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Remediation Of Heavy Metal Contamination In Sediments: Application Of In Situ Treatment Utilizing Emulsified Liquid Membrane An

Deborah Maxwell
University of Central Florida

REMEDIATION OF HEAVY METAL CONTAMINATION IN SEDIMENTS:
APPLICATION OF IN SITU TREATMENT UTILIZING EMULSIFIED LIQUID
MEMBRANE AND ZERO-VALENT METAL TECHNOLOGIES

by

DEBORAH BOLIN MAXWELL
B.S. University of Central Florida, 1978

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ABSTRACT

Heavy metal contamination of soils, sediments and groundwater presents an ongoing source of hazardous and persistent environmental pollution. How best to remediate these contaminants is the impetus of continuing research efforts. Methods include containment, ex situ and in situ techniques. A successful in situ method utilizing a combination of emulsified liquid membranes, ELM, and zero-valent metal, ZVM, and bimetals has demonstrated impressive heavy metal reduction in 100 ppm solutions of Cd, Cu, Ni, Pb, Cr and U.

This promising in situ method has been employed by the Industrial Chemistry Laboratory at the University of Central Florida and it has demonstrated considerable success in treating several environmental threats. Contaminated soils, surfaces, sediments and groundwater with offending agents such as trichloroethene, polychorobiphenyls and heavy metals have been treated utilizing emulsified liquid membrane systems containing zero-valent iron or bimetal particles.

In vial studies, lead spiked sediments have shown repeatable 60% removal of lead after seven days of treatment. A persistent pattern emerged at ten days whereupon remediation levels began to drop. The current study was established to determine the reason for the decline at ten days and beyond. Questions addressed: Does the formation of an impeding oxide layer diminish the remediation capacity of the iron/magnesium system? Does the emulsion reach a maximum capacity to withdraw the contaminant? Do the soil components or the soil structure interfere with the access to the contaminant?

This study has yielded insight into the reasons emulsified liquid membrane systems containing zero-valent metals achieved maximum lead removal at day seven, and thereafter

begin to lose their effectiveness. A three part study was implemented to address and to answer the three questions pertaining to the consistent pattern of diminishing remediation levels exhibited at day ten and beyond. Initially, from Study I results it appeared that the formation of an impeding oxide layer on the bi-metal which was inside the emulsion droplet and which plated or precipitated with the lead was not occurring at day ten. Results indicated that the iron/magnesium was still capable of removing lead. Furthermore, from Study II results the emulsion dose injected appeared adequate to remove the lead, meaning that the emulsion had not reached its maximum capacity for remediation. The emulsion dose was not a limiting factor. Lastly, Study III results seemed to indicate that the drop in remediation after day seven pertained to the soil structure. There appeared to be some merit to the idea that with aging of the sediment, the lead was diffusing and migrating to some inaccessible interior sites within the sediment particles. Additionally, indications from day ten and day fourteen delineated that a second emulsion dose injection might restore lead removal levels to approach those first observed at day seven and consequently be a useful field application.

In order to explore the effectiveness of injecting a second dose of emulsion, another vial study was implemented. The typical pattern of observing sixty percent maximum lead removal at day seven was observed. In separate groups, a second injection of emulsion was added at day five, and then for another vial series, a second dose was added at day seven. The second emulsion dose treatment for either day five or day seven did not yield any increases in percent lead removal. Another theory emerged after viewing micrographs of recovered iron/magnesium compared with fresh ball-milled bimetal. In addition, scanning electron microscopy appeared to confirm the explanation that the emulsified zero-valent metal system might be compromised

after day seven. This would lead to exposure of the iron/magnesium to the air and the elements.

Corrosion of the bimetal might be occurring. With time, release of the plated or precipitated lead

back into the sediment mixture could follow.   The results of Study I had led to the conclusion

that an impeding oxide layer had not formed; however, this conclusion may have been premature

because the recovered iron/magnesium was exposed to lead solution in the vial study. Perhaps if

the recovered iron/magnesium was inserted back into an emulsion and injected into lead spiked

sediments the percent lead removed might give a more accurate picture of the iron/magnesium's

capability to continue performing remediation.

Remediation of sediments contaminated with lead is a complicated task because of the

complex nature of sediment components. Emulsified liquid membranes utilizing zero-valent

bimetals has repeatedly demonstrated impressive results at day seven; however, this treatment

method is not without its limitations. Optimal results appear to be gained at day seven after

emulsion injection. The bimetal and plated or precipitated lead must be removed at that point;

otherwise the effective remediation of the contaminant is progressively reversed

To Michael,
Jessica, Nick, Jacqueline, Daniel, and Joseph, who all believed in me
and who helped me believe that I could achieve my goal

To Sylvio Scola
who was the truest of friends
and who always had a kind and encouraging word for me

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LIST OF ABBREVIATIONS

E^o_{cell} Combined standard reduction potential of a right and left half-cell

EDTA   Ethylenediaminetetraacetic acid

ELM   Emulsified liquid membrane

EZVM   Emulsified zero-valent metal

FAAS   Flame atomic absorption spectroscopy

PRB   Permeable reactive barrier

SEM   Scanning electron microscopy

XPS   X-ray photoelectron spectroscopy

ZVM   Zero-valent metal

CHAPTER ONE: INTRODUCTION

While much is to be said concerning all the advances created by the industrial age and the technological marvels of the previous century, there is an unfortunate legacy of environmental threats and hazards that have been produced and continue to persist with unresolved remediation. Whereas an explosion of knowledge in chemistry and the sciences has resulted in a panoply of advances, it is necessary that an understanding and application of chemistry will provide the remedy.

A sturdy yet harmful group of contaminants are the heavy metals which retain their priority status on the Environmental Protection Agency's National Priority (Superfund) List pertaining to 1200 sites. This list designates cadmium, copper, lead, mercury, nickel, and zinc as the most hazardous, as these pollutants are persistent in the environment and are resistant to bioremediation. Of particular concern is heavy metal contamination of soils and sediments which has arisen from domestic and industrial effluents, the atmosphere, storm water runoff and the earth itself.   More specifically to this research, anthropogenic sources of lead include lead-zinc smelters, soldering processes, and industrial manufacturing of ammunition, glass, piping, insecticides, paints, and lead storage batteries (Mulligan, 1999; Dantas, 2003).

Heavy metal contamination of sediments continues to be problematic with few practical or applicable remediation technologies. Because of the importance of benthic organisms such as worms, crustaceans, insect larvae, and microbes to the aquatic food chain, contaminated sediments introduce pollutants by the process of bioaccumulation which invariably move up the food chain and eventually are consumed by humans. There is always the threat of re-suspension

of the contaminants into the water column which presents its own set of environmental threats to wildlife and humans (EPA, 2003).

How Heavy Metals Bind with Soils and Sediments

Sediments are essentially soil particles that accumulate by the action of wind, snow, ice, and rain eroding and carrying soil by deposition to the bottom of lakes, estuaries, rivers, and oceans. The components of sediments are similar to soil content; however, sediments will often have higher silt, clay, and organic percentages as compared to soils (Mulligan, 2001). The four main components of sediments are inorganic minerals including silicon oxides of iron, aluminum and manganese, clay minerals, organic material and water. An understanding of the sediment composition is helpful to illustrate how heavy metals bond with the different types of sediment particles (Bradl, 2005).

Heavy metals will bind to mineral surfaces by sorption processes which are a partitioning of the sorbate from the aqueous phase to a sorbent. This occurs by metal cations adsorbing onto hydrated iron and manganese oxides formed by surface complexation (Bradl, 2005). In addition, clay minerals will bind metals by surface complexation and ion exchange (Gustafsson, 2003). Colloidal particles of organic matter adsorb a proportionally high percentage of heavy metals, despite the typically lower percentage content that organic matter represents in a sediment mixture (Weng, 2001).

Adsorption at the inorganic surface occurs by accumulation of sorbate at the interface between the aqueous layer above the sediment particle and the solid adsorbent phase itself, and thus resulting in the formation of a two-dimensional structural arrangement, avoiding the development of a three-dimensional molecular arrangement (Bradl, 2005).

This adsorption to mineral surfaces falls into two categories. The first is non-specific, physical outer-sphere adsorption, where the metal cation while retaining its hydration shell of water molecules, is drawn by hydrogen bonding and electrostatic long-range coulombic forces to the negatively charged mineral surface (Ge, 2005; Kim, 2001). The second, specific, chemical inner-sphere adsorption category is a more direct method where the waters of hydration around the metal cation are dispelled and a coordinate covalent chemical bond occurs directly between the cation and the mineral surface. This bond is most often formed between metal cations and oxygen atoms at the surface forming a one-to-one monodentate complex. If two or more oxygen atoms bond with the sorbate then bidentate, tridentate and tetradentate inner-sphere adsorption complexes are formed. An alteration of inner-sphere complexes occurs when the sorbing heavy metal cation either serves as a bridge between a ligand and the surface or is bound through an intermediate bridging ligand to the surface indirectly. These adsorption complexes are designated as ternary surface complexes. Enhanced metal uptake by mineral surfaces has been observed with Pb(II) sorbed to goethite, ($FeO(OH)$), in the presence of sulfates and carbonates (Ge, 2005; Kim, 2005).

Outer-sphere adsorption that occurs by hydrogen bonding and long-range coulombic forces is understandably weaker than the shorter-range electrostatic or covalent bonds formed between metal cation and mineral surface atoms characteristic of inner-sphere adsorption. If the sorption densities exceed a monolayer, then the adsorption description is no longer applicable and the three-dimensional solid formed by the metal on the solid surface is defined as a surface precipitate. This sorption-related surface precipitation can occur at values well below solubility limits due to the nature of the water/surface interface. The reason is that the interface is different from the bulk water overlying the sediment in terms of ordering and structure of the

interface water molecules, the charge distribution, concentration of counterions, and the natural roughness of the surface (Kim, 2005).

Another method observed by which heavy metals bind with soil/sediment particles is illustrated by defining the nature of clay minerals. While the adsorption mechanisms described previously occur with clay, an additional understanding of clay characteristics such as large specific surfaces because of their fine grain structures and negative surface charge is helpful. These characteristics facilitate clay's ability to adsorb cations contributing to clay's assimilation of heavy metals into the internal structure of clay (Kim, 2005). Clay, which is predominately made up of hydrous aluminum silicates, has a sheet-like structure due to the alternating tetrahedral sheets of silicon oxide with octahedral sheets of aluminum oxide. Replacement of some aluminum or silicon atoms within this structure by metal cations of similar size but lesser charge results in a net negative charge at the surface of the clay structure which provides a site for the heavy metals to bind (Manahan, 2005).

The form of precipitation in clay materials occurs through the integration by means of migration, diffusion or encapsulation of the metal cation into the crystalline structure of the clay mineral structure. While this form of sequestration of the metal cation may be significant initially, with aging of the sediment lead and cadmium displays high sorption reversibility caused by decreasing surface areas and lack of structural assimilation over time (Kim, 2005).

Organic matter, while typically just five percent by weight of soil provides a greater adsorbent source for heavy metals than its percentage allotment (Gustafsson, 2003). As stated earlier, sediments often have higher organic content as compared with soils.

Organic matter consists of living organisms, organic decomposition products and humus (Mulligan, 2001). Humic acid and fulvic acids, known as humus, are the most significant of the

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humus components in soil and sediments (Manahan, 2005). Organic matter can be either in the form of bulk materials or coating on particulate matter, accumulating in the surface and subsurface layers of the soil profile (Ge, 2005).

Humic acids include a variety of functional groups such as carboxylic acids, phenolic hydroxyl groups, carbonyls, esters, and methoxy groups. The functional groups along with high cation exchange capacity of humic acids allow for enhanced heavy metal retention ability by means of surface complexation, ion exchange and surface precipitation (Bradl, 2005). More specifically, cation complexation with humic acids occurs through bonds formed either between the heavy metal and the negatively charged surface on the functional group, or by means of nonspecific coulombic sorption to the residual negative charge of the organic molecule (Ge, 2005). Among the numerous humic acids, atomic weight can vary between 20,000 to 100,000 amu, which are comprised of the elements, carbon, oxygen, nitrogen and hydrogen (Bradl, 2005).

Several parameters influence heavy metal adsorption by soils and sediments. They are pH, the type and size of the metal cation and its speciation characteristics, heavy metal competition, soils/sediments composition and aging of the soils/sediments. For example, regarding clay minerals, the number of negatively charged surface sites available to bind with heavy metals increases with pH. The general trend is that as soils/sediments approach a more neutral pH, adsorption of heavy metals onto solid surfaces increases (Bradl, 2005).

How Lead Binds to Soil and Sediment Particles

The culmination of the research in this paper was focused on the heavy metal lead and its remediation. Lead has an atomic number of 82, is a soft, malleable metal of blue gray color with

a bright luster. It is toxic to humans, and especially hazardous to infants and children. Lead

enters the body by inhalation, ingestion or by skin contact. Lead can accumulate in the body

over time causing fatigue, headaches, vomiting, and seizures. Lead can have detrimental effects

upon hemoglobin production and kidney function (Bradl, 2005).

Lead binds specifically to soils and sediments by adsorption to the mineral surfaces, by

precipitation on the surfaces of lesser soluble or highly stable compounds or by reactions with

organic matter. Figure 1 shows the monomeric speciation of lead in an aqueous medium. Lead

is hydrolyzed at a pH of 4 or greater and undergoes multiple hydrolysis reactions as pH

increases. Between the pH of 6 and 10 the predominant lead species is $Pb(OH)^+$ whereas above

a pH of 9, the main species is $Pb(OH)_2$. When lead binds with clay minerals and other mineral

surfaces, carbonate content in the soils increases adsorption. The presence of manganese and

iron in soils/sediments also affects lead adsorption. Affinity between lead and organic matter is

significant and lead appears to form inner-sphere complexes with humic acid (Bradl, 2005).

Lead adsorption demonstrates a biphasic behavior in that there is a fast reaction between

lead and surficial adsorption sites. The reaction can also proceed in a slower manner with

diffusion of the lead and its migration to internal sites occurring as additional adsorption sites

become available. Lead has demonstrated the highest affinity for clays, peat and iron oxides

(Bradl, 2005).
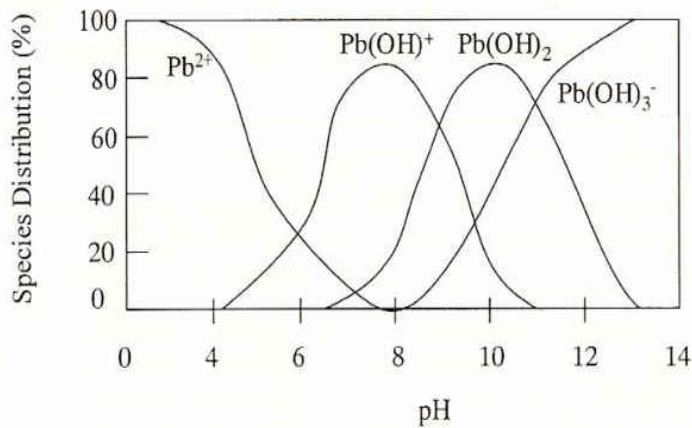
Figure 1 - Predicted aqueous monmeric chemical speciation of lead as a function of pH (Bradl, 2005)

Current Remediation Techniques Employed to Treat Sediments

Remediation of heavy metals is generally classified into three categories: containment or capping, ex situ, and in situ treatments. Containment involves isolating the contaminant and preventing any movement with the application of physical barriers made of steel, cement, bentonite or grout. These methods work either ex situ or in situ; however, commercial availability favors ex situ treatments presently. Containment strategies that follow dredging are performed by means of solidification, which enables the contaminant itself to be contained by solidifying it within a solid matrix or stabilizing it; this containment strategy requires chemical reactions to reduce contaminant mobility. Vitrification is another stabilizing method that utilizes a large amount of energy and the insertion of electrodes, which after the application of electrical current and subsequent cooling will allow for solidification of the contaminant (Mulligan, 2001).

The ex situ methods involve the removal of soil or sediments and then employing various treatment options such as soil washing, physical separation, or hydrometallurgical recovery for

highly contaminated soils. Ex situ methods are performed after dredging of sediments occurs. Each year three hundred million cubic yards of sediments are dredged to maintain the navigability of US waterways. Of those, three to twelve million cubic yards are so heavily contaminated that they require special handling and remediation (Mulligan, 2001). Of particular concern with the dredging of sediments for ex situ treatment is the re-suspension of the offending contaminant into the surrounding water environment during sediment removal, which thus exacerbates the problem (Degtiareva, 2001). Another complication inherent to sediment remediation is the higher levels of silt, clay and organic matter which can impede effective remediation. Sometimes the problems engendered by remediation can be worse than the initial presence of the contaminant. In these cases, the best options may be leaving the sediment as is and implementing continuous monitoring (Milum, 2005).

In situ methods include soil flushing which consists of infiltrating the different soils with extracting solutions with or without chemical additives such as organic or inorganic acids and complexing agents such as ethylenediaminetetraacetic acid, EDTA (Pichtel, 2001). Electrokinetic techniques require electrodes and a low current which promotes the migration of metals and anions to the appropriate electrodes and removal of the metals by electroplating or precipitation (Virkutyte, 2002). Phytoremediation involves certain plant species and their propensity to accumulate metals such as cadmium, copper, lead, nickel and zinc (Mulligan, 2001; Milum, 2005).

Emulsified Liquid Membrane and Zero Valent Metal Technologies

A promising in situ method has been employed by the Industrial Chemistry Laboratory at the University of Central Florida which has demonstrated considerable success at treating several

environmental threats. Contaminated soils, surfaces, sediments and groundwater with offending agents such as trichloroethene, polychorobiphenyls and heavy metals have been treated utilizing emulsified liquid membrane systems and innovative solutions containing zero-valent iron or bimetal particles. One of the remediation techniques involves a combination of ELM, emulsified liquid membrane, and ZVM, zero-valent metal, technologies (Quinn, 2005; Milum, 2005; Brooks, 2006).

An emulsion or an emulsified liquid membrane is the consolidation of two immiscible liquids into a single phase, macroscopically homogeneous, but microscopically heterogeneous. The emulsion is often stabilized by the presence of a surfactant. These colloidial systems have specific properties such as very low interfacial tension, large interfacial surface area, and solubilization capacity for either aqueous or hydrophobic soluble compounds or species (Raghuraman, 1994; Solans, 1997; Dantas, 2003; Milum, 2005).

By using emulsified liquid membrane technology a combination of the extraction and the stripping steps are performed in a single operation, thus removing equilibrium limitations inherent with typical solvent extraction methods. Aqueous streams contaminated with heavy metals have been treated successfully, removing metal ions such as copper, cadmium, chromium, lead, mercury, nickel, and zinc. The extracting agent is located in the interior of the water in oil phase or membrane, inside the water-oil-water emulsion. The stripping reagent is positioned inside the aqueous receiving phase inside the emulsion droplet. Because equilibrium limitations are not in effect, lower concentrations can be achieved in the contaminated environment (Raghuraman, 1994, Okamoto, 2000).

Two possible explanations based on models exist to describe the contaminant transport through the emulsion droplet outer membrane which is hydrophobic. The first model centers on

positioning a reagent in the receiving aqueous interior droplet phase that will react with the transported solute. Transport of the solute is driven by this forced concentration gradient. An example of this mechanism is the extraction of phenol from solution by positioning sodium hydroxide inside the emulsion droplet. After the phenol is transported into emulsion droplet interior, sodium phenolate is produced and will be sequestered there because of its inability to be transported back through the emulsion droplet (Milum, 2005).

The second model explains the transport of the contaminant metal through the emulsion droplet membrane by use of a carrier molecule such as a surfactant which also lends stability to the emulsion. When this model is workable, employing a specific carrier molecule allows for a selective mechanism towards certain molecules or moieties and their transportation across the emulsion droplet membrane (Milum, 2005; Okamoto, 2000). Experiments showed that the carrier molecule model did not explain contaminant transport in the emulsified liquid membrane studies at the University of Central Florida. The surfactant served solely to stabilize the emulsion and did not function as a carrier molecule (DeVor, 2007).

Data from several University of Central Florida studies suggest that a third model best explains the remediation with emulsified zero-valent metal, EZVM. It is possible that a pore structure formed by the surfactant molecules combines with the reactive metal on the interior of the droplet and allows certain moieties to move through the emulsion droplet membrane. This model would appear to be a modification of the first model, incorporating the concentration gradient driving transport through the selective pores in the membrane (Milum, 2005).

Zero-valent metal is incorporated inside the emulsion droplet during the mixing procedure. It is this metal that reduces the contaminant metal and that is central to the remediation strategy. The emulsified liquid membrane functions to deliver the zero-valent metal

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to the contaminant site (Milum, 2004). The surfactant serves to stabilize and help form the

emulsion. The surfactant will also facilitate membrane pore structure formation and be

instrumental in the transport of the contaminant metal through the emulsion droplet hydrophobic

membrane. Once the contaminant metal is inside the emulsion droplet interior it will plate out

with the zero-valent metal or precipitate on the metal surface and thus form an insoluble

compound (Milum, 2005).

Reduction of the contaminant metal by the emulsion metal takes place, facilitating the

plating of the contaminant metal onto the emulsion metal as illustrated by the half-cell reduction

reactions printed below (Milum, 2005; Ponder, 2001; Nurmi, 2005).

$$Fe^{3+} + 3e^- \rightarrow Fe^0 \qquad E_o = -0.037 \text{ V} \qquad (1)$$

$$Fe^{2+} + 2e^- \rightarrow Fe^0 \qquad E_o = -0.447 \text{ V} \qquad (2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad E_o = +0.771 \text{ V} \qquad (3)$$

$$Mg^{2+} + 2e^- \rightarrow Mg^0 \qquad E_o = -2.360 \qquad (4)$$

Iron particles have been demonstrated to reduce copper, lead, mercury, selenium, and

silver to the zero-valent oxidation state (Milum, 2005; Ponder, 2001; Cantrell, 1995). Chromium

when exposed to zero-valent iron undergoes partial reduction, from Cr^{+6} to Cr^{+3}, and potentially

can precipitate out of solution by bonding with hydroxide to form $Cr(OH)_3$ which reduces

dissolved chromium substantially (Milum, 2005; Cantrell, 1995). Zero-valent iron technology

may also be applied to the remediation of radioactive materials such as UO_2^{2+}, by the

immobilization of the uranium species on the iron surface rather than reduction occurring in this

case (Milum, 2005; Qui, 2000). The exact mechanism of the remediation of any listed heavy

metals is unknown; however, it is believed that reduction and adsorption mechanisms play a significant role in the process (Milum, 2005; Brown, 2001)

Initially, iron particles in the form of filings were used in environmental remediation processes. Degradation of trichloroethene and other chlorinated solvents was accomplished with zero-valent iron in emulsified liquid membranes and even better results were realized with the use of micro-scale and nano-scale iron (Quinn, 2005). When remediation of other environmental contaminants such as heavy metals was attempted, zero-valent iron resulted in lower remediation effectiveness as compared to the degradation of chlorinated solvents (DeVor, 2006).

In an attempt to improve the remediation effectiveness of heavy metals by EZVM, a bimetal was produced and used in subsequent experiments. The bimetal was produced by mechanically ball milling 20% by weight zero-valent iron and 80% by weight zero-valent magnesium (Aitken, 2006). The bimetal was then incorporated into the emulsion formulation and thereafter demonstrated impressive contaminant removal. Combining the reduction potentials of magnesium and lead yields an E°_{cell} value of 2.236 V as compared to the reaction between iron and lead yielding an E°_{cell} of 0.321 V, indicating a greater propensity for the magnesium and lead to react versus the iron and lead.

Another factor that illustrates the reason magnesium metal emulsions perform better than iron metal emulsions in the remediation of heavy metals is the density difference between iron (7.86 grams /centimeter^3) and magnesium (1.74 grams/centimeter^3). Since iron has a greater density than magnesium, magnesium has more surface area per mass. Percent contaminant removal with zero-valent metal has been proven to be surface area dependent (Nurmi, 2005). Given that the percent lead removal is based on surface area, it follows that equal masses of magnesium and iron yield a greater surface area of magnesium available for plating out or

precipitating lead. This results in higher concentration of contaminant removal by mass for

magnesium versus the iron. The presence of iron, however, is necessary to facilitate the removal

of the contaminant through the use of a strong magnet. The contaminated sediment is injected

with EZVM and mixed. When the appropriate day arrives, the sample is pulled and a strong

magnet is passed through the mixture several times allowing for removal of the contaminant

plated out or precipitated on the iron/magnesium. The magnet used in the University of Central

Florida Industrial Chemistry Lab is made of neodymium (Milum, 2005).

Figures 2 through 4 illustrate the hydrophilic aqueous phase outside the emulsion droplets

shown, the hydrophobic emulsion droplet membrane and the hydrophilic interior of the emulsion

droplet where the zero-valent metal is located after the emulsion formation (Milum, 2005).
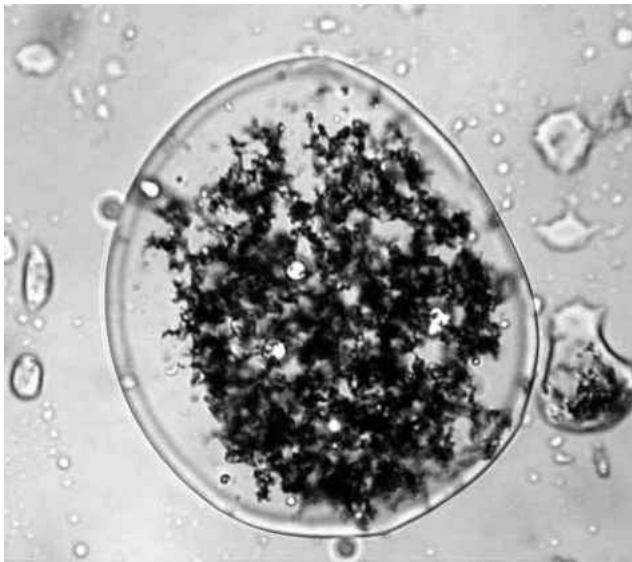
Figure 2 - Micrograph of water- oil-water emulsion droplet containing nanoscale iron particles.

Figure 3 - Micrograph of water-oil-water emulsion droplet containing microscale iron particles.

Figure 4 - Micrograph of water-oil-water emulsion droplet containing microscale magnesium particles.

A typical emulsion formula used in the University of Central Florida Chemical Industrial Laboratory consists of the following: 80.0 mL of corn oil, 100.0 mL of de-ionized water, 3.0 grams of sorbitan trioleate which has the tradename of Span 85, a surfactant, and 20.0 grams of a zero-valent metal or bimetal. These ingredients are mixed in a high speed blender in specific steps. First, the metal is added to the blender and mixed with the de-ionized water at a blending speed for 30 seconds. Continuing with mixing, the corn oil and surfactant mixture are slowly

added until the emulsion is formed, and then mixed beyond that point for one minute (Milum, 2005).

The Proven Effectiveness of Emulsified Liquid Membrane and Zero Valent Metal Technologies

In a series of experiments, emulsified liquid membranes ELM, and zero-valent metal ZVM, combined as emulsified zero-valent metal EZVM, have proven their effectiveness at either degrading chlorinated solvents and polychlorinated biphenyls or plating out or precipitating heavy metals and thus facilitating contaminant removal. Regarding heavy metals, solution studies were run where metal ions in solution were removed by exposure to zero-valent metal emulsion.

Emulsion Effectiveness in Heavy Metal Solutions

Researchers at the University of Central Florida have demonstrated the effectiveness of emulsified liquid membrane technology by conducting a series of vial studies which consisted of injecting different emulsion formulations comprised of Fe, Fe-Mg, and Mg into 100 ppm heavy metal solutions of cadmium, copper, nickel, lead, chromium and uranium. Remediation or percent metal removal was over 80% in most cases while using the magnesium/iron corn oil emulsion, magnesium corn oil emulsion or the magnesium d-Limonene oil emulsion. Results with the nano-iron corn oil emulsion and micro iron corn oil emulsion were mixed. The nano-iron corn oil emulsion did not perform as would be expected. Reason should dictate that with the use of nano scaled metal particles the surface area available for plating out the metal increases; however, the remediation levels that were anticipated were not reached. Nurmi and his colleagues reported that nano-scale iron did not always increase degradation of contaminants in

higher numbers as compared with micro-scale iron (Nurmi, 2005). Micro-scale metal particles appear to provide the optimal performance. Furthermore, the emulsion effectiveness is vastly improved by using the bi-metal system of iron and magnesium (Milum, 2005).
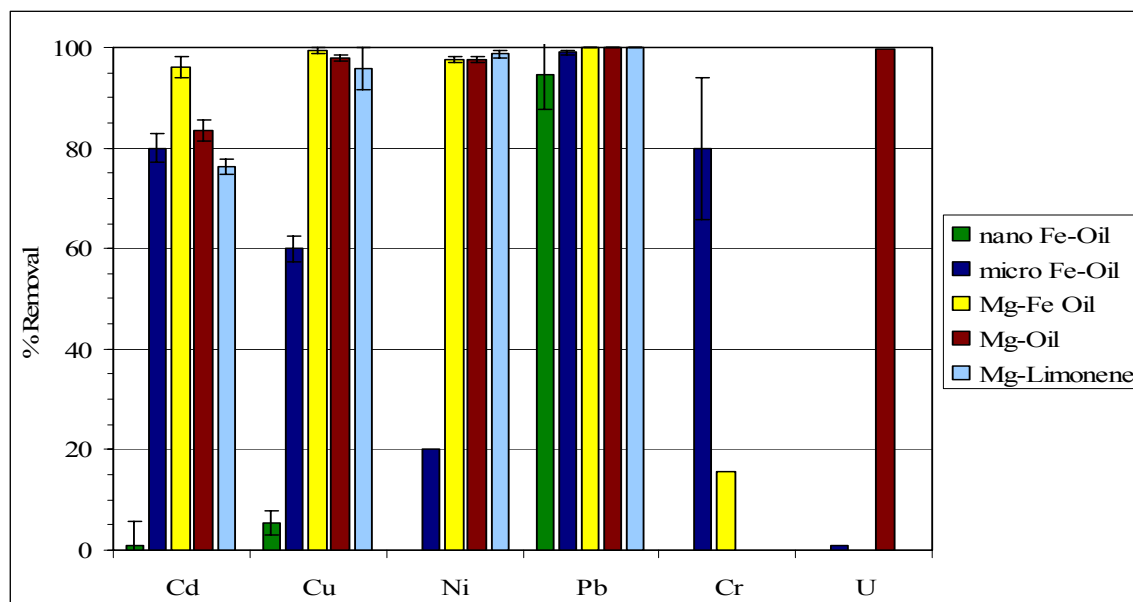
Figure 5 - Removal of heavy metal 100 ppm solutions by various emulsions (Milum, 2005).

The removal capacity of the different emulsion formulations was evaluated by performing experiments in vials with varying emulsion dosages ranging from one to seven grams. Starting at one gram of emulsion and increasing by one gram increments, solutions of 1000 ppm lead solution were mixed with the emulsion doses (Milum, 2005).
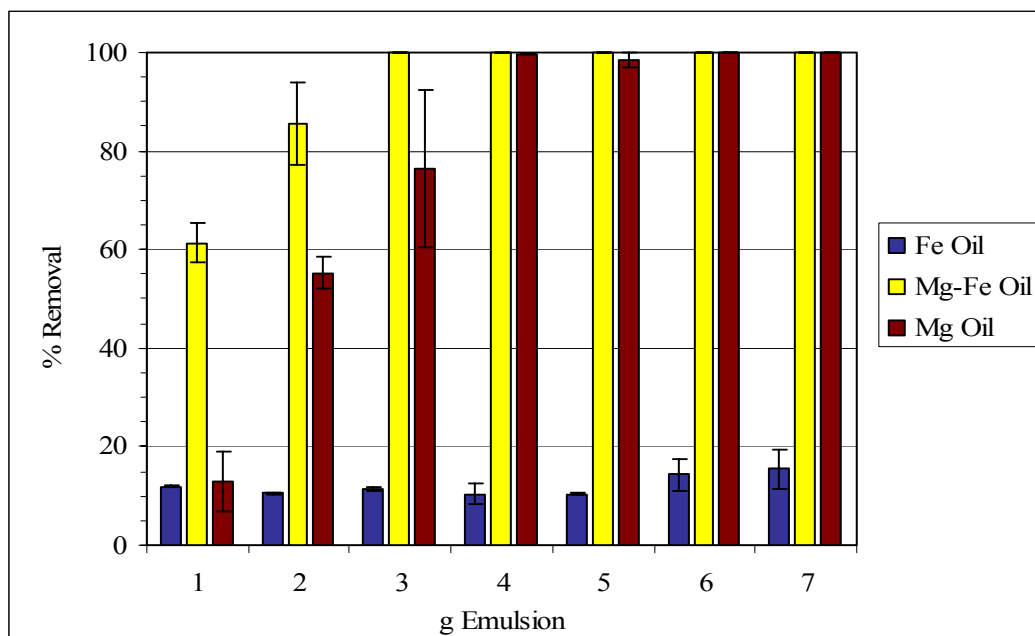
Figure 6 - Removal of lead from a 1000 ppm solution at various levels of emulsion loading (Milum, 2005).

As displayed above, the iron/magnesium emulsion removed 100% of the lead at three grams of an emulsion dose and the magnesium emulsion removed 100% of the lead at four grams. The iron emulsion behaved unimpressively and was only able to remove 100 ppm of the lead at the level of a seven gram emulsion dose (Milum, 2005).

Other studies were performed to survey the emulsion efficacy at removing lead from more complex matrices. The following additives were chosen because they represented different complexing agents that might possibly enhance transport of the heavy metal across the emulsion membrane. One hundred ppm lead solutions with additional 0.01 M adipic acid, succinic acid, sodium citrate, 2-mercapto-1-methlimidazole, or disodium ethylenediaminetetraacetic acid (EDTA) were subjected to emulsion doses. The effect of these chemical species with the exception of the EDTA did not influence or diminish the percent lead removal from the lead solution. The EDTA is a known complexing agent that presumably when bound with the lead,

solubilized it, and thus prevented it from plating out or precipitating on the emulsion metal surface (Figure 7).
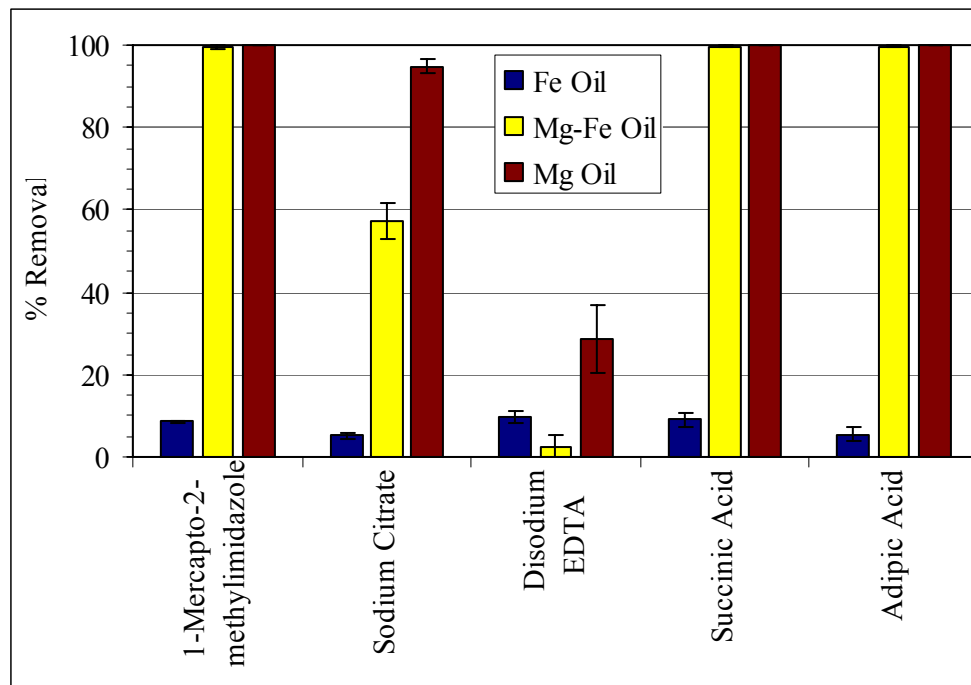
Figure 7 - Removal of lead ions from complex environments (Milum, 2005).

These same solutions were also used in replacement of the de-ionized water in an attempt to alter and possibly enhance the interior aqueous phase inside the emulsion droplet. It was anticipated that the effort would immobilize a greater amount of contaminant inside the droplet. Sodium oxalate solution was also used as a replacement for the de-ionized water component of the emulsion formulation. The results did not produce any increases in percent lead removed over the previous formulations. The sodium citrate solution with the other ingredients separated into different phases and never achieved a stable emulsion state (Milum, 2005).

More matrix effects were explored with the addition of humic acid to the lead contaminant solution and the subsequent injection of the emulsion. Because some studies have suggested that permeable reactive barrier lifetimes are limited in the presence of humic acids,

and that possible breakthrough of heavy metal contaminants occur in column studies, the presence of humic acid and its effect on percent lead removed was analyzed. It was found to have little effect on the emulsion's ability to remove lead (Milum, 2005).

One more matrix consideration was explored with the use of seawater as the solvent for the various heavy metal solutions. It appears that the high ionic strength of seawater doesn't inhibit or affect the percent metal removed of the iron, magnesium or iron/magnesium metals emulsions as compared to using de-ionized water lead solutions as shown in Figure 8 (Milum, 2005).
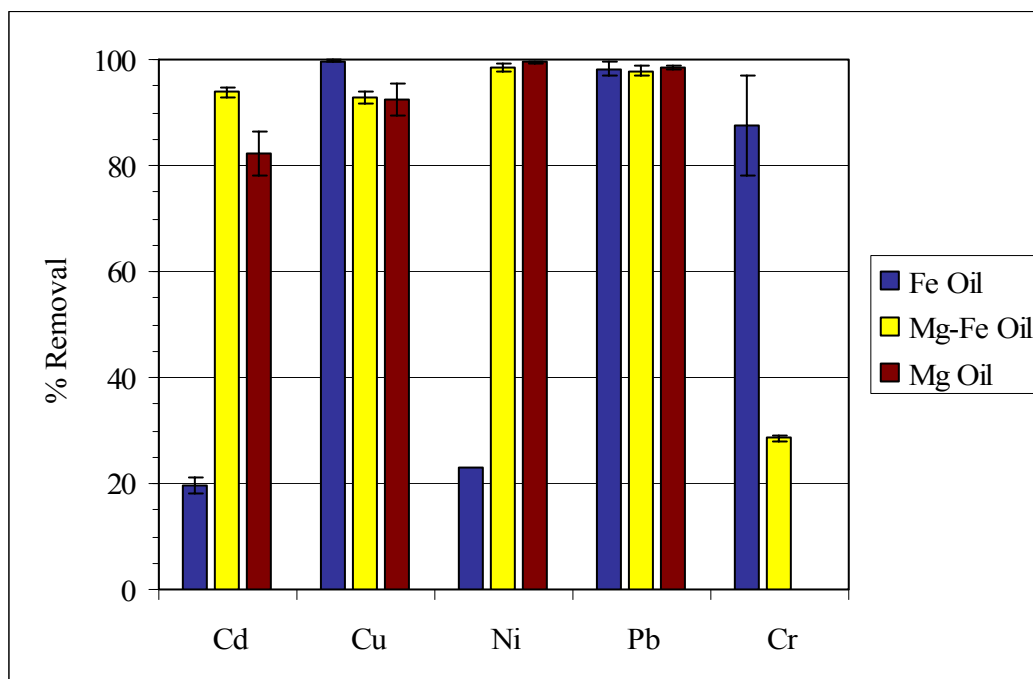
Figure 8 - Removal of metal ions from 100 ppm solutions in seawater (Milum, 2005).

Contaminant Fate and Transport Mechanism

Studies to verify that the contaminant was traversing the emulsion droplet membrane and depositing on the iron/magnesium particle were implemented. Analysis of recovered and

acidified magnesium and iron after having contact with 100 ppm lead solutions demonstrated this after collecting and calculating the percent removal of the recovered lead (DeVor, 2006)

To verify that the destination of the contaminant was the emulsion droplet interior and not the organic phase of the droplet membrane, experiments were conducted using the corn oil/surfactant phase of the emulsion exposed to aqueous 1000 ppm lead solutions. Furthermore, the determination that the surfactant did not perform as a carrier molecule was demonstrated by the following. One thousand ppm lead solution was mixed with corn oil and then in another set of vials with a corn oil and surfactant mixture. Analysis of the lead solution showed no decrease in lead concentration in either set of vials. Since there was 95% plus lead removal with zero-valent iron-magnesium emulsions when introduced into lead spiked solutions, there must be some transport mechanism for the lead to enter the emulsion droplet and gain access to the iron/magnesium for reduction of the lead to occur (Milum, 2005).

Because no lead migrated into the organic phase (even with the surfactant present), it was determined that in the presence of the emulsion, lead was transferring through the membrane to the emulsion interior. These experiments also proved that the surfactant does not 'carry' the lead ions, but instead produced a pore structure that allowed lead transport (DeVor, 2006).

As seen in Figure 9, the hydrophilic components of the organic phase emulsion droplet membrane align as illustrated by micelle behavior in such a way that pores or channels open in the membrane layer. These channels separate the hydrophilic phase of the emulsion droplet exterior from the hydrophobic organic phase of the droplet. As illustrated, the surfactant forms micelles and by their alignment facilitates a pore formation whereby the lead ions followed by counterions traverse the membrane barrier. Because of this theory, it is proposed that a

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concentration gradient between the lead ions in solution and the interior of the emulsion droplet acts as the driving force to facilitate movement of the lead into the emulsion droplet interior (DeVor, 2006).
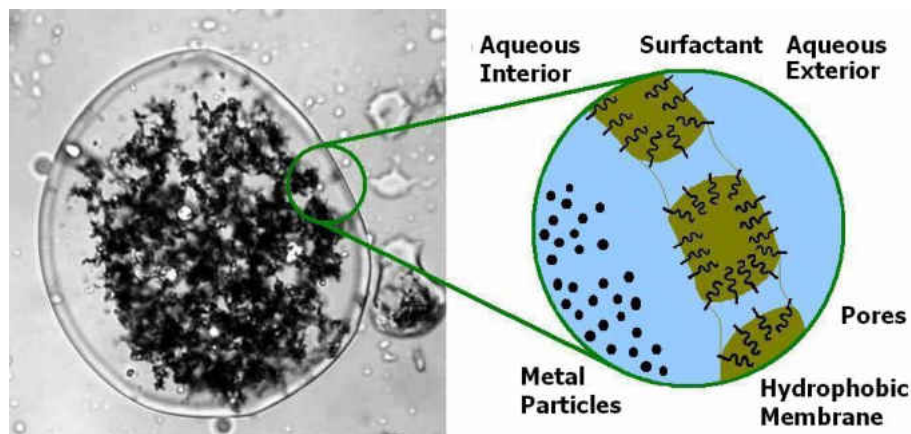
Figure 9 - Cross-sectional view of proposed emulsion membrane structure (Milum, 2005).

To determine if the contaminant once transported into the emulsion droplet interior was reduced to a zero-valent form or adsorbed onto the metal surface while in a higher oxidation state, X-ray photoelectron spectroscopy was performed. Characteristic peak shifts for lead associated with either Pb_3O_4 or $Pb(OH)_2$ were observed, indicating the adsorption of the lead onto the metal particle surface rather than a reduction of lead to the elemental state. This was documented by the fact that elemental lead would have displayed the characteristic binding energy of zero-valent lead (136eV) in the XPS analysis (DeVor, 2006).

Emulsion Effectiveness in Sediments

Soils and sediments present with many more remediation obstacles as compared to heavy metal solutions. Whereas heavy metal remediation of soils has an extensive coverage in the scientific literature, the remediation of heavy metals in sediments does not. Consequently, researchers at University of Central Florida implemented a series of studies using heavy metal

spiked sediments. An artificial sediment was prepared using approximately 80% by weight builders sand, approximately 15% by weight dried kaolinite clay and the remainder made up of organic material in the form of peat (Eimers, 2002). The sediment was spiked with a 100 ppm lead nitrate solution, dried in the oven overnight so as to bind the lead with the sediment particle. The spiked sediment was weighed out in vials and brought to incipient wetness. These vials were later injected with the appropriate emulsion dose (Milum, 2005).

Initially, micro-iron emulsions were injected into the spiked sediment. Results were gathered over a one to four week period. After a peak percent lead removed at around three weeks, remediation levels dropped. It was speculated that lead was beginning to desorb from the iron surface in the emulsion. In Figure 10 the results of this study are shown with the effects of different acidic, neutral and basic conditions displayed (Milum, 2005).
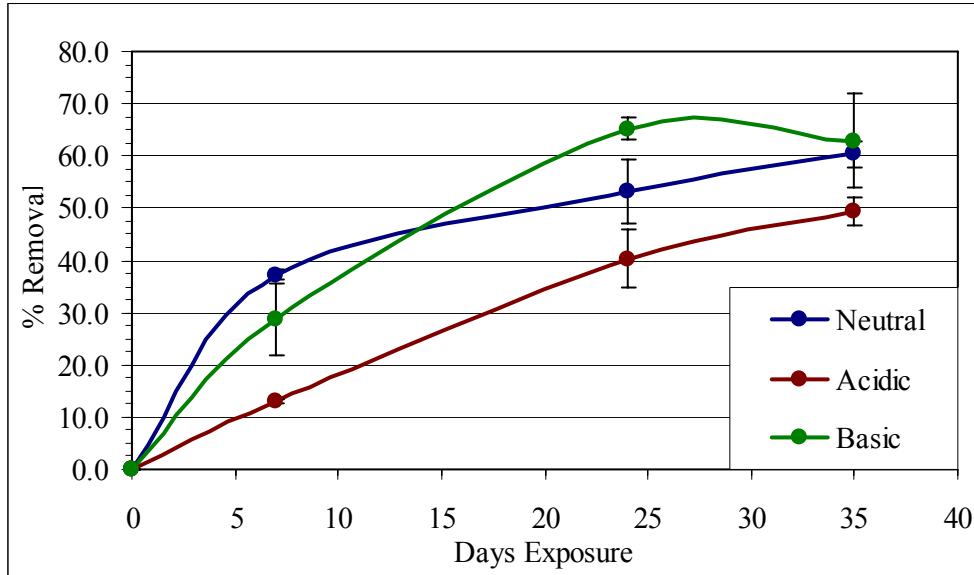
Figure 10 - Removal of lead ions from soil with micro-iron emulsions with different pHs of the emulsion exterior (Milum, 2005)

Microscale iron emulsions were tested for their capability to removed lead from various lead spiked matrices (Milum, 2005). The results are shown in Figure 11.
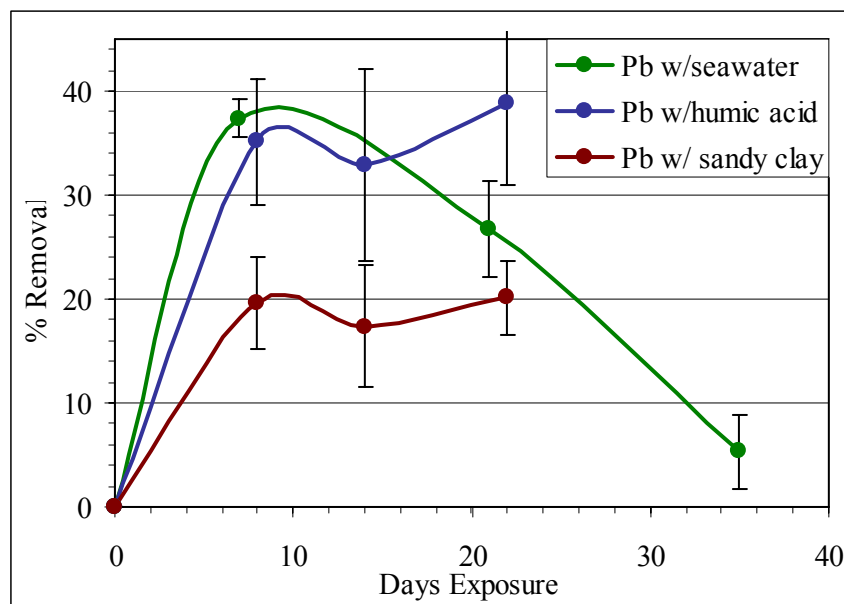
Figure 11 - Lead removal from spiked sediment with matrix variations using microscale iron emulsion, (Milum, 2005).

In an attempt to achieve higher lead remediation levels a new emulsion formulation was developed. The new emulsion that was tested was an iron/magnesium emulsion because it would combine the impressive high lead removal levels achieved with magnesium emulsions and the capability for removal of the emulsion after plating out or precipitation with iron emulsions by use of the magnetic properties of iron. Using a strong magnet to physically separate the contaminant within the emulsion from the sediment provides a relatively easy method for contaminant removal (Milum, 2005).

A vial study with spiked sediment was set up. The initial results using 20% by weight iron and 89% by weight magnesium showed promising results with 60% lead removal after one week of exposure. This level of lead removal was achieved after three to five weeks using an iron emulsion. Figure 12 displays the results of the vial study (Milum, 2005).
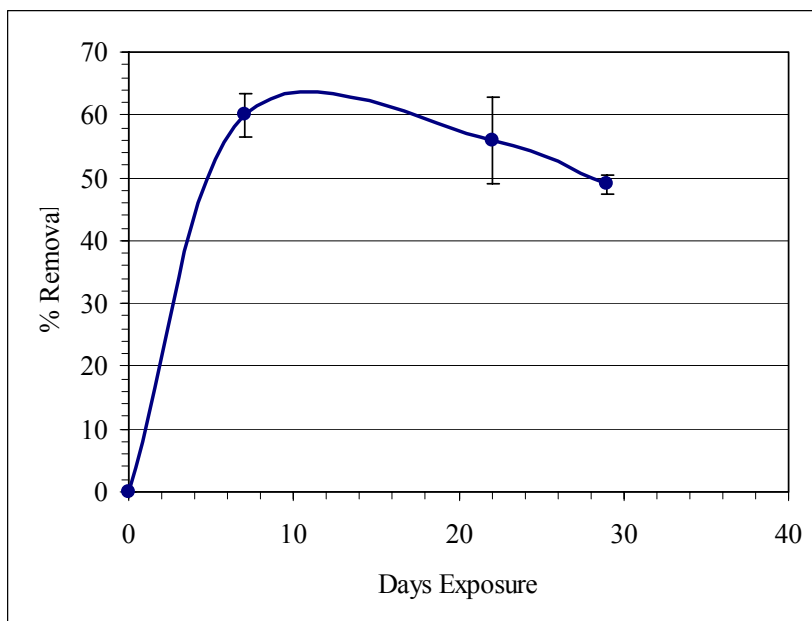
Figure 12 - Lead removal from spiked sediment using a 20 wt % Fe-Mg emulsion.

The next step was to conduct a bench scale study to facilitate eventual application to the field. A wading pool was set up with lead spiked sediment that was based on the previous formulation and brought to incipient wetness. Sixty percent reduction of lead was again achieved after seven days; however, once again, lead removal had dropped off at around the ten day mark. This trend was now an obvious pattern that had been observed in all the previous studies. Figure 13 displays these results and Figures 14 and 15 illustrate the bench scale work (Milum, 2005).
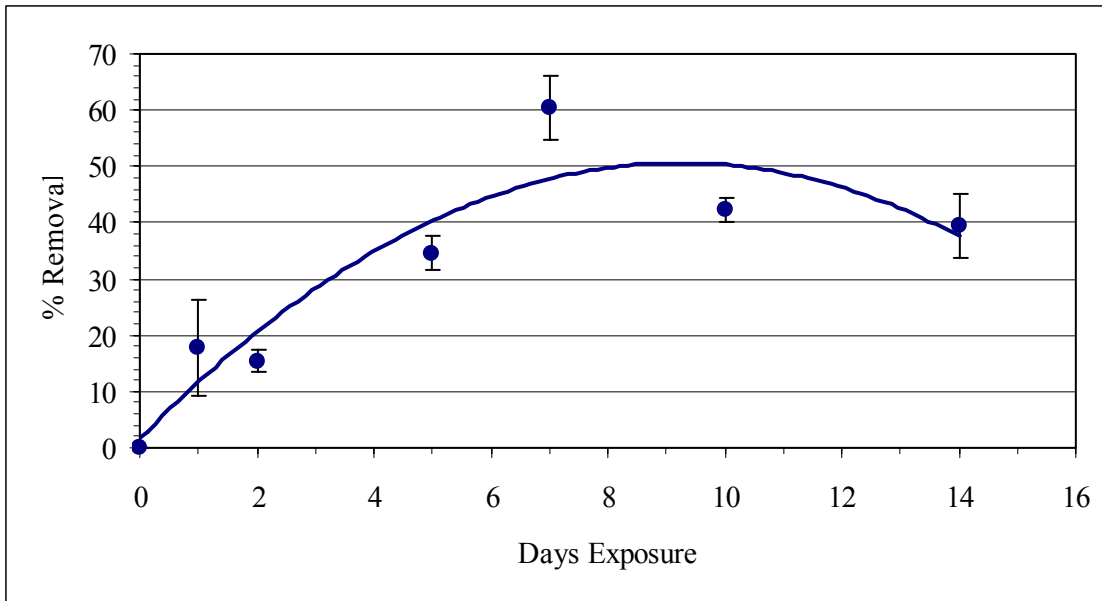
Figure 13 - Lead removal from bench scale spiked sediment study using 20 wt % Fe-Mg emulsion.

Figure 14 - Apparatus for injecting emulsion.

Figure 15 - Action of injected emulsion into sediment.

Figure 16 - Attachment for soil mixing.

Figure 17 - Mixing of emulsion into sediment.
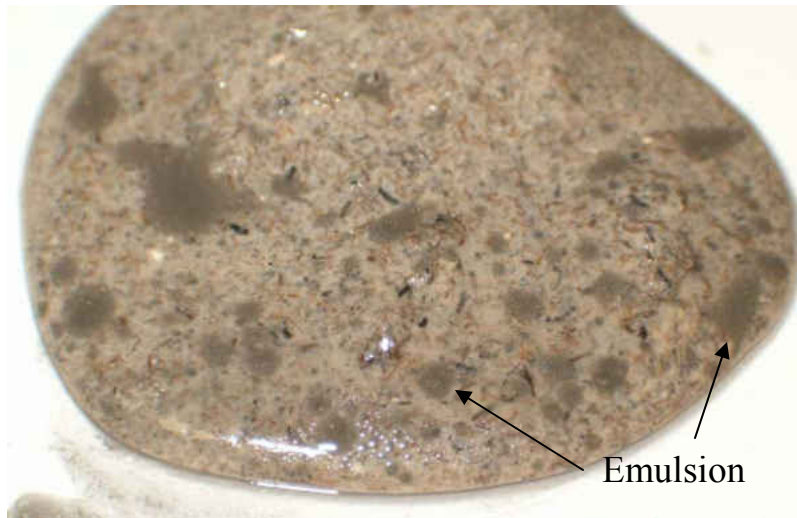
Figure 18 - Sample of sediment after mixing.

How best to address this trend and attempts to understand the reasons for its occurrence would be the subject of the subsequent heavy metal remediation studies.

One further consideration was proposed as a means to facilitate a scale up for adapting this technology to field applications: this was in a set up to allow for the treatment of large amounts of sediments. An experiment was set up such that treated sediments could be vacuumed up and run through a separating unit. Magnets placed at strategic positions along a track would capture metal/emulsion residue and allow the remaining sediment to wash onward down to a collecting vessel. Figures 19-21 show a bench scale set up to illustrate the envisioned method (Milum, 2005).

Figure 19 - Sediment mixed with microscale iron emulsion.

Figure 20 - Emulsion separation process with magnets at regions marked with yellow tape.

Figure 21 -Resulting clean sediment.

<u>Research Objectives: Studies to Investigate the Seven to Ten Day Drop in Remediation</u>

To better understand the demonstrated pattern of drops in remediation after seven to ten days, questions and proposed theories were offered. Emulsion added to the sediment appeared to progressively increase lead removal for seven days. If the sample was pulled after seven days then the maximum amount of lead removal was detected at that period in time. If the emulsion was left until day ten, and the sample was analyzed, the percent lead removal had dropped. One of the questions to be addressed was that after day ten, had the iron/magnesium inside the emulsion droplet oxidized so completely and was thus no longer capable of plating out or precipitating? If the oxidation had occurred to that degree, would this then result in lead released back into the sediment?

Another possible explanation was that perhaps the emulsion dose was inadequate to remove the amount of lead available for deposition on the iron/magnesium particles inside the emulsion droplet. An increase in the initial emulsion dose was proposed to address this theory. Still, another possible explanation could be the soil/sediment structure. As referenced earlier in this work, the biphasic behavior of lead adsorption onto sediment particle sites may cause the lead to assimilate into a more inaccessible site within the soil structure over time. The initial adsorption of the heavy metal onto the soil particles occurs quickly; however, the slower adsorption occurs by diffusion to internal sites (Bradl, 2005).

The current study was implemented for the purpose of determining the reason or reasons for the remediation decrease and to further improve emulsion treatment effectiveness. Accordingly, several questions needed to be answered.

1. Do the Fe/Mg particles in the emulsion form an impeding oxide layer and thus lose their effectiveness at plating out or precipitating lead?

2. Does the emulsion reach a maximum capacity for withdrawing the lead?

3. Are the lead cations trapped within the soil structure prohibiting the emulsion from gaining access to them? Does the chemistry of the soil surface increase consumption of the iron-magnesium particles thereby resulting in a limited 60% removal?

CHAPTER TWO: MATERIALS AND METHODS

In order to answer the preceding questions, a three part lead-spiked soil study was initiated. An artificial soil mixture was mixed with 3.0 kg of builder's sand, 0.50 kg kaolin clay and 800 mL peat for a 25 vol% organic component (Eimers, 2002). This soil mixture was spiked with 100 ppm lead (0.16 g/kg $Pb(NO_3)_2$) in solution and brought to incipient wetness (0.26 mL/g). The mixture was mixed thoroughly with an electric power drill mixing attachment for 30 minutes. The spiked soil was baked overnight in a 140° Celsius oven.

The soil was removed the next day and ground up. Twenty grams of soil was weighed out in 40 mL vials and brought back to incipient wetness with 5.2 mL de-ionized water. Control samples were pulled for acid extraction.

The emulsion formula consisted of the following: 80.0 grams of corn oil, 100.0 mL of de-ionized water, 3.0 grams of sorbitan trioleate, Span 85 (a surfactant), and 20.0 grams of a zero-valent metal or bimetal. This mixture was mixed in a high speed blender in specific steps. First the metal was added to the blender and mixed with the de-ionized water using a blending speed setting for 30 seconds. Continuing with mixing, the corn oil and surfactant mixture were slowly added until the emulsion was formed and then beyond that point for one minute. Appropriate doses of emulsion were injected according to the study specifications. After the zero hour, control samples were drawn; all remaining control samples and emulsion injected samples were placed on a continuous shaker table.

Samples were pulled on days one, two, five, seven, ten, fourteen and twenty-one. The first step was to utilize a neodymium magnet to extract the iron/magnesium with plated out or precipitated contaminant from inside the emulsion droplets. The sample was poured out using

de-ionized water as a rinse into a beaker. The magnet was placed on the bottom and held as the sample was poured into a second beaker. This metal/emulsion residue was placed aside. The neodymium magnet was inserted into a plastic Ziploc bag and drawn through the sediment with numerous motions so as to allow complete removal of any metals and the emulsion itself. This step was repeated once.

The metal/emulsion residue was then rinsed with acetone and de-ionized water until all emulsion was removed with metal remaining at the bottom of the beaker. The metal sample was allowed to air dry overnight. The sample was collected, weighed and cataloged the next day.

To perform the acid extraction for both the control samples and the emulsion injected samples a modified EPA 3050 acid extraction procedure was followed (DeVor). Sediment samples with emulsion and metal having been removed were poured out with de-ionized water over a Whatman filter on a Buchner funnel support with filtration being assisted by the use of a vacuum. The soil sample was dried overnight in a 120° C oven. The next day a 3.0 gram sample was weighed analytically into an Erlenmeyer flask. Twenty mL of concentrated nitric acid was poured onto the soil and the flask was allowed to sit for one hour. The flask was then placed in an ultrasound unit and sonicated for one hour. The soil acid mixture was poured over a fiberglass filter into an Erlenmeyer flask. The extract was poured into a 50 mL volumetric flask and diluted to the mark with de-ionized water. All control samples and emulsion injected samples were analyzed on a Perkin Elmer 5000 Flame Atomic Absorption Spectrophotometer.

Study I was conducted to answer the following question. Do the Fe/Mg particles in the emulsion form an impeding oxide layer and thus lose their effectiveness at plating out lead? Twenty 40 mL vials were set up and injected with three mL of emulsion. On day 10 all 20 vials were pulled and the metal was extracted using a neodymium magnet. The metal was washed

with acetone to remove the emulsion residue. The metal sample was allowed to dry overnight in ambient air. The dried metal was collected and weighed analytically. A 100 ppm Pb solution was prepared. Controls of Pb solution and test vials were set up. Then 0.25 grams of 20 wt% Fe-Mg was poured into each vial and then 20 mL of the 100 ppm Pb spiked solution was added. Zero hour control samples, two and seven day samples were acid extracted and analyzed.

Study II was conducted to answer the question: Does the emulsion reach a maximum capacity for withdrawing the lead? Twenty-eight 40 mL vials were set up with Pb spiked soil and injected with six mL of emulsion which was twice the typical dose of emulsion. Samples were pulled at day 2, day 5, day 7, day 10, day 15 and day 20, and an acid extraction was performed. Extrants were analyzed.

Study III was conducted to answer the following questions. Are the lead cations getting trapped within the soil structure prohibiting the emulsion from gaining access to them? Does the chemistry of the soil surface increase consumption of the iron-magnesium particles thereby resulting in a limited 60% removal? Fifty-six 40 mL vials were set up with Pb spiked soil. Three mL emulsion doses were injected. Samples were pulled at day 2, day 5, day 7 and day 10. At day 10 a fresh batch of emulsion was prepared. A three mL dose of emulsion was injected into the remaining vials. Samples were pulled at day 2, day 5, and day 10. Acid extraction was conducted on the dried samples and then analyzed.

Analysis was performed by use of a Perkin Elmer Model 5000 Flame Atomic Absorption Spectrophotometer. Instrument parameters were set at the following conditions: Using a lead lamp, wavelength 283.3 nm; slit width 0.7 nm; air flow 45 liters/minute; acetylene flow 30; and 10 milliamps. Standard solutions of lead nitrate were run to establish a calibration curve. After

and before every 10-15 samples that were run, three calibration standards were run to verify minimal drift.

After getting the results from the previous study, a variation of the previous three part study was implemented. The goal of the follow-up study was to assess the merit of re-injecting emulsion doses at day 5 and at day 7. The thought was that perhaps increased lead removal values could be achieved. A similar procedure to the three part study was followed.

CHAPTER THREE: RESULTS AND DISCUSSION

Initial Three Part Study

Study I

After two days of exposure 0.25 grams of the Fe-Mg particles showed 92.7% lead removal from 20 mL of a 100 ppm solution. After seven days there was 98.6% lead removal (Figure 18). The results demonstrated that the Fe-Mg particles do not lose their ability to remove lead from solutions and thus must not be forming an impeding oxide layer that prevents the deposition of lead.
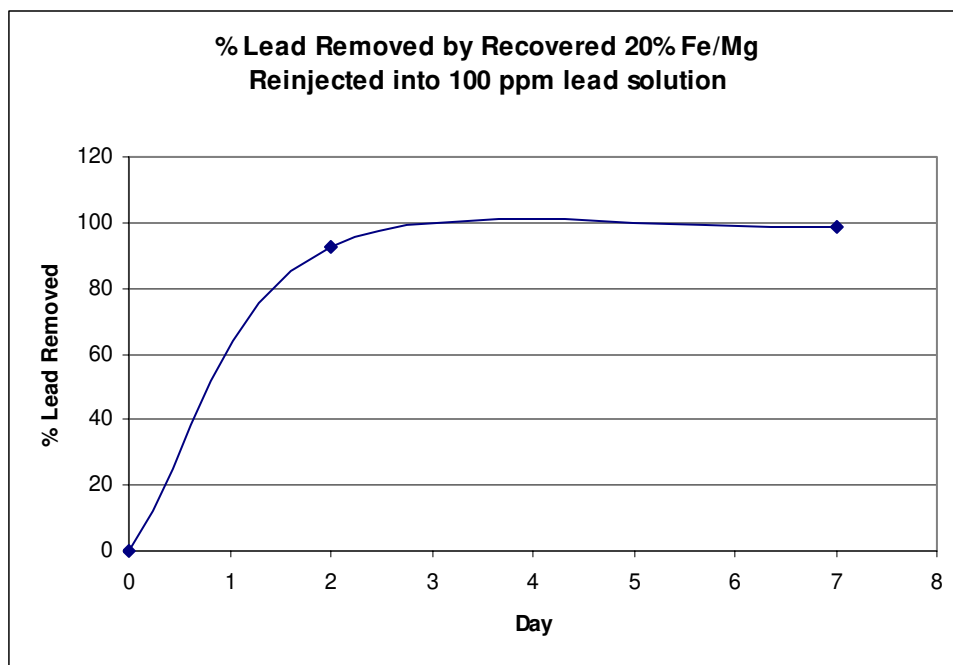
Figure 22 - Percent lead removed by adding 100 ppm Pb solution to recovered iron/magnesium metal from emulsion added to Pb spiked sediments.

Study II

If the emulsion does have a limiting remediation capacity, then a doubling of the emulsion dose should present this with a significant increase in lead removal. Injecting twice the normal dose of emulsion did not show a significant increase in percent lead removal as compared to a single dose injection. Once again the pattern of maximum lead removal at seven days was observed, followed by a decline in remediation (Figure 19). Because there was no substantial increase in percent lead removal from injecting a double dose of emulsion, the decline in remediation after 10 days was not caused by the emulsion reaching a maximum capacity. The emulsion dose was not a limiting factor.
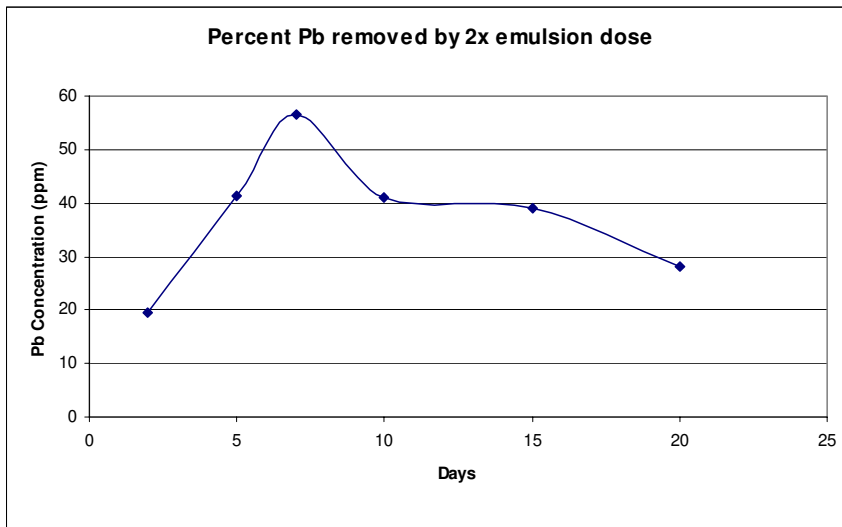
Figure 23 - Study II. Percent lead removed with 2x emulsion dose.

Study III

The vials were injected initially with the typical 3.0 mL dose of emulsion. After day seven samples were pulled for acid extraction, and a second 3.0 mL dose of emulsion was injected into the remaining vials. As the data demonstrate (Figure 20), the first emulsion dose reached a maximum lead removal between 5 and 7 days and thereupon began to diminish. After the re-injection of emulsion, lead removal rates began to rise, albeit not to the first dose levels, yet at a significant removal rate.

% Pb removed by initial injection of 1x (3mL) emulsion dose, followed by reinjection on Day 10
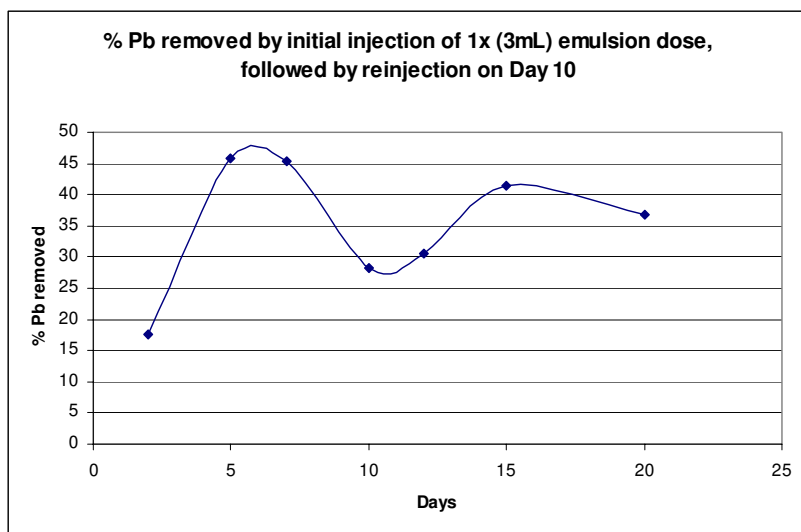
Figure 24 - Study III. Percent lead removed with initial 1x dose followed by reinjection of another 1x dose at 10 days.

Fourteen Day Study

Once again the fourteen day study demonstrated the well-established pattern of achieving maximum lead removed at sixty percent after the emulsion had been present in the sediment for seven days. If the emulsion remained in the sediment thereafter, then when the samples were pulled and analyzed, remediation levels dropped precipitously.

14 Day Study - Percent Pb Removed by Emulsion
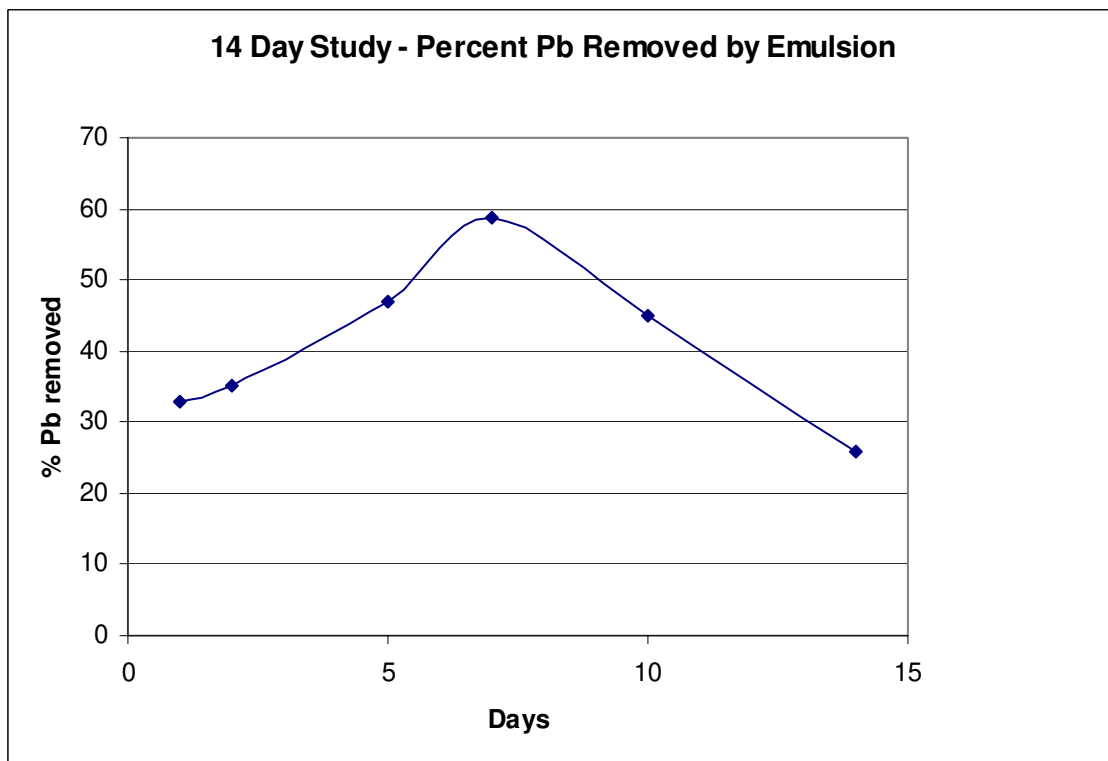
Figure 25 – Fourteen day Study. Emulsion injected into 100 ppm lead spiked sediment.

Five Day Re-injection Study

The vials were injected initially with the typical 3.0 mL dose of emulsion. A second 3.0 mL dose of emulsion was injected into the remaining vials at day 5 after that day's samples were pulled for acid extraction. As the graph of the data demonstrates, the first emulsion dose reached a maximum lead removal between 5 and 7 days and thereupon began to diminish despite the second injected dose of emulsion.
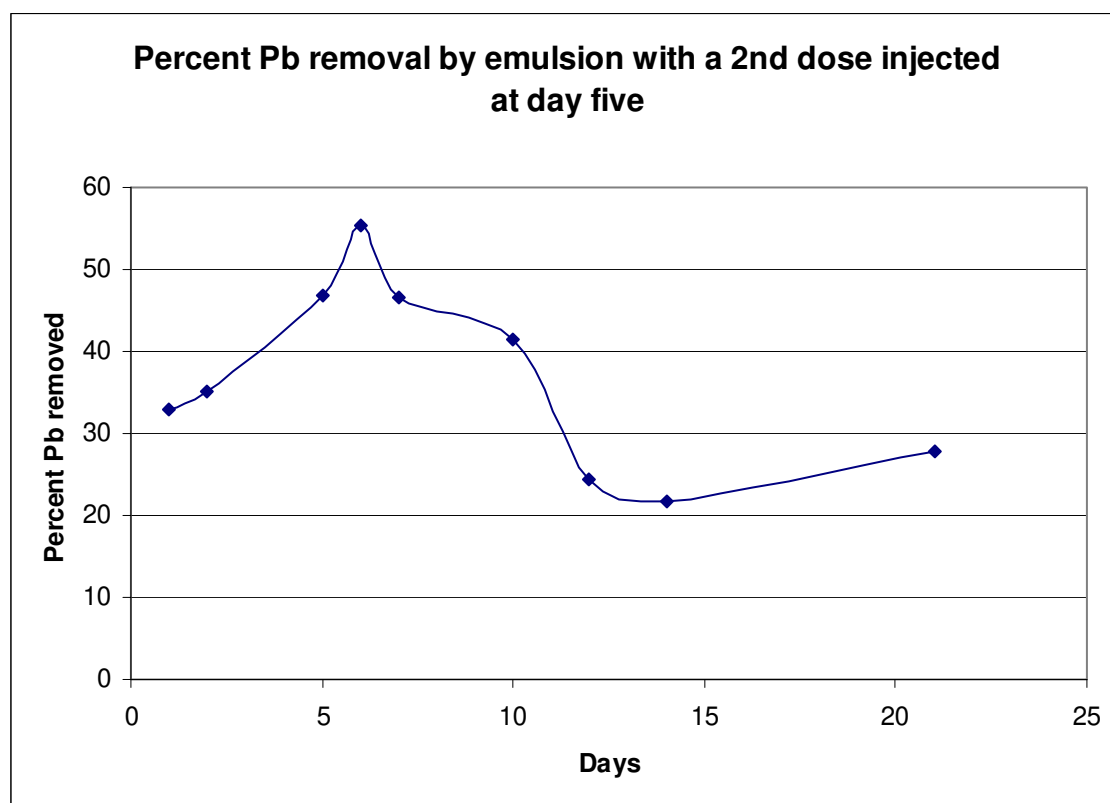
Figure 26 – Initial emulsion injected into 100 ppm lead spiked sediment followed by second emulsion dose injected at day 5.

Seven Day Re-injection Study

The vials were injected initially with the typical 3.0 mL dose of emulsion. A second 3.0 mL dose of emulsion was injected into the remaining vials at day seven after that day's samples

were pulled for acid extraction. As previously seen, the percent lead removed after the maximum remediation levels were obtained, began to diminish with time. Remediation was reversed.
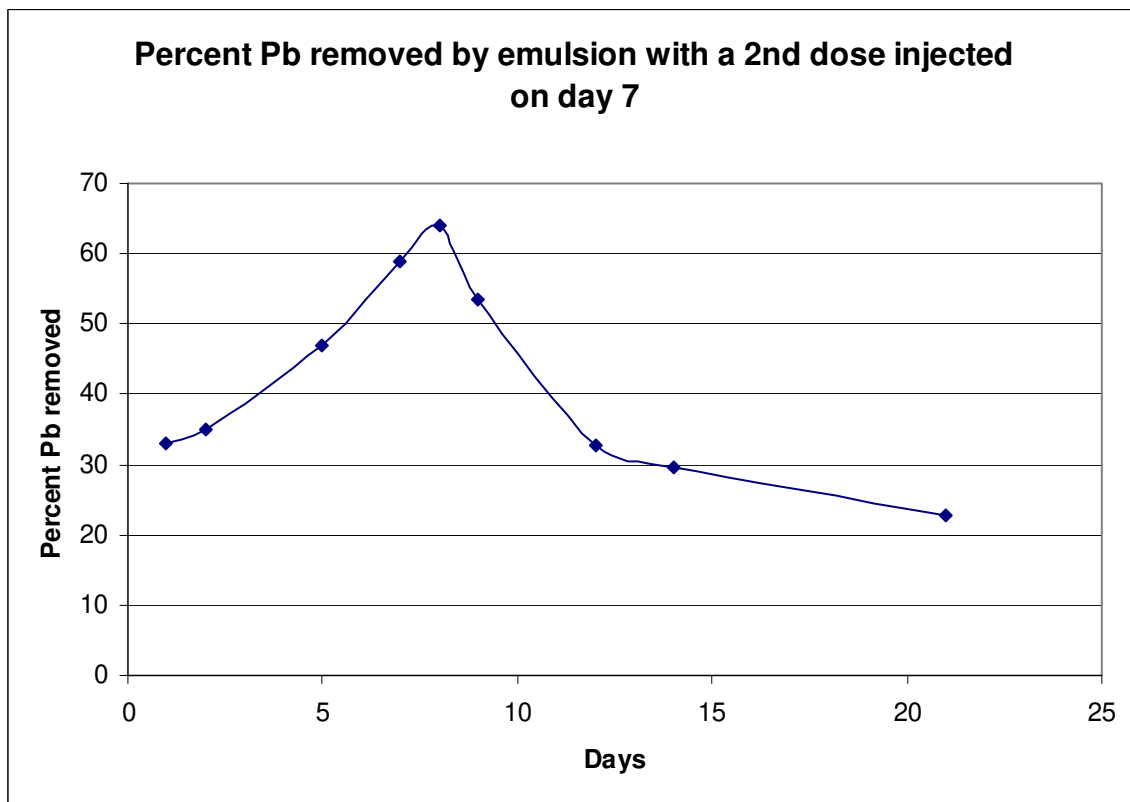
Figure 27 – Initial emulsion injected into 100 ppm lead spiked sediment followed by second emulsion dose injected at day 7.

The results obtained from the five day re-injection study and the seven day re-injection study showed no improvement after day seven. The maximum lead removed is consistent at the day seven mark; it being around 60 percent lead removed. Re-injecting the emulsion dose did not appear to have any effect on ameliorating the downward trend in lead recovery after the seven day high mark for either study.

The next step was to consider what might be going on at the surface of the remediating bimetal system of the iron/magnesium. After seven days, was the iron/magnesium beginning to corrode? Was it no longer able to plate out with the lead and was it releasing any adsorbed lead back into the sediment mixture? Could it be that metal oxide is forming and degrading the iron/magnesium bimetal that was initially inside the emulsion droplet? If so, then during the process the lead could be shed or removed from plating or precipitating onto the iron/magnesium. The physical integrity of the emulsion is jeopardized at this point. There should be some physical evidence of this on the bimetal inside an older vial containing sediment and emulsion. In addition, comparing recovered metal from the various samples to fresh ball-milled iron/magnesium may be instructive.

Is the nature of the remediation limited to the time that emulsion properties remain intact? Does the emulsion break down, re-release plated out lead back into the sediment system and reverse any remediation of the sediment? Is there a limited window of opportunity to inject the emulsion, use the magnet to withdraw the contaminant and remediating metal, because afterwards the emulsion system will undergo irretrievable degradation?

Micrographs of the recovered lead were obtained using an Olympus BH2 microscope. These were compared with micrographs of fresh ball-milled iron/magnesium that had never been used in an emulsion. The recovered metal was from the five day and ten day samples obtained during sample extraction from the fourteen day follow-up study.

Recovered bimetal and fresh iron/magnesium were also viewed using the scanning electron microscope, SEM JEOL 6400F. Once again the images were examined for evidence of corrosion on the bimetal.
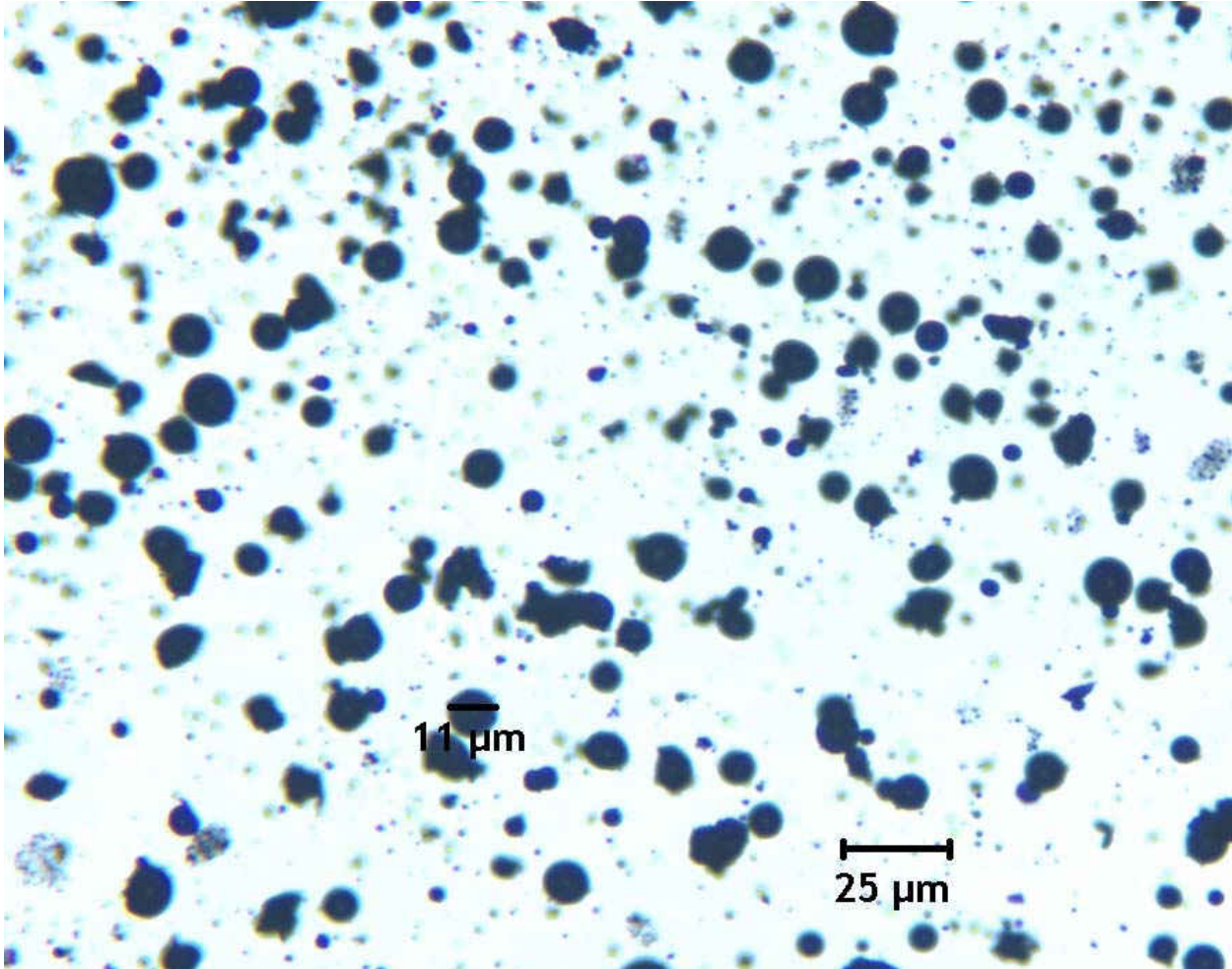
Figure 28 – Micrograph of fresh ball-milled 20 wt. % iron and 80 wt. % magnesium (20x magnification).

The fresh ball-milled bimetal appears to have little plated out or precipitated material on its surface in that it retains a somewhat spherical shape.
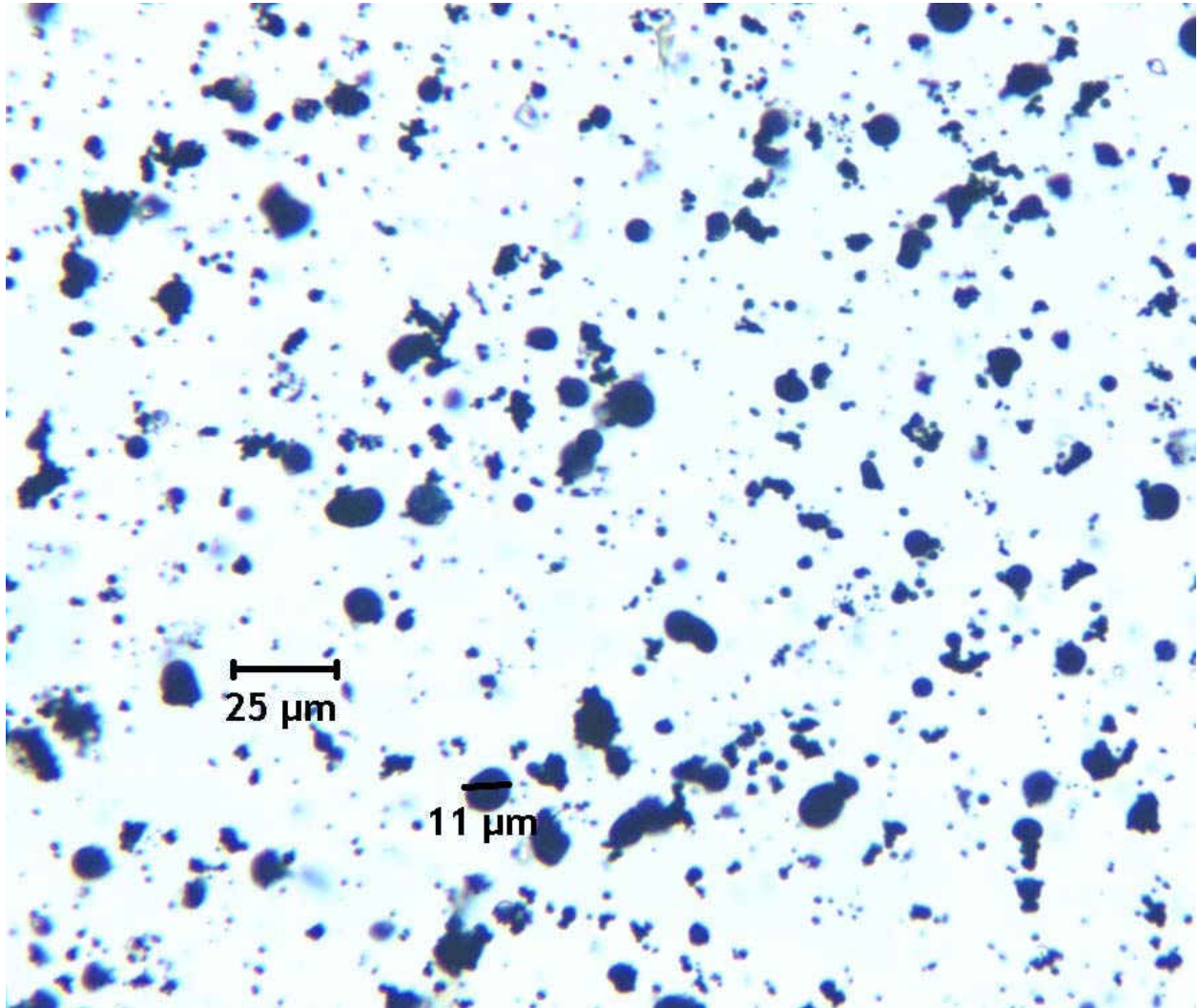
Figure 29 – Micrograph of recovered iron/magnesium from emulsion and sediment mixture after exposure to lead spiked sediment for five days (20x magnification).

The bimetal in the micrograph appears to have impregnated material on its surface as compared to the micrograph of fresh ball-milled iron/magnesium.
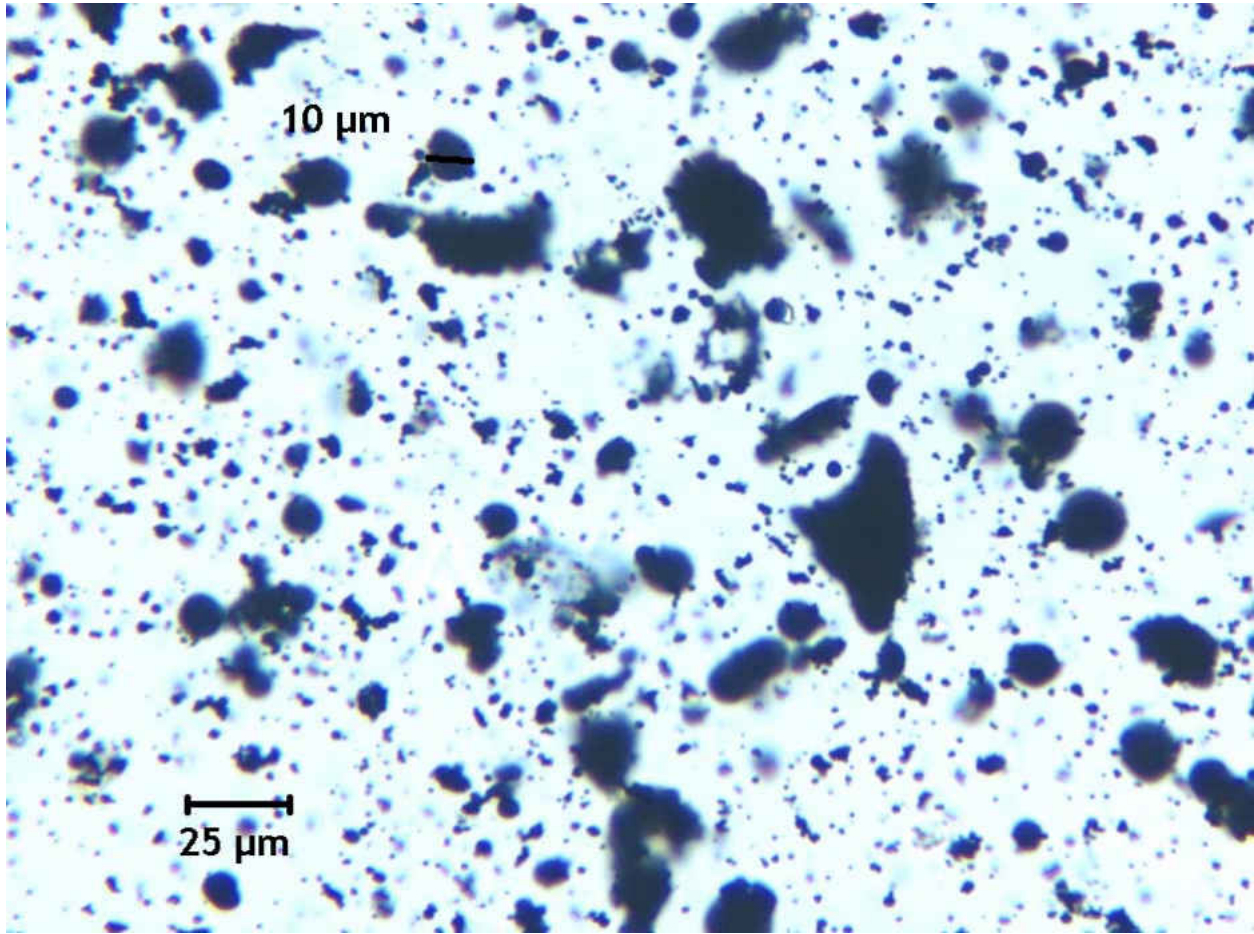
Figure 30 – Micrograph of recovered iron/magnesium from emulsion and sediment mixture after exposure to lead spiked sediment for ten days (20x magnification).

This micrograph taken of iron/magnesium recovered from the emulsion/bimetal removed after being exposed to the lead spiked sediment for ten days has the appearance of even more impregnated material on the surface as compared to the recovered bimetal removed after five days.

MgFe - Fresh   6.0kV   x550   20µm
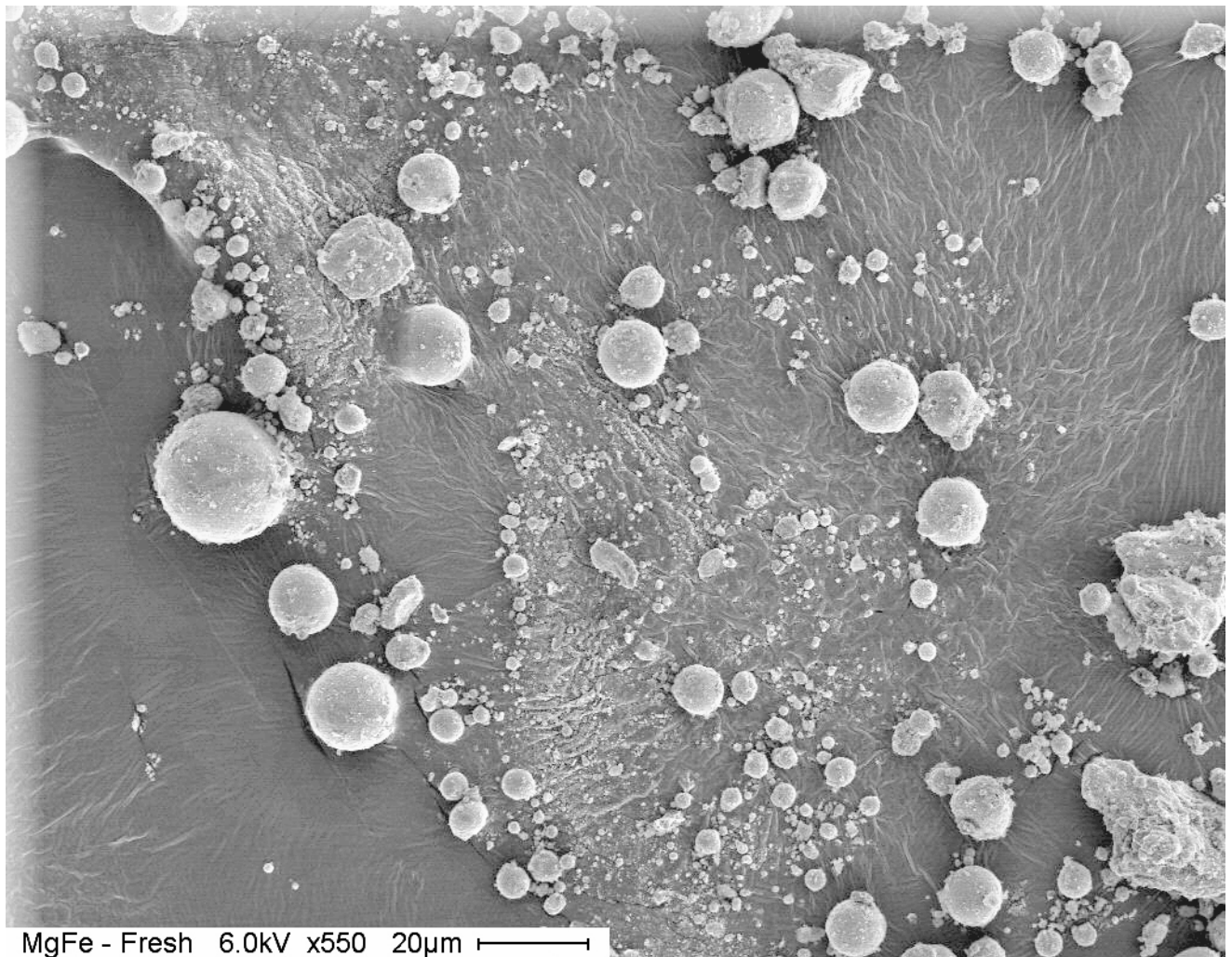
Figure 31 – SEM image of fresh ball-milled 20% by weight iron and 80% by weight magnesium.

The images of the iron/magnesium bimetal appear spherical in shape as they did in the micrograph of fresh ball-milled iron/magnesium.
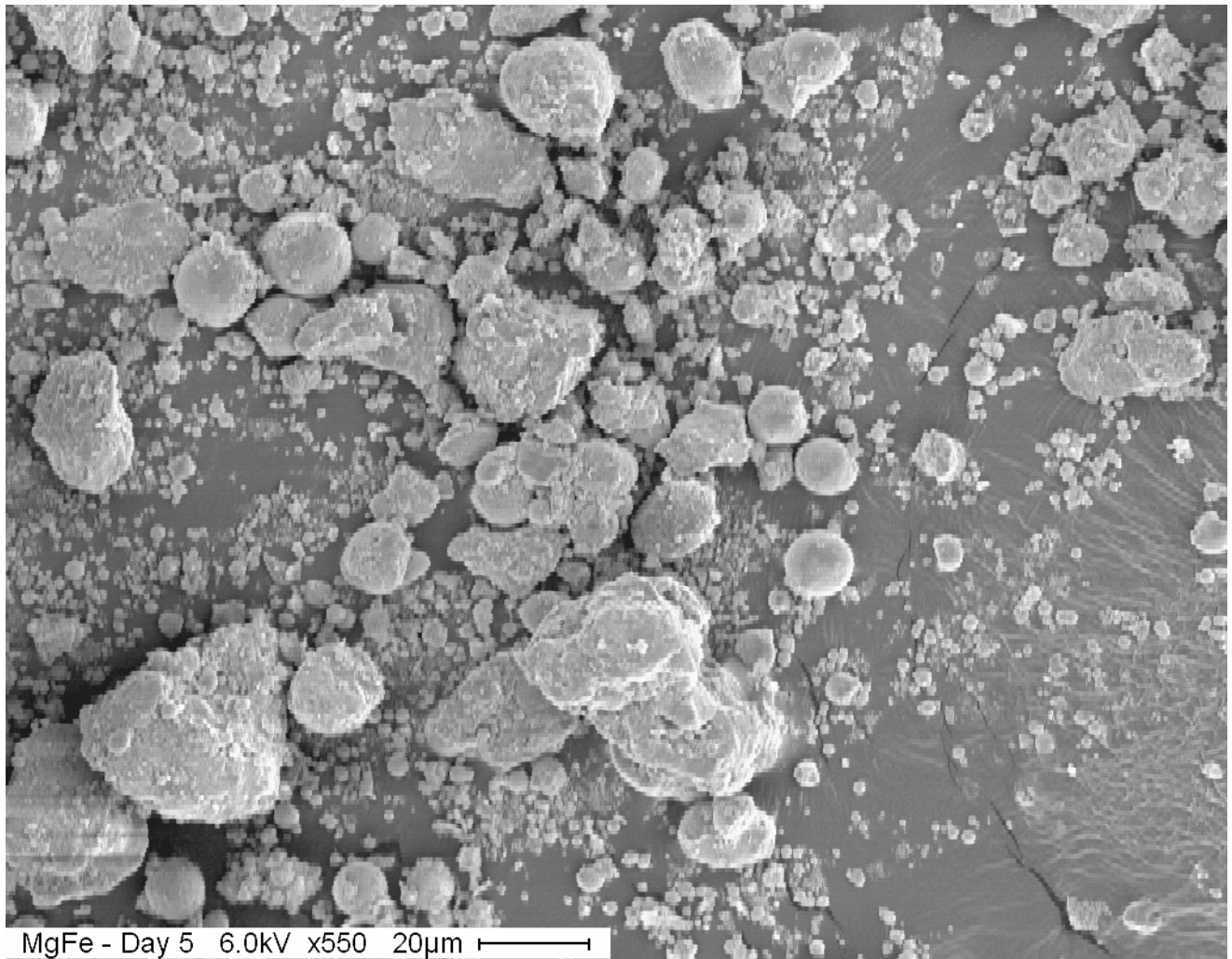
Figure 32 – SEM image of recovered iron/magnesium from emulsion and sediment mixture after exposure to lead spiked sediment for five days.

The appearance of the iron/magnesium has changed and this may be due to the adsorption

of lead onto the surface in addition to more corrosion through the formation of more oxide or

hydroxide layers.
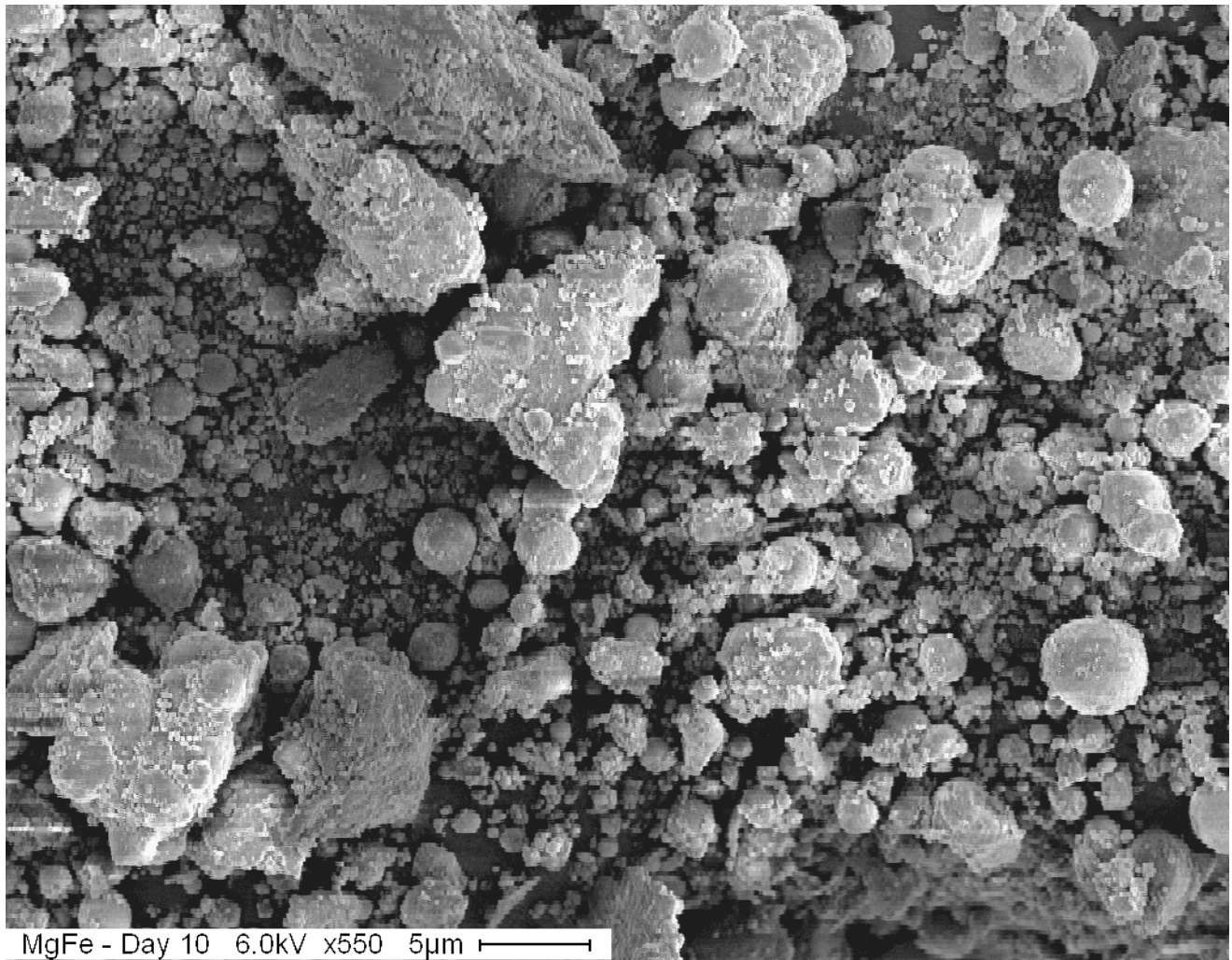
Figure 33 – SEM image of recovered iron/magnesium from emulsion and sediment mixture after exposure to lead spiked sediment for ten days.

The appearance of the iron/magnesium has further progressed from the spherical shapes seen in the SEM image of fresh ball-milled bimetal to suggest significant corrosive characteristics. Even then, the formerly spherical shape of the bimetal is still evident.

Just as the adsorption of lead onto sediment particles is accomplished by complexing through outer or inner sphere processes, the adsorption of lead onto the iron/magnesium bimetal occurs in a similar way. Initially when the emulsion is made, the iron/magnesium has a thin

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oxidation layer which allows for electron transfer through this layer, facilitating the reduction of the lead and its adsorption onto the iron/magnesium. As times passes, the thin oxidation layer on the iron/magnesium inside the emulsion droplet thickens. These corrosive events diminish the available sites for additional lead to further plate with or precipitate on the surface of the iron/magnesium. It is also conceivable with the formation of addition layers formed by that some of the lead in plated out or precipitate form would be released back into the sediment because the active sites are now occupied by oxygen. The oxidation of the iron/magnesium diminishes the surface site availability. Any remediation that had occurred could be reversed.

CHAPTER FOUR: CONCLUSION

For in-situ remediation of heavy metals and more particularly lead contaminated sediment to occur and achieve significant results, the emulsified liquid membrane or emulsion must act to deliver the zero-valent metal to the contaminated sediment. The emulsified liquid membrane is of a water-oil-water formulation which maintains the bimetal, iron/magnesium in its relatively zero-valent form inside the emulsion droplet. The reality is that once the bimetal is positioned inside the emulsion droplet after emulsion formulation, there is a thin oxide or hydroxide layer on the surface of the bimetal. With time this corrosive layer thickens. As the layer thickens beyond ten angstroms, then electron transfer through the oxide layer is no longer feasible to accomplish the reduction to facilitate the plating out or precipitation of lead.

The emulsion facilitates delivery of the bimetal to the lead contaminant sites so that plating out or precipitation of the lead on the bimetal can occur. Since this appears to be only optimally possible up until seven days, it is crucial that removal by a strong magnet be performed at or before the seven days. Otherwise, the remediation efforts will start to diminish and eventually be reversed.

At first, it appeared that the bimetal, iron/magnesium, had maintained a thin layer of oxidation and was still optimally capable of further plating or precipitating with the contaminant lead beyond seven days and into the second week of remediation efforts. This was the conclusion drawn after the Study I results. The purpose of Study I was to measure the ability of the bimetal to plate out with the lead in solution. The micrographs and SEM images showed that the initial spherical shapes of the iron/magnesium had become impregnated with some materials. This could either be adsorbed lead or oxide and/or hydroxide layers or both. This would appear

to suggest that the lead that was so ably removed from the lead solution in Study I was sequestered within the oxide/hydroxide structure that appears to be built up over time on the surface of the iron/magnesium. Whereas significant lead removal from a solution is possible even after the iron/magnesium particle corrodes because of the way the lead is adsorbed within this oxide surficial framework, achieving the same removal rates in sediments with the degraded iron/magnesium is more difficult.

Sediment matrices as compared to solutions present a more challenging environment in regards to the emulsion gaining access to the contaminated lead that is adsorbed by numerous ways onto the sediment particles. As was done in Study I, just exposing the recovered bimetal and injecting it into lead solution may have been too simple a measure to conclude that the recovered bimetal had not formed too thick of an oxide layer and was still in its active state, capable of further plating out or precipitation of lead. A better gauge of the recovered bimetal, iron/magnesium's ability to remediate lead contaminated sediments would have been to prepare a fresh emulsion with the recovered iron/magnesium and inject that into lead spiked sediment. The difficulties are in preparation of enough emulsion, exposing it to an adequate amount of lead spiked sediment and recovering the bi-metal effectively to enable use of the recovered bimetal in preparation of a fresh emulsion batch.

Emulsified liquid membrane combined with zero-valent metals has proven to be a successful in-situ remediation treatment for heavy metal contaminated sediments if the emulsion system is removed at around seven days. There is a limited window to retrieve the plated out or precipitated contaminant. Once this is done then a second treatment of emulsion can be applied to continue on with the remediation efforts. In situ methods although limited to a time frame are more advantageous compared to ex-situ treatments when considering labor and expenses.

A review of the questions that prompted the initiation of this sediment study bear repeating: Does the formation of an impeding oxide layer diminish the remediation capacity of the iron/magnesium system? Does the emulsion reach a maximum capacity to withdraw the contaminant?   Do the soil components or the soil structure interfere with access to the contaminant?

The answers to these questions as they relate to the drop in percent lead removal after the optimal remediation by the zero-valent bimetal in emulsion at seven days appears to be a combination of the first question and the third. It does appear from the micrograph and SEM evidence that an oxide layer and thus a corrosive effect occurs at the surface of the iron/magnesium. Once this corrosive effect ensues, then when removal of the emulsion and bimetal using the magnet occurs, it is possible that during the removal process the impregnated layers of oxide/hydroxide along with the adsorbed lead flake off the iron/magnesium. This desheathing of the iron/magnesium particles reintroduces the contaminant lead back into the sediment and reverses any appreciable remediation. This was evidenced by the results seen in the five day and seven day re-injection studies in the follow-up study. The second dose of emulsion and its fresh iron/magnesium did not appear to have the ability to react with these contaminant–impregnated oxide layers that had desheathed off of the original iron/magnesium bimetal.

Furthermore, it is postulated from the literature that the other limiting factor in this remediation scheme is the aging of the sediment along with the tendency of heavy metal particles to diffuse and to migrate into more inaccessible sites within the complex sediment structure (Bradl, 2005). Data to back up this claim was seen in the lead concentration of control samples

taken throughout the remediation studies. Control samples displayed a progressively downward trend in the measurements of lead content (Appendices A and B).

Remediation of sediments is a complicated task because of the complex nature of sediment components. Emulsified liquid membranes utilizing zero-valent bimetals have demonstrated impressive repeatable results at day seven; however, this treatment method is not without its limitations. Optimal results appear to be gained at day seven after emulsion injection. The bimetal and plated out or precipitated lead must be removed at that point; otherwise the effective remediation of the contaminant is progressively reversed.

APPENDIX A:
STUDY TO EXPLORE REASONS FOR REMEDIATION
LEVEL DROP AFTER SEVEN DAYS

STUDY I, II and III Calibration curve

	Pb	
Calibration curve	solns.	11/21/2006
Blank	0.001	

Con ppm	Absorbance
100	0.26
50	0.13
25	0.064
10	0.025
5	0.013
2	0.006
1	0.002

Calibration Curve Pb solutions

$y = 0.0026x$
$R^2 = 0.9999$

$y = 0.0026x - 0.0003$
$R^2 = 1$

Absorbance vs Concentration (ppm)
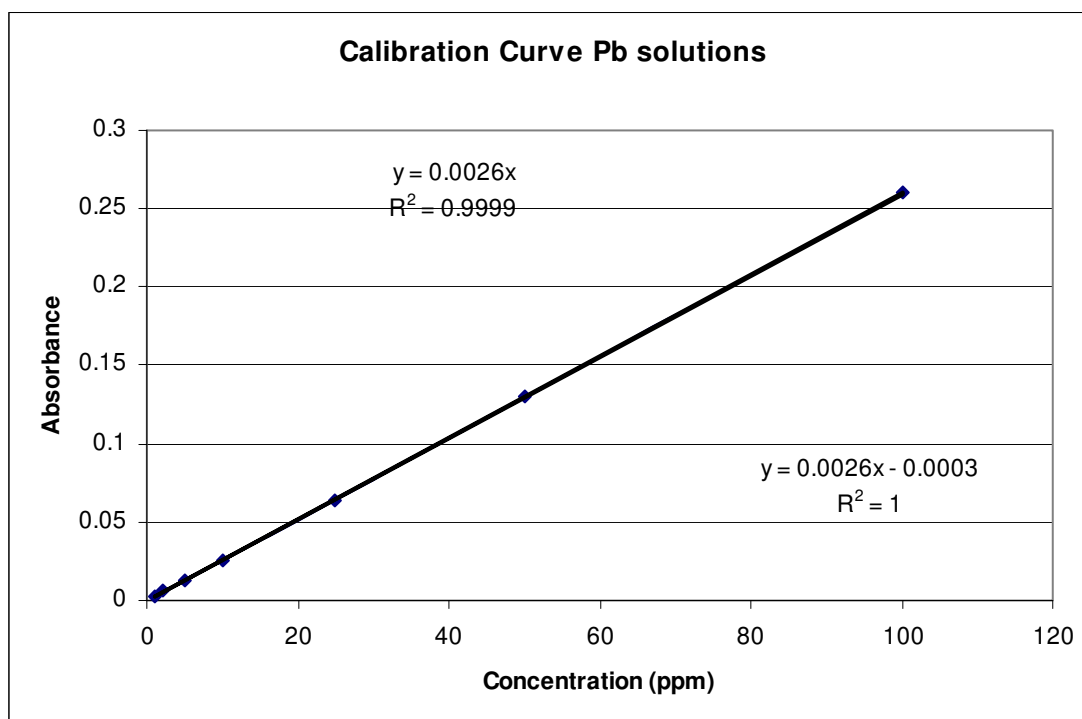
STUDY I RESULTS

Results of recovered Fe/Mg reinjected into
100 ppm Pb solution
0.25 g 20%Fe/Mg placed into 20 mL 100 ppm Pb soln

Day	% Pb rem
0	0
2	92.7
7	98.6

54

% Lead Removed by Recovered 20% Fe/Mg Reinjected into 100 ppm lead solution
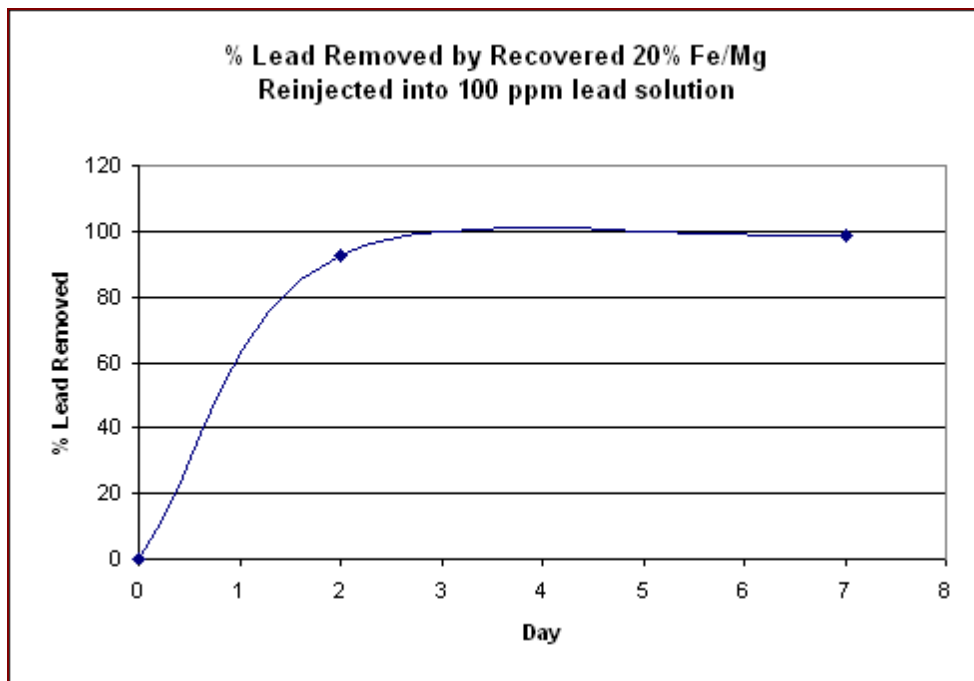
STUDY II and STUDY III RESULTS

Control Samples

20.0 grams of soil brought to incipient wetness with 5.2 mL of deionized water. Acid extraction was performed on each sample for the zero hour value.

Sample	pH	Wt (g)	Absorb.	Conc ppm	Pb con	Avg Pb	Std dev.
1	5.4	3.0046	0.012	4.615385	76.80531		
2	5.37	3.0096	0.011	4.230769	70.2879	73.21148	
3	5.44	3.0285	0.011	4.230769	69.84925		3.65213
4	5.43	3.0403	0.012	4.615385	75.90344		

Each designated day when sediment and emulsion samples were pulled for acid extraction and analysis, two control samples were pulled as well. Acid extraction and analysis gave the following results.

55

Control samples.

Sample	pH	Wt (g)	Absorb.	Conc ppm	Pb con	Avg Pb	Std dev.
Day 2 A	5.78	3.043	0.011	4.230769	69.51642		
Day 2 B	5.61	3.0418	0.012	4.615385	75.86601	72.29921	
Day 5 A	5.6	3.0182	0.011	4.230769	70.08762		7.397974
Day 5 B	5.66	3.01	0.01	3.846154	63.8896		
Day 7 A	5.55	3.038	0.01	3.846154	63.30075		
Day 7 B	5.5	3.0099	0.011	4.230769	70.28089		
Day 10 A	6.1	3.014	0.012	4.615385	76.56577		
Day 10 B	6.08	3.0217	0.011	4.230769	70.00644		
D 12(2) A	5.89	3.0303	0.01	3.846154	63.4616		
D 12(2) B	5.94	3.0256	0.011	4.230769	69.9162		
D 15(5) A		3.0215	0.014	5.384615	89.105		
D 15(5)B		3.0035	0.013	5	83.23622		
D 20(10)A		3.0165	0.012	4.615385	76.50231		
D 20(10)B		3.0025	0.011	4.230769	70.45411		

STUDY II DATA

Twice an emulsion dose (6 mL) was injected into 40 mL vials containing 20.0 grams of 100 ppm Pb spiked sediment brought to incipient wetness with 5.2 mL deionized water. Samples were pulled on the following days. The emulsion formula was 20.0 grams of 20% by weight iron/magnesium; 100.0 mL deionized water, 80.0 mL corn oil and 3.0 grams of Span 85 blended together in a high speed blender for one minute. The typical emulsion dose to be injected into 20.0 grams of sediment is 3.0 mL. Twice the dose is 6.0 mL.

Sample	Wt (g)	Absorb.	Conc ppm	Pb con	Avg Pb	% Pb removed	Avg % Pb removed	St. dev.
Day 2 A	3.0051	0.009	3.461538	57.5944		21.33147		
Day 2 B	3.0339	0.009	3.461538	57.04767	59.00223	22.07825	19.4085	
Day 2 C	3.0139	0.01	3.846154	63.80693		12.84574		4.388482
Day 2 D	3.0069	0.009	3.461538	57.55992		21.37856		
pH of 4	9.66	9.89	9.74	9.57				
Day 5 A	3.0115	0.007	2.692308	44.70044		38.9434		
Day 5 B	3.0206	0.007	2.692308	44.56578	43.00205	39.12734	41.26324	
Day 5 C	3.0129	0.006	2.307692	38.29686		47.69009		4.286931
Day 5 D	3.0288	0.007	2.692308	44.44512		39.29214		
pH	9.76	9.9	9.74	9.47				
Day 7 A	3.0163	0.005	1.923077	31.87808		56.45754		
Day 7 B	3.0401	0.005	1.923077	31.62851	31.88549	56.79842	56.44742	
Day 7 C	3.0049	0.005	1.923077	31.99902		56.29235		0.251531
Day 7 D	3.0014	0.005	1.923077	32.03633		56.24138		
pH	9.6	9.55	9.47	9.78				
Day 10 A	3.0219	0.007	2.692308	44.5466		39.15353		
Day 10 B	3.0115	0.006	2.307692	38.31467	43.059	47.66577	41.18545	
Day 10 C	3.02	0.007	2.692308	44.57463		39.11524		4.322993
Day 10 D	3.0048	0.007	2.692308	44.80011		38.80725		
pH	9.91	9.8	9.78	9.93				
Day 15 A	3.0109	0.007	2.692308	44.70935		38.93123		
Day 15 B	3.0081	0.007	2.692308	44.75097	44.63913	38.87439	39.02714	
Day 15 C	3.0196	0.007	2.692308	44.58054		39.10718		0.149865
Day 15 D	3.024	0.007	2.692308	44.51567		39.19578		
pH								
Day 20 A	3.0113	0.009	3.461538	57.47582		21.49344		
Day 20 B	3.033	0.008	3.076923	50.72409	52.66539	30.71567	28.06403	
Day 20 C	3.004	0.008	3.076923	51.21377		30.04681		4.392571
Day 20 D	3.002	0.008	3.076923	51.24789		30.0002		
pH	9.33	9.6	9.58	9.5				

STUDY II PLOT OF DATA

Day	% Pb removed
2	19.4085
5	41.26324
7	56.44742
10	41.18545
15	39.02714
20	28.06403

Percent Pb removed by 2x emulsion dose

(plot: Pb Concentration (ppm) vs Days)
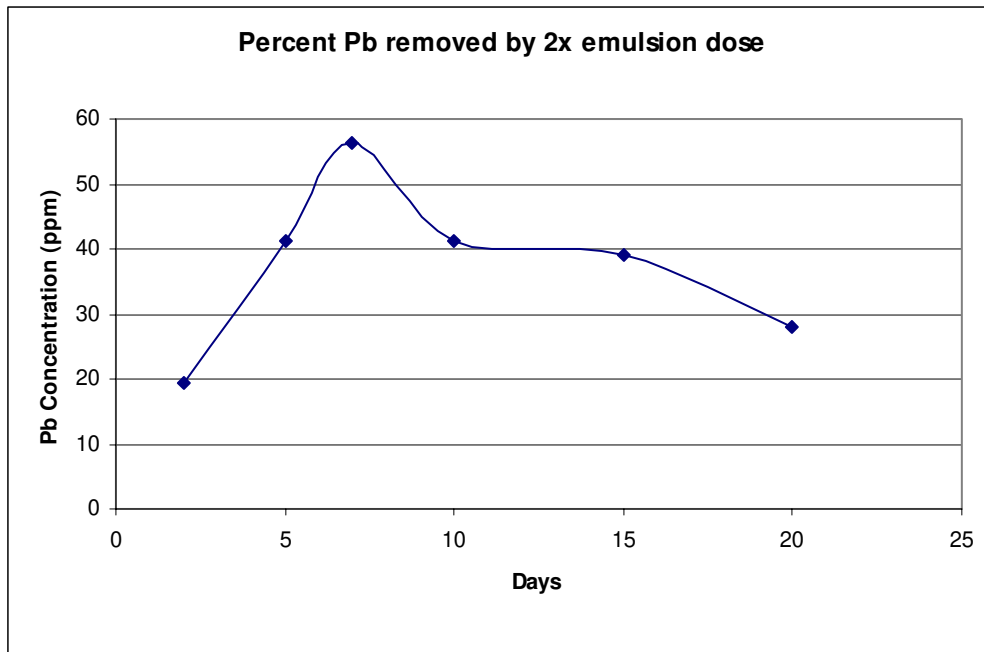
STUDY III DATA

Study III.   A 1x emulsion dose (3 mL) was injecterd into 40 mL vials containing 20.0 grams
Pb spiked dried soil that was brought to incipient wetness   ess with 5.2 mL de-I water. Samples
were pulled on the following days. On day 10 samples were pulled and then another 1x emulsion
dose was injected and stirred into the remaining vials. All vials were placed on a continuous shaker
table throughout the
study.
Emulsion: 20.0 grams 20% Fe-Mg; 100 mL de-I water; 80 mL corn oil; 3.0 g Span 85
Emulsion dose 1x 3.0 mL; 2x 6.0 mL

| | | | | | | % Pb | Avg % Pb | |
Sample	Wt (g)	Absorb.	Conc ppm	Pb con	Avg Pb	removed	removed	St. dev.
Day 2 A	3.0221	0.009	3.4615385	57.270416		21.773996		
Day 2 B	3.0468	0.009	3.4615385	56.806132	60.404095	22.408163	17.493684	
Day 2 C	3.0173	0.01	3.8461538	63.735025		12.943946		5.3150673
Day 2 D	3.014	0.01	3.8461538	63.804808		12.848629		
pH of 4	9.41	9.12	9.09	9.47				
Day 5 A	3.0243	0.007	2.6923077	44.511254		39.201811		
Day 5 B	3.0421	0.005	1.9230769	31.60772	39.699501	56.826825	45.774214	
Day 5 C	3.0372	0.006	2.3076923	37.990457		48.108607		8.5096981
Day 5 D	3.0123	0.007	2.6923077	44.688572		38.959612		
pH of 4	9.44	9.22	9.18	9.13				
Day 7 A	3.0038	0.007	2.6923077	44.815029		38.786883		
Day 7 B	3.0058	0.006	2.3076923	38.387323	39.92659	47.566525	45.46403	
Day 7 C	3.0023	0.006	2.3076923	38.432074		47.5054		4.4568114
Day 7 D	3.0307	0.006	2.3076923	38.071936		47.997315		
pH of 4	9.58	9.53	9.33	9.57				
Day 10 A	3.015	0.009	3.4615385	57.405281		21.589782		
Day 10 B	3.0485	0.008	3.0769231	50.466181	52.488287	31.06794	28.305933	
Day 10 C	3.0172	0.009	3.4615385	57.363424		21.646955		8.3609363
Day 10 D	3.0103	0.007	2.6923077	44.718262		38.919057		
pH of 4	9.51	9.47	9.46	9.75				

After samples were pulled, the remaining vials were reinjected with a 1x (3.0 mL) emulsion dose and stirred. Vials were placed back on shaker table for remainder of study.

D 12(2) A	3.0372	0.008	3.0769231	50.653942		30.811476		
D 12(2) B	3.0282	0.008	3.0769231	50.804489	50.81752	30.605843	30.588045	
D 12(2)C	3.013	0.008	3.0769231	51.060788		30.255763		0.2373042
D 12(2)D	3.0314	0.008	3.0769231	50.750859		30.679097		
pH of 4	9.37	9.33	9.83	9.47				
D 15(5) A	3.0467	0.007	2.6923077	44.183997		39.648813		
D 15(5) B	3.023	0.006	2.3076923	38.16891	42.879243	47.864857	41.430984	
D 15(5) C	3.0021	0.007	2.6923077	44.840407		38.752219		4.3065495
D 15(5) D	3.0371	0.007	2.6923077	44.323659		39.458048		
pH of 4	10.15	10.22	9.9	10.07				
D 20(10)A	3.0276	0.007	2.6923077	44.462738		39.26808		
D 20(10)B	3.0135	0.007	2.6923077	44.670776	46.280992	38.983918	36.784515	
D 20(10)C	3.0045	0.008	3.0769231	51.205243		30.058451		4.4877485
D 20(10)D	3.0058	0.007	2.6923077	44.78521		38.827613		
pH of 4	9.84	9.39	9.62	9.5				

STUDY III PLOT OF DATA

% Pb removed

Day	% Pb removed
2	17.49368
5	45.77421
7	45.46403
10	28.30593
12	30.58804
15	41.43098
20	36.78452

% Pb removed by initial injection of 1x (3mL) emulsion dose, followed by reinjection on Day 10
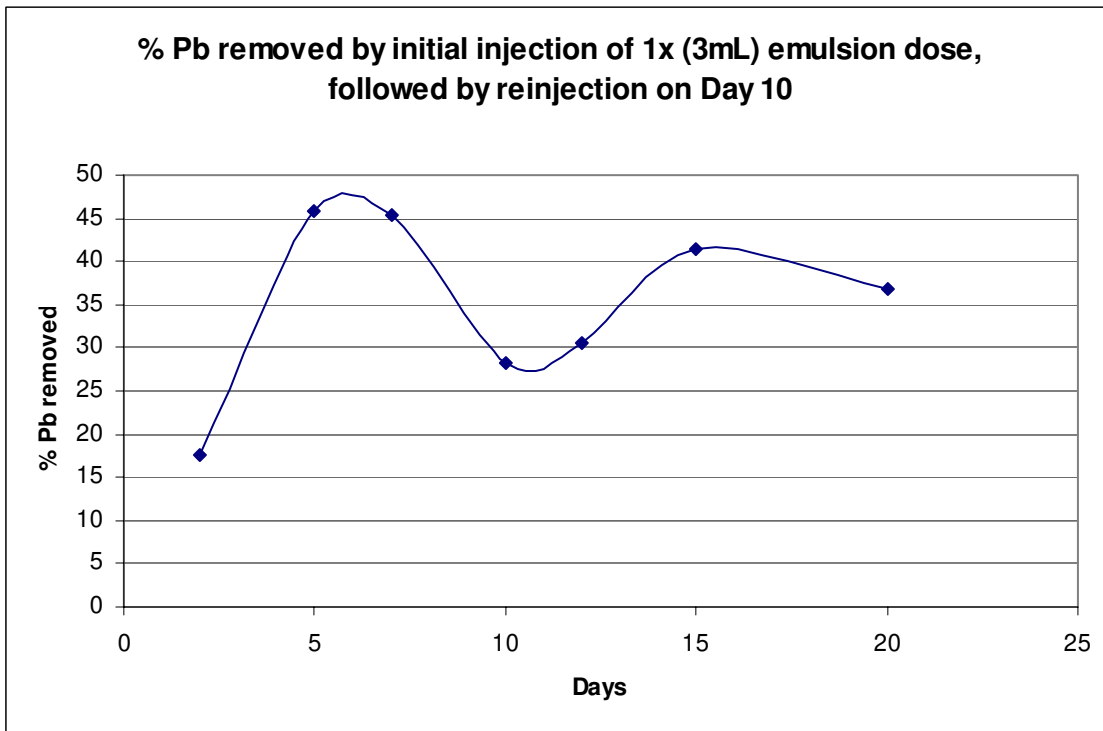
APPENDIX B:
FOLLOW-UP STUDY

FOLLOW UP STUDY

After the November 2006 Pb spiked soil/emulsion remediation study, Dr. Clausen and Dr. Geiger directed a new study for exploring reasons for remediation levels dropping after 10 days. I was directed to reinject emulsion at day 5 and then at day 7 to investigate ways to maintain remediation
levels. Also, one question needs answering - is the emulsion droplet still intact after 7-10 days? If it breaks up, does this action release contaminant Pb back into the soil?
February - March 2007 artificial soil prepared by mixing thoroughly 3.00 kg builder's play sand, 0.50 kg dried ground up clay, and 900 mL peat for a total of 3603.44 kg soil. Mixed with electric drill and attachment for 30 minutes. Brought to incipient wetness with 900 mL deionized water with
6 mL concentrated nitric acid and 0.5761 grams of lead nitrate in solution. Mixed with electric drill and attachment for 30 minutes. Poured in glass baking dish and put in 120 degree Celsius oven overnight. Removed and mixed up dried spiked soil with rubber hammer with soil pieces in double plastic bags. Ground to a fine mixture. Pulled four random samples to perform acid extraction. Distributed and weighed out 20.0 grams of dried soil into 128 40.0 mL vials. Brought to incipient wetness with 5.5 mL deionized water. Pulled four zero hour control samples and performed acid extraction.   Will analyze concentration on Flame Atomic Absorption Spectrophotometer. Spiked soil was mixed to a desired 100 ppm Pb concentration.   (0.16 gr lead nitrate/ kg soil)

Made up four emulsion
batches   with the followiing ingredients.
Emulsion: 20.0 grams 20% Fe-Mg; 100 mL de-I water; 80 mL corn oil; 3.0 g Span 85
Emulsion dose: 3mL
Injected one emulsion dose in each 20 grams of soil brought to incipient wetness vial for 14 day study. Pulled samples accordingly. For 5 day reinject study, made up new batch of emulsion and injected 2nd 3 mL dose into remaining vials and placed on shaker table. For 7 day reinject study, repeated the same procedure.

Prepared Pb solution standards in 1000 mL volumetric flask. Analytically weighed out 0.16 grams lead nitrate and poured into flask with 6.0 mL concentrated nitric acid. Mixed thoroughly and diluted to mark. Used glass pipettes to draw 50 mL, 25 mL, 10 mL, 5 mL, 2 mL, and 1 mL of 100 ppm solution. Mixed in 100 mL volumetric flask and diluted to   k for each
mark.   standard.

Calibration Curve Standards

Calibration curve	Pb solns.
Blank	0.001
Con ppm	Absorbance
100	0.264
50	0.134
25	0.068
10	0.03
5	0.015
2	0.006
1	0.003

Calibration curve standard Pb solutions

$y = 0.0027x$

$R^2 = 0.9996$

Absorbance

Concentration (ppm)
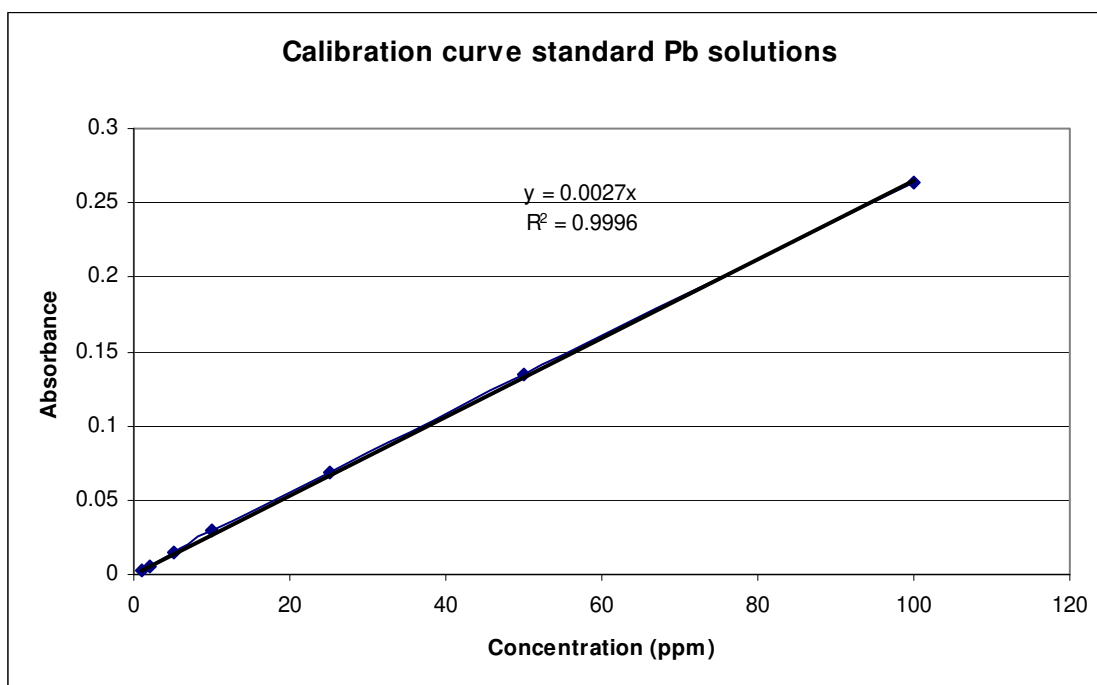
CONTROL SAMPLES

Weighed out 20.0 grams of soil in 128 40.0 mL vials and brought to incipient wetness.

Control Samples. 20.0 grams of soil brought to incipient wetness with 5.2 mL de-I water.
Acid extraction performed.   0 hour

Sample	Wt (g)	Absorb.	Conc ppm	Pb con	Avg Pb	Std dev.
1	3.0237	0.013	4.814815	79.61793		
2	3.0346	0.012	4.444444	73.22949	75.14413	5.90065
3	3.0116	0.011	4.074074	67.63969		
4	3.0059	0.013	4.814815	80.0894		

Each day when emulsion injected samples were pulled, 2 control samples were pulled as well with the following results:

Sample	Wt (g)	Absorb.	Conc ppm	Pb con	Avg day	Overallavg	Std dev.
Day 1 A	3.0333	0.012	4.444444	73.26088	70.48626		
1 B	3.0084	0.011	4.074074	67.71164		70.36861	
Day 2 A	3.0145	0.012	4.444444	73.71777	73.49899		3.591357
2 B	3.0325	0.012	4.444444	73.28021			
Day 5 A	3.0029	0.012	4.444444	74.00254	70.78634		
5 B	3.0147	0.011	4.074074	67.57014			
Day 6 A	3.0335	0.011	4.074074	67.15138	73.39387		
6 B	3.023	0.013	4.814815	79.63637			
Day 7 A	3.0061	0.012	4.444444	73.92376	70.81995		
7 B	3.0082	0.011	4.074074	67.71614			
Day 8 A	3.0198	0.012	4.444444	73.58839	70.31905		
8 B	3.0381	0.011	4.074074	67.0497			
Day 9 A	3.0271	0.011	4.074074	67.29335	67.55886		
9 B	3.0034	0.011	4.074074	67.82437			
Day 10 A	3.0054	0.013	4.0625	67.58668	67.35219		
10 B	3.0264	0.013	4.0625	67.1177			
Day 12 A	3.026	0.014	4.375	72.29015	72.56092		
12 B	3.0035	0.014	4.375	72.8317			
Day 14 A	3.0131	0.014	4.375	72.59965	69.82544		
14 B	3.0294	0.013	4.0625	67.05123			
Day 21 A	2.9911	0.013	4.0625	67.9098	67.45287		
21 B	3.0319	0.013	4.0625	66.99594			

Fourteen Day Study

A fourteen day Pb spiked soil emulsion remediation study was set up. This was to provide a framework to analyze the 5 day reinject and 7 day reinject studies also instituted.
20.0 grams of Pb spiked soil was weighed out in 40.0 mL glass vials, brought to incipient wetness
and injected with a 3.0 mL dose of emulsion, mixed with the long syringe tip and placed on the shaker table for continuous operation for length of study.
Four samples were pulled on designated days. The sample was poured out into a beaker with deionized water. A   neodymium magnet enclosed in plastic bags was run through the sample three times to remove all metal from the sample (Pb plated on Fe/Mg). The sample was washed
with deionized water and acetone to remove the emulsion residue. Sample was poured over filter
through Buchner funnel. Sample was scraped onto watch glass for overnight drying in the oven.
Metal sample was collected in beaker and allowed to dry overnight. Metal sample was collected in
vials and weighed analytically. The dried soil sample was weighed out in 3.0 gram samples in Erlenmeyer flasks. Tweny mL concentrated nitric acid was added and allowed to sit one hour.
Soil samples were sonicated for one hour. Sample was poured over fiberglass filter on glass frit under vacuum quantitatively. Sample was diluted to 50.00 mL in volumetric flask for analysis on Flame Atomic Absorption Spectrophotometer.

Sample	Wt (g)	Absorb.	Conc ppm	Pb con	Avg Pb	% Pb removed	Avg % Pb removed	St. dev.
Day 1 A	3.0037	0.008	2.962963	49.32189	50.41661	34.36354	32.90671	
1 B	3.0492	0.008	2.962963	48.58591		35.34296		4.087794
1 C	3.0303	0.009	3.333333	55.00006		26.80719		
1 D	3.0384	0.008	2.962963	48.75861		35.11314		
Day 2 A	3.0467	0.008	2.962963	48.62577	48.76411	35.28991	35.10581	
2 B	3.0442	0.008	2.962963	48.66571		35.23677		6.330095
2 C	3.0105	0.007	2.592593	43.05917		42.6978		
2 D	3.0466	0.009	3.333333	54.70579		27.19879		
Day 5 A	3.0376	0.007	2.592593	42.67502	39.87211	43.20902	46.93904	
5 B	3.0071	0.006	2.222222	36.94959		50.82826		4.437125
5 C	3.0257	0.007	2.592593	42.84286		42.98566		
5 D	3.0013	0.006	2.222222	37.02099		50.73324		
Day 7 A	3.0068	0.006	1.875	31.17933	31.08697	58.50717	58.63008	
7 B	3.0027	0.006	1.875	31.2219		58.45051		0.178335
7 C	3.0293	0.006	1.875	30.94774		58.81535		
7 D	3.0243	0.006	1.875	30.99891		58.74727		
Day 10 A	3.0205	0.008	2.5	41.38388	41.28232	44.92723	45.06238	
10 B	3.0462	0.007	2.1875	35.90539		52.21785		5.744236
10 C	3.0219	0.008	2.5	41.3647		44.95275		
10 D	3.0258	0.009	2.8125	46.47531		38.15169		
Day 14 A	3.0032	0.011	3.4375	57.23062	55.65246	23.83881	25.93898	
14 B	3.0059	0.011	3.4375	57.17921		23.90722		3.844557
14 C	3.022	0.011	3.4375	56.87459		24.31261		
14 D	3.0443	0.01	3.125	51.32543		31.69728		

Day	Avg % Pb removal
1	32.90671
2	35.10581
5	46.93904
7	58.63008
10	45.06238
14	25.93898

14 Day Study - Percent Pb Removed by Emulsion
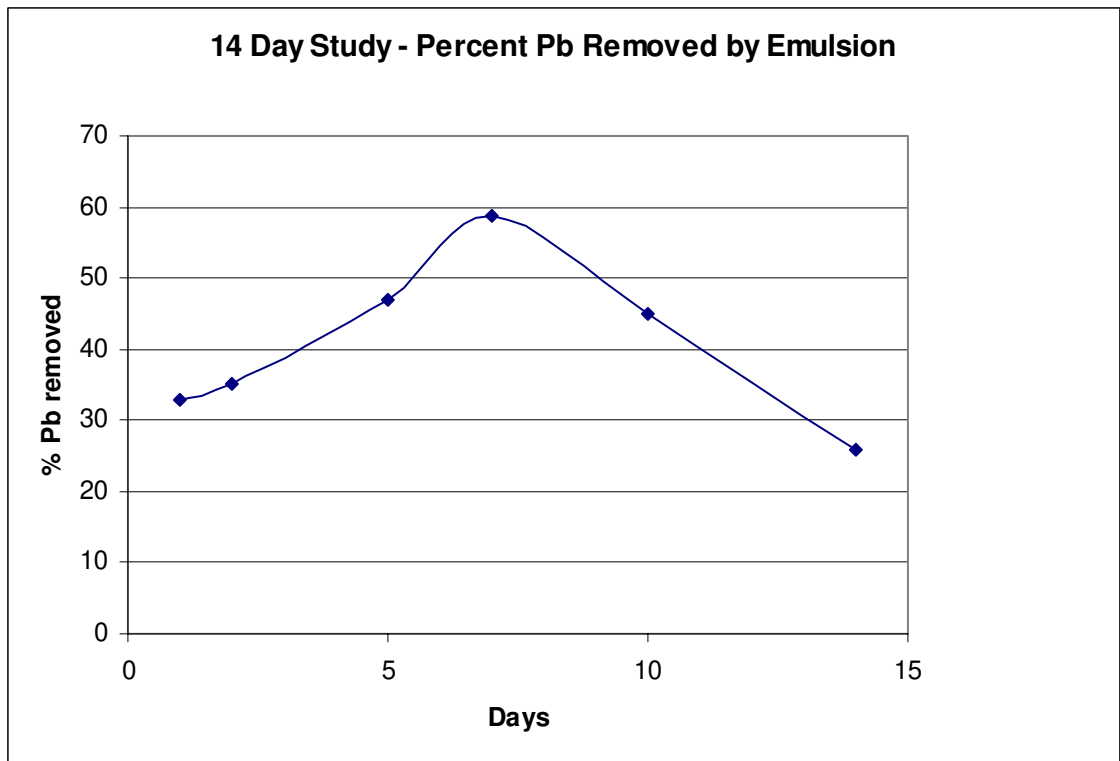
FIVE DAY REINJECTION STUDY

Five day reinjection study. Will remediation levels be maintained by reinjecting a second emulsion dose at 5 days? Can the eventual drop in remediation of Pb after 7-10 days be avoided? Will a second dose of emulsion increase remediation levels beyond 60% Pb removal?

At day 5 the four samples were drawn for acid extraction. A fresh emulsion batch was prepared and 3.0 emulsion doses were injected into each remaining vial.

Sample	Wt (g)	Absorb.	Conc ppm	Pb con	Avg Pb	% Pb removed	Avg % Pb removed	St. dev.
Day 1 A	3.0037	0.008	2.962963	49.32189	50.41661	34.36354	32.90671	
1 B	3.0492	0.008	2.962963	48.58591		35.34296		4.087794
1 C	3.0303	0.009	3.333333	55.00006		26.80719		
1 D	3.0384	0.008	2.962963	48.75861		35.11314		
Day 2 A	3.0467	0.008	2.962963	48.62577	48.76411	35.28991	35.10581	
2 B	3.0442	0.008	2.962963	48.66571		35.23677		6.330095
2 C	3.0105	0.007	2.592593	43.05917		42.6978		
2 D	3.0466	0.009	3.333333	54.70579		27.19879		
Day 5 A	3.0376	0.007	2.592593	42.67502	39.87211	43.20902	46.93904	
5 B	3.0071	0.006	2.222222	36.94959		50.82826		4.437125
5 C	3.0257	0.007	2.592593	42.84286		42.98566		
5 D	3.0013	0.006	2.222222	37.02099		50.73324		

Fresh emulsion prepared. 3 mL dose injected into each vial and stirred. Vials placed back on shaker table. Samples drawn at one, two, five, seven, nine, sixteen day intervals.

Sample	Wt (g)	Absorb.	Conc ppm	Pb con	Avg Pb	% Pb removed	Avg % Pb removed	St. dev.
Day 6(1)A	3.0287	0.006	2.2222222	36.686074	33.619861	51.17894	55.259373	
6(1) B	3.0471	0.005	1.8518519	30.38712		59.561417		4.9481159
6(1) C	3.0038	0.006	2.2222222	36.990183		50.77424		
6(1) D	3.0442	0.005	1.8518519	30.416067		59.522895		
Day 7(2)A	3.0171	0.008	2.5	41.430513	40.077101	44.865169	46.666252	
7(2) B	3.0228	0.007	2.1875	36.18334		51.847965		6.6746
7(2) C	3.0305	0.007	2.1875	36.091404		51.97031		
7(2) D	3.0175	0.009	2.8125	46.603148		37.981566		
Day10(5)A	3.0062	0.007	2.1875	36.383142	43.954368	51.582074	41.506491	
10(5) B	3.0167	0.01	3.125	51.795008		31.07238		11.78424
10(5) C	3.0222	0.007	2.1875	36.190523		51.838405		
10(5) D	3.037	0.01	3.125	51.448798		31.533106		
Day12(7)A	3.0036	0.01	3.125	52.020908	56.893324	30.771757	24.287679	
12(7) B	3.0219	0.011	3.4375	56.876468		24.310109		5.3115763
12(7) C	3.0218	0.011	3.4375	56.878351		24.307605		
12(7) D	3.0341	0.012	3.75	61.797568		17.761244		
D14(9) A	lost							
14(9) B	3.0161	0.011	3.4375	56.985843	58.750729	24.164557	21.815895	
14(9) C	3.0251	0.011	3.4375	56.816304		24.390175		4.2648861
14(9) D	3.0024	0.012	3.75	62.45004		16.892951		
D21(16)A	3.0343	0.011	3.4375	56.644037	54.225205	24.619424	27.838339	
21(16) B	3.0325	0.01	3.125	51.525144		31.431507		3.9318029
21(16) C	3.0198	0.011	3.4375	56.916021		24.257474		
21(16) D	3.0155	0.01	3.125	51.815619		31.04495		

Day	Avg %Pb removed
1	32.90671
2	35.10581
5	46.93904
6	55.25937
7	46.66625
10	41.50649
12	24.28764
14	21.81589
21	27.83834

Percent Pb removal by emulsion with a 2nd dose injected at day five

SEVEN DAY REINJECTION STUDY

Seven day reininjection study. The same questions can be asked as in the five day reinjection.
Will remediation levels be maintained by reinjecting a second emulsion dose at 7 days? Can the
eventual drop in remediation at 7-10 days be avoided? Will a second dose of emulsion increase
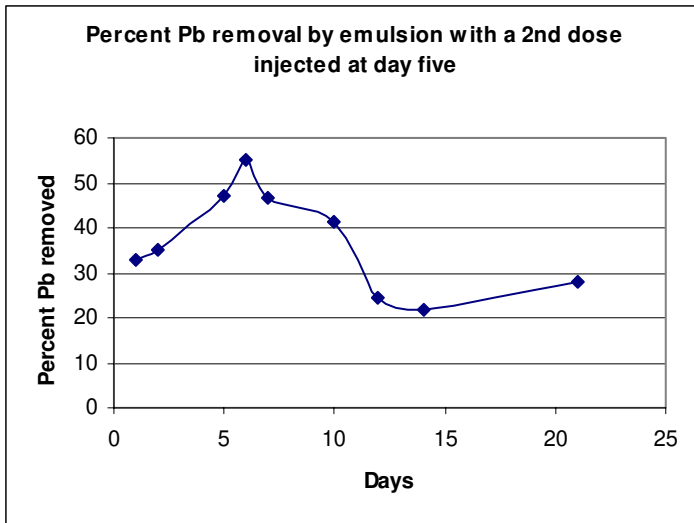remediation levels beyond 60% Pb removal?
At day seven a second fresh batch of emulsion was prepared. 3.0 mL emulsion doses were
injected into each remaining vial.

Sample	Wt (g)	Absorb.	Conc ppm	Pb con	Avg Pb	% Pb removed	Avg % Pb removed	St. dev.
Day 1 A	3.0037	0.008	2.962963	49.321886	50.416613	34.363544	32.90671	
1 B	3.0492	0.008	2.962963	48.585907		35.342964		4.0877942
1 C	3.0303	0.009	3.3333333	55.000055		26.80719		
1 D	3.0384	0.008	2.962963	48.758606		35.113141		
Day 2 A	3.0467	0.008	2.962963	48.625775	48.764111	35.289909	35.105815	
2 B	3.0442	0.008	2.962963	48.665708		35.236767		6.3300955
2 C	3.0105	0.007	2.5925926	43.059169		42.697797		
2 D	3.0466	0.009	3.3333333	54.705792		27.198787		
Day 5 A	3.0376	0.007	2.5925926	42.675016	39.872114	43.209017	46.939044	
5 B	3.0071	0.006	2.2222222	36.94959		50.82826		4.437125
5 C	3.0257	0.007	2.5925926	42.842856		42.985661		
5 D	3.0013	0.006	2.2222222	37.020995		50.733236		
Day 7 A	3.0068	0.006	1.875	31.179327	31.08697	58.50717	58.630076	
7 B	3.0027	0.006	1.875	31.2219		58.450514		0.1783347
7 C	3.0293	0.006	1.875	30.947744		58.815354		
7 D	3.0243	0.006	1.875	30.998909		58.747265		

Fresh emulsion prepared. 3 mL dose injected into each vial and stirred. Vials placed back on shaker table. Samples drawn at one, two, five, seven, and fourteen day intervals.

Day 8(1)A	3.0315	0.006	1.875	30.925285	27.121759	58.845242	63.906871	
8(1) B	3.0165	0.005	1.5625	25.899221		65.533792		6.521562
8(1) C	3.02	0.004	1.25	20.695364		72.458943		
8(1) D	3.0274	0.006	1.875	30.967167		58.789507		
Day 9(2)A	3.0241	0.008	2.5	41.334612	34.966623	44.992791	53.467138	
9(2) B	3.0077	0.005	1.5625	25.974998		65.43295		19.039693
9(2) C	3.0284	0.004	1.25	20.637961		72.535334		
9(2) D	3.0095	0.01	3.125	51.918923		30.907476		
Day12(5)A	3.0259	0.01	3.125	51.637529	50.510894	31.281948	32.781243	
12(5) B	3.0178	0.01	3.125	51.776128		31.097504		3.3558364
12(5) C	3.0092	0.009	2.8125	46.731689		37.810507		
12(5) D	3.0107	0.01	3.125	51.89823		30.935015		
Day14(7)A	3.0185	0.01	3.125	51.764121	52.884161	31.113483	29.622965	
14(7) B	3.0401	0.009	2.8125	46.256702		38.442607		8.9119852
14(7) C	3.0142	0.012	3.75	62.20556		17.218298		
14(7) D	3.0452	0.01	3.125	51.310259		31.717471		
D21(14)A	3.0116	0.011	3.4375	57.070992	58.111456	24.051243	22.666621	
21(14) B	3.0193	0.012	3.75	62.100487		17.358127		3.5551177
21(14) C	3.0248	0.011	3.4375	56.821939		24.382676		
21(14) D	3.0446	0.011	3.4375	56.452408		24.874438		

Percent Pb removed by emulsion with a 2nd dose injected on day 7
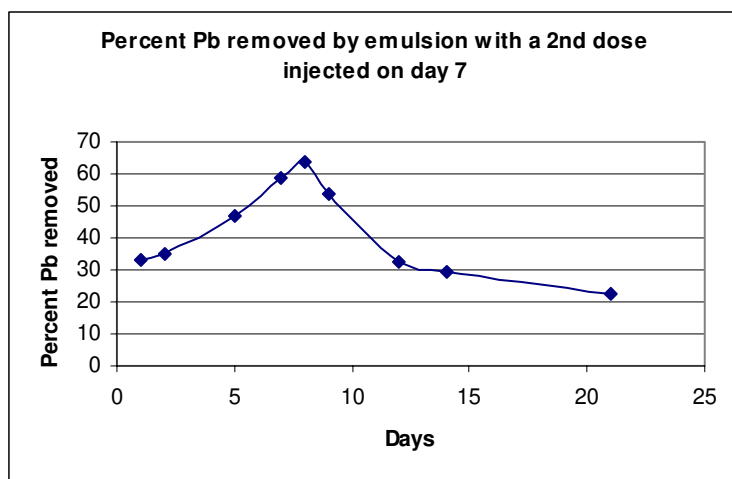
Day	Avg % Pb removed		Day	Avg % Pb removed
1	32.90671		8	63.90687
2	35.10581		9	53.46714
5	46.93904		12	32.78124
7	58.93008		14	29.62296
			21	22.66662

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