

Effect of voltage gradient on integrated electrochemical remediation of contaminant mixtures

Krishna R. Reddy and Madhusudhana R. Karri

Abstract

This paper evaluates the effect of voltage gradient on the efficiency of integrated electrochemical remediation (IECR) of low permeability soils contaminated with both heavy metals and polycyclic aromatic hydrocarbons (PAHs). The IECR remediation process aims to oxidize organic contaminants within the soil by the electro-osmotic delivery of hydrogen peroxide (H_2O_2) and a Fenton-like oxidation process, as well as simultaneously removing heavy metals by electro-osmotic advection and electromigration. In Fenton-like oxidation, the native soil iron is utilized as a catalyst to decompose H_2O_2 to generate free hydroxyl radicals that oxidize PAHs into relatively benign products such as carbon dioxide, water and oxygen. A series of bench-scale experiments was performed on kaolin (a low permeability soil) spiked with nickel (a representative heavy metal) and phenanthrene (a representative PAH) each at a concentration of 500 mg per kg of dry soil under two voltage gradients, 1 and 2 VDC/cm. The H_2O_2 solution in two different concentrations at 5% and 10% was introduced at the anode, and each experiment was conducted for a total duration of four weeks. The results showed that increasing the voltage gradient from 1 VDC/cm to 2 VDC/cm did not increase the electro-osmotic delivery of H_2O_2 significantly. Phenanthrene removal from the soil was negligible in all the experiments; however, 28% and 34% of the phenanthrene were oxidized within the soil in the 5% and 10% H_2O_2 experiments, respectively, under 1 VDC/cm. The phenanthrene oxidation increased to about 32% and 42% under 5% and 10% H_2O_2 concentrations, respectively, under 2 VDC/cm. Nickel migrated towards the cathode and then precipitated close to the cathode, due to high pH conditions in all the experiments. Nickel migration was slightly higher in the case of 2 VDC/cm than in the case of 1 VDC/cm, due to greater migration of the acidic pH front towards the cathode under 2 VDC/cm. Overall, the results showed that an increase in the voltage gradient from 1 VDC/cm to 2 VDC/cm improved overall remedial performance slightly, and alternative strategies to increase H_2O_2 delivery and prevent precipitation of metals near the cathode are required for achieving significantly higher remedial efficiencies.

Key words: chemical oxidation, clays, contaminant mixtures, electrokinetic remediation, heavy metals, organic contaminants, soil

INTRODUCTION

The presence of mixed contaminants in soils poses a great challenge for their remediation. The mixed con-

taminants include combinations of organic compounds, heavy metals, and radionuclides. Very few conventional techniques are found to address the remediation of such mixed contaminant sites (Sharma and Reddy 2004). Moreover, these techniques are ineffective or expensive in the remediation of mixed contaminated sites that contain low permeability and heterogeneous soils. The synergistic effects of one type of contaminant on the remediation of another type of contaminant may

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complicate the treatment of such mixed contaminated sites.

Electrokinetic remediation has been shown to have great potential to remediate organic contaminants and heavy metals when they exist individually, as well as to deliver the reactive agents under different subsurface environments (Acar *et al.* 1995; Reddy and Chinthamreddy 2003; Reddy *et al.* 2003*a,b*; Reddy and Saichek 2004). Electrokinetic remediation essentially involves the installation of electrodes into the contaminated soils and applying a low electric potential across the anodes (positively charged electrodes) and the cathodes (negatively charged electrodes). The contaminants are transported towards the electrodes due to electro-osmosis (the movement of interstitial water generally towards the cathodes) and electromigration (the movement of ionic species to the oppositely charged electrodes). Electrokinetic remediation has been receiving increased attention for *in situ* remediation of contaminated sites, due to its effectiveness in low permeability and heterogeneous soils. Recently, electrokinetic remediation has been investigated for simultaneous removal of heavy metals and organic compounds from low permeability soils (Maturi 2004). To enhance solubilization of contaminants, flushing solutions such as surfactants, cosolvents, chelates and organic acids, were used. The contaminant-laden solutions collected at the electrodes required further treatment, leading to higher treatment costs.

In situ chemical oxidation processes have the potential to provide cost-effective means of rapidly treating organic contaminants in soils (USEPA 1991). Numerous previous studies reveal the strong reactivity of Fenton's reagent with organic contaminants in soils, resulting in effective contaminant destruction (Arnold *et al.* 1995; Gates and Siegrist 1995; Miller and Valentine 1995; Ravikumar and Gurol 1994; Tyre *et al.* 1991). A conventional Fenton's reaction involves catalytic decomposition of hydrogen peroxide (H_2O_2) with iron to yield free hydroxyl radicals ($\cdot OH$), which non-selectively oxidizes many organic contaminants within the soil into relatively benign products such as carbon dioxide, water and oxygen. Therefore, aiming to oxidize organic contaminants within the soil and simultaneously aiming to remove heavy metals from soils has the potential to be an effective and less expensive strat-

egy for the remediation of contaminant mixtures in soils.

Previously, the coupled electrokinetics and Fenton-like oxidation process was investigated for the remediation of polycyclic aromatic hydrocarbons (PAHs) alone in low permeability soils (Chandhuri 2003). In Fenton-like oxidation, the iron native to the soil is utilized as a catalyst to decompose H_2O_2 to generate free hydroxyl radicals (Valentine and Wang 1998; Watts *et al.* 1990, 1997). The native iron in soils can be available as iron oxide (Fe_2O_3) or iron oxyhydroxide phases ($FeOOH$). Recently, the coupled electrokinetics and Fenton-like oxidation process was investigated to remediate clayey soils contaminated with contaminant mixtures, particularly PAHs and heavy metals (Karri 2005). In these studies, batch experiments and bench-scale electrokinetic experiments with different concentrations of H_2O_2 were conducted to determine the remedial efficiency of H_2O_2 on PAHs alone and when PAHs co-exist with heavy metals. Kaolin soil was used as the model clay soil, and phenanthrene and nickel were used as representative PAH and heavy metal, respectively. These studies have concluded that as the concentration of H_2O_2 increased, the oxidation of phenanthrene within the soil also increased. However, high residual phenanthrene concentrations were still observed throughout the soil after electrokinetic testing, implying that the complete oxidation of phenanthrene was not achieved. A gradual increasing trend of nickel concentrations from the anode to the cathode was observed in all the experiments, which implies that nickel migrated towards the cathode in all the experiments, irrespective of the concentration of H_2O_2 used. However, the removal of nickel from the soil was low, which could be due to its precipitation as nickel hydroxides under the high pH conditions created near the cathode. In these experiments, electro-osmotic flow could not be sustained for a greater duration of time. The cumulative flow was less than two pore volumes in all the experiments. Due to low electro-osmotic flow, a sufficient amount of H_2O_2 may not have been delivered into the soil for complete phenanthrene oxidation.

According to the Helmholtz–Smoluchowski theory, electro-osmotic flow is directly proportional to applied electric potential (Reddy and Saichek 2004). When the voltage gradient increases, the electric current can increase due to an increase in the ionic strength in the

electrode solutions and more ions entering into the soil from the respective electrodes. The increased current can result in increased or sustained electro-osmotic flow during the remediation process. In this study, a series of bench-scale experiments was conducted to investigate the effects of voltage gradient on electro-osmotic delivery of H_2O_2 , oxidation of phenanthrene within the soil, and also on the removal of nickel from the soil. In addition, this study investigated whether the naturally available iron in the soil would act as a catalyst to decompose H_2O_2 and oxidize PAHs.

EXPERIMENTAL METHODOLOGY

Table 1 summarizes the variables involved in the experimental programme. The programme made it possible to systematically investigate the effects of voltage gradient on the Fenton-like oxidation of phenanthrene within the soil and the simultaneous removal of nickel from the soil. Replicate experiments were conducted to ensure the accuracy and repeatability of the experimental results.

Table 1. Experimental programme

Experiment*	Voltage gradient (VDC/cm)	Time duration (weeks)	Flushing solution
1	1.0	4	5% H_2O_2
1R	1.0	4	5% H_2O_2
2	1.0	4	10% H_2O_2
2R	1.0	4	10% H_2O_2
3	2.0	4	5% H_2O_2
3R	2.0	4	5% H_2O_2
4	2.0	4	10% H_2O_2
4R	2.0	4	10% H_2O_2

* Experiments 1R, 2R, 3R and 4R are the replicate experiments

Materials

For all the experiments, commercially available laboratory-grade kaolin soil, obtained from VWR Scientific Products and manufactured by EM Science, was used. Kaolin was selected as a model clayey soil due to its low hydraulic conductivity. It consists of mostly fine particles (up to 96%) and near zero organic matter. The composition and properties of kaolin are presented in Table 2.

Phenanthrene was selected as a representative PAH.

Table 2. Properties of kaolin

Property	Test method	Value
Mineralogy		Kaolinite: 100% Muscovite: trace Illite: trace
Specific gravity	ASTM D 854	2.6
Grain size distribution	ASTM D 422	% gravel = 0 % sand = 4 % silt = 18 % clay = 78
Hydraulic conductivity (at porosity = 46%)	ASTM D 2434	1.0×10^{-8} cm/s
pH	ASTM D 2974	4.9
Organic content	ASTM D 2974	Near 0
USCS classification	ASTM D 2488	CL

It is a neutral organic compound with three aromatic rings. It is hydrophobic in nature with very low aqueous solubility of 1.1 mg/L at 25°C. Nickel was selected as a representative heavy metal, due to its occurrence at majority of contaminated sites. For testing purposes, nickel chloride salt ($NiCl_2 \cdot 6H_2O$) was used as the source chemical for nickel. Both contaminants were selected at 500 mg/kg of dry soil each, which represents the typical concentrations at the contaminated sites.

H_2O_2 was used as the flushing solution at the anode in all the experiments. Diluted H_2O_2 stock solutions in 5% and 10% concentrations were prepared from 30% H_2O_2 solution using de-ionized water. Native iron in the kaolin soil alone was used as the iron catalyst for Fenton's reaction.

Contaminated soil preparation

For each experiment, about 300 g of dry kaolin soil were taken in a glass beaker, and the predetermined amount of phenanthrene required to achieve the target concentration was dissolved in hexane in a separate glass beaker. The phenanthrene-hexane mixture was then mixed with the soil. The solution was allowed to mix within the soil homogeneously by constant stirring with stainless steel spoons. Additional amounts of hexane were added to allow thorough mixing of the soil. The mixing was carried out in a fume hood, and care was taken to reduce the volatilization of hexane with phenanthrene. Once the mixing was completed, the soil was kept in the same fume hood for about three days to

dry. After the soil was completely dry, it was transferred into a plastic pan and mixed with nickel chloride solution to yield a nickel concentration of 500 mg per kg dry soil. For this, nickel chloride salt was mixed in a known volume of de-ionized water to achieve an initial target soil moisture content of 35% by weight, and the resulting solution was mixed with the soil. After mixing continuously for homogeneity, a representative sample from the soil was taken for analysing moisture content, pH, and the actual initial concentration of phenanthrene and nickel in the soil.

Electrokinetic experiments

Figure 1 shows a schematic of the bench-scale electrokinetic test set-up used for this study. A detailed description of the test set-up is given by Reddy *et al.* (2001) and Reddy and Saichek (2004). The spiked soil

was uniformly compacted in the electrokinetic cell to achieve a final dry density of 1.24 to 1.37 g/cm³. Once the soil was packed in the cell, filter papers were attached to both ends of the soil and then the cell was closed by electrode assemblies that consisted of porous stone and slotted graphite electrodes on both ends. The anode reservoir was connected to the anode assembly, and a sample collection bottle was placed at the cathode outlet. Initially, the anode reservoir and assembly were filled with 5% or 10% hydrogen peroxide solution and the cathode assembly was filled with de-ionized water. A constant voltage gradient of 1 or 2 VDC/cm was applied across the soil sample. Electric current and the electro-osmotic flow were measured at regular time intervals. Periodically, outflow samples were collected at the cathode.

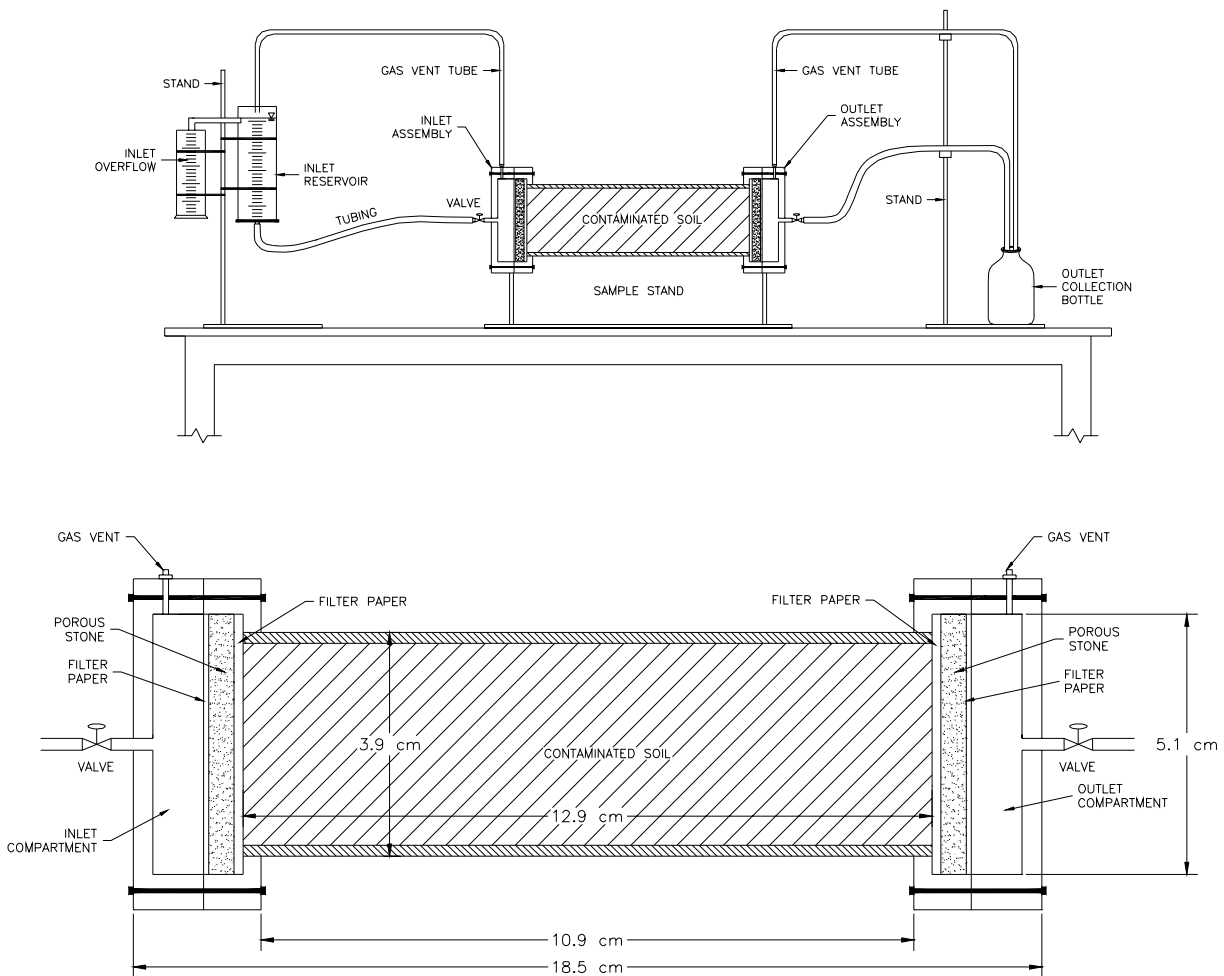


Figure 1. Bench-scale electrokinetic test set-up

At the end of the each experiment, aqueous solutions from anode and cathode reservoirs and the electrode assemblies were collected separately and the volumes were measured. The soil sample was extruded from the electrokinetic cell and sliced into five equal sections. The section close to the cathode was then sliced into two equal subsections to better define the pH and distribution of contaminants near the cathode. Each soil section was stored in a glass jar, and a representative sample was tested for final moisture content using the standard methods ASTM D2216 and ASTM D4972, respectively.

Chemical analysis

Phenanthrene analysis

To determine the residual phenanthrene distribution in the soil at the end of the testing, Soxhlet extractions were first performed on each soil section according to the USEPA test method 3540C (USEPA 1986; Reddy and Saichek 2004; Maturi 2004). For this extraction, about 10 grams of dry soil were taken in a Whatman cellulose extraction thimble and mixed with 10 grams of anhydrous sodium sulphate. About 95 mL of acetylene and 95 mL of methylene chloride were taken in a round-bottomed flask. The thimbles were placed in the Soxhlet extraction tube and these tubes were connected to the round-bottomed flasks containing solvents. The Soxhlet extraction process was operated for at least 24 hours. At the end of the extraction, the final volume of extractant was measured. The same extraction procedure was performed on the initial spiked soil to determine initial phenanthrene concentration in the soil prior to treatment.

For analysing the amount of phenanthrene in the Soxhlet extractants, a gas chromatograph (GC), Hewlett Packard Model HP6890 Series GC system, was used. The GC was equipped with a flame ionization detector (FID) and a column HP-5 (cross-linked 5% PH ME Siloxane) with dimensions 30 m \times 0.32 mm \times 0.25 μ m film thickness. The injection of samples was carried out manually. One μ L sample was injected for each run. Helium was used for make-up flow at a constant pressure of 25 mL/min. The initial oven set-point temperature was 100°C and was ramped at 15°C per minute for ten minutes up to 250°C with a total run time for each sample of eleven minutes. The GC was calibrated by using 2-fluorobiphenyl as an external

standard. Standard phenanthrene solutions were prepared in different concentrations ranging from 1 to 40 mg/L. Based on the surrogate concentrations, the extraction efficiencies were calculated.

The liquid samples collected at the electrodes were analysed for phenanthrene concentration after performing liquid-liquid extraction (Maturi 2004). For this, one mL of the liquid sample was taken in a test tube and it was diluted with water to a 1:10 ratio. Then 200 μ L of 2-fluorobiphenyl were added to the test tube. Later, 2 mL of methylene chloride were added to the mixture and the test tube was then hand-shaken for about 5 minutes. The aqueous and methylene chloride phases were allowed to separate, and then about 1–2 mL of the separated organic phase of the solution were taken into an auto-sampler vial using a syringe. The extractants were analysed for phenanthrene using GC.

Nickel and iron analysis

Acid digestion of the initial spiked soil and all soil sections was performed according to the USEPA 3050 procedure (USEPA 1986). Then the concentrations of nickel and iron were measured using an atomic absorption spectrophotometer (USEPA 1986). Iron was analysed to assess availability of natural iron in the soil to function as a catalyst in Fenton-like oxidation of phenanthrene. For acid digestion, about 2 g of soil sample were taken in a conical flask. Next, 10 mL of 1:1 nitric acid (HNO₃) were added to it, and the soil and acid solution were mixed thoroughly. Then the soil-acid solution was covered with a watch glass, heated to about 95°C, and then refluxed for about 15 minutes. The sample was then allowed to cool and 5 mL of concentrated HNO₃ were added to it. The solution was then refluxed for 30 minutes. After cooling, the last step was repeated one more time. Covering the conical flask with a ribbed glass, the sample was allowed to reflux until it evaporated to about 5 mL. After cooling the sample, about 2 mL of de-ionized water and 3 mL of 30% hydrogen peroxide (H₂O₂) were added. It was heated again to observe the effervescence. As the effervescence subsided, the sample was allowed to cool and another 1 mL of H₂O₂ was added again and the mixture was heated. This addition of H₂O₂ was continued another eight times, so that the total H₂O₂ added was less than 10 mL. Once the sample was allowed to cool, 5 mL of concentrated hydrochloric acid (HCl) were

added with 10 mL of de-ionized water. The mixture was then heated for 15 minutes, and finally cooled. Later, it was centrifuged at about 4000 rpm for about 30 minutes so that both the solid and liquid phases were separated. The supernatant was diluted to 100 mL, and this was then used to determine the concentrations of nickel and iron using an atomic absorption spectrophotometer (AAS). Liquid samples collected at anodes and cathodes were also analysed for nickel and iron using AAS. A calibration curve was prepared based on a range of standard concentrations. Samples with high concentrations were diluted whenever concentrations exceeded the highest standard concentration used in the calibration.

Quality control/quality assurance

In order to ensure the accuracy and reproducibility of the results, all the experiments were conducted in replicates. Uniform testing conditions were maintained in all the experiments by properly sterilizing the electrokinetic cells, electrode assemblies and electrode reservoirs. During the analysis of iron and nickel using the AAS, and of phenanthrene using the GC, care was taken to ensure that the samples were checked for accuracy by regularly checking the instruments for standard concentrations. Also, the mass balance analyses were performed for nickel in all the experiments and for phenanthrene in the baseline experiment using de-ionized water (Karri 2005).

Table 3. Initial properties of contaminated soil

Parameter	Value
Moisture content (%)	34.6
Dry bulk density (g/cm ³)	1.24–1.37
pH	5.80
Nickel concentration (mg/kg–dry)	482
Phenanthrene concentration (mg/kg–dry)	447
Iron concentration (mg/kg–dry)	805

Table 4. Initial properties of flushing solutions

Flushing solution	pH	Electrical conductivity (μS/cm)	Redox potential (mV)
Deionized water	7.87	6.80	122.2
5% H ₂ O ₂	6.32	17.42	218.2
10% H ₂ O ₂	6.48	20.56	209.5

RESULTS AND DISCUSSION

The measured initial properties of the contaminated soil are summarized in Table 3. Also, the initial properties of the flushing solutions, along with de-ionized water, are presented in Table 4. The results of the electrokinetic experiments were analysed to assess the electric current and electro-osmotic flow during the electric potential application as well as the soil pH, and contaminant removal and/or oxidation in the soil at the end of testing.

Figure 2 shows the variation of electric current at different intervals of time throughout the testing period. Electric current increased rapidly and then decreased rapidly during the initial stage of testing within the first 24 hours. With 1 VDC/cm, the current increased to 10 mA, then dropped rapidly to about 3 mA and finally stabilized at 0.3 mA. However, with 2 VDC/cm, the current increased to 44 mA, then dropped rapidly to about 2 mA and finally stabilized at 0.3 mA. The high initial currents in the 2 VDC/cm experiments can be attributed to the higher initial mobility of ions in the soil. These initial high currents are due to the presence of salt precipitates that go into the solution (Mitchell 1993). In addition, due to electrolysis reactions, H⁺ ions are generated at the anode and OH⁻ ions are generated at the cathode. These ions, being constantly generated, possess high mobility into the soil. Due to the inflow of acidic solution, the pH of the soil will be lowered, which may lead to additional mineral dissolution and a higher current. The ions move constantly into the soil due to electromigration and electro-osmosis processes. Over time, these ions are depleted as they move into the electrode chambers, causing the current values to drop as time progresses (Eykholt 1992; Pamukcu 1994; Grundl and Michalski 1996). Although the initial current values are higher for 2 VDC/cm experiments than in 1 VDC/cm experiments, after a period of about 48 hours, all the experiments showed similar values of electric current. As soon as ionic movement progressed into the soil in the 2 VDC/cm experiments, the depletion of ions also occurred at a similar rate. Therefore after a certain time, the ionic strength of the pore solution in the experiments with 2 VDC/cm became equivalent to that in the experiments with 1 VDC/cm.

Figure 3 shows the variation in the electro-osmotic

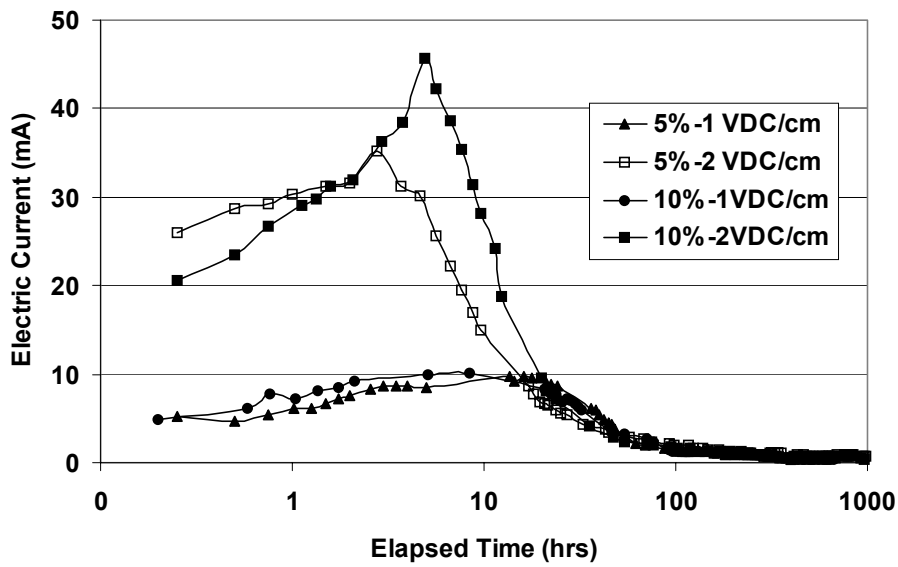


Figure 2. Electric current during testing

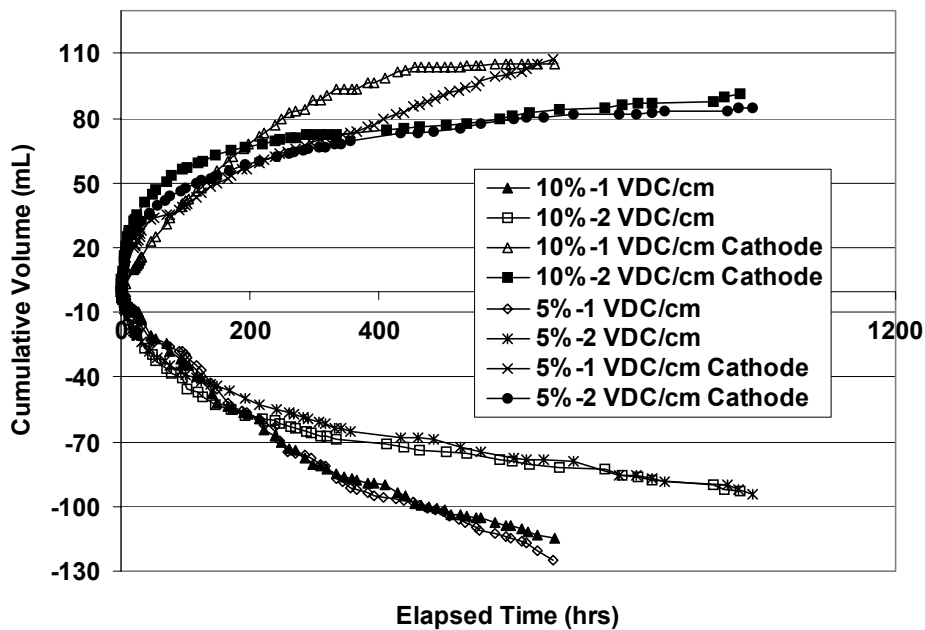


Figure 3. Electro-osmotic flow during testing

flow during the testing process. Flow increased rapidly in the 2 VDC/cm experiments during the initial 24 hours. As much as 30 mL were collected in the first 24 hours of testing and later on, as the current value decreased, the flow rate also decreased simultaneously. The flow rate remained almost constant later during the

remainder of the testing period. During the initial stages, flow increased at a uniform rate in the case of 1 VDC/cm, but not as high as that observed in the experiment with 2 VDC/cm. The flow rate continued to increase during the entire test duration in the experiments with 1 VDC/cm. The cumulative electro-osmotic

flow in the case of 1 VDC/cm was about 107 mL, whereas in the case of 2 VDC/cm it was about 91 mL. This shows that the flow in 1 VDC/cm was comparable to that in the 2 VDC/cm experiment. In the 1 VDC/cm experiments, approximately 1.4–1.6 pore volumes of electro-osmotic flow were obtained near the cathode in the 5% H₂O₂ experiments, and about 1.3–1.5 pore volumes were obtained in 10% H₂O₂ experiments. In the 2 VDC/cm experiments, approximately 1.2 pore volumes were obtained in 5% H₂O₂ experiments, and about 1.3 pore volumes were obtained in 10% H₂O₂ experiments. The high flow rate during the beginning stages was due to high initial currents. The flow rate decreases as ionic movement subsides, which is shown from the lower current values at a later stage of testing. In the 2 VDC/cm experiments, the flow rate decreased gradually, due to the depletion of migrating ions. Also, due to the precipitation of nickel ions at the cathode, the movement of ions could be reduced.

The difference in electro-osmotic flow conditions between 1 VDC/cm and 2 VDC/cm experiments was not significant. Therefore, it appears that increasing the voltage gradient may not necessarily increase the electro-osmotic flow. The reason is that the higher voltage gradient may increase the electrolysis reaction at the anode and consequently increase H⁺ ion generation.

Thus, the soil pH near the anode would be reduced, which causes the charge on the soil mineral surface to be more positive, possibly counteracting the electro-osmotic flow and/or the number of ions in the solution (Reddy and Saichek 2004). Therefore, the low pH conditions can reduce the electro-osmotic flow with time. Thus, there is no appreciable increase in cumulative flow towards the end of the testing in the case of the 2 VDC/cm experiments. Another significant adverse impact on electro-osmotic flow could be the precipitation of nickel ions as nickel hydroxide near the cathode. Consequently, ionic strength decreases, which was shown from the lower current values at a later stage of testing (Figure 2).

As shown in Figure 4, the soil pH increased from anode to cathode in all the experiments. In the first five sections from anode, the soil pH was reduced to values in the range of 2–4 in both the 1 and 2 VDC/cm experiments. In the sixth section, which is near the cathode, high pH values of about 10.5 were observed in the 1 VDC/cm experiment. In the case of the 2 VDC/cm experiment, pH values increased to about 7.5. Lower pH values were observed in the case of the 2 VDC/cm experiment than the 1 VDC/cm experiment. Due to electrolysis reactions, the acidic solution generated by H⁺ ions at the anode migrates into the soil towards the

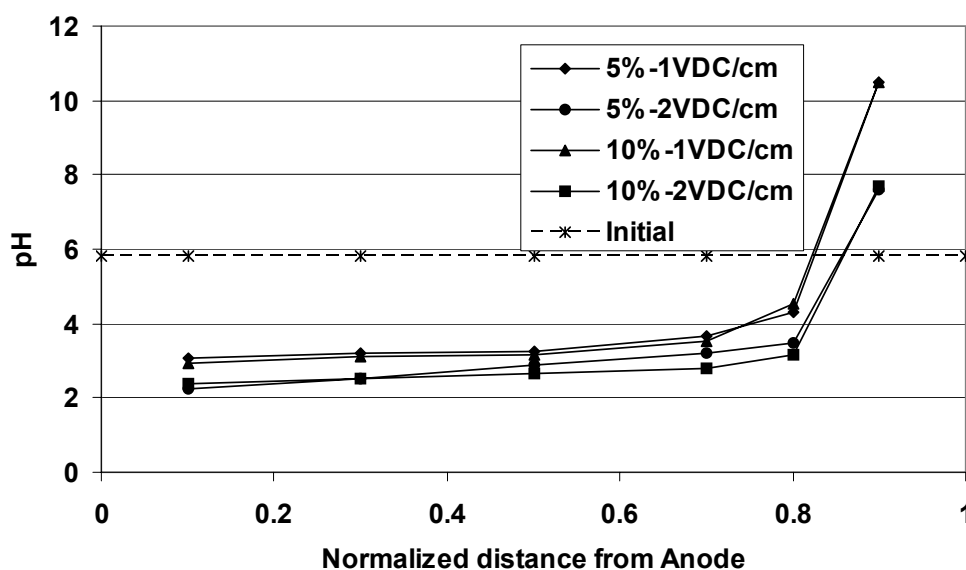


Figure 4. Soil pH distribution after testing

cathode, thereby reducing the soil pH. The alkaline solution generated by OH^- ions at the cathode migrates towards the anode, increasing the soil pH near the cathode. The extent of transport of H^+ ions under 2 VDC/cm was greater than that observed under 1 VDC/cm, resulting in lower pH through most of the soil. The observed non-uniform pH changes significantly affect the surface charge of soil particles (hence the electro-osmotic flow) and solubilization and adsorption/precipitation of heavy metals.

Figure 5 shows the distribution of nickel in various sections of soil from anode to cathode at the end of testing. Nickel concentration remained very low and almost similar in all the experiments throughout the first four sections from the anode. It increased in the fifth and the sixth sections in the case of the 1 VDC/cm experiments. Whereas, in the case of the 2 VDC/cm experiments, the nickel concentration in the fifth section decreased to almost the same as in the first four sections; in the sixth section, however, it increased to a very high value. In general, the concentration of nickel at the cathode was very high in all the experiments, due to the high pH conditions existing near the cathode. Nickel migrates towards the cathode in its cationic state. Under acidic conditions, solubilization of nickel, as well as its hydroxides, is favourable. Therefore, in the first four to five sections from the anode, the concentration of nickel was very minimal. This implies

that nickel was dissolved in the pore solution, and moved towards the cathode due to electromigration and electro-osmosis. The low pH conditions as in the case of the 2 VDC/cm experiments, caused high solubilization of nickel. As a result, the mobility of nickel in most of the sections towards the cathode was higher in the experiments with 2 VDC/cm. However, in the case of the 1 VDC/cm experiments, the pH was comparatively high, implying lesser solubilization and mobility of nickel towards the cathode. Electromigration was the dominant transport process as compared to electro-osmotic advection for the nickel in all experiments. The electric potential was increased, with the premise that it would increase the ionic mobility in the soil, thereby inducing higher electro-osmotic flow. However, the creation of very low pH conditions in the soil near the anode caused the soil mineral surface to become positive, implying a positive zeta potential that decreases electro-osmotic flow towards the cathode. In addition, the rapid flow conditions during the initial stages of testing with 2 VDC/cm could not be sustained, due to faster nickel migration and precipitation near the cathode.

The distribution of residual phenanthrene in the soil after testing is shown in Figure 6. Phenanthrene concentrations decreased throughout the soil as compared to the initial concentration in all the experiments. However, phenanthrene removal into the electrode reser-

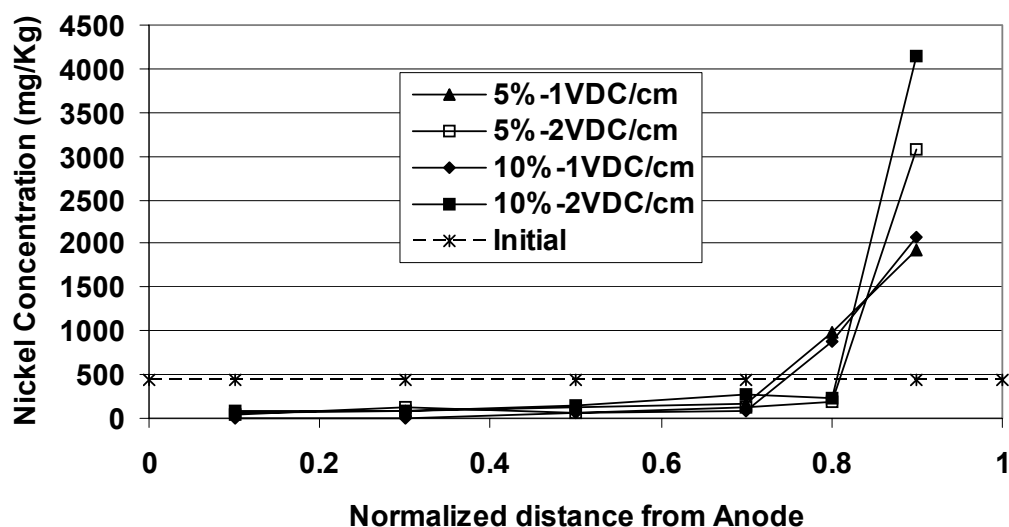


Figure 5. Nickel distribution in the soil after testing

Table 5. Phenanthrene removal, oxidation and overall remedial efficiency

Experiment	Number of pore volumes	Initial mass of phenanthrene in soil (mg)	Final mass in soil (mg)	Mass in effluent (mg)	Mass removed %	Mass oxidized %	Remedial efficiency %
1	1.6	89.8	64.6	0.6	0.7	28.0	28.7
1R	1.4	90.6	66.3	0.6	0.7	26.6	27.6
2	1.5	89.8	62.5	0.5	0.5	30.4	30.9
2R	1.3	88.9	56.2	0.5	0.6	36.9	37.4
3	1.2	93.1	63.5	0	0	31.8	31.8
3R	1.2	88.2	59.8	0	0	32.3	32.3
4	1.3	84.1	49.4	0	0	41.2	41.2
4R	1.2	87.3	49.4	0	0	43.5	43.5

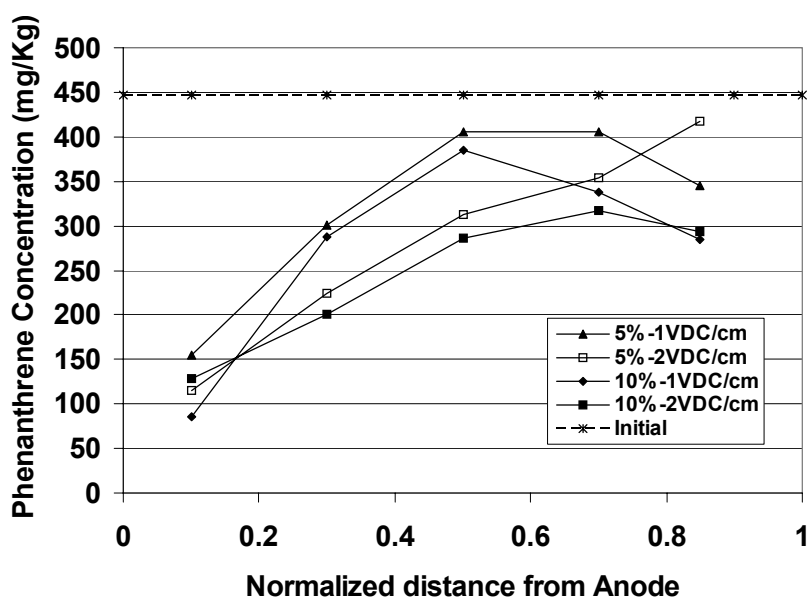


Figure 6. Phenanthrene distribution in the soil after testing

voirs was insignificant in all the experiments. Phenanthrene concentrations were higher from anode to cathode in all the experiments. The concentration of phenanthrene remained lower throughout the first five sections in the case of the experiments with 2VDC/cm than those in the experiments with 1 VDC/cm. However, in the sixth section, the concentration of phenanthrene was comparatively higher in case of the 2 VDC/cm experiments (ranging from 340 mg/kg to 411 mg/kg) than that in case of the 1 VDC/cm experiments (ranging from 323 mg/kg to 360 mg/kg).

Based on the concentrations in effluent as well as the initial and final concentrations of phenanthrene within the soil, the per cent removal, per cent oxidation, and combined remedial efficiencies were calculated, and these results are summarized in Table 5 and Figure 7. These results show that the per cent removal of phenanthrene is negligible and that the overall remedial efficiency of phenanthrene is mainly attributed to oxidation. The remedial efficiency increased with voltage gradient. With 1 VDC/cm, about 28% remedial efficiency was obtained in the 5% H₂O₂ experiment

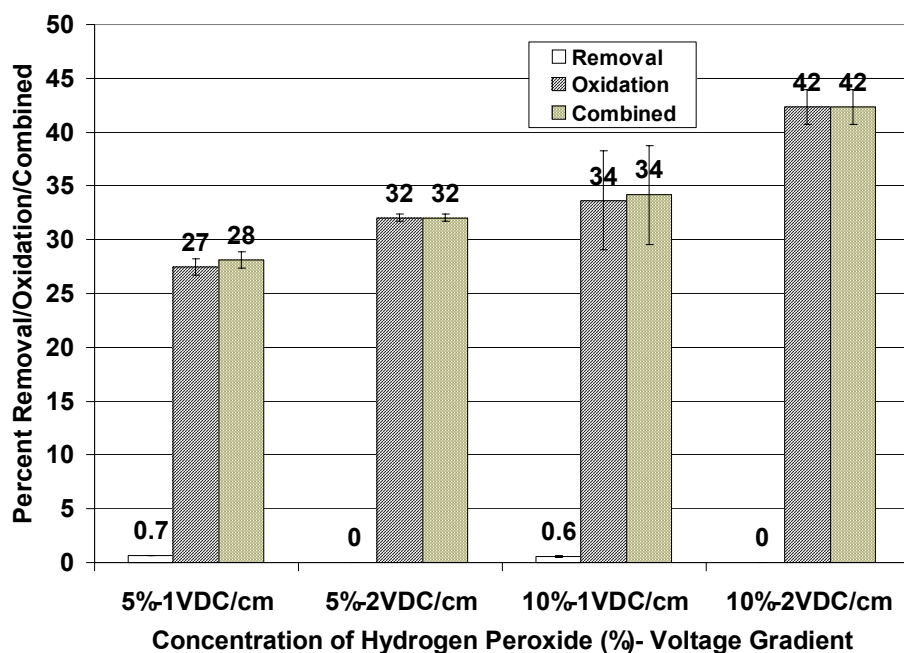
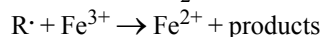
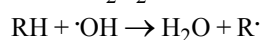
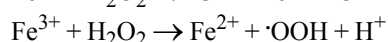
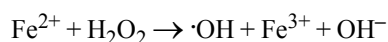


Figure 7. Phenanthrene removal, oxidation and overall remedial efficiencies

and about 34% remedial efficiency was obtained in the 10% H₂O₂ experiment. With 2 VDC/cm, about 32% remedial efficiency was obtained in the 5% H₂O₂ experiment and about 42% remedial efficiency was obtained in the 10% H₂O₂ experiment. The oxidation of phenanthrene can be attributed to the following Fenton-like oxidation reactions (Walling 1975):



In the above reactions, R represents phenanthrene (organic contaminant). In this study, native soil iron served as iron catalyst in the above reactions. H₂O₂ upon reaction with ferrous ion produces hydroxyl radicals which oxidize phenanthrene. Therefore, in all the soil sections of all the experiments, the concentration of phenanthrene reduced significantly. The increasing concentrations of phenanthrene from anode to cathode reflect the extent of H₂O₂ transport into the soil. The H₂O₂ solution was injected from the anode, and, due to electro-osmosis, the more contaminated soil near the

anode was exposed to H₂O₂. As the contaminant comes into contact with H₂O₂, Fenton-like oxidation occurs and therefore more phenanthrene oxidizes near the anode. The transport of H₂O₂ further into the soil depends on the extent of electro-osmotic flow. However, as the current values decreased with time, the electro-osmotic flow also decreased. Therefore, the interaction of H₂O₂ and contaminated soil decreased towards the cathode. Hence, the residual phenanthrene concentrations increased from anode to cathode in all the experiments.

Figure 8(a) shows the residual total iron (Fe) distribution in the soil from anode to cathode in all the experiments. The iron concentration was higher in all the sections from anode to cathode, with the concentrations ranging from 544 to 1200 mg/kg of dry soil. Only a very low amount in the range of about 0.1 to 0.3 mg of iron was removed from the soil in all the experiments. The iron fraction available for Fenton-like oxidation reactions was determined by leaching experiments. These experiments consisted of mixing 2 g of soil with 10 mL of de-ionized water, shaking the mixture, and finally separating and analysing the Fe concentrations

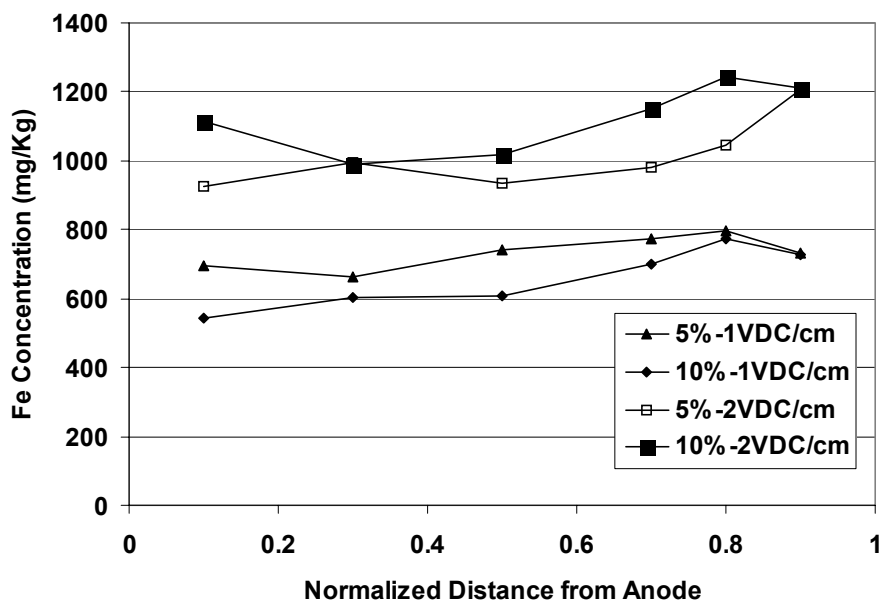


Figure 8(a). Total iron distribution in the soil after testing

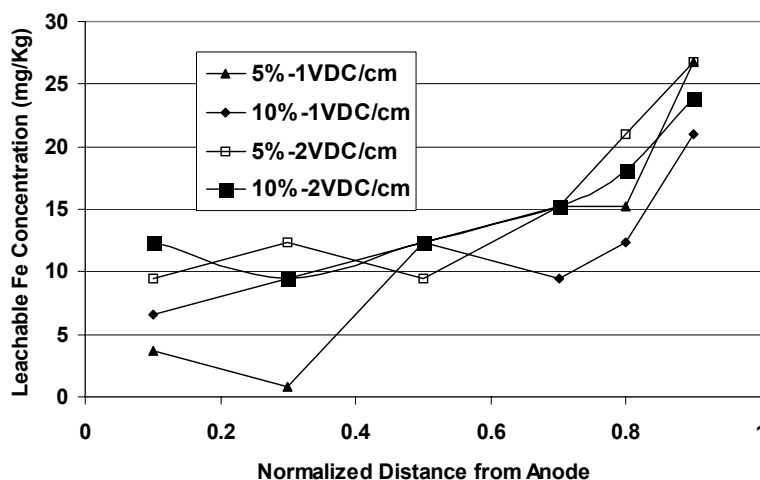


Figure 8(b). Leachable iron distribution in soil after testing

of the supernatant. The distribution of leachable iron (Fe) in different soil sections is shown in Figure 8(b). The leachable Fe concentration increased gradually from anode to cathode in all the experiments. In the case of the 5% H₂O₂ experiment, the concentration increased from 4 to 27 mg/kg of soil from anode to cathode. In the case of the 10% H₂O₂ experiment, the concentration increased from 7 to 21 mg/kg of soil

from anode to cathode. These results show that a considerable amount of native iron was readily available for Fenton-like oxidation, and that it was not the limiting factor for phenanthrene oxidation. The reason for low oxidation of phenanthrene may be due to low electro-osmotic flow, leading to insufficient amount/concentration of H₂O₂ available for the oxidation of phenanthrene. Other factors such as soil-H₂O₂-phen-

anthrene interaction and solubilization may also have affected the overall oxidation of phenanthrene.

CONCLUSIONS

The main objective of this research was to assess the effects of voltage gradient on the remedial efficiency of integrated electrochemical remediation of mixed contaminants in low permeability soils. This remedial strategy aims to deliver H_2O_2 by electro-osmosis to achieve Fenton-like oxidation of PAHs and to remove heavy metals simultaneously by electro-osmosis and electromigration. Generally, clayey soils possess high amounts of iron and it is hypothesized that the native soil iron can serve as a catalyst in Fenton's reaction. A series of bench-scale experiments performed on kaolin soil spiked with nickel and phenanthrene under two different voltage gradient conditions resulted in the following conclusions:

- Significant migration of nickel occurred from anode to cathode in all experiments. However, nickel precipitated near the cathode, due to high pH conditions. Increasing the voltage gradient to 2 VDC/cm reduced pH throughout the soil, as compared to that of the 1 VDC/cm experiment, resulting in greater migration of nickel towards the cathode. However, nickel precipitated in the close vicinity of cathode even in the 2 VDC/cm experiment, due to the high pH conditions. The presence of phenanthrene and the use of hydrogen peroxide solution in the anode did not appear to influence the soil pH distribution and transport of nickel in the soil.
- A significant amount of phenanthrene was oxidized with the injection of hydrogen peroxide from the anode into the soil. Phenanthrene oxidation is mainly attributed to the reactions with the hydroxyl radicals resulting from the oxidation of H_2O_2 in the presence of native iron in the soil. The native iron in the soil acted as an effective catalyst for the oxidation reaction. Clayey soils possess a high iron content, with sufficient fraction existing in easily leachable form available for Fenton-like reaction. The increased voltage gradient induced slightly higher electro-osmotic delivery of hydrogen peroxide, leading to increased phenanthrene oxidation.
- The removal of both nickel and phenanthrene from

the soil was very low. Although phenanthrene removal is not desirable, nickel removal is essential for the effective remediation. In order for integrated electrochemical remediation to be viable, strategies to enhance both phenanthrene oxidation and removal of nickel should be explored. These strategies may encompass increased delivery of H_2O_2 , better interaction of H_2O_2 with phenanthrene, and solubilization of precipitated metals near the cathode.

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