Removal Of Iron, Zinc, And Copper From Waters Impacted By Acid Mine Drainage Using Natural Zeolite

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REMOVAL OF IRON, ZINC, AND COPPER FROM WATERS IMPACTED BY ACID MINE DRAINAGE USING NATURAL ZEOLITE

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DEDICATION

To every master's student struggling to finish a thesis, I would like to quote Ayn Rand's famous book, Atlas Shrugged:

“Devotion to the truth is the hallmark of morality; there is no greater, nobler, more heroic form of devotion than the act of a man who assumes the responsibility of thinking.”

May we all continue our pursuit of knowledge in the name of producing truth.
REMOVAL OF IRON, ZINC, AND COPPER FROM WATERS IMPACTED BY ACID MINE DRAINAGE USING NATURAL ZEOLITE

By

MACKAYLA JANE THYFAULT

THESIS

Presented to the Faculty of the Graduate School of
The University of Texas at El Paso
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of the Requirements
for the Degree of

Master of Science in Environmental Engineering

THE UNIVERSITY OF TEXAS AT EL PASO

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ABSTRACT
In this research, the adsorption behavior of zeolites with respect to iron (Fe), zinc (Zn), and copper (Cu) has been studied in order to assess its application to heavy metal removal in polluted settings caused by acid mine drainage (AMD). The St. Cloud zeolitic deposit used in this project was characterized using a sieve analysis; the effective diameter and coefficient of uniformity were calculated. Batch studies were performed, and the samples were analyzed using ICP-OES. Batch studies used metal concentrations ranging from 50 mg/L to 650 mg/L. Freundlich, Linear, Langmuir, and BET adsorption isotherms were applied and evaluated to the batch study results. Column studies were performed to study the adsorption breakthrough curve for practical application of zeolite treatment of AMD, particularly treatment of concentrations similar to the contaminants of the Gold King Mine, Colorado AMD leakage in August 2015. Breakthrough curves were generated and evaluated to find 80% exhaustion. Regeneration column studies were executed to analyze the possible regeneration use of natural zeolite. A preliminary market analysis and business plan was executed to determine if zeolite would be a profitable commodity in the AMD remediation sector. It was found that the adsorption behavior zeolite possesses has great potential to remove heavy metals from polluted rivers, and the AMD remediation sector could financially provide profit from zeolite.
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A great deal of appreciation is extended to the following people who contributed to this project.

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CHAPTER I

Introduction

‘Heavy metals’ is an ill-defined term used to describe a group of metals that are commonly associated with pollution and toxicity; the vague term includes alkali metals, alkaline earth metals, and metalloids. Many heavy metals are accidently discharged into the aquatic environment, resulting in serious soil and water pollution; the release of such contamination into aquatic ecosystems is mainly from human activities (Alloway, 1997).

One major source of heavy metal pollution is the discharge of Acid Mine Drainage (AMD), which is an environmental pollutant of major concern in mining regions throughout the world. When AMD contamination occurs, the oxidation of pyrite or pyrrhotite acidifies the solution below a pH of 3, leading to the solubization of heavy metals such as Pb, Cd, Zn, Cu, Cr, Ni, and Fe (Lottermoser, 2003). Iron (Fe), Zinc (Zn), and Copper (Cu) are particularly common metals that accumulate in organisms, causing diseases and disorders (Lin, 2002). The high acidity of AMD paired with the large amounts of dissolved heavy metals, such as copper, zinc, manganese, iron, arsenic, and lead generally make AMD extremely toxic to most living organisms (Pentreath, 1994).

Many processes already exist for removing dissolved heavy metals such as activated carbon, reverse osmosis, ion exchange, precipitation, ultrafiltration, electro dialysis, and phytoextraction (Applegate, 1984; Geselbarcht, 1966; Sengupta, 1986). Contamination from AMD in particular is commonly treated with the addition of alkaline materials like lime or fly ash. However, many current processes are costly and not suitable for the natural environment. In the case of the Gold King Mine AMD leakage in Colorado during August
215, experts have estimated that the cleanup cost will be between $338 million and $27.7 billion (Batkins, 2015). Recently alternative low-cost materials have been proposed as possible sorbents for the removal of heavy metal contamination.

Among possible low-cost sorption materials, zeolite is considered to be the most cost-effective. Zeolites are naturally occurring hydrated aluminosilicate minerals with the potential to remove heavy metals from contaminated water. They belong to the class of minerals known as “tectosilicates.” Most natural zeolites are formed by the alteration of glass-rich volcanic rocks with fresh water in playa lakes or by seawater. (Erdem et al., 2004)

Zeolites have a cage-like structure and consist of three-dimensional frameworks of SiO$_4^{4-}$ and AlO$_4^{5-}$ tetrahedrons, as seen in Figure 1. The aluminum and silicon ions occupy the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of the Si$^{4+}$ by Al$^{3+}$ makes a negative charge in the lattice. Typically, the net negative charge is balanced by an exchangeable cation of sodium, potassium, or calcium. These cations are exchangeable with cations in aqueous solutions, such as lead, calcium, and zinc. Because the exchangeable ions (sodium, potassium, or calcium) in zeolite are relatively harmless, zeolite is suitable for the removal or heavy metals from contaminated waters. (Gottardi, 1985)
Though there is a comprehensive method for identifying and assessing the severity of sedimentation contamination to protect aquatic life, there is not a specified system for direct water contamination (Chapman et al., 1998). Table 1 shows the most-recently published U.S. Environmental Protection Agency maximum contamination levels for water supporting aquatic life (EPA, 2015).

Table 1: U.S. Environmental Protection Agency Maximum Contaminant Levels for Drinking Water and Aquatic Life

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
<th>Hg</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drinking Water, in μg/L (1)</td>
<td>5</td>
<td>100</td>
<td>1000</td>
<td>15</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>Water Supporting Aquatic Life, in μg/L (2)</td>
<td>12</td>
<td>100</td>
<td>20</td>
<td>100</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>Natural Sediments, Nonpolluted, in μg/g (3)</td>
<td>-</td>
<td>&lt;25</td>
<td>&lt;25</td>
<td>&lt;40</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>Natural Sediments, Moderately Polluted, in μg/g (3)</td>
<td>25-75</td>
<td>25-50</td>
<td>40-60</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Natural Sediments, Heavily Polluted, in μg/g (3)</td>
<td>&gt;6</td>
<td>&gt;75</td>
<td>&gt;50</td>
<td>&gt;60</td>
<td>&gt;1</td>
<td>-</td>
</tr>
</tbody>
</table>

(1) U.S. Environmental Protection Agency, 1992
(2) U.S. Environmental Protection Agency, 1982
(3) Great Lakes Water Quality Board, Dredging Subcommittee, 1982
(adapted from Garbarino, J.R. et al., 1995)

Though the U.S. Environmental Protection Agency does not have very thorough classifications for contaminants pertaining to wildlife, many states such as California and Alaska have created their own aquatic life water criteria.

By examining the nature of AMD contamination, the possible low-pH sorption properties of zeolite, and feasible market analysis, the possibility of zeolbioites as a
solution for AMD contamination remediation will be assessed.

1.1 Objectives

The overall goal of this project is to study the feasibility of removing iron, zinc, and copper from water using natural zeolite at low pHs typical to AMD. Specific objectives include:

1. Characterize the zeolitic deposit used in this project by performing a sieve analysis and calculating the effective diameter and coefficient of uniformity.

2. Evaluate the adsorption of Fe, Zn, and Cu onto natural zeolite by performing equilibrium and kinetic batch studies at varying concentrations.

3. Evaluate the removal of Fe, Zn, and Cu at concentrations found in the Animas River, CO contamination using columns packed with natural zeolite.

4. Perform a market analysis and preliminary business plan using natural zeolite for AMD river contamination remediation.
CHAPTER II

Literature Review

2.1 Heavy Metal River Contamination

Heavy metals contaminate water sources in many ways; the main anthropogenic sources of heavy metal river contamination are mining and disposal of untreated or partially treated effluents from industrial activity (Hatje et al., 1998). Heavy metal water contamination is a worldwide problem due to heavy metals toxicity, which is aggravated by their persistence in the environment, and their propensity to be bioaccumulated (Nouri et al., 2008). Heavy metal contamination does not only affect aquatic life; it can flow through the food chain to affect humans as well. Bioaccumulation occurs when contaminants enter the aquatic environment and are incorporated into small organisms. Larger organisms eat the smaller organisms, and the contaminants move up the food chain as the cycle continues, increasing the amount of accumulated contaminants with each step. Humans consume metallic elements through both water and food. Some metals such as sodium, potassium, magnesium, calcium, and iron are found in living tissue and are essential to healthy human life. Currently six heavy metals including molybdenum, manganese, cobalt, copper, and zinc, have been linked to human growth, development, achievement, and reproduction (Vahrenkamp, 1979; Friberg et al., 1986). Even these metals, however, can become toxic or aesthetically undesirable at increased concentrations. Several heavy metals, like cadmium, lead, and mercury, are highly toxic at relatively low concentrations, can accumulate in body tissues over long periods of time, and are nonessential for human health. Table 2 shows the metals according to their toxicity to humans.
Table 2: Classification of Naturally Occurring Metals by Toxicity and Hydrologic Activity

[Those that normally do not exist as dissolved species in natural waters or are very rare in crustal rocks in italics]

<table>
<thead>
<tr>
<th>Nontoxic</th>
<th>Low toxicity</th>
<th>Moderate to high toxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Magnesium</td>
<td>Praseodymium</td>
</tr>
<tr>
<td>Bismuth</td>
<td>Manganese</td>
<td>Cerium</td>
</tr>
<tr>
<td>Calcium</td>
<td>Molybdenum</td>
<td>Dysprosium</td>
</tr>
<tr>
<td>Cesium</td>
<td>Potassium</td>
<td>Erbium</td>
</tr>
<tr>
<td>Iron</td>
<td>Strontium</td>
<td>Europium</td>
</tr>
<tr>
<td>Lithium</td>
<td>Rubidium</td>
<td>Gadolinium</td>
</tr>
<tr>
<td>Sodium</td>
<td>Gallium</td>
<td>Terbium</td>
</tr>
<tr>
<td>Germanium</td>
<td>Thulium</td>
<td>Copper</td>
</tr>
<tr>
<td>Gold</td>
<td>Tin</td>
<td>Hafnium</td>
</tr>
<tr>
<td>Holmium</td>
<td>Ytterbium</td>
<td>Neodymium</td>
</tr>
<tr>
<td>Neodymium</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.1.1 Acid Mine Drainage (AMD)

The main cause of Acid Mine Drainage (AMD) is the weathering of pyrite (FeS₂).

Pyrite oxidizes to produce very acidic waters (with pH<3), which in turn solubilizes heavy metals and other toxins; allowing the contaminants to be transported downstream into river bodies, eventually ending up in the ocean. (Pentreath, 1994; Jenkins et al., 2000)

Pyrite is a mineral composed of iron and sulfur (FeS₂). Mineral deposits containing pyrite are usually found beneath the earth’s surface, where there is little or no oxygen. When mining occurs, these minerals are exposed and brought to the surface where a combination of weathering and mining activities results in the production of acid waters:

\[
2\text{FeS}_2(s) + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{+2} + 4\text{SO}_4^{2-} + 4\text{H}^+ 
\]

When sufficient oxygen is dissolved in the water or when the water is exposed to sufficient atmospheric oxygen, another oxidation of Fe⁺² (ferrous iron) to Fe⁺³ (ferric iron) occurs:

\[
2\text{Fe}^{+2} + \frac{1}{2}\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{+3} + \text{H}_2\text{O} 
\]
Ferric iron can either precipitate as Fe(OH)$_3$, which is commonly seen as red-orange precipitate in waters affected by AMD:

$$2\text{Fe}^{3+} + 6\text{H}_2\text{O} \leftrightarrow 2\text{Fe(OH)}_3\text{(s)} + 6\text{H}^+$$

or it can react directly with pyrite to produce more ferrous iron and acidity:

$$14\text{Fe}^{3+} + \text{FeS}_2\text{(s)} + 8\text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + 15\text{Fe}^{2+} + 16\text{H}^+$$

When ferrous iron is produced and sufficient dissolved oxygen is present the cycle of producing acidic conditions and ferric iron continues. Without dissolved oxygen the reaction between pyrite and ferric iron will continue to completion and the affected water will show elevated levels of ferrous iron. (Younger, et al., 2002)

As these acid waters are created, they solubilize some of the elements contained in the mineral deposits, such as iron, copper, zinc, cadmium, and manganese, forming AMD. The elements are not biodegradable and therefore accumulate in living organisms, causing various diseases, disorders, and even death. (Alvarez-Ayuso et al., 2003; Spyrnskyy et al., 2006; Bailey et al., 1999)

### 2.2 Methods for Heavy Metal Removal

Many processes currently exist for the removal of heavy metal contamination including chemical precipitation, reverse osmosis, ion exchange, ultrafiltration, electrodialysis, and phytoextraction (Applegate, 1984; Sengupta, 1986; Geselbarcht, 1966).

#### 2.2.1 Chemical Precipitation

Precipitation is the process of producing solids within a solution. For heavy metal removal, it is desirable to precipitate as much heavy metal in a solid phase as possible so that it can be removed from the water. However, in natural aquatic environments, removing the precipitated contaminates from sediments and soils is problematic.
Lime softening, also known as Clark’s process, is the most common form of chemical precipitation, and uses the addition of limewater (calcium hydroxide) to remove hardness (calcium and magnesium) ions by precipitation. In the lime softening process, calcium hydroxide is added to water, which raises the pH and shifts the equilibrium of carbonate species in the water:

\[
\text{Ca(OH)}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{+2} + 2\text{OH}^-
\]

Dissolved carbon dioxide is changed in bicarbonate after reacting with hydroxide:

\[
\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-
\]

The hydrogen ion is then removed from bicarbonate by hydroxide ions in solution to produce carbonate:

\[
\text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}
\]

Carbonate is then able to precipitate calcium out of solution:

\[
\text{Ca}^{+2} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3
\]

This process can also remove iron, manganese, radium, and arsenic from water. (Mellor, 1941)

Though chemical precipitation is suitable for removing heavy metals from water, it is not suitable in a natural aquatic environment, as it would simply move the contamination to the sediment from where it could easily continue to flow up the food chain.

2.2.2 Reverse Osmosis

Reverse osmosis is a process used for separating a solute from a solvent in the aqueous or gaseous phase. The process includes the solvent flowing through a non-porous membrane from one side and collecting the separated solute from the other side. (Chu et al., 2009). In order for the separation to be possible, an external pressure must be applied
to overcome the osmotic pressure of the solution; causing the solvent to be forced through the membrane with the product being collected at atmospheric pressure. (Greenlee et al., 2009)

Though reverse osmosis is an effective treatment process, it is not suited for on-site treatment of contaminated rivers.

**2.2.3 Ion Exchange**

Ion exchange is a promising technology currently being developed to remove heavy metal contamination. Ion exchange is very cost-efficient compared to other technologies, especially when implementing low-cost natural sorbents such as activated charcoal and zeolites (Kesraoui-Ouki et al., 1994; Orhan et. al, 1993). Natural zeolites have a greater potential to be used as packing material in reactive planes intercepting contaminated water, because activated carbon is generally more expensive.

**2.2.4 Ultrafiltration**

Ultrafiltration is a technology based on particle size exclusion separation membranes. It includes varying small micropores that act as sieves and prevent particles exceeding the pore diameters to pass through. Ultra filtration membranes typically have pore diameters varying in size from 1 nm to 0.1 μm (Vial et al., 2002). It is commonly used as a pretreatment for reverse osmosis to prevent fouling of the system.

Though it is an effective pretreatment system, ultrafiltration will not remove dissolved constituents, as it is a particle removal process. As such, it is not suitable for on-site treatment of AMD contaminated waters.
2.2.5 Electrodialysis

Electrodialysis is a process used to transport ions from one solution to another through an ion exchange membrane under the influence of an applied electric potential difference. (Banasiak et. al, 2007) A diagram of electrodialysis can be seen in Figure 2.

![Diagram of Electrodialysis](University of Guelph, 2016)

Figure 2: Diagram of Electrodialysis
(University of Guelph, 2016)

Though electrodialysis is an effective system for water treatment, it is costly and not suited for on-site treatment of contaminated rivers.

2.2.6 Phytoextraction

Phytoextraction is an approach to remediate an area of land contaminated with heavy metals using hyperaccumulator plants (Chaney et al., 1997). During each growing
cycle, hyperaccumulator plants accumulate metals in their aerial parts, effectively removing the contaminants from the soil, as depicted in Figure 3.

**Figure 3: Phytoextraction Process**
(Biology Online, 2015)

The plants can then be burned into a small, high-pollutant-concentration ash that is safe to dispose of at a landfill (Kumar et al., 1995).

While useful for slow remediation of heavy metal contaminated land, phytoextraction is not suitable for fast remediation of contaminated water.

### 2.3 Zeolite

Zeolites are silicate minerals that share similar chemical compositions, mineral associations, and geologic occurrences. The combination of these aspects makes zeolite a viable choice for treatment of AMD contamination.

#### 2.3.1 Chemical Composition

Chemically, zeolites are classified as hydrated aluminosilicates, meaning they contain water, aluminum and atoms. Zeolite molecules are loosely connected by a
framework structure that is characterized by spaces or pores between the molecule groups. These openings created in the zeolites make up the three-dimensional framework for the SiO$_4^{-4}$ and AlO$_4^{-5}$ tetrahedrons (Gottardi and Galli, 1985). The basic zeolite structure of SiO$_4^{-4}$ and AlO$_4^{-5}$ tetrahedrons are the primary building units (PBU), as depicted in Figure 4.

![Figure 4: Basic Zeolite Structure](The Chemical Engineers' Resource Page, 2011)

Zeolite PBU connect via oxygen ions into secondary building units (SBU), which are then linked into a three-dimensional crystalline structure of zeolite. A three-dimensional representation of this can be seen in Figure 5.
2.3.2 Mineral Association

In mineralogy, zeolites belong to the class of minerals known as “tectosilicates.” Their hardness ranges from 3.5 to 5.5 and they have low densities with specific gravities ranging between 2.0 and 2.4. There are approximately 50 naturally occurring and 150 synthetic zeolites known today. The most common natural zeolites are natrolite, analcime, chabazite, heulandite, phillipsite, clinoptilolite, and stilbite. Zeolites contain a number of different cations including K+, Na+, Mg2+, and Ca2+, which are the most common. These cations are not strongly bound to the zeolite molecule so they can easily be removed and replaced with other cations. (Shaffer et al., 2001; Virta, 2006)

2.3.3 Occurrence of Zeolite

Geographically, zeolites are generally occur in vugs and veins in igneous rocks such as basalt and gabbro, but can also be found in altered volcanic tuff and certain sedimentary deposits. They form when alkaline groundwater reacts with the elements in the basaltic igneous rock. Most natural zeolites are formed by the alteration of glass-rich volcanic rocks with fresh water in playa lakes or by seawater (Erdem et al., 2004). There are significant deposits of zeolite in the United States, Canada, Tasmania, and India. In the United States, deposits have been found in Arizona, California, Idaho, Nevada, Wyoming, Texas, Utah, Oregon and New Mexico. In addition to these extensive natural deposits, synthetic zeolites are currently being developed and produced for various applications. (Minerals Education Coalition, 2015)

About 50 zeolites can be found in nature; the Swedish mineralogist A. F. Cronstedt discovered the first zeolite in 1756.(Poulsen and Oksbierg, 1995).
2.3.4 Adsorption Qualities

The efficiency of ion exchange techniques in removing metal ions from wastewaters depends on varying factors such as initial concentration of metal ions in wastewater, the pH of the system, the possibility of formation of metal hydroxyl anions, previous chemical and thermal modification of zeolite material and the amount of water that needs to be purified. Natural zeolites have excellent resistance to chemical, biological, mechanical or thermal changes.

Table 3 shows the efficiency of the removal of metal cations from wastewater using natural zeolite when supplemented with other physical and chemical methods.

Table 3: Efficiency of the Removal of Metal Cations from Wastewater Using Natural Zeolite

<table>
<thead>
<tr>
<th>Methods</th>
<th>Removal efficiency, %</th>
<th>Cd (II)</th>
<th>Cr(III)</th>
<th>Cu(II)</th>
<th>Ni(II)</th>
<th>Zn(II)</th>
<th>Fe(III)</th>
<th>Mn(II)</th>
<th>Pb (II)</th>
<th>As(III)</th>
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<td>Physical / chemical methods</td>
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<td>Precipitation</td>
<td>96-99</td>
<td>99</td>
<td>80</td>
<td>71-85</td>
<td>99</td>
<td>-</td>
<td>99</td>
<td>92</td>
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<td>Ion exchange</td>
<td>100</td>
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<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
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<td>-</td>
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<tr>
<td>Membrane filtration*</td>
<td>93-99</td>
<td>86-95</td>
<td>98-100</td>
<td>60-100</td>
<td>95-99</td>
<td>90</td>
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<td>99</td>
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<td>-</td>
<td>99</td>
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<td>99</td>
<td>-</td>
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<td>95-98</td>
<td>85-99</td>
<td>70-98</td>
<td>99-100</td>
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<td>-</td>
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<td>77-99</td>
<td>98-99</td>
<td>69-90</td>
<td>96</td>
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<td>78</td>
<td>99</td>
<td>-</td>
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<tr>
<td>Natural zeolite</td>
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<td></td>
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<td></td>
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<tr>
<td>CLI (Clinoptilolite)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>75</td>
<td>85</td>
<td>70</td>
<td>-</td>
<td>95</td>
<td>-</td>
<td>-</td>
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<tr>
<td>M-CLI (Modified Clinoptilolite)</td>
<td>90-99</td>
<td>88</td>
<td>80</td>
<td>37</td>
<td>92</td>
<td>90</td>
<td>70</td>
<td>90-99</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td>CHA (Chabazite)</td>
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<td>98</td>
<td>98</td>
<td>98</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SCO (Scolecite)</td>
<td>59</td>
<td>96</td>
<td>-</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>75</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PHI (Philipsite)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>74</td>
<td>88</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

CLI (Clinoptilolite), M-CLI (Modified Clinoptilolite), CHA (Chabazite), SCO (Scolecite), PHI (Philipsite) (Margeta, K. et al., 2013)

2.4 Adsorption

Adsorption is the adhesion of molecules, atoms, or ions to a solid surface due to the excess of the surface free energy caused by the bond deficiency (Kopecký et al., 1996).

An adsorption process can be described by an adsorption isotherm, which is a representation of the amount of an adsorbate attached to an adsorbent as a function of the
pressure of a gas or the concentration of a solute in solution, at constant temperature.

(Jaroniec, 1975)

2.4.1 Adsorption Models

The equilibrium distribution of metal ions between the natural or modified zeolites and the solution is important in determining the maximum sorption capacity. In most studies Freundlich, Langmuir, and BET models are used (Al-Anerb and Al-Anberb, 2008).

2.4.1.1 Linear Model

If a linear model is applicable, the adsorption capacity of the adsorbant will increase linearly with the equilibrium concentration of the adsorbate. The linear equation is as follows:

\[ X = x/m = s \cdot C \]

where:

- \( s \) = slope of adsorption isotherm
- \( C \) = concentration of the substance in solution after reaching equilibrium (mg/L)

By analyzing the linear model, it can be seen to be the Freundlich model with \( n \) equal to one.

2.4.1.2 Langmuir Model

The Langmuir model relates to adsorption by assuming an adsorbate behaves as an ideal gas at isothermal conditions, which means it assumes the following:

- there is a limited area available for adsorption
- the adsorbed solute material on the surface is only one molecule thick
- the adsorption is reversible and equilibrium is achieved

The Langmuir equation is as follows:
\[ X = \frac{x}{m} = \frac{\text{x}_{\text{max}} K_L C_e}{1 + K_L C_e} \]

where:

\[ x = \text{mass of adsorbed material (mg)} \]
\[ m = \text{mass of adsorbent material (g)} \]
\[ C_e = \text{concentration of the substance in solution after reaching equilibrium (mg/L)} \]
\[ \text{x}_{\text{max}}, = \text{maximum content of sorbed substance (mg/g)} \]
\[ K_L = \text{Langmuir distribution coefficient} \]

The Langmuir equation can be linearized as follows:

\[ \frac{1}{x/m} = \frac{1}{b} + \frac{1}{ab}(1/C) \]

Once the equation has been linearized, the empirical constants can be found and the adsorption model can be plotted.

2.4.1.3 Freundlich Model

The Freundlich model is an empirical equation that represents the relationship between the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the solution. The Freundlich equation is as follows:

\[ X = \frac{x}{m} = K C^{1/n} \]

where:

\[ x = \text{mass of adsorbed material (mg)} \]
\[ m = \text{mass of adsorbent material (g)} \]
\[ C = \text{concentration of the substance in solution after reaching equilibrium (mg/L)} \]
\[ K, n = \text{empirical constants} \]

The Freundlich equation can be linearized to solve for K and n as follows:

\[ \log(x/m) = \log K + \left(\frac{1}{n}\right) log C \]
Once the equation has been linearized, the empirical constants can be found and the adsorption model can be plotted.

2.4.1.4 Brunauer – Emmet – Teller (BET)

The BET model extends the Langmuir model from a monolayer to several molecular layers. Above the monolayer, each additional layer is assumed to equilibrate with the layer below it. The BET equation is as follows:

\[ X = \frac{x}{m} = \frac{ACx_m}{(C_x-C)(1+(A-1)C/C_s)} \]

where:

- \( A \) = constant describing interaction energy for the solute and the surface of the adsorbent material
- \( x_m \) = required amount of solute for forming a uni-molecular layer (mg/g)
- \( C_s \) = saturation concentration of the solute (mg/L)
- \( C \) = concentration of the substance in solution after reaching equilibrium (mg/L)

2.4.2 Fixed Bed Adsorption

Adsorption columns involve non-steady state operation because the amount of contaminate in the solid increases continuously with the passage of fluid through the fixed bed of adsorbent. This changing behavior cannot be analyzed with batch tests, which are under equilibrium conditions. A fixed bed adsorption column is depicted in Figure 6.
The sorption zone is the length of the column where mass transfer occurs and the solute is transferred from the adsorbate to the adsorbent. When upflow is used, the sorption zone moves upward through the fixed bed in the column. Once the sorption zone reaches the top of the column, the breakthrough begins and the effluent concentration increases until the adsorption of the adsorbent is exhausted. An exhausted sample is not the same as a saturated sample, when full initial concentration is reached, but is a sample at 80% of saturation. A typical breakthrough curve is depicted in Figure 7, with \( C_e \) being the concentration effluent (\( C_e \) for this study) and \( C_0 \) being the concentration influent (\( C_i \) in this study).
2.5 Regeneration/Disposal

Possible regeneration of the zeolite for re-use as well as possible re-use of the obtained concentrate metal ions after zeolite regeneration, could have a very positive impact on the revived aquatic environment without creating new waste. Recent studies of the desorption efficiency of metal ions and regeneration of natural zeolite - clinoptilolite are presented in Table 4 and indicate that the adsorption process is reversible in most cases (Katsou et al., 2011).

Table 4: Desorption Efficiency of Metal Ions and Regeneration Natural Zeolite - Clinoptilolite

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>Desorbing Solution</th>
<th>Desorption Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(^{2+})</td>
<td>3 M KCl</td>
<td>&gt;99.5</td>
</tr>
<tr>
<td></td>
<td>0.5 M NaCl</td>
<td>95</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>0.34 NaCl</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>5 g/L EDTA</td>
<td>29</td>
</tr>
<tr>
<td>Cd(^{2+})</td>
<td>1 M KNO(_3)</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>1 M NaCl</td>
<td>97</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>0.34 NaCl</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>5 g/L EDTA</td>
<td>60</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>0.1 M HCl</td>
<td>93</td>
</tr>
</tbody>
</table>

(Margeta, K. et al., 2013)
2.6 AMD from Gold King Mine, Colorado

Gold mining in the hills around Silverton, CO was the primary income and economy for the region until the last mine closure in the area in 1991; the Gold King Mine itself was abandoned in 1923. (Kaplan, 2015) Figure 8 shows the location of Gold King Mine and the surrounding area.

![Figure 8: Map of Gold King Mine’s Spill Path](image)

On August 5, 2015, EPA personnel along with workers for Environmental Restoration LLC (a Fenton, Missouri, company under EPA contract to mitigate pollutants from the closed mine) caused the release of toxic wastewater when attempting to add a tap to the tailing pond for the mine. Workers accidentally destroyed the plug holding water trapped inside the mine, overflowing the pond, spilling three million US gallons (11 ML) of mine waste water and tailings, including heavy metals such as cadmium and lead, and other toxic elements, such as arsenic, beryllium, zinc, iron, and copper into Cement Creek, a tributary of the Animas River in Colorado. (Harder et. al, 2015)
Data measured down the Animas River near Silverton six hours after the contamination incident showed elevated cadmium at 98.3 ppb, zinc at 26,800 ppb, beryllium at 34.8 ppb, aluminum at 91,900 ppb, lead at 150 ppb, and copper at 10,400 ppb. Additionally, the pH levels in Cement Creek upstream Silverton were at 3.74, while the pH levels in the Animas River below Silverton were at 4.8. (Finley and McGhee, 2015; Finley, 2015)

On August 10, 2015, the EPA reported that levels of six metals were above the limits allowed by the Colorado Department of Public Health and Environment for domestic water. The department requires municipalities to cease to use water when the levels exceed the limits. Some metals were found at hundreds of times their limits, such as lead at 100 times the limit, and iron at 326 times the limit. Some of the data EPA officials posted in tables are shown in Table 5. The measurements were taken 15 miles (24 km) upstream from Durango. (Finley and McGhee, 2015)

Table 5: Contaminants Concentrations and Colorado State Limits 15 Miles Upstream from Durango, CO on August 10, 2015

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Concentration (ppb)</th>
<th>Colorado State Limit (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>6.13</td>
<td>5</td>
</tr>
<tr>
<td>Arsenic</td>
<td>264</td>
<td>10</td>
</tr>
<tr>
<td>Iron</td>
<td>326000</td>
<td>1000</td>
</tr>
<tr>
<td>Copper</td>
<td>1120</td>
<td>1000</td>
</tr>
<tr>
<td>Manganese</td>
<td>3040</td>
<td>50</td>
</tr>
<tr>
<td>Zinc</td>
<td>26800</td>
<td>5000</td>
</tr>
</tbody>
</table>

(EPA B, 2015)
CHAPTER III

Materials and Methods

3.1 Characterization of Zeolitic Deposit

A sieve analysis was done to determine the effective diameter and coefficient of uniformity for the zeolite used in this study using the following procedure:

1. 1,000 grams of zeolite were weighed.
2. Six labeled sieves (and one pan) were organized in ascending numbers. The sieve numbers and opening sizes can be found in Appendix A.
3. The zeolite was placed in the upper sieve and shaken for 1 minute.
4. The zeolite that remained in each sieve and pan were weighed.
5. The retained, cumulative retained, and passing percent for each sieve were calculated.
6. The effective diameter and coefficient of uniformity were determined for the zeolite used in this study. The effective size, $E$, was obtained as $P_{10}$, when graphing the sieve size in log scale versus the cumulative percent passing. The coefficient of uniformity, $U$, was obtained by using the ration of $P_{60}$ to $P_{10}$ when graphing the sieve size in log scale versus the cumulative percent passing.

Additionally, the St. Cloud Zeolite specification sheet and product data sheet were analyzed for pertinent information. For more data on St. Cloud Zeolite, the specification sheet can be found in Appendix B and the product data sheet can be found in Appendix C.

3.2 Preparation of Natural Zeolite

For this project, natural zeolite (clinoptilolite) was obtained from the St. Cloud Mine in Winston, NM for use. The samples were used in their natural state ("as
received”) with no chemical modifications, unless stated. The natural zeolite samples were prepared as follows:

1. A #40 Sieve (0.420 mm standard, 0.0165 in. nominal sieve opening) was filled with zeolite to capacity and washed over a large pan with running tap water.
2. As the pan filled, the flowing water removed the fines.
3. The zeolite was mixed by hand, with continuous water flow until the water in the pan was clear.
4. The zeolite was dried in the oven for 100°C for 24 hours.

3.3 Experimental Procedure

Two standard methods are typically applied to study the removal of contaminants from water using zeolites: batch and column methods.

3.3.1 Kinetic Batch Studies

Kinetic batch studies are conducted to establish a timeline for equilibrium between the adsorbent and the adsorbate. A specified amount of adsorbent is placed in contact with a solution of synthetic or real samples of water with varied times of contact. Kinetic batch study results are typically presented as zero or first order reactions.

To begin, a timeline to reach equilibrium was established by placing 5 g zeolite into 50 mL of metal ion solution with a concentration of 5 mg/L. Suspensions were shaken in a multi-function tube rotator with constant hydrodynamic conditions (100 rpm) for 24 hours, and samples were taken at varying times. The amount of heavy metal ions remaining in the liquid phase after equilibration was measured using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) or the Inductively Coupled Plasma – Mass Spectrometer (ICP-MS). The procedure was completed in triplicates.
3.3.2 Equilibrium Batch Studies

An equilibrium batch study is carried out using a specified amount of adsorbent, which is then placed in contact with a solution of synthetic or real samples of water with varied concentrations of contaminants. Equilibrium batch studies are typically held at constant temperature and hydrodynamic conditions, and the amount of immobilized ions on the zeolite is presented as equilibrium distribution of ions between the adsorbent and the solution.

All ion exchange experiments were performed by the batch method, the procedure was as follows:

1. Batch samples were prepared of ferric nitrate in 2% nitric acid solution, zinc oxide in 3% nitric acid solution, and cupric nitrate in 2% nitric acid solution, with the solid/liquid ratio of 5 g zeolite/50 mL of metal ion solution in 50 mL conical centrifuge tubes. Concentrations of the metal ion solutions began with 50 mg/L and increased to 650 mg/L; an additional one combined the three in every concentration. The aqueous solutions pHs were adjusted to 3.5 using hydrochloric acid (HCl).

2. The suspensions were shaken in a multi-function tube rotator with constant hydrodynamic conditions (100 rpm) for 24 hours to ensure equilibrium was reached.

3. After 24 hours, the solutions were filtered using 45 microns filters, and the samples were prepared for testing by ICP-OES by acidifying each filtered 10 mL sample with 200 µL of nitric acid (HNO₃).

4. The procedure was completed in triplicates.
5. The amount of heavy metal ions remaining in the liquid phase after equilibration
was measured using ICP-OES.

3.3.2 Column Studies
In column studies, several parameters affect the dynamics of the cation uptake by
zeolite. Some factors are mainly related to the solution (temperature, pH, the flow rate, the
initial cation concentration being removed by zeolite, the pretreatment solution, the
presence of other competing ions in the solution, characteristics of the heavy metal being
removed by the zeolite), while others are factors specific to the solids (particle size, surface
dust, impurities found in the zeolite sample, the pretreatment procedure type applied to
the zeolite). Results of column studies are presented by breakthrough curves.

Using the natural zeolite, column studies were performed using concentrations
 Corresponding to the values reported from the Animas River, CO AMD contamination in
August 2015 (previously reported in Table 6). The steps for the column studies were as
follows:

1. A Kimble Flex column size 2.5 cm diameter by 10 cm length was packed with 55
grams of the natural zeolite.

2. 4 liters of ferric nitrate in 2% nitric acid solution with a Fe$^{3+}$ concentration of 326
mg/L, 4 liters of zinc oxide in 3% nitric acid solution with a Zn$^{2+}$ concentration of
26.8 mg/L, and 4 liters of cupric nitrate in 2% nitric acid solution with a Cu$^{2+}$
concentration of 1.12 mg/L, were prepared in 1 liter volumetric flasks and poured
into 4 liter Erlenmeyer flasks. The aqueous solutions pHs were adjusted to 3.5 using
hydrochloric acid (HCl).
3. ¼ inch diameter tubing was connected to low flow variable speed VWR peristaltic pumps (B). The tubing required an “in” tube that pumped the solution from the Erlenmeyer flask (A), and an “out” tube that was connected to the bottom end of the Kimble column (C). From the top of the column another tube was connected; this tube was where the effluent was collected for sampling (G). This arrangement is depicted in Figure 9.

![Figure 9: Column Study Diagram](image)

(Alliance of Crop, Soil, and Environmental Science Societies, 2016)

4. The pumps were turned to the maximum setting that gave a flow of 0.3 mL/s.

5. Once the pumps were on and the columns were primed, the flow ran for 24 hours and samples were taken at different set intervals throughout.

6. The samples were prepared for analysis by ICP-OES (and ICP-MS in the case of copper) by acidifying each 10 mL sample with 200 μL of HNO₃.
3.3.3 Regeneration Studies

Using the exhausted zeolite from the previous Zn column test, a column study concerning regeneration was performed using potassium chloride solution (KCl) as well as Zn solution. The steps for the column study are as follows:

1. The Kimble Flex column size 2.5 cm diameter by 10 cm length used for the previous Zn column was prepared for use.

2. 4 liters of KCl solution with a concentration of 100,000 mg/L was prepared in 1 liter volumetric flasks and poured into a 4 liter Erlenmeyer flask.

3. ¼ inch diameter tubing was connected to a low flow variable speed VWR peristaltic pump. The tubing required an “in” tube that pumped the solution from the Erlenmeyer flask, and an “out” tube that was connected to the bottom end of the Kimble column. From the top of the column another tube was connected; this tube was where the effluent was collected for sampling.

4. The pump was turned to the maximum setting that gave a flow of 0.3 mL/s.

5. Once the pump was on and the columns were primed, the flow ran for 24 hours and samples were taken at different set intervals throughout.

6. The samples were then prepared for analysis by ICP-OES by acidifying each 10 mL sample with 200 μL of nitric acid (HNO₃).

   The regenerated zeolite was then tested by the procedure as follows:

1. The Kimble Flex column size 2.5 cm diameter by 10 cm length used for the previous regeneration column was prepared for use.
2. 4 liters of Zn solution with a concentration of 26.8 mg/L was prepared in 1 liter volumetric flasks and poured into a 4 liter Erlenmeyer flask. The aqueous solution’s pH was adjusted to 3.5 using hydrochloric acid (HCl).

3. ¼ inch diameter tubing was connected to a low flow variable speed VWR peristaltic pump. The tubing required an “in” tube that pumped the solution from the Erlenmeyer flask, and an “out” tube that was connected to the bottom end of the Kimble column. From the top of the column another tube was connected; this tube was where the effluent was collected for sampling.

4. The pump was turned to the maximum setting that gave a flow of 0.3 mL/s.

5. Once the pump was on and the columns were primed, the flow ran for 24 hours and samples were taken at different set intervals throughout.

6. The samples were then prepared for analysis by ICP-OES by acidifying each 10 mL sample with 200 μL of HNO₃.

Figure 10 depicts the process for the testing and regeneration of the Zn column.

Figure 10: Testing and Regeneration of Zn Column Flowchart
CHAPTER IV

Results and Discussion

4.1 Characterization of Zeolitic Deposit

Table 6 shows the results from the zeolite sieve analysis.

<table>
<thead>
<tr>
<th>Sieve Number</th>
<th>Opening Size (mm)</th>
<th>Mass Retained (g)</th>
<th>Cum. Retained (g)</th>
<th>Cum. % Retained</th>
<th>% Passing</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/8&quot;</td>
<td>9.51</td>
<td>0</td>
<td>0</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td>4</td>
<td>4.76</td>
<td>0</td>
<td>0</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td>40</td>
<td>0.425</td>
<td>988.5</td>
<td>988.5</td>
<td>98.9</td>
<td>1.1</td>
</tr>
<tr>
<td>100</td>
<td>0.15</td>
<td>3</td>
<td>991.5</td>
<td>99.2</td>
<td>0.8</td>
</tr>
<tr>
<td>200</td>
<td>0.075</td>
<td>2</td>
<td>993.5</td>
<td>99.4</td>
<td>0.6</td>
</tr>
<tr>
<td>Pan</td>
<td>0</td>
<td>6</td>
<td>999.5</td>
<td>100.0</td>
<td>0.0</td>
</tr>
<tr>
<td>total mass</td>
<td></td>
<td>999.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As depicted above, over 99% was retained between the number 40 and the number 200, while less than 1% was retained in the pan, confirming the data included in the St. Cloud zeolite product data sheet.

Figure 11 depicts a gradation curve for the zeolite used for this project as graphed on log scale.
Figure 11: Zeolite Gradation Curve

For the zeolite tested during this study was found to be 0.91mm. Maximum $U$ was found to be 1.318, indicating a relatively uniformly graded sample (Davis and Cornwell, 2008).

According to U.S. Geological Survey 96-065, “St. Cloud’s zeolite is notable for its responsiveness, consistency, attrition resistance, pH buffering characteristics, moisture retention, attractive color, compatibility with other nutrients and additives, product availability, quality control, manufacturing capacity and price.”

In a report comparing St. Cloud Zeolite to some other U.S. zeolites, the United States Geological Survey (USGS) found St. Cloud had the lowest Na$^+$ content and exchangeability, the highest Ca$^{2+}$ content and exchangeability, the highest capacity to adsorb K$^+$, the best pH stability and neutralizing effect, the highest loading capacity of combined Na$^+$-K$^+$-Ca$^{2+}$ in contact with fertilizers of producing properties, and the average total N capacity and most
4.2 Batch Studies

4.2.1 Kinetic Batch Study Results

The results of the kinetic batch study in Figure 12 indicate a conservative equilibrium time of less than 2 hours. This validates the following batch studies as truly reaching a state of equilibrium as they were shaken in a multi-function tube rotator with constant hydrodynamic conditions (100 rpm) for 24 hours before being prepared for the ICP-OES. Though the kinetic batch study was run for 24 hours, concentrations after 1 hour were below the detection limit.

![Kinetic Batch Study](image)

**Figure 12: Equilibrium Batch Study Results**

The results of binding varying concentrations of Fe, Zn, and Cu ions onto natural zeolite demonstrate a higher degree of ion removal at lower initial concentration area of metal ions. The linear nature of the data when plotted on a log scale indicates a first-order
reaction, suggesting that the adsorption found in this study is directly proportional to the concentrations used.

**4.2.1 Equilibrium Batch Study Results**

The plots in Figure 13 show the removal ratio of each heavy metal ion as a function of the initial concentration used in this study. The raw data for the batch studies can be found in Appendix D.

The removal ratio is defined as:

\[
\alpha = \frac{(C_i - C_e)}{C_i} \times 100
\]

where \(C_i\) is the initial concentration, and \(C_e\) is the equilibrium concentration of the particular ion.

The equilibrium experimental results of Fe, Zn, and Cu ions exchanged have been fitted by non-linear equations of the adsorption models; Langmuir, Freundlich, BET, and
linear trend line. Though all were compared, Langmuir was proven to be the best fit for the adsorption isotherms in this study when comparing the linearized models and their R² values.

Figure 14a depicts the linearization of the Langmuir adsorption model for the Fe data. Figure 14b depicts the adsorption isotherm of the Fe batch study in comparison to the Langmuir adsorption model.
When comparing the Fe data to that of Langmuir, Freundlich, BET, and linear models, it was found that the best fit was that of the Langmuir adsorption model for the concentrations tested in this study. It is assumed that the natural zeolite had reached adsorption saturation, and the variances are from the incidental environmental differences found in naturally mined zeolite, which can be seen in the graphical representation of the data. The best fit of the Langmuir model suggests a monolayer removal for heavy metals; an increase in the surface area of the zeolite would positively impact the adsorption.

Figure 15a depicts the linearization of the Langmuir adsorption model for the Zn data. Figure 15b depicts the adsorption isotherm of the Zn batch study in comparison to the Langmuir adsorption model.
When comparing the Zn data to that of Langmuir, Freundlich, BET, and linear models, it was found that the best fit was that of the Langmuir adsorption model when disregarding the data point from the 650 mg/L C_i batch test (furthest to the right on the graph). It is assumed that the 5g of natural zeolite in that batch test differed from the incidental environmental variances found in naturally mined zeolite, which can be seen in the graphical representation of that data. The best fit of the Langmuir model suggests a
monolayer removal for heavy metals; an increase in the surface area of the zeolite would positively impact the adsorption.

Figure 16a depicts the linearization of the Langmuir adsorption model for the Cu data. Figure 16b shows the adsorption isotherm of the Cu batch study in comparison to the Langmuir adsorption model.

![Figure 16a: Cu Linearized Langmuir Model](image)

![Figure 16b: Cu Adsorption Isotherm and Comparative Langmuir Model](image)
When comparing the Cu data to that of Langmuir, Freundlich, BET, and linear models, it was found that the best fit was that of the Langmuir adsorption model when disregarding the data point from the 50 mg/L C_{i} batch test (furthest to the left on the graph). As the number reported from the ICP-OES was 0, it is known that the level was below that of the detection level. Additionally, when including this point the K value is negative, an impossibility that is corrected after removing the value below detection. The best fit of the Langmuir model suggests a monolayer removal for heavy metals; an increase in the surface area of the zeolite would positively impact the adsorption.

Equilibrium studies are useful in determining the selectivity of natural zeolite for heavy metals under controlled experimental conditions (Inglezakis et al., 2002). Figure 17 depicts the selectivity adsorption isotherms from this equilibrium batch study.

![Selectivity Adsorption Isotherms](image)

**Figure 17: Selectivity Adsorption Isotherms**
The selectivity series obtained in this study was: \( \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Fe}^{3+} \). The difference in adsorption capacity of the natural zeolite for the heavy metal ions could be due to a number of factors, including hydration diameters, hydration enthalpies, and solubility of the cations. The hydration radii of the cations are: \( r_{\text{HZn}^{2+}} = 4.30 \text{Å} \), \( r_{\text{HFe}^{3+}} = 4.57 \text{Å} \), and \( r_{\text{HCu}^{2+}} = 4.19 \text{Å} \) (Nightingale, 1959). Ideally, the smallest cations would be adsorbed faster and in larger quantities compared to the larger cations, since the smaller cations can pass through the micropores and channels of the zeolite structure with ease (Erdem et al., 2004). Adsorption could also be described using hydration enthalpy, which is the energy that permits the detachment of water molecules from cations and reflects the ease with which the cation interacts with the adsorbent. Essentially, the more a cation is hydrated the stronger its hydration enthalpy and the less it can interact with the adsorbent (Amarasinghe and Williams, 2004). The hydration energies of the cations are: -2010, -1955, and -4265 kJmol\(^{-1}\) for \( \text{Cu}^{2+} \), \( \text{Zn}^{2+} \), and \( \text{Fe}^{3+} \) respectively (Marcus, 1991; Nightingale, 1959). According to the hydration diameters the order of adsorption should be \( \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Fe}^{3+} \) and according to the hydration enthalpies the order should be \( \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+} \). \( \text{Fe}^{3+} \) has a greater charge density compared to the other cations that have an ionic charge of \( +2 \), hence its greater hydration diameter and enthalpy.

### 4.3 Column Studies

The results of the column studies are analyzed by breakthrough curves. The breakthrough curve represents the evolution of the adsorbate concentration in the flow from the adsorbent bed, commonly as a function of time or bed volume. For this study, the concentrations corresponding to the values reported from the Animas River, Colorado AMD contamination in August 2015 were used for the absorbate concentrations and...
natural zeolite from the St. Cloud Mine in New Mexico was used for the adsorbent bed. The bed column was calculated to be 0.049 L. The raw data for the column studies can be found in Appendix E.

Figure 18 shows the saturation breakthrough curve for Fe.

![Fe Breakthrough Curve](image)

**Figure 18: Breakthrough Curve of Fe**

As depicted in Figure 18, 39,000 bed volumes reached saturation breakthrough and 80% exhaustion occurred near 35,000 bed volumes.

Figure 19 shows the breakthrough curve for Zn.
Figure 19: Breakthrough Curve of Zn

As can be seen from the Figure 19, saturation breakthrough was reached around 150,000 bed volumes for Zn, and 80% exhaustion occurred near 100,000 bed volumes.

Figure 20 shows the column curve for Cu.
As can be seen from Figure 20, saturation breakthrough was never reached for Cu during the 24-hour testing period, meaning saturation breakthrough occurs after 24-hours. This can be interpreted as natural zeolite being an excellent choice for remediation of Cu contamination levels caused by the Gold King Mine, CO AMD.

4.4 Regeneration Studies
The results of the regeneration studies were analyzed with breakthrough curves, similar to the column studies discussed earlier. The first regeneration study involved running the Zn-exhausted column with KCl until reaching saturation breakthrough. The results of the first regeneration column can be seen in Figure 21.
As can be seen in Figure 21, breakthrough was reached between hours 4 and 7 of running, and 80% exhaustion occurred near 4.75 hours. However, in the case of regeneration, 100% exhaustion could be more desirable for reuse purposes.

The second regeneration study involved running the newly regenerated column with the same concentration of Zn previously used until reaching breakthrough. The results of the second regeneration column in comparison to the first Zn run can be seen in Figure 22.
As can be seen in Figure 22, saturation breakthrough was reached very similarly to that of the mined, natural zeolite; 154,000 bed volumes reached saturation breakthrough, and 80% exhaustion occurred near 98,000 bed volumes. There was less than a 2% decrease in the time when 80% exhaustion occurred from the first Zn column to the second Zn column, indicating that while regenerated zeolite maintains the adsorption properties of fresh mined, natural zeolite.
CHAPTER V
Customer Discovery and Market Analysis

5.1 Executive Summary

The modern world poses many threats to nature as a whole, and rivers are no exception. Even with careful precautions, accidents happen and harmful contaminants end up in the waterways.

In the U.S., 40% of the rivers and 46% of the lakes are polluted and are considered unhealthy for swimming, fishing or aquatic life (Hearn, 2011). 206 million pounds of toxic materials are dumped in our waterways each year. Within the U.S. alone, there are approximately 6,000 industrial spills per year with yearly increases. (Environment America, 2014)

In the August of 2015, the Animas River in Colorado was heavily contaminated by accident. The crew misjudged the pressure while trying to remove contaminated water, and the mistake resulted in 80 miles of river pollution. Experts estimate that the cleanup cost for this river is between $338 million and $27.7 billion (Batkins, 2015). In cases such as these, environmental engineers have to fix as much as they can as quickly as they can. It is the environmental engineers responsibility to choose the best method possible once an accident occurs. Zeolites can be used as a new, innovative technology to effectively remove acid mine drainage contamination while keeping costs low.

Only a few effective pollution removal technologies are available today, and the majority of these methods rarely work for flowing rivers at all. Moving water, aquatic wildlife, and portability are central problems for current technologies. Natural zeolites provide a solution to these challenges as well as many others. Zeolites have been proven to remove heavy metal contamination, and are readily available for use. When used with a
system designed with efficiency and customization in mind they can be easy to transport and readily adjusted to provide full coverage for various river sizes. The result is a technology that provides many advantages over ordinary systems on the market and has a very competitive price.

The plan for using natural zeolites as AMD remediation is both cost effective and efficient. The necessary materials – coated steel, natural zeolite, and other synthetics – would be purchased from wholesale companies in bulk, and prototypes would be built and thoroughly tested before mass assembly begins. Estimated startup time, at the completion of the first scaled-up prototype, would be in approximately six months. As accidents happen, the world demands restoration of nature, and natural zeolites will become a very popular choice for cleaning river contamination. This will prove to be a very worthwhile and profitable investment in the future of environmental protection.

5.2 Entrance Strategy
As discussed earlier, zeolite has been established as a low-cost adsorbent that can effectively purify contaminated water commonly found in natural aquatic environments without disturbing aquatic life. The market entrance strategy will involve scaling up prototypes and testing technology in a partnership with environmental engineering consultants who are dealing with their customers who face river contamination issues and are actively bidding for jobs posted by federal and state governments. It is important that an engineering consultant will receive the technology at a discount price, so they will be more motivated to engage their customers.

With the significant maintenance and operating cost that scaling entails, it is expected that a partnership will be in a very good position to i) prove the concept, ii)
technically scale the technology to an industrial level and iii) facilitate the entrance to the market making it easier to approach more customers by demonstrating the value natural zeolite can add to their operations. The pilot program is expected to run for 6 months to gather results and spread public knowledge of the technology. During this period production and quality control will be emphasized, focusing on the highest standards for reliability, effectiveness, and quality. Additionally, the feasibility to enter different markets such as the agricultural sector, industrial water processes, and varying areas of contamination will be explored. After this period it would be possible diversify to provide clean water in more areas of the world while still tackling water decontamination in polluted rivers.

The ideal business plan has several milestones to achieve production and quality controls. The pilot partnership is key to observe and test the technology in an industrial environment instead of a controlled lab environment. The strategic partnership provides the advantage of improving the technology and gaining a competitive advantage over current systems. The focus will be on all industries that operate water treatment processes seeking to decrease contamination among aquatic sites in the United States.

5.3 Intellectual Property
Provisional patents are currently being filed for possible apparatuses for use with natural zeolite. These patents consist of intellectual property for systems and methods for contaminant removal via absorbent technology and for the technology that could be used to implement natural zeolite in natural rivers.

5.4 Market Analysis
The market sector covers the wide range of AMD contaminations in bodies of water,
such as rivers, lakes, and man-made dams. Since an overabundance of impurities can cause damage to aquatic life, careful consideration must be given to the process intended to remove the contaminants.

Natural zeolite river decontamination technology will allow a body of water to eliminate the overabundance of contaminants in the water, and therefore improve the quality and health of the surround environment, increasing their return on investment. There are more than 250,000 rivers in the U.S., all of them with potential for contamination. Partnering with established environmental engineering firms in varying regions of the U.S. is essential to the testing simply because its knowledge and experience with environmental decontamination and innovation. Their business consists in effectively improving the environment; a worthwhile goal to aim for.

Currently, the estimated amount of funds spent on cleaning bodies of water every year by community, state, and federal sources is $22 billion. The industrial sector represents an important percentage of their market segmentation. This strategy is aimed to establish a solid market share in the Southwest and West market within a two-year period, 2017 and 2018, and in the following two years, 2019-2021, the focus is on capturing surrounding states in the Midwest and Southeast.

5.5 Competing Methods and Competitive Advantage

Other methods used to decontaminate AMD contamination involve changing the pH of rivers with either lime or ash to start the precipitation process; then the water must be filtered separately to remove the precipitated contaminants. Some mining companies use CaCO₃ during the mining process to buffer the acidic nature of mining, but the practice is not continued once a mine is abandoned and vulnerable to AMD leakage. The competitive
The advantage of using natural zeolite is the unique process, which does not require a change in pH, allowing removal of contaminants to quickly be removed on-site.

5.6 Business Model

5.6.1 Customer Segments and Relationships

Customer segments have been established that include those who currently want to reduce contamination in natural bodies of water, however, the market does not remain limited to other uses for impurity reduction.

It important to estimate the market size of the competitors, many of which use reverse osmosis, which is more expensive than the developing technology involving natural zeolite. The reverse osmosis market segment would also be evaluated and approached in order to obtain a competitive market share. Currently the market for reverse osmosis membranes and system components reached nearly $5.4 billion in 2014 globally, and it is predicted to rise at a compound annual growth rate of 10.5% to reach $8.8 billion by 2019.

During the first year pilot program, customers would consist of a local water treatment, supply, or service firm or an engineering design firm. These firms operate at more than one facility. It is essential that the highest quality service be provided to the local pilot program in order to expand to more facilities.

5.6.2 Value Proposition

The greatest value to customers is the quality of water, the ability to reduce process costs, and improve return rate on investment. The current water treatment process is not a simple, inexpensive process. The use of natural zeolite is an innovative water purification process that requires less capital and a significant reduction of time for the process to be completed.
5.6.3 Channels
Ideally, the end customers, agencies aiming to reduce aquatic contamination, will be approached by the partner firms that facilitate those processes such as environmental engineering design firms and water services firms. In turn, those firms will be approached with informational sessions that will demonstrate the results the technology produces and the advantages of using the zeolite system. The main focus for the zeolite technology would be to provide these firms with the design and operational information, and the benefits the new technology will enable.

5.6.4 Revenue Streams
Working closely with the partnering engineering consultant to analyze the customer’s needs and present a formal proposal to the communities and engineering design companies will be a top priority. The removal system units will be designed and scaled to satisfy the decontamination levels required by the customer. Additional negotiation with the customer will determine the extent of the maintenance and support that will be needed for the sold units.

5.6.5 Key Resources and Activities
A partnership with an established Environmental Engineering Consultants/ Mining company would be the best choice for a partner. It would be one of our most valuable assets; it provides intellectual property and resources for further technological development. The intellectual property would be strengthened by the ongoing development work by engineers. A key activity would be the continuous improvement on the technology to consistently reach full potential to provide a competitive service. Another Key resource is the ideal management team which description is in Appendix G.
5.6.6 **Key Partners**

In order to guarantee a successful venture, it would be necessary to align strategically within the market, and partner with 1) companies that will produce the necessary process components, 2) companies, like water service and engineering design companies who have and/or will have close relationships with the end users.

**Financial Plan**

Five-year projections are found in Appendix H. The plan incorporates several assumptions:

- Only revenues for removal units that are used for purifying process water have been taken into account
- The first year is focused on West Texas and New Mexico companies who have a significant process water problem
- The second and third years are focused on companies within the Southwest
- Year four and beyond are focused on firms in the Western United States

**5.7 Investment Offering and Exit Strategy**

It would be necessary to seek $52,000 for 2.5% stake with the assumption that a $100,000 seed grant would first be obtained. Exit strategy options include, but are not limited to, the sale to an industrial water-service company or buy out of investors within five years.
CHAPTER VI

Conclusions

In this study, adsorption characteristics of adsorbed Fe, Zn, and Cu by natural zeolite were assessed at varying metal concentrations and conditions. Both batch studies and column studies were performed to evaluate the adsorption behavior of zeolites with respect to Fe, Zn, and Cu in relation to heavy metal removal in polluted settings caused by AMD. A regeneration column study was executed to analyze the possible regeneration use of natural zeolite.

6.1 Zeolite Characterization

By performing a sieve analysis, the effective diameter was found to be 0.91mm. The coefficient of uniformity was calculated to be 1.318, indicating a relatively uniformly graded sample.

6.2 Zeolite Adsorption Properties

The batch study indicated that the best fitting adsorption isotherm for the concentrations of Fe, Zn, and Cu tested in this study is the Langmuir adsorption model. This suggests a monolayer adsorption of Fe, Zn, and Cu, implying that an increase in the surface area of the zeolite would lead to an increase in the adsorption capabilities.

Column studies were preformed to determine the adsorption breakthrough curve for practical application of zeolite treatment of AMD, particularly treatment of concentrations similar to the contaminants of the Gold King Mine, Colorado AMD leakage in August 2015. Natural zeolite proved to be capable of handling the found concentrations caused by the Gold King Mine, Colorado AMD leakage.

6.3 Zeolite Regeneration

By preforming a regeneration column study, it was found that natural zeolite has the
ability to regenerate though its adsorption levels are not as high after being regenerated.

The first time the Zn solution was pushed through the column, it reached 80% exhaustion at 4.6 hours. After being regenerated with KCl, the column was run with the same concentration of Zn solution, reaching 80% exhaustion at 1.75 hours.

6.4 Zeolite Market Analysis

The results of the preliminary market analysis and business plan indicate that natural zeolite can be used effectively in the market for the removal of metal cations from wastewater. Zeolite is a naturally occurring material that could provide a substitute for the use of other materials as an adsorbent due to its availability with the benefit of low cost.

Following the preliminary business plan, zeolite could enter the market for AMD remediation and make profit by year five.

Recommendations/Future Work

The research that has been undertaken for this thesis has highlighted a number of topics on which further research would be beneficial.

As previously discussed, the working concentration of Cu from the Gold King Mine, CO contamination, was too low to conclusively form a complete breakthrough curve. As such, further research could be done as to extending the time period for a Cu and natural zeolite column study, or a higher concentration of Cu could be used with a natural zeolite column to obtain a compete breakthrough curve.

On the statistical side, further work could be done to create an adsorption model that better fits the nature of natural zeolite or the trends associated with regeneration of natural zeolite.
The best fit of the Langmuir adsorption model suggests a monolayer adsorption a previously discussed, which suggests further work in the possible field of using nanotechnology with zeolites.

Concerning regeneration, further studies could be done to increase knowledge of how continuous regeneration affects the adsorption qualities of natural zeolite – for instance, if they will continue to decrease or level out, and how many times zeolite can be effectively regenerated.

Another area that could benefit from further work is studying the varying stages of AMD. In particular, natural zeolite might be evaluated as a possible treatment for AMD as a preventative measure rather than a remediation process. If natural zeolite could be involved in the mining process, accidental AMD contamination could be partially eliminated in the future. Future studies might, for example, evaluate the use of zeolite placed in abandoned mines before leakage occurs.
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## APPENDIXES

### APPENDIX A – Sieve Sizes and Numbers

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<tr>
<th>Sieve Number</th>
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St. Cloud Natural Zeolite
(Clinoptilolite)

Product Information Sheet

Natural zeolites are a unique type of microporous volcanic mineral with sieving and cation exchange properties for use in agriculture, environmental and industrial applications. St. Cloud Mining Company is the largest producer of natural zeolite in North America.

• Uses of St. Cloud Zeolite
St. Cloud Zeolite has hundreds of proven uses, and the list continues to grow. St. Cloud Zeolite is a natural mineral produced by all natural means, and is used as an animal feed supplement that has been shown to improve health and reduce the negative effects of animal waste; as an additive to animal stalls and pens to reduce ammonia and other emissions to air and water; as a soil amendment to retain water and plant nutrients in root zones, which conserves both; for a number of other horticultural and agricultural uses, including being the only zeolite endorsed for use in space by NASA; as a water filtration media that removes ammonia, some heavy metals and other constituents; and dozens of other uses.

• Physical Properties

Bulk Density (In Place, dried) .....................87 lbs/ft³ (1,390 kg/m³)
Bulk Density (Aggregate, dried. Common sizes)
  4 X 6 Mesh .....................44-48 lbs/ft³
  6 X 14 Mesh ....................45-47 lbs/ft³
  14 X 40 Mesh ..................46-49 lbs/ft³
  -40 Mesh ......................48-52 lbs/ft³
  -100 Mesh ......................49-53 lbs/ft³
  -325 Mesh ......................43-47 lbs/ft³
Clinoptilolite content ..................................75 to 85%
Cation Exchange Capacity (CEC) .............0.8 – 1.2 meq/g Surface
Charge density ......................................10.1E-23 meq/Å²
Color .....................................................White (85 optical reflectance)
Crushing Strength ....................................2,500 lbs/in³ (176 kg/m³)
Hardness .............................................3.5-4.0 Mohs LA
Wear (Abrasion Index) ......................... 24
Molecular Ratio .....................................5.1 (Si/Al)
pH (natural) .........................................7.5 to 8.0
pH Stability .........................................0-13
Permeability .........................................10⁻³ m/sec (1.4 – 0.4 mm particles)
Pore Size (diameter) .............................4 - 7 angstroms
Pore Volume ........................................≤ 52%
Resistivity ..........................................~ 9,000 ohms/cm
Specific Gravity .....................................2.2 - 2.4:1
External Surface Area ............................14 to 15 m²/g
Total Surface Area ..................................... ≤ 800 m²/g
Swelling Index ....................................... nil
Thermal Stability ..................................... 1,202° F (650° C)
Other .................................................... non-soluble, non-slaking, free flowing, readily mixable

• Chemical Analysis
  (Ca, Na₂, K₂)(Al₆, SiO)₂4H₂O; Calcium-sodium-potassium aluminosilicate). In approximate weight percent for major oxides:
  CaO  3.4%  MgO 1.5%  Na₂O 0.3%  Fe₂O₃ 1.6%
  K₂O  3.0%  P₂O₅ 0.05%  Al₂O₃ 12.1%  SiO₂ 70.0%

• Chemical Composition
  for selected elements by x-ray fluorescence (in weight % or ppm, as noted)
  Ca  2.4%  Mg  0.9%  Na  0.1%  Fe  0.6%  Cu  10 ppm
  K  1.2%  P  0.01%  Al  3.1%  Si  32.9%  Zn  59 ppm

• Cation Exchange Capacity
  Total exchange capacity of 0.8 – 1.2 meq/g total, and an external exchange capacity of about 0.1 meq/g.

• Major Exchangeable Cations
  Rb, Li, K, Cs, NH₄, Na, Ca, Ag, Cd, Pb, Zn, Ba, Sr, Cu, Hg, Mg, Fe, Co, Al, Cr. (selectivity of above cations is a function of hydrated molecular size and relative concentrations).

• Primary Adsorbing Gases
  CO, CO₂, SO₂, H₂S, HCHO, Ar, O₂, N₂, H₂O, He, H₂, Kr, Xe, CH₂OH, Freon, formaldehyde, and mercaptans.

• Environmental Properties
  Zeolites are natural, inert, non-toxic substances which are federally classified as GRAS (Generally Regarded As Safe) in most applications and exempted from most regulations and reporting when used in accordance with good agricultural practice and when less than 2% in animal feed products (40 CFR, Part 180.1001 and elsewhere). St. Cloud Zeolite is USDA approved as an absorbent for spills in food processing facilities and complies with federal and state environmental requirements. No fibrous silicates have been detected and crystalline silica is present in quantities of less than 0.01%. Reference MSDS Sheet (product CAS No. 1318-02-1) for additional information.

• Location
  St. Cloud’s Zeolite operation is centrally located near Winston, New Mexico, approximately 35 miles west of Interstate 25 midway between Albuquerque, New Mexico and El Paso, Texas.

• Reserves
  An 18.3 million ton zeolite reserve base mined from surface exposures 1.5 miles from plant site.

• Delivery and Freight
  Motor carriers for packaged and bulk products for domestic and international destinations. Bulk rail facilities are available by special arrangement. UPS, LTL, and regional warehousing services also available. Warehouse customer pick-ups 8:00 am-3:00 PM, 5 days per week, or 24 hrs per day or by prior arrangement.

• Trade Names
  Sold by St. Cloud as Stone House® Cat Litter, Floor Drying Material and Natural Zeolite Crystal, and Heaven Scent®. Marketed or included in products by brokers, manufacturers and distributors as Ammo® Chips, Litter and Rocks, Ammonia-X®, A-Stone®, Biolite®, Clinolite®, EcoFresh®, Ecolite®, E-Z Dry®, Hydrosil®, PDZ® Sweet Stall®, Stall Fresh® Zeofresh, ZeoPro and others.
• **Packaging**
  Standard, private label and custom packaging and palletizing available including 10, 25, 50 lb. or other units in paper or plastic with stitch, taped, valve packed or heat sealed closures. Other off-site special packaging services available on request. Bulk packaging in approximately 1-ton and other supersacks or directly loaded in any bulk truck or rail car configuration including top loading or pneumatic carriers.

*Information herein is accurate to the best of our knowledge, but may be subject to change without notice. Suggestions are made without warranty or guarantee of results. Before using, user should determine the suitability of the product for its intended use and user assumes the risk and liability in connection herewith.*

Updated September 2007.
PRODUCT DATA SHEET

NM-Ca *Winston Clinoptilolite
Potassium Aluminosilicate, Natural Clinoptilolite
Zeolite Powder and Granules

TYPICAL PROPERTIES

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TYPICAL CHEMICAL ANALYSIS

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MAJOR EXCHANGEABLE CATIONS

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Information herein is accurate to the best of our knowledge. Suggestions are made without warranty or guarantee of results. Before using, user should determine the suitability of the product for his intended use and user assumes the risk and liability in connection therewith. We do not suggest violation of any existing patents or give permission to practice any patented invention without a license.
APPENDIX D – Kinetic Batch Studies Raw Data

**IRON**

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<th>Fe C&lt;sub&gt;e&lt;/sub&gt; (mg/L)</th>
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**ZINC**

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APPENDIX E – Equilibrium Batch Studies Raw Data

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### IRON – SELECTIVITY

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## APPENDIX F – Column Studies Raw Data

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## APPENDIX G – Regeneration Studies Raw Data

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APPENDIX H – Management Team

The ideal team would comprise of individuals with business, science, and engineering specialties. An environmental engineer would work directly with the development of the removal mill units. A business specialist would be required for marketing research and developing financial statements for the startup. An experienced mechanical engineer would also be necessary for prototype development and testing.
# APPENDIX I – Financials: Balance Sheet Years 1-5

## ASSETS

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## LIABILITIES & EQUITY

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CURRICULUM VITAE

Mackayla Janae Thyfault was born in Midland, Texas. The oldest child of Brook William Thyfault and Nancy Strate Thyfault, she graduated from Captain John L. Chapin High School, El Paso, Texas, in the spring of 2010 with Engineering Magnet Honors and entered Brigham Young University in the fall. While pursuing a bachelor’s degree in Civil Engineering with a minor in Business Management, she worked with greenplex technology and sustainability, and during the summers of 2013 and 2014, interned with the Texas Department of Transportation – El Paso. She was published in 2015 in *Natural Resources* with *Exploring Emergent Vegetation Time-History at Malheur Lake, Oregon Using Remote Sensing*. In the fall of 2015, she entered the Graduate School at The University of Texas at El Paso where she continued her education with a focus on acid mine drainage and zeolite adsorption properties. She plans to further her studies by earning a Doctorate of Philosophy in Civil Engineering from The University of Texas at El Paso.

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El Paso, Texas
79904

Or mackayla.thyfault@yahoo.com