Mechanisms of Radium Adsorption on Silica and Barite

Hamid Hamid

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MECHANISMS OF RADIUM ADSORPTION ON SILICA AND BARITE

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DEDICATION

To my wife Rasha, lovely daughters Dimah and Shadan, who supported me and made my life easier along my scientific journey.
ACKNOWLEDGEMENTS

I would like to acknowledge my supervisor Dr. Joseph R.V. Flora, for his support and advise throughout this research. Special thanks to my dissertation committee Dr. Yeomin Yoon, Dr. Nicole Berge and Dr. Radisav Vidic for their professional comments on the dissertation. Special thanks to Dr. Linkel K. Boateng who support me as a mentor. Finally, I would like to thank my family and friends for their support.
ABSTRACT

The use of experimental studies with computer modeling is vital in the development of cost-effective methods for treating radium containing wastewaters. The goal of this dissertation is to develop a multi-scale model to study radium removal mechanisms onto silica and barite, and the effect of water quality parameters on radium removal. The major tasks to be accomplished in this study are: to develop a multi-component isotherm model for radium removal on different ionized silica surfaces; to re-parameterize sulphate force fields to account for metal-sulfate interactions; and to simulate radium removal on barite under different water quality conditions. We conducted molecular dynamics (MD) simulations to investigate radium removal on different ionized silica surfaces. The results indicate that high solution pH results in high radium removal due to increased silica surface negative charge, while high ionic strength results in less radium removal due to complexation and competition mechanisms with ions in the solution. The barite isotherm illustrate that ionic strength results in reduced radium removal due to complexation and competition mechanisms with the anions and cations in the solution but some inconsistencies were observed. The predicted isotherms for silica were consistent with experimental isotherm data. In order to accurately predict the removal of radium by adsorption onto the surface of barite, re-parameterization of the literature sulphate force fields were performed to account for metal-sulfate interactions. Different parameters were calculated using MD and umbrella sampling simulations to evaluate metal-sulfate interactions for different Me\(^{2+}\)-SO\(_4\) systems. In general, the calculated parameters matched
the experimental data, demonstrating that the re-parametrized force fields can accurately simulate the properties of barite and celestite, and will therefore could be effective for predicting the removal of radium by adsorption onto barite. The adsorption of different cations onto three barite surfaces (100, 010, and 001) were also simulated in the presence of different salts. The results show that radium removal decreases significantly with increasing ionic strength due to ions competitions and complexation mechanisms. In the case of CaCl₂ and MgCl₂ solutions, the isotherm predictions based on the multi-component Langmuir isotherm followed the expected trend while the trend for BaCl₂, SrCl₂, and NaCl solutions were not consistent with experimental isotherms. The findings in this study can elucidate radium removal mechanisms under different conditions to assist in the development of effective treatment technologies.
# TABLE OF CONTENTS

**DEDICATION** .................................................................................................................................................. iii

**ACKNOWLEDGEMENTS** ..................................................................................................................................... iv

**ABSTRACT** ....................................................................................................................................................... v

**LIST OF TABLES** ............................................................................................................................................... x

**LIST OF FIGURES** ........................................................................................................................................... xii

**CHAPTER 1 INTRODUCTION** ........................................................................................................................... 1

1.1 Motivation and significance .......................................................................................................................... 1

1.2 Objectives and scope ..................................................................................................................................... 5

1.3 Dissertation overview and organization ...................................................................................................... 7

**CHAPTER 2 BACKGROUND AND LITERATURE REVIEW** ......................................................................... 9

2.1 Radium contamination ................................................................................................................................. 9

2.2 Radium treatment methods .......................................................................................................................... 9

2.3 Radium removal by lime-soda ash softening from wastewater ..................................................................... 14

2.4 Radium removal from wastewater by silica oxide materials ....................................................................... 15
2.5 Radium removal from wastewater by sulfur oxides ..............................16

2.6 Effect of ions on divalent cations removal by adsorption ....................18

2.7 Free energy of adsorption from MD simulations ...............................19

2.8 Process modeling of adsorption equilibrium .................................21

CHAPTER 3 ELUCIDATING MECHANISMS OF RADIUM ADSORPTION ON SILICA SURFACES USING MOLECULAR SIMULATIONS ..........23

3.1 Introduction ..................................................................................24

3.2 Simulation details .........................................................................26

3.3 Materials and methods ..................................................................31

3.4 Results and discussion ..................................................................34

3.5 Ra$^{2+}$ adsorption isotherms on silica .........................................55

CHAPTER 4 REVISING THE SULFATE FORCE FIELD TO ACCOUNT FOR METAL-SULFATE INTERACTIONS .................................57

4.1 Introduction ..................................................................................57

4.2 Simulation details .........................................................................59

4.3 Results and discussion ..................................................................64

CHAPTER 5 ELUCIDATING MECHANISMS OF RADIUM ADSORPTION ON BARITE SURFACE USING MOLECULAR SIMULATIONS ..........79
5.1 Introduction.............................................................................................................79

5.2 Simulation details...................................................................................................81

5.3 Results and discussion .........................................................................................84

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS ........................................93

REFERENCES .............................................................................................................96
LIST OF TABLES

Table 2.1. Characteristics of produced wastewater from Marcellus shale in Pennsylvania .................................................................10

Table 2.2. Wastewater production per Shale gas well in different Shale gas basins in the U.S. .................................................................10

Table 2.3. Components of No.741 uranium mine waste water (pH 3.88) in China ..........11

Table 3.1. Mean (standard deviation) of free energy of adsorption of Ra²⁺/Na⁺ on different silica surfaces with different number of dissociated silanol groups. Units are in kcal/mol ..............................................................................................................37

Table 3.2. Energy decomposition analysis for the interaction of Ra²⁺, Na⁺, Ra²⁺/Cl⁻ and Ra²⁺/Na⁺ with silica of different surface charge due to different dissociated silanol groups. All energies are in kcal/mol ..............................................................................................................39

Table 3.3. Morokuma energy decomposition analysis for the interaction of RaCl⁺ with one molecule of Silica. All energies are in kcal/mol .................................................................47

Table 4.1. Non-Bonded Force Field Parameters for Sulfate .........................60

Table 4.2. Bonded Force Field Parameters for Sulfate .................................61

Table 4.3. Non-Bonded Force Field Parameters for Metal Cations .................61

Table 4.4. Solid densities calculated with different sulfate and metal force field combinations ..............................................................................65
Table 4.5. Association constants calculated with different sulfate and metal force field combinations .............................................................................................................66

Table 4.6. Coordination numbers and hydration free energies calculated with different sulfate force fields ........................................................................................................................................66

Table 4.7. Range of unbonded sulfate force field parameters that satisfy barite and celestite density ........................................................................................................................................69

Table 4.8. Mean (Standard Deviation) of Associated Constants and C₄ Values for Different Cases of Unbonded Sulfate Parameters in Table 4.7 ..............................................................................73

Table 4.9. Mean (Standard Deviation) of Barite and Celestite Densities for Different Cases of Unbonded Sulfate Parameters in Table 4.7 and C₄ values in Table 4.8 .........................74

Table 4.10. Unit cell dimensions for barite and celestite in angstroms ........................................74

Table 4.11. Water coordination number calculated for different cases of unbonded sulfate parameters in Table 4.7 ....................................................................................................................77

Table 4.12. Hydration free energy calculated for different cases of unbonded sulfate parameters in Table 4.7 ....................................................................................................................78

Table 5.1. Mean (standard deviation) of free energy of adsorption of Ra²⁺/Ba²⁺ and cations on (001) barite surface with different salt concentrations. Units are in kcal/mol 91
LIST OF FIGURES

Figure 3.1. Representative models of silica (a) side view and (b-f) top view with 1-20 dissociated silanol sites. The dissociated silanol site is represented with oxygen Van der Waals (VDW) radii in red. The rest of the silica is represented with CPK models with red oxygen atoms, yellow silica atoms and white hydrogen atoms. .................................27

Figure 3.2. (a) Side view and (b) top view of silica cluster used for Density Functional Theory calculations. The different dissociated silanol sites are labeled O1 to O6 and are shown using oxygen VDW radii in red.................................................................30

Figure 3.3. Potential of mean force (PMF) for different number of dissociated silanol groups (number of sites) for (a) charged silica surface with Ra\(^{2+}\), (b) silica surface with Na\(^+\) cations in solution and RaCl\(_2\), (c) silica surface with Na\(^+\) cations in solution and RaCl\(_2\) with 1M NaCl, (d) charged silica surface with Na\(^+\), (e) silica surface with Na\(^+\) cations in solution and NaCl, and (f) silica surface with Na\(^+\) cations in solution and NaCl with 1M NaCl....36

Figure 3.4. Interaction energy of Ra\(^{2+}\) or Na\(^+\) with a silica surface with one dissociated silanol group calculated using Density Functional Theory.................................................................42

Figure 3.5. Top view snapshots of Ra\(^{2+}\) interacting with: (a) one (b) two and (c) three dissociated silanol groups. The silica is represented with CPK models with red oxygen atoms, yellow silica atoms, white hydrogen atoms, and pink Radium ion.................42

Figure 3.6. Interaction energy of Ra\(^{2+}\) with a silica surface with one to three dissociated silanol group calculated using density functional theory.................................................................42

Figure 3.7. DFT-optimized geometry of (a) Ra\(^{2+}\) (b) Ra\(^{2+}\)and Na\(^+\), and (d) Ra\(^{2+}\)and Cl\(^-\) on a negatively charged silica surface with O2 dissociated silanol group. RHF-optimized geometry of (c) Ra\(^{2+}\)and Na\(^+\), and (e) Ra\(^{2+}\)and Cl\(^-\) but with Ra\(^{2+}\) offset 10 Å from the original optimized location in (b) and (d) along the z direction. All calculations were done in PCM water. Oxygen, silica, hydrogen, radium, sodium, and chloride are represented with CPK models with the colors red, yellow, white, pink, blue, and cyan respectively..44
Figure 3.8. Interaction energy of Ra$^{2+}$ with a silica surface in the presence of (a) Na$^+$ and (b) Cl$^-$ with one to three dissociated silanol groups calculated using density functional theory. .................................................................45

Figure 3.9. Probability density distribution of (a) distance between Ra$^{2+}$ to the closest dissociated silanol group (b) distance between Na$^+$ to the same dissociated silanol groups in (a), and (c) distance between Ra$^{2+}$ to the nearest Cl$^-$ in the absence of additional NaCl. (d)-(f) correspond to (a)-(c) but with additional 1M NaCl. ...............................48

Figure 3.10. Zeta potential of silica SiO$_2$ as a function of pH and ionic strength. ..........50

Figure 3.11. Ion and water distribution as a function of distance from the silanol groups of the silica surface with different numbers of dissociated sites and ionic strength conditions .........................................................................................................................54

Figure 3.12. Surface charge density as a function of (a) Number of sites (b) pH. .............55

Figure 3.13. Experimental and predicted isotherms of Ra$^{2+}$ adsorption on silica surface showing (a) the effect of solution pH (b) the effect of ionic strength.................................56

Figure 4.1. Three-dimensional model of barite and celestite mineral used in this work...62

Figure 4.2. Umbrella sampling snapshots at (a) large and (b) small metal-sulfate distances ........................................................................................................................................63

Figure 4.3. Umbrella sampling snapshots where sulfate is (a) outside and (b) within the water droplet. ..............................................................................................................................64

Figure 4.4. Densities calculated with different sulfur charges and VDW $R_{\text{min}}$ for (a) barite and (b) celestite, respectively for $\alpha=1.2$ Å$^3$, $\epsilon=0.155$ kcal/mol. Densities calculated with different $\alpha$ and epsilon for (c) barite and (d) celestite, respectively for $S_{\text{charge}}=2$ e, $R_{\text{min}}=1.74$ Å.................................................................68

Figure 4.5. Potential of mean force for (a) BaSO$_4$ (b) CaSO$_4$ (c) MgSO$_4$ (d) SrSO$_4$ for case 4 in Table 4.7 as a function of the distance between Me$^{2+}$ and SO$$_4$$-S$. .................................70
Figure 4.6. Association constants for (a and b) BaSO₄, (c and d) CaSO₄, (e and f) MgSO₄ and (g and h) SrSO₄ calculated with varying C₄ values for the different cases of unbonded sulfate parameters in Table 4.7. ........................................................................................................72

Figure 4.7. Radial distribution function for (a) Ba-O_SO₄ (b) S_SO₄-O_SO₄ in barite (c) Sr-O_SO₄ (d) S_SO₄-O_SO₄ in celestite for different cases of unbonded sulfate parameters in table 4.7 and C4 values in table 4.8.................................................................75

Figure 4.8. Comparison of model and experimental distances for (a) Ba-O_SO₄ (b) S_SO₄-O_SO₄ in barite (c) Sr-O_SO₄ (d) S_SO₄-O_SO₄ in celestite.................................................................76

Figure 4.9. Radial distribution function for (a) S_SO₄-O_w (b) O_SO₄-H_w for different cases of unbonded sulfate parameters in table 4.7.................................................................76

Figure 4.10. Potential of mean force of hydration free energy for case 4 in table 4.8 as a function of the distance between SO₄-S and the center of the water sphere.........................78

Figure 5.1. Potential of mean force (PMF) for different cations onto different barite surfaces for (a) 100, (b) 010, (c) 001 in DI water.................................................................85

Figure 5.2. Potential of mean force (PMF) for different (a) Ionic mass (b) Lennard Jones forces for different cations onto 100 barite surface in DI water.........................................86

Figure 5.3. Charge density for different ions onto different barite surfaces. (a)100 (b) 010 (c) 001 in DI, while (d)100 (e) 010 (f) 001 in 0.1M concentration. .................................86

Figure 5.4. Mass density for different ions onto different barite surfaces. (a)100 (b) 010 (c) 001 in 0.1M concentration, while (d)100 (e) 010 (f) 001 in 1M concentration.................88

Figure 5.5. Average structures barite (a) 100 (b) 010 (c) 001 side view with 1M BaCl₂ concentration. The barite is represented with CPK models with red oxygen atoms, pink barium atoms. The blue clouds are water-hydrogen, red is water-oxygen, and white is barium in the solution. .................................................................89
Figure 5.6. Potential of mean force (PMF) of Radium onto (001) barite surface with different salts and concentrations in the solution (a) BaCl\(_2\) (b) CaCl\(_2\) (c) SrCl\(_2\) (d) MgCl\(_2\) (e) NaCl.

Figure 5.7. Experimental and predicted isotherms of Ra\(^2+\) adsorption on (001) barite surface showing the effect of ionic strength (a) BaCl\(_2\) (b) CaCl\(_2\) (c) SrCl\(_2\) (d) MgCl\(_2\) (e) NaCl.
CHAPTER 1

INTRODUCTION

1.1. Motivation and significance

Radium is a radioactive alkaline earth metal with a half-life of 1620 years. It is classified as a hazardous material due to its health risks and persistent effect on the environment (Barbot et al., 2013; Warner et al., 2013). Generally, there are two essential industries which generate radium; first, from hydraulic fracturing and second, from uranium mill and mining.

For hydraulic fracturing, the increase in the world’s energy consumption, coupled with elevated oil costs have encouraged governments to explore alternative energy resources like unconventional shale gas. This new extraction method is considered a rapidly growing section of the U.S. energy industry and has a significant role in establishing international oil independence. The U.S. Information Administration (EIA) reports that the United States has 2203 trillion cubic feet of natural gas in stock which is enough for ninety-two years (U.S. EIA, 2014a, 2014b). Furthermore, the United States is ranked first in the world in natural gas production and fourth in its guaranteed stock of natural gas (U.S. EIA, 2013). In 2012, the percentage of natural gas of total consumed energy in the United States was 27% and this rate is expected to increase in 2040 (U.S. EIA, 2014). Hydraulic fracturing is used by companies as a well activation method by injecting liquid and proppant (usually sand) into the bottom of wellbores with elevated pressure to generate fractures in the rocks which have hydrocarbons. These fractures are
initiated at the injection well and expand to hundreds of meters within the shale. These processes produce large quantities of wastewater created by mixing water and chemicals. Each step of the fracturing process requires about 1100 to 2200 m$^3$ of water. The total demand for a single well is about 9000 to 29000 m$^3$ of water which accounts for 98% of the liquid, with the remaining 2% being 150 to 180 m$^3$ of chemical addition (Wood et al., 2011). The water is injected into the ground to generate the fractures and release the gas. 10-40% of this consumed water becomes wastewater and flow back to the surface as hydraulic fracturing wastewater (Blauch et al., 2009; Gregory et al., 2011; Barbot et al., 2013; Halusczak et al., 2013). The flowback/produced wastewater from fracturing has a radium-226 concentration of about 267 times higher than the standards allowed for disposal of wastewaters, and thousands of times higher than drinking water standards, which is about 5 pCi/L (Hopey et al., 2011; USEPA, 2013). The characteristics of this wastewater varies significantly depending on different factors such as geological composition, the fluid used in fracking, depth, and others. Naturally Occurring Radioactive Materials (NORM) are considered to be the most hazardous pollutants in hydraulic fracturing wastewater with radium-226 being the essential isotope of NORM (Rowan et al., 2011).

The second source of radium from industry is uranium mill tailings. Before 1940s, natural uranium was used as a coloring agent, and solutions containing uranium was disposed of with the waste products of the process. However, after nuclear fuel was invented, the value of uranium elevated, and uranium mining became more significant. Also, due to the increase in nuclear power plants all over the world, uranium mining has become more prominent and has resulted in an increase in the amount of waste generated; about 1 billion tons initiated from 4000 sites in the world. Decomposition of uranium to
radium is considered the main reason for uranium radiation which is produced from uranium mill tailings. Each site produces about $938 \times 10^6$ m$^3$ waste with radioactivity varying between 1 to 100 Bq/g, depending on the ore mined (Abdelouas, 2006; Sethy et al., 2011; Campbell et al., 2015).

Fracking wastewater does not only affect surface water, but also has a negative impact on groundwater. This impact has been reported by researchers and the US Environmental Protection Agency (USEPA). The USEPA reported about fracking contaminated groundwater in Pavilion, Wyoming. The evidence in this report was drawn from several tests that were conducted on groundwater. The results indicated the presence of hydrocarbons and some chemicals related to fracking liquids and digging processes in deep wells, as well as high pH which is produced from using potassium hydroxide in the process (DiGiulio et al., 2011). Also, uranium mill tailings is a significant source of contamination of both surface and groundwater close to uranium mills. (Abdelouas, 2006). In order to reduce the potential health risk of radioactive chemicals, wastewater containing radioactive pollutants should be treated and disposed of properly. In this work, we focused onto silica and barite to remove the radium from the solution in different conditions.

Silica in both amorphous and crystalline forms of silicon dioxide is considered one of the most abundant substances on earth. The crystalline form, $\alpha$-quartz ($\alpha$-SiO$\text{$_2$}$) is available in soil, clay, and rocks. Hydraulic fracturing processes produce fractures that expands to hundreds of meters within the shale, with silica being one of its components. As a result, hydraulic fracturing wastewater can potentially flow through silica layers, thus making silica layers an adsorbent for radium and the quartz-water interface an important case to study by researchers. The fate and transport of radium in ground water, as well as
its decomposition and adsorption to aquifers is still not well understood. Modeling of radioactive pollutants in groundwater can provide an in-depth understanding of the movement of these pollutants and its retardation due to interaction with confined sandy aquifers (Reynolds et al., 2003). In addition, there are different types of proppants for making fractures in rocks. Many of these proppants have silica sand with different percentages of total contents. Therefore, there is the capability for radium to be adsorbed onto the silica (Hu et al., 2014). Furthermore, it has been previously shown that radium-226 can be efficiently removed from aqueous solutions by adsorption using different silica oxides such as zeolite (Kosarek, 1979). The adsorption of Ra$^{2+}$ by silica depends on different conditions. These are the key motivations for choosing silica as an adsorbent medium for radium removal and investigate the factors that influence the adsorption process.

Silica surfaces in water are usually wrapped with acidic hydroxyl groups, silanols Si-OH, and their protonation depends on the pH of the system. When pH is high, deprotonation of the silanol groups increases and the surface charge becomes more negative (Kroutil et al., 2015). Due to the significant role of pH on the efficiency of silica adsorption capabilities, different pH conditions were investigated to evaluate the impact of pH on adsorption. Also, due to the presence of different cations and anions in wastewater, the effect of ionic strength (1M NaCl) on the adsorption of Ra$^{2+}$ onto different ionized silica were studied.

Barite (BaSO$_4$) is considered the most prevailing barium comprise mineral at the crustal plate as well as an active mineral (Frenier and Ziauddin, 2008; Curti et al., 2010). Moreover, experiments have showed that barite have efficiency to remove radium, which
if a key motivation for studying the barite and its ability to remove cations from the DI water or from solutions with high ionic strength.

The approach to this study is as follows: first, the adsorption of radium onto different silica clusters under different water quality conditions is simulated using MD and umbrella sampling. Second, the sulfate forcefield is reparametrized to produce barite and celestite densities and metal sulfate association constants consistent with experiments. Third, the effect of competitive cations (Mg$^{2+}$, Ba$^{2+}$, Sr$^{2+}$, Ca$^{2+}$, and Na$^{+}$) on the adsorption of Ra$^{2+}$ onto different barite surfaces in different solutions is investigated. A process model was developed based on multi-component Langmuir adsorption and the molecular dynamics simulations results were integrated into the process model to predict theoretical isotherms in order to compare with experimental isotherms for the mentioned cases.

1.2. Objectives and scope

The main goal of this project is to investigate radium removal from hydraulic fracturing and uranium mining wastewaters with different ionized silica surfaces and barite surfaces under different water quality conditions. Molecular modeling is conducted to quantify the interaction between radium/sodium ions and dissociated silanol group on silica surface and to understand the mechanism of radium adsorption. Also, simulations are performed to understand radium removal onto barite in the presence of different cations after developing an appropriate force field for sulfate. The molecular scale results are incorporated into a multi-component Langmuir process model to calculate theoretical isotherms of radium removal and compare with experimental isotherm data.

Although several researchers have investigated the efficiency of silica in removing different ions from wastewater (Chałupnik et al., 2013), a multiscale model that simulates
the removal of Ra\(^{2+}\) by different ionized silica at the molecular and process levels have not been developed. This unique multiscale framework will provide a deeper understanding for the removal of radium from wastewater by silica. Also, there is lack of theoretical information related to the adsorption of radium onto barite.

The results from the simulation will also play a critical role in evaluating the performance of the treatment process by calculating radium removal and investigating the factors that affect radium adsorption onto silica and barite. The main objectives of this research are as follows:

1. Simulate the adsorption of radium onto silica surfaces with different number of dissociated silanol groups (1, 5, 10, 15, 20 sites) using MD simulations.
2. Investigate the effect of different parameters (pH, ionic strength (NaCl)) on the interaction of Ra\(^{2+}\) and Na\(^+\) on different silica surfaces.
3. Perform Morokuma Energy Decomposition Analysis (MEDA) to analyze the different components of the interaction energy (electrostatic, exchange repulsion, polarization, high order coupling) and evaluate the predominant adsorption mechanisms.
4. Re-parameterize the sulfate force field to produce barite and celestite densities and metal sulfate association constants consistent with experiments.
5. Simulate the adsorption of radium onto barite with and without cations using MD simulations.
6. Integrate the molecular modeling results into a multi-component Langmuir process model to calculate theoretical isotherms and compare with experimental isotherms for both silica and barite.
1.3. Dissertation overview and organization

The main goal of this study is to investigate the adsorption mechanisms of radium on both silica and barite adsorption media, and the effect of water chemistry conditions on radium removal using molecular and process modeling approaches. The individual tasks in this study are accomplished using MD simulations and process level modeling. Before conducting the MD simulations, the specific molecular models for the adsorbents, adsorbates and solvents are built to mimic experimental structure and properties.

To investigate the impact of silica surface charge on radium removal, various dissociated silanol groups representing their corresponding pH were performed. Surface charge was simulated to study the effect of pH on radium removal by silica. Also, ionic strength was simulated to evaluate the influence of different ions in the solution on radium removal by both silica and barite. MD simulations coupled with multi-component Langmuir process modeling were performed to predict theoretical isotherms to compare with experimental isotherms to access model accuracy and evaluate radium removal.

The organization of the dissertation is as follows: Chapter 1 represents a brief introduction and discusses the motivation and overall significance of this study. Chapter 2 focuses on reviewing related literature and background information as part of highlighting some of the significant studies in this area and independent studies on the main tasks of this study. Chapter 3 discusses the mechanism of radium removal by silica under different conditions. Chapter 4 presents the re-parameterization of the sulphate forcefields for barite simulation and Chapter 5 discusses the removal of radium by barite and describes the mechanisms of the removal process. Finally, Chapter 6 presents a summary of the
dissertation and the main conclusions from the studies as well as recommendations for future work.
CHAPTER 2
BACKGROUND AND LITRATURE REVIEW

2.1. Radium contamination

Hydraulic fracturing and uranium mining sites produce different types of wastewaters with different characteristics. These characteristics and quantities vary widely depending on different parameters such as well depth, compositions of the subsurface layers, and the type of proppant used. Table 2.1 shows the characteristics of produced wastewater from Marcellus shale in Pennsylvania (Barbot et al., 2013). The quantities of the produced wastewater are shown in Table 2.2 (Lutz et al., 2013; Vengosh et al., 2014). It should be noted that the high concentration of average total dissolved solids (TDS) 106390 mg/l in the hydraulic fracturing wastewater make it a significant parameter when selecting the proper radium treatment method. uranium mining wastewater has different characteristics as described in Table 2.3.

2.2. Radium treatment methods

The growth of hydraulic fracturing and uranium mining industries, restricted legislations, cost, and the environmental and health effects are the most significant factors which have encouraged researchers to find alternative methods and techniques to remove NORM from water and wastewaters. These methods vary between physical (e.g. membrane filtration), chemical (e.g. precipitation), and physicochemical (e.g. adsorption). Membrane filtration techniques such as reverse osmosis, nanofiltration, ultrafiltration,
microfiltration and electrodialysis for removing radium from water and wastewater have been studied by researchers; these techniques have been applied either separately or combined with other treatment methods (Montaña et al., 2013; Khedr, 2013).

Table 2.1. Characteristics of produced wastewater from Marcellus shale in Pennsylvania (Barbot et al., 2013).

<table>
<thead>
<tr>
<th>Component</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDS (mg/L)</td>
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<td>345,000</td>
<td>106,390</td>
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</tr>
<tr>
<td>COD (mg/L)</td>
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</tr>
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</tr>
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</tr>
<tr>
<td>Fe²⁺ dissolved (mg/L)</td>
<td>0.1</td>
<td>222</td>
<td>40.8</td>
</tr>
<tr>
<td>Fe²⁺ total (mg/L)</td>
<td>2.6</td>
<td>321</td>
<td>76</td>
</tr>
<tr>
<td>Gross alpha (pCi/L)</td>
<td>37.7</td>
<td>9,551</td>
<td>1,509</td>
</tr>
<tr>
<td>Gross beta (pCi/L)</td>
<td>75.2</td>
<td>597,600</td>
<td>43,415</td>
</tr>
<tr>
<td>Ra²²⁸ (pCi/L)</td>
<td>0</td>
<td>1,360</td>
<td>120</td>
</tr>
<tr>
<td>Ra²³⁰ (pCi/L)</td>
<td>2.75</td>
<td>9,280</td>
<td>623</td>
</tr>
<tr>
<td>U²³⁵ (pCi/L)</td>
<td>0</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>U²³⁸ (pCi/L)</td>
<td>0</td>
<td>497</td>
<td>42</td>
</tr>
</tbody>
</table>

aData for Northeast Pennsylvania only

Table 2.2 Wastewater production per Shale gas well in different Shale gas basins in the U.S.

<table>
<thead>
<tr>
<th>Basin</th>
<th>Wastewater per well (m³)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marcellus Shale, PA (2008–2011)</td>
<td>5200ᵃ</td>
<td>Lutz et al., 2013</td>
</tr>
<tr>
<td>Marcellus Shale, PA (2012)</td>
<td>3500ᵃ</td>
<td>Vengosh et al., 2014</td>
</tr>
<tr>
<td>Niobrara, CO (2012)</td>
<td>4000ᵇ</td>
<td>Vengosh et al., 2014</td>
</tr>
</tbody>
</table>

ᵃMarcellus Shale in PA (m³/well) calculated for 2012
ᵇThe Niobrara Shale in CO calculated from the Colorado Oil and Gas Conservation Commission.
Table 2.3. Components of No.741 uranium mine waste water (pH 3.88) in China (Chen et al., 2017).

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (mg/l)</th>
<th>Component</th>
<th>Concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U⁶⁺</td>
<td>1.65</td>
<td>Cr⁶⁺</td>
<td>6.37</td>
</tr>
<tr>
<td>K⁺</td>
<td>39.1</td>
<td>Cu²⁺</td>
<td>54.4</td>
</tr>
<tr>
<td>Na⁺</td>
<td>635</td>
<td>Zn²⁺</td>
<td>435.8</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>424.5</td>
<td>Pb²⁺</td>
<td>169.9</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>223.6</td>
<td>Ra²⁺</td>
<td>3400</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>41</td>
<td>SO₄²⁻</td>
<td>2049</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>24.2</td>
<td>NO₃⁻</td>
<td>23.15</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>0.751</td>
<td>Cl⁻</td>
<td>1064</td>
</tr>
</tbody>
</table>

*US Nuclear Regulatory Commission, 2001

However, several challenges have been encountered in the practical applications of these techniques including membrane fouling, complexity, energy requirements, difficulty to regenerate the membrane, and the cost of some filtration technologies such as reverse osmosis (IAEA, 2001; Rana et al., 2013; Mohammad et al., 2015). For instance, high concentrations of salts and organics and other pollutants in fracking wastewater can cause fouling and other membrane related problems (Barbot et al., 2013; He et al., 2013). These disadvantages have made membrane filtration less attractive for removing radium from fracking wastewater.

Chemical addition to remove radium from water and wastewater have been extensively studied by researchers over the past years. Commonly used coagulants in water treatment plants for removing radium and other modified chemicals such as ferric sulfate, ferric chloride, aluminum sulfate, aluminum polyhydroxychlorosulfate, lime, iron hydroxide, were investigated (Valentine et al., 1985; Frey and Logsdon, 1997; Baeza et al., 2006). Some of these studies have focused on the parameters impacting the process efficiency such as the decontamination factor (DF), solid-liquid separation step, pH, dose, and type of chemicals (Valentine et al., 1985; IAEA, 2001; Baeza et al., 2006).
Ion exchange has also been widely applied as a chemical technique to remove radium using different chemicals such as mixing strong base anion (SBA) resin with strong acid cation (SAC) resin, clinoptilolite, and barite (Clifford and Zhang, 1994). There are several disadvantages of this technique that limits its usefulness for wastewater treatment, such as increased levels of sodium ion in product water, generating polluted water (used for backwashing, rinsing the media) with high level of radioactivity compared to the raw water (about 100 times) especially when fracking wastewater is classified as strongly polluted wastewater (Munter, 2013; He et al., 2013; He et al., 2014).

Physicochemical methods such as adsorption is still an efficient treatment method adopted by many researchers over the past years. Nowadays, researchers focus on NORM adsorption using adsorbents with different chemical and physical characteristics that work separately or combined with other techniques to improve process efficiency. Commonly used adsorbents include schwertmannite (i.e. iron oxy hydroxy sulfate and zirconium-ferrite), titanite nanofibers, granulated wood charcoal, iron-manganese solids and BaSO$_4$ impregnated alumina (Clifford et al., 1988; Mott et al., 1993; Yang et al., 2008; Miro et al., 2008; Nishimura et al., 2009). Factors that influence radium adsorption such as pH, the structure of solids, and competitive cations have been investigated by researchers (Mott et al., 1993). Despite its effectiveness, major disadvantages of this technique include time requirement, decreased efficiency in the case of treating liquid with high concentrations, leaching of small particles from treating basins to wastewater when using certain some adsorbents, by-products and problems of adsorbent regeneration (Arthur et al., 2005; Chałupnik et al., 2013). These factors hinder the effective use of adsorption processes for removing radium from large quantities of fracking wastewater with different
composition (He et al., 2014). Although some adsorbents can achieve acceptable radium removal efficiency for certain types of wastewater (e.g. using MnO$_2$ bearing material for radium removing from low salt concentration water), these adsorbents may not be suitable for treating fracking wastewater with high salinity (Moon et al., 2003).

Despite the major problems associated with radium removal from fracking wastewater, several studies have evaluated the effectiveness of current techniques for radium treatment. For instance, Gas Technology Institute (GTI) accomplished an evaluation of water management options venture with contributions from a consortium of 23 companies in 2011 (Hayes and Smith, 2011). The consortium identified NORM treatment from gas shale wastewater as one of the critical problems that should be addressed by researchers in order to develop the industry. They concluded that there is no available commercial material in the market that has the ability to effectively remove NORM from gas shale wastewaters. Also, after evaluating the efficiency of different adsorbents for removing radium from hydraulic fracturing wastewater, they reported that as of the time of the report there was no cost-effective technique for removing NORM from wastewater (Hayes and Smith, 2011). In another study, Vengosh et al. (2014) illustrated that the treatment facilities of hazardous pollutants (NORM, heavy metals, and halogens) in unconventional flow back/produced wastewater is still insufficient which increases the possibility of surface water pollution and environmental problems. Furthermore, in (Pennsylvania) and due to insufficient treatment, they concluded that the treated outflow has a high concentration of radium and other pollutants which can cause surface water contamination (Ferrar et al., 2013). The above treatment challenges have necessitated the
need for researchers to identify alternative treatment methods for radium removal from hydraulic fracturing and uranium mining wastewater.

The availability of silica in large quantities and in different forms makes it readily available for radium removal. Understanding the movement of radium in groundwater and its attachment to silica in deep silica layers and possibility to retard, adsorption likelihood by silica used in proppants, and the ability of different types of zeolites to adsorb radium from the solution, make silica quartz a good alternative adsorbent to remove radium from hydraulic fracturing and uranium mining wastewater. Related to barite, experimental results of cations removal by barite as well as its availability motivated us to study its ability in radium adsorption.

2.3. Radium removal by lime-soda ash softening from wastewater

Lime soda ash softening is considered an effective process for removing hardness (Johnson et al., 1989) and has been employed in industrial fields for more than a century (Acharya, et al., 2011). The process generates different minerals including CaCO$_3$, MgCO$_3$, BaCO$_3$, SrCO$_3$, BaSO$_4$, and SrSO$_4$. This process is not only useful for removing hardness but also for removing radium-226 and radium-228 (Hammer et al., 2012). There are many advantages of applying lime-soda ash softening to remove radium by co-precipitation from hydraulic fracturing wastewater. These benefits are related to efficiency, cost, energy, treating volumes, and basin size.

Regarding radium removal efficiency, Yoshida et al. (2008) showed that lime soda ash softening has removal efficiency higher than predicted and could also remove other metals (Ca$^{2+}$, Mg$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$) by co-precipitation with carbonates. In addition to that, lime-soda ash softening is a suitable technique to minimize hardness in flow back
wastewater to less than 2000 mg/l concentration and raise the quality of water to meet the reuse requirement (Acharya et al. 2011; Karrs and Altman, 2014). Another significant merit is that lime soda ash softening is considered a low-cost process (Sorg, 1988; Lee and Bondietti, 1983; Arthur et al., 2005). Regarding energy consumption, lime softening requires less energy and pretreatment compared with membrane treatment to remove certain pollutants in produced water (Arthur et al., 2005). This process has proved its elevated clarifying efficiency, simplifying sludge collection as well as saving volume and energy (Mehta, 2014).

Despite its predicted efficiency to remove radium from hydraulic fracking wastewaters, there is still limited theoretical and experimental (He et al., 2014), investigations on the use of sodium carbonate (Na₂CO₃) for the removal of radium from wastewater. Furthermore, due to the possibility of finding SrSO₄ and quartz silica in the same liquid, impregnated quartz silica with SrSO₄ could be modeled to compute the effect of celestite on radium silica removal and compare the adsorption of radium on silica with and without celestite.

2.4. Radium removal from wastewater by silica oxide materials

Silicon dioxide (SiO₂) in its both crystalline and amorphous forms is one of the most abundant substances on earth. (Kroutil et al., 2015). However, only a very few studies have focused on the investigation of Ra²⁺ adsorption onto silica quartz surfaces. Therefore, alternative silica forms such as zeolite will be discussed in this section. Regarding silica surface characteristics, Emami et al. (2014) showed that the charge of the silica surface plays a significant role in radium adsorption depending on the pH of the solution (increasing pH leads to increasing surface charge which achieves more cation removal).
Clinoptilolite, a natural zeolite was used to remove radium from hydraulic fracturing wastewater due to its high selectivity for \( \text{Ba}^{2+} \), \( \text{Sr}^{2+} \) and increased attraction to the larger ionic radius cations such as \( \text{Ba}^{2+} \), \( \text{Sr}^{2+} \), \( \text{Na}^{+} \), \( \text{Ca}^{2+} \), \( \text{Fe}^{2+} \), \( \text{Mn}^{2+} \), and \( \text{Mg}^{2+} \) which are all less than the radius of \( \text{Ra}^{2+} \) (148pm). This form of zeolite indicated a good removal efficiency for \( \text{Ra}^{2+} \) (Bish, 1999; Fan et al., 2016). In another instance, Decalso, an artificial zeolite, was used to remove radium from lime-neutralized water and achieved a high removal efficiency of approximately 95% (Kosarek, 1979).

The limited data related to the removal efficiency of \( \text{Ra}^{2+} \) by silica, and the hypothesis that silica will be a good adsorbent for \( \text{Ra}^{2+} \) due to its structure, and the possibility of interaction with hydraulic fracturing and uranium mining wastewater components motivated us to investigate different ionized silica surfaces for radium removal under different conditions.

2.5. Radium removal from wastewater by sulfur oxides

Radium in hydraulic fracturing wastewaters with elevated concentration of barium, strontium, and salinity, is eliminated by co-precipitation with barium or some other alkaline earth metals. In the past years, the removal of radium by co-precipitation and formation of \( \text{RaBa(SO}_4 \) complexes has been investigated (Rosenberg et al., 2013). This research area is still of interest with recent modifications to get more radium removal with less cost.

Zhang et al. investigated the equilibrium and kinetics of co-precipitation of radium with \( \text{BaSO}_4 \) and \( \text{SrSO}_4 \) as binary and ternary systems in different ionic strength to simulate the real characteristics of hydraulic fracturing wastewater. They found that the radium distribution coefficient with \( \text{SrSO}_4 \) and \( \text{BaSO}_4 \) is 237 and 1.54, respectively. Also, the results of their study indicated that in ternary system, radium removal by co-precipitation
with BaSO$_4$ was higher than SrSO$_4$ due to rapid nucleation of BaSO$_4$ and similarity in ionic radii of Ra$^{2+}$ with Ba$^{2+}$ than Sr$^{2+}$ (Zhang et al., 2014).

In another study, Doerner and Hoskins investigated the removal of radium by sulfate ion in the presence of barium experimentally. Their study showed that when there is more barium than radium, sulfate components combines with radium and remove it by precipitation and the solubility product of RaSO$_4$ is not exceeded (Doerner and Hoskins, 1925).

Langmuir and Riese (1985) elaborated the thermodynamics of trace radium solid solution in the presence of sulfate and carbonate components and explained the equation that estimate the removal. Langmuir and Melchior (1985) also investigated the geochemistry of Ra$^{2+}$, Ba$^{2+}$, Sr$^{2+}$, and Ca$^{2+}$ sulfates in some American brines to find the geochemical controls on radium and some other radioactive elements. Kondash et al., (2013) reported that mixing of hydraulic fracturing fluid with acid mine drainage improves the removal of radium by sulfate oxide under different conditions.

Brandt et al. (2015) studied barite recrystallization during radium uptake as a function of time using both experimental and modeling techniques. They concluded that the recrystallization mechanism of is complex and unpredictable even with some observed probabilities. Heberling et al. (2018) studied the long term batch barite recrystallization in the presence of $^{226}$Ra and $^{133}$Ba, they showed that the recrystallization process is very slow compared to previous work. According to the recrystallization model, the time required to complete bulk barite equilibration is 1400-16,900 years.

Recent studies have focused on studying radium removal in the presence of barium and sulfate ions experimentally. Rosenberg et al. (2013) studied the removal of radium in
a large-scale field system consisting of six sequential evaporation ponds and proved that
the formation of RaBa(SO$_4$) solid solution controlled the removal of radium.

Although several studies have investigated radium removal via different processes,
the use of molecular and process modeling for predicting adsorption isotherms to describe
radium removal have not yet been investigated.

2.6. Effect of ions on divalent cations removal by adsorption

Adsorption of divalent ions on silica and barite in the presence of other ions such
as Ba$^{2+}$, Sr$^{2+}$, Ca$^{2+}$, Mg$^{2+}$ Na$^+$ and Cl$^-$ has been investigated by several studies due to its
significance in environmental applications. For instance, Hayes and Katz (1996) studied
the adsorption of Zn (II) and Ca$^{2+}$ on silica/electrolyte under different conditions and they
reported that there was competition between the ions. According to Robertson and Leckie
(1997), the main reason for this competition is that both cations adsorb on the same
hydroxyl groups. Also, the adsorbed Ca$^{2+}$ generates outer sphere complex while Zn$^{2+}$
generates inner sphere complex (Hayes and Katz, 1996; Robertson and Leckie, 1997;
Janusz et al., 2003).

Srivastava et al. (2005) studied single and multi-element systems on Kaolinite
under different conditions. They found that the adsorption isotherm for multi-component
systems follow the order Cu$^{2+}$ > Pb$^{2+}$ > Zn$^{2+}$ > Cd$^{2+}$. Based on these studies, we conclude
that divalent cations have a significantly effect on radium removal by silica, and this effect
should be investigated to understand the underlying mechanisms and its effects on radium
removal within an experimental time frame.

Rosenberg et al. (2018) studied the effect of sodium chloride on radium removal by
barite and other minerals within seawater evaporation in different ponds. They modeled
the removal by empirical laws and proved that sodium and chloride ions reduce the ability of barite to remove radium. They further used a batch system to elaborate the effect of sodium chloride on radium removal with barite co-precipitation in a neutral system at ambient temperature and focused on nucleation and growth kinetics of RaBa(SO₄) in presence of sodium and chloride ions. They derived an equation to describe the dependency of partitioning coefficient on the degree of barite saturation.

In another study, Rosenberg et al. investigated the fate of radium in the presence of high concentrations of Na⁺ and Cl⁻ ions and their activity in reducing radium removal by co-precipitation explained the thermodynamics of radium removal using Pitzer formalism (Rosenberg et al., 2011).

2.7. Free energy of adsorption from MD simulations

The type and mechanism of adsorption reactions can be related by three essential thermodynamics parameters: Free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). The Gibbs free energy (ΔG°) indicates the degree of spontaneity of the adsorption reaction; thus, a more negative ΔG° value indicates a more energetically favorable adsorption reaction between the adsorbate and adsorbent in solution. The ΔG° for adsorption reaction can be calculated from the thermodynamic relation below:

$$\Delta G = -RT\ln K_a$$  (2.1)

Where K_a is a thermodynamic equilibrium constant (dimensionless), T is the absolute temperature (Kelvin), R is the ideal gas constant with a value of 8.314 (J/mol.K). The relationship between the thermodynamics parameters is expressed by the following equations:
\[
\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad \text{(2.2)}
\]

\[
\ln K_a = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad \text{(2.3)}
\]

From the relations above, \(\Delta H^\circ\) and \(\Delta S^\circ\) can be estimated from the slope and intercept of \(\ln K_a\) vs. \(1/T\) plot. A positive and negative value of \(\Delta H^\circ\) refers to an endothermic process (take heat from surrounding) and exothermic process (release heat to surrounding), respectively. Low values of \(\Delta S^\circ\) indicates no randomness while high values suggest high randomness during adsorption (Liu, 2009).

Studies have applied the above thermodynamic relations with Langmuir isotherm model to study different adsorption processes. For instance, Liu (2009) investigated and reported that for charged or uncharged adsorbate in the bulk, the equilibrium Langmuir constant is very close to the thermodynamic Langmuir constant, which allows the use of the equilibrium constant for computing free energy (\(\Delta G^\circ\)), enthalpy (\(\Delta H^\circ\)), and entropy (\(\Delta S^\circ\)) for adsorption processes.

Yousef et al. (2011) studied four essential adsorption characteristics which include kinetics (pseudo-first order and pseudo-second order models), mechanism (intraparticle diffusion model), isotherms (Langmuir, Freundlich, Temkin, and Redlich–Peterson), and thermodynamics (\(\Delta G^\circ\), \(\Delta H^\circ\) and \(\Delta S^\circ\)) of the adsorption of phenol by Jordanian zeolite. Based on the application of the thermodynamics parameters, they concluded that adsorption of phenol onto Jordanian zeolite was physical in nature. In our present study, we will relate Langmuir isotherms to molecular dynamics by relating the Langmuir coefficients to the free energy which calculated from molecular dynamics simulations.
2.8. Process modeling of adsorption equilibrium

Adsorption isotherms such as Langmuir and Freundlich are essential for describing the interaction between adsorbates and adsorbent surfaces in solution. The Langmuir model which is used in this study, assumes that adsorption is mono-layer and the structure of the adsorbent is homogeneous and adsorption sites are identical and energetically equivalent. The Langmuir isotherm model is given by the following equation:

\[ q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \]  

(2.4)

\[ \frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m} \frac{1}{C_e} \]  

(2.5)

where \( q_m \) is the maximum amount of adsorbed pollutant per unit mass of adsorbent (mg/g). \( C_e \) is concentration of adsorbate in the solution at equilibrium (mg/l), and \( K_L \) is the Langmuir constant related to the energy of adsorption (l/mg). both \( K_L \) and \( q_m \) can be calculated from a linear plot of \( 1/C_e \) versus \( 1/q_e \) (Vimonses et al., 2009).

Liu (2009) have developed a unique model to relate the multicomponent Langmuir isotherm to the free energy of adsorption from MD simulation. The Langmuir coefficient of the model is illustrated in the following equation:

\[ b = \frac{\exp \left( \frac{-\Delta G}{RT} \right)}{1 \text{mol/L}} \]  

(2.6)

where 1 mol/L refers to the standard reference concentration, \( R \) is the universal gas constant, and \( T \) is the absolute temperature.

In this study, we developed an equilibrium process model composed of a dual and triple component Langmuir isotherm, coupled with mass balances over a batch system and
calculated the theoretical isotherms. The calculated isotherms are compared with experimental isotherms to verify the agreement between modeling and experimental data.
CHAPTER 3

ELUCIDATING MECHANISMS OF RADIUM ADSORPTION ON SILICA SURFACES USING MOLECULAR SIMULATIONS

ABSTRACT

Molecular dynamics (MD) simulations coupled with umbrella sampling and umbrella integration were performed to extract the free energy of adsorption of radium and sodium on a silica surface with 1 to 20 dissociated silanol groups (corresponding to a pH range of 2 to 10) and in the presence of different concentrations of sodium and chloride in solution. The free energies of adsorption increased (were more negative) with more dissociated silanol groups and at lower concentration of ions in solution. Energy decomposition analyses demonstrated that electrostatic interactions were the dominant mechanism for radium adsorption on the silica surface. Radium adsorption energies increased with more dissociated silanol groups because of the increase in negative surface charge. Sodium competition with radium on a dissociated silanol group and chloride complexation with radium were the main mechanisms for the decrease in adsorption free energies in presence of ions in solution. The surface charge density in the Stern layer for different dissociated silanol groups obtained from MD simulations were in reasonable agreement with the calculated surface charges based on experiments at different pH values. Isotherm predictions based on the multi-component Langmuir isotherm were in reasonable agreement with experimental results.
Keywords: Competitive Adsorption, Complexation, Energy Decomposition Analysis, Ionic Strength, Isotherms, Molecular Dynamics, pH, Surface Charge

3.1. Introduction

Radium is a daughter product of the decay of uranium and thorium and can be found in soils near uranium and radium mining sites (Carvalho et al., 2007; Campbell et al., 2015). Radium is also a major component of naturally occurring radioactive materials found in hydraulic fracturing (fracking) wastewaters. Fracking flowback/produced wastewater from Marcellus Shale can have median Ra-226 concentrations >164 times the wastewater disposal standards (Geltman and LeClair, 2017), and > 492 times drinking water standards (Rowan et al., 2011; US EPA, 2016). Because radium has a half-life of 1622 years (Zapecza and Szabo, 1986), understanding the mechanisms associated with removal and fate of radium is critical for environmental protection.

Radium removal from water can be achieved through membrane filtration or transfer to a solid phase. Solid phase transfer can involve engineering of a process through the addition of precipitants or through adsorption onto a solid (Kosarek, 1979). The fate of radium in the environment is usually dictated by adsorption or ion exchange onto mineral inorganic surfaces (Tanner, 1964; Kraemer and Reid, 1984). This study focuses on elucidating the mechanisms of adsorption of radium on silica. Silica is a widely researched material in engineering and natural science fields (Zhuravlev, 2000). The crystalline form (α-SiO₂) is found in soil and rocks (Blume et al., 2016), and radium contamination has been found in pore waters of sandy aquifers (Reynolds et al., 2003; Grundl and Cape, 2006). Furthermore, proppants used in fracking contain a large percentage of silica (Mader, 1989; Liang et al., 2016).
The objective of this study is to understand mechanisms of adsorption of radium on silica using molecular simulations and to compare model predictions with experimental adsorption isotherms. The same modeling approach can also be used to elucidate mechanisms of radium adsorption and transport in aquifers (Grundl and Cape, 2006) or to study the effects of proppant coatings (e.g., fly ash and other minerals, Enderle (2017) developed to keep radium in the subsurface during hydraulic fracturing. Silica have surface silanols Si-OH whose degree of protonation depends on the system pH (Emami et al., 2014; Kroutil et al., 2015). Radium has been detected in aquifer systems in a pH range of 4.0-9.3 (Szabo et al., 2012) and in fracking wastewaters in a pH range of 4.9-12.0 (Abualfaraj et al., 2014). A mean ± standard deviation of pH ranging from 3.4 ± 0.4 to 8.7 ± 0.5 has been reported in waters in different locations within a uranium mine tailing site (Campos et al., 2011), from which radium will be produced due to uranium decay. Furthermore, the total dissolved solids (TDS) in fracking wastewater has been reported to be as high as 5 times that of seawater (Gregory et al., 2011). In this study, simulations and experiments were performed in different water characteristics ranging from a pH of 2.0 to 10.0 with and without the addition of 1M NaCl as ionic strength. These water qualities represent the extreme ranges reported in the literature.

The molecular simulations used in this study combine molecular dynamics with umbrella sampling and umbrella integration to extract the free energy of adsorption of radium on silica in the presence of competing ions. Theoretical studies of ion exchange in the literature have been limited. Korolev et al. (1999) studied the competitive binding of monovalent cations on DNA using a continuum model using Monte Carlo simulations and found qualitative agreement between predicted ion selectivity and experiments. Wang and
Sun (2013) calculated relative free energies between ammonium and sodium in zeolite using molecular (MD) simulations and thermodynamic integration to predict the experimental distribution of the two ions. Salmas et al. (2013) used MD simulations to calculate kinetics of ion exchange between sodium and silver in a zeolite. To our knowledge, this is the first theoretical study that calculates free energies of adsorption of radium under different water quality conditions and elucidates the mechanisms of competitive adsorption/ion exchange. Radium isotherm predictions calculated with this approach is compared with experimental isotherms.

3.2. Simulation details

3.2.1. Silica model

The model for quartz silica used in the MD simulations was obtained from Emami et al. (2014) and is shown in Figure 3.1. They expanded an α-quartz unit cell to a 7×4×3 supercell, cut the {001} surface and protonated the dangling oxygen groups. The model has a silanol density of 9.4 SiOH groups per nm², with the degree of dissociation dependent on the pH of the solution. They forwarded that a solution pH of 2.0, 7.0 and > 9.0 corresponds to 0, 10, and 20 dissociated silanol groups, with each dissociated group having a corresponding Na⁺ ion in solution.

The silica used in this study was similar to Emami et al. (2014) but with dissociated silanol groups ranging from 1 to 20 (see Figure 3.1). Only the top surface had silanol groups while the bottom surface was completely protonated. Surfaces with 10 and 20 sites were directly adapted from Emami et al. (2014), which they selected at random, with the silanol groups of the 10 sites model composed of a subset of the 20 sites model. The surface with 15 sites was generated by randomly protonating 5 sites of 20 site model that is not part of
the 10 sites model. Similarly, the surface with 5 sites was generated by randomly protonating 5 sites of 10 site model. Each system was solvated with 2500 water molecules.

Figure 3.1 Representative models of silica (a) side view and (b-f) top view with 1-20 dissociated silanol sites. The dissociated silanol site is represented with oxygen Van der Waals (VDW) radii in red. The rest of the silica is represented with CPK models with red oxygen atoms, yellow silica atoms and white hydrogen atoms.

Three solvated silica systems were simulated: (1) a silica surface without any neutralizing cations in solution, (2) a silica surface with Na$^+$ neutralizing the surface charge, and (3) a silica surface with Na$^+$ neutralizing the surface charge and with additional
1 M NaCl to simulate the effects of ionic strength. For the first system, either one atom of Ra$^{2+}$ or Na$^+$ was added adjacent to a dissociated silanol group without any Cl$^-$ in the bulk. For the second and third systems, Cl$^-$ was added to ensure the system is electrically neutral. The additional Cl$^-$, NaCl, and water molecules were added randomly using Packmol (Martínez et al., 2003, 2009).

3.2.2. Force fields

The interface force field developed by Emami et al. (2014) was used to model silica and the Na$^+$ cation. The silica force field was calibrated with the heat of immersion and was designed to be compatible with different platforms, including the AMBER force field. The Na$^+$ cation was calibrated with hydration free energy. The force fields for Ra$^{2+}$ and Cl$^-$ were obtained from Li et al. (2013, 2015), which were also developed to be compatible with the AMBER force field. Values calibrated to the hydration free energy and compatible with TIP3P model water were used.

3.2.3. MD simulations

A series of molecular dynamics (MD) simulations were performed on the built silica systems. The energy of each system was minimized to remove bad contacts, followed by constant volume heating to 300K for 0.1 ns, constant temperature simulation for 0.9 ns, and constant pressure equilibration at 300K for 2 ns. The Nose-Hoover thermostat was used with a time step of 1 fs, the velocity Verlet algorithm, and the shake algorithm to constrain the water molecule geometry. The Ra$^{2+}$ or Na$^+$ ion was constrained to be adjacent to the targeted dissociated silanol group along the z-axis using a spring couple with a spring constant of 10 kcal/mole-$\text{Å}^2$. A 12 Å cut-off for van der Waals interactions was used in conjunction with a $10^{-6}$ accuracy for the particle-particle particle-mesh solver. Umbrella
sampling was performed using collective variables defined by the projection of the distance between the Ra\(^{2+}\) or Na\(^+\) ions and the targeted dissociated silanol group along the z-axis with a force constant of 30 kcal/mole-Å\(^2\) (Torrie and Valleau, 1977; Fiorin et al., 2013). The simulation length of each umbrella sampling window was 2.1 ns, with the first 0.1 ns of simulation discarded as equilibration. Distances between the ion and the surface along the z-direction were extracted every 0.1 ps. The potential of mean force was calculated using the umbrella integration procedure developed by Kästner et al. (2009). All MD simulations were performed with LAMMPS (Plimpton et al., 1995). VMD software with topotools was used to visualize the results (Humphrey et al., 1996).

### 3.2.4. Quantum chemical calculations

Quantum chemical calculations using a 129 atoms silica cluster was performed to ascertain the nature of the interaction of Ra\(^{2+}\) with silica in the presence of other ions. A quartz unit cell was obtained from the American Mineralogist Crystal Structure Database (Downs et al., 1993, 2003), expanded to produce a 4×4×2 cell, and trimmed to create a cluster similar to the surface used in our MD simulations (see Figure 3.2). All dangling oxygen atoms were protonated. Initial constrained geometry optimization of the silica cluster was performed at the RHF level using the 6-31G(d) basis set with all Si and O atoms fixed at their crystallographic positions to obtain optimal locations of the added protons. Select surface silanol groups were deprotonated (shown in Figure 3.2(b) as O1-O6), and different combinations of ions (Ra\(^{2+}\), Na\(^+\), and Cl\(^-\)) were added to the surface at different initial locations. Subsequent constrained geometry optimization was performed at the RHF level using the CRENBL basis set and effective core potential for Ra\(^{2+}\) and the 6-31G(d)
basis set for all other atoms. Only the topmost layer of H and O were relaxed; all other atoms were fixed at their previously optimized and crystallographic positions.

(a) 

(b)

Figure 3.2 (a) Side view and (b) top view of silica cluster used for Density Functional Theory calculations. The different dissociated silanol sites are labeled O1 to O6 and are shown using oxygen VDW radii in red.

A Morokuma energy decomposition analysis (EDA) (Kitaura et al., 1976) was performed to investigate the interaction of Ra$^{2+}$ with the silica surface at the optimized geometry. A final constrained geometry optimization was performed using Density Functional Theory (DFT) with the B3LYP functional and in the polarizable continuum model (PCM) of water. Variations in the total interaction energy of Ra$^{2+}$ with the silica surface was calculated by offsetting the Ra$^{2+}$ position along the z-axis and re-optimizing the system, relaxing only the topmost layer of H and O and keeping the rest of the atoms and Ra$^{2+}$ fixed. All geometry optimization and DFT calculations were performed using TeraChem (Ufimtsev et al., 2009; Titov et al., 2012; Song et al., 2015; Liu et al., 2015;
Goumans et al., 2009). Morokuma EDA calculations were performed using Firefly (Granovsky, 2014; Schmidt et al., 1993)

3.3. Materials and methods

The experiments reported in this dissertation were performed by collaborators at the University of Pittsburgh.

3.3.1. Radium adsorption isotherms

Radium chloride (RaCl$_2$) concentrated stock solution with activity of 1440 µCi/L, measured by using gamma spectroscopy (Canberra BE 202), was a donation from Pennsylvania State University. The stock solution was diluted to 8,650 pCi/L with DI water (Synergy, Millipore, Billerica, MA). Silica (SiO$_2$) powder (Alfa Aesar, Ward Hill, MA) was used as an adsorbent for Ra-226. 1 pCi/L is taken to be 1 pg/L for the MD simulations (US EIA, 1997).

Radium uptake experiments were conducted to investigate the effect of pH and ionic strength on the ability of silica to remove radium from aqueous solution. Silica particles at concentrations ranging from 50 to 5,000 mg/L were mixed with 50 mL of 8,650 pCi/L RaCl$_2$ solution in Falcon polypropylene conical centrifuge tubes (Fisher Scientific, Pittsburgh, PA). Solution pH was adjusted by adding HCl and/or NaOH and the ionic strength was adjusted by adding NaCl prior to the addition of silica. Samples were mixed for 24 hours in a horizontal shaker (Darts Control Inc., Zionsville, IN) at a speed of 30 rpm to ensure adsorption equilibrium. 10 mL of each sample was filtered through 0.45 µm mixed cellulose esters membrane (Millipore, Billerica, MA) to separate silica solids from aqueous solution and Ra-226 concentration was analyzed using Liquid Scintillation
Counter (LSC, LS 6500, Beckman Coulter, Brea, CA). Radium uptake was calculated using
\[
q = \frac{(C_0 - C_e)V}{A}
\]
where \( q \) (pCi/cm\(^2\)) is adsorption capacity for Ra-226 per unit surface area of silica, \( C_0 \) and \( C_e \) (pCi/L) are the initial and final Ra-226 concentration in the liquid phase, \( V \) (mL) is the volume of the sample and \( A \) (cm\(^2\)) is the mass of the adsorbent.

Ra-226 concentration was quantified using LSC (Blackburn and Al-Masri, 1992; Escobar et al., 1996; Zhang et al., 2014) that was calibrated using gamma spectroscopy (Johnston and Martin, 1997). Measurements were done for 40 min per sample at 170-230 keV. This method is selective for radium and overestimation of activity due to the possible presence of other radium isotopes (i.e., Ra-223, Ra-224 and Ra-228) is negligible (Köhler et al., 2002). Therefore, 2 ml of the sample was first mixed with 0.364 ml of 100 mM BaCl\(_2\) solution and 20 ml of 1 M H\(_2\)SO\(_4\) to co-precipitate Ra-226 in the form of (Ra,Ba)SO\(_4\) solid solution. Samples were heated at 50 °C for 60 min until the supernatant was clear. (Ra,Ba)SO\(_4\) solids were filtered through 0.45 µm pore size mixed cellulose esters membrane and carefully transferred into glass vials using 3 ml of 0.25 M EDTA. Samples were then heated at 60 °C until solids were completely dissolved. 14 ml of liquid scintillation cocktail Ultima Gold (Perkin Elmer, Waltham, MA) was added prior to measurements by LSC.

### 3.3.2. SiO\(_2\) particle characterization

Zeta potential measurements were conducted using Litesizer 500 (Anton Paar, Ashland, VA). A total of 50 mg of SiO\(_2\) powder was dispersed in 10 ml of DI water and the solution pH was adjusted from 2-10 using HCl and/or NaOH. The impact of ionic
strength was investigated by adding 10 mM, 100 mM and 1 M NaCl to the solution. Electrophoretic mobility of SiO$_2$ particles was measured in polycarbonate cuvettes with gold electrodes on each side and zeta potential was automatically calculated using Smoluchowski equation (Hunter, 2013).

Surface charge density was calculated using Gouy-Chapman equation for symmetric binary electrolyte (Gouy, 1910; Chapman and Li, 1913).

$$\sigma = \sqrt{8 C_\infty \varepsilon k T \sinh \left( \frac{z e \psi_0}{2 k T} \right)} \quad (3.2)$$

where $C_\infty$ is the concentration of electrolyte in solution, $\varepsilon$ is the water permittivity, $k$ is the Boltzmann constant, $T$ is the temperature, $z$ is the ion valence and $\psi_0$ is the surface potential. Surface potential was approximated using Gouy-Chapman model for the distribution of electrokinetic potential in the double layer (Hiemenz, 1986):

$$\tanh \left( \frac{\psi(x)}{4} \right) = \tanh \left( \frac{\psi_0}{4} \right) e^{-K x} \quad (3.3)$$

where, $x$ is the distance from the particle surface, $\psi(x)$ is the potential at the distance $x$ (i.e., measured zeta potential) and $K$ is the Debye parameter that was calculated using the following equation (Kohonen et al., 2000):

$$K = \left( \frac{e^2 \Sigma z^2 n_i}{\varepsilon k T} \right)^{1/2} \quad (3.4)$$

where, $e$ is the elementary charge and $n$ is the number density of ion species in the bulk solution. Zeta potential is the electrokinetic potential measured at the shear plane that is located between the Stern boundary layer and the screening length (i.e., Debye length $K^{-1}$) (Hiemenz, 1986). Although the exact location of the shear plane is not known, recent studies suggested that it is located close to the screening length, (Ding et al., 2015; Li et al., 2003) which is the assumption used to calculate the surface charge density.
Particle characterization was performed by measuring particle size distribution and specific surface area of silica powder using Litesizer 500 (Anton Paar, Ashland, VA) and nitrogen Brunauer-Emmett-Teller (BET) adsorption/desorption analysis (Micromeritics ASAP 2020, Micromeritics, Norcross, GA), respectively. Since expected particle size was 1 μm or bigger, a minimal concentration of 0.1 mg/ml of silica in the solution was necessary to perform successful particle size distribution analysis using Litesizer. BET analysis was performed using 0.5 g of SiO₂. Before adsorption/desorption measurements, degassing was done for 2 hours at 200 °C under high vacuum. Surface area was obtained based on the typical 6-point BET analysis at relative pressure (P/P₀) from 0.05 and 0.25 (Brunauer et al., 1938).

MD simulations were coupled with umbrella sampling (Torrie and Valleau, 1977) and the potentials of mean force of Ra²⁺ and Na⁺ interacting with the silica were calculated using the umbrella integration procedure developed by Kästner et al. (2009). All MD simulations were performed with LAMMPS (Plimpton et al., 1995). Density Functional Theory (DFT) calculations and Morokuma energy decomposition analyses (EDA) (Kitaura et al., 1976) using a 129 atoms silica cluster were performed using Terachem (Ufimtsev et al., 2009) and Firefly (Granovsky, 2014), respectively, to ascertain the nature of the interaction of Ra²⁺ with silica in the presence of other ions.

3.4. Results and discussion

3.4.1. Free energy of adsorption on silica

The PMF obtained from umbrella sampling calculations is a potential energy surface (Truhlar, 1992) that illustrates the interaction of Ra²⁺ or Na²⁺ with the silica surface. Figure 3.3 shows representative sample PMF curves obtained with different surfaces and
solution conditions. The PMF shows the free energy as a function of distance of the ion with the dissociated silanol group along the z-direction. All PMF curves were shifted to have a value of 0 kcal/mol at 10 Å. A negative PMF indicates attraction while a positive PMF represents repulsion relative to the free energy at 10 Å.

The PMF is flat at large distances from the surface (approaching 10 Å), indicating negligible interaction between the Ra²⁺ or Na²⁺ ions and silica. The PMF curves show a series of local minima and maxima as the ions approach the surface, after which a global minima is observed. These phenomena is also observed when simulating a cation-anion pair in solution (Winstein et al., 1954; Ghosh et al., 2012) where a local minima is associated with a solvent separated ion pair and a global minima occurs when the ion pair is in contact with each other. This trend is evident when the silica surface has a single dissociated silanol group. When the silica surface has multiple dissociated silanol groups, one cannot clearly delineate solvent separation between the ions and the surface because of multiple possible points of interaction between the cation and the negative surface. As the Ra²⁺ or Na⁺ ions approach the surface, the PMF increases, indicating the onset of repulsive forces. The free energy of adsorption of Ra²⁺ or Na⁺ ions with the silica surface is taken as the difference between the PMF at 10 Å and at the global optimum.

Table 3.1 shows the mean and standard deviation of the free energies of adsorption obtained from 20 umbrella sampling simulations for each condition corresponding to (a) through (f) in Figure 3.3. The free energy of adsorption of Ra²⁺ with the silica surface is more negative than Na⁺ under the same conditions, indicating that Ra²⁺ adsorption is preferred. This preference is due to the higher positive charge of Ra²⁺ compared to Na⁺. This is confirmed with a Morokuma EDA (see Table 3.2) which shows the decomposition
of the energies of interaction between the ions and the silica cluster into different components.

Figure 3.3 Potential of mean force (PMF) for different number of dissociated silanol groups (number of sites) for (a) charged silica surface with Ra$^{2+}$, (b) silica surface with Na$^+$ cations in solution and RaCl$_2$, (c) silica surface with Na$^+$ cations in solution and RaCl$_2$ with 1M NaCl, (d) charged silica surface with Na$^+$, (e) silica surface with Na$^+$ cations in solution and NaCl, and (f) silica surface with Na$^+$ cations in solution and NaCl with 1M NaCl.

A comparison of Case 1 and Case 2 in Table 3.2 shows the total Ra$^{2+}$ interaction energy with various sites on the silica cluster is more favorable than Na$^+$. The mean ±
standard deviation of the total interaction of Ra$^{2+}$ with a silica surface with one dissociated silanol group is $-319 \pm 8$ kcal/mol, while that of Na$^+$ with the same sites is $-153 \pm 9$ kcal/mol.

Table 3.1 Mean (standard deviation) of free energy of adsorption of Ra$^{2+}$/Na$^+$ on different silica surfaces with different number of dissociated silanol groups. Units are in kcal/mol.

<table>
<thead>
<tr>
<th>Case</th>
<th>Number of dissociated silanol groups (sites)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>a. Charged silica surface with Ra$^{2+}$</td>
<td>-6.7 (1.1)</td>
</tr>
<tr>
<td>b. Silica surface with Na$^+$ cations in solution and RaCl$_2$</td>
<td>-6.8 (1.6)</td>
</tr>
<tr>
<td>c. Silica surface with Na$^+$ cations in solution and RaCl$_2$ with 1M NaCl</td>
<td>-7.0 (1.0)</td>
</tr>
<tr>
<td>d. Charged silica surface with Na$^+$</td>
<td>-1.9 (0.6)</td>
</tr>
<tr>
<td>e. Silica surface with Na$^+$ cations in solution and NaCl</td>
<td>-2.3 (0.8)</td>
</tr>
<tr>
<td>f. Silica surface with Na$^+$ cations in solution and NaCl with 1M NaCl</td>
<td>-1.6 (1.0)</td>
</tr>
</tbody>
</table>

The ion interaction with the negatively charged silica cluster is predominantly due to the electrostatic interaction term, with Ra$^{2+}$ having values of $-295 \pm 11$ kcal/mol, while that of Na$^+$ is $-146 \pm 14$ kcal/mol. The electrostatic component is the most significant component of the total energy and depends on the static charge distribution of each monomer (i.e., silica and Ra$^{2+}$/Na$^+$) in the combined system without considering the antisymmetric product of the monomer atomic orbitals. The polarization component is the difference in energy between the relaxed charge distribution and the static charge distribution. The exchange component is the difference energy between the non-
antisymmetric and antisymmetric product of the monomer orbitals in the combined wavefunction. Charge transfer is due to the interaction of valence molecular orbitals on one monomer with the unoccupied orbitals on the other monomer. The higher order coupling is the difference in energies between the fully relaxed antisymmetric wavefunction of the system and the sum of each of the other components (Phipps et al., 2015). In many studies, differences in electrostatic interaction energy has been used to rationalize changes in the total interaction energy because it is the largest component compared to the others (Glendening, 1996; Thellamurege et al., 2013). Note that the values of the interaction energy from the EDA (Table 3.2) cannot be directly compared to the free energies of adsorption (Table 3.1) since the EDA calculations are only available in vacuum (with no explicit water). These trends are also consistent with DFT calculations in PCM water.

Figure 3.4 shows DFT calculations in PCM water confirming that Ra$^{2+}$ interaction with silica is more favorable than Na$^+$. The interaction energy at large distances are relatively flat, indicating minimal interaction of the ions with the silica surface. As the ion approaches the surface, only a single global optimum is observed because the simulations were performed in implicit (PCM) water. As the ion further approaches the surface, an increase in the interaction energy is observed as the ions experience repulsive forces. Direct comparisons in the absolute values between Figure 3.4 and Tables 3.1 and 3.2 in the main text cannot be made because of differences in the simulation conditions. For the same ions, Figure 3.4 shows different interaction energies calculated for different dissociated silanol groups (O1, O2, O3, and O4 as shown in Figure 3.2). Thus, during MD simulations, depending on the location of the different silanol groups on the surface and the surrounding
atoms, different free energies of adsorption may be calculated. This illustrates the extent of the variability of the energy calculations for similar numbers of dissociated silanol sites at the silica surface.

Table 3.1 also shows that the free energy of adsorption of both Ra$^{2+}$ and Na$^+$ becomes more favorable as the silica surface becomes more negative with an increase in the number of dissociated silanol groups. Figure 3.5 shows snapshots of simulations of Ra$^{2+}$ on a silica surface containing 20 dissociated silanol groups. Ra$^{2+}$ may interact with 1, 2, or 3 silanol groups at various times during different umbrella sampling simulations, resulting in an increase in the interaction of Ra$^{2+}$ with the surface when silica has more dissociated silanol groups. When comparing Cases 2, 3, and 4 in Table 3.2, the EDA for Ra$^{2+}$ with 1, 2, and 3 dissociated silanol groups shows the total interaction energy becomes more negative with average values of -319, -487, and -630 kcal/mol, respectively. The change in the energy is due to the change in the electrostatic energy component, with the average values of -296, -463, and -612 kcal/mol for 1, 2, and 3 dissociated silanol groups. This change in the electrostatic component is due to the increase in total negative surface charge of silica. Figure 3.6 shows that Ra$^{2+}$ may interact with 1, 2, or 3 silanol groups at various times during different umbrella sampling simulations. This results in an increase in the free energy of adsorption of Ra$^{2+}$ with increasing negative surface charge. Figure 3.6 also shows similar trends in both increases in Ra$^{2+}$ interaction with the silica surface in PCM water and with variations in calculations with different site combinations.
Table 3.2 Energy decomposition analysis for the interaction of Ra\(^{2+}\), Na\(^{+}\), Ra\(^{2+}/Cl^−\) and Ra\(^{2+}/Na^+\) with silica of different surface charge due to different dissociated silanol groups. All energies are in kcal/mol.

<table>
<thead>
<tr>
<th>Case # / Ion</th>
<th>Surface charge (Dissociated Silanol Group)</th>
<th>Total interaction energy</th>
<th>Energy Decomposition Components</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Polarization</td>
</tr>
<tr>
<td>1 / Na(^{+})</td>
<td>Silica(^-) (O1)</td>
<td>-165</td>
<td>-164</td>
</tr>
<tr>
<td></td>
<td>Silica(^-) (O2)</td>
<td>-152</td>
<td>-137</td>
</tr>
<tr>
<td></td>
<td>Silica(^-) (O3)</td>
<td>-144</td>
<td>-133</td>
</tr>
<tr>
<td></td>
<td>Silica(^-) (O4)</td>
<td>-150</td>
<td>-149</td>
</tr>
<tr>
<td>2 / Ra(^{2+})</td>
<td>Silica(^-) (O1)</td>
<td>-323</td>
<td>-307</td>
</tr>
<tr>
<td></td>
<td>Silica(^-) (O2)</td>
<td>-313</td>
<td>-285</td>
</tr>
<tr>
<td></td>
<td>Silica(^-) (O3)</td>
<td>-328</td>
<td>-302</td>
</tr>
<tr>
<td></td>
<td>Silica(^-) (O4)</td>
<td>-310</td>
<td>-288</td>
</tr>
<tr>
<td>3 / Ra(^{2+})</td>
<td>Silica(^2-) (O1-O2)</td>
<td>-489</td>
<td>-461</td>
</tr>
<tr>
<td></td>
<td>Silica$^2-$ (O2-O3)</td>
<td>-484</td>
<td>-464</td>
</tr>
<tr>
<td>---</td>
<td>-------------------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>4 / Ra$^{2+}$</td>
<td>Silica$^3-$ (O2-O3-O5)</td>
<td>-634</td>
<td>-613</td>
</tr>
<tr>
<td></td>
<td>Silica$^3-$ (O2-O3-O6)</td>
<td>-626</td>
<td>-610</td>
</tr>
<tr>
<td></td>
<td>Silica$^-$ (O2 with Na$^+$)</td>
<td>-202</td>
<td>-174</td>
</tr>
<tr>
<td></td>
<td>Silica$^-$ (O2-O3) with Na$^+$</td>
<td>-342</td>
<td>-319</td>
</tr>
<tr>
<td></td>
<td>Silica$^3-$ (O2-O3-O5) with Na$^+$</td>
<td>-482</td>
<td>-460</td>
</tr>
<tr>
<td>5 / Ra$^{2+}$</td>
<td>Silica$^-$ (O2)</td>
<td>-190</td>
<td>-183</td>
</tr>
<tr>
<td></td>
<td>Silica$^2-$ (O2-O3)</td>
<td>-297</td>
<td>-290</td>
</tr>
<tr>
<td></td>
<td>Silica$^3-$ (O2-O3-O5)</td>
<td>-401</td>
<td>-389</td>
</tr>
</tbody>
</table>

*See Figure 3.2 for site description of specific dissociated silanol groups.
Figure 3.4 Interaction energy of Ra\(^{2+}\) or Na\(^+\) with a silica surface with one dissociated silanol group calculated using density functional theory.

(a)  (b)  (c)

Figure 3.5 Top view snapshots of Ra\(^{2+}\) interacting with: (a) one (b) two and (c) three dissociated silanol groups. The silica is represented with CPK models with red oxygen atoms, yellow silica atoms, white hydrogen atoms, and pink Radium ion.

Figure 3.6 Interaction energy of Ra\(^{2+}\) with a silica surface with one to three dissociated silanol group calculated using density functional theory.

In the presence of neutralizing Na\(^+\) cations, the free energy of adsorption of Ra\(^{2+}\) on the silica surface become less favorable. This can be seen when comparing Figure 3.3a
and 3.3b as well as Table 3.1 sections a and b. In the presence of additional ions (1 M NaCl), the free energy becomes even less favorable as seen in Figure 3.3b and 1c as well as Table 3.1 sections b and c. This can be explained by a competing ion effect due to Na\(^+\) and a reduction in the effective charge of Ra\(^{2+}\) due to complexation with Cl\(^-\).

Figure 3.7a shows the DFT-optimized location of Ra\(^{2+}\) on a silica surface with one dissociated silanol group (O2 in Figure 3.2b). When Na\(^+\) is added to the system, Figure 3.7b shows Na\(^+\) occupying a location opposite that of Ra\(^{2+}\) with the dissociated silanol group located between the two cations. The distance between Ra\(^{2+}\) and O2 in Figure 3.7a is 2.61 Å. The optimized distance between Na\(^+\) and O2 in the absence of Ra\(^{2+}\) is 2.10 Å. When both ions are present (Figure 3.7b), the O2-Ra\(^{2+}\) and O2-Na\(^+\) distances are 2.81 Å and 2.31 Å, respectively. Hence, Na\(^+\) is effectively competing with Ra\(^{2+}\) for the same adsorption site.

The effect of Na\(^+\) competition is further seen when comparing the interaction energy of Ra\(^{2+}\) with silica in the absence and presence of Na\(^+\) on the surface in EDA calculations. Table 3.2 shows the total interaction energy of Ra\(^{2+}\) is on average 135 kcal/mol higher (less favorable) in the presence of Na\(^+\) (Case 5) compared to cases when Na\(^+\) is not present for the same corresponding dissociated surface silanol groups (Cases 2 to 4). There is a corresponding average increase of 136 kcal/mol in the electrostatic component due to the presence of Na\(^+\). The average changes in the polarization, exchange repulsion, charge transfer, and higher order coupling terms are all less than 9 kcal/mol,
indicating that changes in the static charge distribution of the monomers due to the presence of Na$^+$ imparts the greatest influence on Ra$^{2+}$ interaction with the surface.

Figure 3.7 DFT-optimized geometry of (a) Ra$^{2+}$ (b) Ra$^{2+}$ and Na$^+$, and (d) Ra$^{2+}$ and Cl$^-$ on a negatively charged silica surface with O2 dissociated silanol group. RHF-optimized geometry of (c) Ra$^{2+}$ and Na$^+$, and (e) Ra$^{2+}$ and Cl$^-$ but with Ra$^{2+}$ offset 10 Å from the original optimized location in (b) and (d) along the z direction. All calculations were done in PCM water. Oxygen, silica, hydrogen, radium, sodium, and chloride are represented with CPK models with the colors red, yellow, white, pink, blue, and cyan respectively.

EDA calculations with Ra$^{2+}$ in the same optimized position for Case 5 but in the absence of Na$^+$ shows a difference in average total interaction energy of 14 kcal/mol. Thus,
changes in the distance between Ra$^{2+}$ and the dissociated silanol groups have minimal effect on the overall interaction of Ra$^{2+}$ with silica compared to the effect of the presence of Na$^+$. Figure 3.7c shows that when Ra$^{2+}$ is offset 10 Å from its optimized location in Figure 3.7b, Na$^+$ stays in the same vicinity at a distance of 2.13 Å from the dissociated silanol group, close to its optimal distance.

Interaction energy profiles of Ra$^{2+}$ as a function of distance calculated using DFT in PCM water also shows consistently shallower profiles in the presence of Na$^+$ (Figure 3.8a). This reduction in the attraction of Ra$^{2+}$ for the surface is another demonstration of the competing ion effect. Figure 3.8b shows interaction energy profiles of RaCl$^+$ are also consistently shallower compared to the Ra$^{2+}$ profiles, demonstrating the effect of complexation in reducing the interaction energy.

![Figure 3.8 Interaction energy of Ra$^{2+}$ with a silica surface in the presence of (a) Na$^+$ and (b) Cl$^-$ with one to three dissociated silanol groups calculated using density functional theory.](image)

The Cl$^-$ anion has a different role and mechanism from Na$^+$ in the reduction of the interaction energy of Ra$^{2+}$ with the dissociated silanol groups. Figures 3.7d and 3.7e show that Cl$^-$ effectively attaches to Ra$^{2+}$, forming a RaCl$^+$ complex. The distance between Ra$^{2+}$ and Cl$^-$ is 3.11 Å while the distance between Ra$^{2+}$ and O2 is 2.79 Å in Figure 3.7d. The presence of Cl$^-$ results in a larger O2-Ra$^{2+}$ distance because of the smaller effective charge
of the complex compared to the Ra$^{2+}$ ion. When Ra$^{2+}$ is offset 10 Å in the z-direction from its optimum location, Cl$^-$ maintains its complex with Ra$^{2+}$ and the Ra$^{2+}$-Cl$^-$ distance decreases to 2.85 Å because of a decrease in interaction between the dissociated silanol group and the Cl$^-$ anion.

Because the effect of Cl$^-$ on Ra$^{2+}$ interaction with silica is due to complexation, EDA calculations were performed evaluating the interaction of the complex with different silanol groups. Table 3.2 shows the total interaction energy of RaCl$^+$ with is on average 181 kcal/mol higher (Case 6) compared to cases when Cl$^-$ is not present for the same corresponding dissociated surface silanol groups (Cases 2 to 4). The increase is due primarily to a higher electrostatic component (average increase of 167 kcal/mole). We were unable to calculate the charge transfer component due to convergence issues. Numerous studies have shown this component to be smaller in magnitude (Li et al., 2006), which we also further confirmed with EDA calculations using a silicate molecule (See Table 3.3). EDA calculation with Ra$^{2+}$ in the same optimized position for Case 6 but in the absence of Cl$^-$ shows a difference in average total interaction energy of 14 kcal/mol. Thus, changes in the distance between Ra$^{2+}$ and the dissociated silanol groups have minimal effect on the overall interaction of Ra$^{2+}$ with silica compared to the effect of the presence of Cl$^-$. DFT calculations support the mechanisms forwarded on the reduction of interaction energy of Ra$^{2+}$ for the silica surface due to ion competition and complexation. Table 3.3 demonstrates that the electrostatic component is still the dominant mechanism associated with RaCl$^+$ interaction with the silica surface. Other components are relatively minor.
Table 3.3 Morokuma energy decomposition analysis for the interaction of RaCl+ with one molecule of Silica. All energies are in kcal/mol.

<table>
<thead>
<tr>
<th>Case</th>
<th>Electrostatic</th>
<th>Exchange repulsion</th>
<th>Polarization</th>
<th>Charge transfer</th>
<th>High order coupling</th>
<th>Total interaction energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO4H21- - RaCl+</td>
<td>-191</td>
<td>50</td>
<td>-30</td>
<td>-20</td>
<td>8</td>
<td>-183</td>
</tr>
<tr>
<td>SiO4H22- - RaCl+</td>
<td>-351</td>
<td>85</td>
<td>-50</td>
<td>-41</td>
<td>14</td>
<td>-343</td>
</tr>
</tbody>
</table>

When comparing Table 3.2 Cases 5 and 6, the presence of Cl− has a larger effect on the reduction of Ra2+ interaction with dissociated silanol groups compared to Na+, indicating that complexation may have a greater influence than competing ions on Ra2+ adsorption on silica. These calculations were performed at the quantum level. To relate this to the MD calculations, the distribution of O-Na+ and Ra2+- Cl− distances were analyzed during umbrella sampling of Ra2+ using the silica model with 10 dissociated silanol groups.

The projection of the distance between the Ra2+ ion and the target dissociated silanol group was constrained along the z-axis during umbrella simulations. Beyond a certain z-distance, the influence of the target silanol group on Ra2+ diminishes, allowing Ra2+ to move more freely in the x-y plane. To verify the competitive ion effect of Na+, the nearest distance between Ra2+ and a dissociated silanol group is plotted against the nearest distance between the same silanol group and a bulk Na+ ion. Similarly, to verify the complexation of Cl−, the distance between Ra2+ and the nearest Cl− ion is plotted as against the nearest distance between Ra2+ and a dissociated silanol group. Figures 3.9a and d both show an uneven distribution of distance between Ra2+ and the nearest dissociated silanol group during umbrella sampling with a z-axis constraint. Majority of the Ra2+ resides at an
overall distance of 2.5 Å with distinct minima at 3.5 Å. The boundary of 3.5 Å can be taken as the defining distance between an adsorbed Ra\(^{2+}\) and Ra\(^{2+}\) in the bulk solution.

Figure 3.9 Probability density distribution of (a) distance between Ra\(^{2+}\) to the closest dissociated silanol group (b) distance between Na\(^+\) to the same dissociated silanol groups in (a), and (c) distance between Ra\(^{2+}\) to the nearest Cl\(^-\) in the absence of additional NaCl. (d)-(f) correspond to (a)-(c) but with additional 1M NaCl.
Figure 3.9b shows that when Ra-O < 3.5 Å, the probability of finding Na⁺ at a distance < 3.2 Å is 0.05 compared to 0.32 when Ra-O > 3.5 Å in the absence of additional NaCl. The value of 3.2 Å corresponds to the minimum after the first peak in the probability density and can be taken as the defining distance between an adsorbed Na⁺ and bulk Na⁺. Na⁺ ions in the system come from the bulk cations needed to neutralize the negative silica surface. A probability of 0.05 when Ra²⁺ is adsorbed coupled with the increase in probability when Ra²⁺ is transferred to the bulk solution indicates Na⁺ is actively competing with Ra²⁺ for the same site. Figure 3.9e shows that in the presence of 1 M NaCl, the probability of finding Na⁺ at a distance less than 3.2 Å increases to 0.15 and 0.52 for Ra-O < 3.5 Å and Ra-O > 3.5 Å, respectively, because of the increase in available Na⁺ to compete for the site.

The probability of finding Cl⁻ at a distance close to Ra²⁺ is minimal without additional NaCl (see Figure 3.9c) because of the small number of chloride ions in solution. The Cl⁻ in the system comes primarily from RaCl₂. Thus, the primary reason for the decrease in free energy of adsorption of Ra²⁺ in this case is Na⁺ ion competition. When 1 M NaCl is added, Figure 3.9f shows a first peak in the Ra-Cl distance at 3.3 Å followed by a second peak at 5.3 Å. The first peak corresponds to the contact ion pair and the second corresponds to the solvent separated ion pair (Winstein et al., 1954; Ghosh et al., 2012). The probability of a having RaCl⁺ ion pair is 0.08 when Ra-O < 3.5 Å and 0.11 when Ra-O > 3.5 Å. This increase in probability is consistent with the reduction in Ra-Cl distances for the RaCl⁺ complex when far from the negative silanol surface as shown earlier in the DFT calculations. This indicates that RaCl⁺ complexes form in the presence of 1M NaCl, and these complexes contribute to the reduction. Thus, both complexation and ion
competition contribute to the decrease in free energy of adsorption of Ra\(^{2+}\) on the silica surface.

**3.4.2. Surface charge density and pH**

The zeta potential of SiO\(_2\) was a subject of several previous studies (Yukselen-Aksoy and Kaya, 2011; Rodriguez and Araujo, 2006; Xu et al., 2003) and the results were highly dependent on experimental conditions. Zeta potential directly reflects the surface charge of SiO\(_2\) (Hunter, 2013), which is largely due to deprotonation of silanol (SiOH) groups (Iler, 1979). The reported isoelectric point (IEP) (i.e., pH at which the zeta potential is zero) was in the range of 1.2-2.5 (Yukselen-Aksoy and Kaya, 2011; Rodriguez and Araujo, 2006; Xu et al., 2003), and the zeta potential as a function of pH depends on the concentration and valence of ions in the solution (Yukselen-Aksoy and Kaya, 2011). The zeta potential of silica obtained in this study is shown in Figure 3.10. The IEP at the ionic strength of 10 and 100 mM was 2.3 and 2.9, respectively, which is in agreement with previous studies. However, zeta potential at 1M ionic strength was much less negative with an IEP 4.8. Such behavior is most likely due to the presence of very high concentration of Na\(^+\) cations in the electric double layer, which results in a reduced surface charge (Chorom and Rengasamy, 1995).

![Figure 3.10 Zeta potential of silica SiO\(_2\) as a function of pH and ionic strength.](image-url)

Figure 3.10 Zeta potential of silica SiO\(_2\) as a function of pH and ionic strength.
Based on the measured zeta potential (see Figure 3.10) the surface charge density on silica particles were determined using the Gouy-Chapman model (Gouy, 1910; Chapman and Li, 1913) and is shown in Figure 3.12a. The surface charge density ranged from +0.03 to -0.18 C/m² with the silica surface becoming more negative with increasing pH due to the increased deprotonation of silanol groups. The increase in NaCl concentration in solution decreases the surface charge density due to the screening of deprotonated SiO₂⁻ groups by high concentration of Na⁺.

To relate the experimentally measured surface charge density to the silica model used, MD simulations were performed with 1-20 dissociated silanol groups in DI water (with bulk neutralizing Na⁺) and with the addition of 0.1 M and 1 M NaCl (see Figure 3.11).

The concentration of Na⁺, Cl⁻, and H₂O as a function of distance along the z-direction from the surface silanol groups is shown in Figure 3.11. The first Na⁺ peak corresponds to inner sphere surface complexes of Na⁺ with the dissociated silanol groups. This layer of Na⁺ can be considered to be tightly bound the surface and represents the start of the Stern layer (Bourg and Sposito, 2011, Tournassat et al., 2009). Integration of the total charges due to Na⁺, Cl⁻ and H₂O from the SiO₂ surface to the head of the Stern layer gives the surface charge density.

Figure 3.12 shows the surface charge density calculated from MD simulations are in the same order of magnitude as those calculated from experiments and follows the same general trends. A higher number of dissociated sites results in a more negative surface charge density, and higher ionic strength results in a less negative surface charge density.
Figure 3.11 Ion and water distribution as a function of distance from the silanol groups of the silica surface with different numbers of dissociated sites and ionic strength condition
When comparing Figure 3.12a and 3.12b, assignment of a solution pH of 2.0, 7.0, and 10.0 to 0, 10, and 20 sites by Emami et al. (2014) is justified and will be used when comparing experimental isotherms to model calculations.

![Figure 3.12 Surface charge density as a function of (a) Number of sites (b) pH.](image)

3.5 Ra\(^{2+}\) adsorption isotherms on silica

The multicomponent Langmuir isotherm model is used to describe the competitive adsorption of Ra\(^{2+}\) and Na\(^{+}\) on the silica surface,

\[
q_{Ra^{2+}} = q_{max} \frac{b_{Ra^{2+}} C_{Ra^{2+}}}{1 + b_{Ra^{2+}} C_{Ra^{2+}} + b_{Na^{+}} C_{Na^{+}}}
\]  

(3.1)

\[
q_{Na^{+}} = q_{max} \frac{b_{Na^{+}} C_{Na^{+}}}{1 + b_{Na^{+}} C_{Na^{+}} + b_{Ra^{2+}} C_{Ra^{2+}}}
\]  

(3.2)

Where \(q\) is the equilibrium surface concentration, \(q_{max}\) is the surface concentration of dissociated silanol groups, \(b\) is the Langmuir coefficient, and \(C\) is the equilibrium bulk concentration. Using the adsorption free energies (\(\Delta G\)) for both Ra\(^{2+}\) and Na\(^{+}\) in Table 3.1, the Langmuir coefficient can be calculated from (Liu, 2009)

\[
b = \frac{\exp(\frac{\Delta G}{RT})}{1 \text{mol/L}}
\]  

(3.3)
where 1 mol/L refers to the standard reference concentration, R is the universal gas constant, and T is the absolute temperature. $\Delta G$ values calculated for the different solution conditions already account for solute activity. Using the BET specific surface area of 2.82 m$^2$/g SiO$_2$ measured, $q_{max}$ is calculated based on the number of dissociated silanol groups that corresponds to the solution pH.

Figure 3.13 shows the model predictions of the isotherms agree reasonably well with the experimental data for different solution conditions. An increase in pH results in an increase in the removal of Ra$^{2+}$ from solution because of the increase in the number of dissociated silanol groups on the silica surface. An increase in ionic strength results in a decrease in the Ra$^{2+}$ removal due to Na$^+$ competition for the dissociated silanol groups and Cl$^-$ complexation with Ra$^{2+}$. This demonstrates that the modeling approach has utility in both explaining mechanisms and potential utility for predicting Ra$^{2+}$ removal from solution under different water quality conditions.

![Figure 3.13 Experimental and predicted isotherms of Ra$^{2+}$ adsorption on silica surface showing (a) the effect of solution pH (b) the effect of ionic strength.](image)
CHAPTER 4

REVISING THE SULFATE FORCE FIELD TO ACCOUNT FOR METAL-SULFATE INTERACTIONS

ABSTRACT

Force fields is considered the most significant parameter in the molecular dynamics (MD) simulations. In order to accurately predict the removal of radium by adsorption onto the surface of barite, re-parameterization of the literature sulphate force fields were performed to account for metal-sulfate interactions. Different parameters were calculated using MD and umbrella sampling simulations to evaluate metal-sulfate interactions for different Me$^{2+}$-SO$_4$ systems. In general, the calculated parameters matched the experimental data, demonstrating that the re-parametrized force fields can accurately simulate the properties of barite and celestite, and will therefore be effective for predicting the removal of radium by adsorption onto barite.

4.1. Introduction

Molecular dynamics simulations have been used to understand the mechanism of ion interaction with different molecules in chemical and biological systems (Kubiak et al., 2016). This type of simulation requires a force field that describes various properties of the atoms and molecules, including bond length, bond angle, bond dihedral angle, atomic charges, and non-bonded electrostatic and Van der Waals interactions. To obtain realistic
simulation results, the force fields are typically calibrated to reproduce thermodynamic, dynamic, and structural properties of the system of interest (Ríos-López et al., 2018).

Metal-SO$_4^{2-}$ is considered very common in the environment including water, soil, rocks, as well as industrial wastewater such as hydraulic fracturing flowback wastewater. Barite (BaSO$_4$) interacts strongly with divalent cations in solution with ionic minerals, and many studies have proved the mineral ability to remove different types of cations (Ca$^{2+}$, Sr$^{2+}$) from the solution (Sánchez-Pastor et al., 2005; YuHang et al., 2007; Hang et al., 2007; Williams, 2016; Bracco et al., 2018; Weber et al., 2018). Therefore, sulfate compounds have attracted the attention of researchers to investigate them either experimentally or theoretically.

Ionic force fields have generally been parameterized to reproduce hydration free energies. Cannon et al. (1994) first parameterized the surface force field sulfate to have a similar hydration free energy relative to xenon. Wang et al., 2004 published a general Amber force field developed primarily for biological molecules, and parameters for sulfate could be extracted using the antechamber module within the software. Williams et al. (2014) used a sulfate forcefield parameterized to structurally reproduce \textit{ab initio} calculations (Huige and Altona, 1995). They further revised this forcefield to reproduce hydration free energies (Williams and Carbone, 2015). All these force fields used harmonic bond and angle parameters and 12-6 Van der Waals’ parameters. Other recent studies involving sulfate force field parameterization include using a rigid ion force field and Buckingham non-bonded potentials to reproduce solvation free energies, water
coordination shells, and CaSO$_4$ structures, (Byrne et al., 2017), and investigating the effects of adding polarizability terms (Jungwirth et al., 2003).

A recent review paper details the development of metal ion force fields used in molecular mechanics (Li and Merz, 2017). Because of the absence of bonded terms, metal cations are typically parameterized by comparing with the solvation free energy (e.g., Mamatkulov et al., 2013). Li and co-workers (2013, 2014, and 2015) published a series of papers that demonstrated it was not possible to have a single set of metal ion forcefields that describe both hydration free energies and metal-water coordination numbers simultaneously. They suggested either using a compromise set of parameters or a revised van der Waal’s force field that account for polarizability of the ions.

As shown in Chapter 2 of this thesis, we are most interested in the removal of radium on mineral surfaces and the effect of ions on that removal. Preliminary simulations using the forcefields published in the literature were not consistent with the experimental radium removal results. We attribute this to the inadequate parameterization of the force fields to account for metal-sulfate interactions. The approach taken in this study is to revise the sulfate force field and re-parameterize the interaction of the metal parameter to fit with the barite and celestite densities and metal-sulfate association constants. This force field will then be used to predict the removal of radium by adsorption onto the surface of barite.

4.2. Simulation details

Tables 4.1 and 4.2 show the sulfate parameters used in this study that are directly compatible with the Amber force field within the Amber suite of programs. These parameters were used in the initial evaluation of metal-sulfate interactions. The total molecular charge of sulfate is -2, but there is a large variation in the partial charges assigned
to each atom of sulfate. The $\text{SO}_4$-S charge varies from +0.8 to +2.3 (which corresponds to $\text{SO}_4$-O charge varying from -0.7 to 1.075. There is less variation in the $R_{\text{min,SO}_4}$-S and $\epsilon$ but a larger variation in $R_{\text{min,SO}_4}$-O. Table 4.3 also show the recent metal parameters published by Li and Merz, (2013) and Li et al., (2013). HFE refers to parameters fitted with hydration free energy, CM refers to a compromise between fitting to hydration free energy and water coordination numbers, and 12-6-4 refers to parameters fitted to both hydration free energy and water coordination numbers but using a new $C_4$ term for van der Waals interactions (Li et al., 2013, 2015). This new potential equation is shown in equation 4.1,

$$U_{ij}(r_{ij}) = \epsilon_{ij} \left[ \left( \frac{R_{\text{min,ij}}}{r_{ij}} \right)^{12} - 2 \left( \frac{R_{\text{min,ij}}}{r_{ij}} \right)^{6} \right] - \frac{e^2 Q_i Q_j}{r_{ij}} + K_c (r-r_0)^2 + K_b (\theta-\theta_0)^2 \quad (4.1)$$

where, $e$ is the proton charge, $Q_i$ and $Q_j$ are the partial charge of two particles and $r_{ij}$ is the distance between the two particles. $R_{\text{min,ij}}$ is the distance at which two particles have a minimum in the L J potential, $\epsilon_{ij}$ is the well depth,$C_{4ij}$ is the new 12-6-4 LJ term that accounts for species polarizability.

$$C_{4,i} = \frac{C_{4ij}(\text{H}_2\text{O})}{\alpha_{\text{H}_2\text{O}}} \alpha_i \quad (4.2)$$

Table 4.1 Non-bonded force field parameters for sulfate.

<table>
<thead>
<tr>
<th>Atom(i)</th>
<th>$q_i$ (e)</th>
<th>$R_{\text{min,i}}$ (Å)</th>
<th>$\epsilon_i$ (kcal/mol)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>2.30</td>
<td>1.992</td>
<td>0.2</td>
<td>Williams et al, 2014</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>1.992</td>
<td>0.2</td>
<td>Williams and Carbone, 2015</td>
</tr>
<tr>
<td></td>
<td>1.5408</td>
<td>1.9825</td>
<td>0.282</td>
<td>Wang et al., 2004</td>
</tr>
<tr>
<td>O</td>
<td>-1.075</td>
<td>1.824</td>
<td>0.1554</td>
<td>Williams et al, 2014</td>
</tr>
<tr>
<td></td>
<td>-0.7</td>
<td>2.065</td>
<td>0.1554</td>
<td>Williams and Carbone, 2015</td>
</tr>
<tr>
<td></td>
<td>-0.8852</td>
<td>1.7107</td>
<td>0.1463</td>
<td>Wang et al., 2004</td>
</tr>
</tbody>
</table>
Table 4.2. Bonded force field parameters for sulfate.

<table>
<thead>
<tr>
<th>S-O</th>
<th>O-S-O</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_f$ (kcal/mol·Å²)</td>
<td>$r_{eq}$ (Å)</td>
<td>$k_o$ (kcal/mol·rad²)</td>
</tr>
<tr>
<td>525.5</td>
<td>1.487</td>
<td>128.2</td>
</tr>
<tr>
<td>683.03</td>
<td>1.453</td>
<td>140</td>
</tr>
</tbody>
</table>

Table 4.3. Non-bonded force field parameters for metal cations.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Method</th>
<th>$R_{min,i}$ (Å)</th>
<th>$\epsilon_i$ (kcal/mol)</th>
<th>C4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$^{2+}$</td>
<td>HFE</td>
<td>1.825</td>
<td>0.234</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>CM</td>
<td>1.980</td>
<td>0.371</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>12-6-4</td>
<td>1.937</td>
<td>0.332</td>
<td>85.8</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>HFE</td>
<td>1.520</td>
<td>0.046</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>CM</td>
<td>1.635</td>
<td>0.098</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>12-6-4</td>
<td>1.634</td>
<td>0.097</td>
<td>89.0</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>HFE</td>
<td>1.288</td>
<td>0.004</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>CM</td>
<td>1.360</td>
<td>0.010</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>12-6-4</td>
<td>1.429</td>
<td>0.021</td>
<td>122.2</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>HFE</td>
<td>1.659</td>
<td>0.112</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>CM</td>
<td>1.794</td>
<td>0.208</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>12-6-4</td>
<td>1.778</td>
<td>0.195</td>
<td>96.3</td>
</tr>
</tbody>
</table>

12-6-4, C4 from (Li and Merz, 2013), all other from (Li et al., 2013)

Different combinations of these Amber compatible force fields were tested for predicting the density of barite and celestite, the association constant of different metal sulfates, the water coordination numbers, and hydration free energy. The methods used to calculate these parameters are described in the following sections.

Density. Unit cell structures for barite and celestite were obtained from (Hill, 1977). A 4×6×5 crystal structure was built using Vesta (Momma and Izumi, 2008), and Figure 4.1 shows the final crystal configuration used in this work. Up to 100,000 steps were taken to minimize the crystal structure, followed by 0.1 ns of heating to 298 K, and 100 kPa anisotropic constant pressure screening simulations for 2.1 ns. Densities were obtained every 0.1 ns and averaged over the last 2.0 ns. Final constant pressure simulations were performed for 11 ns after force field selection. Calculation of density, unit cell parameters,
interatomic distances, and radial distribution functions were performed on configurations obtained over the last 10 ns of simulations.

![Three-dimensional model of barite and celestite mineral used in this work.](image)

**Figure 4.1** Three-dimensional model of barite and celestite mineral used in this work.

Metal Sulfate Association Constants. A system consisting of one molecule of metal sulfate surrounded by approximately 2000 molecules of SPC/E water was built using the Antechamber module of Amber (Wang et al., 2001). The system was minimized for up to 100,000 steps, heated to 298 K for 0.1 ns, and the density adjusted at a constant isotropic pressure for 1 ns. Umbrella sampling simulations were then performed where a constant spring potential was applied between the metal and SO$_4^-$ atom to keep the window centers ranging from 2.0 to 10.0 Å for 2.1 ns per window. The potential of mean force (PMF) was obtained by umbrella integration (Kästner et al., 2009) with application of the Jacobian correction (Trzesniak et al., 2007; Khavrutskii et al., 2008) and assigning a PMF value of zero at 10 Å. Final umbrella sampling simulations were performed after force field selection using 11 ns per window. Figure 4.2 shows snapshots of the umbrella sampling simulations with windows where the metal sulfate distances are large and small.
Hydration free energy. Hydration free energies have been calculated in the literature using a thermodynamic integration approach or umbrella sampling (Caleman et al., 2011; Li and Merz, 2013). An umbrella sampling approach similar to Caleman et al., 2011 was used in this work (Caleman et al., 2011). A spherical system consisting of one sulfate molecule and 1024 molecules of water was constructed. One water molecule was fixed to the center of the droplet using a force constant of 200 kcal/mol/Å². The spherical geometry was maintained by applying a parabolic force constant of 2 kcal/mol/Å² between the oxygen atom of each water molecule and the oxygen atom of the central water molecule when the distance exceeded 19.44 Å, effectively maintaining the system density at 1 g/cm³. The system was heated to 298 K for 0.1 ns, followed by umbrella sampling simulations where a constant spring potential was applied between the oxygen atom of the central water molecule and the SO₄⁻S atom to keep the window centers ranging from 12.0 to 42 Å for 2.1 ns per window. The potential of mean force was obtained by umbrella integration (Kästner et al., 2009) with application of the Jacobian correction (Trzesniak et al., 2007; Khavrutskii et al., 2008) and assigning a PMF value of zero at 42 Å. Final umbrella sampling simulations were performed after force field selection using 11 ns per window.
Figure 4.3 shows snapshots of the umbrella sampling simulations showing the central water molecule and the sulfate is outside and within the water droplet.

![Figure 4.3. Umbrella sampling snapshots where sulfate is (a) outside and (b) within the water droplet.](image)

Coordination Numbers. A system consisting of one molecule of sulfate surrounded by approximately 2000 molecules of SPC/E water was built using the Antechamber module of Amber (Wang et al., 2001). The system was minimized for up to 100,000 steps, heated to 298 K for 0.1 ns, followed by a 1 ns constant pressure run where the density was adjusted at a constant isotropic pressure of 100 kPa, followed by a final equilibration step at constant volume for 11 ns. The water coordination numbers surrounding the sulfate molecule and radial distribution functions were calculated over that last 10 ns of the equilibration step. The system is similar to Figure 4.2 but without the metal ion.

### 4.3. Results and discussion

#### 4.3.1. Assessment of current combinations of metal and sulfate force fields

Table 4.4 shows the density of barite and celestite obtained using different combination of force fields from previous studies. The reported densities for both barite and celestite deviate from the experimental values of 4.5 and 3.9-4 g/cm³, respectively (Dehairs et al., 1980; Hemmersbach and Braun, 2006; Zhang et al., 2014; Kaminskii et al., 2010; Kaminskii et al., 2011; Mackay et al., 2015; Kuang et al., 2017). The best candidates
would be the combination of the Williams et al. (2014) sulfate force field with the metal force field fitted with hydration free energy or the Wang et al. (2004) with the CM metal force field.

Table 4.4 Solid densities calculated with different sulfate and metal force field combinations.

<table>
<thead>
<tr>
<th>SO₄²⁻</th>
<th>Me²⁺</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Barite</td>
</tr>
<tr>
<td>Williams et al, 2014</td>
<td>CM&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.08</td>
</tr>
<tr>
<td></td>
<td>HFE&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.56</td>
</tr>
<tr>
<td></td>
<td>12-6-4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.21</td>
</tr>
<tr>
<td>Williams and Carbone, 2015</td>
<td>CM&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.44</td>
</tr>
<tr>
<td></td>
<td>HFE&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.81</td>
</tr>
<tr>
<td></td>
<td>12-6-4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.55</td>
</tr>
<tr>
<td>Wang et al., 2004</td>
<td>CM&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.53</td>
</tr>
<tr>
<td></td>
<td>HFE&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.13</td>
</tr>
<tr>
<td></td>
<td>12-6-4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.69</td>
</tr>
</tbody>
</table>
<sup>a</sup>Li et al., 2013; <sup>b</sup>Li and Merz, 2014

Table 4.5 shows the association constants for BaSO₄, CaSO₄, SrSO₄, and MgSO₄ obtained using various combinations of force fields. The reported values do not match with experimental values; for instance, the calculated association constant for SrSO₄ varies from 1.45-3.02 while the reported experiment values are (1.86) (Felmy et al., 1990) and (2.29) (Reardon and Armstrong 1987). And these values were not corresponding for BaSO₄, CaSO₄, and MgSO₄, which have experimental association constant values 2.72 for BaSO₄ (Felmy et al., 1990), 2.17 for CaSO₄ (Katayama, 1976), and 2.22 for MgSO₄ (Rull et al., 1994; Akilan et al., 2006). As shown in Table 4.6, the coordination number of water molecules surrounding the sulfate molecule varies from 13-15.2 for different force fields which is higher than the experimental value (less than 12) (Ohtaki and Radnai, 1993; Vchirawongkwin et al., 2007; Byrne et al., 2017). Also, the hydration free energy which is the energy released when the sulfate molecule is transferred from a fixed position in the
Table 4.5 Association constants calculated with different sulfate and metal force field combinations.

<table>
<thead>
<tr>
<th>SO_4^{2-}</th>
<th>Me^{2+}</th>
<th>log K_{assoc}</th>
<th>BaSO_4</th>
<th>CaSO_4</th>
<th>SrSO_4</th>
<th>MgSO_4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Williams et al., 2014</td>
<td>CM^a</td>
<td>1.59</td>
<td>2.98</td>
<td>2.29</td>
<td>15.36</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HFE^a</td>
<td>1.74</td>
<td>5.91</td>
<td>2.58</td>
<td>17.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12-6-4^b</td>
<td>1.76</td>
<td>2.18</td>
<td>1.73</td>
<td>8.89</td>
<td></td>
</tr>
<tr>
<td>Williams and Carbone, 2015</td>
<td>CM^a</td>
<td>1.99</td>
<td>1.72</td>
<td>1.57</td>
<td>6.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HFE^a</td>
<td>1.70</td>
<td>2.16</td>
<td>1.45</td>
<td>3.39</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12-6-4^b</td>
<td>1.47</td>
<td>1.60</td>
<td>1.68</td>
<td>1.94</td>
<td></td>
</tr>
<tr>
<td>Wang et al., 2004</td>
<td>CM^a</td>
<td>1.93</td>
<td>3.21</td>
<td>2.46</td>
<td>16.87</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HFE^a</td>
<td>2.00</td>
<td>5.52</td>
<td>3.02</td>
<td>16.74</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12-6-4^b</td>
<td>2.04</td>
<td>3.10</td>
<td>2.91</td>
<td>8.60</td>
<td></td>
</tr>
</tbody>
</table>

^aLi et al., 2013; ^bLi and Merz, 2014

Gas phase to a fixed position in water is not consistent with reported experimental values. Our method of calculation uses umbrella sampling and is different from thermodynamic integration methods in the literature.

Table 4.6 Coordination numbers and hydration free energies calculated with different sulfate force fields.

<table>
<thead>
<tr>
<th>SO_4^{2-}</th>
<th>Water Coordination Number</th>
<th>Hydration Free Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Williams et al., 2014</td>
<td>13.0</td>
<td>-235.4</td>
</tr>
<tr>
<td>Williams and Carbone, 2015</td>
<td>15.2</td>
<td>-201.0</td>
</tr>
<tr>
<td>Wang et al., 2004</td>
<td>13.0</td>
<td>-248.3</td>
</tr>
</tbody>
</table>

Based on the discrepancies between the reported literature values and experimental data, it can be concluded that the metal sulphate force fields used in these studies will be inadequate for future calculations of metal adsorption onto barite. The approach taken in this study is to revise the sulfate force field and re-parameterize the interaction of the metal parameter to fit with the barite and celestite densities and metal-sulfate association constants. Obtaining an accurate mineral structure coupled with metal sulfate interaction is critical for describing metal adsorption onto barite.
4.3.2 Revising the sulfate force field

The development and parametrization of accurate force fields requires the use of appropriate force field equations and initial parameters. In this study, the 12-6-4 force field equation will be used to describe the interactions between the Me\(^{2+}\)-SO\(_4\) systems. The 12-6-4 uses an additional C\(_4\) term that can be used to calibrate metal-sulfate interactions in a manner similar to Panteva et al. (Panteva et al., 2015). The approach taken was to vary the sulfate force field, by keeping the bonded terms of Williams et al., 2014 and Williams and Carbone (2015) in Table 4.2, as well the non-bonded van der Waal’s sulfur terms in Table 4.1. The sulfur charge (and hence oxygen charge), R\(_{\min,O}\), \(\epsilon_O\), and \(\alpha_O\) was varied.

A full factorial set of calculations were used to calculate barite and celestite densities over a range of sulfur charge (1.4, 1.7, 2.0, and 2.3), R\(_{\min,O}\) (1.71, 1.74, 1.77, 1.80, and 1.83), \(\alpha_O\) (0.6, 0.9, 1.2, and 1.5) and \(\epsilon_O\) (0.135, 0.145, 0.155, and 0.165). Figure 4.4 shows a slight decrease in densities with increasing sulfur charge. Although an increase in sulfur charge coincides with a more negative SO\(_4\)-O charge which should result in more electrostatic attraction between the Ba\(^{2+}\) and Sr\(^{2+}\), the increased repulsion among the more numerous SO\(_4\)-O results in an overall lower density. The densities for both metals decrease with increasing Lennard-Jones R\(_{\min,O}\) and \(\epsilon_O\) parameters. Analyzing only the interaction between Ba\(^{2+}\)/Sr\(^{2+}\) atoms and negative SO\(_4\)-O, equation (4.1) results in barite and celestite structures dominated by the electrostatic attraction. Furthermore, considering that the
Figure 4.4 Densities calculated with different sulfur charges and VDW $R_{\text{min}}$ for (a) barite and (b) celestite, respectively for $\alpha=1.2$ Å$^3$, $\epsilon=0.155$ kcal/mol. Densities calculated with different $\alpha$ and epsilon for (c) barite and (d) celestite, respectively for $S_{\text{charge}}=2$ e, $R_{\text{min}}=1.74$ Å.

Experimental distances between the nearest Ba$^{2+}$/Sr$^{2+}$ atoms and negative SO$_4$-O atoms are between 2.7 and 2.5 Å for barite and celestite, the Lennard Jones parameters in equation (4.1) are repulsive in this region. Increasing $\epsilon_O$ decreases the electrostatic attraction and decreases the density. Increasing $R_{\text{min,O}}$ shifts the Lennard Jones curve to the right, thereby increasing repulsion in the region and decreasing the density. Density is relatively insensitive to $\alpha_O$ because the overall contribution of the 4th term in equation (4.1) is small in the region.

A generalized linear regression analysis was performed based on the results from Figure 4.4 and the following equations were obtained relating the barite and celestite densities to different parameters.
Barite density=10.35-3.094 R_{min}-0.06 S_{charge}-2.352\epsilon+0.00000250\alpha \quad (4.3)
Celestite density=9.604-3.094 R_{min}-0.0755 S_{charge}-2.188\epsilon+0.0000121\alpha \quad (4.4)

Based on the above regression models, the barite and celestite densities are sensitive to the R_{min}, S_{charge}, and \epsilon parameters but insensitive to \alpha parameter. Thus, the value of alpha (\alpha) in both equations is not critical which provides flexibility in using this parameter to fit the association constants. The above regression models are be used to initiate the development of a new set of force field parameters. Using the experimental densities of 4.5 and 3.98 g/cm^3 for barite and celestite, respectively and specifying values for \epsilon, the corresponding values of R_{min} and S_{charge} were calculated as shown in Table 4.7. The parameters presented in the table indicate the range of unbonded sulfate force field parameters that satisfy barite and celestite density for the specified \epsilon values. As observed from the table, the different values of \epsilon produces a tight range of values for R_{min} and S_{charge}.

Table 4.7 Range of Unbonded Sulfate Force Field Parameters that Satisfy Barite and Celestite Density.

<table>
<thead>
<tr>
<th>Case</th>
<th>R_{min} (Å)</th>
<th>S_{charge} (e)</th>
<th>\epsilon (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.747</td>
<td>2.116</td>
<td>0.135</td>
</tr>
<tr>
<td>2</td>
<td>1.743</td>
<td>2.132</td>
<td>0.140</td>
</tr>
<tr>
<td>3</td>
<td>1.739</td>
<td>2.149</td>
<td>0.145</td>
</tr>
<tr>
<td>4</td>
<td>1.735</td>
<td>2.166</td>
<td>0.150</td>
</tr>
<tr>
<td>5</td>
<td>1.731</td>
<td>2.182</td>
<td>0.155</td>
</tr>
<tr>
<td>6</td>
<td>1.727</td>
<td>2.199</td>
<td>0.160</td>
</tr>
<tr>
<td>7</td>
<td>1.723</td>
<td>2.216</td>
<td>0.165</td>
</tr>
</tbody>
</table>

In this section, we present the PMF obtained from umbrella sampling calculations and the calculated association constants for the different Me^{2+}-SO_4 systems. Figure 4.5 shows representative sample PMF curves for BaSO_4, CaSO_4, MgSO_4 and SrSO_4 as a function of the distance between Me^{2+} and SO_4-S. In general, the PMF curves indicate a series of local minima is observed. The PMF is flat at large distances from surface.
(Approaching 10 Å), indicating negligible interaction between the Me\(^{2+}\) and SO\(_4\)\(^{-}\). A negative PMF indicates attraction while a positive PMF represents repulsion relative to the free energy at a separation of 10 Å.

Figure 4.5 Potential of mean force for (a) BaSO\(_4\) (b) CaSO\(_4\) (c) MgSO\(_4\) (d) SrSO\(_4\) for case 4 in Table 4.7 as a function of the distance between Me\(^{2+}\) and SO\(_4\)\(^{-}\).

Association constants are calculated based on the Me\(^{2+}\)-SO\(_4\) free energies from the umbrella sampling simulations. The association constants obtained using the same alpha values for the sulphates did not indicate a good fit. In a related study involving the 12-6-4 force field, researchers varied the C4 parameter in the AMBER force fields to obtain better fits. Based on this, the C4 parameter between the SO\(_4\) and Me\(^{2+}\) was varied to obtain optimum fits for the association constants. In calculating the values for C4 using equation
the alpha parameter was estimated using the regression models and the values specified in Table 4.7.

Figure 4.6 shows the association constants for the $\text{Me}^{2+}$-$\text{SO}_4$ systems calculated with varying values of $C_4$ for the different cases in Table 4.7 The left figures show the association constants for the range of $C_4$ investigated while the right figures represent a blown out section for the $C_4$ range of interest. Some cases are point estimates where the association constant was calculated with short 2 ns umbrella sampling windows. In the points where a standard deviation is shown, the mean represents the association constant calculated with 10 ns windows while the standard deviation comes from calculations of the association constant with the same simulations divided into five 2 ns umbrella windows. In general, higher values of $C_4$ produces higher association constants for the different cases. Considering the standard deviations of the association constants in Table 4.8, these values are within the experimental data. The case of $\text{MgSO}_4$ is still problematic, with extremely large variation in the association constants. This is due to the sharpness of the peaks in the PMF around 3.8 Å in Figure 4.6c, causing a relatively large variation in the PMF with corresponding variations in the association constant calculations. In order to assess the accuracy of the force fields parameters, the parameters were used in simulations to calculate the association constants, density, coordination number, hydration free energy, and unit cell dimension and compared with experimental data.
Figure 4.6 Association constants for (a and b) BaSO$_4$, (c and d) CaSO$_4$, (e and f) MgSO$_4$ and (g and h) SrSO$_4$ calculated with varying C$_4$ values for the different cases of unbonded sulfate parameters in Table 4.7.
Table 4.8 Mean (Standard Deviation) of Associated Constants and C₄ Values for Different Cases of Unbonded Sulfate Parameters in Table 4.7.

<table>
<thead>
<tr>
<th>Case</th>
<th>BaSO₄</th>
<th>SrSO₄</th>
<th>CaSO₄</th>
<th>MgSO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \log K_{assoc} )</td>
<td>( C_4 )</td>
<td>( \log K_{assoc} )</td>
<td>( C_4 )</td>
</tr>
<tr>
<td>1</td>
<td>2.62  (0.16)</td>
<td>116.5</td>
<td>2.37  (0.18)</td>
<td>73.2</td>
</tr>
<tr>
<td>2</td>
<td>2.61  (0.20)</td>
<td>117.6</td>
<td>2.28  (0.23)</td>
<td>68.0</td>
</tr>
<tr>
<td>3</td>
<td>2.60  (0.23)</td>
<td>116.5</td>
<td>2.28  (0.31)</td>
<td>70.0</td>
</tr>
<tr>
<td>4</td>
<td>2.62  (0.20)</td>
<td>118.3</td>
<td>2.26  (0.22)</td>
<td>68.4</td>
</tr>
<tr>
<td>5</td>
<td>2.69  (0.12)</td>
<td>118.8</td>
<td>2.21  (0.14)</td>
<td>61.7</td>
</tr>
<tr>
<td>6</td>
<td>2.68  (0.03)</td>
<td>117.6</td>
<td>2.39  (0.06)</td>
<td>68.0</td>
</tr>
<tr>
<td>7</td>
<td>2.63  (0.08)</td>
<td>117.6</td>
<td>2.21  (0.16)</td>
<td>68.0</td>
</tr>
</tbody>
</table>

Using the best fit C₄ parameters and the unbonded sulfate parameters in Table 4.7, the barite and celestite densities were computed for the Me²⁺-SO₄ systems. As presented in Table 4.9, the calculated barite density matches the experimental density of 4.5 g/cm³ in all cases. For the case of the celestite, the calculated density varies between 3.97-3.98 g/cm³, which is close to the target experimental density of 3.9-4.0 g/cm³ (Kaminskii et al., 2010; Kaminskii et al., 2011; Mackay et al., 2015; Kuang et al., 2017), indicating the appropriateness of the developed force fields for Me²⁺-SO₄ simulations.

To further demonstrate the accuracy of the developed force fields, the unit cell dimensions from the simulations were compared with experimental unit cell data for barite and celestite. Table 4.10 shows the average of the unit cell dimensions for the different cases of unbonded sulfate parameters. As seen from the table, the unit cell dimensions for both barite and celestite match the experimental data indicating the effectiveness of the developed force fields. The radial distribution function (RDF) for Ba-O_SO₄ and S_SO₄-O_SO₄
were generated to further study the cation structure around the $\text{SO}_4^{2-}$ for both barite and celestite. For barite, the first peak distance for $\text{Ba-O}_{\text{SO}_4}$ occurs around 2.785 Å, while the first peak distance for $\text{S}_{\text{SO}_4}$-$\text{O}_{\text{SO}_4}$ occurs around 1.468 Å as shown in Figure 4.7 (a and b). In the case of celestite, the first peak distance for $\text{Sr-O}_{\text{SO}_4}$ occurs at 2.61 Å and the peak for $\text{S}_{\text{SO}_4}$-$\text{O}_{\text{SO}_4}$ occurs at 1.46 Å as shown in Figure 4.7 (c and d).

The interatomic distances for $\text{Ba-O}_{\text{SO}_4}$ and $\text{S}_{\text{SO}_4}$-$\text{O}_{\text{SO}_4}$ were also computed and compared to experimental data to assess the accuracy of the structures. Figure 4.8 a and b shows the comparison between model and experimental distances for $\text{Ba-O}_{\text{SO}_4}$, $\text{S}_{\text{SO}_4}$-$\text{O}_{\text{SO}_4}$ in barite. As shown, the calculated interatomic distances are consistent with the experimental distances; for $\text{Ba-O}_{\text{SO}_4}$, the first calculated distance is 2.73 Å, which compares well with the experimental distance of 2.765 Å. In the case of $\text{S}_{\text{SO}_4}$-$\text{O}_{\text{SO}_4}$, the first pair of calculated and experimental distances are 1.45 and 1.462 Å, respectively (Hill, 1977).

Table 4.9 Mean (Standard Deviation) of Barite and Celestite Densities for Different Cases of Unbonded Sulfate Parameters in table 4.7 and C4 values in table 4.8.

<table>
<thead>
<tr>
<th>Case</th>
<th>Density (g/cm$^3$)</th>
<th>Barite</th>
<th>Celestite</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.50 (0.00)</td>
<td>3.98 (0.00)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4.50 (0.00)</td>
<td>3.98 (0.00)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4.50 (0.00)</td>
<td>3.98 (0.00)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4.50 (0.00)</td>
<td>3.98 (0.00)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4.50 (0.00)</td>
<td>3.98 (0.00)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>4.50 (0.00)</td>
<td>3.97 (0.00)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>4.50 (0.00)</td>
<td>3.97 (0.00)</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.10 Unit cell dimensions for barite and celestite in Angstroms.

<table>
<thead>
<tr>
<th>Axis</th>
<th>Barite</th>
<th>Celestite</th>
<th>Model$^a$</th>
<th>Experimental</th>
<th>Model$^a$</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>8.89 (0.00)</td>
<td>8.8842$^d$</td>
<td>8.38 (0.00)</td>
<td>8.371$^b$, 8.3545$^c$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>y</td>
<td>5.46 (0.00)</td>
<td>5.4559$^d$</td>
<td>5.37 (0.00)</td>
<td>5.355$^b$, 5.3458$^c$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>z</td>
<td>7.10 (0.00)</td>
<td>7.1569$^d$</td>
<td>6.82 (0.00)</td>
<td>6.870$^b$, 6.8671$^c$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Average of the different cases of unbonded sulfate parameters in table 4.7 and C4 values in table 4.8. 

Figure 4.7 Radial distribution function for (a) Ba-O\textsubscript{SO\textsubscript{4}} (b) S\textsubscript{SO\textsubscript{4}}-O\textsubscript{SO\textsubscript{4}} in barite (c) Sr-O\textsubscript{SO\textsubscript{4}} (d) S\textsubscript{SO\textsubscript{4}}-O\textsubscript{SO\textsubscript{4}} in celestite for different cases of unbonded sulfate parameters in table 4.7 and C4 values in table 4.8.

Figure 4.8 c and d shows the comparison between theoretical and experimental distances for Sr-O\textsubscript{SO\textsubscript{4}} and S\textsubscript{SO\textsubscript{4}}-O\textsubscript{SO\textsubscript{4}} in celestite with experimental distances taken from Miyake et al. 1978. In both cases for barite and celestite, the theoretical interatomic distances were consistent with experimental distances indicating that the proposed forcefields can accurately simulate the structures of barite and celestite.

Water structure surrounding SO\textsubscript{4}\textsuperscript{2\textsuperscript{−}} was investigated and presented as RDFs in Figure 4.9 The first peak of the S–O\textsubscript{w} radial distribution function is observed around 3.7
Å, which is in the range of 3.7-3.9 Å as estimated by X-Ray diffraction studies (Ohtaki and Radnai, 1993; Byrne et al., 2017). The distance for $O_{SO4}-H_w$ was approximately 1.66 Å.

Figure 4.8 Comparison of model and experimental distances for (a) Ba-$O_{SO4}$ (b) $S_{SO4}-O_{SO4}$ in barite (c) Sr-$O_{SO4}$ (d) $S_{SO4}-O_{SO4}$ in celestite.

Figure 4.9 Radial distribution function for (a) $S_{SO4}-O_w$ (b) $O_{SO4}-H_w$ for different cases of unbonded sulfate parameters in table 4.7.
Table 4.11 shows the mean and standard deviation and mode of coordination numbers for the seven cases for two conditions. The first condition depends on the interaction between the sulfur of the sulfate and the oxygen of the water (S\textsubscript{SO4}-O\textsubscript{w}) while the second depends on the interaction between the oxygen of the sulfur and hydrogen of the water (O\textsubscript{SO4}-H\textsubscript{w}). In all cases, the CN indicate a tight standard deviation and the mean CNs are consistent with experimental CNs (Vchirawongkwin et al., 2007) which validates the performance of the proposed force fields.

Table 4.11 Water Coordination Number Calculated for Different Cases of Unbonded Sulfate Parameters in Table 4.7.

<table>
<thead>
<tr>
<th>Case</th>
<th>S\textsubscript{SO4}-O\textsubscript{w}</th>
<th>O\textsubscript{SO4}-H\textsubscript{w}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean (stdev)</td>
<td>mode</td>
</tr>
<tr>
<td>1</td>
<td>13.02 (0.84)</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>12.93 (0.83)</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>12.94 (0.83)</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>13.02 (0.86)</td>
<td>13</td>
</tr>
<tr>
<td>5</td>
<td>12.92 (0.83)</td>
<td>13</td>
</tr>
<tr>
<td>6</td>
<td>12.95 (0.85)</td>
<td>13</td>
</tr>
<tr>
<td>7</td>
<td>12.83 (0.81)</td>
<td>13</td>
</tr>
</tbody>
</table>

Figure 4.10 shows the PMF obtained from umbrella sampling simulations to estimate the hydration free energy. As indicated, the PMF flattens out as SO\textsubscript{4}-S moves further away from the center of the water sphere. The corresponding hydration free energies for different cases of unbonded sulfate parameters are presented in Table 4.12. The results vary from −248.6 ± 0.69 to −250.9 ± 0.94 kcal/mol which is within the limits of 233 to 260 kcal/mol reported by Marcus (1994) and as referenced by Byrne et al. (Byrne et al., 2017). Noting that we obtained a sulfate free energy of 201 using the parameters of Williams and Carbone (2015) that was specifically calibrated force field to replicate the lower value of 233 kcal/mol using thermodynamic integration, it is likely that the same methods using our force field parameters would severely overestimate the sulfate hydration.
free energy. Our objective was not to explicitly fit the hydration free energy, but to obtain force field parameters that better describe metal-sulfate interaction that can be used to evaluate removal of radium on the surface of barite, as described in the previous Chapter.

Figure 4.10 Potential of mean force of hydration free energy for case 4 in table 4.8 as a function of the distance between SO$_4^-$ and the center of the water sphere.

Table 4.12 Hydration free energy calculated for number calculated for different cases of unbonded sulfate parameters in table 4.7.

<table>
<thead>
<tr>
<th>Case</th>
<th>Hydration Free Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-248.6 (0.69)</td>
</tr>
<tr>
<td>2</td>
<td>-248.7 (0.65)</td>
</tr>
<tr>
<td>3</td>
<td>-248.8 (0.62)</td>
</tr>
<tr>
<td>4</td>
<td>-248.9 (0.55)</td>
</tr>
<tr>
<td>5</td>
<td>-250.1 (0.55)</td>
</tr>
<tr>
<td>6</td>
<td>-250.9 (0.77)</td>
</tr>
<tr>
<td>7</td>
<td>-250.9 (0.94)</td>
</tr>
</tbody>
</table>
CHAPTER 5

ELUCIDATING MECHANISMS OF RADIUM ADSORPTION ON BARITE SURFACE USING MOLECULAR SIMULATIONS

ABSTRACT

Adsorption of different cations onto three barite surfaces (100, 010, and 001) were investigated using molecular simulations. The free energy of adsorption obtained from umbrella sampling simulations indicate that 100 is the most desirable surface for adsorption to occur. Further simulations were conducted to evaluate the adsorption of radium onto the surfaces in the presence of different salts (BaCl$_2$, CaCl$_2$, SrCl$_2$, MgCl$_2$, and NaCl) and different concentrations (DI, 0.1M, and 1M). Radium removal decreased significantly with increasing ionic strength due to ions competition and complexation mechanisms. Isotherm predictions based on the multi-component Langmuir model follows the expected trend for CaCl$_2$ and MgCl$_2$ solutions but not BaCl$_2$, SrCl$_2$, and NaCl solutions. The discrepancy is attributed to the inconsistent differences in the magnitudes of the free energies calculated from the simulation.

5.1. Introduction

Radium is considered one of the most significant element of naturally occurring radioactive materials (NORM) and generated by its parent isotopes ($^{227}$Th, $^{228}$Th, $^{230}$Th, $^{232}$Th) which
is originally generated from the decay of the most common radioactive elements in the earth (uranium and thorium). Radium has a half-time of approximately 1600 years (Webster et al., 1995) with high concentration in hydraulic fracturing wastewater thereby making it fall outside of the wastewater disposal standards (Rowan et al., 2011; US EPA, 2016; Geltman and LeClair, 2017). These reasons necessitate the need to study the mechanism of radium removal to understand its fate under environmental conditions.

Barite is the most prevalent barium containing mineral in the earth crust. It has numerous effects on the environment and industries due to its structure, availability, and reactivity. For instance, the long-term radium sequestration and scaling inside pipelines by barite layer in hydraulic fracturing (Frenier and Ziauddin, 2008; Curti et al., 2010).

Hydraulic fracturing wastewaters has high concentrations of radium, barium, strontium, and salinity. These conditions enhance radium removal by co-precipitation mechanism with barium or other alkaline element in the ternary solution (Doerner and Hoskins, 1925; Gordon and Rowley, 1957; Zhang et al., 2014; Brandt et al., 2015). This mechanism includes three sub-essential mechanisms (adsorption, occlusion, and inclusion) and caused by both prompt barite nucleation and similarity of ionic radii of $\text{Ra}^{2+}$ and $\text{Ba}^{2+}$ (Zhang et al., 2014; Brandt et al., 2015). In addition, Barite has different surfaces, however, according to Wulff’s construction, barite $\{210\}$ and $\{001\}$ are considered the most stable surfaces (Redfern and Parker, 1998; Geysermans and Noguera, 2009). These reasons motivated us to investigate the ability of barite for radium removal.

The objective of this study is to understand the mechanisms of adsorption of radium onto barite using molecular dynamics (MD) simulations associated with Langmuir multi-components model and comparing the generated model isotherms with experimental
isotherms. Moreover, all simulations and experiments will be performed under different ionic strength to evaluate its effect on adsorption. This ionic strength represents the extreme ranges reported in the literature.

5.2. Simulation details

The sulfate forcefields used in this study were obtained from Table 4.7 of the previous Chapter. Because of the similarity of densities, association constants, hydration free energies, and coordination numbers calculated from the different cases, the forcefield for case 4 was arbitrarily selected. This forcefield also had a value for the $C_4$ term of MgSO$_4$. The cation and anion 12-6-4 forcefields were obtained from Li and co-workers (2014, 2015). Since Ra$^{2+}$ was not explicitly parameterized for the 12-6-4 forcefield and Li et al (2013) assigned the same force field for Ra$^{2+}$ and Ba$^{2+}$ for the HFE and CM cases, the 12-6-4 forcefield for Ba$^{2+}$ was used but revised to account for the difference in Ra$^{2+}$ polarity. Using high level ab initio (perturbed relativistic coupled cluster theory) calculations, Chattopadhyay et al (2013) showed similar static dipole polarizabilities of Ba$^{2+}$ reported by Li et al. (2013). The value of $\alpha_{Ra^{2+}} = 1.911$ reported by Chattopadhyay et al (2013) is used in this work.

The unit cell structure for barite was obtained from Hill (1977) and three identical 4×6×5 crystal structures was initially built using Vesta (Momma and Izumi, 2008). One half layer of a unit cell layer was removed along one axis (i.e., x, y, and z) for each structure to preserve crystal symmetry perpendicular to the 100, 010, and 001 planes. The coordinates of each atom dimension parallel to each plane was adjusted to dimensions that would correspond to a crystal with unit cell dimensions shown in Table 4.10 from the previous Chapter. Each crystal structure was solvated with 5555 SPC/E water molecules.
and with different metal chlorides at concentrations corresponding to 0M 0.1M and 1M using Packmol (Martínez et al., 2003, 2009). The volume of the salt solution was kept constant at the corresponding experimental density (Fabus et al., 1966; Isono, 1984).

The hydrated barite structure was minimized at a constant volume for up to 100,000 steps to remove bad contacts and heated to 298 K for 0.1 ns at a constant volume with the barite molecules held at their initial positions using a force constant of 20 kcal/mol/Å². A constant volume equilibration run was performed for 1 ns prior to umbrella sampling simulations. A final constant volume equilibration run was performed for 11 ns, with trajectory information extracted from the last 10 ns for analysis of density and charge distribution.

Umbrella sampling simulations with a single NaCl or MeCl₂ in solution (Me = Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺) with 0, 0.1M, and 1M NaCl or MeCl₂. Similar calculations were performed with a single RaCl₂ in the presence of the same concentrations of these salts. A constant spring potential was applied between the metal and the first layer of the SO₄⁻S atoms perpendicular to the 100, 010, or 001 surfaces to keep the window centers ranging from 1.0 to 12.0 Å for 11 ns per window. The potential of mean force (PMF) was obtained by umbrella integration (Kästner et al., 2009) assigning a PMF value of zero at 10 Å.

Adsorption Experiments. The experiments reported in this dissertation were performed by collaborators at the University of Pittsburgh. Similar to Section 3.3.1, adsorption of Ra²⁺ on barite was performed using the standard bottle point technique. Different masses of barite were added to 50 mL of a 12,463 pCi/L RaCl₂ solution containing different metal chloride salt solutions. The solution pH was adjusted to 8.0 by
adding HCl and/or NaOH. Samples were mixed for 24 hours in a horizontal shaker. 10 mL of each sample was filtered through 0.45 µm mixed cellulose esters membrane (Millipore, Billerica, MA) to separate silica solids from aqueous solution and the Ra-226 concentration was analyzed using Liquid Scintillation Counter (LSC, LS 6500, Beckman Coulter, Brea, CA).

Adsorption Isotherm Calculations. The multicomponent Langmuir isotherm model is used to describe the competitive adsorption of Ra\(^{2+}\), Ba\(^{+}\), and other counterions on the silica surface,

\[
q_{Ra^{2+}} = q_{\text{max}} \frac{b_{Ra^{2+}} C_{Ra^{2+}}}{1 + b_{Ra^{2+}} C_{Ra^{2+}} + b_{Ba^{2+}} C_{Ba^{2+}} + b_{Me} C_{Me}} \tag{5.1}
\]

\[
q_{Ba^{2+}} = q_{\text{max}} \frac{b_{Ba^{2+}} C_{Ba^{2+}}}{1 + b_{Ra^{2+}} C_{Ra^{2+}} + b_{Ba^{2+}} C_{Ba^{2+}} + b_{Me} C_{Me}} \tag{5.2}
\]

\[
q_{Me} = q_{\text{max}} \frac{b_{Me} C_{Me}}{1 + b_{Ra^{2+}} C_{Ra^{2+}} + b_{Ba^{2+}} C_{Ba^{2+}} + b_{Me} C_{Me}} \tag{5.3}
\]

where \(q\) is the equilibrium surface concentration, \(q_{\text{max}}\) is the surface concentration of dissociated silanol groups, \(b\) is the Langmuir coefficient, and \(C\) is the equilibrium bulk concentration. A triple component system is required because the solubility product of BaSO\(_4\) adds Ba\(^{2+}\) ions to solution. For simplicity, ionic strength effects are neglected, and the Ba\(^{2+}\) in solution due to BaSO\(_4\) dissolution is set at \(10^{-5}\)M. Equation 3.1 is used to relate free energies calculated from molecular dynamics simulations to the Langmuir b coefficient.
5.3. Results and discussion

5.3.1. Free energy of adsorption

The PMF obtained from umbrella sampling calculations is a potential energy surface (Truhlar, 1992) that clarify the interaction of different cations with various barite surfaces (100, 101, 001) as showed in Figure 5.1. Surface adsorption mechanism was studied initially to understand and investigate the potentially of their removal onto various surfaces where the cations interact directly onto barite surface.

Figure 5.1a shows the potential mean force of six cations (Ba\(^{2+}\), Ca\(^{2+}\), Mg\(^{2+}\), Ra\(^{2+}\), Sr\(^{2+}\), and Na\(^{+}\)) onto 100 barite surface in DI water. The PMF graph for Mg\(^{2+}\) shows that there is no interaction between the cation and the barite surface. while (Ra\(^{2+}\), Ba\(^{2+}\), Sr\(^{2+}\), Ca\(^{2+}\), and Na\(^{+}\)) have interaction energies \(-32.7\), \(-29.4\), \(-25.6\), \(-19.9\), \(-15.6\) kcal/mol respectively. This indicates that radium has the most removal opportunity due to the more negative value of its interaction energy. Figure 5.1b shows that in general there is no interaction between all six minerals and (010) barite surface and all PMF curves are very shallow. Figure 5.1c shows the interaction of the six metals with (001). The curves show that the magnesium will not adsorb due to its shallow PMF curve, while radium has the most opportunity to adsorb due to its deep PMF curve (\(-18.9\) kcal/mol). To elucidate the behavior of the divalent (Ba\(^{2+}\), Sr\(^{2+}\), Mg\(^{2+}\), Ca\(^{2+}\)) on the same surface, the potential mean force with different Lennard-Jones force fields and ionic mass were computed as shown in Figure 5.2. Figure 5.2a shows that varying the mass of ions while keeping the same Lennard-Jones forcefield for Ba\(^{2+}\) the same for all cases does not have impact on the interaction energy. Figure 5.2b shows that keeping the mass of Ba\(^{2+}\) the same while varying the Lennard-Jones forcefield parameters to corresponds to the values of Mg\(^{2+}\), Ca\(^{2+}\), Sr\(^{2+}\),
and \( \text{Ba}^{2+} \) had an impact on the PMF. Barium has the most negative PMF value -29.55 kcal/mol followed by strontium -25.5, calcium -19.29, and magnesium -1.85 respectively, which is consistent with the order of the interaction energy of the divalent cations in Figure 5.1. Thus, since the charges of the divalent cations are the same, differences in the Lennard Jones parameters, which account for the atomic radius and van der Waal’s interactions, dictate the strength of adsorption on barite.

![Figure 5.1 Potential of mean force (PMF) for different cations onto different barite surfaces for (a) 100, (b) 010, (c) 001 in DI water.](image)

Figure 5.3 shows charge density curves obtained with different surfaces and solution conditions. The curves show the charge density as a function of distance of the ion

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85
Figure 5.2 Potential of mean force (PMF) for different (a) Ionic mass (b) Lennard Jones forces for different cations onto 100 barite surface in DI water.

Figure 5.3 Charge density for different ions onto different barite surfaces. (a)100 (b) 010 (c) 001 in DI, while (d)100 (e) 010 (f) 001 in 0.1M concentration.
with the first SO$_4$-S layer of the barite surface along the z-direction. A negative value of the charge density indicates negative charge while a positive value represents positive.

Figure 5.4 shows the mass density of ions and water as a function of distance from the first SO$_4$-S layer of the barite surface along the z-direction for various barite surfaces and solution conditions. The curves are plateau at large distances from the barite surface (approaching 7 Å), which constitute the bulk solution. There is a structuring of ions and water near the surface, with the critical distance of 2 to 3 Å, corresponding to the optimum PMF in Figure 5.1. At this critical distance, Figure 5.4 a, b, and c shows the peak barium ion densities are 0.72, 0.0, and 0.169 g/cm$^3$ respectively for 100, 010, and 001 barite surfaces in a 0.1M BaCl$_2$ salt concentration. The peak increases to 3.24, 0.44, and 0.77 g/cm$^3$ respectively in Figure 5.4 d, e, and f for a 1M BaCl$_2$ solution. This confirms that the 100 barite surface 100 is most attractive to the cations, followed by the 001 and the 100 surfaces.

Figure 5.5 shows the average densities of the solution components over the average barite structure for different barite surfaces with a 1M BaCl$_2$ solution. In Figure 5.5a, barium is located near the surface due to high negativity of the surface. Figure 5.5b shows that barium is farther from the surface because the neutral charge of the surface reduces electrostatic interaction with the barium. Figure 5.5c, barium has a similar distance from the surface as Figure 5.5a but has a lower density overall.

Figure 5.6 shows the potential mean force for radium onto (001) barite surface in DI, 0.1M, and 1M salt solution (BaCl$_2$, CaCl$_2$, SrCl$_2$, MgCl$_2$, and NaCl). In Figure 5.6a, b, and c, the PMF show that radium has the most interaction with the barite surface followed by 0.1M and 1M salt concentrations. For example, in Figure 5.6a, the minimum
potential mean force of radium with barite surface is -18.97 kcal/mol and this decreased to -15.4 and -14.5 kcal/mol for 0.1M and 1M SrCl$_2$ respectively. The reason of this reduction

Figure 5.4 Mass density for different ions onto different barite surfaces. (a)100 (b) 010 (c) 001 in 0.1M concentration, while (d)100 (e) 010 (f) 001 in 1M concentration.
Figure 5.5 Average structures barite (a) 100 (b) 010 (c) 001 side view with 1M BaCl$_2$ concentration. The barite is represented with CPK models with red oxygen atoms, pink barium atoms. The blue clouds are water-hydrogen, red is water-oxygen, and white is barium in the solution.

is complexation and ion competition for the surface, as discussed in Chapter 3, with increasing effects at higher salt concentrations. However, Figures d and e show that higher concentrations result in the opposite effect where Ra$^{2+}$ appears to adsorb stronger at higher BaCl$_2$ and NaCl concentrations. The reason is not clear at this point. It is possible that longer simulations have to be performed to obtain a fully converged PMF.
Table 5.1 shows the mean and standard deviation of the free energies of adsorption. The table elucidate that the interaction of radium or barium with barite surface will be reduced due to ionic strength. The mean reason of this reduction is the complexation and competition mechanism as illustrated in Chapter 3. Values in this table are used to calculate the Langmuir b coefficient (equation 3.3), which is then used in the multi-component isotherm equations (5.1 to 5.3).

Figure 5.6 Potential of mean force (PMF) of Radium onto (001) barite surface with different salts and concentrations in the solution (a) BaCl$_2$ (b) CaCl$_2$ (c) SrCl$_2$ (d) MgCl$_2$ (e) NaCl.
Table 5.1 Mean (standard deviation) of free energy of adsorption of Ra\(^{2+}\)/Ba\(^{2+}\) and cations on (001) barite surface with different salt concentrations. Units are in kcal/mol

<table>
<thead>
<tr>
<th>Filename</th>
<th>Mean</th>
<th>stdev</th>
<th>Filename</th>
<th>Mean</th>
<th>stdev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra(^{2+}) adsorption in DI water</td>
<td>-19.0</td>
<td>2.3</td>
<td>Ra(^{2+}) adsorption in the presence of 0.1 M of salt</td>
<td>BaCl(_2)</td>
<td>-11.8</td>
</tr>
<tr>
<td>Ba(^{2+}) adsorption in DI water</td>
<td>-17.0</td>
<td>1.9</td>
<td></td>
<td>CaCl(_2)</td>
<td>-15.7</td>
</tr>
<tr>
<td>Ra(^{2+}) adsorption in the presence of 0.1 M of salt</td>
<td>MgCl(_2)</td>
<td>-15.6</td>
<td>1.8</td>
<td>MgCl(_2)</td>
<td>-15.7</td>
</tr>
<tr>
<td>Ba(^{2+}) adsorption in the presence of 0.1 M of salt</td>
<td>NaCl</td>
<td>-12.5</td>
<td>2.2</td>
<td>NaCl</td>
<td>-18.3</td>
</tr>
<tr>
<td>Ba(^{2+}) adsorption in the presence of 1 M of salt</td>
<td>SrCl(_2)</td>
<td>-15.4</td>
<td>1.4</td>
<td>SrCl(_2)</td>
<td>-14.2</td>
</tr>
<tr>
<td>Ca(^{2+}) with CaCl(_2)</td>
<td>-4.7</td>
<td>0.8</td>
<td>Ca(^{2+}) with CaCl(_2)</td>
<td>BaCl(_2)</td>
<td>-8.8</td>
</tr>
<tr>
<td>Mg(^{2+}) with MgCl(_2)</td>
<td>-0.2</td>
<td>0.2</td>
<td>Mg(^{2+}) with MgCl(_2)</td>
<td>CaCl(_2)</td>
<td>-16.7</td>
</tr>
<tr>
<td>Na(^{+}) with NaCl</td>
<td>-5.9</td>
<td>0.5</td>
<td>Na(^{+}) with NaCl</td>
<td>MgCl(_2)</td>
<td>-17.3</td>
</tr>
<tr>
<td>Sr(^{2+}) with SrCl(_2)</td>
<td>-10.4</td>
<td>0.9</td>
<td>Sr(^{2+}) with SrCl(_2)</td>
<td>NaCl</td>
<td>-9.9</td>
</tr>
</tbody>
</table>

5.3.2. Ra\(^{2+}\) Adsorption isotherms on (001) barite

Figure 5.7 shows that the model predictions of the isotherms do not agree well with the experimental data for the different salts. It was expected that similar to Section 3.4.3, an increase in salt concentration should lead to a decrease in the adsorption capacity of the barite for Ra\(^{2+}\). While this is demonstrated in the experiments, the model results are inconsistent. The model follows the expected trend for CaCl\(_2\) and MgCl\(_2\) solutions. The model performance is poor for BaCl\(_2\), SrCl\(_2\), and NaCl solutions. The disagreement is due to the inconsistent differences in the magnitudes of the free energies calculated from the simulation. Further studies are needed to ascertain the exact source of these inconsistencies.
One possible study includes obtaining better estimates of the PMF, such as running longer simulations or using more advanced methods of extracting the PMF from umbrella simulations. Another study would require obtaining better parameterization of the 12-6-4 Ra\(^{2+}\) forcefield.

Figure 5.7 Experimental and predicted isotherms of Ra\(^{2+}\) adsorption on (001) barite surface showing the effect of ionic strength (a) BaCl\(_2\) (b) CaCl\(_2\) (c) SrCl\(_2\) (d) MgCl\(_2\) (e) NaCl.
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Radium removal mechanisms onto silica and barite, and the effect of water quality parameters on the removal are investigated using atomistic simulations and process level modeling. MD simulations are conducted to obtain parameters that describe the removal mechanisms and these parameters are incorporated into a process model to make process level predictions. This approach provides an avenue to integrate atomistic simulations into process level modeling and compare predictions with experimental data to get a holistic understanding of radium removal mechanisms.

A multi-component Langmuir isotherm model is developed using information from MD simulations to investigate radium removal on different ionized silica surfaces. Isotherms based on radium adsorption onto silica and barite are predicted and compared with the experimental isotherms. The results indicate that high solution pH results in high radium removal due to increased silica surface negative charge, while high ionic strength results in less radium removal due to complexation and competition mechanisms with ions in the solution. The barite isotherm illustrates that ionic strength results in reduced radium removal due to complexation and competition mechanisms with the anions and cations in the solution.

Preliminary simulations using the forcefields published in the literature were not consistent with barite and celestites densities as well as metal sulfate association constants. This led to the development of a force field parameterization framework to re-parameterize
sulphate force fields to account for metal-sulfate interactions. MD and umbrella sampling simulations were performed to calculate parameters to evaluate metal-sulfate interactions for different Me\(^{2+}\)-SO\(_4\) systems. The results of regression analysis indicated that the barite and celestite densities are insensitive to the \(\alpha\) parameter thereby providing flexibility in fitting the association constants. The calculated barite and celestite density values matched the experimental density. The cation structure around the SO\(_4^{2-}\) for both barite and celestite were investigated using radial distribution functions for Ba-OSO\(_4\) and SSO\(_4\)-OSO\(_4\) and the results were in agreement with experimental data. Association constants calculated based on the Me\(^{2+}\)-SO\(_4\) free energies from umbrella sampling simulations indicated a good fit and were consistent with experimental data except the case of MgSO\(_4\) which had extremely large variations in the association constants. The results also indicate that the proposed forcefields can accurately simulate the structures of barite and celestite based on the agreement between the theoretical and experimental interatomic distances for Ba-O\(_{SO4}\) and S\(_{SO4}\)-O\(_{SO4}\). Moreover, the CN and hydration free energy values were in agreement with experimental data indicating the effectiveness of the force field parameterization framework. Thus, the consistency between the calculated and experimental data indicates that the proposed approach can successfully capture the interactions of the metal parameter to fit barite and celestite properties. Thus, the developed forcefields will be suitable for predicting the removal of radium by adsorption onto the surface of barite.

The adsorption of different cations onto three barite surfaces (100, 010, and 001) were investigated using molecular simulations. The free energy of adsorption obtained from umbrella sampling simulations indicate that 100 is the most desirable surface for
adsorption to occur. The effect of different salts (BaCl$_2$, CaCl$_2$, SrCl$_2$, MgCl$_2$, and NaCl) were also investigated. The results further indicate that radium removal decreases significantly with increasing ionic strength due to ions competitions and complexation mechanisms. In the case of CaCl$_2$ and MgCl$_2$ solutions, the isotherm predictions based on the multi-component Langmuir isotherm followed the expected trend while the trend for BaCl$_2$, SrCl$_2$, and NaCl solutions were not consistent with experiment. The discrepancy is attributed to the inconsistent differences in the magnitudes of the free energies calculated from the simulation. In order to address this discrepancy, future studies will conduct longer simulations for each umbrella window to improve the PMF estimates or adopt advanced methods of extracting the PMF from umbrella simulations. The effectiveness of the force field used in the simulations will also be investigated by obtaining better parameterization of the 12-6-4 Ra$^{2+}$ forcefield. The results of this study can potentially be useful for elucidating the mechanisms associated with radium adsorption onto different adsorbents under different environmental conditions.
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