In Situ Remediation Of Heavy Metal Contaminated Sediments Using Emulsified Zero-valent Metal Particles

Kristen Marie Milum
University of Central Florida

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IN SITU REMEDIATION OF HEAVY METAL CONTAMINATED SEDIMENTS USING EMULSIFIED ZERO-VALENT METAL PARTICLES

by

KRISTEN M. MILUM
B.S. University of Central Florida, 2003

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science
in the Department of Chemistry
in the College of Arts & Sciences
at the University of Central Florida
Orlando, Florida

Summer Term
2005
ABSTRACT

Sediments can act as both a sink for pollutants and a source for aquatic contaminants. Natural and human disturbances of the sediments can release the contaminants to the overlying water where bottom dwelling, or benthic, organisms may be exposed through direct contact, ingestion of sediment particles, or uptake of dissolved contaminants present in the water. Dredging, the most common remediation technology for heavy metals, exacerbates this process. The in situ use of emulsified metal has been studied for its ability to pull heavy metals from aqueous solution and from saturated soils. It has proven successful in the laboratory with removal of lead, cadmium, copper, nickel, and uranium from aqueous solution and removal of lead and cadmium from saturated spiked soils.

The use of zero-valent metal particles, particularly those of zero-valent iron (Fe$^0$), as an in situ remediation technique, is currently undergoing evaluation. The basic mechanism for removal appears to be reduction of contaminant metals followed by the subsequent precipitation of their insoluble forms. This is accompanied by the oxidation of the zero-valent metal. In the case of iron, Fe$^0$ undergoes oxidation to Fe$^{2+}$ and then to the Fe$^{3+}$ state. Particulate Fe$^0$ has been shown to precipitate Cr$^{6+}$ to Cr$^{3+}$ and Pb$^{2+}$ undergoes reduction to Pb$^0$. Initially, zero-valent iron filings were used to reduce the metal
contaminants, but it has been shown that smaller size iron particles, such as nano-scale iron, have higher initial reduction rates as well as a higher concentration of contaminant removal per mole of iron. Emulsion liquid membrane (ELM) technology has been employed as a remediation technique for the removal of metals from wastewater where extraction and stripping processes are performed in a single operation. The ELMs are made by forming an emulsion between two immiscible liquids, such as oil and water, and are often stabilized by a surfactant.

We have attempted to demonstrate the application of the combination of these two technologies through the use of emulsified zero-valent metal (EZVM) to treat sediments with heavy metal contamination. Emulsions were prepared using vegetable oil, water, Span 85, and either nanoscale Fe, 1-3 μm Fe, 4 μm Mg, or a 20 wt % Fe-Mg mixture. The results presented in this study demonstrate that EZVM is a viable technique for in situ remediation of heavy metals in sediments. Laboratory scale studies have shown high levels of removal of lead and cadmium from solution using emulsified zero-valent iron. Additionally, the use of emulsified magnesium has shown the ability for high levels of removal of copper, cadmium, nickel, lead, and uranium from solution. A variety of solution matrices were also explored for a lead solution including seawater, the presence of complexing agents and humic acids. Small-scale laboratory studies have shown 65% removal of lead and 45% removal of cadmium from saturated, spiked soils. A bench scale test to demonstrate the applicability of this technique in the environment revealed similar results for the removal of lead.
To Mom & Dad,

For never letting me think that I couldn’t.
ACKNOWLEDGMENTS

I would like to thank Dr. Cherie Geiger, my advisor, for all the support and wisdom that she shared. I would also like to thank Dr. Chris Clausen, Dr. Steve Kuebler, and Dr. Jackie Quinn for the guidance and encouragement. To my colleagues: Brian Aitken, Kathy Brooks, Rachel Calabro, Larry Collier, Bobby DeVor, Debbie Maxwell, and Gena Ward, thank you for all the work that you have done to make this thesis possible.
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<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic acid</td>
</tr>
<tr>
<td>ELM</td>
<td>Emulsion liquid membrane</td>
</tr>
<tr>
<td>EZVM</td>
<td>Emulsified zero-valent metal</td>
</tr>
<tr>
<td>FAAS</td>
<td>Flame atomic absorption spectroscopy</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively coupled plasma-mass spectroscopy</td>
</tr>
<tr>
<td>PRB</td>
<td>Permeable reactive barrier</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>ZVI</td>
<td>Zero-valent iron</td>
</tr>
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</table>
INTRODUCTION

Of the 1200 sites in the US on the National Priority List for contaminated soil treatment, approximately 63% of the sites contain heavy metal contamination. Lead, chromium, cadmium, and copper were found at 15, 11, 8, and 7% of the sites, respectively. The heavy metals, cadmium, lead, mercury, nickel, and zinc are considered by the Environmental Protection Agency to be the most hazardous and are all located on the EPA's list of priority pollutants. Once heavy metals reach the environment, from sources including domestic and industrial effluent, they are persistent, as they cannot be biodegraded. The sediments can act as both a sink for pollutants and a source for aquatic contaminants. Natural and human disturbances of the sediments can release the contaminants to the overlying water where bottom dwelling, or benthic, organisms may be exposed through direct contact, ingestion of sediment particles, or uptake of dissolved contaminants present in the water. Exposure of toxic chemicals to benthic organisms can sometimes kill them, resulting in a decrease of available food to larger organisms. Alternatively, consumption of the contaminated benthic organisms by larger animals can result in bioaccumulation.

When considering the available treatment options for a contaminated site, it is important to also consider the speciation and distribution of the heavy metal contaminants. Using
lead as an example, alkyllead compounds, a very toxic form of lead, is rarely reported in sediments,\(^4\) while lead carbonates are significantly more prevalent.\(^5\) Primarily, metals are found associated with soils and sediments in one of four primary mechanisms, listed in order of decreasing bioavailability:

1. A small portion is present in adsorbed or exchangeable forms.
2. The metals can be organically bound to the soil, but can be released over time.
3. They can be found associated with carbonates and oxides of iron and manganese.
4. They can be in a residual form, consisting of insoluble compounds, such as sulfides.\(^5\)

**Current Remediation Technology**

The high levels of clay, silt and organic matter provide a much greater obstacle for the treatment of heavy metal contaminated sediment than for that of soil or groundwater. Frequently, dredging of sediments is required and *ex situ* treatment is performed. There are a great deal of concerns following this course of action, particularly due to the risk of introducing contaminants into previous uncontaminated areas. This is caused by the resuspension of sediments during the dredging process and spills or leaks during transport.\(^6\) Prior to the transport, however, full characterization, analysis and assessment of the sediment must be obtained.\(^7\) Each treatment process comes with a variety of limitations. Many require specific conditions for operation to combat significant decreases in effectiveness and are only of use for a select number of contaminants.\(^7\) For
these reasons, it is often not possible to completely remediate contaminated sediment with a single treatment technology. Frequently treatment stages are employed with the first being dewatering of the sediment.

There are several remediation options to be considered: leaving the sediment in place, containing or capping, *in situ* treatment, or dredging followed by *ex situ* treatment. It is important to remember: “No remedial alternative can remove, contain, or treat contaminated sediment without some disturbance and consequent release of contaminants. Disturbing sediment causes resuspension of contaminants into the water column. The remedial option must minimize the contaminant release.”

There are situations where no action is warranted: if the sediment will not be disturbed by human or natural activities, the contaminant discharge has ceased, there is rapid natural burial of the sediment, and the environmental impact of the clean-up effort is more damaging than the “no action” alternative. Similar requirements are in place when selecting capping as a treatment option. Treatment is accomplished by depositing a layer of ‘clean’ sediment on top of the contaminated region to limit the disturbance of the contaminated sediment. While capping is considered to be an *in situ* treatment technology, others are available although they have very limited application for the remediation of heavy metals. Generally, they are infrequently used due to the possibility for secondary contamination from toxic reagents or treatment products and the difficulty associated with mixing of the treatment reagents in the sediment.
A variety of processes are available for *ex situ* treatment of heavy metals contaminated sediment, including soil washing, thermal desorption, electrokinetics, and vitrification. Solidification and stabilization technologies have been found to be the most effective.

Soil washing is a water-based process designed to remove contaminants by mechanical scrubbing. Contaminants are either dissolved or suspended in a wash solution which is later treated by conventional means. While this process is effective on coarse material like gravel, finer particles such as clay and silt tend to pass through the treatment system. Soluble metals may be treated by this method, but insoluble metals often require the addition of acid or a chelating agent to the wash water for successful treatment.\(^6\)

Thermal extraction or desorption is effective for sediments contaminated with mercury, arsenic, and cadmium compounds that can be evaporated at 800 °C with the appropriate air control systems. However, moisture content of sediments and treatment capacity of the units limit the applicability of this technique.\(^7\)

Electrokinetic treatment of heavy metals contaminated sediments is accomplished by passing a low intensity electric current between a cathode and an anode imbedded in the sediments. The technology has been effectively demonstrated in Europe although high levels of oxides, carbonates, moisture content and other contaminants can interfere with efficient removal.\(^7,8\)
Vitrification is an immobilization technique whereby a current is passed through the sediment, causing temperatures to reach as high as 3000 °C, which solidifies as it cools. Although toxic gases may be produced during treatment, cadmium, chromium, and lead have been successfully reduced using this technique. High organic content of the dredged sediment can decrease efficiency.  

**Zero-Valent Iron Technology**  
The use of zero-valent iron (Fe\(^0\)) is an *in situ* remediation technique that is currently undergoing evaluation. The basic mechanism for removal initially proposed involves the reduction of contaminant metals followed by the subsequent precipitation of their insoluble forms. Fe\(^0\) undergoes oxidation to Fe\(^{2+}\) and then to the Fe\(^{3+}\) state with standard half cell reactions shown in reactions 1-3.

\[
\begin{align*}
\text{Fe}^{3+} + 3\text{e}^- & \rightarrow \text{Fe}^0 \quad E_o = -0.037 \, \text{V} \\
\text{Fe}^{2+} + 2\text{e}^- & \rightarrow \text{Fe}^0 \quad E_o = -0.447 \, \text{V} \\
\text{Fe}^{3+} + \text{e}^- & \rightarrow \text{Fe}^{2+} \quad E_o = +0.771 \, \text{V}
\end{align*}
\]

Initially, iron filings were used, but it has been shown that smaller iron particles, such as nano-scale iron, have higher initial reduction rates as well as a higher concentration of contaminant removal by mass. This has been attributed to the specific surface area of the
iron particle, which has a direct relationship to the number of active surface sites on the iron that are available to the contaminant metals. If the size of the particle is decreased, the specific surface area is increased, which leads to an increased rate of reduction.\textsuperscript{9,10} Previous studies have demonstrated the ability of iron particles to reduce copper, silver, mercury, selenium, and lead to their zero-valent forms,\textsuperscript{9,11} while other metals such as chromium are partially reduced. Particulate Fe\textsuperscript{0} has been shown to reduce Cr\textsuperscript{6+} to Cr\textsuperscript{3+} rapidly, which can then form Cr(OH)\textsubscript{3} and subsequently precipitate out of solution, greatly reducing the concentration of dissolved chromium.\textsuperscript{11} Further work has been done to demonstrate the application of the ZVI technology to radioactive materials such as UO\textsubscript{2}\textsuperscript{2+}, where it was discovered that the uranium species is immobilized on the iron surface without any reduction occurring.\textsuperscript{12} In addition to these metals, a number of experimental conditions have been explored regarding the effect of dissolved gases, including oxygen and carbon dioxide, as well as the form of iron used. No definite mechanism for the removal of each of these heavy metals from solution has been determined due to the complex redox chemistry involved, though most indicate the mechanism to proceed by reduction, adsorption, or a combination of the two. Independently, extensive research into the adsorption of heavy metals onto iron oxide surfaces has been performed.\textsuperscript{13,14}
**Emulsion Liquid Membrane Technology**

Emulsion liquid membrane (ELM) technology has been employed as a remediation technique for the removal of metals from wastewater where extraction and stripping processes are performed in a single operation. The ELMs are made by forming an emulsion between two immiscible liquids, such as oil and water, and are often stabilized by a surfactant.

Several models have been devised to describe transport through the membrane, and these can be described using two different mechanisms. Type I involves maximizing the concentration gradient by including a reagent in the receiving phase to react with the transported solute. For example, phenol extraction can occur by this process where the interior of the emulsion droplet contains sodium hydroxide. When the phenol is transported to the interior of the emulsion droplet, it reacts forming sodium phenolate which is not capable of transporting back through the membrane out of the emulsion droplet. Type II mechanisms involve the incorporation of a carrier molecule into the membrane of the emulsion droplet to facilitate transfer of the solute, typically this process is used for the removal of metal ions and complexes.

The ability of emulsion systems to remove metal ions from waste streams has been extensively documented, though virtually all involve the use of carrier molecules to facilitate the transport. The metal-carrier complex must be soluble in the membrane...
phase and insoluble in the feed or receiving phase. The carrier molecules selected can serve both to enhance the removal capacity of the emulsion system as well as provide an element of selectivity for the emulsion system. In addition to varying the carrier molecule, other factors including drop size and ratio of organic to water in the emulsion were investigated.

**Emulsified Zero-Valent Metal**

We have attempted to demonstrate the application of the combination of these two remediation technologies, emulsion liquid membranes and zero-valent metal, through the use of emulsified zero-valent metal (EZVM) to treat sediments with heavy metal contamination.

An emulsion system consisting of an organic component, corn oil or d-limonene, water, Span 85, a surfactant, and nano- or microscale metal particles has been developed. The design allows for the emulsion system to act as both a protective barrier around the metal particles and to concentrate the heavy metal contamination in the interior of the droplet. The following figures are micrographs of emulsion droplets.
Figure 1: Micrograph of oil-water emulsion droplet containing nanoscale iron particles.

Figure 2: Micrograph of oil-water emulsion droplet containing microscale iron particles.
Use of the EZVM technology for treatment of contaminated sediments would not only provide a novel *in situ* treatment technology, but in contrast to current *in situ* heavy metal treatment technologies, EZVM can provide a method to remove the contaminants from the site. After the EZVM has been injected into the sediments, the heavy metal contaminants transport through the emulsion membrane and deposit onto the iron surface. Then, taking advantage of the magnetic properties of iron, a magnetic removal process could be used to separate the emulsion from the sediments and thereby removing the contamination with it.
**Research Objectives**

Current remediation technologies are unable to effectively treat heavy metal contamination *in situ*. The goals of this research were to determine the ability of EZVM to remove metal ions from solution and the effect of more complex matrices on the ability of the emulsion system to remove heavy metal ions was explored. Once this was established, it was necessary to verify the transport of the heavy metal contaminants to the interior of the emulsion droplet and its subsequent immobilization on the metal surface.

After the emulsion system was successfully shown to remove contaminants in various solution matrices, it was then necessary to determine the ability of the emulsion to remove metals from saturated, spiked sediments. Also, it was necessary to establish the feasibility of employing EZVM as a remediation technique through a small-scale demonstration.
EXPERIMENTAL

Methods & Materials

Materials

Micro-scale iron (1-3 \( \mu \)m and <10 \( \mu \)m) was obtained from BASF Corporation and Alfa Aesar and washed with a 5% sulfuric acid solution prior to use. Nano-scale iron was obtained from the Toda Corporation and was used as received. Magnesium (approximately 4 \( \mu \)m) was obtained from Hart Metals, Inc. and used as received. Lead solutions were prepared from dried lead nitrate with 1% HNO\(_3\). Cadmium, copper, nickel, and chromium solutions were prepared from 1000 ppm reference solutions obtained from Aldrich and Fisher Scientific. Uranium solutions were prepared from 1000 ppm reference solution obtained from Solutions Plus, Inc.

A 20 wt % iron-magnesium mixture was prepared by ball-milling 64 g Mg with 16 g Fe in a stainless steel canister (inner dimensions 5.5 cm by 17 cm) with a 16 steel ball bearings at a total mass of 261.15g.
Figure 4: Stainless steel canister used in preparation of iron-magnesium mixture.

The material was milled for 30 minutes using a Red Devil 5400 series paint mixer.

Figure 5: Red Devil mixer used in preparation of magnesium-iron mixture.
Sediment Preparation

To prepare the spiked soil, a quantity of soil, which had been dried and sieved using a US Standard Sieve No. 45 (42 mesh), was brought to incipient wetness with the appropriate concentration of heavy metal solution to yield a final concentration of 100 mg / kg soil. The soil was then dried overnight in an oven at 110 °C.

For the small-scale study, an artificial sediment system similar to previously developed systems was prepared. The mixture consisted of 85 wt % silica sand and 15 wt % kaolin clay. Ground peat was added at 10 vol %. To spike the sediment, the mixture was brought to incipient wetness using a lead solution for a final concentration of 600 mg Pb / kg soil.

Figure 6: Artificial sediment mixture.
Emulsion Preparation

Emulsions were prepared immediately prior to use with a formulation of corn oil or d-limonene, water, metal, and Span 85, a surfactant. To obtain acidic and basic emulsions, the pH of the water component was adjusted to a pH of 4-5 with hydrochloric acid and to a pH of 9-10 with sodium hydroxide, respectively. Unless otherwise noted, all emulsions used have a neutral interior water phase.

Analysis

Samples were analyzed by atomic absorption spectroscopy on a Varian SpectrAA 20Plus Spectrophotometer according to the parameters indicated in Table 1. All solutions containing lead, cadmium, copper or nickel were analyzed using an air-acetylene flame atomization apparatus.

Table 1. Flame atomic absorption analysis parameters.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Wavelength (nm)</th>
<th>Lamp Current (mA)</th>
<th>Slit Width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>228.8</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>Chromium</td>
<td>357.9</td>
<td>7</td>
<td>0.2</td>
</tr>
<tr>
<td>Copper</td>
<td>324.7</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>Lead</td>
<td>283.3</td>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>Nickel</td>
<td>352.4</td>
<td>4</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Prior to analysis each day, calibration curves for the elements to be analyzed were obtained. In addition, after every 20-30 samples analyzed, a standard was reanalyzed to verify the system was still calibrated. Typical calibration curves are shown below in Figures 7-10.

Figure 7: Calibration curve for the determination of cadmium by flame atomic absorption analysis at 228.8 nm.
y = -7E-06x^2 + 0.0022x + 0.002

R^2 = 0.9999

Figure 8: Calibration curve for the determination of copper by flame atomic absorption analysis at 324.7 nm.

y = -5E-05x^2 + 0.0156x + 0.0013

R^2 = 1

Figure 9: Calibration curve for the determination of lead by flame atomic absorption analysis at 283.3 nm.
Figure 10: Calibration curve for the determination of nickel by flame atomic absorption analysis at 352.4 nm.

Chromium samples were analyzed on the Varian SpectrAA 20Plus Spectrophotometer outfitted with a GTA 96 Graphite Tube Atomizer. The furnace program used is outlined below in Table 2.
Table 2. Graphite furnace program for chromium analysis

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (sec)</th>
<th>Argon Flow (L/min)</th>
<th>Signal Acquisition</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>5</td>
<td>3.0</td>
<td>No</td>
</tr>
<tr>
<td>95</td>
<td>40</td>
<td>3.0</td>
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</tr>
<tr>
<td>120</td>
<td>10</td>
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<tr>
<td>1000</td>
<td>5</td>
<td>3.0</td>
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<td>3.0</td>
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<td>2600</td>
<td>1.2</td>
<td>0.0</td>
<td>Yes</td>
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<tr>
<td>2600</td>
<td>2</td>
<td>0.0</td>
<td>Yes</td>
</tr>
<tr>
<td>2600</td>
<td>2</td>
<td>3.0</td>
<td>No</td>
</tr>
</tbody>
</table>

$y = 0.0015x + 0.0031$

$R^2 = 0.9997$

Figure 11: Calibration curve for the determination of chromium by graphite furnace atomic absorption analysis at 357.9 nm.
Uranium samples were analyzed by Galbraith Laboratories, Inc. using inductively coupled plasma-mass spectroscopy (ICP-MS).

Humic acid samples were analyzed by UV-visible absorption. Measurements were obtained at 254 nm on an Agilent 8453 UV-visible spectrometer. A featureless spectra with a general increase in absorbance toward lower wavelengths was observed, which agrees with previously reported data. Humic acid concentrations were determined at 254 nm; the spectra and calibration curve are shown in Figures 12 and 13.

![Figure 12: UV-Visible spectra of humic acid standard solutions.](image-url)
A series of studies were prepared to verify the removal of metal ions in solution by the emulsion. In each study, vials were assembled containing 5 g of emulsion and 10 mL of solution. Control vials containing only 10 mL of the respective solution were also prepared. The solution was analyzed for the presence of the metal after 5 days using atomic absorption analysis.

Six different metals were chosen for testing removal from solution using the EZVM technology: cadmium, chromium, copper, lead, nickel, and uranium. These studies were performed with the metals present in solutions of DI water and seawater.
For the oil emulsion formulations, experiments were performed to determine the removal capacity of the emulsions. Vials containing between 1 and 7 g emulsion, in one gram increments and 10 mL of 1000 ppm lead solution.

Additional analysis was performed regarding the ability of the emulsion to remove lead from more complex matrices. Solutions of 100 ppm lead and approximately 0.01 M adipic acid, succinic acid, sodium citrate, 2-mercapto-1-methylimidazole, or disodium ethylenediaminetetraacetic acid were prepared.

The effect of humic acids on the removal of lead from solution with the EZVM was also examined. Solutions of 100 ppm lead and 20 ppm humic acid solution were prepared and analyzed after five days of exposure to emulsion. Remaining lead concentration was determined by atomic absorption spectroscopy and UV-visible spectroscopy was used for the determination of humic acid levels remaining in the solution.

**Emulsion Formulation**

Variations of the emulsion were prepared to determine how the presence of complexing agents in the interior of the emulsion droplet would affect its ability to remove lead from solution. Emulsions were prepared with the same formulation, while amendments were
added to the water component of the emulsion. Solutions of approximate 0.1 M of sodium chloride, succinic acid, adipic acid, sodium citrate, sodium oxalate, 2-mercapto-1-methylimidazole, and disodium ethylenediaminetetraacetic acid and a 100 ppm lead solution were prepared. Vials were then assembled, containing 5 g of the modified emulsion and 10 mL, 100 ppm lead solution, to test the ability of these emulsions to remove lead from solution. The solution was separated after five days and analyzed for the presence of lead by flame atomic absorption spectroscopy.

**Contaminant Fate**

**Lead Partitioning**

A series of experiments were set up to show the partitioning of lead between an oil and water system. Vials contained 10 mL oil and 10 mL of a 10 ppm lead solution. Additional experiments were also set up: the first involved the addition of 0.40 g Span 85 to the oil layer, the second included 0.50 g of ethylenediaminetetraacetic acid (EDTA).

A series of complimentary experiments were set up to determine the partitioning of lead in a d-limonene and water system. Vials contained 10 mL of d-limonene and 10 mL of 10 ppm lead solution. Additional vials were also set up containing d-limonene, lead solution and 1.3 g Span 85.
For both experiments, the quantity of surfactant used was based upon the ratio of the organic component to surfactant in the emulsion formulation.

**Plating Studies**

A series of vials were prepared to verify that the lead was precipitating onto the metal in the interior of the emulsion droplet. The vials were assembled with 5 g of emulsion and 10 mL of 1000 ppm Pb solution. Control vials were also assembled containing 5 g emulsion and 10 mL deionized water. For emulsions containing iron, the samples were separated by placing a magnet on the bottom of the vial to separate the metal from solution. For the magnesium containing emulsions, the emulsion was filtered using a glass filter with a medium frit. The separation was followed by rinsing the recovered metal with sequential 5 mL portions of hexane, acetone, and hexane.

**SEM**

Samples were prepared for analysis by scanning electron microscopy (SEM). Vials were prepared containing 5 g iron emulsion and 10 mL of 100 ppm lead solution. Control vials were also prepared containing emulsion and water. After five days, the iron was recovered from the interior of the emulsion using a magnet and washed with 5 mL
portions of hexane, acetone, and hexane. The residual hexane was evaporated under a nitrogen stream.

Measurements were obtained on a LEO 1455 scanning electron microscope with a four quadrant back scatter detector (4QBSD) configured in compositional (atomic contrast) mode. Samples were analyzed using an accelerating voltage of 13 kV.

**XPS**

Samples were prepared for analysis by x-ray photoelectron spectroscopy (XPS) containing 0.5 g iron and 10 mL of 1000 ppm lead solution. After five days, the solution was separated from the vial and analyzed by FAAS and the iron was recovered from the samples using a magnet. The iron was subsequently washed with 5 mL portions of hexane, acetone, and hexane. The residual hexane was allowed to evaporate under an argon atmosphere. Samples were placed into the ultrahigh vacuum, $10^{-9}$ Torr, using a flat sample bar holder with holes as received; no tape was used for mounting.

Measurements were performed on a Kratos AxisUltra XPS using monochromatic Al K$_\alpha$ X-ray source, an electron flood gun for charge neutralization and hemispherical analyzer with multichannel photomultiplier detector. Survey spectra were acquired at a pass energy of 80 eV for elemental identification. Survey acquisition time was four minutes.
Higher resolution spectra were then acquired at a pass energy of 20 eV for quantitative analysis. Acquisition times for high-resolution spectra of carbon 1s and oxygen 1s was 4 minutes, while that of iron 2p and lead 4f was at 5 and 10 minutes respectively.

**Sediment Studies**

A series of vials were prepared containing 20 g of the spiked sediment, which was brought to incipient wetness with deionized water, 3 mL of iron emulsion was injected into the soil, and 5 mL of additional deionized water was added to the vials. Control vials were also assembled containing only 20 g of soil brought to incipient wetness and 5 mL of additional water. The vials were placed on a shaker table for varying amounts of time before being separated for analysis. To separate the samples, the contents of the vial were placed in a zipper closed plastic bag with a small puncture hole at the bottom of the bag. The bag was placed against a powerful magnet and the soil and water were allowed to drain through the hole into a beaker while the iron was held in the plastic bag by the magnet. The process was repeated until all of the emulsion was removed from the sediment. The water and soil sample was transferred to a Büchner funnel, filtered, and washed with DI water. The soil samples were dried and analyzed using a variation of EPA Method 3050b. A 5 g sample of the dried soil was placed in an Erlenmeyer flask and 20 mL of concentrated nitric acid was added to the flask. This was allowed to digest for approximately 1 hour, and then the flask was placed in an ultrasound bath for 45 minutes at full power. The sample was then filtered using a Büchner funnel with vacuum
filtration and washed with DI water. The filtrate was diluted to a final volume of 50.00 mL and analyzed by flame atomic absorption spectroscopy.

**Small-Scale Demonstration**

A small pool was prepared to demonstrate that ability of the EZVM system for the treatment of contaminated sediments. The pool was filled with 105 lbs of the artificial sediment system. Samples of the sediment were obtained prior to the beginning of the experiment to act as controls. The magnesium-iron emulsion was chosen for the demonstration and injected into the emulsion system using the apparatus shown below.

Figure 14: Peristaltic pump used for injecting emulsion.
Figure 15: Apparatus for injecting emulsion.

The emulsion was injected through the tubes affixed to each of the prongs while moving the apparatus through the sediment. After injecting the emulsion, soil mixing, shown below, was performed to completely distribute the emulsion in the sediment. This was accomplished by using a mixing attachment with a cordless power drill.

Figure 16: Apparatus for soil mixing.
After mixing was complete, a several samples of the sediment were obtained to ensure thorough mixing had been achieved. A photo of which is shown below in Figure 17.

![Figure 17: Sample of sediment after mixing.](image)

The gray spots shown in the picture above are emulsion, which was found distributed through all of the sediment samples obtained.

Samples were obtained from the pool at set time intervals to monitor the lead reduction. The emulsion was separated from the sediment and analyzed using the same techniques as described for the vial studies using a variation of EPA Method 3050b.
RESULTS & DISCUSSION

**Metal Removal from Solution**

Initial work began with investigating the ability of the microscale iron emulsion to remove lead ions from solution. While this was found to be successful, the initial removal rates were not optimal, and while not drastically different, the results did have small variations when repeated. As the variation between each experiment was determined to be the iron used in the emulsion, an investigation was performed to determine the best technique to acid wash the iron. The results are summarized in the table below.
Table 3: Comparison of acid-washing techniques.

<table>
<thead>
<tr>
<th>Sample</th>
<th>#</th>
<th>Conc. (ppm)</th>
<th>% Removed</th>
<th>Average Removed</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
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<td>Pb Control</td>
<td>C</td>
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<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
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<td>2</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>61.16</td>
<td>24.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>79.28</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unwashed</td>
<td>2</td>
<td>55.04</td>
<td>31.6</td>
<td>22.0</td>
<td>14.1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>61.16</td>
<td>24.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>79.28</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid Wash - No Stirring</td>
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<td>41.52</td>
<td>48.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>37.56</td>
<td>53.4</td>
<td></td>
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<td>4</td>
<td>43.08</td>
<td>46.5</td>
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<td>Acid Wash - With Stirring</td>
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<td>86.8</td>
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<td></td>
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<td>4</td>
<td>15.11</td>
<td>81.2</td>
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</tr>
</tbody>
</table>

Although several studies have shown that the smallest metal particles have the highest capacity for remediation, this relationship did not directly correlate to the emulsion system. The nanoscale iron emulsion showed similar removal rates for lead as the microscale iron emulsion in this particular experiment; however that was not the case for all metals tested.

Emulsion loading experiments were performed in order to determine the removal capacity of each emulsion formulation. The magnesium-oil emulsion has a far greater capacity for lead removal, as 4 mL of emulsion is able to remove 1000 ppm Pb from solution, whereas a larger quantity of iron-oil emulsion has only been shown to remove 100 ppm Pb from solution.
Figure 18: Removal of lead from a 1000 ppm solution at various levels of emulsion loading.

At an initial contaminant concentration of 100 ppm, the microscale iron emulsion was found to be able to remove a portion of the metals from solution, but the nanoscale iron emulsion did not perform as well. Magnesium emulsions were able to remove a majority of all metal ions tested from solution. The average percent removal for each element is outlined in Figure 19 below.
Figure 19: Removal of metal ions from 100 ppm solutions.

This drastic difference in performance between the iron and magnesium emulsions could be attributed to two different factors: reduction potential and surface area. Using the standard reduction potentials as a guide, the reaction between magnesium and lead ions has a large $E^{\circ}_{\text{cell}}$ value, 2.246 V, while that of iron and lead is significantly smaller, 0.321 V. Additionally, the density of magnesium, 1.74 g/cm$^3$, is less than that of iron, 7.86 g/cm$^3$. As the metal component of the emulsion is measured by mass, there is a much larger amount of comparably sized material, resulting in more surface area available for reaction.
The removal of uranium from solution was only tested using the magnesium and microscale iron oil emulsion formulations. As uranium contamination is rarely found in seawater, analysis in that matrix was not performed.

Results for the removal of the above metals from seawater were similar for the iron emulsion. The Mg emulsion showed high rates of removal for all metals tested, indicating that high ionic strength solutions do not have a significant effect on the removal capacity of the emulsion.

![Figure 20: Removal of metal ions from 100 ppm solutions in seawater.](image)
Contaminant Fate & Transport

A variety of studies were performed to determine the fate of the contaminant in the emulsion droplet and a possible mechanism by which the metal ions are transporting through the emulsion membrane.

Acid Digestion of Recovered Metal

Initial testing was performed to verify the transport of the contaminant to the interior of the emulsion droplet with deposition onto the metal surface. Analysis of the recovered and acidified iron and magnesium exposed to lead is shown in the table below.
Table 4. Concentration of lead found on recovered metal.

<table>
<thead>
<tr>
<th>Emulsion Formulation</th>
<th>Sample</th>
<th>Weight Metal Recovered (g)</th>
<th>Theoretical Pb Conc. (ppm)</th>
<th>Observed Pb Conc. (ppm)</th>
<th>% Pb Plated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Oil Emulsion</td>
<td>C1</td>
<td>0.4134</td>
<td>0.00</td>
<td>0.4</td>
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<tr>
<td></td>
<td>C2</td>
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<td></td>
<td>1</td>
<td>0.3076</td>
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<td>0.2655</td>
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</tr>
<tr>
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<td>3</td>
<td>0.2824</td>
<td>1.48</td>
<td>0.9</td>
<td>60.86</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.3799</td>
<td>1.96</td>
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<tr>
<td></td>
<td>5</td>
<td>0.2629</td>
<td>1.36</td>
<td>0.9</td>
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<tr>
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<tr>
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<tr>
<td>Mg-Limonene Emulsion</td>
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<td></td>
<td>C2</td>
<td>1.03</td>
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<tr>
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<td>4</td>
<td>0.97</td>
<td>100.0</td>
<td>72.3</td>
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</tr>
</tbody>
</table>

The results of each of these experiments clearly indicate the transport of the contaminant through the emulsion membrane followed by precipitation to the metal surface.
**Lead Partitioning**

Several vials were assembled to investigate the possibility of lead being trapped in the oil layer. As expected, the vials containing only lead solution and corn oil or limonene showed no lead transport into the organic layer. However, vials containing lead solution, organic, and surfactant also showed no lead transport.

**Proposed Transport Mechanism**

This contradicts the idea that the surfactant is acting as a phase transfer agent to transport the lead into the interior of the droplet. Based on this information, it is believed that lead transport occurs through channels formed in the membrane during the emulsion process. Descriptions of this type of structure in membranes and emulsions has been reported previously.$^{26, 27}$ In these models, the hydrophilic components of the membrane align to form pores or channels in the membrane between the hydrophobic membrane and the hydrophilic exterior phase.

Based on this model, the lead ions could be transporting through the pores and the removal process could be driven by the concentration gradient established when the metal ions are removed from solution in the interior of the emulsion.
A visualization of this process is shown in Figure 21 where the surfactant molecules align to form a pore structure allowing the lead ions to transport through the membrane to the interior of the emulsion droplet.

Figure 21: Cross-sectional view of proposed emulsion membrane structure.

In an attempt to determine the reaction taking place at the iron surface, the solution separated from vials containing iron emulsion was analyzed for iron content. Unfortunately, it was determined that the iron content in solution did not depend on the amount of lead reacted, but was dependent on the acid content in the lead stock solution. The relationship is shown below.
Figure 22: Relationship of resulting iron content in exterior solution with percent acid in lead stock solution.

Scanning Electron Microscopy

Samples of iron recovered from the interior of an emulsion exposed to a lead solution were analyzed by scanning electron microscopy (SEM) with electron diffraction spectroscopy (EDS) to identify lead on the surface. However, the lead concentration was below detection limits.
Figure 23: SEM image of iron particles recovered from an emulsion (3700x).

Figure 24: SEM image of iron particles recovered from an emulsion (5000x).
A large particle size difference was observed on the recovered iron, presumably from the acid washing step. These variations that occur during the acid washing may also be a significant reason for the deviations in the performance of the iron emulsion.

**X-Ray Photoelectron Spectroscopy**

While previous analysis does confirm the transport of the contaminant to the interior of the droplet, it is unclear if the contaminant is reduced to a zero-valent form after undergoing an oxidation-reduction reaction or is adsorbed onto the metal surface while in a higher oxidation state. To determine this, samples of recovered iron were analyzed by XPS, the resulting spectra is shown below in Figure 25.
As it is presumed that the reaction of neat iron in contact with a lead solution will proceed via the same mechanism as it would in the aqueous interior of the emulsion droplet, neat iron was used in order to expose it to a higher concentration of lead thus providing a higher signal to noise ratio. A high resolution spectrum of the lead $4f_{5/2}$ and $4f_{7/2}$ peaks is shown below in Figure 26.
Figure 26: Calibrated high resolution XPS spectrum of Pb 4f peaks.

The 4f\textsubscript{7/2} peak centered on 138.5 eV has a peak shift characteristic of Pb\textsubscript{2}O\textsubscript{4} or Pb(OH)\textsubscript{2}, both indicative of the lead adsorbing to the iron surface rather than undergoing reduction to a zero valent form. Zero-valent lead has a characteristic binding energy of approximately 136 eV.\textsuperscript{28}
Matrix Effects in Solution

To probe any limitations that may be in effect for the transport of the metal ions across the emulsion membrane, a variety of solutions were prepared with different complexing agents present in solution with lead ions. The percent removal of lead from each of the different solutions using the iron emulsion and the magnesium emulsion is outlined below in Figure 27.

![Figure 27: Removal of lead ions from complex environments.](image)

Again, the magnesium-based emulsions have outperformed the iron emulsion. However, none of the emulsions showed any significant removal when lead ions were in solution.
with disodium EDTA. One possible reason could be that the size of the EDTA complex is larger than what is able to be transported through the pores of the membrane. Further work must be done to more extensively probe pore sizes of the membrane with the different emulsion formulations.

**Effect of Humic Acid in Solution**

Previous studies by Dries *et al.* have indicated that the presence of humic acid can shorten the lifetime of zero-valent iron permeable reactive barriers. Also, in column studies, it can cause breakthrough of heavy metal contaminants faster than systems in the absence of humic acid.

The presence of humic acid on the performance of the emulsion was found to have little to no effect on its ability to remove lead ions. The presence of the emulsion versus neat iron, however, did have an effect on the levels of humic acid that remained in solution as determined by UV-Visible spectroscopy. It was found that samples containing emulsion had higher levels of humic acid remaining in the exterior solution than that of the equivalent mass of neat iron. The results are summarized in Table 5 as well as Figure 28.
Table 5. Removal of lead in solution with humic acid.

<table>
<thead>
<tr>
<th></th>
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<th></th>
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<th></th>
<th></th>
<th></th>
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<tbody>
<tr>
<td>Control</td>
<td>C</td>
<td>94.10</td>
<td>------</td>
<td>------</td>
<td>----</td>
<td>22.061</td>
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<td>2.644</td>
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<td>------</td>
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<td>12.811</td>
<td>16.091</td>
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<td>6</td>
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<td>99.0</td>
<td>15.609</td>
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46
Figure 28: Removal of lead ions in solution with humic acid.

The results of this experiment indicate that the presence of humic acid should not have the same effect on emulsion as it does on neat iron. It is assumed that the reaction between neat iron and humic acid has reached equilibrium in the sample vials shown. Since the amount of humic acid which reacted with the emulsion is less than that of the neat iron, it can be concluded that the amount of surface area of the iron in the emulsion rendered unreactive by the humic acid is also less. Therefore, the emulsion system should not experience the same shortened lifetime in the presence of humic acids as zero-valent iron.
Varying Emulsion Formulations

A variety of emulsions were prepared where the interior water component was modified in an attempt to enhance contaminant removal. Solutions of 0.1 M of a complexing agent were substituted for the water phase in hopes of providing a way to immobilize a larger amount of contaminant in the interior of the emulsion. In addition to the formulations shown below in Figure 29, an emulsion containing a 0.1 M sodium citrate solution was also attempted, however the mixture separated into three phases immediately after being prepared.

![Figure 29: Removal of lead ions from solution by modified iron emulsions.](image-url)
No further work was explored as none of the modified emulsion formulations indicated a removal capacity greater than that of the standard emulsion formulation.

**Metal Removal from Sediment**

The ability of the iron emulsion to remove metal ions from sediment was demonstrated with varied outcomes. Initial experiments showed promising results. However, upon repetition the results indicated a maximum removal capacity of the emulsion after 1-3 weeks, possibly indicating a reversible adsorption of the heavy metal ions to the surface of the iron. The initial results of studies performed with lead spiked soil are shown in Figure 30. Trendlines have also been used in the following figures to help visualize the data; no modeling was performed.

![Figure 30: Removal of lead ions from soil with varying emulsion pH.](image-url)
Repetition of these experiments yielded the following results for lead removal from spiked sediment and from spiked sediment with various matrix variations, shown in Figures 31 and 32, respectively.

Figure 31: Lead removal from spiked sediment using microscale iron emulsion.
Figure 32: Lead removal from spiked sediment with matrix variations using microscale iron emulsion.

Removal of cadmium from spiked sediments showed the same variations upon repetition using the iron emulsion, with the best results obtained at 45% removal.
Figure 33: Cadmium removal from spiked sediment using microscale iron emulsion.

While removal of the contaminants was observed using the microscale iron emulsion, new emulsion would be required to retreat the sediment in order to achieve desirable remediation levels. The development of the magnesium-iron system potentially allows for the combination of high removal levels obtained with the magnesium emulsions in solution while also providing the magnetic properties necessary for the physical separation of the emulsion from the sediment. Initial studies using this system show very promising results with 60% removal occurring after just one week of exposure. These results are equal to that of the best results obtained after 3-5 weeks using an iron emulsion.
Figure 34: Lead removal from spiked sediment using a 20 wt % Fe-Mg emulsion.

For all of the vial studies a similar trend in the data was observed—an initial maximum followed by a decrease or in the best cases a plateau, in the removal of lead. This could be a result of a number of reasons. It is possible that the iron in the emulsion is oxidizing to an antiferromagnetic form such as goethite which would cause some of the metal to be left behind during the removal process causing a false reading of residual lead in the sediments. Analysis of the soil extracts for the presence of iron or magnesium would reveal if any emulsion was left behind and digested with the soil. Another possibility is if the lead contamination is present in a part of the soil structure inaccessible to the emulsion. This theory could be tested by separating emulsion from a sample of soil and reapplying new emulsion to determine if any further removal is possible.
Based upon these results, the small-scale demonstration was performed using the 20 wt % iron-magnesium emulsion. Samples were obtained from the pool at varying locations every 2-3 days. The separated sediment was subjected to a modification of EPA Method 3050b to determine the amount of lead remaining on the sediment.

The results obtained from the scale-up demonstration agree with those obtained in the vial study of the same system. Although the lead concentration in the pool was significantly higher than that of the vials, the emulsion still showed 60% removal after only one week of exposure. However, like the vial studies, the % removal appeared to decrease after the first week to only 40-50% removal. The results of this analysis are shown below in Figure 35 and Table 6.

Figure 35: Lead removal from spiked sediment using 20 wt % Fe-Mg emulsion.
Table 6: Lead removal from spiked sediment using 20 wt % Fe-Mg emulsion.

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<th>Pb Conc. (mg/kg soil)</th>
<th>Avg. Lead Conc.</th>
<th>% Pb Removal</th>
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The standard deviation observed in day one samples is very high, which is to be expected as these samples were obtained pre-mixing. Standard deviation values decreased for those samples obtained post-mixing.
**Emulsion Recovery**

Use of the EZVM technology for treatment of contaminated sediments would not only provide a novel *in situ* treatment technology, but in contrast to current *in situ* heavy metal treatment technologies, EZVM can provide a method to remove the contaminants from the site. After the EZVM has been injected into the sediments, the heavy metal contaminants transport through the emulsion membrane and deposit on the iron surface. Then, taking advantage of the magnetic properties of iron, a magnetic removal process could be used to separate the emulsion from the sediments and thereby removing the contamination with it. For large scale processes, a method has been envisioned where the treated sediments are vacuumed up and run through a separating unit. As the recovered sediment and water mixture is passed through the separating unit, a series of magnets will capture the emulsion allowing the clean sediment and water to pass through. A small-scale demonstration of this is shown below in Figure 36.
Initial studies were developed using formulations containing either nano- or microscale iron particles. While this was very effective for the physical separation from the sediment, the contaminant removal ability was less than desired and had fluctuations as a result of the acid washing step. Recently it was discovered that emulsions formulated using microscale magnesium were very effective for heavy metal removal, but the envisioned sediment separation process did not work. For this reason a 20 wt % Fe-Mg system was developed to take advantage of the removal properties of magnesium and the magnetic properties of iron.
CONCLUSIONS

Summary of Objectives

The goals of this research were:

- To determine the ability of EZVM to remove metal ions from solution and sediments
- To verify the transport the contaminants to the interior of the emulsion droplet and subsequent immobilization on the metal surface
- To establish the feasibility of employing EZVM as a remediation technique through a small-scale demonstration.

Several different emulsion formulations were tested for the removal of metal ions from both solution and saturated, spiked soils. While all were able to demonstrate removal of the metal ions, the emulsion formulations containing magnesium proved to be the most effective. The incorporation of a small weight percent iron into the emulsion system allowed for the both effective treatment and the use of the previously demonstrated physical separation of the emulsion from the sediment.
Based upon the results obtained herein, the use of emulsified zero-valent metal particles is a viable technique for the remediation of heavy metal contaminated sediments.

**Future Recommendations**

Based on the results of this research, the following recommendations are made for future research:

1. Further investigation into the fate of the contaminant in the interior of the emulsion droplet, to better understand the mechanism of removal. Once this is understood, it will provide greater direction for the optimization of the emulsion system.

2. Probe the size and structure of the pores formed in the emulsion membrane to determine limiting parameters.

3. Explore the removal capacity of the emulsion for the remediation of additional inorganic contaminants, such as arsenic, mercury, and selenium.

4. Optimize field-scale delivery and recovery methods of the emulsion in sediment systems. Additionally, explore the environmental impact of such techniques to ensure minimal negative influence in the event of incomplete remediation.
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