for all ions under all conditions. Langmuir theory also assumes that adsorption forms a monolayer of adsorbate (Koretsky, 2000). As shown in Equation 2.2, Langmuir theory takes into account the available surface sites of a mineral, giving a more broadly applicable adsorption constant than the $K_d$ approach in higher concentration solutions. One of the disadvantages of using Langmuir isotherms is its limitation on assuming a single surface site as minerals may exhibit more than one site. In the case of HFO, both “strong” and “weak” hydroxyl functional sites have been observed (Dzombak and Morel, 1990). Natural sediments composed of aggregates of minerals will have many different types of surface sites. Similar to distribution coefficients, Langmuir constants are empirical and can only be applied to the measured system (Koretsky, 2000). Unlike Langmuir isotherms, Freundlich isotherms account for multiple surface sites of different surface energy, and this approach is more suitable for heterogeneous sediments. Similar to distribution coefficients and Langmuir isotherms, the adsorption constants derived from Freundlich isotherms are valid only for the conditions under which the experiment was conducted. The models do not consider changes in adsorption as a function of pH or other chemical or physical factors such as composition and ionic strength of solution, different chemical species and sorbent-sorbate ratio (Koretsky, 2000).

The second group of adsorption models includes the SCMs, of which there are many different formulations depending on how the solid surface and its charge distribution is envisaged. The greatest advance of SCMs is their emphasis on using
equilibrium thermodynamics to explain the molecular interactions in adsorption reactions (Dzombak and Morel, 1990). Another major improvement of SCMs over isotherms is the incorporation of activity coefficients to correct for the non-ideal situation resulting from the long range electrostatic field, as well as from the ionic interactions in solution (Dzombak and Morel, 1990). Positive or negative charges at mineral surfaces arise from the chemical reactions of adsorbed species and surface functional groups (Dzombak and Morel, 1990). Adsorbing ions thus have to travel through the electrical field generated by the surface charges to react chemically with the surface (Dzombak and Morel, 1990). SCMs are system independent: the equilibrium constants derived from SCMs have already incorporated the influence of chemical and physical conditions, such as pH, solution composition and ionic strengths (depending on the model used) as well as sorbent-sorbate ratio. Five common SCMs are: the diffuse layer model, or DLM (Stumm et al., 1970), the constant capacitance model (Stumm et al., 1980) the triple layer model (Davis et al., 1978) the Stern variable-charge, variable-surface potential model (Bowden et al., 1980), and the one-pK model (van Riemsdijk et al., 1986). All SCMs share four mutual assumptions (Dzombak and Morel, 1990):

(1) Adsorption takes place at specific functional groups at the mineral surface.

(2) Adsorption reactions can be described by thermodynamic mass law equations.

(3) Surface charges are a direct result of surface chemical reactions (adsorption).

(4) The effect of variable electric potential can be corrected by applying a coulombic correction factor derived from Electric Double Layer (EDL) to the equilibrium constant.
SCMs vary in the way EDL is described, and accordingly in the calculation of electric potential, as well as in the number of surface functional sites used (Koretsky, 2000). A detailed discussion of the DLM will be presented here as it is the SCM used for calculation and modeling in this research.

2.2.2 Diffuse Layer Model (DLM)

The DLM was developed by Stumm and co-workers during the 1970s. The DLM portrays the interface between mineral and solution as two discrete charge layers (Figure 2.6): a surface layer with firmly held adsorbed charges, and a diffuse layer of counter ions (Dzombak and Morel, 1990). As shown in Figure 2.6, the surface layer has excessive positive charges, hence there are more negatively charged ions in the swarm of counter ions in the diffuse layer to balance the charges. Charges on the surface layer are the result of protonation, deprotonation and adsorption reactions (Dzombak and Morel, 1990). Counter ions in the diffuse layer act to neutralize the charged surface, as a result, they cause an electrokinetic potential between the surface and an arbitrary point in the solution. This potential difference is referred to as the surface potential. The extent of the surface potential depends on the surface charge density (σ) and the thickness of the diffuse layer. As shown in Figure 2.6, the potential decreases exponentially through the diffuse layer, reaching zero at the margin of the double layer where electrokinetic potential is absent.
In the DLM, the distribution of ions in diffuse layer as well as the relationship between the charge density (σ) and electric potential (ψ) is derived from Gouy-Chapman double layer theory (Dzombak and Morel, 1990). Charge density (σ) can be represented by Equation 2.4 (Dzombak and Morel, 1990).

Equation 2.4
\[
\sigma = (8RT \epsilon \epsilon_0 c \cdot 10^3)^{1/2} \cdot \sinh (Z\psi F/2RT)
\]

where
- R: Molar gas constant (8.314 J/mol.K)
- T: Absolute temperature (K)
- \( \epsilon \): Dielectric constant of water (78.5 at 25°C)
- \( \epsilon_0 \): Permittivity of free space (8.854 \cdot 10^{-12} \text{ C/V·m})
- c: Molar electrolyte concentration
- Z: Electrolyte valence

Figure 2.6: (Top) Schematic representation of surface layer and diffuse layer of DLM. (Bottom) Electric potential plot correspond to the top schematic representation (modified from www.chemistry.nmsu.edu/studntres/chem435/Lab14/double_layer.html).
The ionic strength (I) of electrolyte is defined in Equation 2.5 as (Dzombak and Morel, 1990):

\[
\text{Equation 2.5} \\
I = 0.5 \sum (Z_i^2 \cdot c_i)
\]

Therefore, at 25°C, Equation 2.4 becomes Equation 2.6 (Dzombak and Morel, 1990).

\[
\text{Equation 2.6} \\
\sigma = 2.5 I^{1/2} \psi
\]

This relationship of charge density (σ) and electric potential (ψ) will be included along with the thermodynamic mass law equations to develop acidity and adsorption equilibrium constants. To delineate the surface acidity constants, titration experiments were performed to stimulate transfer of H⁺ between the surface of UO₂ and bulk solution. UO₂ is amphoteric, meaning it can deprotonate or protonate so as to reach equilibrium with H⁺ and OH⁻ in bulk solution. At a certain pH, called the pH of pristine point of zero charge (pHppzc), UO₂ surface has a net zero charge. Above the pHppzc, the UO₂ surface is negatively charged as more deprotonation than protonation is taking place. Vice versa, UO₂ surface has excess H⁺ below pHppzc. Equations 2.7 and 2.8 express the protonation and deprotonation activities of UO₂ surface hydroxyl groups respectively with corresponding acidity constants.

\[
\text{Equation 2.7 Protonation} \\
\text{Protonation} \\
>\text{U-OH}_2^+ \leftrightarrow >\text{U-OH}^- + \text{H}^+ \\
K_+^{\text{app}}
\]

\[
\text{Equation 2.8 Deprotonation} \\
\text{Deprotonation} \\
>\text{U-OH} \leftrightarrow >\text{U-O}^- + \text{H}^+ \\
K_-^{\text{app}}
\]
As described by Dzombak and Morel, 1990, the apparent acidity constant or apparent equilibrium constant is the measured constant where influence of surface charge is included. Therefore, the mass law equations are written as

\[
\text{Equation 2.9} \\
K_+^{\text{app}} = \frac{[\text{>U-OH}]}{[\text{>U-OH}_2^+]} \{\text{H}^+\} \\
\text{Equation 2.10} \\
K_-^{\text{app}} = \frac{[\text{>U-O}]}{[\text{>U-OH}]} \{\text{H}^+\}
\]

Where \{\text{H}^+\} indicates activity of \text{H}^+ in bulk solution, away from both the surface and diffuse layers (Dzombak and Morel, 1990). \{\text{H}^+\} encompasses the influence of the surface charge as \text{H}^+ has to travel through the potential field to arrive at the bulk solution from the mineral surface. The intrinsic equilibrium constant (\(K^{\text{int}}\)) is a constant independent of surface charge effect, and is calculated from the measured \(K^{\text{app}}\) by applying a coulombic term as expressed in Equation 2.11 (Dzombak and Morel, 1990).

\[
\text{Equation 2.11} \\
K^{\text{int}} = K^{\text{app}} \exp (\Delta Z F \psi / RT) \\
\]

Therefore, Equation 2.9 and 2.10 become:

\[
\text{Equation 2.9a} \\
K_+^{\text{int}} = K_+^{\text{app}} \exp (\Delta Z F \psi / RT) \\
\text{Equation 2.10a} \\
K_-^{\text{int}} = K_-^{\text{app}} \exp (\Delta Z F \psi / RT)
\]

Mathematically, this system can be solved using mass law equations of water hydrolysis, protonation and deprotonation of mineral surface; mole balance equations of proton and surface hydroxyl groups; total surface charge from the coordination and

37
dissociation of proton; as well as charge-potential relationship (Equation 2.6) (For
details, please refer to Table 2.1, Dzombak and Morel, 1990). Calculation of each
reaction and delineation of \( K_+^{\text{int}} \) and \( K_-^{\text{int}} \) is performed using Protocfit (Chapter 3.3.1:
Titration Modeling). Chemical species involved in this acid-base system are \( >\text{U}-\text{OH}_2^+ \), \( >\text{U}-\text{OH} \), \( >\text{U}-\text{O}^- \), \( \text{H}^+ \) and \( \text{OH}^- \). The adsorption system includes all the species in
the acid-base system, with the addition of the adsorbed metal and its complexes, for
example, \( \text{Pb}^{2+} \), \( \text{PbOH}^+ \), \( \text{Pb(OH)}_2 \), and \( >\text{U}-\text{O-Pb}^+ \). The \( K_+^{\text{int}} \) and \( K_-^{\text{int}} \) resulting from the
acid-base, metal-free system will be used as constraints to solve for the new
unknowns (metal adsorption constant(s), \( K^{\text{int}}_M \)) in adsorption model calculation.

Adsorption of a metal ion (eg. \( \text{Pb}^{2+} \)) by \( \text{UO}_2 \) can be expressed by the release
of a proton from the surface hydroxyl group of \( \text{UO}_2 \) and the coordination of \( \text{Pb}^{2+} \) with
the deprotonated surface of \( \text{UO}_2 \). For example,

\[
\text{Equation 2.12}
\quad >\text{U}-\text{OH} + \text{Pb}^{2+} \leftrightarrow >\text{U}-\text{O-Pb}^+ + \text{H}^+
\]

\( K_{\text{Pb}}^{\text{app}} \)

As described above, binding and release of \( \text{H}^+ \) depends on the pH of the
solution. Because deprotonation takes place at higher pH to equilibrate with the
excess \( \text{OH}^- \) in bulk solution, cation metal adsorption is expected to increase at higher
pH values (Dzombak and Morel, 1990). Similar to the case described above for acid-
base titration, an intrinsic equilibrium constant is used to quantify the surface
electrostatic effect (Dzombak and Morel, 1990), according to:

\[
\text{Equation 2.13}
\quad K_{\text{Pb}}^{\text{int}} = K_{\text{Pb}}^{\text{app}} \exp (\Delta Z F \psi / RT)
\]
The chemical species and equations used to solve for this adsorption system are analogous to those for the acid-base titration system, with the addition of appropriate metal aqueous complexation species and surface complexation species. Overall, these include mass law equations of water hydrolysis, metal aqueous complexation, metal surface complexation, protonation and deprotonation reactions; mole balance equations of H\(^+\), metal and surface sites; and the surface layer charge calculation, based on the charge-potential relationship derived from Gouy-Chapman EDL (For details, please refer to Table 2.8, Dzombak and Morel, 1990). This calculation is performed using an equilibrium aqueous speciation computer algorithm, JCHESS (Chapter 3.3.2: Adsorption Modeling). With previously determined \( K_{\text{int}} \) and \( K_{\text{int}}' \) from the titration results, \( K_{\text{Pb} \text{ int}} \) or \( K_{\text{M} \text{ int}} \) (any metal or its complexes) can hence be quantified.

The greatest advantage of using the DLM is its simplicity (Dzombak and Morel, 1990). The DLM has the least number of parameters needed for calculation or data regression compared to other SCMs, including \( K_{\text{int}} \), \( K_{\text{int}}' \) and \( K_{\text{M} \text{ int}} \) (Koretsky, 2000). The DLM assumes a single surface layer, which avoids the need for estimations of capacitance for different layers as needed in TLM. Neither is capacitance a fitting parameter in the single layer, because it is calculated by Gouy-Chapman theory. Besides that, as described by Dzombak and Morel, the most important feature of a selected SCM is its ability to fit a given set of titration and adsorption data. If such data cannot be fit using a simple SCM, a more complicated SCM such as TLM may be recommended. If a good fit can be achieved, it is more favorable to use a simpler model. One of the disadvantages of using the DLM is that
the derived K is a function of the electrolyte solution. To overcome this problem, electrolyte solution of NaCl was used throughout the series of experiments as NaCl is the major component of many surface waters and groundwaters.

The fate and transport of metals, radionuclide and organics can be predicted using reactive transport models such as MODFLOW and Mintran. For simplicity purposes, adsorption has typically been addressed using $K_d$, $K_L$ and $K_F$, even in the industrial practices (Zhu et al., 2001). However, this is often inadequate to depict the complex geochemical reactions that control the distribution of solutes between groundwater and the aquifer matrix in subsurface environments, especially in mining sites where acid mine drainage problem prevails (Zhu et al., 2001). A single retardation factor has been demonstrated to fall short in its ability to incorporate the multiple solutes that dominate the geochemistry of such a complex system. The leaching of acidic fluid into the aquifer will produce chemical heterogeneities, which also change through time (Zhu et al., 2001). Hence it is impractical to use solely a constant $K_d$ or to know the variation of $K_d$ values with time and space (Zhu et al., 2001). A more accurate approach is to use a coupled reactive transport model in which the advective–dispersive transport equations are solved together with an adsorption constant that incorporate both the mass-action and mass-balance equations for chemical reactions (Zhu et al., 2001). An equilibrium adsorption constant derived from SCM could overcome all the shortcomings described above to better delineate the extent of a plume.
CHAPTER III

METHODS AND MATERIALS

3.1 Materials

Materials prepared for experiments include UO$_2$ powder, PbCl$_2$ solution, Cd and La standard solutions. Sodium chloride (NaCl) at different ionic strengths was used as background electrolyte as NaCl, because it is not expected to participate significantly in most sorption reactions. DI water used was purified with a Barnstead E-pure (Model D4641) water system to $>17.6$ mΩ·cm.

3.1.1 Adsorbent Preparation - UO$_2$

Fine-grained synthetic UO$_2$ obtained from a commercial source (International Bio-Analytical Industries, Inc.) was used throughout the series of experiments. Under standard atmospheric condition, a thin layer of oxidized U(VI) was found coating the surface of UO$_2$ particulates. This resulted in uneven data distribution in both titration and adsorption experiments, due to blocking of surface sites by adsorbed U(VI). This inhibited exchange of other ions between the UO$_2$ surface and aqueous solution at certain pH range until the U(VI) was dissolved in solution. Therefore, in this study UO$_2$ particles were treated with 0.5 M NaHCO$_3$ solution to remove surface U(VI) coatings. Uranium(VI) strongly complexes with aqueous carbonate ions, so carbonate or bicarbonate can be used to effectively leach soluble U(VI) from solids onto which it has adsorbed (Zielinski and Meier, 1988). Raw UO$_2$ powder was introduced into 0.5M NaHCO$_3$ and allowed to equilibrate for 24 hours under strictly anoxic
conditions inside a Coy (®) type B glove box anaerobic chamber under an atmosphere of 95% N₂ / 5% H₂. At the end of 24 h of exposure to 0.5 M NaHCO₃, suspended UO₂ particles were removed by centrifugation from the supernatant and resuspended in a fresh solution of 0.5 M NaHCO₃ for an additional 24 h. This procedure was repeated two more times, for a total of four separate bicarbonate washes, after which the UO₂ particles were rinsed three times in DDI water to remove residual NaHCO₃. In all steps of this washing procedure the solutions of DDI and 0.5 M NaHCO₃ used were deoxygenated for 24 h in the anaerobic chamber prior to mixture with UO₂, to minimize the possibility of U(IV) oxidation. Supernatant solutions from the UO₂ wash procedure were analyzed for dissolved total U by ICP-OES. Results are shown in Chapter 4, Figure 4.1. Initial exposure of raw UO₂ to bicarbonate solutions eluted up to 40 ppm total U, likely in the form U(VI), and that total eluted U(VI) increased with time up to a steady state value after approximately 400 min. Subsequent exposure of UO₂ to a second and third wash with bicarbonate eluted less U(VI), as shown in Figure 4.1. At the final wash step, less than 0.5 ppm U(VI) was removed by bicarbonate from solid UO₂, representing a diminution of elutable U(VI) by approximately 98.5% from the original raw UO₂. Washed UO₂ was freeze-dried in a LabConco ® laboratory vacuum freeze-drier for 24 hours and then stored in the anaerobic chamber. Throughout the procedure described above, UO₂ was maintained under strictly anoxic conditions, except during freeze-drying when momentary exposure to normal air occurred when UO₂ was placed inside or removed from the freeze-drier.
3.1.2 Adsorbates Preparation - Pb, Cd and La

Lead ion (Pb$^{2+}$) was obtained by dissolving reagent-grade PbCl$_2$ in DDI water. This PbCl$_2$ stock solution of 100 ppm total Pb was used to prepare starting solutions for Pb adsorption experiments. Cadmium (Cd) and lanthanum (La) in adsorption experiments were prepared from 1000 ppm Cd and La atomic absorption standard solutions in HNO$_3$ (Fisher Scientific). Stock solutions were diluted to the desired concentrations as needed in adsorption experiments.

3.2 Experimental Methods

This study examined the surface chemical properties of UO$_2$, through an approach focused on controlled laboratory experiments and thermodynamic modeling of experimental data to regress fundamental parameters for individual reactions governing ion coordination at the UO$_2$-water interface. A comprehensive depiction of the experimental methodology is provided below.

3.2.1 Titration of UO$_2$

Potentiometric acid-base titrations of UO$_2$ were performed in this study using an automated digital titration apparatus (Mettler-Toledo ® DL-58). Titrations measured proton exchange by the UO$_2$ surface as a function of pH and solution ionic strength (salinity) in a background NaCl electrolyte solution at 0.001, 0.01 and 0.1 mol/L, under anoxic atmospheric conditions in the anaerobic chamber.

Prior to each titration experiment, 50ml of electrolyte solution was placed in the titration sample cup and constantly stirred while pH was monitored for at least 12
hours, to eliminate dissolved $O_2$ and $CO_2$ from the solution. An increase of pH was normally observed after 12 hours as an indication of oxygen and carbon dioxide removal. Approximately 0.24g of $UO_2$ was added to the deoxygenated NaCl solution and stirred for another 2 h to allow for equilibrium between $UO_2$ and solution. Constant pH was used as an indication of equilibrium. The pH at equilibrium is called the immersion pH and was recorded. Standard solutions of commercially-calibrated, reagent grade (Titrastar) 0.1M NaOH and 0.1M HCl were used as titrants. Each experiment started with a base titration (NaOH added to solution) from the immersion pH to pH 10, then was followed by an acid titration (HCl added) to pH 3.5-4, then another base titration to bring the pH back to 10. At each step, 0.01ml of titrant was added to the solution. All titrations used a pH drift threshold of 0.5 mV per minute between titrant addition steps, with a maximum of 900 s equilibration time at each step. Results are shown in Chapter 4 Figure 4.2 in the form of titrant volume versus pH for each titration leg of all titrations conducted in this study.

3.2.2 Reversibility of Sorption

Prior to conducting adsorption experiments, tests were run to measure the reversibility of metal adsorption onto $UO_2$. This project is based on the theory of Double Layer Model (See Chapter 2: Adsorption), which assumes cations adsorb reversibly to a charged surface as a result of interactions between protons ($H^+$) in solution and unsatisfied bonds among lattice components at the solid surface. Cation penetration to the crystal lattice structure is negligible for an adsorption reaction. Therefore, adsorbed cations are able to desorb rapidly from the solid surface if there
is a surplus of H\(^+\) in the solution. Reversible metal uptake can be tested by comparing the rates of uptake and release, where a surface having adsorbed cations is titrated back to a very low pH to induce desorption. Equilibration times necessary for adsorption experiments can also be measured using kinetic tests, which determine the rate of metal ion uptake and release, and the results of such trials were used in this study to inform the design of adsorption experiments.

In the reversibility experiments, 500 ml of a solution containing 0.001-0.1 M NaCl and 10 ppm of adsorbing metal (Pb, Cd, or La) was prepared in a beaker with 0.5g of UO\(_2\). Solution pH was raised to 10 where it is anticipated that metal adsorption would be complete. Samples were extracted from the batch solution incrementally over 24 h. Samples were taken every 5-15 min for the first hour; every 30 min for the second to third hour; every hour from the 4\(^{th}\) - 10\(^{th}\) hour; and every 6 h after the 11\(^{th}\) hour. Immediately after withdrawal from the batch solution, samples were removed in closed centrifuge tubes from the anaerobic chamber, centrifuged using a Fisher Scientific Centrifuge, returned closed to the anaerobic chamber, and filtered using 0.2 µm Millex syringe filters. After the first 24 h of adsorption, the batch solution was titrated to pH 2 to induce desorption of metals, and samples were taken over time in a similar manner to the adsorption phase of the experiments. All samples were acidified with 5% HNO\(_3\) and analyzed by ICP-OES for total dissolved adsorbate (Pb, Cd or La) metal and U (See 3.2.4: ICP-OES Analysis).
3.2.3 Adsorption Experiments

The surface coordination properties of UO$_2$ were measured via metal adsorption experiments. Reversible adsorption (surface complexation) of dissolved metal ions was measured in parallel 15 mL vessels containing solid UO$_2$ (1 g/L) and an electrolyte solution of NaCl (0.001 – 0.1 mol/L) along with variable concentrations (0.1 – 10 ppm) of individual dissolved metals (Pb, Cd, La). Metal adsorption was measured at a range of pH from 2-12, under three different ionic strength conditions (0.001M, 0.01M and 0.1M NaCl) and three different solid/solute concentrations. Table 3.1 illustrates the design of the experiments.

Pb and La were designed to range from 1-10ppm due to their strong affinity for adsorption onto UO$_2$ surfaces. Higher concentrations of the adsorbates shift the adsorption edge to higher pH values, but with this range of sorbate/sorbent ratio the complete adsorption edges could be observed in the pH range of 2-11. On the other hand, Cd concentrations ranged from 0.1-10ppm due to its lower adsorption affinity,
which causes the adsorption edge to occur at higher pH. These experiments were
designed with a wide range of parameters so that standard thermodynamic
equilibrium constants independent of system conditions such as pH, ionic strengths
and adsorbate/adsorbent concentration, could be derived.

The following procedure was used for each metal adsorption edge experiment.
First, 500ml of NaCl solution was prepared and stirred in the anaerobic chamber for
at least 12 hours to eliminate any possible dissolved oxygen and carbon dioxide. As
for pH titrations, an increase in pH was noted after 12 hours. Hydrochloric acid (HCl)
was added to the NaCl solution to bring the pH down to about 2, before addition of
each adsorbate (Pb, Cd and La). This prevents any adsorption of the adsorbate to the
beaker wall. Pb, Cd and La from previously prepared stock solutions or standard
solution were transferred to the NaCl solution using a pipettor. The volume
transferred varied according to the desired final concentration. For example, 5ml of
1000ppm Cd standard solution is added to formulate 10ppm Cd in a 500ml batch
electrolyte solution. A blank sample was taken to ensure accuracy of adsorbate added.
Approximately 0.5g washed UO$_2$ powder was then weighed and transferred to the
batch solution. The batch solution was constantly stirred with a magnetic stir rod until
the solid and liquid phase were mixed homogeneously. Different concentrations of
NaOH were used as base titrant to precisely raise the pH of batch solution at
increments of 0.3-0.5 pH unit. At each pH increment, 10ml of representative sample
was extracted from the batch solution to a 15ml centrifuge tube. At the end of the
experiment, samples at different pHs in the 15ml centrifuge tubes were placed on a
Fisher Scientific Bioplus shaker to be vibrated for 24 hours to allow for thorough
mixture and equilibrium. Previous kinetic tests illustrated adsorption of Pb, Cd and La took place within the first 20 minutes (see Chapter 4.4 Reversibility Tests). However, 24 hours was used in these experiments to ensure complete equilibration. pHs of all samples were remeasured and recorded after the 24 hour equilibration period. The samples were then centrifuged using a Fisher Scientific Centrifuge to separate the solid and liquid phase. 0.2µm Millex pore size syringe filter units were used to further filter out the solid UO₂. Filtered supernatant was placed in a clean tube with 5% HNO₃, for later concentration analysis using ICP-OES. The reason for 5% HNO₃ addition is to prevent any adsorption of ions onto the tube wall (Kinniburgh and Jackson, 1981; Sposito, 2004).

3.2.4 ICP-OES Analysis

Adsorption was measured by analyzing the extent of metal removal from solutions using inductively-coupled plasma optical emission spectroscopy (ICP-OES) of filtered (0.2 µm) supernatant solutions from the kinetic and adsorption experiments. ICP-OES can measure element concentrations in solution as low as a few part per billion (ppb) for Pb, Cd, La and U. Calibration was done against standard solutions of ions with known concentrations ranging from 10 ppb-10 ppm so as to include the entire range of possible adsorbate concentrations. Supernatants were pumped from 15 ml vials to the nebulizer, where they are mixed with Ar and converted to a fine spray so as to increase the exposed surface area. The fine spray was then carried into the plasma and instantaneously excited by the high temperature. Ionized elements returned to their ground state by emitting a characteristic wavelength of radiation.
Element concentrations could be quantitatively determined as the radiation intensity is proportional to the element concentration.

3.2.5 Surface Area Analysis

Specific surface area (m$^2$/g solid) was measured through quantitative 11-point BET N$_2$(g) gas-surface exchange using a Quantachrome ® Nova 2200 BET (Brunauer, Emmett and Teller) surface area analyzer. Approximately 2 g of UO$_2$ powder was placed in a glass cell and was heated and degassed overnight to remove any possible moisture or contaminant. It was reweighed after removal of moisture and any other contaminants. A dewar filled with nitrogen gas was used to contain the glass cell so as to maintain a constant temperature throughout the experiment. N$_2$ gas was slowly injected into the glass cell and N$_2$ molecules would adsorb onto the UO$_2$ surface to form a monolayer that covered the entire surface of the UO$_2$ powder. The number of N$_2$ molecules that adsorbed onto UO$_2$ was quantified and multiplied with the surface area of N$_2$ molecules to yield the total surface area of UO$_2$ sample. Specific surface area was then calculated by dividing the total surface area by the total weight of UO$_2$.

3.3 Calculations and Modeling

3.3.1 Titration Modeling

Titrations measured the capacity of the surface to exchange H$^+$ with the bulk solution across a range of pH from 3.5-10, and these data were used to regress
electrolyte-independent and pH-independent thermodynamic equilibrium constants for surface H\(^+\) exchange reactions, according to a double-layer model of the surface electrostatic field (Dzombak and Morel, 1990). Regression calculations were conducted using experimental data, along with a surface protonation computer algorithm, called *Protofit*, which is designed to calculate protonation constants from titration data. *Protofit* was written by Benjamin Turner from Notre Dame University. Besides calculating protonation and deprotonation constants, it could also calculate the pristine point of zero charge (pH\(_{ppzc}\)) and could be used to optimize the constants based on several datasets simultaneously (Turner, 2005). In this case, several datasets referred to the titration results at various ionic strength of NaCl.

To optimize the experimental data to the model calculated result, *Protofit* calculated the sum of squares between a dataset adsorbent derivative function and a model adsorbent derivative function (Turner, 2005). *Protofit* first converted the original experiment data from volume of acid added versus pH to the net protons added or removed from a surface (Q\(_{ads}\)) over pH (Turner, 2005). The derivative of this function with regard to pH is the rate of proton transfer per pH unit, defined in *Protofit* as the dataset derivative function, Q\(^*\)\(_{ads}\) (Turner, 2005).

Equation 3.1a and 3.1b represent the deprotonation and protonation reactions of the functional group on solid surface, as written in *Protofit*.

\[
\text{Equation 3.1a} \\
>\text{RH}_0 = \text{RO}^- + \text{H}^+ \\
\]

\[
\text{Equation 3.1b} \\
>\text{RH}_2^+ = \text{RH}_0^+ + \text{H}^+ \\
\]
Based on Equation 3.1a and 3.1b, mass action expressions were derived using the DLM (Equation 3.2a and 3.2b) (Turner, 2005).

**Equation 3.2a: Deprotonation mass action (from Eq. 3.1a)**

\[
\frac{\{>RO^-\}[H^+]}{\{>ROH^0\}} = K_1 \exp \left( \frac{-\Delta Z \cdot F \cdot \Psi}{RT} \right)
\]

**Equation 3.2b: Protonation mass action (from Eq. 3.1b)**

\[
\frac{\{>ROH^0\}[H^+]}{\{>ROH^-\}} = K_2 \exp \left( \frac{-\Delta Z \cdot F \cdot \Psi}{RT} \right)
\]

Equation 3.3 represents the mass balance equation of the overall system (Turner, 2005).

**Equation 3.3: Mass balance equation**

\[
\{>ROH\}_w = \{>ROH^0\} + \{>RO^-\} + \{>ROH^-\}
\]

Surface charge (\(\sigma\)) and surface potential (\(\Psi\)) were calculated using Equation 3.4 and Equation 3.5, respectively (Turner, 2005).

**Equation 3.4: Surface charge calculation**

\[
\sigma = F \sum_j \left( \frac{-\{>RO^-\}_j + \{>ROH^-\}_j}{SSA} \right)
\]

**Equation 3.5: Surface potential calculation**

\[
\Psi = \frac{2RT}{zF} \sinh^{-1} \left( \frac{\sigma}{\sqrt{8RT \cdot C_0 \cdot C}} \right)
\]

Estimates of the intrinsic protonation and deprotonation adsorption constants (\(K_{+ int}^\text{int}\) and \(K_{- int}\)) and site concentration (\(C\)) provided by the user allow Prototif to solve equation 3.2a-3.5 simultaneously by iteration over pH (Turner, 2005). Prototif then calculated the model adsorbent derivative function \(F_{ads}^*\) using Equation 3.6 (Turner, 2005).
Equation 3.6: Model adsorbent derivative function $F_{ads}^*$

$$F_{ads}^*(i) = \frac{(\sigma_i - \sigma_1) \cdot SSA}{F_r}$$

where:
- $K$  
  Equilibrium constant
- $F_r$  
  Faraday's constant
- $\Delta Z$  
  Change in surface charge
- $\Psi$  
  Surface potential
- $R$  
  Ideal gas constant
- $T$  
  Absolute temperature
- $\sigma$  
  Surface charge
- $\psi$  
  Surface potential
- $SSA$  
  Specific surface area of UO$_2$
- $\varepsilon_o$  
  Dielectric constant of water
- $\varepsilon$  
  Permittivity of space
- $z$  
  Counter ion valence
- $c$  
  Counter ion concentration

$F_{ads}^*$ calculated was compared to $Q_{ads}^*$. *ProtoFit* would iterate over several starting guesses to generate several different optimized parameter sets where the sum of squares between $F_{ads}^*$ and $Q_{ads}^*$ was minimized (Turner, 2005). The optimized parameter set with reasonable estimation of $K_+, K_{int}$, $C$ and $\text{pH}_{ppzc}$ was selected and applied in the following adsorption modeling.

### 3.3.2 Adsorption Modeling

Experimental results were used to regress optimal model-dependent values for stoichiometries and thermodynamic equilibrium constants for adsorption reactions governing reversible metal coordination at the UO$_2$ surface. JCHESS was developed by Van Der Lee and de Windt in 1999, and was designed to model heterogeneous chemical equilibria in a geochemical context. JCHESS software is an equilibrium
aqueous speciation computer algorithm, which can be used to iteratively fit theoretical mass law and mass action parameters to experimental data trends.

Speciation of Pb, Cd and La with NaCl solution was simulated in JCHSS so that all reasonable complexes could be considered in the adsorption modeling. The protonation and deprotonation adsorption constants ($K_{+i}^{int}$ and $K_{-i}^{int}$) and surface site densities ($C$) resulting from the metal-free system used for acid-base titrations were used as constraints to solve for the new unknowns (metal adsorption constant(s), $K_{M}^{int}$). By setting up initial estimates of adsorption constants for all possible adsorbate complexes onto UO$_2$, JCHESS would calculate the resulting speciation of the adsorbed and dissolved (non-adsorbed) complexes in the system. The result could be presented in several ways, including the concentration of adsorbed solute over a designated pH range. These results were visually compared to and fit with the experimental results. In theory, the thermodynamic equilibrium constants that were estimated using JCHESS are able to provide a close fit to all the experimental results for Pb, Cd and La adsorption onto UO$_2$ over a wide range of conditions, including different concentrations of UO$_2$ or adsorbate, ionic strengths and pH (see Chapter 3.2.3 Adsorption Experiments and Table 3.1 Experiment Design).

Thermodynamic properties obtained in titration and adsorption experiments on UO$_2$ could be used to develop a quantitative assessment of the coordinative reactivity of the mineral surface. Results were used to evaluate the relative potential reactivity of UO$_2$, on the quantitative basis of reaction affinity, ion exchange capacity, and specific surface area. The results provide useful recommendations with respect to predicting the stability of Pb, Cd and La on UO$_2$ in aquifer settings.
CHAPTER IV

RESULTS

4.1 Bicarbonate Wash

Under standard atmospheric conditions, a thin layer of oxidized U(VI) was found coating the surface of the UO₂ particulates. In this study, UO₂ particles were treated with NaHCO₃ (sodium bicarbonate) solution to remove surface U(VI) coatings. U(VI) strongly complexes with aqueous carbonate ions, thus washing with NaHCO₃ can be used to effectively leach soluble U(VI) from solids onto which it has adsorbed (Zielinski and Meier, 1988). To determine the most effective concentration of NaHCO₃, a comparison test was performed by treating 5 g/L of UO₂ with different concentrations of NaHCO₃ (0.05 M, 0.1 M, 0.5 M and 0.7 M). Raw UO₂ powder was introduced into different concentrations of NaHCO₃ and allowed to equilibrate for 24 hours under strictly anoxic conditions inside an anaerobic chamber. Within the 24 h, aliquots were removed approximately every hour in the first 6 h and every 3-6 h for the remaining 18 h. At the end of 24 h exposure to NaHCO₃, suspended UO₂ particles were removed by centrifugation from the supernatant and resuspended in a fresh solution of NaHCO₃ for an additional 24 h. Similar aliquot sampling procedures were performed. The procedure of mixing and sampling was repeated one more time, for a total of three separate bicarbonate washes. The sampled aliquots contained dissolved U(VI) that was formerly adsorbed on the UO₂ surface. Dissolution of U(VI) was visually observed during the experiment as the clear wash solution turned a yellowish
color. Dissolved U(VI) was analyzed using ICP-OES and plotted over time (Figure 4.1a to c).

Figure 4.1: Removal of U(VI) over time by 0.7 M, 0.5 M, 0.1 M and 0.05 M NaHCO₃ for a) 1st wash (0-24 h), b) 2nd wash (24 – 48 h) and c) 3rd wash (48 – 72 h).
Although the same quantity of UO₂ powder was used in the different concentrations of NaHCO₃ solutions, the exact amount of oxidized U(VI) in each solution is unknown. Therefore, attention should be paid to the trend of U(VI) removal rather than the absolute concentration. Figure 4.1a displays the concentration of extracted U(VI) from the surface of UO₂ within the first 24 hours. The removal of U(VI) increases over time until all the available carbonate ions are coordinated with U(VI). The removal strengths of each NaHCO₃ solution are nearly proportional to their concentrations. After about 400 min, leached U(VI) concentrations plateau as all NaHCO₃ solutions became saturated with U(VI), thus, fresh solutions were needed to extract the remaining U(VI). During the 2⁰ wash (Figure 4.1 b), U(VI) removal by 0.7 M and 0.5 M remains nearly constant throughout 24 h, while 0.05 M and 0.1 M NaHCO₃ were able to remove U(VI) increasingly over time because there was more U(VI) left on the UO₂ surface from the 1⁰ wash as compared to what remains after the 0.5 M and 0.7 M NaHCO₃ washes. In the 3⁰ wash, 0.7 M and 0.5 M NaHCO₃ extracted only <0.6 mg/L of U(VI), with the concentration remaining nearly constant throughout the 24 h. This implies thorough removal of U(VI) from the UO₂ surface, with a 98.5% reduction in the amount of U(VI) removed between the first wash (60-70 mg/L) and third wash (~0.6 mg/L). Both 0.7 M and 0.5 M NaHCO₃ exhibit comparable ability to remove adsorbed U(VI). NaHCO₃ at 0.5 M is the optimal concentration; NaHCO₃ concentration greater than 0.5 M can only be as good as 0.5 M. Therefore, 0.5M NaHCO₃ is chosen as the leachant concentration to remove U(VI) from the surface of UO₂.
4.2 UO₂ Surface Area

UO₂ surface area was measured using a Novachrome BET analyzer with an 11-point N₂ adsorption isotherm. The average surface area was estimated to be 3.505 m²/g from 2 runs. Previous studies by other workers show a variety of results, from 0.0113 m²/g (Torrero et al., 1996) to 4.6 m²/g (Olsson, 2002). The discrepancy may arise from the supplying sources as well as the surface treatment of UO₂ to remove U(VI). No surface treatment was reported in Torrero, 1996; while Olsson treated UO₂ with HClO₄.

4.3 pH Titration

4.3.1 pH Titration Results

Figure 4.2a-c displays titration curves of 4.8 g/L of UO₂ in 0.1 M, 0.01 M and 0.001 M NaCl. The results are plotted as volume of titrant versus pH. Negative volumes of base on the y-axis correspond to net addition of acid. Each plot consists of three titration curves that are completed in one experiment. The ‘1st leg’ represents a base titration from the immersion pH to pH ~10. It is followed by a ‘2nd leg’ which is a reverse titration from pH 10 to 3.5 or 4, and a final titration step (3rd leg) back to pH 10. Multiple steps were performed to insure that acid-base titrations for UO₂ were reproducible with minimal hysteresis.

Hysteresis was observed between the three titration steps. Such hysteresis is often observed in acid-base titrations of oxide minerals (Dzombak and Morel, 1999, Stén. 2002). The specific causes are unknown, but there are a few sensible speculations. In the acid-base studies of BaTiO₃ (Paik, 2003), an oxide-rich surface
was caused by Ba dissolution during acid titration. When BaTiO$_3$ is titrated back to pH 10, dissolved Ba is adsorbed and/or precipitated onto the mineral surface (Paik, 2003). The joint effects of dissolution and subsequent adsorption/precipitation results in titration hysteresis (Paik, 2003). This could be a possible explanation for hysteresis in UO$_2$ titration as UO$_2$ tends to dissolve at low pH.

4.3.2 Thermodynamic Modeling of Titration Data

The results of titration experiments were used to determine an optimal description of the thermodynamic properties of the functional groups on the UO$_2$ surface, including the intrinsic protonation and deprotonation adsorption constants ($K^+_{\text{int}}$ and $K^\text{int}$, see Chapter 2.2.2 Double Layer Model) and site densities (C). To facilitate the extraction of thermodynamic values from the titration data, the computer code Protofit was used to test the appropriateness of differing chemical mass-action and mass-law relations in describing the proton-exchange behavior of UO$_2$ surface functional groups (See Chapter 3.3.1: Titration Modeling). Protofit was used to perform optimization on three titration datasets simultaneously (4.8 g/L UO$_2$ in 0.1, 0.01 and 0.001M NaCl) to constrain the optimized parameters ($K^+_{\text{int}}$, $K^\text{int}$, C) over a wide range of physical and chemical conditions. Because the number and properties of surface functional groups are unknown, three different site models were compared in Protofit for optimization: a one acid-site model, a one base-site model and a two site model (one amphoteric-site, one acid-site). Table 4.1 summarizes the results of Protofit optimization for the three sets of titration data. The accuracy of each site model and optimized parameters ($K^+_{\text{int}}$, $K^\text{int}$, C) obtained may be evaluated by direct
Figure 4.2: Acid-base potentiometric titration data for UO$_2$ at different concentrations and different ionic strengths of background electrolytes. a) 0.1, b) 0.01 and c) 0.001 M NaCl. All experiments were conducted using 4.8g UO$_2$. 
comparison with observed experimental values (Figures 4.3a-c) and by seeking to minimize the weighted sum of squares generated by the regression algorithm ($W_{sos}$). For comparison purposes, ratios of $W_{sos(i)}/W_{sos(1)}$ are calculated to evaluate $W_{sos}$ of the $i$th model relative to the smallest $W_{sos}$, obtained from the two site model (one amphoteric-site, one acid-site), shown as Model 1 in Table 4.1.

Table 4.1: Results of Protofit optimizations of differing DLM stoichiometries representing the UO$_2$ surface. $W_{sos(i)}/W_{sos(1)}$ values are weighted sums of squares ratio of the $i$th site model to model 1.

<table>
<thead>
<tr>
<th>Model 1:</th>
<th>Sites: One amphoteric and one acidic</th>
<th>$W_{sos2}/W_{sos1}$: 2.17</th>
<th>$W_{sos3}/W_{sos1}$: 2.23</th>
</tr>
</thead>
<tbody>
<tr>
<td>reactions:</td>
<td>$&gt;U(\text{amp})\text{-OH} \rightarrow &gt;U(\text{x})\text{-O}^- + H^+$</td>
<td>$&gt;U(\text{amp})\text{-OH} + H^+ \rightarrow &gt;U(\text{x})\text{-OH}_2^+$</td>
<td>$&gt;U(\text{acd})\text{-OH} \rightarrow &gt;U(\text{acd})\text{-O}^- + H^+$</td>
</tr>
<tr>
<td></td>
<td>log $K_{int}^i$: -6.6</td>
<td>log $K_{int}^i$: 1.5</td>
<td>log $K_{int}^i$: -4.4</td>
</tr>
<tr>
<td></td>
<td>log C: -0.7 mol/kg</td>
<td></td>
<td>log C: -1.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Model 2:</th>
<th>Sites: One amphoteric</th>
<th>$W_{sos2}/W_{sos1}$: 2.17</th>
</tr>
</thead>
<tbody>
<tr>
<td>reactions:</td>
<td>$&gt;U(\text{amp})\text{-OH} \rightarrow &gt;U(\text{x})\text{-O}^- + H^+$</td>
<td>$&gt;U(\text{amp})\text{-OH} + H^+ \rightarrow &gt;U(\text{x})\text{-OH}_2^+$</td>
</tr>
<tr>
<td></td>
<td>log $K_{int}^i$: -5.4</td>
<td>log $K_{int}^i$: 2.1</td>
</tr>
<tr>
<td></td>
<td>log C: -0.6 mol/kg</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Model 3:</th>
<th>Sites: One acidic</th>
<th>$W_{sos3}/W_{sos1}$: 2.23</th>
</tr>
</thead>
<tbody>
<tr>
<td>reactions:</td>
<td>$&gt;U(\text{acd})\text{-OH} \rightarrow &gt;U(\text{acd})\text{-O}^- + H^+$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>log $K_{int}^i$: -5.37</td>
<td></td>
</tr>
<tr>
<td></td>
<td>log C: -0.6 mol/kg</td>
<td></td>
</tr>
</tbody>
</table>

The third model is the simplest; UO$_2$ surface is assumed to behave as a monoprotic acid. This one-acid-site model provides a poor fit to the titration data, yielding a high ratio of $W_{sos3}/W_{sos1}$ of 2.23. A single-site amphoteric model (Model
2) provides a considerably better fit to the experimental data \((W_{sos\,2}/W_{sos\,1} = 2.17)\) when compared with the one-acid-site model. A two-site model (one amphoteric-site, one acid-site, Model 1) provides the best fit to the titration data when compared with previous models. Application of this model to the titration data at different ionic strengths yields similar values for the pH_{ppzc}. Figures 4.3a-c serve to compare the accuracy of each site model with its specific optimized parameter sets to the actual experimental data. The two-site model fits the experimental data more closely throughout the measured pH range at different electrolyte ionic strengths than either the amphoteric or acidic models. As a conclusion, UO\(_2\) has two surface functional sites: an amphoteric site and an acidic site. The amphoteric site has \(\log K_{\text{int}}\) of -6.6, \(\log K_{+\text{int}}\) of 1.5 and site density (log C) of -0.7 mol/kg. The acidic site has \(\log K_{\text{int}}\) of -4.4 and site density (log C) of -1.1 mol/kg. The amphoteric site is more abundant with a site density about half an order magnitude higher than the acidic site. Protofit was also used to perform calculations for pH_{ppzc}, the pH at which the surface has net zero charge (i.e., \([>U-O^-] = [>U-OH^+])\). pH_{ppzc} of UO\(_2\) is 3.16. The estimation of pH_{ppzc} by Protofit is supported by zeta potential measurements of the same material. The isoelectric point of UO\(_2\) was estimated to be between pH 3-3.5 for UO\(_2\) in 0.1 M and 0.01 M NaCl using zeta potential measurements.
Figure 4.3: Comparative plots of experimental and Protofit regressed potentiometric titration curve of UO$_2$ in a) 0.1M NaCl, b) 0.01M NaCl and c) 0.001M NaCl. Experimental results are represented by diamond symbols while the Protofit regressed models are represented by lines.
A minor disagreement between experimental and Protofit regressed titration curves can be observed at background electrolyte of 0.001M NaCl (Figure 4.2c), particularly in the pH range from 5-9. The observed pH is lower than the predicted pH after 0.08 ml of base has been added. It indicates that the solution has excess H\(^+\) from surface deprotonation compared to the prediction from the regressed protonation/deprotonation stability constants. The specific reason is unclear, but it may be caused by a minor acidic (deprotonatable) site that becomes more prominent at lower ionic strength as this phenomenon is not observed in both 0.01M and 0.1M electrolyte. Addition of a second acidic site was attempted to improve the optimization of 0.001M, but this creates problems for the fits of titrations with 0.1M and 0.01M NaCl. Therefore, it is assumed that the second acidic site has an insignificant contribution to the system, especially at moderate ionic strengths (0.01M and 0.1M NaCl), and the model with a single amphoteric and a single acidic site is used to model adsorption (see below).

4.4 Reversibility Tests

Reversibility tests were performed to check the reversibility of cation adsorption (Chapter 3.2.2 Reversibility of Sorption), a basic assumption of the DLM, as well as the time needed to reach adsorption equilibrium. Figure 4.4a displays the adsorbed fraction over time of 7.45 ppm Pb, 10 ppm Cd and 10 ppm La onto 1 g/L UO\(_2\) in 0.01M NaCl at pH ~ 10 where cations are expected to be fully adsorbed. La exhibits the greatest uptake rate, all La ions were adsorbed shortly after introduction to the UO\(_2\). Cd and Pb show slower adsorption where total adsorption takes place
after ~10 min and ~30 min of mixing, respectively. After the first 24 h of adsorption, reverse adsorptions were induced by titrating the solution to pH ~2 at which pH total desorption of cations is anticipated.

Figure 4.4: Reversibility test results. a) Adsorption curve at pH ~ 10 and b) Desorption curve at pH ~ 2, of 7.45 ppm Pb, 10 ppm Cd and 10 ppm La with 1 g/L UO₂ in 0.01M NaCl.
Figure 4.4b displays the desorption rate of 7.45 ppm Pb, 10 ppm Cd and 10 ppm La from 1 g/L UO$_2$ in 0.01M NaCl at pH ~ 2. La once more exhibits the greatest reaction rate with complete desorption from UO$_2$ surface after ~ 10 min. Pb removal fluctuates over time with very rapid release occurring in the first 10 minutes, followed by more gradual release. Cd demonstrates the slowest release rate from UO$_2$ initially, and reaches equilibrium after ~ 50 min. Because the coordination of Pb, Cd and La can fully reverse in a rather short period, the mechanism of sorption is assumed to be surface adsorption, because complete reversibility indicates negligible ion penetration into the crystal lattice of UO$_2$. Therefore, implementation of the DLM in preceding calculations of titration and subsequent calculations of adsorption should be valid.

4.5 Cation Adsorption

4.5.1 Results of Adsorption Experiments

4.5.1.1 Pb Adsorption

The results of Pb adsorption experiments involving UO$_2$ are shown in Figure 4.5. The percentage of available Pb taken up by UO$_2$ as function of pH is shown at two different Pb:UO$_2$ concentration ratios (Fig. 4.5a) and three different ionic strengths (Fig. 4.5b). Sorption of Pb strongly depends on pH, as it increases with increasing pH. Pb uptake from 0% to 100% occurs over a fairly wide range of pH, from 2 - 5.6 for 1 ppm Pb or 2 - 6.25 for 10 ppm Pb experiments. A similar wide pH range for Pb adsorption has also been observed for the sorbent hydrous ferric oxide (HFO; Dzombak and Morel, 1990). The adsorption edge of Pb on HFO occurs over 3 - 4 pH units. As Pb:UO$_2$ concentration ratios increase from 1 mg/g to 10 mg/g, the
adsorption edges shift towards higher pH, indicating lower adsorbed fraction for higher Pb: UO₂ at the same pH. Ionic strength appears to have negligible effect on Pb adsorption, as can be seen in Fig 4.5b, data collected for Pb:UO₂ of 1 mg/g at 0.001 M, 0.01 M and 0.1 M NaCl are nearly identical.

Figure 4.5: Experimental data for Pb sorption onto UO₂ as a function of pH at different a) Pb:UO₂ concentration ratios and b) ionic strengths. UO₂ concentration was 1 g/L for all experiments.
4.5.5.2 Cd Adsorption

The results of Cd adsorption experiments involving UO₂ are shown in Figure 4.6a and 4.6b. The percentage of available Cd taken up by UO₂ as a function of pH versus is shown for three different Cd:UO₂ concentration ratios (Fig. 4.6a) and two different ionic strengths (Fig. 4.6b). Sorption of Cd strongly depends on pH, and increases with increasing pH. Cd uptake from 0% to 100% occurs over a narrower range of pH as compared to Pb, from 6 - 7.5 for 0.1 ppm Cd or 6 - 8 for 1 ppm Cd. Similar narrower pH range of Cd adsorption have also been observed for HFO (Dzombak and Morel, 1990). Adsorption edges of Cd onto HFO occur over 2 - 2.5 pH units. As seen for Pb, as Cd:UO₂ concentration ratios increase from 0.1 mg/g to 10 mg/g, the adsorption edges shift towards higher pH. Complete adsorption of the Cd is observed beyond pH ~8, 9 and 10 for 0.1, 1 and 10 ppm Cd respectively. Ionic strength has a strong effect on Cd adsorption (Fig 4.5b), increasing the concentration of the electrolyte from 0.01 to 0.1 M NaCl caused a decrease in Cd adsorption. Similarly strong ionic strength dependence has been observed for Cd adsorption on HFO (Dzombak and Morel, 1999), natural soils (Parto, 1997), and gram negative bacteria (Borrok and Fein, 2005). The largest decrease in adsorption is observed at pH ~7.4 where 0.1M adsorbed 45% less than in 0.01M NaCl.
Figure 4.6: Experimental data for Cd sorption onto UO$_2$ as a function of pH at different a) Cd: UO$_2$ concentration ratio and b) ionic strengths. UO$_2$ concentration was 1 g/L for all experiments.
4.5.5.3 La Adsorption

The results of La adsorption experiments involving UO$_2$ are shown in Figure 4.7. The percentage of available La taken up by UO$_2$ as a function of pH is plotted for two different La:UO$_2$ concentration ratios (Fig. 4.7a) and three different ionic strengths (Fig. 4.7b). Similar to Pb and Cd, sorption of La strongly depends on pH and increases with increasing pH. Overall, La adsorption displays a gradual uptake (gentle slope) in the first 2-3 pH units, followed by a dramatic increase in adsorption (nearly vertical slope) within 0.5-1 pH unit until 100% adsorption is achieved. Similar to Pb and Cd, as La:UO$_2$ concentration ratios increase from 1 mg/g to 10 mg/g, the adsorption edges shift towards higher pH. For example, 50% La uptake occurs at pH ~5.4 for 1 ppm La and pH ~6 for 10 ppm La. 100% adsorption of La is also observed beyond pH 7 - 8 for all solute:sorbent ratios. Ionic strength has only a minor effect on La adsorption (Fig 4.7b); the positions of the adsorption edges for the experiments conducted at 0.001, 0.01, and 0.1 M ionic strengths are generally similar.
Figure 4.7: Experimental data for La sorption onto UO₂ as a function of pH at different a) La: UO₂ concentration ratio and b) ionic strengths. UO₂ concentration was 1 g/L for all experiments.
4.5.2 Thermodynamic Modeling of Adsorption

Pb, Cd and La adsorption data for UO₂ was modeled using the DLM approach to derive intrinsic adsorption constants that could account for observed changes in adsorption as a function of electrolyte ionic strength and metal:UO₂ ratio. To derive the intrinsic adsorption constants for different metals or their complexes, metal adsorption models were constrained using the protonation and deprotonation constants (K⁺ₐ, K⁻ₐ), as well as site densities (C) of each surface site, developed from the modeling of acid-base titrations (Table 4.1 Model 1). Adsorption calculations were performed using JCHESS. Selection of adsorption constants are determined by testing the fits of models involving individual metals or metal-complexes binding onto various combinations of the two functional sites. Due to the change of pH during the experiments, metal complexation to form a variety of complexes, such as hydroxide, oxide and chloride, can change during the experiment. Changes in metal speciation as a function of pH or solution composition are also calculated using JCHESS.

4.5.2.1 Pb

The best fit intrinsic Pb adsorption constants are compiled in Table 4.2. Because a single model is not able to flawlessly fit all the datasets at different conditions of ionic strengths and Pb:UO₂ ratio, the best-fit model for each dataset is presented, together with the best average-fit. The average log K_{Pb}^{int} for the amphoteric site is -2.725 with a standard deviation of 0.30 and the average log K_{Pb}^{int} for the acidic site is -0.575 with a standard deviation of 0.41. The acidic site demonstrates a greater
affinity for Pb adsorption in all cases compared to the amphoteric site. The individual best fit and average fit models for each dataset are compared with the measured adsorption data in Figures 4.8 and 4.9. The distribution of the adsorbed Pb across the individual surface sites is also shown. Figures 4.8a-c compares calculated predictions to experimental data at constant ionic strength for increasing Pb:UO$_2$ ratios from 1 mg/g to 10 mg/g. Figures 4.9a-b compare calculated predictions to experimental data for different ionic strengths at a constant Pb:UO$_2$ ratio of 1 mg/g.

Table 4.2: Log intrinsic adsorption constants for best-fit adsorption models for 1 g/L UO$_2$ experiments conducted with 1, 10 and 1 ppm Pb at 0.001, 0.01, and 0.1 M ionic strengths.

<table>
<thead>
<tr>
<th>Pb conc. / ionic strength</th>
<th>log $K_{\text{Pb}}^{\text{int}}$</th>
<th>&gt;U(amp)-O-Pb$^+$</th>
<th>&gt;U(acd)-O-Pb$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ppm / 0.01M</td>
<td>-2.8</td>
<td>-0.55</td>
<td></td>
</tr>
<tr>
<td>10 ppm / 0.01M</td>
<td>-3.0</td>
<td>-1.10</td>
<td></td>
</tr>
<tr>
<td>1 ppm / 0.001M</td>
<td>-2.8</td>
<td>-0.55</td>
<td></td>
</tr>
<tr>
<td>1 ppm / 0.1M</td>
<td>-2.3</td>
<td>-0.10</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>-2.725</td>
<td>-0.575</td>
<td></td>
</tr>
<tr>
<td>standard deviation</td>
<td>0.30</td>
<td>0.41</td>
<td></td>
</tr>
</tbody>
</table>

4.5.2.2 Cd

The best fit intrinsic Cd adsorption constants are compiled in Table 4.3. Because a single model is not able to flawlessly fit all the datasets at ionic strengths and Cd:UO$_2$ ratios, the best-fit model for each dataset is presented, as well as the fit for the average log K. The log $K_{\text{Cd}}^{\text{int}}$ derived for the amphoteric site for all data sets is -7, and the log $K_{\text{Cd}}^{\text{int}}$ of the acidic site is -5.2 with a standard deviation of 0.23. The best fit model for each dataset is compared with the measured adsorption data in Figures 4.10 and 4.11, together with the distribution of adsorbed Cd across individual
Figure 4.8: Measured Pb adsorption data (diamonds) and calculated DLM results for 1 g/L UO₂ with a) 1, b) 10 ppm Pb. All adsorption experiments were conducted using 0.01M NaCl.
surface sites. Figures 4.10a-c compare calculated results to experimental data at constant ionic strength and increasing Cd:UO₂ ratios from 0.1 mg/g to 10 mg/g. As Cd:UO₂ ratios increases, preference for Cd adsorption switches from the acidic site to the amphoteric site. Figures 4.11a-b compares calculated results to experimental data at different ionic strengths (0.01 and 0.1M NaCl) and a constant Cd:UO₂ ratio of 1 mg/g.
Table 4.3: Log intrinsic adsorption constants for best-fit adsorption models for 1 g/L UO\(_2\) experiments conducted with 0.1, 1 and 10 ppm Cd at 0.01, and 0.1 M ionic strengths.

<table>
<thead>
<tr>
<th>Cd conc. / ionic strength</th>
<th>(\log K_{cd}^{int})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&gt;U(amp)-O-Cd[+]</td>
</tr>
<tr>
<td>0.1 ppm / 0.01 M</td>
<td>-7</td>
</tr>
<tr>
<td>1 ppm / 0.01 M</td>
<td>-7</td>
</tr>
<tr>
<td>10 ppm / 0.01 M</td>
<td>-7</td>
</tr>
<tr>
<td>1 ppm / 0.1 M</td>
<td>-7</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td>-7</td>
</tr>
<tr>
<td><strong>Standard deviation</strong></td>
<td>0.00</td>
</tr>
</tbody>
</table>

Figure 4.10: Measured Cd adsorption data (diamonds) and calculated DLM results for 1 g/L UO\(_2\) with a) 0.1, b) 1, c) 10 ppm Cd. All adsorption experiments were conducted using 0.01 M NaCl.
Figure 4.10: Continued.

Figure 4.11: Measured Cd adsorption data (diamonds) and calculated DLM results for 1 g/L UO$_2$ with 1 ppm Cd at a) 0.01, b) 0.1 M NaCl.
4.5.2.3 La

A single model is able to fit all the datasets at different conditions of ionic strength and La:UO₂ ratios. However, stability constants derived with the DLM are not able to match the slope and shape of the adsorption curves if only the free ion La³⁺ coordination to surface site (>U-O-La²⁺) is considered. Therefore, multiple common La complexes, including LaOH²⁺ and LaO₂H⁺ were tried to attempt to fit the experimental data. Speciation of 10⁻⁴ M La in 0.01M NaCl from pH 0-12 is plotted in Figure 4.12. La³⁺, LaOH²⁺ and LaO₂H are the most abundant La complexes under the pH and solution conditions of the adsorption experiments. All combinations of these La complexes binding to the two surface sites were tested using JCHESS to fit the experimental data. The best fit model is comprised of >U-O-La²⁺ and >U-O-LaO₂H⁺, as La³⁺ is the most abundant species below pH ~9.5 and LaO₂H prevails above that. The best fit intrinsic La adsorption constants are compiled in Table 4.4. The acidic site demonstrates a greater affinity for La³⁺ and LaO₂H⁻ adsorption at the lower La:UO₂ ratio compared to the amphoteric site. The best fit model for each dataset is compared with the experimental data in Figures 4.11a-e, along with the distribution of adsorbed La species. Figures 4.13a-c compare DLM results to the experimental data at constant ionic strength and increasing La:UO₂ ratios from 0.1 mg/g to 10 mg/g. Binding of La³⁺ onto the amphoteric and acidic sites is significant at low La:UO₂ ratio. As La:UO₂ increases, LaO₂H⁻ surface coordination becomes more substantial than La³⁺. Figures 4.14a-c compare DLM derived results to experimental data at different ionic strengths (0.01 and 0.1M NaCl) at a constant Cd:UO₂ ratio of 10 mg/g.
Table 4.4: Log intrinsic DLM adsorption constants for best-fit adsorption models for 1 g/L UO\textsubscript{2} experiments conducted with 1, 10 and 50ppm La at 0.001, 0.01, and 0.1 M ionic strengths.

| Log $K_{La}^{int}$ | >U(amp)-O-La[2+]  
>U(acd)-O-La[2+] | -6  
-4.7 |
| Log $K_{LaO_2H}^{int}$ | >U(amp)-O-LaO_2H[-]  
>U(acd)-O-LaO_2H[-] | -21  
-19 |

Figure 4.12: Speciation of $10^{-4}$ M La in 0.01M NaCl. Major species: La$^{3+}$ (pH < 9), LaOH$^{2+}$ (9 < pH > 9.9) and LaO$_2$H$^-$ (pH > 9.9).
Figure 4.13: Measured La adsorption data (symbols) and DLM results (lines) for 1 g/L UO$_2$ with a) 1, b) 10 ppm La, including the distribution of the adsorbed La species. All adsorption experiments were conducted using 0.01M NaCl.
Figure 4.14: Measured La adsorption data (symbols) and DLM results (lines) for 1 g/L UO₂ with 10 ppm La at a) 0.001 b) 0.1 M NaCl, together with the calculated distribution of adsorbed La species.
5.1 Acid-Base Properties of UO₂

Optimal model fits to the titration data indicate that UO₂ can be reasonably approximated as a hydroxylated surface having one major type of amphoteric site (>U(amp)-OH) and one major type of negatively ionizing (acidic) site (>U(acd)-OH). The amphoteric site is responsible for both release and uptake of protons depending on the pH of solution, while the acidic site only releases protons over the pH range used in these experiments. Titration data modeled with a DLM, yield optimal values of log \( K_{\text{int}} \) and log \( K_{s,\text{int}} \) for the >U(amp)-OH site of -6.6 and 1.5 with an estimated total site concentration of 34 sites/nm² \((10^{-0.7} \text{ mol/kg})\) UO₂ (Table 5.1). For the acidic site, the derived log \( K_{s,\text{int}} \) is about 2 orders of magnitude greater at -4.4, while the site concentration is smaller at 13 sites/nm² \((10^{-1.1} \text{ mol/kg})\) UO₂ (Table 5.1). Under the same chemical and physical conditions, the acidic site possesses a higher buffering capacity as compared to amphoteric site. This phenomenon is also observed in adsorption experiments where the initial adsorption at lower pH frequently takes place at the acidic site.
Table 5.1: Surface sites of UO₂. U(amp)-OH represents amphoteric site while U(acd)-OH represents the acidic site.

<table>
<thead>
<tr>
<th>Sites: One amphoteric and one acidic</th>
</tr>
</thead>
<tbody>
<tr>
<td>reactions: &gt;U(amp)-OH → &gt;U(x)-O⁻ + H⁺</td>
</tr>
<tr>
<td>log K&lt;sub&gt;int&lt;/sub&gt;: -6.6</td>
</tr>
<tr>
<td>log C: -0.7 mol/kg</td>
</tr>
<tr>
<td>&gt;U(acd)-OH → &gt;U(y)-O⁻ + H⁺</td>
</tr>
<tr>
<td>log K&lt;sub&gt;int&lt;/sub&gt;: -4.4</td>
</tr>
<tr>
<td>log C: -1.1 mol/kg</td>
</tr>
</tbody>
</table>

The two-surface-site model suggested by Protofit optimization can be useful for inferring the composition or the structure of UO₂. Three major hypotheses are proposed to account for this multi-site model: a) small quantities of amorphous hydrous oxide UO₂ (am), (b) partial oxidation of UO₂ or c) distinct properties of unsaturated atoms at different UO₂ surface planes. First, the existence of UO₂ (am) or any impurities in UO₂ can cause a second surface site because the impurity phase would presumably have different surface properties than the crystalline UO₂. The formation of UO₂(am) or accidental mixing of impurities can happen during the manufacturing processes of UO₂ from uraninite, or during the experimental procedures in the case of UO₂(am). The formation of UO₂(am) has been observed in natural system as well as in the process of microbial reductive precipitation of U(VI) (Arthur et al., 2006; Haas et al., 2004). In the Tono region of central Japan, a U deposit is leached by oxidizing groundwater and reduced back to uraninite, coffinite and the metastable UO₂(am) upon contact with a more reducing environment (Arthur et al., 2006). At this site, rapid precipitation from U(VI), reportedly results in UO₂ that is poorly crystalline or amorphous. Partial oxidation of UO₂ sample may also be a reason for the second surface site because oxidation can create structural defects. In
crystalline UO₂, each U atom bonds with 8 O atoms. When UO₂ is partially oxidized, some of the U atoms will bond with more than 8 O atoms, leading to a smaller surface binding energy for cations. Partial oxidation of natural uraninite has been frequently reported, with the formula UO₂₊ₓ, where x ranges from 0 to 0.25 (Janeczek and Ewing, 1992).

Koretsky et al. (1998) have studied the number and types of surface sites exposed at a few idealized mineral planes for periclase (MgO). The selected planes can represent the cleaved and exposed plane of MgO particulates in nature, as well as perfect growth faces of MgO (Koretsky et al, 1998). The crystal system of MgO resembles is the same as UO₂: they are both isometric – hexoctahedral. Therefore, studies completed by Koretsky et al. (1998) on MgO are used as a reference to explain the surface reactive sites of UO₂. At the surface of every mineral, because there are no coordinative atoms/ molecules on the exterior side, bonds are broken, or “coordinatively unsaturated”. In the study of Koretsky et al. (1998), planes of {100}, {111} and {110} of MgO were examined. Figure 5.1 a-c illustrates the unsaturated atoms on each plane of MgO. At each type of surface plane, several different atom configurations can be formed. For example, at plane {111}, a Mg is coordinated with 3 O atoms in Figure 5.1b(i) while an O atom is bonded with 3 Mg atoms in Figure 5.1b(ii), resulting in different unsaturated bonds of different charges and energy. The 3-fold coordinated Mg atoms in Figure 5.1b(i) may hydroxylate to form >Mg⁴⁺OH. After hydroxylation, the Mg atom will become 4-fold as it is bonded to 4 O atoms. In this case, OH⁻ is bonded with just one Mg. On the other hand, the 3-fold coordinated O atoms in Figure 5.1b(ii) may protonate to form >Mg₃OH, where OH⁻ is coordinated
with 3 Mg atoms. Because these two surface hydroxyl groups are bonded to different combinations of Mg and O, they are expected to be different in their protonation and deprotonation properties. The OH\(^-\) bonded with multiple Mg is more polarized than the one bonded with single Mg, so it is easier to deprotonate and may represent a more acidic site (Dzombak and Morel, 1990). Similar conditions likely exist for UO\(_2\), where multiple surface sites can be formed due to the different coordinatively unsaturated atoms exposed at the surface. This may also explain the two-surface-site model optimized from titration data.

Study of the UO\(_2\) crystallinity is beyond the scope of the current study due to the time constraint for a master's thesis. Recommended future work includes crystallinity determination by techniques such as TEM (Transmission Electron Microscopy) or EXAFS (Extended X-ray Absorption Fine Structure). TEM could be used to assess the morphology and crystallinity of particles, and to look for chemical impurities with resolution to the submicron scale. High resolution TEM could also be used to detect atomic-scale defects in areas a few nanometers in diameter. The Protofit optimized site density for the amphoteric site of 34 sites/nm\(^2\) is higher than expected. Typically, the threshold of available surface sites is assumed to be 20-25 sites/nm\(^2\) based on the physical size constrains of an atom. The reasons behind this unexpectedly high site density are unclear, but there are some possible explanations. Titration was conducted by transferring H\(^+\) from solution to UO\(_2\) surface or vice versa. Since the H\(^+\) radius is the smallest among all atoms (0.32 Å) (Chang, 1998), more H\(^+\) atoms are able to adsorb onto per unit surface area of solid than other cations. Therefore, the site density optimized by Protofit is reasonable for H\(^+\), but
Figure 5.1: Schematic representation of coordinately unsaturated atoms at MgO planes of \{100\}, \{111\} and \{110\}. Dashed lines protruding out from the “surface” are the unsaturated bonds (Koretsky et al., 1998).

perhaps too large for other larger atoms. To overcome this shortcoming, future work may include application of the new approach of surface complexation model standard states, suggested by Sverjensky (2003). He suggested using a site density of 10 sites/
nm$^2$ and a specific surface area of 10 m$^2$/g as thermodynamic standard sates for surface complexation modeling. He showed that the equilibrium constants of the same mineral derived by different group of scientists may vary due to the different site densities and specific surface areas of samples, and that it is not valid to compare equilibrium constants derived using different physical conditions. Therefore, correction is needed to standardize so that all constants are comparable (Sverjensky, 2003). He also derived an analytical relationship to convert stability constants derived without using his suggested sytandard state site densities and specific surface area to standard state values.

5.2 Adsorption of Metals onto UO$_2$

Adsorption experiments of various cations onto UO$_2$ demonstrate a pH, matrix-concentration and ionic strength (Cd only) dependence that are analogous to those exhibited by other mineral surfaces (Dzombak and Morel, 1990) and bacteria (Haas et al., 2004). Surface complexation models involving only one surface site do not closely reproduce the experimental data, but model fits are improved by the inclusion of a second surface site.

5.2.1 Comparison of Different Site Models

As previously mentioned in Chapter 4: Thermodynamic Modeling of Titration Data, a two-site model is needed to better fit the model optimized result to experimental data. Here, a comparison of fits with a one-amphoteric (Model 2 from Table 4.1) against those from a two-site model is performed to prove the necessity of
the two-site model. Figure 5.2a and b shows the comparison of different site type models for 10 ppm of Pb and Cd adsorption in 0.01 M NaCl. In both cases, the 1-amphoteric site model fails to match the slope of the experimental data. The 1-site model estimates too small a fraction of adsorbed Pb and Cd at the same pH as compared to the two-site model. This is because these models lack the acidic site that can increase the deprotonated surface sites available for cation adsorption under the pH conditions of the experiment.

Figure 5.2: Comparison of 1-site and 2-site model adsorption results. a) 10ppm Pb and b) 10ppm Cd, both with 1 g/L UO₂ in 0.01M NaCl.
5.2.2 Comparison of Metals Adsorption

Table 5.2 presents a summary of adsorption constants for each metal along with the pH$_{50}$, which is the pH at which 50% of the metal is adsorbed. Based on the intrinsic adsorption constants, the affinity of metal binding to the surface of UO$_2$ in decreasing order is: Pb > La > Cd. Similarly, the adsorption constant for Pb on HFO is also greater than Cd (Dzombak and Morel, 1990). La cannot be used as comparison in the case of HFO as there is no information available to date. pH$_{50}$ is inversely proportional to the log $K^\text{int}_M$. An increase of pH$_{50}$ from Pb, to La and Cd represents a shift of the adsorption edge with increasing pH from Pb, to La and Cd, which also implies decreasing adsorption affinity. This is consistent with the optimized adsorption constants.

Table 5.2: Summary of adsorption constants of Pb, Cd and La with pH$_{50}$.

<table>
<thead>
<tr>
<th>M</th>
<th>pH$_{50}$</th>
<th>$\log K^\text{int}_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>5.02</td>
<td>-0.575</td>
</tr>
<tr>
<td>Cd</td>
<td>8.16</td>
<td>-5.2</td>
</tr>
<tr>
<td>La</td>
<td>6.28</td>
<td>-4.7</td>
</tr>
</tbody>
</table>

Minimum and maximum uptake of cations is a function of the adsorbate. Minimal uptake was observed in this study at pH values below 2 for Pb, below 5 for Cd and below 4 for La, which are also in accordance to the adsorption constants. In all cases, the lower-pH part of adsorption edge is dominated by the acidic site. This dominance is shifted to the amphoteric site at a basic pH value that depends on the individual metal. As metal:UO$_2$ ratios increase, this transition pH decreases. This may be explained by the deprotonation of the amphoteric site as pH increases, which then competes with the acidic site for sorbates. Initial available adsorption sites are provided by the acidic site, which deprotonate at lower pH. As pH increases, the
available acidic site for adsorption decrease, and the amphoteric site account for most of the adsorbing cations.

Only a weak dependence of Pb and La adsorption on ionic strength was observed over the range 0.001-0.1 M NaCl. This is indicative of the formation of inner-sphere complexes as opposed to the outer-sphere complexes mostly likely formed by Cd, which does show significant ionic strength dependency (Davis and Kent, 1990). This inference is based on the idea that formation of outer-sphere complexes is driven primarily by electrostatic attraction. As ionic strength increases, Na\(^+\) and Cl\(^-\) concentrations increase dramatically in the bulk solution as well as near the solid surface, this will lessen the effect of the surface electrostatic field, and therefore decreases the adsorption of Cd. Inner-sphere complexes formed by Pb and La are mainly covalent as they are directly adsorbed to the surface without hydration shell. Ionic strength has little influence on the adsorption of inner-sphere complexes as they are not predominantly electrostatically driven.

5.2.3 Correlation of \(K_{M}^{\text{int}}\) to Other Thermodynamic Properties of Metals

It is impractical to experimentally determine the adsorption constants (\(\log K_{\text{ads}}\)) for every ion onto every possible mineral. Therefore, a linear free energy approach has been adopted by few groups of scientists (Dzombak and Morel 1990, Fein et al., 2001, Langmuir, 1979) to predict the equilibrium constants for adsorption. In this study, adsorption constants for cations on UO\(_2\) are correlated to the first hydrolysis constants (\(\log K_{\text{OH}}\)) of the adsorbed species because adsorption involves complexation of the metal with surface hydroxyl groups. Once the correlation is established, it can
be used to predict the adsorption constants for ions that have not been measured experimentally. Figure 5.3 illustrates the correlation between the $\log K_{\text{ads}}$ and $\log K_{\text{OH}}$ where squares represent $\log K_{\text{ads}}$ of the acidic site and diamonds represent $\log K_{\text{ads}}$ of the amphoteric site. Langmuir (1979) and Dzombak and Morel (1990) divided the adsorbed species into monovalent, bivalent and trivalent groups while Fein (2001) did not subdivide sorbates by valence. In this study, because adsorption was only examined for two bivalent and one trivalent metal, it is not possible to subdivide correlations by valence and get meaningful results. Therefore, a simple linear relationship is used to fit all of the available data. The linear regression shows poor correlation between the data as $R^2$ (determination of coefficient) is fairly low. Therefore, the derived linear equation for both surface sites will probably not be able to provide an accurate estimation of adsorption constants for other cations. However, there is an obvious trend linking the bivalent and trivalent cations for both the acidic and amphoteric sites. For both surface sites, La appears to have smaller adsorption constants than if it were inline with the bivalent cations. If only the bivalent cations are considered in the correlation, the linear regression at both surface sites will produce comparative slopes of 1.80 and 1.94. It may be possible that the cations of different valences have distinct correlations to the first hydrolysis constants. However, more adsorption data with different cations is needed to confirm any correlation.
Figure 5.3: Correlation plots showing calculated adsorption constants for UO₂ as a function of first hydrolysis constants for Pb, Cd and La.

Figure 5.4 compares the adsorption constants of Pb and Cd on UO₂ to the adsorption constants on HFO. Unfortunately, no surface complexation data for La onto HFO is available to be used in this comparison study. Some inferences can be drawn from this comparison, but these must be confirmed using more adsorption data with different cations. In Figure 5.4, the adsorption constants of Pb and Cd onto UO₂ are plotted as a function of the adsorption constants on HFO. The slopes of both lines exhibit a nearly 1:1 relationship. This indicates that the relative ratio of Pb and Cd adsorption constants onto UO₂ is similar to those for HFO. If the assumption is true, it can be used to estimate the adsorption constants of most cations for UO₂ by only knowing the adsorption constant of the cation of interest for HFO. This relationship also shows that adsorption has a stronger dependency on the adsorbed species, than on the adsorbents.
Figure 5.4: Correlation plots showing calculated adsorption constants for UO₂ as a function of adsorption constants for HFO. Adsorption data for HFO is obtained from Dzombak and Morel (1990).

5.3 Conclusion

In this research project, the fundamental surface properties of UO₂ were examined by specific surface area and zeta potential measurements, titration experiments and adsorption experiments using Pb, Cd and La. Specific surface area of UO₂ was measured at 3.505 m²/g by N₂ BET. This number is important for determining the number of reactive surface sites per unit surface area responsible for transferring protons or cations in titration and adsorption. Titration data was optimized to derive surface site densities (C) as well as acid-base equilibrium constants (log K_{int}, log K_{+int}) for crystalline UO₂. Titrations indicate that UO₂ has two major surface sites: 1) an amphoteric site with log K_{int} and log K_{+int} at -6.6 and 1.5, and a computed site concentration of 34 sites/nm² and 2) an acidic site with K_{+int} at -4.4 and a calculated site concentration of 13 sites/nm². The two major surface sites may
be caused by the presence of a secondary phase (UO$_2$(am)) , by partial oxidation of UO$_2$, or by the presence of multiple exposed planes that have distinct properties of coordinatively unsaturated surface atoms.

Pb exhibits a strong adsorption onto UO$_2$, followed by La and Cd. Adsorption of free aquo cations of Pb and Cd only is able to account for all of the observed adsorption behavior, but adsorption of La alone cannot. Therefore, adsorption of aqueous LaO$_2$H, a second major species of La, is necessary to fit the measured data. A linear free energy approach was used to correlate the derived adsorption constants for each metal on UO$_2$ with its first hydrolysis constant and also to the adsorption constants of each metal on HFO. When correlated with the first hydrolysis constants, no significant linear correlation is observed. However, on both surface sites, adsorption constants of La are off the regressed line by nearly equal amounts. It is hypothesized that trivalent cations may have a different relationship to the first hydrolysis constants than bivalent cations. However, this will have to be proved by additional adsorption work.

Future work to supplement the results and conclusions of this project may include studies of UO$_2$ morphology, crystallinity and impurities, and additional adsorption studies of bi- and trivalent cations. Crystallography studies of UO$_2$ could be performed by TEM or EXAFS to determine the cause of the two-surface site model suggested by titration data. Additional adsorption experiments using additional bi- and trivalent cations should delineate a better correlation to thermodynamic properties of cations so as to generate a better predictive of metal adsorption on UO$_2$. 
Appendix

Copyright Permission Letter
November 9, 2006

Dr. Carla Koretsky
1121 Rood Hall
Kalamazoo MI 49008

Dear Dr. Koretsky,

I would like to request your permission to include an excerpt from the following item in my thesis:


The schematic representation of unsaturated atoms of periclase will be used as a reference to uranium dioxide surface structure in my thesis. The source will receive full credit in the manuscript.

For your convenience, I am including a space for your signature to indicate your permission for my use of the above mentioned material. By signing below, you give Western Michigan University the right to supply copies of this material on demand as part of my thesis.

[Signature]

[Name]

Nov 16, 2006

[Date]

Sincerely,
Koi Ling Lim
1121 Rood Hall
Kalamazoo MI 49008
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