ELECTRIC POWER
RESEARCH INSTITUTE

Advanced Oxidation Techniques for Soils Containing Manufactured Gas Plant (MGP) Hydrocarbons

1010139

Advanced Oxidation Techniques for Soils Containing Manufactured Gas Plant (MGP) Hydrocarbons

1010139

Technical Update, March 2006s

EPRI Project Manager

J. Lingle

ELECTRIC POWER RESEARCH INSTITUTE
3420 Hillview Avenue, Palo Alto, California 94304-1395 ▪ PO Box 10412, Palo Alto, California 94303-0813 ▪ USA
800.313.3774 ▪ 650.855.2121 ▪ askepri@epri.com ▪ www.epri.com

DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

THIS DOCUMENT WAS PREPARED BY THE ORGANIZATION(S) NAMED BELOW AS AN ACCOUNT OF WORK SPONSORED OR COSPONSORED BY THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, THE ORGANIZATION(S) BELOW, NOR ANY PERSON ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS DOCUMENT IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

(B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS DOCUMENT OR ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT.

ORGANIZATION(S) THAT PREPARED THIS DOCUMENT

PRD Tech, Inc.

This is an EPRI Technical Update report. A Technical Update report is intended as an informal report of continuing research, a meeting, or a topical study. It is not a final EPRI technical report.

NOTE

For further information about EPRI, call the EPRI Customer Assistance Center at 800.313.3774 or e-mail askepri@epri.com.

Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc.

Copyright © 2006 Electric Power Research Institute, Inc. All rights reserved.

CITATIONS

This document was prepared by

PRD Tech, Inc.
1776 Mentor Avenue; Mail Box Suite # 107
Cincinnati, OH 45212

Principal Investigator
R. Govind

This document describes research sponsored by the Electric Power Research Institute (EPRI).

This publication is a corporate document that should be cited in the literature in the following manner:

Advanced Oxidation Techniques for Soils Containing Manufactured Gas Plant (MGP) Hydrocarbons, EPRI, Palo Alto, CA: 2006. 1010139.

ABSTRACT

This report presents the results of a bench-scale experimental study using a combination of chemical oxidation and electrotreatment of polycyclic aromatic hydrocarbon (PAH) contaminated soils from former Manufactured Gas Plant (MGP) sites. Electroosmotic movement of water and movement of charged surfactant micelles due to the electro-gradient were used to introduce persulfate oxidant into the contaminated soil matrix. Results showed that greater than 80% removal of the PAHs were obtained in 20 days of treatment time. Experiments with aqueous ozone, introduced as gas aphrons into the soil matrix, demonstrated 100% removal of the PAHs present in the contaminated soil. These experiments show that combining chemical oxidation with electrotreatment can be a viable treatment strategy for PAH contaminated soils.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

1
INTRODUCTION

Manufactured gas plants (MGPs) played a key role in the modernization of the United States. From about 1850 to 1950 these plants manufactured illuminating and heating gas from coal or oil and literally lighted the way for modern civilization. It is estimated that there were from 1100 to 3000 MGPs in the United States (Harkins *et al.*, 1988). Coal tar with its polycyclic aromatic hydrocarbon (PAH) and benzene/toluene/ethylbenzene/xylene (BTEX) constituents is often the primary cleanup issue at MGP sites.

Most in-situ oxidation studies have addressed removal of the contamination species that are dissolved in the aqueous phase and do not address the difficulties associated with a true separate phase. Oxidation reactions chemically convert contaminants to less toxic compounds that are more stable, less mobile, and/or inert. The oxidizing agents most commonly used for treatment of contaminants are ozone, hydrogen peroxide, or sodium persulfate. Chemical oxidation is a short-to-medium-term technology. The main problems in chemical oxidation are: (1) subsurface heterogeneity can cause uneven distribution of oxidants; {2) there is no control of the subsequent movement of the oxidant after its release. Hence, recirculation is sometimes the preferable delivery system.

Most PAHs have extremely low aqueous solubility, low vapor pressures, and high octanol/water partitioning coefficients (Peters and Luthy, 1993; Haines and Sandler, 1995). As a consequence of these chemical properties, PAHs have a high affinity for association with organic carbon material (humus) in soil (Alexander, 1995). In addition to the strong sorption of PAHs to soil particles, PAH mixtures/tars behave in such a way that upon exposure to air and water, low molecular weight compounds with comparatively high aqueous solubility and volatilities are preferentially lost resulting in the formation of semi-rigid skin-like films at tar-water interfaces (Luthy *et al*., 1993). These films are composed of complex, high molecular weight, water-insoluble compounds. The development of these interfacial skins can result in reduced mass transfer rates of even low molecular PAHs into adjacent water layers. With MGP soils, which most often have been contaminated and subsequently weathered for decades, the sorption of PAHs to soil and the formation of interfacial films combine to severely limit the bioavailability of PAHs in soil and even complicates the accurate analysis of PAHs in soil (Alexander, 1995; Hatzinger and Alexander, 1995).

Coal tar wastes at Manufactured Gas Plants (MGPs) are mainly composed of complex mixtures of polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs) and several inorganic chemicals. Currently, there are no demonstrated, effective *in-situ* solutions for treating MGP contaminated soils with low hydraulic permeability conditions, due to the nature of the tars and the Dense Non-aqueous Phase Liquids (DNAPL) present at these sites.

Remediation technologies for contaminated soil are broadly classified into two major groups: (1) in-situ treatment technologies and (2) ex-situ treatment technologies.

The primary problems in in-situ bioremediation are: (a) low conversion rates due to limited availability of oxygen and nutrients; (b) difficulty in introducing oxygen and nutrients, especially in soils with high clay content, which exhibit low hydraulic permeability; and (c) strong adsorption of the contaminants to the soil phase, which limits the bioavailability of the chemicals. Ex-situ remediation technologies are affected from similar constraints clayey soils, with hydraulic conductivities in the order of 10^{-8} cm/sec, require enormous amounts of pumping pressure (up to 800 atm) to obtain significant groundwater movement. Therefore, conventional removal processes are often impractical and highly costly for such soil media.

Technologies that have been tried with limited success include:

- Thermal processes for DNAPL remediation
    - ➢ Steam or hot water heating
    - ➢ Six Phase Heating (SPH) and Resistive heating
    - ➢ High temperature conductive heating processes
    - ➢ Low temperature solidification
    - ➢ EPRI thermal oxidation process
- Electro processes for DNAPL treatment
    - ➢ Lasagna Process (Electro-osmotic)
    - ➢ In-situ applications of electro-kinetic enhanced processes
- Other processes under development
    - ➢ In-situ polymer or solvent flushing
    - ➢ Chemical oxidation (In-situ)
    - ➢ Enhanced desorption and bioremediation

The objective of this study was to investigate the feasibility of hybrid technologies for treating contaminated soils. Hybrid technologies use a combination of treatment approaches to increase their efficacy, range and kinetics. The work consisted of a bench-scale feasibility study to investigate the use of free radicals and their movement by electro-kinetics to remediate PAH contaminated MGP soils. This study consisted of an *in-situ* electrokinetic process involving application of low intensity direct electrical current across electrode pairs placed in the test cell on each side of a contaminated volume of soil. The electrical current induced electro-osmosis and ion migration which, coupled with application of surfactant or chemical oxidants, has been investigated to treat PAH contaminants in MGP soils. This process is especially unique due to its ability to work in low permeability soils, applicable to a broad range of organic and inorganic contaminants, with the advantages of uniform water flow, no channeling, control of flow direction and low energy consumption.

Background

Groundwater in its natural state is consistently moving. This movement can be described by basic hydraulic principles. The flow of groundwater through porous media can be expressed by Darcy's law:

$$Q = K_h \cdot A \cdot \frac{dh}{dL} \qquad (1)$$

$$V = \frac{Q}{A} = K_h \cdot \frac{dh}{dL} \qquad (2)$$

Where:

Q is the groundwater flow rate (m^3/s)

K_h is the hydraulic conductivity (the measure of the ability of the porous medium to transmit water (m/s)

A is the cross-sectional surface area (m^2)

dh/dL is the hydraulic gradient in the flow direction

V is the apparent velocity (m/s)

The actual velocity of the fluid particles varies from point throughout the medium and can be evaluated by dividing the apparent velocity with the effective porosity. Darcy's law serves as the basis for present-day knowledge of groundwater flow. It indicates that groundwater flows in accordance to the hydraulic gradients and that the fluid velocity depends on certain properties of the soil medium and the pore fluid. In the utilization of Darcy's law, it is important to know the validity range within which it is applicable. Laminar flow and saturation of the soil mass are prerequisites for using Darcy's theory. For almost all natural groundwater motion, the flow pattern can be assumed laminar. In case of unsaturated soils, the hydraulic gradient and the effective porosity need to be modified according to the moisture content of the soil area.

The difference in the hydraulic head across the soil medium forms a hydraulic gradient. In fluid mechanics the mechanical energy content of the fluid is described by hydraulic head,

$$h = \frac{V^2}{2g} + \frac{p}{\rho \cdot g} + z \qquad (3)$$

Equation 3 shows that the hydraulic head is the sum of the velocity head, which is the kinetic energy per unit weight, the pressure head, which is a measure of the ability of the fluid to do work, and elevation head, which is the potential energy per unit weight. For subsurface flow the velocity head is negligible. In case of a horizontal field the elevation head can be neglected as well. Thus the hydraulic head becomes a direct measure of the externally applied pressure across the soil.

Contaminant Transport and Treatment

Contaminant transport in groundwater can be described by a partial differential equation, including a velocity term, a dispersion/diffusion term, and a retardation term. The equation can be as follows below in one dimension:

$$\frac{\partial}{\partial x}[D \cdot \frac{\partial c}{\partial x}] - \frac{\partial}{\partial x}(c \cdot V) - \lambda \cdot c \cdot R = R \cdot \frac{\partial c}{\partial t} \qquad (4)$$

Where

D is the dispersion coefficient (m^2/s)

c is the contaminant concentration (g/l)

R is the retardation factor

λ is the decay constant (i.e. biological, physical, or chemical decay, l/s)

t is the time (s)

x is the Cartesian coordinate

Experience has shown that pump and treat, as well as soil vapor extraction systems, can be very effective for the removal of groundwater contaminants. However, in low permeable, fine grained soils, (i.e. clay) these processes are often ineffective and very costly. The primary reason for this is the low hydraulic conductivity (10^{-7}-10^{-8} cm/s) of such soils. The dependence of the hydraulic conductivity to the grain size has been studies in details and can be obtained from hydrogeology literature (Shephard 1989, Mitchel 1976). Results demonstrate that particle sizes in the order of micrometers will result in very low hydraulic conductivities. Therefore, in order to get significant groundwater movement, enormous pressure needs to be applied across the contaminated soil area. (10^{-2}-10^{-3} atm)

Remediation methods such as in-situ chemical treatment or in-situ bioremediation suffer from the similar limitation of moving nutrients, oxygen and treatment chemicals through low permeable areas using hydraulic gradients. Although fine grained soils create difficulties in promoting groundwater movement and chemical transport, they are generally efficient in sequestering large quantities of inorganic and organic contaminants. (Hatfield, 1993) Hence, there exists a need for cost effective and efficient technologies to rapidly remediate low permeable soils in-situ.

Theory of Electrokinetic Remediation

Electrokinetic remediation can be broadly defined as the removal of contaminants under the action of an electrical field applied across the soil-water system. The phenomenon consists of a complex set of mechanisms which lead to the movement of the pore fluid. The principle processes involved are electroosmosis, electromigration, chemical diffusion and electrophoresis. The contribution of each of these mechanisms to the remediation process varies with the type and activity of soil medium, electrolyte concentration in the pore fluid, amount of colloids in the system, and properties of the target contaminant.

Electroosmosis can be defined as the movement of the fluid phase under the impact of a DC electrical field, while the solid phase remains stationary. If electric potential is applied across a soil mass that contains an electrolyte solution, the positive ions (cations) move towards the cathode and the negative ions (anions) move towards the anode. In ion exchanging soils such as clays and silts, there is a net negative charge on the soil particles. Hence, an excess amount of cations are present to neutralize the medium. The majority of these cations are positioned near the charged surface of the soil and as they migrate towards the cathode they drag pore fluid with them.

Electroosmosis was first discovered by Reuss in 1808. In 1879, Helmholtz provided a mathematical basis for the phenomenon and explained it analytically His description, later refined by Smoluchowski in 1914, is considered as the fundamental model of electroosmosis and is still extensively used in electrokinetic studies (Smoluchowski 1921). The Helmholtz-Smoluchowski equation is as follows:

$$Qe = \left(\frac{\xi \cdot \varepsilon \cdot n}{\mu}\right) \cdot A \cdot \frac{dE}{dL} \qquad (5)$$

where Qe is the quantity of liquid moved per unit time (cm^3/hr), dE/dL is the uniform electric field strength (V/m), n is the porosity of the soil column, ε is the permittivity of the pore liquid (C/V), μ is the viscosity of the pore liquid (g/cm·sec), A is the total cross section area (cm^2), ζ is the zeta potential (V).

Electromigration describes the transport of ionic species present in the pore fluid. This process is largely responsible for generating the electrical current, and it includes the migration of H^+ and OH^- towards the oppositely charged electrode.

When an electric potential is applied electrolysis of water occurs at the electrodes according to the following reactions:

At the anode: $2H_2O \rightarrow O_2\,(g) + 4H^+ + 4e^-$ (6)

At the cathode: $4H_2O + 4e^- \rightarrow 2H_2\,(g) + 4OH^-$ (7)

As seen from these equations, the electrolysis reactions cause an acidic solution to be generated at the anode and an alkaline solution to be generated at the cathode. (Reddy, 2003)

As a result, an acid front develops at the anode side and a base front is generated at the cathode side. Subsequently, the acid front migrates towards the cathode while the base front migrates towards the anode. Since the ionic mobility of the H^+ ion is higher than the ionic mobility of the OH^- ion, the acid front movement will generate a net flow towards the cathode. In addition to the migration of the H^+ and OH^-, metal ions such as Na^+, Ca^+, Cd^+, Pb^+ and anions such as Cl^-, NO_3^-, CO_3^{-2}, SO_4^{-2}, PO_4^{-3} are set in motion with the effect of the electric field. *Electromigration* can become the principal mechanism in highly active (containing large amounts of ionic species) soils with low water content or in systems were target contaminant is actually a charged particle (e.g., metals).

Ionic diffusion can be described as the movement of ions as a result of a concentration gradient which occurs due to the natural availability of the ion or as a result of electrolysis reactions. Ionic diffusion can become important in highly active soils with large chemical concentration gradients. Unless there is an exceptionally high chemical gradient, the concentration of ionic diffusion to the macroscopic flow is negligible.

Electrophoresis is defined as the migration of a charged particle relative to a stationary liquid phase. Electrophoresis can be thought as the mirror image process of electroosmosis, where the liquid phase is mobile and the solid phase is stationary. Electrophoresis becomes significant in electrokinetic remediation when colloidal particles are present in the soil-water matrix. The introduction of surface active agents and, consequently, the formation of micelles, increase the impact of electrophoresis on the process. Especially in cases where the colloids contain or absorb the target contaminant, electrophoresis plays a major role in the remediation process.

Electrokinetic Remediation

A comprehensive review of the physico-chemical processes that are involved in electrokinetics has been provided in several previous studies, such as those by Eykholt and Daniel (1994), Yeung (1994), Acar et al. (1995), and Alshawabkeh and Bricka (2000). Furthermore, although electrokinetics is commonly used for toxic metal contamination, researchers, such as Acar et al. (1992), Bruell et al. (1992) and Shapiro and Probstein (1993), have performed laboratory investigations and have found that electrokinetics can be successfully used for the remediation of soluble organic contaminants, such as benzene, toluene, and phenol.

The mass flux transported during the electrokinetic process depends on the transient geochemistry that takes place under the influence of an induced electrical field. Specifically, the sorption-desorption, precipitation-dissolution, and oxidation-reduction behavior of the contaminants during the electrokinetic process significantly affect the remediation efficiencies. Sorption refers to the partitioning of the contaminants from the solution or pore fluid to the solid phase or soil surface. Sorption includes adsorption and ion exchange and it is dependent on (1) the type of contaminant, (2) the type of soil, and (3) the pore fluid characteristics. Desorption is the reverse process and is responsible for the release of contaminants from the soil surface. Both sorption and desorption are affected by soil pH changes caused by the migration of H^+ and OH^- ions, which are produced by the electrolysis reactions (Acar and Alshawabkeh, 1993). The pH dependent sorption-desorption behavior is generally determined by performing batch experiments using the soil and contaminant of particular interest.

Casagrande conducted field studies in consolidation of soils by electroosmosis. (Casagrande, L. 1952) Sunderland used electroosmosis in dewatering of limestone, mine tailings and sewage, thickening construction sites and drying cellulosic materials. (Sunderland J.G. 1987) Lo conducted the application of electroosmosis causing improvements in stress strain behavior, consolidation and an increase in salinity and plasticity. (Lo, K.Y. 1991)

Reddy presents the results of an experimental investigation which studied the feasibility of using the electrokinetic process to remediate contaminated clays of glacial origin, otherwise known as glacial tills, this investigation suggests that the electrokinetic process has significant potential for remediating glacial tills contaminated with metals.(Reddy and Shirani, 1996).

Experiments of effect of pH control at the anode have been carried out. The test using deionized water with pH control generated a higher electroosmotic flow than the equivalent test performed without pH control, but the electroosmotic flow difference between the surfactant and cosolvent tests with and without pH control was minor compared to that observed with the deionized water tests. Controlling the pH was beneficial for increasing contaminant solubilization and migration from the soil region adjacent to the anode, but the high contaminant concentrations that resulted in the middle or cathode soil regions indicates that subsequent changes in the soil and/or solution chemistry caused contaminant deposition and low overall contaminant removal efficiency. (Reddy, 2003) Lee and Yang found the operable period was extended and the removal efficiency for lead II was also increased using circulation system in electrokinetic soil remediation. It was observed that most of the effluent lead II from the cathode compartment was electroplated onto the cathode and that residual effluent lead II did not precipitate onto, or adsorb to, the clay at the anode compartment during circulation. Therefore, there was no need to treat the electrolyte because there was virtually no effluent from the cathode compartment in the circulation system. It was also found that the electrolyte volume required to sustain the electrolytic reaction was sufficient for the whole electrokinetic remediation process. (H.Lee and J.Yang, 2000)

Electrokinetic Remediation by Surfactant

Tsuda T. developed the physical and geometrical parameters of electroosmosis and electrophoresis. (Tsuda T.1982) Terabe used free zone electrophoresis in electrokinetic separation of different organic compounds with micellar solutions. (Terabe, S. 1985) Experiments were done in capillary tubes. Anionic surfactants (SDS) appeared to create an opposing electrophoretic flow whereas cationic surfactants (CTAC) changed the surface charge of the capillary wall. (Li.,H and Gale, J., 1994)

Recently PAHs extraction with nonionic surfactants based in the cloud point phenomenon has been proposed. Use of this methodology offers some advantages for the extraction of PAHs compared with solvent extraction:

1. Ability to concentrate the PAH with high recoveries and very high pre-concentration factors,

2. Safety and cost benefits; very small amounts of the relatively nonflammable and nonvolatile surfactant are required,

3. Easy disposal of the surfactant,

4. Compatibility with micellar or hydro-organic mobile phase,

5. Ability to minimize losses due to the sorption of PAHs onto containers and

6. Possibility to determine PAHs associates to humic acids.

Advantages of the use of anionic surfactants over nonionic ones in cloud point extraction schemes include:

1. The absence of an aromatic moiety in their molecules which results in low fluorescence signal even at excitation wavelengths lower than 300 nm

2. Their polar character which results in low retention times. (Silicia, D et.al 1999)

Tsomides conducted a laboratory study to determine whether commercial surfactants (like Triton X 100) enhance the bioremediation of PAH contaminated sediments. The results suggest that many surfactants are toxic to PAH degrading microorganisms and while surfactant addition may not always have adverse effects on biodegradation the use of surfactants might not be desirable to achieve complete contaminant removal. (Tsomides, et.al 1995)

The effect of nonionic surfactants on the solubility and biodegradation of polycyclic aromatic hydrocarbons (PAHs) in the aqueous phase and in the soil slurry phase, as well as the fate of these surfactants, were investigated. (Kim, 2001)

Chemical Oxidation

Biodegradation has been successfully employed for remediation of soils contaminated with low-molecular-weight PAHs. However, bioremediation strategies often have limited applicability when soils and aquifers are contaminated with mixtures of high-molecular-weight PAHs (Madsen 1991; Macdonald and Kavanaugh 1994), probably due to the tendency of these compounds to sorb strongly to natural soil organic matter (Means et al. 1980), the resonance energies and stabilities of their structures, and their low water solubility (Klevens, 1950).

In-situ chemical oxidation processes may be used to overcome the limitations imposed by the low aqueous solubility of PAHs on their rates of biodegradation and dissolution. Chemical oxidation of these compounds is likely to enhance both their biodegradability and aqueous solubility, since the oxidation products would be more polar than the parent compounds (Gilbert, 1987). An advantage of chemical oxidation processes is that they are not subject to some of the rate limitations imposed on biodegradation processes, since the chemical oxidants may diffuse in the aqueous and gaseous phase to the reaction site.

Various oxidizing agents can be used to treat organics and PAHs in soils. Application of electric potential in conjunction with ions from the oxidizing agent can improve ability of these ions to penetrate small pores in the compacted soils, such as in clays. In addition, temperature can be increased to accelerate the kinetics of the treatment system. Examples of oxidizing agents are given below in Table 1-1.

Table 1-1
Examples of Oxidizing Agents

Oxidant	Half Reaction	Redox Potential (E^o)Volts)
Fluorine (F_2)	$F_2(g) + 2H^+ + 2e^- \rightarrow 2HF$ (aq)	3.06
Hydroxy radical (OH*)	$OH^* + e^- \rightarrow OH^-$	2.70
Sulfate radical ($SO_4^{-}*$)	$SO_4^{-}* + e^- \rightarrow SO_4^{2-}$	2.60
Atomic Oxygen (O)	$O(g) + 2H^+ + 2e^- \rightarrow H_2O$	2.42
Ozone (O_3)	$O_3(g) + 2H^+ + 2e^- \rightarrow O_2(g) + H_2O$	2.07
Persulfate anion ($S_2O_8^{2-}$)	$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	2.01
Hydrogen peroxide (H_2O_2)	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.77
Permanganate	$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.70
Hypochlorous Acid (HCLO)	$HCLO$ (aq) $+ H^+ + 2e^- \rightarrow Cl^- + H_2O$	1.49
Chlorine (Cl_2)	$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	1.36
Chlorine dioxide (ClO_2)	$ClO_2(g) + e^- \rightarrow ClO_2^-$	1.16
Bromine (Br2)	$Br_2(g) + 2e^- \rightarrow 2Br^-$	1.09
Iodine (I2)	$I_2 + 2e^- \rightarrow 2I^-$	0.54

Ozone Oxidation

Ozone is a very strong oxidant ($E_0 = +2.07$ V) that has been used successfully in wastewater treatment for the oxidation of organic contaminants (Stover et al. 1982; Peyton and Glaze 1988). Ozone oxidizes organic compounds either by direct oxidation or through the generation of hydroxyl radicals, or both. Organic compounds treated with ozone are transformed to oxygenated intermediates which are more soluble and hence more biodegradable (Legube et al. 1981; Gilbert 1983; Gilbert 1987).

In-situ Ozonation

The use of gaseous ozone for in situ chemical oxidation has significant advantages over aqueous based systems for the treatment of unsaturated soils. As the diffusivity of ozone gas is much greater than that for aqueous species, the mass of ozone that one can contact with the target contaminants is much greater than that which is possible with dissolved oxidants. Additionally, as volatilization of the target chemical is also not required, it can overcome mass transfer limitations associated with soil venting. *In-situ* ozonation may also be used to treat the region near the water table by using sparging. *In-situ* ozonation would likely be more rapid than biodegradation or soil venting processes, thereby reducing the remediation time and possibly treatment costs.

Conceptually, in situ ozonation is similar to soil venting. Vertical or horizontal injection wells can be used to inject ozone into the subsurface. Extraction wells may, if necessary, be used to control the direction of ozone flow in the subsurface. Horizontal wells could also be used to inject ozone. Nelson and Brown have claimed that the technique is more effective for the introduction of ozone into unsaturated soils than is the use of vertical wells. Horizontal wells are also advantageous when using ozone in combination with sparging technologies. However, while horizontal wells may have some advantages, it is not clear that these advantages warrant the additional cost necessary to install such wells.

Steffen Robbertson and Kirsten consulting engineers and scientists and Mcculloch Environmental Equipment Sales have conducted three field-scale soil remediation efforts using ozone. In all cases, the contaminants of interest have been chlorinated solvents. The largest of these remediation efforts was at a site in Carson City, NV. This site had been contaminated with Tetrachlorethylene (TCE). It was estimated that it would take 5 years to clean up this site using conventional pump-and-treat methods. The owner, a property developer, wanted to accelerate this process, so that the site could be developed. Thirteen sparge wells a three horizontal vapor extraction wells were installed. After initial sparging and venting with air, ozone was used in both sparging and soil vapor extraction wells. Samples taken after 4.5 months of operation indicated that the site had been remediated and the site is now closed (McCulloch, W., personal communication). The site was closed at the end of the third month. At a smaller site in Cape Cod, MA groundwater clean-up was achieved in less than 2 weeks (McCulloch, W., personal communication).

Nelson and Brown (1994) have described the use of ozone sparging to remove trichloroethylene (TCE) and dichloroethylene (DCE) from a site in Kansas. Prior to ozonation, air sparging was used to remove the bulk of the contaminants. Groundwater samples collected from monitoring wells ranging from 5 to 20 ft from the injection point indicated that the reaction TCE concentrations were reduced from 54 to 100%. The lowest level of TCE removal (14%) was seen at a sampling location 5 ft from the ozone injection well. DCE removal efficiencies ranged from 94% to 100% (with the exception of the nearby sampling point, where the removal was 30%).

To assess the applicability of *in-situ* ozonation, the effect of soil organic matter, soil moisture and soil texture on the ozone demand exerted by the soil has been studied. Along with the reactivity of selected PAHs with ozone in the soil and the byproducts formed from the reaction of ozone with PAHs.

Transport of Ozone in Unsaturated Soils

One of the major concerns with the use of *in-situ* ozonation has been the ability to transport ozone any considerable distance in saturated soils. The concentrations of ozone in the gas phase are orders of magnitude higher than that obtainable in aqueous solutions. Ozone is more stable in the gas phase than in water. In water, OH catalyzes the auto-decomposition of ozone (Langlais et al., 1991). Also higher flow velocities can be achieved in the vadose zone than is possible in aquifers.

We have investigated the transport of ozone in several geological materials (Day and Masten, 1992; Day, 1994; Hsu, 1995; Cole et al., 1996). Ozonation was conducted by passing humidified gaseous ozone through 10 cm long soil columns. Details of the procedures used in these experiments are described by Cole et al. (1996), Hsu (1995) and Day (1994) found that ozone is readily transported through columns packed with Ottawa sand there is rapid initial breakthrough of ozone (within 1.5 pore volumes). However, complete breakthrough is not achieved until nearly 5 pore volumes have been passed through the column. Work has also been conducted with Metea subsoil. The ozone demand exerted by the Metea subsoil is greater than that of the Ottawa sand; breakthrough in a 10 cm column is observed in approximately 600 pore volumes. For Borden sand, 90% ozone breakthrough is achieved in a 30 cm column in approximately 300 pore volumes (Day, 1994). Similar results were also obtained with Wurtsmith soil (Cole et al. 1996). The ozone demand of the Wurtsmith soil was completely satisfied within 30 min (approximately 60 pore volumes).

The rate of ozone degradation in soil columns is very slow after the ozone demand is met (Day, 1994). Ottawa sand exerts little ozone demand (less than 0.04 mg O_3 per gram sand). For Metea subsoil the ozone demand is approximately 2 mg O_3 per gram sand (Day, 1994). For Wurtsmith soil, the ozone demand is approximately 0.215 mg O_3 per gram soil at a moisture content of 6.8%. Once the initial ozone demand is met, little degradation of ozone is observed.

The effect of moisture content on the degradation of ozone in soils was investigated (Day, 1994). It was found that increasing the moisture content in Ottawa sand resulted in an increase in the ozone demand exerted by the soil and an increase in the time required to achieve a constant ozone concentration in the effluent stream from the column. Air-dried Ottawa sand had an ozone demand of 0.036 mg per gram soil, while the ozone demand for the moist soils (12 and 37% moisture contents) were 0.048 and 0.062 mg per gram soil, respectively. It is thought that this increase is due to the dissolution of gaseous ozone into the soil pore water and the subsequent self-decomposition of ozone once it is dissolved in the water.

Ozone Reactions in Aqueous Solutions and in Soil Slurries

Ozone reacts directly with aromatic compounds via a 1, 3-dipolar cyclic addition of ozone across the double bond to yield an unstable intermediate, known as a trioxalane. These intermediates rapidly decompose to form catechols, phenols and carboxylic acid (Bailey, 1982). Phenol will be further oxidized by ozone to form a number of organic acids and aldehydes (Jarret and Bermond 1983). The PAHs are reactive with both ozone and OH radicals (formed from the self-decomposition of ozone). As such, the remediation of soils contaminated with the PAHs has considerable promise.

Much work has been accomplished in our laboratory investigating the aqueous decomposition products formed from the ozonation of pyrene (Yao, 1997). Numerous products are produced, but the intermediates formed are mostly biphenyls substituted with carboxylic acid and aldehyde functional groups. Toxicity testing using gap junction intercellular communication as a biological endpoint has revealed that the products formed upon the ozonation of pyrene at dosages of at least 4.5 mol of ozone per mole of pyrene are not epigenetic toxicants to rat liver epithelial cells (Upham et al., 1994, 1995)

In- situ Ozonation of PAH Contaminated Soils

PAHs are very reactive with ozone and as such, ozone is very effective for the removal of PAHs from soil. The degradation of pyrene, naphthalene, chrysene and phenanthrene in soils has been studied. (Yao and Masten, 1992; Day, 1994) For a soil containing 100 mg kg^{-1} of pyrene, 81% of removal of pyrene could be achieved using an ozone dosage of approximately 500 mg kg^{-1} of soil (Day, 1994). The degradation was complete in 15 minutes, demonstrating that the rate of disappearance of pyrene was fast. Hydrophobic PAHs react more slowly than would be expected on the basis of their reactivity with ozone in water (Yao and Masten, 1992). In Ottawa sand, it was observed that in dry soil, approximately 65% of the naphthalene was removed after 37 h of venting with air; in moist soil when ozone venting was applied, the residual naphthalene concentration obtained was approximately two orders of magnitude lower than that obtained when using air venting alone (Hsu et al., 1993).

Nam and Kukor combined chemical oxidation with biological degradation, using a sequential treatment process consisting of ozonation and biodegradation, finding great biodegradation efficiency improvement for naphthalene, fluorene, phenanthrene, pyrene, and chrysene. But transformation of benzo(a)pyrene was not as pronounced as for the other PAHs in the soil (Nam and Kukor, 2000).

Persulfate Oxidation

The peroxydisulfate ion is one of the strongest oxidizing agents known in aqueous solution. The standard oxidation-reduction potential for the reaction

$$2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2e^- \qquad (8)$$

is estimated to be -2.01 volts. Reactions involving this ion, however, generally are slow at ordinary temperatures. Many peroxydisulfate oxidations have been studied kinetically. Persulfate was used to remove and oxidize amorphous soil/sediment organic matter (SOM).

The compositional changes upon persulfate oxidation were similar to the compositional changes upon humification, which supports the idea that weathered SOM is more condensed than the original material (Cuypers et al. 2002). The alkaline persulfate oxidation converts all N into nitrate, which is an easy and rapid method for determination total dissolved nitrogen (Hagedorn and Schleppi, 2000). There is a discussion of total oxidant demand (TOD) testing with sodium persulfate (Hoag et al., 2002) and with hydrogen peroxide (Fenton's reagent).

Persulfate oxidation of dissolved trichloroethylene (TCE) was investigated in aqueous and soil slurry systems under a variety of experimental conditions. the conditions under which transition metal ions (e.g., ferrous ion, Fe^{2+}) could activate the persulfate anion ($S_2O_8^{2-}$) to produce a powerful oxidant known as the sulfate free radical ($SO_4^{-\cdot}$) with a standard redox potential of 2.6 V. was examined (Liang et al. 2004).

Hybrid Electrochemical Transport and Chemical Oxidation

Electrochemical remediation uses a DC current between electrodes placed in the soil, to which chemical oxidant has been introduced. The charged species formed by addition of chemical oxidant are transported through the soil by electrical forces and then separated from soil to be treated. A variety of organic contaminants which are normally recalcitrant to other treatment techniques can be treated by this hybrid method of using chemical oxidants and electrochemical transport. In addition, temperature enhancements coupled with chemical oxidation and electrochemical transport can be an effective treatment strategy.

The oxidants selected for this study were sodium persulfate and aqueous ozone. Both oxidants exhibit two mechanisms for oxidation: (1) direct oxidation of the organic molecule; and (2) free radical oxidation. The later type of oxidation is more effective and kinetically much faster than direct oxidation. The use of an electrogradient in conjunction with these oxidants promotes free radical oxidation over direct oxidation. Previous studies on the use of sodium persulfate for *in-situ* chemical oxidation of contaminants have demonstrated its effectiveness for organics such as monochlorobenzene in dense non-aqueous phase liquids (DNAPLs) (Brown and Robinson, 2003). Persulfate decomposes upon oxidation to sulfate ion, and depending on the rate of reaction, the concentration of sulfate ion may temporarily exceed groundwater quality guidelines, such as the United States Environmental Protection Agency (USEPA) secondary standard of 250 mg/L for sulfate as a nuisance chemical. However, it is expected that the sulfate ion will be generated slowly and will attenuate naturally. In previous field-scale studies using persulfate solutions (ERM, 2002), no statistically significant increase in sulfate concentration was observed during the in-situ sodium persulfate pilot study, based on the comparison of the mean sulfate concentrations in the 12 pilot study wells, before and 2 months after persulfate injections.

Ozone has several advantages over other chemical oxidants, which includes:

- Produces hydroxyl radicals in aqueous phase, which is one of the strongest oxidants, as listed in Table 1-1;

- The only by-product from the ozone is oxygen which enhances biodegradation. There are no salts left behind, as in the case of Fenton's reagent, which increases the ionic strength of the soil, thereby inhibiting subsequent biodegradative processes;

- The half lives of several high molecular weight PAHs in the presence of aqueous ozone are low (Trapido et al., 1995), as shown below in Table 1-2.

Table 1-2
Half-lives of High Molecular Weight PAHs in the Presence of Aqueous Ozone

Ozone (ppm)	Benzo(k)fluoranthene	Benzo(a)pyrene	Benzo(b)fluoranthene
0.19	3.9 hrs	0.58 hrs	4.2 hrs
0.70	3.1 hrs	0.20 hrs	3.6 hrs
2.28	0.9 hrs	0.08 hrs	1.9 hrs

Application of electrokinetic treatment has several effects, which includes:

- Generates an acid front in the anode compartment, which is transported across the soil column and desorbs contaminants, such as metals, from the soil;

- Initiates electromigration of species in the soil pore fluid; and

- Establishes an electric potential which results in electroosmosis movement of species. Electroosmotic occurs due to inherent negative charge on clay and mineral surfaces. The extent of negative charge varies as follows:

  Sand < silt < kaolinite < Illite < Montmorillonite

- Ionic species move due to electromigration and also due to water movement by electroosmosis;

- Use of surfactants with electrokinetic treatment enhances water movement in the pores and also enhances desorption of hydrophobic contaminants from the soil into the surfactant micelles;

- Micellar transport during electrokinetic treatment has been studied before (Govind, 2004); and

- The use of charged micelles enhances water movement since the micelle movement is caused also by the electro-gradient and the micelle size is much bigger than the ionic species.

2

PROJECT OBJECTIVES

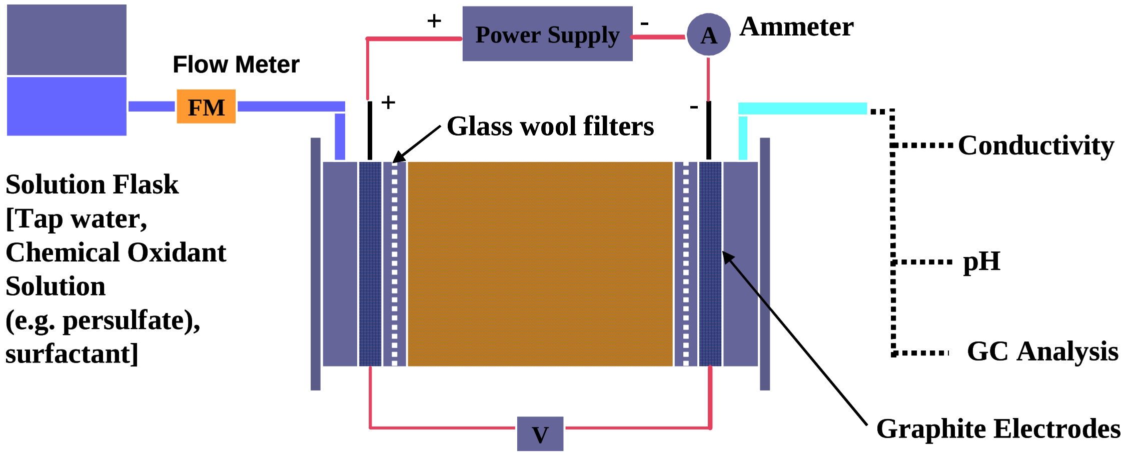
The objectives of the proposed study were as follows:

- Investigate at the bench-scale level, the effectiveness of using hybrid treatment methods, specifically the use of either surfactant addition or chemical oxidation coupled with electrochemical transport;
- Study PAH degradation with oxidant solutions including activated persulfate or ozone;
- Investigate the effectiveness of electrical potential in moving contaminants and the products of chemical oxidation through soils;
- Determine degradation levels for soils containing PAH and coal-tar contaminants.

3

EXPERIMENTAL PLAN

A bench-scale experimental system was constructed, as shown in Figure 3-1. The main cell consisted of a cylindrical glass tube with dimensions of 4” inside diameter and 12” length, two graphite plate electrodes, having dimensions of 4” diameter and 1/4” thickness (with 1/8” diameter holes drilled to allow liquid transport), two glass disk to support and seal the system, inlet and outlet ports for introducing and withdrawing processing fluid, and ports for screwing copper rods into the sides of the electrodes for electrical connections. Glass-wool filters were inserted between the soil specimen and the electrodes to avoid contact and plugging of the porous electrodes. Chambers on either side of the electrodes were used to introduce the chemical oxidant solution and separate the solution and reaction products. A liquid flow meter (FM) was used on the feed side to control the influent flow rate. A Kepco Constant Current/Voltage Power Supply is used to maintain a constant voltage difference between the electrodes of 5V DC, which gives a gradient of 5.08V/ft across the column. The amperage declined from initial values of 4.7 mA to 2.8 mA, mainly due to ion starvation within the column material, precipitation of metal hydroxides near the cathode and desorption of metal cations in the acidic region near the anode.



Constant Current: 1 – 5 mA (average 3 mA; current density = 0.037 mA/cm^2) applied across the soil column
Soil Column: 4” ID, 12” Length with two graphite plate electrodes (1/4” thick with 1/8” holes) and glass wool filters; Constant Voltage

Figure 3-1
Schematic of the Experimental Set-up

Analysis of products was conducted using pH, electrical conductivity and GC analysis. The surfactant used in this study was Cetyltrimethylammonium chloride (CTAC), a cationic surfactant, at a constant concentration of 2mM. Positively charged CTAC micelles improve the flow rate by dragging the pore fluid towards the cathode. A cooperative effect of electrophoresis and electroosmosis is demonstrated in this particular application.

Before experimentation was begun, the soil was homogenized and several samples were taken from this homogenized soil to analytically achieve less than 15% variation in the compound concentrations, as determined by GC/MS analysis using EPA 3540 and 8270C methods. This homogenized soil was then weighed and packed inside the column. After 10 days, the soil was removed, homogenized and then sampled for analysis. The next experiment was begun with the originally homogenized soil, keeping the same weight of soil for each experiment, and was removed and analyzed after 20 days.

With surfactant only studies, PAHs were desorbed and solubilized in the surfactant micelles and were eluted out the soil column into the receiving flask. Although attempts were made to extract and analyze this eluted water, difficulties were encountered with foaming and the analytical results were inconclusive. Hence, only the soil analysis data was used in all subsequent experiments to determine the treatment efficacy in this study.

4

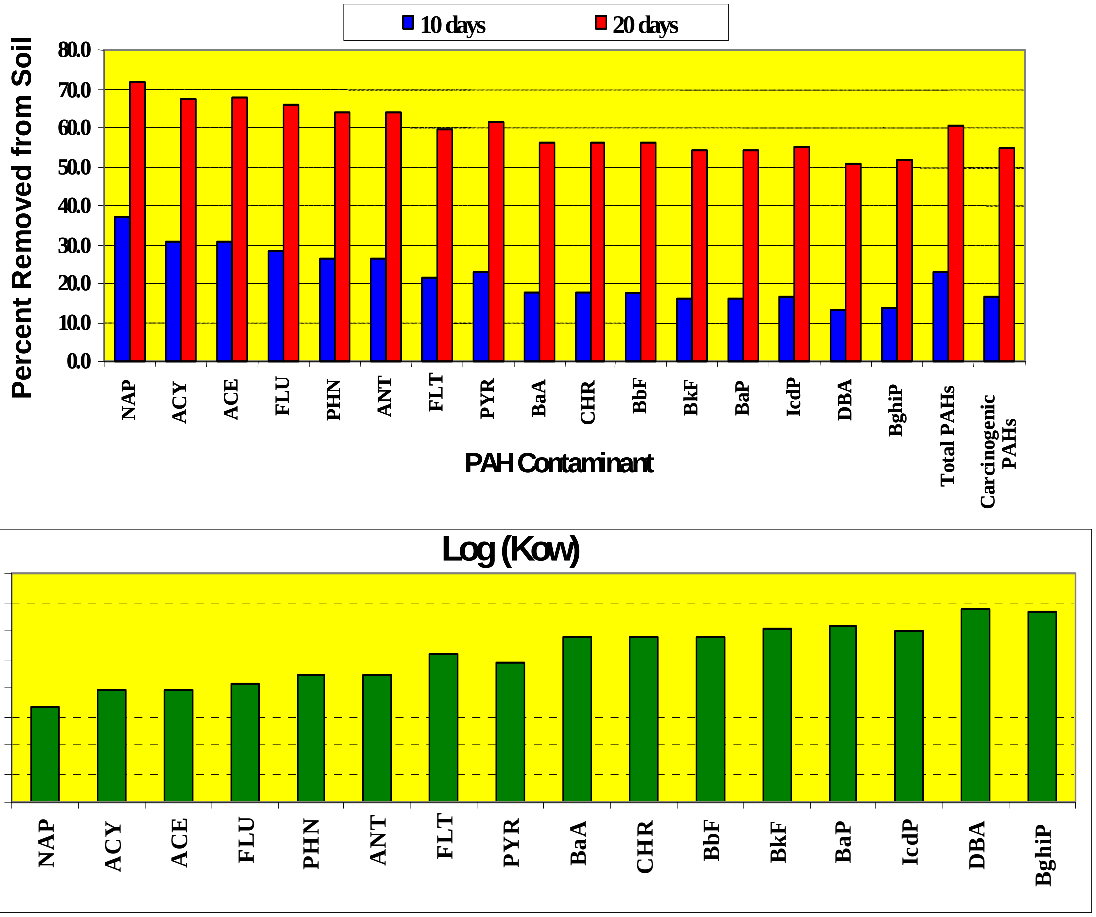
EXPERIMENTAL RESULTS

The surfactant used in this study was Cetyltrimethylammonium chloride (CTAC), since previous studies had shown its effectiveness in removing PAH contaminants from soil (Govind, 2004). The contaminated soil obtained for this study had PAHs ranging from 2 rings to 6 rings, as shown in Table 4-1. The sample consisted of a high clay content soil; however no specific soil properties were measured or provided.

Table 4-1
Analysis of PAHs in the Contaminated Soil

PARAMETER	CONC (mg/Kg)	RING SIZE
Naphthalene (NAP)	80.7	2
Acenaphthylene (ACY)	35.2	3
Acenaphthene (ACE)	9.8	3
Fluorene (FLU)	38.6	3
Phenanthrene (PHN)	326.8	3
Anthracene (ANT)	47.8	3
Fluoranthene (FLT)	107.5	4
Pyrene (PYR)	230.2	4
Benzo(a)anthracene (BaA)	71.3	4
Chrysene (CHR)	81.8	4
Bennzo(b)fluoranthene (BbF)	50.7	5
Benzo(k)fluoranthene (BkF)	47.3	5
Benzo(a)pyrene (BaP)	110.3	5
Benzo(g,h,i) perylene (BghiP)	59.5	5
Indeno(1,2,-3-cd) Pyrene (IcdP)	47.8	6
Dibenz(ah)anthracene (DBA)	9.5	6
TOTAL PAHs	1354.8	
Carcinogenic PAHs (BaA, CHR, BbF, BkF, BaP, BghiP, IcdP, DBA)	478.2	

The total PAHs were 1354.8 mg/Kg and the carcinogenic PAH were 478.8 mg/Kg. Figure 4-1 shows the results of PAH concentrations in the soil as a function of treatment time. Soil samples were extracted using EPA Method 3540 and the extracts were analyzed using EPA Method 8270C. The soil dry weight was measured using EPA 160.3 or ASTM D2216. The soil concentrations are shown below in Figure 4-1. A plot of the log of the Octanol-Water coefficient (logKOW) is also shown alongside to illustrate the fact that the contaminant removal decreases as the KOW increases, since high KOW contaminants are more tightly bound to the organic matter of the soil and hence are more difficult to desorb into the surfactant micelle.



Operating Conditions were: Voltage 5 V; Surfactant: CTAC; Temperature: 25°C

Figure 4-1
Surfactant Enhanced Electrokinetic Treatment

The above removals are mainly by desorption of the contaminant from the soil into the surfactant, CTAC, micelle, and them removal of the contaminant as the micelle moves through the soil matrix under the applied electro-gradient. This is physical removal of the contaminants rather than treatment.

Figure 4-2 shows the use of a chemical oxidant: sodium persulfate at 1 molar (1M) concentration in water, which is allowed to move through the soil under an applied electro-gradient.

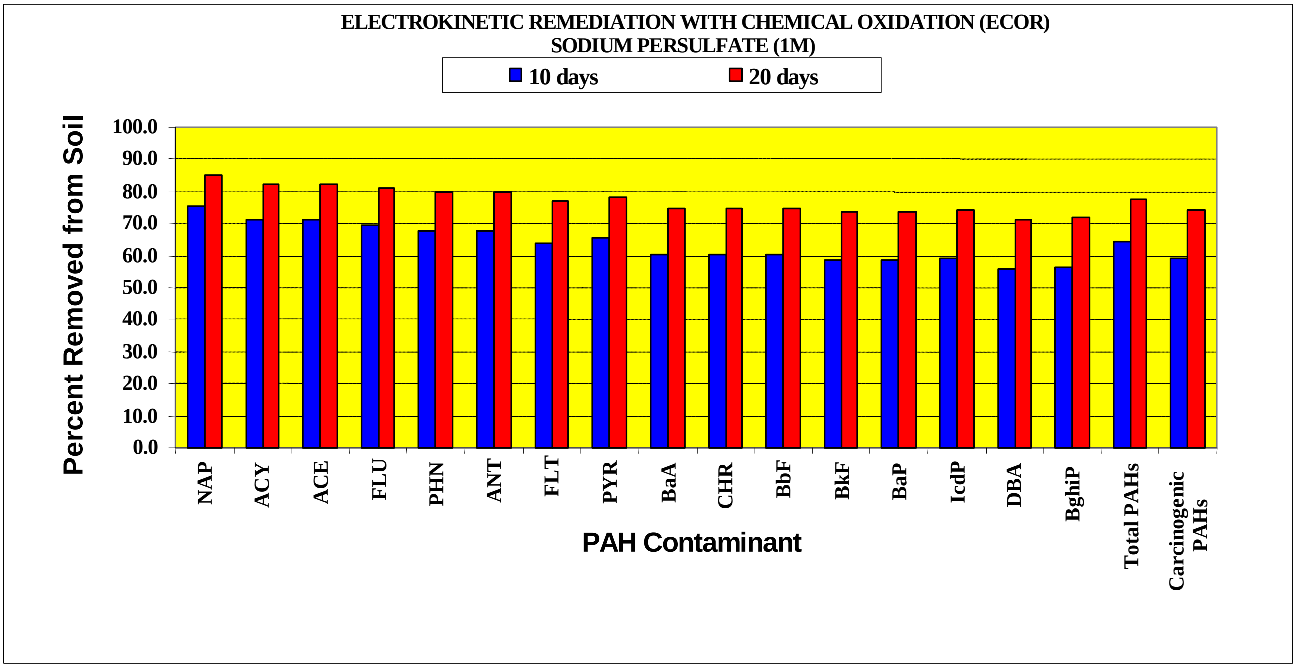


Figure 4-2
Electrokinetic Remediation with Chemical Oxidation Using Persulfate

Clearly, the percent removal is greater than with surfactant alone. Persulfate is a strong oxidizing agent and it initiates three mechanisms:

1. Solubilization of the hydrophobic contaminants in water: Partial oxidation of the PAHs results in the introduction of a hydroxyl group on the molecular structure, which increases the aqueous solubility of the PAH in the water; this increases the removal efficiency as the water moves through the soil;

2. Accelerated humification of the PAH contaminant: Humification is the chemical bonding of the contaminant to soil's organic matter, resulting in organic matter. Hydroxylation of the PAH molecule results in its chemical bonding to the soil's organic matter, which makes the PAH molecule indistinguishable from the organic matter; and

3. The oxidant causes partial destruction of the PAH molecule.

Computer simulation of this humification process was conducted using the SPARTAN PRO computer program and Figure 4-3 shows the bond formation with Syringic Acid, which is often used as an analog of soil's organic matter. In this figure, phenanthrene is shown bonding with Syringic Acid.

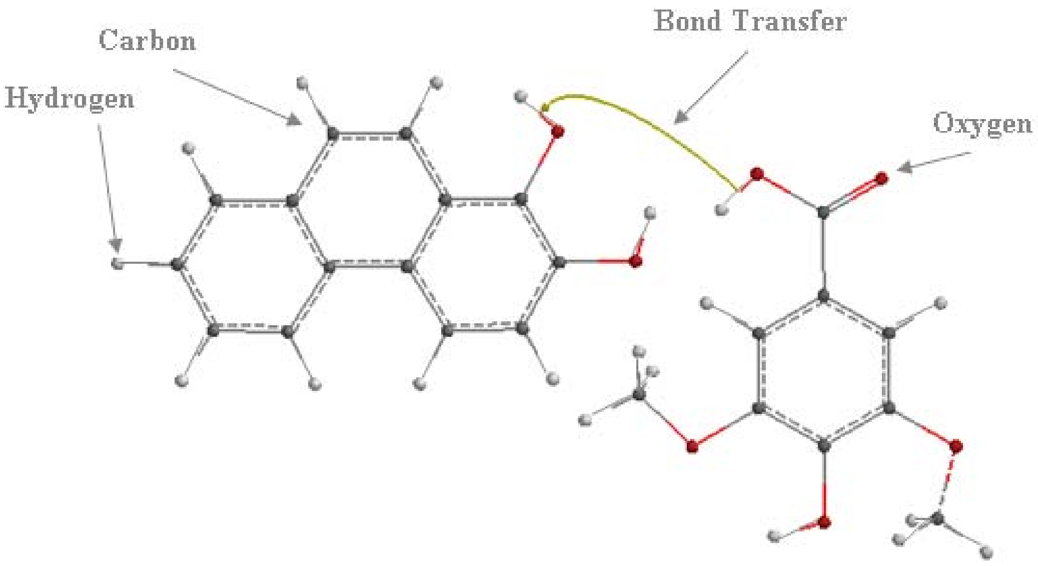
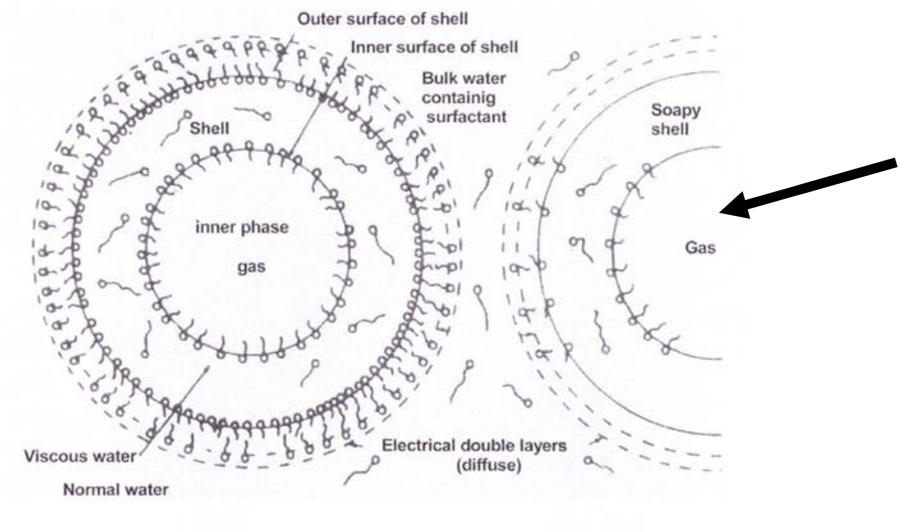


Figure 4-3
Chemical Bonding of Phenanthrene with Syringic Acid, an analog of Soil's Organic Matter

Studies were also conducted with aqueous ozone as the oxidizing agent in conjunction with electrochemical treatment. Ozone was first dissolved in water and surfactant solution at a concentration of 0.56 kg/m^3 to create gas aphrons using CTAC concentrations of 2 and 4 milli molar (mM) at pH 8.0. This was achieved by stirring 400 mL of CTAC solution using a stirrer rotating at 8,000 rpm for minutes at room temperature. The rapid mixing resulted in the formation of gas aphrons, as shown below in Figure 4-4. These gas aphrons are very stable, lasting for several weeks once created in the liquid phase. Since these gas aphrons contain ozone gas, the aqueous concentration of ozone in the liquid phase can be easily maintained above 3 ppm.



Ozone inside Gas Aphron

Figure 4-4
Gas Aphron with Ozone formed by rapid stirring of CTAC solution

The aqueous liquid containing these ozone gas aphrons were introduced into the electrotreatment apparatus and allowed to move across the soil under the electro-gradient. The soil concentrations of PAHs were determined after 10 days and 20 days by removing several soil samples from the column and extracting them. Figure 4-5 shows the results of aqueous ozone treatment of the PAH contaminated soil. Soil concentration data are provided in Appendix A

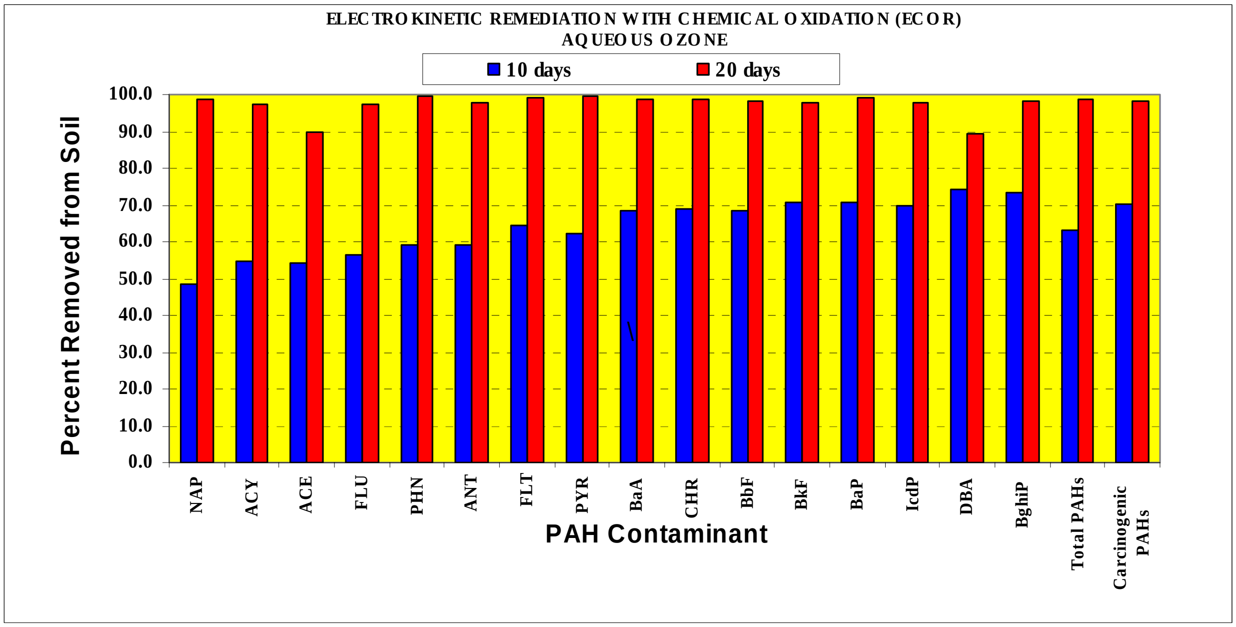


Figure 4-5 Aqueous Ozone Treatment of the PAH Contaminated Soil

Aqueous ozone is able to treat all the PAHs present in the soil in 20 days, with no detectable PAHs remaining at the end of the 20 day treatment time. These data show that aqueous ozone is a much stronger oxidizing agent than persulfate and can be easily used in the field. The Quantitation Limit for PAHs in this study was 1 mg/Kg on a dry weight basis with recoveries of 85% - 89%. The estimated quantitation limit for PAHs by EPA Method 8270C is 0.66 mg/Kg.

5

CONCLUSIONS

The following conclusions can be drawn from this study:

1. Chemical oxidation coupled with electrokinetic treatment is a viable method for treating PAH contaminated soils;

2. The use of surfactants enhances the efficacy of the electrotreatment process due to the partitioning of the hydrophobic PAHs in the surfactant micelles;

3. Experimental studies with CTAC surfactant demonstrated that PAHs can be successfully removed from contaminated soil using an electro-gradient to move the charged micelles through the soil matrix;

4. Two chemical oxidants were studied: (1) persulfate; and (2) aqueous ozone. Both these oxidants demonstrated significant PAH treatment in 20 days. Aqueous ozone was able to treat significant contaminant levels of PAHs and achieved non-detect PAH levels in 20 days.

5. Further studies are needed at the field-scale level to further demonstrate the technical and economic viability of these technologies in treating PAH contaminated soils at MGP soil sites.

6
REFERENCES

Brown, Richard A., and David Robinson. Response to Naturally Ocurring Organic Material: Permanganate vs Persulfate. Presented at the 8th International Conference on Soil-Water Systems, 12-16 May, Gent, Belgium, 2003.

Casagrande, L. Journal of the Boston Society of Civil Engineers, 39(1952) 51-83.

Chambers, D. C.,Willis, J., Giti-Pour, S., Zieleniewski, J. L., Rickabaugh, J. F., Mecca, M. I., Pasin,B., Sims, R. C., Sorensen, D. L., Sims, J. L., McLean, J. E., Mahmood, R., Dupont, R. R. and Wangner, K.: 1991, In Situ Treatment of Hazardous Waste Contaminated Soils, 2nd ed., ndc, New Jersey, p.98.

Choi,Y.S. and Lui,R., A mathematical model for the electrokinetic remediation of contaminated soil, Journal of Hazardous Materials 44(1995) 61-75

Cuypers, C, Grotenhuis, T, Nierop, Klaas G.J., Franco, E.M., Jager, A.D, Rulkens, W., Amorphous and condensed organic matter domains: the effect of persulfate oxidation on the composition of soil/sediment organic matter, Chemosphere 48(2002) 919-931

ERM. Residual Dense Non-Aqueous Phase Liquid Investigation, Acid Plant Area, ATOFINA Chemicals, Inc., Facility, Portland, Oregon, 2002.

Gilbert, E (1983), Investigations on the changes of biological degradability of single substances induced by ozonation. Ozone Sci. Eng. 5: 137–149

Gilbert, E (1987), Biodegradability of ozonation products as a function of COD and DOC elimination by example of substituted aromatic substances. Water Res. 21: 1273–1278

Govind R, Ramani, M (2004) Computer Simulation of Soil Humification Processes, Paper presented at the Annual AIChE Meeting.

Hagedorn, F. Schleppi, P. Determination of total dissolved nitrogen by persulfate oxidation, J. Plant Nutr.Soil Sci. 163(2000),81-82

Hoag, G. E., Chheda, P. V., Woody, B. A., & Dobbs, G. M. (2002). U.S. Patent No.6,019,548, Washington, D.C.: U.S. Patent and Trademark Office.

Kim, I.S, Park, J., Kim, K., Enhanced biodegradation of polycyclic aromatic hydrocarbons using nonionic surfactants in soil slurry, Applied chemistry 16 (2001) 1419-1428

Kim, S., Moon, S., Kim K., Removal of heavy metals from soils using enhanced electrokinetic soil processing, Water, Air and Soil Pollution 125(2001) 259-272.

Klevens HB (1950), Solubilization of polycyclic hydrocarbons. J. Phys. Colloid Chem. 54: 283–298

Legube B, Langlais B, Sohm B & Dore M (1981) Identification of ozonation products of aromatic hydrocarbon micropollutants: effect on chlorination and biological filtration. Ozone Sci. Eng.3: 33–48

Li, H. and Gale, R.J. Emerging Technologies in Hazardous Waste Management VI, Book of Abstracts for the I&EC Special Symp. ACS, Atlanta Georgia, September 19-21, 1994, 1188-1191

Liang, C. Bruell, C.J., Marley, M.C. Sperry, K.L. Persulfate oxidation for in situ remediation of TCE. II. Activated by chelated ferrous ion, Chemosphere 55 (2004) 1213-1223

Liang, C. Bruell, C.J., Marley, M.C. Sperry, K.L. Persulfate oxidation for in situ remediation of TCE. II. Activated by chelated ferrous ion, Chemosphere 55 (2004) 1225-1233

Lo, K.Y. and Ho, K.S., Can.Geotech.J. 28(1991), 763-770

Macdonald JA & Kavanaugh MC (1994) Restoring contaminated groundwater: an achievable goal? Environ. Sci. Technol. 28:362A–368A

Madsen EL (1991) Determining in situ biodegradation: facts and challenges. Environ. Sci. Technol. 25: 1662–1673

Means JC, Ward SG, Hassett JJ & Banwart WL (1980) Sorption of polynuclear aromatic hydrocarbons by sediments and soils. Environ. Sci. Technol. 14: 1524–1528

Peyton GR and Glaze WH (1988), Destruction of pollutants in water with ozone in combination with ultraviolet radiation. Environ. Sci. Technol. 22: 761–767

Probstein, R. F. and Renaud, P. C.: 1986, *Proc*. Workshop on Electrokinetic Treatment and its Application in Environmental Geotechnical Engineering for Hazardous Waste Site Remediation, University of Washington, Seattle, Augustus 4–5, Hazardous Waste Engineering Research Laboratory, EPA, Cincinnati, U.S.A.

Reddy, K.R. Xu, C.Y, Chinthamreddy, S., Assessment of electrokinetic removal of heavy metals from soils by sequential extraction analysis, Journal of Hazardous Materials B84 (2001) 279-296.

Ribeiro,A.B. and Mexia,J.T., A dynamic model for the electrokinetic removal of copper from a polluted soil, Journal of Hazardous Materials 56(1997) 257-271

Shapiro, A. P.: 1990, ‘Electroosmotic Purging of Contaminants from Saturated Soils’, Ph.D. thesis, Massachusetts Institute of Technology, Cambridge, U.S.A.

Sicilia, D. Rubio, S., Perez-Bendito, D., Maniasso, N., Zagatto, E.A.G., Anionic surfactants in acid media: a new cloud point extraction approach for the determination of polycyclic aromatic hydrocarbons in environmental samples, Analytica Chimica Acta, 392 (1999) 29-38

Stover EL, Wang L-W and Medley DR (1982) Ozone assisted biological treatment of industrial wastewaters containing biorefractory compounds. Ozone Sci. Eng. 4: 177–194

Sunderland, J.G. journal of Applied Electrochemistry, 17(1987), 889-898

Sunderland, J.G. journal of Applied Electrochemistry, 17(1987), 1048-1056

Terabe, S. OTusuka, K. Ando, T. Analytical Chemistry, 57 (1985), 834-841

Trapido, M., Veressinina, Y. and Munter, R. Ozonation and advanced oxidation processes of polycyclic aromatic hydrocarbons in aqueous solutions – a kinetic study. *Environ. Technol.*, **16**, 729-740, 1995.

Tsomides, H.J., Hughes, J.B., Thomas, M.J., Ward, H.C., Effect of surfactant addition on phenanthrene biodegradation in sediments, Environmental Toxicology and Chemistry, 14 (1995) 953-959

Tsuda, T., Nomura, K. and Nakagawa, G., Journal of chromatography, 248(1982) 241-247

A
APPENDIX

LABORATORY DATA

Surfactant Enhanced Electrokinetic Remediation (SEER)
Conditions: 5 V; Room Temp 30 C; Surfactant: CEC

Contaminant	**Conc. (mg/Kg)**	**Ring Size**	**Day10**	**Day 20**	**log(Kow)**
Naphthalene (NAP)	80.7	2	50.7	22.7	3.3
Acenaphtylene (ACY)	35.2	3	24.4	11.5	3.94
Acenaphthene (ACE)	9.8	3	6.8	3.2	3.92
Fluorene (FLU)	38.6	3	27.6	13.2	4.18
Phenanthrene (PHN)	326.8	3	241.1	117.6	4.46
Anthracene (ANT)	47.8	3	35.2	17.2	4.45
Fluoranthene (FLT)	107.5	4	84.6	43.3	5.16
Pyrene (PYR)	230.2	4	177.0	88.9	4.88
Benzo(a)anthracene (BaA)	71.3	4	58.6	31.2	5.76
Chrysene (CHR)	81.8	4	67.5	36.0	5.81
Benzo(b)fluoranthene (BbF)	50.7	5	41.7	22.3	5.78
Benzo(k)fluoranthene (BkF)	47.3	5	39.7	21.6	6.11
Benzo(a)pyrene (BaP)	110.3	5	92.8	50.5	6.13
Indeno(123-cd)pyrene (IcdP)	47.8	6	39.9	21.6	6
Dibenz(ah)anthracene (DBA)	9.5	6	8.2	4.7	6.75
Benzo(ghi)perylene (BghiP)	59.5	5	51.4	28.8	6.63
Total USEPA PAHs	1354.8		1047.2	534.3	
Carcinogenic PAHs	478.2		399.9	216.8	

Note: Day 10 and day 20 concentrations are in mg/Kg dry soil.

Electrokinetic Remediation with Chemical Oxidation (ERCO)
Conditions: 5 V; Room Temp 30 C; Oxidant: Sodium persulfate (1M concentration)

Contaminant	Conc. (mg/Kg)	Ring Size	Day10	Day 20	log(Kow)
Naphthalene (NAP)	80.7	2	20.1	12.3	3.3
Acenaphtylene (ACY)	35.2	3	10.2	6.3	3.94
Acenaphthene (ACE)	9.8	3	2.8	1.7	3.92
Fluorene (FLU)	38.6	3	11.8	7.3	4.18
Phenanthrene (PHN)	326.8	3	105.1	65.3	4.46
Anthracene (ANT)	47.8	3	15.3	9.5	4.45
Fluoranthene (FLT)	107.5	4	38.9	24.4	5.16
Pyrene (PYR)	230.2	4	79.6	49.8	4.88
Benzo(a)anthracene (BaA)	71.3	4	28.1	17.8	5.76
Chrysene (CHR)	81.8	4	32.5	20.6	5.81
Benzo(b)fluoranthene (BbF)	50.7	5	20.0	12.7	5.78
Benzo(k)fluoranthene (BkF)	47.3	5	19.5	12.5	6.11
Benzo(a)pyrene (BaP)	110.3	5	45.6	29.1	6.13
Indeno(123-cd)pyrene (IcdP)	47.8	6	19.4	12.4	6
Dibenz(ah)anthracene (DBA)	9.5	6	4.2	2.7	6.75
Benzo(ghi)perylene (BghiP)	59.5	5	26.1	16.8	6.63
Total USEPA PAHs	1354.8		479.3	301.4	
Carcinogenic PAHs	478.2		195.4	124.7	

Note: Day 10 and day 20 concentrations are in mg/Kg dry soil.

Electrokinetic Remediation with Chemical Oxidation (ERCO)
Conditions: 5 V; Room Temp 30 C; Oxidant: Aqueous Ozone

Contaminant	Conc. (mg/Kg)	Ring Size	Day10	Day 20	log(Kow)
Naphthalene (NAP)	80.7	2	41.7	BDL	3.3
Acenaphtylene (ACY)	35.2	3	16.0	BDL	3.94
Acenaphthene (ACE)	9.8	3	4.5	BDL	3.92
Fluorene (FLU)	38.6	3	16.7	BDL	4.18
Phenanthrene (PHN)	326.8	3	133.9	BDL	4.46
Anthracene (ANT)	47.8	3	19.6	BDL	4.45
Fluoranthene (FLT)	107.5	4	38.3	BDL	5.16
Pyrene (PYR)	230.2	4	86.7	BDL	4.88
Benzo(a)anthracene (BaA)	71.3	4	22.5	BDL	5.76
Chrysene (CHR)	81.8	4	25.6	BDL	5.81
Benzo(b)fluoranthene (BbF)	50.7	5	16.0	BDL	5.78
Benzo(k)fluoranthene (BkF)	47.3	5	13.9	BDL	6.11
Benzo(a)pyrene (BaP)	110.3	5	32.4	BDL	6.13
Indeno(123-cd)pyrene (IcdP)	47.8	6	14.4	BDL	6
Dibenz(ah)anthracene (DBA)	9.5	6	2.5	BDL	6.75
Benzo(ghi)perylene (BghiP)	59.5	5	15.8	BDL	6.63
Total USEPA PAHs	1354.8		500.6	0.0	
Carcinogenic PAHs	478.2		143.0	0.0	

Note: Day 10 and day 20 concentrations are in mg/Kg dry soil.

BDL = below detection level. The detection level was < 1 mg/kg for all parameters

Export Control Restrictions

Access to and use of EPRI Intellectual Property is granted with the specific understanding and requirement that responsibility for ensuring full compliance with all applicable U.S. and foreign export laws and regulations is being undertaken by you and your company. This includes an obligation to ensure that any individual receiving access hereunder who is not a U.S. citizen or permanent U.S. resident is permitted access under applicable U.S. and foreign export laws and regulations. In the event you are uncertain whether you or your company may lawfully obtain access to this EPRI Intellectual Property, you acknowledge that it is your obligation to consult with your company's legal counsel to determine whether this access is lawful. Although EPRI may make available on a case-by-case basis an informal assessment of the applicable U.S. export classification for specific EPRI Intellectual Property, you and your company acknowledge that this assessment is solely for informational purposes and not for reliance purposes. You and your company acknowledge that it is still the obligation of you and your company to make your own assessment of the applicable U.S. export classification and ensure compliance accordingly. You and your company understand and acknowledge your obligations to make a prompt report to EPRI and the appropriate authorities regarding any access to or use of EPRI Intellectual Property hereunder that may be in violation of applicable U.S. or foreign export laws or regulations.

The Electric Power Research Institute (EPRI)

The Electric Power Research Institute (EPRI), with major locations in Palo Alto, California, and Charlotte, North Carolina, was established in 1973 as an independent, nonprofit center for public interest energy and environmental research. EPRI brings together members, participants, the Institute's scientists and engineers, and other leading experts to work collaboratively on solutions to the challenges of electric power. These solutions span nearly every area of electricity generation, delivery, and use, including health, safety, and environment. EPRI's members represent over 90% of the electricity generated in the United States. International participation represents nearly 15% of EPRI's total research, development, and demonstration program.

Together…Shaping the Future of Electricity

Printed on recycled paper in the United States of America

1010139

ELECTRIC POWER RESEARCH INSTITUTE
3420 Hillview Avenue, Palo Alto, California 94304-1395 • PO Box 10412, Palo Alto, California 94303-0813 • USA
800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com