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Inorganic Sorption in Polymer Modified Bentonite Clays

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Inorganic Sorption in Polymer Modified Bentonite Clays

by

Melody Schwartz Nocon

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Environmental Engineering
Department of Civil and Environmental Engineering
College of Engineering
University of South Florida

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DEDICATION

For my family.
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TABLE OF CONTENTS

LIST OF TABLES ............................................................................................................. iv

LIST OF FIGURES ........................................................................................................... vi

ABSTRACT..................................................................................................................... xiv

CHAPTER ONE: INTRODUCTION..................................................................................1
  1.1 Significance ......................................................................................................1
  1.2 Objective ...........................................................................................................2
  1.3 Scope of Work ..................................................................................................2

CHAPTER TWO: THEORETICAL BACKGROUND ......................................................3
  2.1 Material Classification ......................................................................................3
    2.1.1 General Clay Classification ....................................................................3
    2.1.2 Classification of Sodium Bentonite .......................................................6
    2.1.3 General Synthetic Water Soluble Polymer Classification ......................7
      2.1.3.1 Structure and Water Soluble Polymers ........................................7
      2.1.3.2 Polyelectrolytes ............................................................................7
      2.1.3.3 Polymerization .............................................................................8
      2.1.3.4 Polyacrylamide ...........................................................................9
  2.2 Clay Dispersions ................................................................................................10
    2.2.1 Colloids and Sols .....................................................................................10
    2.2.2 The Diffuse Double Layer ......................................................................10
      2.2.2.1 Surface Complexation in the Stern Layer ..................................13
      2.2.2.2 Diffuse Ions in the Guoy-Chapman Layer ................................15
      2.2.2.3 Polymer Interactions in the Diffuse Double Layer ......................15
    2.2.3 Sol Destabilization ..................................................................................17
      2.2.3.1 Addition of Neutral Salts ............................................................17
      2.2.3.2 Addition of Polyelectrolytes ........................................................18
  2.3 Sorption Isotherms ...........................................................................................18
    2.3.1 Linear Isotherm .....................................................................................19
    2.3.2 Freundlich Isotherm ..............................................................................19
    2.3.3 Langmuir Isotherm ...............................................................................20

CHAPTER THREE: EXPERIMENTAL BACKGROUND .............................................21
  3.1 Water Chemistry .............................................................................................21
  3.2 Atomic Adsorption ..........................................................................................22
    3.2.1 Flame Atomic Absorption Spectrometry (FAAS) ..................................22
      3.2.1.1 Source Instrumentation ................................................................22
3.2.1.2 Flame ..................................................................................23
3.2.1.3 Sample Introduction and Atomization ...............................24
3.3 Scanning Electron Microscopy (SEM) ...........................................25
  3.3.1 Basic Instrumentation ..............................................................25
    3.3.1.1 Electron Optical Column ..................................................26
    3.3.1.2 Vacuum System ...............................................................27
    3.3.1.3 Electronics and Display System ....................................27
  3.3.2 Operational Parameters .........................................................29
    3.3.2.1 Condenser Lens .................................................................29
    3.3.2.2 Accelerating Voltage ........................................................29
    3.3.2.3 Scan Speed .................................................................29
    3.3.2.4 Working Distance ............................................................30
    3.3.2.5 Aperture Size and Alignment ...........................................30
3.4 Energy Dispersive X-Ray (EDX) Analysis ..................................30

CHAPTER FOUR: METHODOLOGY ..................................................34
4.1 Instrumentation ...........................................................................34
  4.1.1 Reverse Osmosis and Deionization Unit ...............................34
  4.1.2 Glassware ..............................................................................34
  4.1.3 Plastic Containers .................................................................34
  4.1.4 Mixer .......................................................................................35
  4.1.5 Tube Rotator ........................................................................35
  4.1.6 Sample Bottles for Preservation ...........................................35
  4.1.7 Syringes and Syringe Filters ..................................................35
  4.1.8 Sample Containers for FAAS ................................................36
  4.1.9 Pipettes and Pipette Tips .........................................................36
  4.1.10 FAA Machine .......................................................................36
  4.1.11 pH Electrode .........................................................................36
4.2 Testing Materials ..........................................................................36
4.3 Initial Media Preparation .............................................................37
4.4 Desorption ...................................................................................38
4.5 Time to Equilibrium ....................................................................38
4.6 Batch Sorption Tests ...................................................................40
  4.6.1 Slurries .........................................................................................40
    4.6.1.1 Bentonite and Bentofix Slurries ......................................40
    4.6.1.2 HC or MA Bentonite Slurries .........................................40
  4.6.2 Spike Solutions ......................................................................41
  4.6.3 Initial Concentration Spiking and Agitation ........................41
  4.6.4 Quality Control ...................................................................41
  4.6.5 Sample Preparation ..............................................................42
    4.6.5.1 Supernatant .....................................................................42
    4.6.5.2 Solid Media ..................................................................42
4.7 Sample Analysis ..........................................................................42
  4.7.1 Flame Atomic Adsorption (FAA) ...........................................42
    4.7.1.1 Sodium .........................................................................42
LIST OF TABLES

Table 1.1: Leachate Properties........................................................................................................2
Table 4.1: Polymer Material Data..................................................................................................37
Table 5.1: Sodium Sorption Test Results .......................................................................................47
Table 5.2: Calcium Sorption Test Results ......................................................................................48
Table A.1: Desorption Tests ..........................................................................................................60
Table A.2: Na\textsuperscript{+} 500 ppm Kinetic Test .......................................................................63
Table A.3: Na\textsuperscript{+} 50 ppm Kinetic Test .............................................................................65
Table A.4: 500 Ca\textsuperscript{2+} ppm Kinetic Test ..........................................................................67
Table A.5: Spike Calculations for Sodium Sorption Experiments .............................................69
Table A.6: Spike Calculations for Calcium Sorption Experiments ...........................................69
Table A.7: Unexposed Bentonite Elemental Composition..............................................................109
Table A.8: Unexposed Bentofix Elemental Composition..............................................................111
Table A.9: Unexposed Medium Anionic Polymer Elemental Composition.................................113
Table A.10: Unexposed High Cationic Polymer Elemental Composition .....................................115
Table A.11: Sodium Exposed Bentonite Elemental Composition..................................................117
Table A.12: Sodium Exposed Bentofix Elemental Composition..................................................119
Table A.13: Sodium Exposed 3% Medium Anionic Elemental Composition ............................121
Table A.14: Sodium Exposed 3% High Cationic Elemental Composition ....................................123
Table A.15: Calcium Exposed Bentonite Elemental Composition...............................................125
Table A.16: Calcium Exposed Bentofix Elemental Composition................................................127
Table A.17: Calcium Exposed 3% Medium Anionic Elemental Composition ...............129
Table A.18: Calcium Exposed 3% High Cationic Elemental Composition .................131
LIST OF FIGURES

Figure 2.1 (a) Silica Tetrahedral Sheet (b) Alumina Octahedral Sheet ........................................3

Figure 2.2: Interlayer Bonding Via Hydration/Dipole Attraction ........................................4

Figure 2.3: Synthesis Patterns for Clay Minerals ........................................................................5

Figure 2.4: The Semi-Basic Unit Layer of Montmorillonite (a) Two Dimensional Representation with Charge Distribution and Average Range of Thickness (b) Three Dimensional Representation Including the Interlayer ...........6

Figure 2.5: Polyacrylamide .......................................................................................................9

Figure 2.6: A Stable Sol .............................................................................................................10

Figure 2.7: Precipitate Salts and Interlayer Cations ................................................................10

Figure 2.8: Process of Hydration for NaCl ............................................................................11

Figure 2.9: (a) Picture of Ionic Distribution Near the Surface of Clay (b) Ionic Concentration as a Function of Distance from the Clay Surface ..........12

Figure 2.10: (a) The Diffuse Double Layer (b) Molecular View of the Diffuse Double Layer ......................................................................................12

Figure 2.11: An Inner Sphere Surface Complex .......................................................................13

Figure 2.12: An Outer Sphere Complex ....................................................................................14

Figure 2.13: Inner and Outer Sphere Complexation ................................................................14

Figure 2.14: Ions in the Stern and Guoy-Chapman Layer .....................................................15

Figure 2.15: The Process of Adsorption for an Uncharged Polymer Molecule at the Clay Surface ......................................................................................16

Figure 2.16: Destabilization and Coagulation by Suppression of the Diffuse Double Layer ......................................................................................17

Figure 2.17: Colloid Agglomeration via Particle Bridging .....................................................18
Figure A.29: Freundlich Isotherm Estimation-3% HC Na .....................................................81
Figure A.30: Freundlich Isotherm-3% HC Na.................................................................81
Figure A.31: Langmuir Isotherm Estimation-3% HC Na ................................................82
Figure A.32: Langmuir Isotherm-3% HC Na .................................................................82
Figure A.33: Linear Isotherm-1% MA Na .........................................................................83
Figure A.34: Freundlich Isotherm Estimation-1% MA Na ...............................................84
Figure A.35: Freundlich Isotherm-1% MA Na .................................................................84
Figure A.36: Langmuir Isotherm Estimation-1% MA Na .................................................85
Figure A.37: Langmuir Isotherm 1% MA Na .....................................................................85
Figure A.38: Linear Isotherm-3% MA Na ..........................................................................86
Figure A.39: Freundlich Isotherm Estimation-3% MA Na ...............................................87
Figure A.40: Freundlich Isotherm-3% MA Na .................................................................87
Figure A.41: Langmuir Isotherm Estimation-3% MA Na .................................................88
Figure A.42: Langmuir Isotherm-3% MA Na .................................................................88
Figure A.43: FAA Calibration Curve for Calcium Samples 500 ppm, 100 ppm, and 
10 ppm Initial Concentrations.........................................................................................89
Figure A.44: FAA Calibration Curve for Calcium Samples 50 ppm, 1 ppm, and 0.1 ppm Initial Concentrations .................................................................89
Figure A.45: Linear Isotherm-Bentonite Ca ......................................................................90
Figure A.46: Freundlich Isotherm Estimation-Bentonite Ca ............................................91
Figure A.47: Freundlich Isotherm-Bentonite Ca .............................................................91
Figure A.48: Langmuir Isotherm Estimation-Bentonite Ca .............................................92
Figure A.49: Langmuir Isotherm-Bentonite Ca .............................................................92
Figure A.50: Linear Isotherm-Bentofix Ca ......................................................................93
Figure A.97: Sodium Exposed Bentofix x25000.............................................................118
Figure A.98: Sodium Exposed Bentofix Spectrum..........................................................119
Figure A.99: Sodium Exposed 3% Medium Anionic x500..............................................120
Figure A.100: Sodium Exposed 3% Medium Anionic x10000........................................120
Figure A.101: Sodium Exposed 3% Medium Anionic x25000........................................120
Figure A.102: Sodium Exposed 3% Medium Anionic Spectrum....................................121
Figure A.103: Sodium Exposed 3% High Cationic x500................................................122
Figure A.104: Sodium Exposed 3% High Cationic x5000..............................................122
Figure A.105: Sodium Exposed 3% High Cationic x25000............................................122
Figure A.106: Sodium Exposed 3% High Cationic Spectrum.........................................123
Figure A.107: Calcium Exposed Bentonite x500............................................................124
Figure A.108: Calcium Exposed Bentonite x10000........................................................124
Figure A.109: Calcium Exposed Bentonite x25000........................................................124
Figure A.110: Calcium Exposed Bentonite Spectrum.....................................................125
Figure A.111: Calcium Exposed Bentofix x500..............................................................126
Figure A.112: Calcium Exposed Bentofix x10000..........................................................126
Figure A.113: Calcium Exposed Bentofix x25000..........................................................126
Figure A.114: Calcium Exposed Bentofix Spectrum ......................................................127
Figure A.115: Calcium Exposed 3% Medium Anionic x500..........................................128
Figure A.116: Calcium Exposed 3% Medium Anionic x10000......................................128
Figure A.117: Calcium Exposed 3% Medium Anionic x25000......................................128
Figure A.118: Calcium Exposed 3% Medium Anionic Spectrum...................................129
Figure A.119: Calcium Exposed 3% High Cationic x500...............................................130
Figure A.120: Calcium Exposed 3% High Cationic x10000...........................................130
Figure A.121: Calcium Exposed 3% High Cationic x25000...........................................130
Figure A.122: Calcium Exposed 3% High Cationic Spectrum........................................131
INORGANIC SORPTION IN POLYMER MODIFIED BENTONITE CLAYS

Melody Schwartz Nocon

ABSTRACT

In 1986, geosynthetic clay liners (GCLs) were invented and successfully used as a replacement for the soil layer in composite lining systems. In some applications an additive (polymer) is mixed with the bentonite to increase performance, especially in those that have low concentrations of sodium bentonite (EPA 2001).

Studies showing significant increases in hydraulic conductivity values for bentonite in the presence of high salt concentrations are frequently documented and there is a risk of early breakthrough due to performance failure of the GCL clay component. (Ashmawy et al, 2002). It has also been stated that sodium, potassium, calcium, and magnesium have such a high affinity for the clay’s surface other chemical species have little chance of attenuation (EPA 2001). For these reasons, researching sorption in the presence of major salt cations and polymers gains great importance.

Distribution coefficients were extrapolated from Linear, Freundlich and Langmuir sorption isotherms for sodium and calcium cations modeled from data collected from batch tests of sodium bentonite and various manufactured and custom mixed polymer modified bentonites. Surface characterization before and after calcium or sodium solution exposure of all tested media was accomplished by use of scanning electron microscopy and energy dispersive x-ray analysis.
CHAPTER ONE
INTRODUCTION

1.1 Significance

In 1986, geosynthetic clay liners (GCLs) were invented and successfully used as a replacement for the soil layer in composite landfill lining systems (EPA 2001). GCLs normally consist of either bentonite clay sandwiched between two geotextiles or a layer of bentonite clay adhered to the surface of a geomembrane. GCLs have become a popular component to include in composite landfill lining systems because bentonite clay has a high swell potential and very low hydraulic conductivity. However, the original values of hydraulic conductivity for the bentonite component of a GCL can increase significantly after installation and exposure to highly concentrated inorganic leachate (Petrov et al, 1997; Shackelford et al, 2000; and Elhajji et al, 2001). According to Elhajji et al (2001), additional polymer treatment of the bentonite component of GCLs can counteract this negative effect and help maintain low values of hydraulic conductivity in the presence of highly concentrated inorganic single specie solutions. Recent research has been performed in regards to this suggestion with mixed results for performance to hydraulic conductivity (Schenning, 2004).

Estimating specific discharge by experimentally defining hydraulic conductivity can be useful in reference for predictions to time, but defining distribution coefficients for various isotherm models can also be helpful in transport modeling for the amount of exposure to inorganic species.
1.2 Objective

One purpose of this research was to define distribution coefficients of polymer modified bentonite clay in the presence of single inorganic species solutions. Sodium and calcium, two inorganic species commonly found in incinerator fly ash leachates at very high concentrations, were used as challenge chemicals. Typical characteristics for incinerator fly ash leachates are listed in the table below.

Table 1.1: Leachate Properties (Ashmawy et al, 2002)

<table>
<thead>
<tr>
<th>TEST LEACHATE</th>
<th>L-1</th>
<th>L-2</th>
<th>L-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>LANDFILL TYPE</td>
<td>Co-disposal</td>
<td>Co-disposal</td>
<td>Ash monofill</td>
</tr>
<tr>
<td>pH</td>
<td>6.30</td>
<td>6.55</td>
<td>7.24</td>
</tr>
<tr>
<td>Ca(^{2+}) (mg/L)</td>
<td>1,150</td>
<td>2,625</td>
<td>5,120</td>
</tr>
<tr>
<td>Na(^{+}) (mg/L)</td>
<td>2,200</td>
<td>300</td>
<td>1,640</td>
</tr>
</tbody>
</table>

Distribution coefficients for sodium and calcium were extrapolated from experimental data modeling of Linear, Freundlich, and Langmuir sorption isotherms.

In addition to defining distribution coefficients, surface characterization of polymer modified bentonite clays before and after exposure to the challenge chemicals were described by use of scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX).

1.3 Scope of Work

One manufactured polymer modified clay, Bentofix, was tested. High cationic polyacrylamide and low anionic polyacrylamide-bentonite solutions at one and three percent by solid weight concentrations were tested. Untreated sodium bentonite was tested to provide a point of reference.

Fixed experimental variables included temperature, pH, and initial sodium or calcium concentrations. The modified variable was the amount of solids in solution. Data was fit to empirical Linear, Freundlich, and Langmuir isotherms.
CHAPTER TWO
THEORETICAL BACKGROUND

2.1 Material Classification

2.1.1 General Clay Classification

All clay minerals belong to the phyllosilicate mineral family, where they primarily differ from each other by their structural arrangement of silicon tetrahedron and aluminum or magnesium octahedron sheets. These sheets bond to each other in 1:1 or 2:1 ratios of silicon tetrahedron to aluminum octahedron in order to form semi-basic unit layers.

![Silica Tetrahedral Sheet](a) ![Alumina Octahedral Sheet](b) (Mitchell, 1993)

Additionally, specific clays within the same clay mineral group can be further distinguished from other group members by the type and extent of isomorphous substitutions that occur in their structural arrangement. Isomorphous substitutions in clays occur when other cations are present in positions of the crystal structure where aluminum or silicon cations should have been during the formation process of the clay.
These cations often have a smaller positive charge than that of aluminum or silicon cations and, consequently, result in a net negative charge present at the surface of the clay.

Net negative surface charges present on the semi-basic unit layers facilitate the attraction of cations from their natural surrounding solution in order to achieve neutrality. These surface cations can often be replaced by other types of cations, and, as such, are termed exchangeable cations. Cation exchange capacity is a sorptive property of a specific clay used to describe the quantity of exchangeable cations and is commonly expressed in units of milliequivalents per 100 grams of dry clay (Mitchell, 1993).

During interlayer bonding between semi-basic unit layers, these surface cations become interlayer cations. Interlayer bonding between semi-basic unit layers can be controlled by interlayer cations and/or polar molecules, such as water. Some bonds involving interlayer cations between the semi-basic unit layers can be so strong that the layers will not separate in the presence of water or any other polar molecules. At other times, interlayer cations will hydrate in the presence of polar molecules to form a weaker bond between semi-basic unit layers and will result in swelling of the clay.

![Figure 2.2: Interlayer Bonding Via Hydration/Dipole Attraction (Mitchell, 1993)](image)
Interlayer bonding for neutral semi-basic unit layers can also be attributed to by van der Waals forces and/or hydrogen bonding.

Figure 2.3: Synthesis Patterns for Clay Minerals (Mitchell, 1993)
2.1.2 Classification of Sodium Bentonite

Bentonite clay is commonly used in geosynthetic clay liners. Bentonite clay, an alteration product of volcanic ash, is primarily composed of montmorillonite, which is the most common type of smectite mineral. Montmorillonite has a 2:1 aluminosilicate semi-basic unit layer, where the 2:1 ratio refers to two tetrahedral sheets sandwiching an octahedral sheet in between.

![Figure 2.4: The Semi-Basic Unit Layer of Montmorillonite (a) Two Dimensional Representation with Charge Distribution and Average Range of Thickness (b) Three Dimensional Representation Including the Interlayer (Mitchell, 1993)](image)

The outsides sheets of montmorillonite consist of silica, where each silicon ion in the sheet is surrounded by four oxygen ions. The middle sheet of montmorillonite consists of aluminum, where each aluminum ion is surrounded by six oxygen ions.
In montmorillonite, isomorphous substitution is demonstrated by the presence of a magnesium cation for every sixth position in the octahedral sheet meant for an aluminum cation. The formula per unit cell for montmorillonite is \((\text{OH})_4\text{Si}_8(\text{Al}_{3.34}\text{Mg}_{0.66})\text{O}_{20}\). In sodium bentonite, sodium is the exchangeable interlayer cation. Interlayer cations in smectites form weak bonds between semi-basic unit layers and are easily hydrated by polar molecules. This phenomenon gives smectites the ability to swell to large proportions upon full hydration.

2.1.3 General Synthetic Water-Soluble Polymer Classification

2.1.3.1 Structure and Water Soluble Properties

Structurally, a polymer, or macromolecule, is essentially a long string of joined monomers, where monomers are simple molecules. Characteristic properties of polymers are controlled by functional groups located within their chemical structure. Functional groups are comprised of one or more atoms attached to the hydrocarbon chain of a polymer (Hill & Petrucci, 1999). Polar functional groups in the polymer chain are responsible for both water solubility and interactions at the clay surface (Theng, 1979).

2.1.3.2 Polyelectrolytes

Polyelectrolytes are water soluble polymers that disassociate in water to create either polycations or polyanions along with an equivalent amount of ions with a small charge and opposite sign. The corresponding ions may also have no charge at all.
2.1.3.3 Polymerization

Polymerization is the chemical process in which a monomer is converted to a polymer. Copolymerization is the chemical process in which more than one monomer is converted to a polymer. The general reaction for polymerization is defined as

\[ nM \rightarrow [\ldots M \ldots]_n \]

Where M stands for monomer, and n stands for the degree of polymerization. A “high” polymer has a high molecular weight and high degree of polymerization. Polymerization can be divided into two groups according to the mechanism of polymer formation: Step-Growth or Chain.

Step-Growth polymerization occurs when functional groups of multiple monomers have reactions that create a link between the monomers. Chain or addition polymerization occurs when either an ionic or free radical catalyst opens the double bond of an unsaturated monomer to form an activated monomer. Additions of monomers to the activated monomer give rise to polymers. Free-radical, anionic, and cationic polymerization are all chain processes (Alger, 1989).

In 1979, Theng classified the three main groups of synthetic polyelectrolytes based on their net ionic charge: nonionic, anionic, and cationic. Nonionic polymers have no charge, anionic polymers have a negative charge, and cationic polymers have a positive charge.
2.1.3.4 Polyacrylamide

Polyacrylamide is created from the free radical polymerization of acrylamide. It is commonly used as a flocculating agent and gel for electrophoresis because of its high affinity for water (Alger, 1989). Polyacrylamide’s high affinity for water is due to its chemical structure.

![Polyacrylamide structure](image)

Figure 2.5: Polyacrylamide

The –NH$_2$ groups allow unlinked amides to form hydrogen bonds with water. However, ions present in solution can interfere with the hydrogen bonds and cause the polyacrylamide gel to release the water molecules.

Testing materials for this study were created by the ionic polymerization of polyacrylamide. High cationic and medium anionic polymers with polyacrylamide backbones were tested.
2.2 Clay Dispersions

2.2.1 Colloids and Sols

Clay particles naturally occur in water as colloids. Colloids are particles with a high surface area to mass ratio that are suspended in water due to their extremely small size, state of hydration, and surface electric charge. A colloidal dispersion in water is also known as a sol (Viessman and Hammer, 2004). Repulsion or attraction between particles is dependent upon the pH and the ionic strength of the solution.

![Figure 2.6: A Stable Sol (Viessman and Hammer, 2004)](image)

2.2.2 The Diffuse Double Layer

Sodium is present in dry sodium bentonite clay as strongly bonded interlayer or surface cations and, in excess, as salt precipitate (Mitchell, 1993).

![Figure 2.7: Precipitate Salts and Interlayer Cations (Santamarina, 2001)](image)
When bentonite clay is placed in water, salt precipitates are separated into anions and cations through the thermal agitation of water molecules. These newly created ions are surrounded by hydration shells (Santamarina, 2001).

The hydrated cations diffuse away from the surface of the bentonite in the direction of the concentration gradient to fulfill the laws of solution equilibrium. This phenomenon creates an ionic distribution around the clay particle that is influenced by both the net negative surface charge of the clay and the concentration gradient (Mitchell, 1993).

Figure 2.8: Process of Hydration for NaCl (Santamarina, 2001)
A basic model for ionic distribution around the surface of a colloid is the Diffuse Double Layer model.
2.2.2.1 Surface Complexation in the Stern Layer

The layer closest to the surface of the colloid is the Stern Layer, which consists of a fixed layer of cations electrostatically attracted to the negative surface of the clay. Within the Stern layer, both inner and outer sphere complexes are present.

Inner sphere complexes are ions that have lost all or a partial amount of their hydration shells and are oriented in such a way that there are no water molecules located between the bonded ion and clay particle surface.

Figure 2.10 (continued)

Figure 2.11: An Inner Sphere Surface Complex (Sposito, 2004)
Outer sphere complexes are still at a fixed position relatively close to the surface of the clay particle, but they still retain their primary hydration shell. Outer sphere complexes are exchangeable cations.

![Outer Sphere Complex](image1.png)

**Figure 2.12: An Outer Sphere Complex (Sposito, 2004)**

![Inner and Outer Sphere Complexation](image2.png)

**Figure 2.13: Inner and Outer Sphere Complexation (Santamarina, 2001)**
2.2.2.2 Diffuse Ions in the Guoy-Chapman Layer

The layer surrounding the Stern layer is a diffuse ion swarm called the Guoy-Chapman Layer. Counterions, or diffuse ions, located in the Guoy-Chapman layer are also exchangeable.

![Diagram showing ions in the Stern and Guoy-Chapman Layer](image)

Figure 2.14: Ions in the Stern and Guoy-Chapman Layer (Sposito, 1989)

2.2.2.3 Polymer Interactions in the Diffuse Double Layer

Up to this point of discussion, sorptive properties of the clay surface have only been addressed in reference to simple cations. For this research, it is also important to address polymer interactions at the surface of the clay. Polymer molecules must have a molecular or coil size that is small enough to penetrate through the interlayer spacing of clay in order to interact with the surface of the clay.

Nonionic polymer molecules sorb to the clay surface only after desorption of a large amount of solvent (water) molecules previously present at the clay surface. Adsorption of the polymer chain is dependent on flexibility and properties of its functional groups. At the clay surface, polymer chains orient themselves into various shapes that allow attachment to the surface via segment-surface bonds.
Figure 2.15: The Process of Adsorption for an Uncharged Polymer Molecule at the Clay Surface (Theng, 1979)

For polycations, adsorption at the surface of the clay occurs by exchange of the many cations for one polycation. The amount of polycations adsorbed to the surface of the clay is dependent on the charge density of the polycation and the cation exchange capacity of the clay.

For polyanions, there are many different mechanisms of adsorption. These include electrostatic attraction, hydrogen bonding, Van der Waals forces, surface complexation, ionic bonding to other cations in the diffuse double layer, and anionic exchange at the positive crystal edges of the octahedral sheet (Theng, 1979).
2.2.3 Sol Destabilization

Destabilization of hydrophobic sols, or colloidal dispersions, can be achieved by increasing Van der Waals Forces and Brownian movement. Increasing Van der Waals forces, the forces of attraction felt between two particles, and Brownian movement, the random motion of colloids in solution, increases the likelihood of flocculation, or agglomeration, between particles. Colloids are also destabilized by the addition of a coagulant, which can be a salt or cationic polymer.

2.2.3.1 Addition of Neutral Salts

Salt cations in solution serve as counterions that reduce the thickness of the diffuse double layer around colloids enough to permit contact between particles. Van der Waals forces of attraction increase as the particles become closer and facilitates flocculation.

Figure 2.16: Destabilization and Coagulation by Suppression of the Diffuse Double Layer (Viessman & Hammer, 2005)
2.2.3.2 Addition of Polyelectrolytes

The long chains of cationic polymers allow them to be excellent coagulants, as they are able to adsorb to the surfaces of multiple colloids. This phenomenon creates a bridging effect between the colloids that results in flocculation.

![Figure 2.17: Colloid Agglomeration via Particle Bridging (Viessman & Hammer, 2005)](image)

2.3 Sorption Isotherms

A sorption isotherm is an equation that expresses the relationship between the amount of sorbed phase species to the amount of solution phase species for the same species in a system that is in equilibrium. The distribution coefficient, often denoted as $K_d$, is present in all sorption isotherms and is a ratio of the sorbed phase concentration to the solution phase concentration. When graphing a sorption isotherm, the sorption density, often denoted as $Q_s$, is labeled on the y axis and the equilibrium concentration, often denoted as $C_e$, is labeled on the x-axis (Benjamin, 2002). The three types of isotherms selected for data modeling in this research included Linear, Freundlich, and Langmuir Isotherms. Equations and typical units used for modeling sorption isotherms are further discussed in Chapter 5.
2.3.1 Linear Isotherm

A linear sorption isotherm is the simplest type of isotherm. It expresses a proportional relationship between sorption density and equilibrium concentration. One faulty attribute of this type of isotherm is its lack of a theoretical upper limit for sorption capacity.

![Figure 2.18: A Typical Linear Isotherm](image)

2.3.2 Freundlich Isotherm

A Freundlich isotherm displays an exponential relationship between the sorption density and equilibrium concentration. The Freundlich isotherm has the same faulty attribute of the linear isotherm; it lacks a theoretical upper limit for sorption capacity.

![Figure 2.19: A Typical Freundlich Isotherm](image)
2.3.3 Langmuir Isotherm

A Langmuir sorption isotherm displays a finite relationship between the sorption density and the equilibrium concentration. Modeling with a Langmuir sorption allows for an establishing of a theoretical upper limit for the sorption density.

Figure 2.20: A Typical Langmuir Isotherm
CHAPTER THREE
EXPERIMENTAL BACKGROUND

3.1 Water Chemistry

A pC-pH diagram was used to predict when the precipitation of CaCO$_3$(s) would occur. Constants used for calculations include an assumed $P_{CO_2}=10^{-3.5}$ atm, $pK_{a1}=6.35$, $pK_{a2}=10.33$ for $H_2CO_3$, and $pK_{so}=8.48$ for CaCO$_3$(s) (Benjamin 2002). Species included in calculations included $H^+$, $OH^-$, $H_2CO_3$, $HCO_3^-$, and $CO_3^{2-}$, $Ca^{2+}$ and CaCO$_3$ (s).

![pC-pH Diagram: Calcium Solubility Curve, $P_{CO_2}=10^{-3.5}$ atm](image)

Figure 3.1: Calcium Carbonate Solubility Curve

Precipitation of CaCO$_3$(s) occurs in the shaded region of the pC-pH diagram between the $pC_T$ line and the $pCa^{2+}$ lines. For all experiments, the working pH ranged from 6.75 to 7.25 and the maximum concentration of Ca$^{2+}$ was 500 mg/L or 0.012476 mol/L. 0.012476 mol/L Ca$^{2+}$ corresponds to a pC value of 1.9. No CaCO$_3$(s) is predicted to form.
3.2 Atomic Absorption

Absorption spectroscopy involves the process in which the radiation absorbed by atoms is measured. Atomic absorption is the absorption of light radiation by atoms and occurs when light of the correct wavelength excites an atom in ground state to a higher energy level. The transition from a ground state \((E_0)\) to an excited state \((E_j)\) can be written as \(E_0 \rightarrow E_j\). The following mathematical expression is used to describe atomic absorption:

\[
A = \log \left( \frac{I_0}{I} \right) = k_v l \log e
\]

Where \(A\) is absorbance, \(I_0\) is the incident light intensity, \(I\) is the transmitted light intensity, \(k_v\) is the absorption coefficient, and \(l\) is the path length. Absorbance, \(A\), of light is directly proportional to the number of atoms, or concentration, that absorbed the light. Therefore, a linear expression can be used to describe the relationship between absorption and concentration (Ebdon et al, 1998).

3.2.1 Flame Atomic Absorption Spectrometry (FAAS)

3.2.1.1 Source Instrumentation

FAAS can use either a hollow-cathode lamp or an electrodeless discharge lamp as a source in its instrumentation. This research utilized hollow-cathode lamps for source instrumentation, and a general schematic for this lamp can be seen below:

Figure 3.2: The Hollow-Cathode Lamp (Ebdon et al, 1998)
The hollow cylindrical cathode is specifically coated with a metal of interest. The glass envelope is filled with an inert gas at 1 to 5 Torr, which creates the proper conditions to allow discharges to concentrate in the hollow cylindrical cathode when a voltage potential of 500 V is applied between the electrodes. Ions are created at the anode due to the charging of the inert gas and these ions subsequently accelerate and bombard the cathode. This bombardment causes the metal atoms in the coating to sputter out of the cathode cup. Further collisions excite the metal atoms and a characteristic spectrum of the metal is produced.

3.2.1.2 Flame

The purpose of the flame in atomic absorption spectrometry (AAS) is to produce ground-state atoms. Gas mixtures are used as fuels for flames. Air acetylene mixtures are generally sufficient enough to produce ground-state atoms, but nitrous oxide-acetylene mixtures are required when refractory compounds are used or interferences are commonly encountered. The slot burner in AAS controls path length and orients the proper portion of the flame for viewing. Components for a flame are as follows:

![Flame Diagram](image)

Figure 3.3: A Premixed Flame (Ebdon et al, 1998)
Because atoms are not uniformly distributed, height of the burner should be adjusted until the region of optimum absorption can be found.

3.2.1.3 Sample Introduction and Atomization

Analytes are introduced into the process through a concentric nebulizer system.

Figure 3.4: Concentric Nebulizer System for a Premixed Burner (Ebdon et al, 1998)

Analytes are drawn through the capillary tube and leave the nebulizer orifice as a mist due to the pressure drop created by the incoming oxidant. As the nebulized sample moves through the plastic expansion chamber any large droplets will collect on the baffles in order to ensure that only the smallest particles reach the flame.

Upon introduction to the flame, droplets undergo desolvation in the preheating zone. Most vapors break down spontaneously to atoms in the flame, but some vapors can be refractory (Ebdon et al, 1998).
3.3 Scanning Electron Microscopy (SEM)

Images produced by the SEM are dependent on the deflection of secondary and backscattered (elastically scattered) electrons present at the sample surface. These electrons are deflected by bombarding incident electrons produced by the electron beam. Various other interactions that may occur by the bombardment of incident electrons in the SEM include no scattering of electrons at the sample surface, inelastic scattering, photon production, auger electron production, x-ray production, cathodoluminescence, and electron energy loss.

Figure 3.5: SEM Surface Interactions (Goldstein et al, 1992).

3.3.1 Basic Instrumentation

The three main components of the SEM include the electron optical column, vacuum system, and the electronics and display system.
3.3.1.1 Electron Optical Column

The basic electron optical column contains an electron gun, anode disc, condenser lens, scan coils, objective lens, the specimen sample holder, and the detector. A beam of electrons is produced by the electron gun. Thermoionic emission of freed electrons is produced via the heating of a filament in the electron gun. A high voltage potential, called the acceleration voltage, is produced between the filament in the electron gun and the anode disc and a beam of electrons are accelerated away from the filament. The beam first passes through a series of lenses which are responsible for focusing the beam. The diameter of the beam is reduced from about 50 micrometers to five nanometers by the condenser lenses, and can be even further reduced by manually changing the size of the aperture. The objective lens ensures that the beam has its smallest diameter when it strikes the specimen surface. Horizontal and vertical scan coils control the scanning direction of the beam as it passes next to them (Lawes, 1987).
3.3.1.2 Vacuum System

The beam of the electrons passing through the electron optical column and onto the sample surface cannot exist in the open atmosphere. In this environment, the beam would only travel a few millimeters before becoming scattered by gas molecules naturally present in the air. The vacuum system attached to the electron optical column removes these molecules and allows the beam to travel from the electron gun to the sample without any interference. Vacuum systems may consist of a series of ion pumps, rotary pumps and a turbo molecular pump.

3.3.1.3 Electronics and Display System

The basic electronics and display system consists of a signal amplifier, waveform generator, magnification control, scan coils, a cathode ray tube (CRT) brightness control, a CRT display screen, and a computer. In order to produce an image, the electron beam must scan over the sample for the detector in the electron optical column to take information, or signals, over many points as it moves along the surface of a sample. In all SEM systems, the diameter of a point is equal to the diameter of the electron beam as well as the thickness of a line on a raster scan. The width of a line on the raster scan consists of 1,000 points. One frame has a thickness of a thousand lines. Therefore, the SEM must scan over 1,000,000 points to produce a single image in a raster scan.
Vertical and horizontal scan coils in the electron optical column are connected to the magnification control and waveform generator. The waveform generator supplies the vertical and horizontal scan coils in the electron optical column with specific current waveforms. The movement of the electron beam over the sample is dictated by the scan coils in the electron optical column. The waveform generator is also connected to a pair of vertical and horizontal scan coils belonging to the CRT brightness control and display screen. In this way, the image on the CRT screen corresponds to the raster scan and the screen resolution is ultimately dictated by the magnification control. The following equation expresses the relationship between magnification, screen resolution, and beam diameter:

\[
magnification = \frac{\text{screen resolution}}{\text{beam diameter}}
\]
3.3.2 Operational Parameters

Changing the operational parameters in the SEM can enhance or reduce the quality of the image collected. Understanding and adjusting operational parameters is essential in order to attain the level of quality desired.

3.3.2.1 Condenser Lens

As seen in the prior equation, screen resolution is inversely proportional to beam diameter at a certain value magnification. Decreasing the beam diameter will enhance the screen resolution. Increasing the condenser lens setting will concentrate the beam and produce higher signals and resolution.

3.3.2.2 Accelerating Voltage

Image resolution is directly proportional to acceleration voltage, therefore, the highest resolution commonly corresponds to adjusting the SEM controls to the highest maximum acceleration voltage value possible. However, high acceleration voltage can cause charging and damage of a specimen due to higher beam energies and specimen interaction volumes.

3.3.2.3 Scan Speed

One raster scan consists of one collected signal per point scanned on the sample. Because the efficiency of the SEM detector and interactions at the surface is very low, one raster scan in itself has a very low quality. Increasing the scan speed increases the amount of raster scans or images displayed per unit time. Therefore, increasing the scan speed should result in a higher quality image. However, signal amplifiers attached to the detector will pick up more random electrons in addition to the signal electrons when the scan speed is increased. The presence of random electrons can be interpreted in an image.
as “noise” and, therefore, a noisy image is produced at very high scan speeds. Therefore, pictures should be collected at an acceptable scan speed that is not too high or too low—often this is still the “lowest” scan speed available on the SEM.

3.3.2.4 Working Distance

Working distance is the physical distance between the final lens in the electron optical column and the surface of the sample. The working distance can be manually changed by adjusting the Z-axis of the specimen sample holder. The working distance should always be within the depth of focus of the lens, or the image will not be in focus. The depth of focus can be manually changed by controls on the SEM, and the control on the SEM is often labeled “working distance.” Resolution is proportional to the depth of focus, therefore decreasing the depth of focus and working distance increases the resolution of the image.

3.3.2.5 Aperture Size and Alignment

Decreasing the aperture size decreases the beam diameter and, therefore, increases the resolution of an image. Also, the aperture should always be aligned at a position in which it does not block any portion of the passing electron beam. Incorrect aperture alignment will result in darkened edges around the image.

3.4 Energy Dispersive X-Ray (EDX) Analysis

The EDX spectrometer can be attached to a spare vacuum port in an SEM when EDX analysis is desired.

X-rays can be produced when incident electrons from the electron beam interact with the specimen. A bombarding incident electron can eject a shell electron in an atom belonging to the specimen and, if the shell electron belongs to an inner shell (K,L, or M),
a photon of electromagnetic radiation is produced that is an X-ray when an electron from a lower energy shell drops down to fill the vacancy.

Figure 3.8: X-Ray Production in Valence Shells (Lawes, 1987)

The three types of X-rays that can be produced from interactions in the inner shells of a specific atom consist of $K_\alpha$, $K_\beta$, and $L_\alpha$. Where $\alpha$ denotes a one level rise in energy, and $\beta$ denotes a two level rise in energy.

Figure 3.9: The X-Ray Family (Lawes, 1987)
Radiation produced from interactions of the electron beam and sample specimen leave the surface of the specimen and strike a crystal. Radiation will only emerge from the crystal if they are within a range of wavelengths corresponding to x-rays (0.1-1 nm) of specified Elements (Bragg’s Law).

![The Electromagnetic Spectrum](image)

Figure 3.10: The Electromagnetic Spectrum (Lawes, 1987)

The x-rays leaving the crystal enter a gas flow proportional detector. The output current pulse from the gas flow proportional detector is proportional to the energy of the detected x-ray. The output current pulse is passed through an amplifier into a pulse shaping circuit. An x-ray count is produced from a computer that counts the number of pulses at a certain value energy level. In this way, an x-ray spectrum is produced, with count values labeled on the y-axis and energy levels labeled on the x-axis.
The peaks are identified according to corresponding $K_\alpha$, $K_\beta$, and $L_\alpha$ elemental peaks.

Elemental composition can also be calculated by comparing count values between different x-ray counts. However, elemental composition computed in this way may be misleading, because counts are dependant on operating conditions and the location of the beam on the sample surface.
CHAPTER FOUR
METHODOLOGY

4.1 Instrumentation

4.1.1 Reverse Osmosis and Deionization Unit

Prior to application, all water used for experimental preparation and during experiments was treated by an EASYpure Reverse Osmosis and Deionization (RODi) unit. Product water specifications include an ASTM Type I resistivity, a total organic carbon (TOC) concentration ranging from 1-5 ppb and a bacterial concentration less than 1 CFU/mL. Whilst resistivity was confirmed with an internal monitor, TOC and bacterial concentration was not verified prior to use in experiments.

4.1.2 Glassware

A set of 10 ±0.02, 100 ±0.08, 500 ±0.20, and 1000 ±0.3 mL PYREX volumetric flasks were used to create standards for calibration of the FAA machine. All used glassware was soaked in a 5% Liquinox cleaning detergent, rinsed with water, immersed in a 1 N Nitric acid bath for twenty-four hours, and rinsed with water once more before placing on drying racks. All flasks contained stoppers at their mouths and beakers were covered with parafilm during storage.

4.1.3 Plastic Containers

All used plastic containers, including polycarbonate and polypropylene containers, were soaked in a 5% Liquinox cleaning detergent, rinsed with water, immersed in a 0.1 N sodium hydroxide base bath for an hour, rinsed with water, soaked
in a 0.1 N nitric acid bath for an hour, and rinsed with water once more before placing on drying racks. All open test tubes and caps were kept in clean closed plastic bags during storage. RODi produced water was used for all rinsing.

4.1.4 Mixer

An ECE Compact Laboratory Mixer (CLM) 6 was used for batch solutions. The six sample jars are made with a poly acrylic and all used jars were limited to a cleaning procedure consisting of rinsing with water, soaking in 5% Liquinox detergent, and a final rinse with water before placing on drying racks. The non-removable paddles and shafts were made out of stainless steel and were also limited to a cleaning procedure consisting of rinsing with water, soaking in 5% Liquinox detergent, and a final rinse with water. All lab jars were also triple-rinsed with water immediately before use.

4.1.5 Tube Rotator

A large size Barnstead/Thermolyne Labquake Tube Rotator with a fourteen tube capacity clip bar was used to perform end over end agitation of sample bottles during sorption tests.

4.1.6 Sample Bottles for Preservation

50 mL Nalgene Oak Ridge Polycarbonate Centrifuge Tubes with rubber seal caps were used as reactors in calcium sorption experiments. 30 mL Nalgene Oak Ridge Polycarbonate Centrifuge Tubes with rubber seal caps were used as reactors in sodium sorption experiments. All sample bottles were triple-rinsed with water before testing.

4.1.7 Syringes and Syringe Filters

B-D polypropylene 20 mL capacity sterile disposable syringes with a luer lock tip and a 0.02 micron pore diameter sterile Whatman Anotop disposable syringe filter with
an anopore inorganic medium and polypropylene housing were used to separate supernatant and solids in sorption tests.

4.1.8 Sample Containers for FAAS

Filtered samples were acidified and stored in 8 mL capacity polypropylene round bottles. Immediately before FAA analysis, samples were diluted in sterile BD Falcon 15 mL polypropylene conical bottom graduated tubes.

4.1.9 Pipettes and Pipette Tips

A set of 10-100μL, 25μL, 20-200μL 100-1000μL, and 1000-5000μL Eppendorf pipettes were used for volumetric measurements during research experiments.

4.1.10 FAA Machine

A VARIAN Fast Sequential Atomic Absorption Spectrometer (AA240FS) was used to analyze solutions.

4.1.11 pH Electrode

An Accumet (AP63) portable pH/mV/Ion meter was used to analyze solutions. The gel pH electrode was calibrated daily with 4, 7, and 10 pH standards.

4.2 Testing Materials

Extra high yield, premium grade powdered Bentonite packaged in a fifty pound paper bag from Wyo-Ben, Inc. was used in experiments as a control. Medium anionic and high cationic polymers used in experiments were produced by Emerging Technologies, Inc.
Table 4.1: Polymer Material Data (Schenning 2004)

<table>
<thead>
<tr>
<th>PRODUCT</th>
<th>CHARGE</th>
<th>BULK DENSITY (lbs/ft³)</th>
<th>MOLECULAR WEIGHT (Daltons x 10⁶)</th>
<th>WEIGHT PERCENT IONIC</th>
<th>SOLUTION VISCOSITY 0.5% in Dist. Water (CP)</th>
<th>EFFECTIVE pH RANGE</th>
<th>EXPERIMENTAL CHARGE DENSITY (Schenning, 2004) (mEq/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10G-80A</td>
<td>Medium Anionic</td>
<td>44</td>
<td>3-4</td>
<td>40</td>
<td>&gt;4500</td>
<td>6-13</td>
<td>423.9</td>
</tr>
<tr>
<td>10G-100C</td>
<td>High Cationic</td>
<td>38</td>
<td>10</td>
<td>55</td>
<td>&gt;5000</td>
<td>1-13</td>
<td>294.7</td>
</tr>
</tbody>
</table>

The manufactured polymer modified bentonite component was directly extracted from a donated Bentofix® GCL sample by cutting the sheet open and shaking out the contents.

Figure 4.1: Direct Extraction of Bentofix

4.3 Initial Media Preparation

Bentonite powder, the Bentofix sample, and the polymers were all stored at room temperature and humidity. The bentonite and Bentofix samples were stored in loosely sealed containers. Under regular storage exposure conditions, both the bentonite and Bentofix were already partially hydrated and contained initial sodium concentrations at their surface. Polymers were stored in tightly sealed, dark storage containers. The bentonite powder, Bentofix sample, and the polymers were all used with no initial preparation.
4.4 Desorption

In order to estimate the amount of leachable sodium and calcium available from the reference material, desorption tests were performed on the bentonite. Desorption experiments were modeled to describe desorption characteristics at a pH of 7. A clean mix jar belonging to the ECE mixer was triple rinsed and filled with a liter of water. Approximately one gram of bentonite powder was weighed out and placed in the water. The mixer was turned up to 360 rpm for 10 minutes and then slowed down at 70 rpm. The pH value of the solution was continuously monitored and manual 10 μL incremental additions of 0.1 N nitric acid or sodium hydroxide was added to the solution until it stabilized at a pH value 7±.25. Eleven 5 mL samples were withdrawn at specific times over a period of 3 days, filtered, and acidified to 5% nitric acid with a small addition of concentrated nitric acid. Results for sodium and calcium desorption tests are included in Appendix A: Results.

4.5 Time to Equilibrium

Kinetic experiments were performed in order to estimate time to equilibrium and to choose acceptable initial sodium and calcium concentrations for sorption tests. Time to equilibrium experiments were modeled to describe sorption characteristics at a pH of 7.

For sodium kinetic experiments, a 500 mg/L solution of Na\(^+\) was created by weighing out approximately 1.27 grams of NaCl pellets and dissolving it in a triple rinsed 1 L volumetric flask filled with water. A clean mix jar belonging to the ECE mixer was triple rinsed and filled with 1 L of the 500 mg/L Na\(^+\) solution. One gram of bentonite powder was weighed out and placed in the water. The mixer was turned up to 360 rpm for 10 minutes and then slowed down at 70 rpm. The pH value of the solution was
continuously monitored and manual 10 μL incremental additions of 0.1 N nitric acid or sodium hydroxide was added to the solution until it stabilized at a pH value of 7±.25. Eleven 5 mL samples were withdrawn at specific times over a period of 3 days, filtered, and acidified to 5% nitric acid with a small addition of concentrated nitric acid. A second sodium kinetic experiment was also performed in the same manner as described above, but a 50 mg/L solution of Na⁺ was used in place of the 500 mg/L solution of Na⁺.

For calcium kinetic experiments, a 500 mg/L solution of Ca²⁺ was created by weighing out approximately 1.38 grams of CaCl₂ pellets and dissolving it in a triple rinsed 1 L volumetric flask filled with water. A clean mix jar belonging to the ECE mixer was triple rinsed and filled with 1 L of the 500 mg/L Ca²⁺ solution. One gram of bentonite powder was weighed out and placed in the water. The mixer was turned up to 360 rpm for 10 minutes and than slowed down at 70 rpm. The pH value of the solution was continuously monitored and manual 10 μL incremental additions of 0.1 N nitric acid or sodium hydroxide was added to the solution until it stabilized at a pH value 7±.25. Eleven 5 mL samples were withdrawn at specific times over a period of 3 days, filtered, and acidified to 5% nitric acid with a small addition of concentrated nitric acid. Results for sodium and calcium kinetic tests are included in Appendix A: Results.
4.6 Batch Sorption Tests

Sorption tests for fixed slurry concentrations of Bentonite, Bentofix, and polymer modified bentonite mixes were performed at six different initial concentrations (500, 100, 50, 10, 1, and 0.2 mg/L of Na\(^+\) or Ca\(^2+\)). Batch sorption experiments were modeled to describe sorption characteristics at a pH of 7.

4.6.1 Slurries

4.6.1.1 Bentonite and Bentofix Slurries

A clean mix jar belonging to the ECE mixer was triple rinsed and filled with a liter of water. Approximately one gram of bentonite powder was weighed out and placed in the water. The mixer was turned up to 360 rpm for 10 minutes and than slowed down at 70 rpm. The pH value of the solution was continuously monitored and manual 10 μL incremental additions of 0.1 N nitric acid or sodium hydroxide was added to the solution until it stabilized at a pH value 7±.25. The solution was allowed to equilibrate overnight before testing. The same procedure was repeated using approximately one gram of Bentofix.

4.6.1.2 HC or MA Bentonite Slurries

Two clean mix jars belonging to the ECE mixer were triple rinsed and filled with a liter of water. For the 1% HC-Bentonite slurry, approximately 0.01 grams of high cationic polymer and approximately 0.99 grams of bentonite powder was weighed out and placed in 1 L of water in a mix jar. For the 3% HC-Bentonite slurry, approximately 0.03 grams of high cationic polymer and approximately 0.97 grams of bentonite powder was weighed out and placed in 1 L of water in a mix jar. The mixer was turned up to 360 rpm for 10 minutes and than slowed down at 70 rpm. The pH value of the solution was
continuously monitored and manual 10 μL incremental additions of 0.1 N nitric acid or sodium hydroxide was added to the solution until it stabilized at a pH value 7±.25. The solution was allowed to equilibrate overnight before testing. The same procedure was repeated using medium anionic polymer instead.

4.6.2 Spike Solutions

A 10,000 mg/L Na⁺ solution was created daily during sorption experiments by adding approximately 2.54 grams of solid NaCl pellets into 100 mL of water in a volumetric flask. A 500 mg/L Na⁺ solution was created daily during sorption experiments by adding approximately 1.27 grams solid NaCl pellets into 1 L of water in a volumetric flask. 10,000 mg/L and 500 mg/L Ca²⁺ solutions were also made the same way, but using 2.76 grams and 1.38 grams, respectively, of CaCl₂ pellets instead.

4.6.3 Initial Concentration Spiking and Agitation

For a specific slurry (bentonite, bentofix, 1% HC-bentonite, 3% HC-bentonite, 1% MA-bentonite, 3% Ma-bentonite), a set of seven triple rinsed centrifuge tubes were labeled, capped and weighed empty. These tubes were filled with a specific volume of the slurry and weighed again. The tubes were spiked with a specific volume of 10,000 or 500 mg/L of Na or Ca²⁺ to create six different initial concentrations of Na⁺ or Ca²⁺ and were weighed once more. Calculations for specific volumes for spiking solutions and slurries are included in the Appendix A: Results. Sets of tubes were placed in the tube rotator and were agitated for at least 24 hours.

4.6.4 Quality Control

A baseline concentration was established as a quality control measurement in order to account for any leachable sodium or calcium concentrations initially available on
the six slurries. This was accomplished by taking a 5 mL sample from each unexposed slurry, syringe filtering, and preserving the sample at 5% HNO₃.

Another quality control measure taken during sorption experiments was running a blank at the lowest concentration of the sorption experiment in order to account for any bottle sorption of sodium or calcium.

4.6.5 Sample Preparation

4.6.5.1 Supernatant

After agitation, the slurries were placed in a test tube rack and the media settled to the bottom by gravity. Approximately 5 mL of supernatant was carefully extracted from the top of the solution in a centrifuge tube with a sterile disposable transfer pipet, placed in a syringe and filtered, and preserved at 5% nitric acid before FAA analysis. This was repeated for the rest of the set.

4.6.5.2 Solid Media

The final pH of the remaining slurry was taken and the slurry was poured into a triple rinsed glass funnel lined with labeled filter paper. After full filtration, the filter paper and extracted media were placed in a drying oven at 50°C for at least three days. After drying, a portion of the filter paper was cut out and placed in a sample bottle for SEM and EDX analysis.

4.7 Sample Analysis

4.7.1 Flame Atomic Adsorption (FAA)

4.7.1.1 Sodium

Blank, 0.1, 0.5, 1, and 1.5 mg/L sodium standards were used to create a linear calibration curve during FAA analysis. Sodium standards were created by spiking a
certain volume of 2 g/L 2% HNO₃ potassium (K⁺) matrix modifier with a certain volume of 10,000 mg/L 5% HNO₃ Na⁺ standard. The 2 g/L K⁺ matrix modifier was created by dissolving approximately 6.71 grams of potassium nitrate (KNO₃) pellets in 1 L of 2% HNO₃ solution. The 2% HNO₃ solution was created by adding 28.57 mL of 70% concentrated HNO₃ to a triple rinsed clean 1 L volumetric flask and filling the remaining volume with water. 5% HNO₃ preserved and concentrated supernatants collected from desorption, kinetic, and sorption experiments were also diluted with the 2 g/L K⁺ 2% HNO₃ samples before FAA analysis.

Fixed working conditions included a 5 mA lamp current, an air flow of 13.5 L/min and an acetylene flow of 2 L/min. Variable working conditions were set at a 589 nm wavelength, a 0.5 nm slit width, and the background correction turned on.

4.7.1.2 Calcium

Blank, 0.1, 0.5, 1, 3, and 5 mg/L calcium standards were used to create a linear calibration curve during FAA analysis. Calcium standards were created by spiking a certain volume of 2 g/L 2% HNO₃ potassium (K⁺) matrix modifier with a certain volume of 1,000 mg/L 5% HNO₃ Ca²⁺ standard. The 2 g/L K⁺ matrix modifier was created by dissolving approximately 6.71865 grams of potassium nitrate (KNO₃) pellets in 1 L of 2% HNO₃ solution. The 2% HNO₃ solution was created by adding 28.57143 mL of 70% concentrated HNO₃ to a triple rinsed clean 1 L volumetric flask and filling the remaining volume with water. 5% HNO₃ preserved and concentrated supernatants collected from desorption, kinetic, and sorption experiments were also diluted with the 2 g/L K⁺ 2% HNO₃ samples before FAA analysis.
Fixed working conditions included a 10 mA lamp current, a nitrous oxide (N₂O) flow of 10.34 L/min and an acetylene flow of 6.55 L/min. Variable working conditions were set at a 422.7 nm wavelength, a 0.5 nm slit width, and the background correction was turned on.

4.7.2 Scanning Electron Microscopy (SEM)

A small sample of dried media and filter paper was mounted on top of a piece of carbon tape attached to an aluminum sample holder. No special coatings were used on the sample. Pictures were taken on a Hitachi S800 scanning electron microscope at working conditions synonymous with high resolution pictures, including the smallest possible working distance, the smallest size aperture setting, the highest possible acceleration voltage (25 kV), and a high condenser lens setting. Pictures were taken at the lowest possible scan speed and imported into a computer. Pictures were formatted using EDAX Genesis software.

4.7.3 EDX Analysis

A small sample of dried media and filter paper was mounted on top of a piece of carbon tape attached to an aluminum sample holder. No special coatings were used on the sample. EDX spectrums were taken using an EDAX detector attached to the SEM. Working conditions used to take spectrums included an acceleration voltage of 25 kV, a 30° tilt, a take off angle of 36.31°, and a working distance corresponding to the maximum amount of x-ray counts. The acquisition time for spectrum collection was at least one minute. After the spectrums were collected, peak identification and a percent elemental composition analysis was performed.
CHAPTER FIVE
DATA ANALYSIS AND DISCUSSION

5.1 Sorption Experiments

Data sets received from AA analysis for samples consisted of initial and final concentrations of sorption experiments. $Q$, the sorption density was calculated from the following equation:

$$\frac{\text{MassSorbed}}{\text{MassSorber}} = \frac{\text{Volume of Solution} \times (\text{Initial Aqueous Concentration} - \text{Final Aqueous Concentration})}{\text{Media Mass}}$$

Isotherms were constructed with $Q$ (mg/kg), the sorption density, on the y-axis and $C_e$ (mg/L), equilibrium concentration on the x-axis.

Quality control measurements implemented during the experiments are accounted for in the data by implementation of the following equation:

$$\text{Final Con.} = \text{FAA Final Con.} - \text{Baseline Con.} + \text{Bottle Sorption Con.}$$

Where $\text{Final Con.}$= the final calculated concentration (mg/L) accounting for quality control measurements, $\text{FAA Final Con.}$= the final concentration of the sorption supernatant reported by the FAA machine (mg/L), $\text{Baseline Con.}$=the baseline concentration of the exposed slurry supernatant reported by the FAA machine (mg/L), and the $\text{Bottle Sorption Con.}$= the amount of bottle sorption that occurred as a difference between the initial and final concentration of the blank (spiked solution only, no media) sample ran in sorption experiments as reported by the FAA machine (mg/L).
5.1.1 Empirical Isotherm Calculations

5.1.1.1 Linear Isotherm

An equation for a linear isotherm was calculated from a linear regression of $Q$ and $C_e$, with the following expression:

$$Q = k_d C_e$$

Where $C_e$ (mg/L) is proportional to $Q$ (mg/kg) by a factor $k_d$ (kg/L).

5.1.1.2 Freundlich Isotherm

An equation for a Freundlich isotherm was calculated from the linear regression of the logarithmic plot of $Q$ and $C_e$, with the following expression:

$$Q = K_F C_e^{n_F}$$

Where the slope of the logarithmic linear regression is equal to a dimensionless factor $n_F$, and $10^{y}$-intercept of linear regression is equal to $K_F ([mg]^{-n_F}[L]^{n_F}/kg)$

5.1.1.3 Langmuir Isotherm

An equation for a Langmuir isotherm was calculated from the linear regression of the plot of $1/Q$ and $1/C_e$, with the following expression:

$$Q = \frac{Q_{max} K_L C_e}{1 + K_L C_e}$$

Where (y-intercept of the linear regression)$^{-1}$ is equal to $Q_{max}$ (mg/kg) and $\frac{1}{slope \cdot Q_{max}}$ is equal to $K_L$ (L/mg).
5.1.2 Distribution Coefficients

Distribution coefficients \((k_d, K_F, K_L)\) and other constants calculated for the empirical isotherms are summarized in Tables 5.1 and 5.2 for sodium and calcium sorption tests, respectively.

For sodium sorption tests, \(k_d\) distribution coefficients had values close in range with the exception of the high cationic polymer tests. \(K_F\) distribution coefficients varied widely in range. High cationic polymer tests had the smallest values—with the higher percentage of cationic polymer resulting in a smaller \(K_F\). \(K_L\) distribution coefficients had values close in range for all sorption tests.

For calcium sorption tests, \(k_d\) distribution coefficients ranged from about 53 kg/L to 130 kg/L. \(K_F\) distribution coefficients were fairly close in range, with the exception of the 3% high cationic polymer test. \(K_L\) distribution coefficients had values ranging from 0.03 to 0.08 L/mg.

Table 5.1: Sodium Sorption Test Results

<table>
<thead>
<tr>
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<th>FINAL pH</th>
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<td></td>
<td>LINEAR</td>
<td>FREUNDLICH</td>
<td>LANGMUIR</td>
</tr>
<tr>
<td>(k_d) kg/L</td>
<td>(n_F)</td>
<td>(K_F) [mg(^{1-n_F})] [L]^[n_F] /kg</td>
<td>(Q_{max}) mg/kg</td>
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<tr>
<td>Bentonite</td>
<td>1291.7</td>
<td>0.9329</td>
<td>1654</td>
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<tr>
<td>Bentofix</td>
<td>1006</td>
<td>0.8187</td>
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<td>1% High Cationic</td>
<td>725.01</td>
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<td>3% High Cationic</td>
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<tr>
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<td>3% Medium Anionic</td>
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Table 5.2: Calcium Sorption Test Results

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<td>$k$ [mg/L]</td>
<td>$n_F$</td>
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<td>3% Medium Anionic</td>
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5.1.3 Sorption Isotherm Discussion

Empirical equations for Linear, Langmuir, and Freundlich isotherms were, with a chosen range of input $C_e$ values, plotted against the raw values of $C_e$ and $Q$. This allowed a comparison of how well the empirical isotherm represented the raw data and, thus, the accuracy of the fit.

The best fitting empirical equations were created by using data corresponding to only the three or four highest final concentrations of the experiment. Analysis of the results reveals that the empirical Freundlich isotherms had the best fit for the data. However, kinetic tests revealed that very little sorption occurred at 50 mg/L or greater for Na$^+$ and 500 mg/L for Ca$^{2+}$. Theoretically, Freundlich isotherms represent substances that have unlimited sorption capacity. Ideally, a consistency between kinetic tests and sorption data would have revealed an empirically calculated Langmuir isotherm as the best fit for all raw data—where the plateau for Na$^+$ begins at an equilibrium concentration of approximately 50 mg/L and the plateau for the Ca$^{2+}$ equilibrium concentration begins at approximately 500 mg/L.
Inconsistency between kinetic and sorption data reveals that another mechanism removed a significant amount of sorbate from the supernatant besides sorption. Surface precipitation is a very possible mechanism. Although precipitation within the solution was considered in Chapter 4, precipitation forming at the surface of the clay was not accounted for. Figure 5.1 describes how surface precipitation influences the shape of strong and weak Langmuir isotherms.

Figure 5.1: (a) Isotherms for Adsorption and Surface Precipitation Separately (b) Apparent Isotherms for Simultaneous Adsorption and Surface Precipitation (Benjamin, 2002)
Another reason for an inaccurate fit of the empirical Langmuir isotherm may be because it is based on a single site type. Multisite Langmuir isotherms account for situations were both strong and weak bonding sites influence sorption, and the apparent Langmuir isotherm is a result of the sum of two different bonding sites (Figure 5.2).

![Multisite Sorption Isotherm](image_url)

Figure 5.2: Multisite Sorption Isotherm (Benjamin, 2002)

Competitive sorption between the ions and the polyions was not considered before beginning experiments. Isotherms may not perfectly fit empirical single-specie isotherms because other species may have occupied sites that had a higher affinity than the species in question.

5.2 SEM Pictures

SEM pictures taken at a maximum of magnification of 25,000 revealed that there were no significant changes in the surfaces or the pores of the exposed regular bentonite slurry and the polymer modified bentonite slurries. Particle charging imposed difficulties of taking quality resolution pictures of the bentonite clay above a magnification of 25,000.
5.3 EDX Analysis

Peak identification of the collected spectrums consisted of using the automatic identification feature of the EDAX genesis software and also manually identifying peaks of common elements expected to be seen in the sample. In many cases during compositional analysis of the dried slurries, exposures of the polymer modified and regular bentonite to high concentrations of sodium or calcium resulted in the principles of mass action, where very high concentrations of any type of chemical species is capable of replacing another capable species at a much lower concentration. Through mass action, sodium, a lower valence cation, was able to replace a higher valence cation. Mass action occurred in various sample to the point where counts of the replaced ion was so low that the peak for it was unidentifiable.

The pure bentonite slurry exposed at the highest solution concentration of sodium (500 ppm) revealed that there was no change in the weight percent of sodium but there was a small reduction in the weight percent of calcium in comparison to the unexposed bentonite powder. The pure bentonite slurry exposed at the highest solution concentration of calcium (500 ppm) revealed that there was a large increase in the weight percent of calcium (1.56%) in comparison to the unexposed bentonite powder (0.55%) and sodium was undetectable in the exposed sample—indicating that the process of mass action had likely occurred.

The Bentofix slurry exposed at the highest solution concentration of sodium (500 ppm) revealed that there was a large increase in the weight percent (2.32 %) of sodium in comparison to the unexposed Bentofix powder (1.09%), and calcium was undetectable—indicating the occurrence of mass action. The Bentofix slurry exposed at the highest
solution concentration of calcium (500 ppm) revealed that there was a decrease of calcium (0.54%) present at the surface in comparison to the unexposed Bentofix powder (1.25%) and sodium was undetectable. The decrease of calcium is not an expected result, and it could be explained by the possibility of an inaccuracy in the EDX sampling, where the measurement was taken at a location on the sample where the true composition of the exposed slurry was not well represented. This can be further attributed to the fact that there is a large jump in the weight percent of carbon (43.02%) from the unexposed Bentofix powder (15.52%)—counts coming off of the carbon tape into the EDX detector could have shifted the weight percent composition off.

The 3% by weight high cationic polymer-bentonite slurry exposed at the highest solution concentration of sodium (500 ppm) revealed that there was a large change in the weight percent of sodium (2.34%) in comparison the unexposed bentonite powder (1.09%), and a decrease in the weight percent of calcium (0.28%) in comparison to the unexposed bentonite powder (0.55%). The 3% by weight high cationic polymer-bentonite slurry exposed at the highest solution concentration of calcium (500 ppm) revealed that there was a large change in the weight percent of calcium (1.2%) in comparison the unexposed bentonite powder (0.55%), and sodium was undetectable—indicating that the process of mass action had likely occurred.

The 3% by weight medium anionic polymer-bentonite slurry exposed at the highest solution concentration of sodium (500 ppm) revealed that there was a moderate change in the weight percent of sodium (1.92%) in comparison the unexposed bentonite powder (1.09%), and virtually no change in the weight percent of calcium (0.54%) in comparison to the unexposed bentonite powder (0.55%). The 3% by weight high cationic
polymer-bentonite slurry exposed at the highest solution concentration of calcium (500 ppm) revealed that there was a large change in the weight percent of calcium (1.12%) in comparison the unexposed bentonite powder (0.55%), and sodium was undetectable—indicating that the process of mass action had likely occurred.
6.1 Summary
Empirical distribution coefficients for sodium and calcium were extrapolated from Linear, Langmuir, and Freundlich isotherms models based on resulting data from batch sorption tests of bentonite, a commercially manufactured GCL component (Bentofix), a 3% by weight high cationic-bentonite slurry, a 1% by weight high cationic-bentonite slurry, a 3% by weight medium anionic-bentonite slurry, and a 1% by weight medium anionic-bentonite slurry. Pictures of the exposed dry slurry surfaces revealed that there was no significant change in comparison to polymer modified bentonite mixes and natural bentonite. EDX analysis of the exposed dried slurry surfaces comparison to unexposed bentonite and Bentofix revealed changes in weight percentages of sodium and bentonite before and after exposure, indicating mass action had occurred.

6.2 Conclusions
The use of high cationic polymers to modify the surfaces of bentonite results in a large reduction of distribution coefficients of linear and Freundlich isotherms in comparison to the other slurries. A reduction in the distribution coefficient results in a smaller Q, sorption density, value at a particular equilibrium concentration for both linear and Freundlich isotherms. Therefore, the addition of high cationic polymers to the surface
of bentonite clays results in a negative effect of its sorptive affinity towards sodium and calcium.

Modeled Langmuir isotherms for all sorption tests revealed a poor fit in comparison to the test data. Results from kinetic tests reveal that very little sorption occurs for sodium for a concentration of 50 ppm for regular bentonite. These results are not in harmony with data collected from sorption tests, where a reduction in concentration is seen even at an initial concentration of 500 ppm. This could be due to the fact that a conventional single-site, single-species Langmuir isotherm may not represent the data well if there is multi-site and competitive sorption occurring at the clay surface.

Polymer modification of bentonite at 1 and 3% by weight results in very little change of the physical appearance of the surface of the clays as seen by a scanning electron microscope up to a magnification of 25,000.

Polymer modified bentonite samples as well as regular sodium bentonite experienced an increase in the weight percent of calcium measured at the surface by EDX analysis after exposure to a 500 ppm Ca\(^{2+}\) solution. However, polymer modified bentonite samples, with the exception of Bentofix, experienced an increase in the weight percent of sodium measured at the surface after exposure to a 500 ppm Na\(^+\) solution in comparison to sodium bentonite, which had no change in percent by weight sodium present at the surface after the same exposure. EDX analysis suggests that polymer modified bentonite is a better sorbent for sodium than sodium bentonite, but polymer modified bentonite and sodium bentonite are both effective sorbents for calcium.
6.3 Recommendations

Results of this research may be used for modeling applications to characterize GCL performance in the presence of inorganic leachates that contain high concentrations of sodium and calcium. With a distribution coefficient and other relevant parameters pertaining to the properties of the clay component of the GCL, it is possible to model the contaminant transport equation and the concentration history assuming conditions for equilibrium are present.

In order to correctly predict GCL performance from results of lab-scale batch sorption studies one must keep in mind that lab-scale batch sorption studies are performed with a high ratio of concentrated sorbate (calcium or sodium) to sorbent (clay component). For most engineering applications of GCLs in landfills, it is just the opposite: there is a high ratio of adsorbent to sorbate. Thus, increasing the presence of sorbent in comparison to the sorbate increases the sorptive potential of the GCL relative to all sorbates.

Another consideration during modeling is that distribution coefficients in this research were extrapolated from single-species, single-site isotherm models. It is highly unlikely that inorganic leachates will contain only sodium or calcium, and competing ions may increase or decrease the affinity of the clay surface for a certain chemical species.
REFERENCES


APPENDICES
Appendix A: Results

Table A.1: Desorption Tests

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Appendix A: (Continued)

**Figure A.1: FAA Calibration Curve for Sodium Desorption**

**Figure A.2: Sodium Desorption Curve**
Appendix A: (Continued)

Calcium Desorption Calibration Curve

\[ y = 0.1929x + 0.0069 \]

\[ R^2 = 0.9957 \]

Figure A.3: FAA Calibration Curve for Calcium Desorption

Figure A.4: Calcium Desorption Curve
## Appendix A: (Continued)

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**Figure A.5: FAA Calibration Curve for Sodium 500 ppm Kinetic Test**

**Figure A.6: Sodium 500 ppm Kinetic Test**
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<td>22.7°C</td>
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Appendix A: (Continued)

![Sodium 50 ppm Calibration Curve](image)

**Figure A.7: FAA Calibration Curve for Sodium 50 ppm Kinetic Test**

![Na Kinetics: 50 ppm](image)

**Figure A.8: Sodium 50 ppm Kinetic Test**
Appendix A: (Continued)

Table A.4: 500 Ca\textsuperscript{2+} ppm Kinetic Test

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<th>pH INITIAL</th>
<th>ACID/BASE</th>
<th>pH</th>
<th>TEMP</th>
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<td>HNO\textsubscript{3} 10µL</td>
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</table>
Appendix A: (Continued)

Figure A.9: FAA Calibration Curve for Calcium 500 ppm Kinetic Test

Figure A.10: Calcium 500 ppm Kinetic Test
### Table A.5: Spike Calculations for Sodium Sorption Experiments

<table>
<thead>
<tr>
<th>STOCK SOLUTION CONCENTRATION (mg/L)</th>
<th>FINAL SAMPLE CONCENTRATION (mg/L)</th>
<th>FINAL SAMPLE VOLUME (mL)</th>
<th>SLURRY VOLUME (mL)</th>
<th>STOCK SPIKE VOLUME (mL)</th>
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<td>28.500</td>
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<tr>
<td>500</td>
<td>0.20</td>
<td>30</td>
<td>29.990</td>
<td>0.010</td>
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### Table A.6: Spike Calculations for Calcium Sorption Experiments

<table>
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<th>STOCK SOLUTION CONCENTRATION (mg/L)</th>
<th>FINAL SAMPLE CONCENTRATION (mg/L)</th>
<th>FINAL SAMPLE VOLUME (mL)</th>
<th>SLURRY VOLUME (mL)</th>
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<tr>
<td>500</td>
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<td>0.010</td>
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<tr>
<td>500</td>
<td>0.20</td>
<td>25</td>
<td>24.990</td>
<td>0.010</td>
</tr>
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</table>
Appendix A: (Continued)

Figure A.11: FAA Calibration Curve for Sodium Sorption

Figure A.12: FAA Calibration Curve Sodium Baseline Samples
Appendix A: (Continued)

Figure A.13: Linear Isotherm-Bentonite Na

\[ y = 1291.7x \]
\[ R^2 = 0.9911 \]
Appendix A: (Continued)

Freundlich Isotherm Estimation-Bentonite Na

\[ y = 0.9329x + 3.2186 \]

\[ R^2 = 0.9584 \]

\[ K_F = 10^{3.2186} = 1654 \]

\[ S = 1654C^{0.9329} \]

Figure A.14: Freundlich Isotherm Estimation-Bentonite Na

Freundlich Isotherm-Bentonite Na

\[ Q(mg/kg) \]

\[ C_{e Na} (mg/L) \]

Figure A.15: Freundlich Isotherm-Bentonite Na
Appendix A: (Continued)

\[ y = 0.0006x + 6E-06 \]
\[ R^2 = 0.9116 \]

Figure A.16: Langmuir Isotherm Estimation-Bentonite Na

\[ S = 166666 \times (0.01C) / (1 + 0.01C) \]

Figure A.17: Langmuir Isotherm-Bentonite Na
Appendix A: (Continued)

Figure A.18: Linear Isotherm-Bentofix Na

$y = 1006x$
$R^2 = 0.9923$
Appendix A: (Continued)

**Figure A.19: Freundlich Isotherm Estimation-Bentofix Na**

\[ y = 0.8187x + 3.3955 \]

\[ R^2 = 0.9929 \]

\[ n = 0.8187 \]

\[ K_F = 10^{3.3955} = 2486 \]

\[ S = 2486^{0.8187} \]

**Figure A.20: Freundlich Isotherm-Bentofix Na**
Appendix A: (Continued)

\[ y = 0.0006x + 5 \times 10^{-6} \]
\[ R^2 = 0.9703 \]

\[ \frac{1}{S_{\text{max}}} = 5 \times 10^{-6}, \quad S_{\text{max}} = 200000 \]
\[ K_L = \frac{1}{(\text{Slope} \times S_{\text{max}})} = 0.01 \]

Figure A.21: Langmuir Isotherm Estimation-Bentofix Na

\[ S = 200000 \times (0.01C)/(1+0.01C) \]

Figure A.22: Langmuir Isotherm-Bentofix Na
Appendix A: (Continued)

Figure A.23: Linear Isotherm-1% HC Na

Linear Isotherm-1% HC Na

\[ y = 725.01x \]

\[ R^2 = 0.9917 \]
Appendix A: (Continued)

Freundlich Isotherm Estimation-1% HC Na

\[ y = 1.1092x + 2.6977 \]

\[ R^2 = 0.8875 \]

\[ n = 1.1092 \]

\[ K_f = 10^{2.6977} = 499 \]

\[ S = 499^{1.1092} \]

Figure A.24: Freundlich Isotherm Estimation-1% HC Na

Freundlich Isotherm-1% HC Na

Figure A.25: Freundlich Isotherm-1% HC Na
Appendix A: (Continued)

Langmuir Isotherm Estimation-1% HC Na

\[ y = 0.0006x + 9\times 10^{-6} \]

\[ R^2 = 0.8864 \]

\[ \frac{1}{S_{\text{max}}} = 9\times 10^{-6}, \quad S_{\text{max}} = 111111 \]

\[ K_L = \frac{1}{\text{Slope} 	imes S_{\text{max}}} = 0.02 \]

Figure A.26: Langmuir Isotherm Estimation-1% HC Na

Figure A.27: Langmuir Isotherm-1% HC Na
Figure A.28: Linear Isotherm-3% HC Na
Appendix A: (Continued)

Freundlich Isotherm Estimation-3% HC Na

\[ y = 1.2358x + 2.3878 \]

\[ R^2 = 0.8816 \]

\[ n_f = 1.2358 \]

\[ K_f = 10^{2.3878} = 244 \]

\[ S = 244C^{1.2358} \]

Figure A.29: Freundlich Isotherm Estimation-3% HC Na

Figure A.30: Freundlich Isotherm-3% HC Na
Appendix A: (Continued)

Langmuir Isotherm Estimation - 3\% HC Na

\[ y = 0.0008x + 9E-06 \]

\[ R^2 = 0.871 \]

\[ \frac{1}{S_{\text{max}}} = 9E-06, S_{\text{max}} = 111111 \]

\[ K_L = \frac{1}{\text{Slope} \times S_{\text{max}}} = 0.02 \]

\[ S = 111111 \times \frac{0.02C}{1 + 0.02C} \]

Figure A.31: Langmuir Isotherm Estimation - 3\% HC Na

Langmuir Isotherm - 3\% HC Na

Figure A.32: Langmuir Isotherm - 3\% HC Na
Appendix A: (Continued)

Figure A.33: Linear Isotherm-1% MA Na
 Appendix A: (Continued)

Figure A.34: Freundlich Isotherm Estimation-1% MA Na

Figure A.35: Freundlich Isotherm-1% MA Na
Appendix A: (Continued)

Langmuir Isotherm Estimation-1% MA Na

\[ y = 0.0005x + 9 \times 10^{-6} \]

\[ R^2 = 0.7696 \]

\[ S = \frac{111111 \times (0.02C)}{1 + 0.02C} \]

\[ K_L = \frac{1}{(\text{Slope} \times S_{\text{max}})} = 0.02 \]

Figure A.36: Langmuir Isotherm Estimation-1% MA Na

Figure A.37: Langmuir Isotherm 1% MA Na
Figure A.38: Linear Isotherm-3% MA Na
Appendix A: (Continued)

Freundlich Isotherm Estimation-3% MA Na

\[ y = 1.0869x + 3.0563 \]

\[ R^2 = 0.9532 \]

\[ n_f = 1.0869 \]

\[ K_f = 10^{3.0563} = 1138 \]

\[ S = 1138C^{1.0869} \]

Figure A.39: Freundlich Isotherm Estimation-3% MA Na

Freundlich Isotherm-3% MA Na

Figure A.40: Freundlich Isotherm-3% MA Na
Appendix A: (Continued)

Figure A.41: Langmuir Isotherm Estimation-3% MA Na

Figure A.42: Langmuir Isotherm-3% MA Na
Appendix A: (Continued)

Figure A.43: FAA Calibration Curve for Calcium Samples 500 ppm, 100 ppm, and 10 ppm Initial Concentrations

Figure A.44: FAA Calibration Curve for Calcium Samples 50 ppm, 1 ppm, and 0.1 ppm Initial Concentrations
Appendix A: (Continued)

![Linear Isotherm-Bentonite Ca](image)

**Figure A.45: Linear Isotherm-Bentonite Ca**

\[ y = 53.873x \]

\[ R^2 = 0.6387 \]
Appendix A: (Continued)

Figure A.46: Freundlich Isotherm Estimation-Bentonite Ca

Figure A.47: Freundlich Isotherm-Bentonite Ca
Appendix A: (Continued)

Langmuir Isotherm Estimation-Bentonite Ca

\[ y = 0.0021x + 6E-05 \]
\[ R^2 = 0.9841 \]

\[ 1/S_{\text{max}} = 6E-5, \quad S_{\text{max}} = 16666 \]
\[ K_L = \frac{1}{(\text{Slope} \times S_{\text{max}})} = 0.03 \]

\[ S = 16666 \times (0.03C) / (1 + 0.03C) \]

Figure A.48: Langmuir Isotherm Estimation-Bentonite Ca

FIGURE A.48: Langmuir Isotherm Estimation-Bentonite Ca

Langmuir Isotherm-Bentonite Ca

\[ Q(\text{mg/kg}) \]

\[ C_e \text{ Ca (mg/L)} \]

Plot Data
Empirical Isotherm

Figure A.49: Langmuir Isotherm-Bentonite Ca

FIGURE A.49: Langmuir Isotherm-Bentonite Ca

92
Appendix A: (Continued)

Figure A.50: Linear Isotherm-Bentofix Ca

Linear Isotherm-Bentofix Ca

\[ y = 77.63x \]

\[ R^2 = 0.6391 \]
Appendix A: (Continued)

Freundlich Isotherm Estimation-Bentofix Ca

\[ y = 0.3886x + 3.4642 \]
\[ R^2 = 0.9933 \]

Figure A.51: Freundlich Isotherm Estimation-Bentofix Ca

Freundlich Isotherm-Bentofix Ca

\[ K_F = 10^{3.4642} = 2912 \]
\[ n_F = 0.3886 \]
\[ S = 2912^{0.3886} \]

Figure A.52: Freundlich Isotherm-Bentofix Ca
Appendix A: (Continued)

Langmuir Isotherm Estimation-Bentofix Ca

\[ y = 0.0006x + 5 \times 10^{-5} \]
\[ R^2 = 0.9459 \]

\[ S = 20000 \times \frac{(0.08C)}{(1+0.08C)} \]

\[ K_L = \frac{1}{(\text{Slope} \times S_{\text{max}})} = 0.08 \]

Figure A.53: Langmuir Isotherm Estimation-Bentofix Ca

Langmuir Isotherm-Bentofix Ca

Figure A.54: Langmuir Isotherm-Bentofix Ca
Appendix A: (Continued)

![Linear Isotherm-1% HC Ca](image)

Figure A.55: Linear Isotherm-1% HC Ca

\[ y = 89.422x \]
\[ R^2 = 0.9233 \]
Appendix A: (Continued)

Figure A.56: Freundlich Isotherm Estimation-1% HC Ca

Figure A.57: Freundlich Isotherm-1% HC Ca
Appendix A: (Continued)

\[ y = 0.0013x + 7E-05 \]

\[ R^2 = 0.8479 \]

\[ 1/S_{max} = 7E-5, S_{max} = 14286 \]

\[ K_L = 1/(Slope * S_{max}) = 0.05 \]

\[ S = 14286 * (0.05C) / (1 + 0.05C) \]

Figure A.58: Langmuir Isotherm Estimation-1% HC Ca

Figure A.59: Langmuir Isotherm-1% HC Ca
Appendix A: (Continued)

Figure A.60: Linear Isotherm-3% HC Ca
Appendix A: (Continued)

Figure A.61: Freundlich Isotherm Estimation-3% HC Ca

Figure A.62: Freundlich Isotherm-3% HC Ca
Appendix A: (Continued)

Langmuir Isotherm Estimation-3% HC Ca

\[ y = 0.0036x + 0.0002 \]
\[ R^2 = 0.5002 \]

\[ S = 5000 \times (0.06C) / (1 + 0.06C) \]

\[ 1/S_{\text{max}} = 0.0002, \quad S_{\text{max}} = 5000 \]
\[ K_L = 1/(\text{Slope} \times S_{\text{max}}) = 0.06 \]

Figure A.63: Langmuir Isotherm Estimation-3% HC Ca

Langmuir Isotherm-3% HC Ca

Figure A.64: Langmuir Isotherm-3% HC Ca
Appendix A: (Continued)

Figure A.65: Linear Isotherm-1% MA Ca

\[ y = 134.18x \]

\[ R^2 = 0.9876 \]
Appendix A: (Continued)

Freundlich Isotherm Estimation-1% MA Ca

\[ y = 0.5873x + 3.0029 \]
\[ R^2 = 0.8317 \]

\[ n = 0.5873 \]
\[ K_F = 10^{3.0029} = 1007 \]
\[ S = 1007C^{0.5873} \]

Figure A.66: Freundlich Isotherm Estimation-1% MA Ca

Freundlich Isotherm-1% MA Ca

Figure A.67: Freundlich Isotherm-1% MA Ca
Appendix A: (Continued)

Langmuir Isotherm Estimation-1% MA Ca

\[ y = 0.001x + 8 \times 10^{-5} \]

\[ R^2 = 0.7889 \]

\[ \frac{1}{S_{\text{max}}} = 8 \times 10^{-5}, \quad S_{\text{max}} = 12500 \]

\[ K_L = \frac{1}{(\text{Slope} \times S_{\text{max}})} = 0.08 \]

\[ S = \frac{12500 \times (0.08C)}{1+0.08C} \]

Figure A.68: Langmuir Isotherm Estimation-1% MA Ca

Figure A.69: Langmuir Isotherm-1% MA Ca
Linear Isotherm-3% MA Ca

$y = 88.265x$

$R^2 = 0.882$

Figure A.70: Linear Isotherm Estimation-3% MA Ca
Appendix A: (Continued)

Figure A.71: Freundlich Isotherm Estimation-3% MA Ca

Figure A.72: Freundlich Isotherm-3% MA Ca
Appendix A: (Continued)

Langmuir Isotherm Estimation-3% MA Ca

\[ y = 0.002x - 8\times 10^{-5} \]
\[ R^2 = 0.379 \]

\[ K_L = \frac{1}{\text{Slope} \times S_{\text{max}}} = 0.04 \]

\[ S = 12500 \times 0.04C / (1 + 0.04C) \]

Figure A.73: Langmuir Isotherm Estimation-3% MA Ca

Figure A.74: Langmuir Isotherm-3% MA Ca
Appendix A: (Continued)

Figure A.75: Unexposed Bentonite x100

Figure A.76: Unexposed Bentonite x250

Figure A.77: Unexposed Bentonite x3500
Appendix A: (Continued)

Figure A.78: Unexposed Bentonite Spectrum

Table A.7: Unexposed Bentonite Elemental Composition

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<th>ELEMENTAL PEAK</th>
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<td>O K</td>
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<td>Na K</td>
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<td>Mg K</td>
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<td>0.56</td>
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<td>Al K</td>
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<tr>
<td>Si K</td>
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<td>7.84</td>
</tr>
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<td>S K</td>
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<td>0.08</td>
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<tr>
<td>Ca K</td>
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<td>0.22</td>
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<td>Fe K</td>
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Appendix A: (Continued)

Figure A.79: Unexposed Bentofix x100

Figure A.80: Unexposed Bentofix x500

Figure A.81: Unexposed Bentofix x2000
Appendix A: (Continued)

Figure A.82: Unexposed Bentofix Spectrum

Table A.8: Unexposed Bentofix Elemental Composition

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<td>O K</td>
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<td>Na K</td>
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<td>Mg K</td>
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<tr>
<td>Al K</td>
<td>11.29</td>
<td>7.71</td>
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<tr>
<td>Si K</td>
<td>21.23</td>
<td>13.93</td>
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<tr>
<td>S K</td>
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<td>0.17</td>
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<tr>
<td>Ca K</td>
<td>1.25</td>
<td>0.57</td>
</tr>
<tr>
<td>Fe K</td>
<td>3.86</td>
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Appendix A: (Continued)

Figure A.83: Unexposed Medium Anionic Polymer x100

Figure A.84: Unexposed Medium Anionic Polymer x600

Figure A.85: Unexposed Medium Anionic Polymer x3000
Figure A.86: Unexposed Medium Anionic Polymer Spectrum

Table A.9: Unexposed Medium Anionic Polymer Elemental Composition

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<tr>
<td>N K</td>
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<tr>
<td>O K</td>
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<td>23.01</td>
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<tr>
<td>Na K</td>
<td>4.38</td>
<td>2.57</td>
</tr>
<tr>
<td>Mg K</td>
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<td>0.32</td>
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<tr>
<td>Si K</td>
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<td>0.28</td>
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<tr>
<td>Fe K</td>
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Appendix A: (Continued)

Figure A.87: Unexposed High Cationic Polymer x70

Figure A.88: Unexposed High Cationic Polymer x1000

Figure A.89: Unexposed High Cationic Polymer x10000
Appendix A: (Continued)

Figure A.90: Unexposed High Cationic Polymer Spectrum

Table A.10: Unexposed High Cationic Polymer Elemental Composition

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<td>O K</td>
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<td>Cl K</td>
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Appendix A: (Continued)

Figure A.91: Sodium Exposed Bentonite x500

Figure A.92: Sodium Exposed Bentonite x10000

Figure A.93: Sodium Exposed Bentonite x25000
Appendix A: (Continued)

![Graph: Sodium Exposed Bentonite Spectrum](image)

Figure A.94: Sodium Exposed Bentonite Spectrum

Table A.11: Sodium Exposed Bentonite Elemental Composition

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<th>ELEMENTAL PEAK</th>
<th>WEIGHT PERCENT</th>
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<tr>
<td>C K</td>
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<td>O K</td>
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<td>Mg K</td>
<td>0.82</td>
<td>0.57</td>
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<tr>
<td>Al K</td>
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<td>3.92</td>
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<tr>
<td>Si K</td>
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<td>10.42</td>
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<tr>
<td>Ca K</td>
<td>0.26</td>
<td>0.11</td>
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<tr>
<td>Fe K</td>
<td>1.79</td>
<td>0.54</td>
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<td>Total</td>
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Appendix A: (Continued)

Figure A.95: Sodium Exposed Bentofix x500

Figure A.96: Sodium Exposed Bentofix x10000

Figure A.97: Sodium Exposed Bentofix x25000
Appendix A: (Continued)

Figure A.98: Sodium Exposed Bentofix Spectrum

Table A.12: Sodium Exposed Bentofix Elemental Composition

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<tr>
<td>C K</td>
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Appendix A: (Continued)

Figure A.99: Sodium Exposed 3% Medium Anionic x500

Figure A.100: Sodium Exposed 3% Medium Anionic x10000

Figure A.101: Sodium Exposed 3% Medium Anionic x25000
Appendix A: (Continued)

Figure A.102: Sodium Exposed 3% Medium Anionic Spectrum

Table A.13: Sodium Exposed 3% Medium Anionic Elemental Composition

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<tr>
<td>Mg K</td>
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<td>1.27</td>
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<td>Al K</td>
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Appendix A: (Continued)

Figure A.103: Sodium Exposed 3% High Cationic x500

Figure A.104: Sodium Exposed 3% High Cationic x5000

Figure A.105: Sodium Exposed 3% High Cationic x25000
Appendix A: (Continued)

Figure A.106: Sodium Exposed 3% High Cationic Spectrum

Table A.14: Sodium Exposed 3% High Cationic Elemental Composition

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<td>1.26</td>
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<td>Al K</td>
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<td>6.11</td>
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<td>Si K</td>
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Appendix A: (Continued)

Figure A.107: Calcium Exposed Bentonite x500

Figure A.108: Calcium Exposed Bentonite x10000

Figure A.109: Calcium Exposed Bentonite x25000
Figure A.110: Calcium Exposed Bentonite Spectrum

Table A.15: Calcium Exposed Bentonite Elemental Composition

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<td>Al K</td>
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<td>Si K</td>
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<td>Ca K</td>
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Appendix A: (Continued)

Figure A.111: Calcium Exposed Bentofix x500

Figure A.112: Calcium Exposed Bentofix x10000

Figure A.113: Calcium Exposed Bentofix x25000
Appendix A: (Continued)

Figure A.114: Calcium Exposed Bentofix Spectrum

Table A.16: Calcium Exposed Bentofix Elemental Composition

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Appendix A: (Continued)

Figure A.115: Calcium Exposed 3% Medium Anionic x500

Figure A.116: Calcium Exposed 3% Medium Anionic x10000

Figure A.117: Calcium Exposed 3% Medium Anionic x25000
Appendix A: (Continued)

Figure A.118: Calcium Exposed 3% Medium Anionic Spectrum

Table A.17: Calcium Exposed 3% Medium Anionic Elemental Composition

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<th>WEIGHT PERCENT</th>
<th>ATOMIC PERCENT</th>
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<td>C K</td>
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<td>O K</td>
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<td>60.91</td>
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<td>Mg K</td>
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<td>1.14</td>
</tr>
<tr>
<td>Al K</td>
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<td>Si K</td>
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<td>Fe K</td>
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Appendix A: (Continued)

Figure A.119: Calcium Exposed 3% High Cationic x500

Figure A.120: Calcium Exposed 3% High Cationic x10000

Figure A.121: Calcium Exposed 3% High Cationic x25000
Appendix A: (Continued)

Figure A.122: CalciumExposed 3% High Cationic Spectrum

Table A.18: Calcium Exposed 3% High Cationic Elemental Composition

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<td>Al K</td>
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