Treatability Study Work Plan (TSWP)
For The Mercury Refining Site - Colonie, New York

Prepared for:
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The attached Treatability Study Plan (TSP) for the Bench Scale Treatability Study for the Electrokinetic Remediation of Soil from the Mercury Refining Site, Colonie, New York is hereby recommended for approval.

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1 INTRODUCTION

1.1 Background

The purpose of the work described in this Treatability Study Work Plan (TSP) is to develop the information to determine the feasibility of electrokinetics (EK) as a remediation technology to remove mercury (Hg) from a contaminated soil. This study is not intended to generate data required to scale from the bench study to full scale EK field implementation but are limited to identifying the possibility of using EK as a Hg removal technique. This study is limited to identifying a “go – no go” situation for pilot evaluation of EK for Hg removal and thus is limited in scope.

Effective electrokinetic remediation depends on the solubilization and transport of the contaminant. EK remediation of Hg-contaminated soil may be difficult due to the low solubility of different Hg complexes formed in natural soils. Therefore, the evaluation of different extraction agents to form soluble complexes will be studied. This study will also determine the rate of Hg transport, the effects of amendments on the effectiveness of EK treatment, as well as identifying any adverse affects of the EK processing. Data will also be collected to determine the rate of power consumption during the laboratory EK treatability study.

1.2 General Site Location and Description

The facility of interest is located at 26 Railroad Avenue, between Interstate 90 and Central Avenue in the towns of Colonie and Guilderland located in Albany County, New York. The site encompasses 0.63 acres of a 2.8 acre parcel. The Mercury Refining Company (MERECO) began operations in 1955. Figures 1 and 2 show the site location and the area of interest, respectively (CDM 2004). The areas to the north, east, and west of the site are principally light industrial with some commercial use and warehouses. The closest residence is located...
approximately 1/4 mile north of the site. An unnamed tributary to Patroon Creek and active railroad tracks form the southern boundary of the site. Beyond the railroad tracks are electrical powerlines and undeveloped land that extends to Interstate 90.

Historically, the MERECO facility has reportedly received spent metal contained material from off-site facilities, stored this waste on-site, reclaimed silver and other precious metals, and reclaimed metallic Hg from off-specification metallic Hg, Hg batteries, and other Hg bearing wastes. The Hg was reclaimed using retort (condensation) furnaces at the facility. This facility was a licensed and permitted for hazardous material treatment and storage because much of the Hg bearing material was received as a hazardous substance from various generators. In 1998, MERECO discontinued its Hg reclamation operations but continued reclaiming precious metals at the facility. While the Hg reclamation operations have been stopped, the precious metal reclamation process continues at the facility. In 1998, MERECO’s permitted hazardous waste storage building was leased to Mercury Waste Solutions - New York, Inc. (MWS), which became a co-permit holder at this time. However, in 2003 MWS surrendered its lease for the permitted hazardous waste storage building and ceased all hazardous waste operations.

Currently, two buildings (Figure 3) are present at the site. These consist of the “Phase I & IA Building”, which was constructed in 1991 to replace the “Hand Shop” building and to house most of the company’s operations, and the 2,635 square foot “Container Storage Building,” was leased by MWS and was used as a transfer facility for Hg waste materials until 2003. The Container Storage Building was constructed in 1989 with an impervious base that includes a sump to collect spilled materials (MERECO 1997).

The northern half of the property is covered by asphalt, concrete, and/or the buildings, and is surrounded by a chainlink fence. The remainder of the property is a grassy area between the Container Storage Building and the railroad. This is the area that was excavated, backfilled, and capped with a clay cap during a 1985 excavation and removal of Hg and polychlorinated biphenyl (PCB) contained soil and debris (CDM 2001). The western side of the grassy area slopes down to the bank of the unnamed tributary that feeds Patroon Creek.
Remedial investigation and remediation at this facility is currently governed under the authority of the United States Environmental Protection Agency (USEPA) Superfund program. Originally, it was governed under the authority of the New York State Department of Environmental Conservation (NYSDEC). A hazardous waste permit was issued to the facility by the NYSDEC, under 6 NYCRR Part 373, on December 31, 1996. A permit also was issued by USEPA in September 1997 under the Hazardous and Solid Waste Amendments (HSWA) of the Resource Conservation and Recovery Act (RCRA), which authorized the storage of hazardous wastes and set out conditions for waste minimization, land disposal restrictions, organic air emissions requirements, and other RCRA requirements. The New York State’s 6 NYCRR Part 373 permit authorized the storage of hazardous wastes that are solely regulated by NYSDEC, and imposed general operating conditions upon the facility and corrective action requirements for solid waste management units (SWMUs). The corrective action module of the 6 NYCRR Part 373 permit identified 11 SWMUs and 7 Areas of Concern (AOCs) that required investigation. On May 8, 1998, NYSDEC signed a consent order for corrective action with MERECO and Mercury Waste Solutions. Under the consent order, MERECO would manage the investigation and any required cleanup. However, due to the slow pace of work under the consent order, NYSDEC later requested (in a letter dated November 17, 1999) that the project be transferred to the USEPA for managing the clean-up under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

USEPA accepted this request and sent a follow up response to NYSDEC in which they outlined the steps that will be taken in the CERCLA remedial investigation. As required by the corrective action module of the 6 NYCRR Part 373 permit, the Remedial Investigation and Feasibility Study (RI/FS), for which the USEPA Superfund program now has the lead, would delineate the extent of Hg contamination. This includes the legal bounds of the property, some portion of the properties that adjoin the facility, and contaminated sediments of Patroon’s Creek, which runs along the facility. Additionally, the RI/FS would fully delineate the contaminated ground water plume, which may not have been completely delineated by previous investigations.
Investigations by USEPA and NYSDEC have found Hg and PCB contamination in the soil, ground water, surface water, and sediments. Mercury is the primary contaminant of concern (for this study) due to its high concentration in the soils [more detailed site information can be found in the Remedial Investigation Study (CDM 2003). Other metals (such as lead and/or arsenic) are of secondary interest, and therefore, much less of a concern.

There is a potential for contaminant migration and adverse impacts on downstream recreation areas within the Patroon Creek system. A human risk assessment has been prepared to evaluate the impact of this site on human health.

1.3 EK Technologies and Mercury

The focus of this TSWP is to present an overview of EK technologies, their potential for application to the MERECO soil, and the details of how the study will be conducted. The following sections present a brief overview of the EK technology, Hg chemistry and its sources, results of previous EK studies where Hg was the main contaminant, the objective of the study, and the details of the experimentation associated with the study.

1.3.1 Technology Description

EK remediation of soil is accomplished through the application of a low-voltage direct current (DC) to electrodes placed in a soil matrix (Figure 4). The current density is generally on the order of milliamperes per square centimeters (mA/cm²). EK can be applied either in-situ or ex-situ where the electrodes can be placed either horizontally or vertically. The application of EK has several effects on the soil, water, and the contaminants, including:

- Electromigration
- Electro-osmosis
- Changes in the soil and pore fluid pH
- Electrophoresis

1.3.1.1 Electromigration

Electromigration refers to the movement of cations and anions under the influence of an electrical field. Cations (positively charged ions) tend to migrate towards the negatively charged
cathode, and anions (negatively charged ions) migrate towards the positively charged anode. Cations that migrate include alkali metals (i.e. sodium and potassium), alkali earth metals (i.e. calcium and barium), and transition metals (i.e. cadmium and mercury). Anions that migrate include (but are not limited to): chromates, chlorides, arsenates, nitrates, and phosphates. These ions concentrate in the solutions near the electrodes or may undergo reactions at the electrodes, which can plate the metals onto the electrodes and liberate gaseous compounds.

1.3.1.2 Electro-osmosis
Electro-osmosis is the bulk transport of water that flows through the soil as a result of the applied electrical field. The water movement towards the cathode is the result of the difference of electrical potential across the soil and its pore fluid. This phenomenon is a result of the electrical field effect on the boundary film of water immediately adjacent to the soil particles. The surface of the soil particles exhibits a charge that aligns water molecules (which are polar) with opposite electric charge, thus forming a boundary film of water molecules on the soil surface. The molecules immediately adjacent to the surface are affected by electrical charges. Other water molecules, although associated with the soil, are not tightly bound and may move. In the presence of an applied electric field, these movable water molecules will in general move toward the cathode (Cabrera-Guzman, et al. 1990). Studies indicate that electro-osmosis is most effective in fine-grained soil; however, it is less predominant in sandy soils.

1.3.1.3 EK pH Changes
pH changes occur under the influence of the current as a result of electrolysis reactions at the electrodes. Oxidation of water occurs at the anode and generates hydrogen (H\(^+\)) ions (Equation 1). Generation of H\(^+\) ions produces an acid front, which migrates towards the cathode. In contrast, reduction of water occurs at the cathode and generates hydroxyl (OH\(^-\)) ions (Equation 2), which migrate as a base front towards the anode (Acar and Alshawabkeh 1996).

\[
\begin{align*}
2H_2O - 4e^- & \rightarrow O_2 + 4H^+ & \text{(eq 1.)} \\
4H_2O + 4e^- & \rightarrow 2H_2 + 4OH^- & \text{(eq 2.)}
\end{align*}
\]

The transport of the H\(^+\) ions is approximately two times faster than the OH\(^-\) ions. Thus, the acid front moves at a greater rate than the base front (Acar and Alshawabkeh 1996). Unless the
transport of the proton (H\(^+\) ion) is retarded by the soil buffering capacity, the soil between the electrodes will be acidified. This acidification results in solubilization of contaminants due to desorption and dissolution of species from soil. Once contaminants are present in ionic form in the soil pore fluid, they migrate to the electrode opposite in polarity under the applied electric field and/or via electro-osmosis, leading to their extraction from the soil at the electrodes.

1.3.1.4 Electrophoresis
Electrophoresis refers to the movement of charged and suspended particles under the influence of the electric field. As with electromigration, positively charged particles migrate towards the cathode and negatively charged particles migrate towards the anode. While electrophoretic transport occurs in soil, it is suspected to have less influence on contaminant treatment than the other phenomena discussed above. This is a result of the soil acting as a filter and reducing the range of particle transport.

Of the electrokinetic phenomena discussed, the application of electrokinetic remediation to mobilize Hg in the MERECO soil is expected to be predominantly influenced by electromigration and electro-osmosis. Electrophoresis, for this system, is considered to be a less significant contributor to Hg movement due to the soil's high silt content. Silt typically resides in the interstitial pore space between the sand particles slowing the movement of suspended particles.

1.3.1.5 Other EK Phenomena
Heavy metals tend to precipitate under conditions of elevated pH; thus, as the base front moves through the soil it will meet the advancing cationic metals and acid front. As the acid is neutralized, the metals will precipitate from solution, hence slowing or even stopping the migration of the cations (Acar and Alshawabkeh 1996; Shapiro and Probstein 1993). This precipitation decreases the concentration of the ionic species in the pore fluid, subsequently decreasing the electrolyte strength and producing a zone of low electric conductivity in the soil adjacent to the cathode compartment. The formation of this zone results in a significant increase in the voltage gradient across the soil coupled with an increase in the energy expenditure. Experimental studies indicate that as the electrokinetic remediation process is continued,
eventually the soil will be plugged with precipitating metal complexes, stopping electro-osmotic flow as well as electromigration.

Based on the fundamental understanding of the process, various methods have been proposed to enhance transport and extraction of cationic species under electric fields and to prevent formation of immobile precipitates. The main objective of these methods is to add an amendment that neutralizes the cathode water (the OH⁻ ions produced by EK), thus reducing the number of OH⁻ ions and their transport into the soil. Simultaneously, the counter ion added (anion) as part of the amendment is chosen to maximize the contaminant solubilization. Neutralization of the cathode electrolysis reaction will eliminate the formation of a base front and the subsequent precipitation of soluble metals. In addition, if the counter ion is chosen properly, this may also aid in metal solubilization. Such amendments should assist in decreasing the electrical potential difference across the electrodes, decreasing energy expenditure, and lowering the ultimate cost of using the treatment process.

1.3.2 Hg Chemistry
Mercury, in recent years, has gained environmental notoriety due to its highly toxic nature and relative high mobility. Mercury can exist in many forms in the environment. The environmental effects of Hg compounds are largely dependent upon their solubility. Table 1 presents the solubility product constant (Ksp) and solubility of various Hg compounds found in the environment. As seen in this table, different Hg species have varying solubilities. Mercury’s environmental toxic effects vary, depending on the chemical form of Hg, as well as its route of exposure.

Mercury contamination, at this site, is often found as elemental mercury (Hg⁰) or in a cation form (Hg^{2+}). Factors such as pH, redox potential, and microbial activity effect the stability of the various Hg ionic complexes (i.e. HgS, HgCl₂, and Hg(OH)₂). This can also effect Hg’s toxic effects through the formation of organic complexes like dimethylmercury [(CH₃)₂Hg] that are generated in-situ and highly toxic. Divalent mercury (Hg^{2+}) in the presence of water tends to form strong ligand complexes with chloride ions (Cl⁻), hydroxyl ions (OH⁻), and organic carbon. In contrast, (CH₃)₂Hg is the most toxic form of Hg found in the environment. It can have detrimental effects on the immune system, damage the nervous system, and alter genetic and
enzymatic patterns. (CH₃)₂Hg is readily absorbed and retained in the body (not easily excreted) over longer period of times. Elemental mercury (Hg⁰) is much less toxic than (CH₃)₂Hg, and when ingested, it absorbs slowly and can pass through the digestive system with little adsorption. Other forms of Hg such as HgCl₂, are more easily adsorbed than Hg⁰ (USGS 2000). Thus, the form of the Hg in the soil is extremely important, but difficult and expensive to uncover.

1.3.3 Mercury Solubility
Elemental mercury and salts of mercury (I) and mercury (II) are the main contributors to the pollution at the Colonie site. A basic knowledge of solubility and related solution equilibrium is necessary to model transport and inorganic transformation in aqueous/soil systems. Mercury salt complexes are sparingly soluble due to the varying complexity of their chemistry which include:

a) the reproportionation equilibrium \( \text{Hg}(I) + \text{Hg}^{2+}(aq) = \text{Hg}_2^{2+}(aq) \)
b) the tendency of solid mercury salts to hydrolyze to stable basic solid salts under certain conditions of pH and temperature.
c) the acid nature of mercury cations, especially the Hg²⁺ ion, which results in a number of hydrolysis products.
d) the tendency of the mercury cations to form stable complexes in aqueous solution
e) the activity effects due to ionic strength on the solubility, reproportionation, hydrolysis, complexing, and other equilibria associated with the solution process.

Mercury reprotoportionation equilibrium refers to the formation of mercury (I) and mercury (II) complexes. Many mercury (I) compounds such as Hg₂O, Hg₂S and others are not stable in the presence of water and in contrast mercury (II) compounds are stable but are very insoluble in water. Thus, mercury (I) disproportionation converts the solid mercury (I) compound to the mercury (II) compound in aqueous solutions. A complete discussion of mercury (II) complexes is far too extensive to be presented in this TSWP but numerous sources have been consider and are summarized in Table 1.

The solubilities of Hg salts are pH and temperature dependent (Figures 5 - 6). In the case of carbonates and sulfides, the solubility depends on carbon dioxide or hydrogen sulfide partial pressure as well as the pH. The solubility of elemental mercury in aqueous systems has shown little deviation at various pHs and it is generally listed as insoluble. A commonly accepted solubility limit for elemental mercury is around 70 µg/L. Elemental mercury in groundwater or
soil-equilibrated water may be dissolved at concentrations around 30-70 ppb. The most sighted value for the solubility of mercury in water is 3.03 X10^{-7} mol kg^{-1} or 0.060779 ppm at 298.15°K. This review indicates that Hg can exist in numerous soluble complexes. The most soluble complexes include: mercury (I) chloride, mercury (II) chloride, mercury (I) iodide, mercury (II) iodide, mercury (I) sulfate, mercury (II) sulfide, and mercury (I) sulfite.

1.3.3.1 Mercury (I) Compounds
Mercury (I) chloride, commonly known as mercurous chloride, is a white insoluble crystalline compound. It is manufactured by heating a mixture of mercury (II) sulfate, mercury, and sodium chloride. Mercury (I) chloride is volatile and sublimes. Mercury (I) chloride slowly decomposes in light, and when dissolved in dilute nitric acid mercury (I) nitrate is formed. Mercury (I) nitrate is the only readily soluble salt of univalent mercury. Mercury (I) nitrate hydrolyzes in aqueous solutions to form basic nitrate Hg_2(OH)NO_3. Once in contact with air, mercury (I) nitrate oxidizes to mercury (II) nitrate. Mercury (I) sulfide, Hg_2S, is unstable and decomposes to mercury and mercury (II) sulfide in the presence of hydrogen sulfide.

1.3.3.2 Mercury (II) Compounds
When a strong base is added to mercury (II) compounds the oxide, HgO precipitates. When precipitated from cold solutions mercury (II) oxide is yellow, while hot solutions forms a red precipitant. Mercury (II) hydroxide is unstable. Mercury (II) chloride, HgCl_2, is formed by heating the metal with excess chlorine, by dissolving mercury (II) oxide in hydrochloric acid, or by the reaction of aqua regia and mercury. The common name of HgCl_2 is bichloride of mercury. It is moderately soluble in water, on the order of (0.269 +/- 0.003) mol kg^{-1} or 73,033 ppm, at room temperature. Mercury (II) chlorine hydrolyzes in water and ammonolyzes in ammonia. Iodide ions precipitate mercury (II) ions from solution as HgI_2, which may exists in three crystalline forms, red, yellow, and orange. The solubility of mercury (II) iodide is reported at 0.68 x 10^{-4} mol kg^{-1} or 63ppm, at ambient conditions. In solutions containing mercury salts, the addition of hydrogen sulfide precipitates out black mercury (II) sulfide, HgS. Interaction between mercury chloride and hydrogen sulfide produces precipitations that are first white, then yellow, then red, and ultimately end up as a fine black soil.
(II) sulfide exists in several crystalline forms. At room temperature the stable form is red α-HgS, or cinnabar while the high temperature form is black β-HgS or metacinnabar. The third form occurs at even higher temperatures, hypercinnabar a form of HgS.

1.3.4 Sources of Mercury
Although atmospheric deposition is the dominant source of Hg, manufacturing practices such as chloro-alkali production, metal processing, gold mining and refining, and medical and hazardous waste disposal contribute greatly to anthropogenic Hg environmental concentration. In contrast, natural sources of atmospheric Hg include geological deposits, volcanic eruptions, and volatilization from the ocean floor (USGS Fact Sheet 146-00, Oct. 2000). Figure 7 presents the estimated contribution of anthropogenic Hg.

Coal-fired power plants (CFPP) are the single largest source of Hg pollution in the United States (US). CFPP are responsible for approximately 33% of total Hg emissions. The source of CFPP Hg is the relatively high level of Hg found in the coal feed. This Hg can be volatilized and released to the atmosphere during the combustion process. In addition, medical and hazardous waste incinerators emit Hg when wastes containing Hg are burned. Mercury from medical waste accounts for up to approximately 10% of total anthropogenic Hg pollution. Mercury in medical waste originates from devices such as thermometers and blood pressure devices. Municipal Hg waste accounts for 18% of anthropogenic Hg pollution. Sources of Hg in municipal waste streams stem from discarded appliances such as thermostats, fluorescent lights, and lamps. Chloro-alkali plants account for 5% of the total anthropogenic Hg, and the single largest source of chloro-alkali Hg is from Hg amalgam cells used to manufacture caustic soda and chlorine (USEPA 1977).

1.3.5 EK Treatment of Hg Contaminated Soil
Electrokinetics (EK) is one of the most promising in situ (and ex situ) innovative soil remediation processes. Due to the focus of this study on Hg remediation, it is desired to study the application of EK to the MERECO soil. Unfortunately, only limited studies could be identified that have focused on the EK treatment of Hg contaminated soils. Previous studies by Reddy et al. (2003a), Reddy et al. (2003b), Cox, et al.(1996), Suer and Lifvergren (2003), and
Suer and Allard (2003) have shown relative success in removing Hg containments under the influence of EK treatment.

Reddy et al. (2003a) studied the desorption potential of Hg using three extraction agents [potassium iodine (KI), sodium chloride (NaCl), and ethylene-diaminetetraacetic acid (EDTA)] under the influence of EK. Batch testing was performed on two types of soil, kaolin and glacial till, spiked with mercury (II) to determine its desorption under various pH conditions. This study focused on the treatment of Hg contaminated soil using 0.1 molar (M) concentration of each extractant under a direct current (DC) at a voltage (V) gradient of 1.0 V/cm. The batch testing and bench scale EK testing indicated that for both soils, KI was the most effective extraction agent for enhancing Hg extraction. As shown in Table 2, the treatment effectiveness for the two soils varied. For the kaolin soil, electrokinetic treatment using KI removed approximately 97% of the initial Hg contamination (500 mg/kg of Hg (II)), leaving a residual concentration of 16mg/kg of Hg in the soil. Treatment of the glacial till soil was less effective. In this soil the KI amended KE treatment only removed 56% of the initial Hg (500 mg/kg Hg (II)), leaving a residual of 220 mg/kg of Hg in the soil. Reddy et al. attributed this variability to the difference in soil composition. The glacial till soil had a higher percentage of carbonates and organic matter, which the authors suggested, produced stronger Hg soil adsorption, and the formation of insoluble mercury complexes, thus, resulting in a more difficult to treat soil.

In the study by Cox et al. (1996), a mixture and iodide/iodine (I₂/I⁻) extractant to mobilize Hg from a cinnabar (HgS) spiked soil, was investigated. In this study, a laboratory contaminated loam soil (LCL) and a field contaminated soil from East Fork Poplar Creek in Oak Ridge TN, containing about 4% organic matter was used. This study focused on exploring the effects of varying the extractant concentration on Hg removal. Several test were performed using I⁻ alone and a mixture of I⁻ and I₂. The fist two experiments ran used I⁻ as the extractant. It was determined that very little Hg was mobilized, however improved removal was observed when a 0.1M NaI extraction solution was added to the anode. A second experiment differed only in the fact that an acid solution was slowly added into the cathode in an attempt to complex sulfide released by the cinnabar. It was determined that some Hg mobilization occurred near the anode where oxidizing conditions prevailed. A third experiment consisted of using a combination of I⁻
and I₂ as the extractant. It was observed that mercury removal was dramatically increased (greater 74%) than using I⁻ alone. Under these test conditions it was found that most of the mobile Hg (greater than 90%) could be speciated as HgL⁻. The improved Hg removal was attributed to the oxidative dissolution of cinnabar. In a fourth experiment the conditions were kept as those used for the third experiment except that the current was doubled in an attempt to increase the rate of Hg transport in the soil. While the higher current enhanced the transport of I⁻ ions, little benefit was observed in transporting HgL⁻. Additional experiments were performed with a 0.1 M NaI anode amendment solution and NaCl addition. The purpose of the NaI amendment was to lower the pH of the anode chamber to a value near 10. The goal of the NaI amendment was the oxidation of I⁻ and I₂, with the goal of increasing Hg recovery for the anode solution. However the addition of the NaI solution significantly increased the conductivity of the cell, thus reducing the steady state voltage and slowing Hg transport. This reduced Hg transport resulted because the electro-migration of amendment to the cell decreased and this reduced the dissolution of HgS. Overall, it was found that 90% of Hg could be removed from the LCL Hg contaminated soils using a mixture of NaCl and I₂/I⁻ at a concentration of 0.01 M.

Suer and Lifvergren (2003) investigated EK treatment using I₂/I⁻ amendments (without NaCl) for removing Hg from a contaminated soil collected from chloro-alkali facility. Initial characterizations indicated that the soil contained over 29% rocks, 42% sand and silts, and 29% clays. To assist with laboratory testing, the soil was sieved to remove the large cobbles and rocks. Thus, only the <2.0 mm fraction was used in the laboratory phase of this study. Iodide added to the cathode compartment was transported through the soil and oxidized to iodine near the anode. As a result mercury was mobilized and transported to the anode as a mercury-iodide complex. The EK cell setup was performed in a closed cell, where the air could be pumped and washed in 1 M nitric acid solution. This allowed the scrubbing of volatile elemental mercury from the offgas from the cell. The total duration of the experiment was 122 days, but it was observed that after 5 days more than 50% of the total Hg had migrated to the anode, while another 25% was recovered from the soil water in the vicinity of the anode. This study reports that over 90% of the Hg was removed from the <2.0 mm soil fraction in less than six days using a voltage gradient of less than 1.4 V/cm.
1.4 Study Objectives

The main objective of this study is to determine if EK treatment has the potential for economically removing Hg from the MERECO soil to a level of 31 mg/kg. This study will also attempt to identify chemical additives that enhance the Hg removal and will attempt to track the movement of Arsenic (As) and Manganese (Mn). The time for conducting this study is limited, so the goal of 31 mg/kg Hg soil concentration may be unachievable; therefore, the rate of Hg treatment will be studied. Extrapolation of the result will be used to determine if there is a potential for the Hg treatment goal to be achieved in the field. Specific sub-objectives of this study include:

- Determining if the treatment goal of 31 mg/kg of Hg in the soil can be achieved through the use of EK treatment
- Accessing the relative rate of Hg transport and if possible As and Mn transport.
- Determining the reduction in Hg mobility in the post treated soil as the result of EK treatment
- Screening and identifying at least three amendments that are effective in increasing the solubility of Hg contained in the MERECO site soil
- Determining the effects of amendments on improving the efficiency of the EK treatment
- Identifying obvious adverse effects of using the amendments
- Determining the rate of power consumption for the bench scale study.

1.5 Regulatory Drivers

As stated previously a treatability goal of 31 mg/kg of Hg for the MERECO soil has been established and referenced by CDM (CDM 2004). While the background information used to support the development of this 31 mg/kg was not available at the time this TSWP was prepared, it is assumed that for this site soil treatment is based on Applicable or Relevant and Appropriate Requirements (ARARs) established under the CERCLA as amended by the Superfund Amendments and Reauthorization Act of 1986 (SARA). Under the guidance of CERCLA applicable or ARARs are used to establish site specific clean-up goals. RCRA, the Clean Water Act (CWA), the Safe Drinking Water Act (SDWA), and Federal as well as local ground water protection policies are commonly used in the supporting framework to establish these goals. Thus, for this study, if the treatability goal of 31 mg/kg (wet weight) for the soil can be achieved, it will be proposed that the soil remain in place.
It addition to the 31 mg/kg goal, the Toxicity Characteristic Leach Procedure (TCLP) as outlined in 40 CFR 2003 (CFR 2003a) will also be applied to all treated soil samples. This will be used to determine if soil not meeting the treatment goal of 31 mg/kg will be classified as hazardous, and this also will be compared to the universal treatment standards (UTS) as outlined in 40 CFR 2003 (CFR 2003b). The TCLP leachate concentration for Hg is set at < 0.2 mg/l and the UTS is <0.025 mg/l.

As a final note, Mn and isolated concentrations of As has also previously been identified in the soil at the MERECO Site. Due to these findings, the USPEA has requested that As and Mn concentrations be tracked as part of this study.
Figure 1. Mercury Refining Company (MEREÇO) Site Location (Source: CDM 2004).
Figure 2. Mercury Refining Company (MEREKO) Site Plan (Source: CDM 2004).
Figure 3. Building Locations at the MERECO (Source: CDM 2004).
Figure 4. General Schematic of Electrokinetic Remediation.
Figure 5. The solubility of Mercury in water at varying temperatures (Source: Clever 1985)
The solubility of mercury(II) sulfide (metacinnabar) as a function of pH at 293 K. Circles, data of Schwarzenbach and Widmer (Ref. 160); heavy line, calculated solubilities based on the summation of the concentrations of the complexes as outlined by the light curves. The total sulfide concentration, $H_2S + HS^-$, is 0.02 mol kg$^{-1}$. The concentrations of the complexes were calculated from the equilibrium constants at 293 K given in Table 23. (Figure reproduced from Barnes, Romberger, and Stemprok (Ref. 153) by permission of the Economic Geology Publishing Co.)

The stoichiometries of mercury sulfide complexes at different acidities and sulfide activities at 293 K. The solubility contours are for metacinnabar and may be converted to those for cinnabar by multiplying by 0.8. The lower horizontal dotted line represents a total sulfide concentration of 0.02 mol kg$^{-1}$, as in Fig. 7. (Barnes, Romberger, and Stemprok (Ref. 153), Barnes (Ref. 34). Reproduced from Ref. 153 by permission of the Economic Geology Publishing Co.)

Figure 6. The solubility of various Hg complexes at varying pH (Source: Clever 1985)
Figure 7. Sources and Contributions of Anthropogenic Hg (Source: USEPA 1997).
Table 1. Ksp and Solubilities for Various Mercury Compounds

<table>
<thead>
<tr>
<th>Mercury Compound</th>
<th>Ksp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg₂Br₂</td>
<td>5.6 x 10⁻²³</td>
</tr>
<tr>
<td>Hg₂Cl₂</td>
<td>1.3 x 10⁻¹⁸</td>
</tr>
<tr>
<td>Hg₂CO₃</td>
<td>8.9 x 10⁻¹⁷</td>
</tr>
<tr>
<td>Hg₂(CN)₂</td>
<td>5.0 x 10⁻⁰⁰</td>
</tr>
<tr>
<td>Hg₂CrO₄</td>
<td>2.0 x 10⁻⁹</td>
</tr>
<tr>
<td>Hg₂C₂O₄</td>
<td>2.0 x 10⁻¹³</td>
</tr>
<tr>
<td>Hg₂(OH)₂</td>
<td>2.0 x 10⁻²⁴</td>
</tr>
<tr>
<td>Hg₂(IO₃)₂</td>
<td>2.0 x 10⁻²⁴</td>
</tr>
<tr>
<td>Hg₂I₂</td>
<td>4.5 x 10⁻²⁹</td>
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<tr>
<td>Hg₂O</td>
<td>1.6 x 10⁻²³</td>
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<tr>
<td>Hg₂(N₃)₂</td>
<td>7.1 x 10⁻¹⁰</td>
</tr>
<tr>
<td>Hg₂HPO₄</td>
<td>4.0 x 10⁻¹³</td>
</tr>
<tr>
<td>Hg₂S</td>
<td>1.0 x 10⁻⁴⁷</td>
</tr>
<tr>
<td>Hg₂SO₄</td>
<td>7.4 x 10⁻⁷</td>
</tr>
<tr>
<td>Hg₂SO₃</td>
<td>1.0 x 10⁻⁷</td>
</tr>
<tr>
<td>Hg₂SeO₃</td>
<td>8.4 x 10⁻¹⁵</td>
</tr>
<tr>
<td>HgS red</td>
<td>4.0 x 10⁻⁵³</td>
</tr>
<tr>
<td>HgS black</td>
<td>1.6 x 10⁻³²</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mercury Compound</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg⁰</td>
<td>0.06078 mg/L @ 25°C</td>
</tr>
<tr>
<td>HgCl₂</td>
<td>70,000 mg/L @ 20°C</td>
</tr>
<tr>
<td>Hg₂Cl₂</td>
<td>0.269 mol/kg @ 20°C</td>
</tr>
<tr>
<td>HgO</td>
<td>53 mg/L @ 20°C</td>
</tr>
<tr>
<td>Hg(C₂H₅O₂)₂</td>
<td>400,000 mg/L @ 10°C</td>
</tr>
<tr>
<td>Hg₂I₂</td>
<td>0.000123 mol/kg @ 20°C</td>
</tr>
<tr>
<td>Hg₂I</td>
<td>60 mg/L @ 25°C</td>
</tr>
<tr>
<td>Hg₂(NO₃)₂·2H₂O</td>
<td>Soluble &gt; 100,000 mg/L</td>
</tr>
<tr>
<td>Hg(NO₃)₂</td>
<td>Very Soluble &gt; 500,000 mg/L</td>
</tr>
</tbody>
</table>

Sources: Linke (1958), Dean (1992), and Windhoz (1996)
Table 2. Results of various EK amended studies for Hg contaminated soil

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Soil</th>
<th>Contaminant Conc. (Hg)</th>
<th>Ending Conc. (Hg)</th>
<th>Current/ Voltage</th>
<th>Treatment Efficiency</th>
<th>Extraction Additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reddy et al 2003a and</td>
<td>Kaolin</td>
<td>500 mg/kg</td>
<td>16 mg/kg</td>
<td>1.0 DC/cm</td>
<td>97%</td>
<td>KI</td>
</tr>
<tr>
<td>Reddy et al. 2003b</td>
<td>Glacial Till</td>
<td></td>
<td>116 mg/kg</td>
<td>1.5 DC/cm</td>
<td>77%</td>
<td></td>
</tr>
<tr>
<td>Cox et al. 1996</td>
<td>LCL</td>
<td>500 mg/kg</td>
<td>&lt;450 mg/kg</td>
<td>0.38 – 0.538 ma/cm²</td>
<td>&lt;90%</td>
<td>NaCl/ Iodine/ iodine</td>
</tr>
<tr>
<td>Suer and Lifvergern 2003</td>
<td>Silty-Clay</td>
<td>90 mg/kg</td>
<td>10 mg/kg</td>
<td>30 V</td>
<td>&gt;90%</td>
<td>Iodine/ iodine</td>
</tr>
</tbody>
</table>
2 DETAILS OF THE EK STUDY

2.1 Study Overview

The testing regime proposed to be used in this EK treatability test for the MERECO Hg contaminated soils consist of a five phase approach as shown in Figure 8. These phases involve:

Phase I: Sample Homogenization – In this phase of study all samples will be thoroughly mixed in an attempt to provide a uniform soil for all tests conducted as part of this treatability study.

Phase II: Soil Characterization Methods - During this phase of the investigation, the homogenized samples will be tested to determine how much Hg is contained in the soil, the degree of leaching for the Hg contaminant, and the physical properties of the soil. While the objective of this study is focused on Hg mobility and removal, previous soil analysis have shown that the soil may contain elevated levels of As and high concentrations of Mn. Therefore, As and Mn will also be analyzed to establish baseline levels of these metals in the soil collected from the MERECO site.

Phase III: Batch Tests – In the batch testing phase of the study, tests will be conducted to identify the effectiveness of the Hg extractants, and the effective concentrations of the Hg extractants.

Phase IV: Laboratory Treatability Studies Using EK – In this phase of the study, eight EK test cells will be conducted to determine if EK has the potential to remove Hg and As from the MERECO soil. Mn concentrations will also be tracked.

Phase V: Data Analysis and Reporting – In this final phase of the study, after the data are collected, statistics will be utilized to interpret the data. Graphs and data tables will be prepared and two draft reports will be completed and submitted for review. These reports will consist of a Quality Assurance Report and the Final Treatability Study Report subjected to EPA review policies.
The specifics of each of these phases of study are discussed in detail in the following sections of this report.

2.2 Phase I: Sample Homogenization

The contaminated soil and groundwater to be used in this study will be collected through a separate contract, under the supervision of EPA Region 2. For this study 20 gallons of soil from the “hot spot” and a separate 20 gallons of soil that represents the average Hg site concentration should be collected. The USEPA will be responsible for all soil sampling and it is understood that core samples will be collected. These core samples should be kept refrigerated at (4°C) and shipped to MSU for study. In addition, 55 gallons of site groundwater should be collected in 5-gallon plastic containers, kept refrigerated (4°C), and shipped to MSU for use in this study. Once the soil samples have been received at MSU, all samples will stored at a temperature of 4°C until required for testing. Contaminated soil homogenization will be accomplished by mixing the soil in a large container prior to study. Immediately prior to soil homogenization, the soil will be slowly warmed to room temperature. After warming, the soil will be scalped using a ¼” sieve. Scalping is intended to remove the debris, roots, and cobbles contained in the soil. If the soil is clumpy a determination will be made to either remove the clumps or to break the clumps by hand to pass through the sieve as part of the scalping process. Soil passing the sieve will be used in all testing. This process will remove the large rocks and/or cobbles that may interfere with testing. After the soil is scalped, the soil will be thoroughly homogenized by first placing all the soil in a large plastic container. The soil will initially be mixed by turning the soil with a shovel by hand. After the initial mixing the soil will be placed in 4 – five gallon plastic pails. The contents of 2 of the five-gallon pails will be placed in a Red Lion Big Cat mixer and mixed for two hours. After mixing 1/4 of the mix soil will be placed in 4 separate five gallon containers. This process will be repeated until all soil is mixed and the new five gallon container are filled. After this mixing process all the soil will be placed back into the large plastic container and remixed using a shovel. After mixing samples will be placed back into the 5 gallon containers. Two of the 5 gallon containers will be passed through a soil riffler un-biasly dividing the soil into two portions, and this soil will be placed into 2- five gallon pails. When all soils have been passed through the riffler and stored in the pails the contents of 2 pails will be mixed in the Red Lion Big Cat mixer for two additional hours. This process will be repeated for the remaining two
pails and the contents of all four pails will be placed back into the large plastic container and mixed using a shovel. The entire process will be repeated two additional times to ensure soil homogeneity. This homogenization process is modeled after that of Marino (1997). After homogenization, duplicate samples will be collected from the top third, middle third, and bottom third of each bucket (total 24 samples). These samples of the homogenized soil will be analyzed for moisture content and total Hg, As, and Mn concentrations (Bricka et al. 1992, and USPEA 1998). These data will be used to assess the degree of homogenization and to establish the variability within the homogenized soil. Once the soil is determined to be homogenized, the 5-gallon containers will be sealed and kept refrigerated at 4°C until required for testing. If the variability of the samples is high and homogenization of the soil is determined to be incomplete, the process described above will be repeated.

2.3 Phase II: Soil Characterization and Methods

To gain a better understanding of the soil collected from the MERECO site, a series of tests will be performed to assist in its characterization. The characterization tests to be performed are outlined in Table 3 and briefly discussed in the following sections.

2.3.1 pH (EPA Method 9045C) and Acid Neutralization (Stegmann & Cote 1991)

pH- To measure pH, 20 grams of sample will be added to a 50 ml beaker and mixed with 20 ml of reagent water for 30 minutes. After mixing is stopped, the sample will be allowed to settle. After 30 minutes without agitation, the pH of the slurry will be measured and recorded.

Acid Neutralization – The Acid Neutralization Procedure (ANP) consists of first passing a dried sample of soil through an ASTM #100 sieve. After the soil is sieved, an acid screening procedure is conducted to identify the proper schedule for acid testing. Screening consists of placing 15 g of soil in 3 centrifugal tubes (5 g each). To each tube, the appropriate amount of 2N HNO₃ is added as indicated in the table listed in appendix A. The tubes are shaken and placed in an end-over-end tumbler and rotary extracted for 24 hours. After the tumbling, the tubes are centrifuged and the pH of the supernatant is determined. Based on the pH of the three tubes, the appropriate schedule is chosen as specified in Appendix A – table 7.1.
Based on the screening test 10 tubes are filled with 5g of the sieved soil. To each tube the appropriate amount of water and 2N HNO₃ is added as specified in Appendix A - table 7-2. This mixture is rotary extracted for 48 hours and the centrifuged. The pH is determined and recorded as shown in Appendix A – record sheet 7.

2.3.2 Oxidation-Reduction (REDO) Potential (ASTM – D1498)

Using the solution prepared for the pH measurement, REDOX measurements will be taken as soon as the sample completes the 30-minute settling period. The REDO potential will be measured following the ASTM D1498 protocol using a pH meter coupled with an oxidation/reduction probe.

2.3.3 Moisture Analysis (Bricka et al. 1992)

Moisture content will be conducted following a method outlined by Bricka et al. (1992). This method involves placing 10 grams of soil in a pre-weighed aluminum pan, and recording the total mass of the specimen and pan. The sample is then placed in an oven maintained at 105°C +/-5°C for approximately 24 hours or until constant weight is achieved. After drying for 24 hours, the sample and pan are re-weighed, and moisture content determined as described in the method.

2.3.4 Cation Exchange Capacity (EPA Method 9081 – USEPA 1998)

The Cation Exchange Capacity of the soil will be conducted following USEPA SW846 – 9081 (USPEA 1998). This method involves collecting 4 gram sub-samples of the homogenized soil and placing them in 50 ml centrifuge tubes containing 33 ml of 1.0 N sodium acetate. The samples are then mixed for five minutes using an end over end tumbler. After mixing, the samples are centrifuged until no visible solids remain in the supernatant liquid. The supernatant is decanted and another 33 ml of 1.0 N sodium acetate solution is added to the soil. This procedure is repeated. After the last centrifugation step, the sodium acetate solution is discarded and 33 ml of 99% isopropyl alcohol is added to the sample. The soil is mixed for an additional 5 minutes, the mixture centrifuged and the liquid discarded. As before, this is repeated three times. After washing with isopropyl alcohol, 33 ml of 1.0 N ammonium acetate are added to the soil, mixed and centrifuged. The supernatant from this process is transferred into a 100 ml flask.
This step is also repeated twice. The combined supernatants are diluted to 100 ml with ammonium acetate and this sample is analyzed for Na by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

2.3.5 Acid Digestion and Total Metals Content (EPA Methods 3050 or 3051 + 6010b)  
Samples will be digested according to the SW846 methods 3050 or 3051 (USEPA 1998) for liquids and solids, respectively. These methods are similar and are described in detail in their respective method. In brief, the extraction consists of placing a small portion of liquid (or soil) in a Teflon vessels. The sample is heated to 175°C using a laboratory microwave and held at this temperature for 4.5 minutes. After this is completed, the samples are removed and cooled. After cooling, the sample is filtered using a Millipore HA cellulose acetate filter, then quantitatively transferred to a 100 ml volumetric flask. Using 2% HNO₃, the liquid is diluted to 100ml. This liquid is placed in high-density polyethylene (HDPE) bottles and stored at 4°C until analyzed according to SW846 method 6010b (USPEA 1998) for Hg, As and Mn as listed in Table 3.

2.3.6 Toxicity Characteristic Leaching Procedure (TCLP) (EPA Method 1311 USEPA 1998)  
The TCLP is designed to evaluate the mobility of both organic and inorganic analytes present in liquid, solid, and multi-phase wastes. For this study, the TCLP will only be conducted to determine the leachability of Hg and As. According to the TCLP method, if Hg is detected in the TCLP leachate at concentration in excess of 0.2 mg/l and/or As is detected at 5 mg/l in the leachate, the soil will be designated as a hazardous waste. SW846 method 1311 (USPEA 1998) will be the method used for this testing.

Briefly, this method consists of a pretest to determine which of two extraction fluids will be used for the extraction. One extraction fluid is a glacial acetic acid (CH₃COOH) solution at pH 2.88, and the second contains a mixture of glacial acetic acid and sodium hydroxide (NaOH) at pH 4.95. The selection of the extraction fluid is based on the buffering capacity of the soil.

After extract fluid selection, soil is placed into a HDPE extraction vessel and the appropriate extraction fluid is added to the soil at a 20:1 liquid-to-solid ratio. While the method calls for a soil sample of 100 g, this will be reduced to 12.5 grams (keeping the liquid to solid ration at 20:1) for this experiment to reduce sample use and waste generation. After the soil/extraction
fluid is placed in the extraction vessel, the sample is tumbled end over end for 18 +/- 2 hours at 30 +/- 2 rpm. When tumbling is complete, the mixture is then vacuum-filtered using Whatman GF/F filters, and the final pH of the extract is recorded. Then the filtered samples are preserved by adding concentrated nitric acid to reduce the pH of the sample to < 2.0. Preserved samples are placed in a HPDE bottle and stored at 4°C for analysis. All TCLP sample are analyzed for Hg, As and Mn according to SW846 method 6010b (USEPA 1998).

2.3.7 Particle-Size Analysis of Soils (EM 1110-2-1906 Appendix V-21)
Soil samples will be prepared by thorough air-drying, followed by sieving through standard sieves as detailed in the US Army (1970) report. After the soils have been prepared and sieved, the particle size distribution of the soil will be determined following the hydrometer method of particle-size analysis (ASTM D 422-63). The hydrometer method is a widely used method to quantitatively determine the distribution of particle sizes in soils. The distribution of particle sizes larger than 75 μm (retained on a No. 200 sieve) is determined by sieving, while the distribution of particle sizes smaller than 75 μm (typically the size class ranging from approximately 0.77 to 0.001 mm) is determined by the hydrometer method. One of the principal utilities of the hydrometer method is in obtaining the clay percentage of a soil or sediment. The hydrometer method is based on the relationship between the velocity of falling spheres in a fluid, the diameter of the sphere, the specific weight of the sphere and of the fluid, and the viscosity of the fluid.

2.3.8 Permeability of Soils (EM 1110-2-1906 Appendix VII-13)
The coefficient of permeability is a constant of proportionality defining the ease with which a fluid passes through a porous medium. Permeability will be determined following procedures detailed by the US Army (1970). The method provides for the determination of the coefficient of permeability by a falling-head method. The procedure establishes representative values of the coefficient of permeability for granular soils that may occur in natural deposits. This procedure is limited to granular soils containing less than 10% soil retained on the 75-μm (No. 200) sieve.

2.3.9 Bulk Density (Modified ASTM D-698-91)
The bulk density of treated and untreated soils will be evaluated following procedures modified from ASTM D 698-91. Modifications to the compaction requirement and mold size have been made to the method. ASTM D 698-91 calls for a compactive effort of 12,400 ft-lbf/ft³ to be
applied by a compaction hammer to a soil sample. This is the compaction effort delivered in the standard proctor test. The molds used in ASTM D 698-91 require a large volume of sample and produce a large volume of hazardous waste requiring special handling and treatment. To minimize the amount of material used, ASTM C 109-93 molds will be used in this study. This test involves the use of two 2- x 2- x 2-inch ASTM C 109-93 molds. The base plate from one of the molds is removed and the two molds are stacked on top of each other and secured to the base plate. The reason for this is that the bottom molds can be filled to a point that is above the 2-inch level and can be compacted to where any excess can be trimmed to the desired 2-inch level. This ensures that the cube is filled with material that has been subjected to a known compactive effort.

In addition to using the stacked molds, modifications to the compaction hammer were necessary. These modifications will ensure that the compaction hammer would fit the mold and deliver the required compactive effort. The hammer can be modified by attaching a 1.9- x 1.0- x 5-inch brass head to the end of a conventional ASTM D 698-91 compaction hammer. The procedure for making the samples begins with assembly of the stacked molds. These molds consist of a gang of three 2 x 2 x 2-inch cube samples. For the compaction of the first lift, the sample is placed in each cube until it is filled 3/4 full. The soil is then compacted by positioning the hammer on one side of the mold, raising the weight as far as possible and releasing it. The hammer is moved to the opposite side of the cube and the process is repeated. The hammer is then rotated 90° so that the hammer is on the adjacent side and the weight is then raised and dropped again. This is performed five times for each cube. This process is illustrated below.

After the five compactions, the second lift is compacted by adding additional soil to the cubes until the bottom cube is completely filled and the cube stacked above the first is filled to approximately one quarter of its total volume. This lift is compacted with five additional blows of the hammer as shown below.
Positioning for hammer for the second lift

When the last five compactions are complete, the top mold is removed. There should be a small amount of excess soil over the lip of the bottom mold. This is trimmed off ensuring that the 2 x 2 x 2-inch cube is completely filled. The mold is then taken apart by the use of two latches on either end. This exposes each 2-inch cube of sample of soil. All the soil is transferred to a tared weight boat and the weight of the soil is recorded. The density of the sample is then determined by the formula:

\[
\text{BulkDensity} = \frac{SM}{SV}.
\]  

(3.7)

where:

\[
\begin{align*}
SM & = \text{mass of the sample determined from the test.} \\
SV & = \text{volume of the sample (8 in}^3). 
\end{align*}
\]

2.4 Phase III: Batch Testing

As stated earlier in this TSWP, Hg species will affect the solubility of Hg. While the information regarding the effectiveness of EK on Hg\textsuperscript{0} transport is limited, it is suspected that transformation of Hg\textsuperscript{0} to an ionic form will increase the effectiveness of EK treatment. In an attempt to address this issue batch test are proposed.

Preliminary test indicate that solutions of NaCl, and KI are effective in transforming Hg\textsuperscript{0} to Hg\textsuperscript{2+} EDTA has also shown to significantly effect the solubility of Hg. In an effort to determine the effective concentration and /or combinations of such amendments, batch screening tests are proposed. This test will take the form of batch shake (isotherm) tests as describe as follows.
Batch testing will be performed on mercury-contaminated soil to identify and evaluate effective extractants as well as their concentrations capable of desorbing Hg from the contaminated soil. Extractant concentration will be optimized by maximizing Hg extraction. Batch shake (isotherm) method as outlined by Bailey (1994) and Neal (1995) will be followed using site groundwater and the liquid. A minimum of five extraction agents will be selected for batch testing including chelators such as: EDTA, NaCl, and KI. By varying the pH of the soil-solution mixtures along with the concentration of the extractant, the optimal pH and extractant concentration will be determined. For this study, pH with and without the amendments will be investigated. Prior investigations by Reddy et al. (2003a) suggest that KI, followed by Na-EDTA was an effective extractant combination for EK applications (Reddy, Chaparro, Saichek 2003). Unfortunately, little information regarding the concentration utilized for this study is available. In addition, it is known that the properties of the soil will affect the chelator’s effectiveness. Thus, a series of batch tests are proposed to screen the extractants and to develop a preliminary assessment of the chelator’s ability for Hg solubilization and cost effectiveness. As part of this study As concentrations will also be measured and tracked.

2.4.1 Sample Preparation
The first step in the batch test is to determine the solid-to-liquid (S/L) ratio to be utilized for study. Previous studies indicate that S/L ratios ranging from 0.01 – 1.0 are effective using an extraction period of 24 hours to achieve equilibrium (Neale 1995, and Bailey 1994). For this study, the optimal S/L ratio will be studied using the KI /NaCl/ EDTA extractant combinations.

Batch extractions studies will be conducted by placing 5 grams of soil (+/-0.01g) into a 125-ml Nalgene bottles and adding the desired concentration of the extraction agent and site groundwater to the soil. The pH will be measured and adjusted between the range of 2.0 - 8.0 (the operational pH of the EK treatment) with dilute nitric acid. The total volume of the soil/chelator/acid mixture will be kept constant by diluting the mixture to 100 ml. After dilution, the pH will be recorded as the initial pH. The bottles will be tightly capped and tumbled in an end-over-end fashion for at least 24 hours at 18 +/- 2 revolutions per minute (rpms). A contact time of 24 hours is assumed to be adequate but regardless, the time for equilibrium will be verified. Periodically the tumbler will be stopped, and the pH and redox potential of the mixture will be measured and recorded. The pH value will be compared to the desired final pH value,
and the pH will be adjusted. At the end of the 24 hour extraction period, the pH and redox will be measured, and if the pH is not at the desired value additional pH adjustment and tumbling will be continued until the final pH values is correct. After the batch samples complete the tumbling cycle, the soil will be separated from the liquid by passing the liquid through a Millipore Type HA 0.45-micron filter. Filtration will be conducted using a vacuum filtration device, and the liquid will be preserved at 4°C until required for Hg analysis (<28 days). This liquid will be analyzed by ICP-AES according to EPA method 6010B. Using the data from these batch absorption tests, extraction isotherms will be plotted and the best complexing agent (highest mercury solublization) will be identified for EK testing.

2.5 Phase IV: Laboratory Treatability Studies Using EK

After the three most effective Hg extraction agents for removing Hg from the MERECO soil have been identified, a series of laboratory EK treatability tests will be conducted. Currently it is proposed to run four sets of experiments as listed below:

- Duplicate EK cells using un-amended soils
- Duplicate EK cells using soils amended with Hg extractant 1 and cathode buffering
- Duplicate EK cells using soils amended with Hg extractant 2 and cathode buffering
- Duplicate EK cells using soils amended with Hg extractant 3 and cathode buffering

Details of the EK experimental set-up and sampling are provide in the following sections.

2.5.1 Cell Fabrication

A schematic diagram of the entire cell is shown in Figure 9 and a photograph is presented in Figure 10. This cell is constructed of 3” inside diameter clear polyvinyl-chloride pipe. As shown in Figure 9 this cell is divided into three parts; a) anode half-cell b) cathode half-cell, and c) middle cell section that holds the soil. The middle cell section measures one foot in length. Along the longitudinal axis of the middle cell section, three pore sample ports were placed at 3” intervals. As illustrated in Figure 9, the sample ports are used to sample the soil pore fluid to determine the ionic mobility of Hg, As and Mn. Figure 11 presents a photograph of the middle section of the cell with pore sampling ports and secondary electrode ports. Pore sample ports will consist of a Dionex Model 38260 end line filter which will be connected to low pressure
Teflon® tubing (Dionex Model 14157), and a ¼”-28 fitting (Dionex Model 37627). These ports will be plugged using Dionex Model 37628 ¼-28 plug fittings. These plugs will be removed when collecting the pore fluid sample.

Secondary ports will be placed along the cell above the pore sample ports and fitted with 1/8” male NPT-fittings, as shown in Figure 11. This serves as an insertion point for secondary electrodes as well as sealing around the electrode preventing pore fluid leakage. These secondary electrodes are made of 0.03” tungsten wire and will be used to measure the voltage gradient across the cell.

The anode and cathode half-cells are shown in Figure 9. These will be constructed of clear PVC-tees glued to flanges on one end and capped with blind flanges on the other end. All flanges will be attached to the middle cell section using 5/8” stainless steel bolts. A 3/16” neoprene-gasket will be placed in between the middle section flange and the anode half-cell flange (cathode half cell flange) to seal the cell. To hold the electrodes in place during the experiment, a small piece of PVC-pipe will be cut, and a slot will be made in this pipe. This slotted piece will be glued to the bottom center of the PVC-tee, as illustrated in Figure 9, and the electrode is placed into this slot. To separate the soil from the respective electrode reservoir fluids and hold the soil in place, 1/8” sintered polyethylene (PE) plates will be placed at the junction of the middle cell and the electrode section. These sintered PE plates will be cut to circular sections, 3.25” in diameter, which fit into the center opening of a neoprene gaskets. These neoprene gaskets with the PE plates will be used to hold the soil in place and seal the cell while permitting liquid to move from the half-cell to the middle section of the cell.

2.5.2 Electrodes
The electrodes will be constructed of a proprietary resin-impregnated carbon material purchased from Bay City Carbon, Michigan. Disks 2.5” in diameter and 0.4” in thickness will be cut from this material and used as electrodes. Tungsten-clean-straight wire purchased from Ed Fagan, Inc., will be used as a connecting wire and will be fastened to the carbon electrode material using a conductive-silver-epoxy purchased from McMaster-Carr Supply Company. A 0.059” diameter, 0.5” deep hole will be drilled in the carbon electrode and the wire will be placed into the hole and sealed with silver epoxy. After excess epoxy is removed from the surface of the electrode,
the electrodes will be baked in the oven for 12 hours. Then, the electrodes will be cooled and heat-shrinkable tubing will be applied to the tungsten wire connecting the wire to the electrode, insulating the wire. To seal the junction between the heat-shrinkable tubing and the electrode, silicon caulk will be applied and allowed to cure for 24 hours. This process will be used to prepare all the anode and cathode electrodes used in this study.

2.5.3 Power Supplies and Wiring
Direct current (DC) power supplies (Agilent Technologies Model E3612A) will be used for this study. The power supplies can be operated using either constant current or constant voltage. Power supplies are to be connected to the half-cells electrode wire using 12-gauge braided wire. As described earlier, clean-straight tungsten wire will secure into the NPT-fittings along the cell and will be used for measuring the voltage gradients. A 12-gauge braided wire will connect the tungsten wire and a voltage-measuring block, as shown in Figure 10. Voltage gradients across the cell will be measured by connecting a Wavetex Model Meterman 23XT Multimeter to the appropriate leads on the voltage block.

2.5.4 Experimental Procedure
This effort will focus primarily on the transport of elemental Hg and Hg-complexes, from the soil under the application of an EK field. The batch tests will be performed on contaminated soil to determine the most effective pH and chelator concentration for Hg solubilization. Once optimal conditions (conditions where Hg extraction are maximized in the batch tests) are established, EK testing will commence. The testing will involve running the EK cells as described below.

2.5.4.1 Cell Setup
The first step in conducting an experimental run is cleaning the cell. Cleaning consists of removing any solids or soil using soap and water. After removing the soil, the cell is rinsed with a 20% nitric acid solution followed by triple rinsing with deionized water. After the cells are cleaned, the empty cells are readied by securing the pore fluid sample devices in the ports, as well as secondary electrodes. Then, the middle section of the cell will be placed in a vertical position with one end of the cell sealed with a blind flange. At the open end of the cell, the soil
will be compacted in lifts using the standard proctor capacitive effort as described in the Bulk Density test of this TSWP (section 2.3.8). Excess soil at the top of the cell will be removed after compacting the soil, and the end of the cell will be cleaned. After loading, the top end of the cell will be sealed with a blind flange and the cell will be placed in a horizontal position. After filling the column with soil, the cell will be rotated axially every 8 hours over a 24-hour period to ensure uniform moisture content across the cell.

After the 24-hour period, the blind flanges from the middle cell section will be carefully removed so that the soil will not be disturbed. Anode and cathode half-cells will be attached to the middle section of the cell and secured with a gasket fitted with sintered PE plate. The secondary electrodes, fitted in their respective ports along the cell, will then be secured to a voltage-measuring block, as shown in Figure 10. The carbon electrodes will be placed in the slots in the half-cells. Then, the cathode and anode half-cells will be filled with site groundwater. To avoid migration of ions by hydraulic gradient, the half-cells will be filled at the same time, and the liquid levels in both the half-cells will be maintained at the same level while being filled.

2.5.4.2 Cell Operation
After the cells are assembled and the anode and cathode half-cells filled, the pH in the cathode half-cell will be adjusted by adding 1 molar nitric acid (HNO₃) as determined in the batch test. Samples will be collected from the sample fluid ports to monitor the ionic transport. The power will be switched on and set to operate under constant current conditions. The pH in the cathode half-cell will be maintained at the desired pH during the experiment using a pH control and nitric acid addition. The hydraulic gradient in the half-cells will be manually maintained at zero by monitoring the levels of the half-cells at regular intervals. All liquids added to the cell will be logged to assist with the mass balance calculations.

2.5.4.3 Analysis and Measurements During Experiments
To evaluate Hg, As and Mn movement along the cell, liquid samples will be drawn from the middle cell’s section, pore sample ports. Samples will be collected (as required to measure metal’s transport) by removing the pore sampling port’s plug fittings quickly, to avoid considerable time lag in the sample collection across the three ports. Approximately 10-ml of the pore fluid will be collected using gravity flow into 15-ml conical graduated tubes. In addition,
samples from the anode and cathode half-cells will also be collected. Anode and cathode half-cell solutions will be mixed (using a glass rod) prior to sampling to ensure uniform ion concentrations. After the half-cell solutions are mixed, the 10 ml of sample will be collected. All liquid samples will be analyzed using ICP-AES according to Method 6010B (USEPA 1998) for Hg, As and Mn. These samples will also be analyzed to determine the concentration of amendments according to the methods listed in Table 3. The pH of all liquid samples will also be measured.

In addition, the voltage across the cell will be measured at each sampling period. The anode will be used as the reference electrode while taking the voltage gradients. Current supplied to the cell and the voltage gradients across anode-port1 (A-V1), anode-port2 (A-V2), anode-port3 (A-V3), and anode and cathode (A-C) will be measured using a digital multimeter (Allied Electronics, Inc, model 23XT).

2.5.4.4 Cell Breakdown and Post-Run Analysis

Prior to or at 75 days of operation, the power supplies will be turned off and the electrode wires disconnected from the carbon electrodes. Anode and cathode solutions will be collected into 5-liter containers from the half-cells simultaneously by tilting the cell slowly without disturbing the soil contained in the middle cell section. Approximately 200 ml of these solutions will be transferred into a 250-ml high-density polyethylene (HDPE) bottles. Then each solution will be digested according to EPA method 3050 (US EPA 1998). After the liquid from each half-cell is removed, the half-cells will be detached from the middle cell section carefully so that the soil will not be disturbed. Then the pore fluid sampling port devices and secondary ports will be removed from the middle cell section. The soil will then be pushed from the cell’s middle section as a core and this core will be divided into 4-equal sections and transferred separately into plastic containers. After the soil is homogenized, 3 - five gram of sub-sample will be taken from each container and dried to determine the moisture content. To determine the Hg As, and Mn concentration of the soil, separate sub-samples of the homogenized soil will be collected from each plastic container and will be digested according to EPA method 3051 (USEPA 1998) and analyzed by ICP-AES (USEPA Method 6010B) for Hg, As and Mn as well as the amendments.
The results of this test will be used to determine the rate of Hg, As and Mn transport and the removal efficacy of Hg and As from the soil. Liquid as well as ion mass balances will be conducted and closure of the mass balances will assist in data interpretation.

A minimum of 125 liquid samples and 12 soil samples will be collected for each run. Thus, a total of over 1,000 liquid samples and 96 soil samples will be collected and analyzed for Hg as part of this laboratory EK treatability portion of the study. The collected samples will be analyzed for pH and Hg, As and Mn content.

2.6 Phase V: Data Analysis and Reporting

Periodically, as results become available, the USEPA Remediation Program Manager will be briefed via telephonic communications with regard to the progress of treatment. Written monthly progress reports will also be supplied to the USEPA Remediation Program Manager. When the final results are available an Analysis of the Variance (ANOVA) statistical procedure will be used to determine if there is a significant difference between the various treatments. The final result of this study will be documented in a final report and provided to EPA for review and comment in accordance to EPA review protocol.
2.7 Schedule and Milestones

While the start date for this study is yet to be determined the following schedule is offered regarding the TSWP. This table includes the projected month the task will be completed and the products that will be provided to the USEPA.

<table>
<thead>
<tr>
<th>Item</th>
<th>Description</th>
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<tr>
<td>a.</td>
<td>Approval of TSWP</td>
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<td>b.</td>
<td>Sample Collection and Shipment to MSU (onsite visit by MSU during sampling activities)</td>
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<td>c.</td>
<td>Receipt of Samples at MSU First formal briefing to USEPA project team</td>
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<td>d.</td>
<td>Sample Homogenization</td>
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<td>e.</td>
<td>Sample Characterization</td>
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<tr>
<td>f.</td>
<td>Batch Testing Second formal briefing to USEPA project team</td>
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<td>g.</td>
<td>Figure 1. The solubility of Mercury in water at varying temperatures Third formal briefing to USEPA project team</td>
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<td>Figure 1. The solubility of Mercury in water at varying temperatures Fourth formal briefing to USEPA project team</td>
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<td>i.</td>
<td>Data analysis</td>
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<td>j.</td>
<td>Draft Report and Review USEPA</td>
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<td>k.</td>
<td>Final Report provided to USEPA</td>
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</table>
Figure 8. Flowchart of the laboratory EK experimental runs.
Figure 9. Drawing of the EK cell.
Figure 10. Photographs of an assembled EK cell.
Figure 11. Photograph of the middle section of cell.
Table 3. Test Methods for Soil Characterization and Liquid Analysis

<table>
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<tr>
<th>Soil Characterization Parameter</th>
<th>Method and Citation</th>
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<tr>
<td>PH Acid Neutralization Procedure</td>
<td>EPA Method 9045c (USPEA 1998)</td>
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<td>REDOX</td>
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<td>Moisture Analysis</td>
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<td>Cation Exchange Capacity</td>
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<td>Liquid</td>
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<td>Soil Analysis</td>
<td>EPA Method 6010b (USPEA 1998)</td>
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<td>I- and Cl-</td>
<td>EPA Methods 9056 and 9253 (USEPA 1998)</td>
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<td>TCLP</td>
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<td>Particle Size Distribution</td>
<td>EM 1110-2-1906 Appendix V-21 (US Army 1970)</td>
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<td>Bulk Density</td>
<td>Modified ASTM D 698-91 (ASTM 1991)</td>
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3 REFERENCES


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www.coe.neu.edu/~aalsha/shortcourse.pdf


Marino, Michael Angelo. 1997. “Evaluation of physical separation techniques to remediate heavy metal contaminated soil form select military installations,” Thesis, Mississippi State University, Mississippi State, MS.


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Appendix A-
Acid Neutralization Capacity Procedure
Method 7.0

Stegemann and Cote (1991)
7.0 ACID NEUTRALIZATION CAPACITY

7.1 Apparatus and Chemicals

Drying oven set at 60 ± 3°C (in a fume hood).
Grinder capable of reducing sample to -100 mesh.
ASTM No. 100 (150 μm) sieve.
Balance, having a precision of ± 0.01 g.
Two 50 ml burets, each having a precision of ± 0.05 ml.
2 N nitric acid. (128 ml Reagent grade conc. HNO₃)
Distilled water.
50 ml beaker.
Eleven 50 ml polypropylene centrifuge tubes with round bottoms and leak proof screw closures.
HBS-design rotary extractor.
Centrifuge.
pH meter (with electrode).

7.2 Procedure

This test shall be started between 56 and 84 days after sample preparation. 150 g of crushed sample (dry weight) from any type of mold may be used.

Dry the sample to constant weight at 60 ± 3°C. Grind the dried sample to pass on ASTM No. 100 sieve.

7.2.1 Selection of an Acid Addition Schedule

Rinse three centrifuge tubes with distilled water, and label them with the sample identification number, and with the numbers 1, 2, and 3. Weigh out 5.0 g of the ground sample for each test tube, and add the appropriate amounts of 2N nitric acid and distilled water as indicated in Table 7.1. Shake each test tube manually.
Place the centrifuge tubes in the rotary extractor and allow to tumble for 24 h. After removing the tubes from the tumbler, centrifuge for 10 minutes at 14 000 rcf. Measure the pH of the supernatant in each tube and record the values on Record Sheet 7.

For the procedure in Section 7.2.2, choose the schedule of acid addition from Table 7.2 with the same number as the tent tube of lowest number in which the final pH of the supernatant was less than 3.

### 7.2.2 Measurement of Acid Neutralization Capacity

Rinse all ten of the centrifuge tubes with distilled water. Label each tube with the sample identification number, and the numbers from 0 to 10.

Weigh out 5.0 g of the ground sample for each tube. Then using the 50 mL burets, measure out the appropriate amounts of distilled water and 2 N HNO₃ for each tube as indicated in Table 7.2, using the schedule chosen in Section 7.2.1. Shake each test tube manually until the contents appear mixed.

Place the centrifuge tubes in the rotary extractor and allow to tumble for 48 ± 1/2 h at room temperature. Record the room temperature on Record Sheet 7. After removing the tubes from the tumbler, centrifuge for 10 minutes at approximately 14 000 rcf. Measure the pH of the supernatant in each tube and record the value on Record Sheet 7. The extraction liquid may be filtered and acidified to pH 2 and stored in a plastic bottle for metals analysis if so desired.
### TABLE 7.1

<table>
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<tr>
<th>Centrifuge Tube No.</th>
<th>Amount of Distilled Water (mL)</th>
<th>Amount of 2N HNO₃ (mL)</th>
<th>Amount of 2N HNO₃ (meq/g dry waste)</th>
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### TABLE 7.2

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RECORD SHEET 7: ACID NEUTRALIZATION CAPACITY

Sample Id. No.: ________________________________
Date of Test: _________________________________
Laboratory: _________________________________
Technician: _________________________________

Section 7.2.1
pH in Centrifuge Tube No. 1: ________________________________

Section 7.2.2
Room Temperature (°C): ________________________________

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7.4