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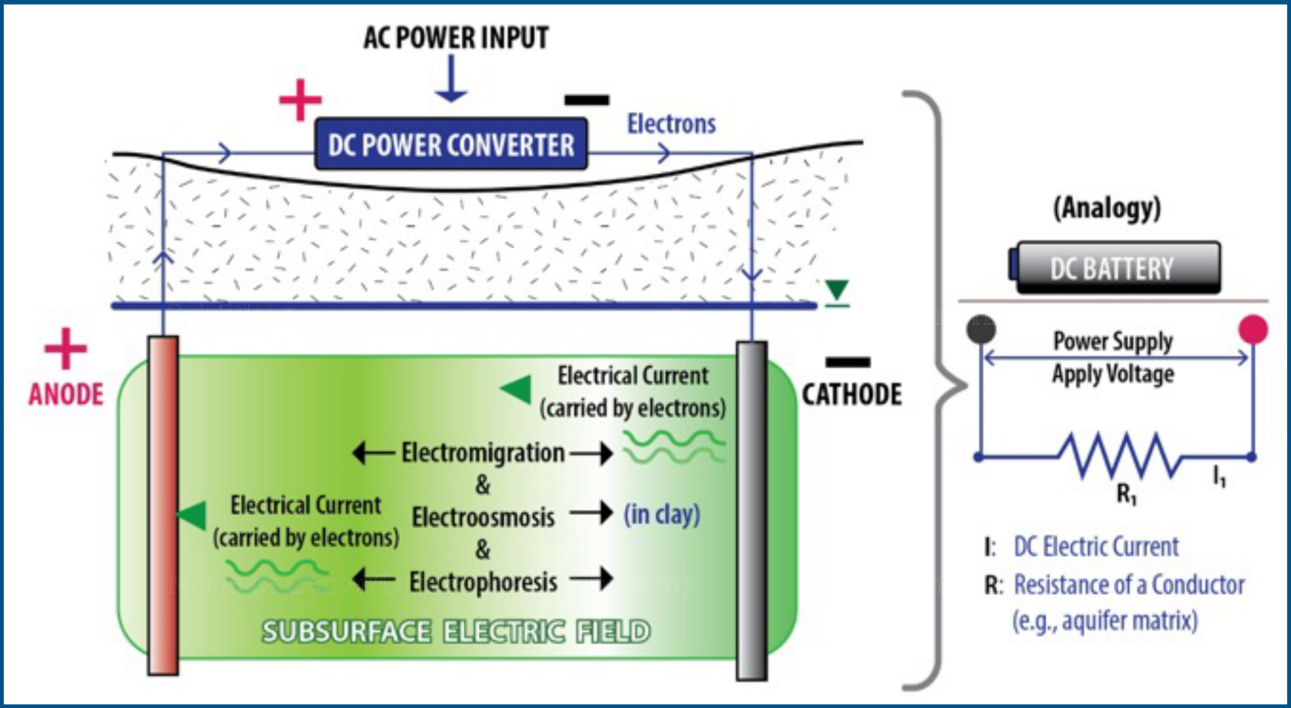
Electrokinetic (EK) Enhanced *In Situ* Remediation

ENGINEERING ISSUE PAPER



Office of Research and Development
Center for Environmental Solutions and Emergency Response
Technical Support Coordination Division

Electrokinetic (EK) Enhanced In Situ Remediation

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Foreword:

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Gregory Sayles, Director
Center for Environmental Solutions and Emergency Response

Table of Contents

APPENDICES

Figures

Tables

Acknowledgments

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This EIP is intended as an overview of EK-enhanced *in situ* remediation technologies for EPA staff, regional program offices, RPMs, and state governmental environmental staff. Interested parties should further consult the body of literature and experience that constitutes the state-of-the-science.

Web links are provided for readers interested in additional information; these weblinks, while accurate at the time of publication, are subject to change. As of the date of this publication, questions may be addressed to:

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Acronyms, Abbreviations, and Symbols

°C	Degrees Celsius
2-D	Two-dimensional
A	Ampere
AC	Alternating current
AOP	Advanced oxidation process
ARAR	Applicable or Relevant and Appropriate Requirements
bgs	Below ground surface
c_i	Dissolved concentration of compound *i* in the pore fluid
cDCE	cis-1,2-Dichloroethene
CESER	Center for Environmental Solutions and Emergency Response
cm	Centimeter
COC	Contaminants of concern
CSM	Conceptual site model
CVOC	Chlorinated volatile organic compounds
DC	Direct current
Dhc	*Dehalococcoides*
DHG	Dissolved hydrocarbon gases
DNAPL	Dense nonaqueous phase liquid
DNT	Dinitrotoluene
DO	Dissolved oxygen
DoD	Department of Defense
DPT	Direct push technology
EIP	Engineering Issue Paper
EISB	Enhanced *in situ* bioremediation
EK	Electrokinetic
EK-BIO	EK-enhanced *in situ* bioremediation
EK-ISCO	EK-enhanced *in situ* chemical oxidation
EK-ISCR	EK-enhanced *in situ* chemical reduction
EPA	U.S. Environmental Protection Agency
ERH	Electrical resistance heating
ESTCP	Environmental Security Technology Certification Program
ETSC	Engineering Technical Support Center
FRTR	Federal Remediation Technologies Roundtable
FS	Feasibility study
ft	Foot / Feet
g	Gram
gpm	Gallon per minute
GWTSC	Groundwater Technical Support Center
HDPE	High-density polyethylene
i_e	Voltage gradient applied
ISCO	*In situ* chemical oxidation
ISCR	*In situ* chemical reduction
J_i^e	Rate of mass transport of compound *i* by electroosmosis
J_i^m	Rate of mass transport of compound *i* by electromigration
K_e	Coefficient of electroosmotic permeability of the soil
kg	Kilogram

K_h	Hydraulic conductivity
kW-hr	Kilowatt-hour
L	Liter
low-k	Low-permeability
m	Meter
mA	Milliamp
mg	Milligram
MTBE	Methyl tertiary-butyl ether
mV	Millivolt
NAS	Naval Air Station
NOD	Natural oxidant demand
NRC	National Research Council
NVOC	Non-volatile organic carbon
nZVI	Nanoscale zero-valent iron
O&M	Operation and maintenance
OLEM	Office of Land and Emergency Management
OM&M	Operation, Maintenance, & Monitoring
ORD	Office of Research and Development
ORP	Oxidation-reduction potential
OSC	On-scene coordinator
OU	Operable unit
PCB	Polychlorinated biphenyl
PCE	Tetrachloroethene
PFAS	Per- and polyfluoroalkyl substances
PVC	Polyvinyl chloride
RAO	Remedial action objective
Redox	Oxidation-reduction
RG	Remediation goals
RI	Remedial investigation
ROD	Record of Decision
RPM	Remedial project manager
sec	Second
SEMD	Superfund and Emergency Management Division
SSZ	Saturated source zone
TCE	Trichloroethene
TIFSD	Technology Innovation and Field Services Division
TOC	Total organic carbon
U_i^*	Effective ionic mobility of compound *i* under one unit of voltage gradient
µM	Micromole
V	Volt
VC	Vinyl chloride
vcrA	Vinyl chloride reductase genes
VFA	Volatile fatty acid
VOC/SVOC	Volatile/Semi-volatile organic compounds
W	Watt
ZVI	Zero-valent iron

Executive Summary

The U.S. Environmental Protection Agency (EPA) Engineering Issue Papers (EIPs) are a series of technology transfer documents that summarize the latest information on selected waste treatment and site remediation technologies and related issues and present it in a conveniently accessible manner to the user community. This EIP summarizes the current knowledge on electrokinetic (EK)-enhanced *in situ* remediation technologies that are available for addressing contaminants in low-permeability (low-k) subsurface environments where conventional hydraulic delivery technologies often face challenges.

Various *in situ* remediation technologies, such as enhanced *in situ* bioremediation (EISB), *in situ* chemical oxidation (ISCO), and *in situ* chemical reduction (ISCR), are well-established and have been demonstrated as effective when applied properly. However, experiences over the past decades indicate that *in situ* remediation implementation can be especially challenging at sites with low-k formations. Within low-k materials, diffusive transport of the remediation reagents is a predominant transport mechanism leading to a lengthy remediation timeframe and sometimes rendering remedial options infeasible or impractical. The most prominent underlying limitation of applying EISB/ISCO/ISCR in low-k materials via conventional hydraulics-based techniques is the challenge of achieving effective delivery of the remediation amendments to the target treatment zone where the contaminant mass resides. While reagent emplacement techniques via pneumatic or hydraulic fracturing have been developed to enhance delivery, potentially uneven (less controlled) distributions and other possible limitations (e.g., injection daylighting) associated with these techniques require careful consideration of site constraints.

EK-Enhanced Amendment Delivery

EK-enhanced amendment delivery for *in situ* remediation is a technology that does not rely on hydraulic mechanisms to deliver the treatment reagents to a target zone. The overarching concept of this technology is to establish an electric field in the subsurface to provide an enhanced transport mechanism for the remediation reagents. Through this process, a more rapid and broader distribution of the reagents, relative to diffusive transport, in low-k materials can be achieved. EK-enhanced *in situ* remediation is implemented by applying a low-voltage direct current (DC) to the individual electrodes installed in an aquifer. With an external power supply source delivering a direct electrical current and voltage to the electrodes, an electric field is created in the subsurface between cathodes and anodes. As shown in **Figure ES-1**, this is conceptually analogous to a DC battery-driven electrical circuit with the aquifer between electrodes acting as an electrical conducting unit. While the amendment distribution is through the connected pores within the aquifer materials, amendment transport is driven by EK processes (i.e., electromigration, electroosmosis, and electrophoresis), not hydraulic mechanisms. Therefore, the EK approach can enhance reagent transport in low-k materials where diffusion, a slow process, is the key hydraulic transport mechanism. EK is an amendment delivery technique that can be used to deploy EISB, ISCO, and ISCR, respectively referred to as EK-BIO, EK-ISCO, and EK-ISCR.

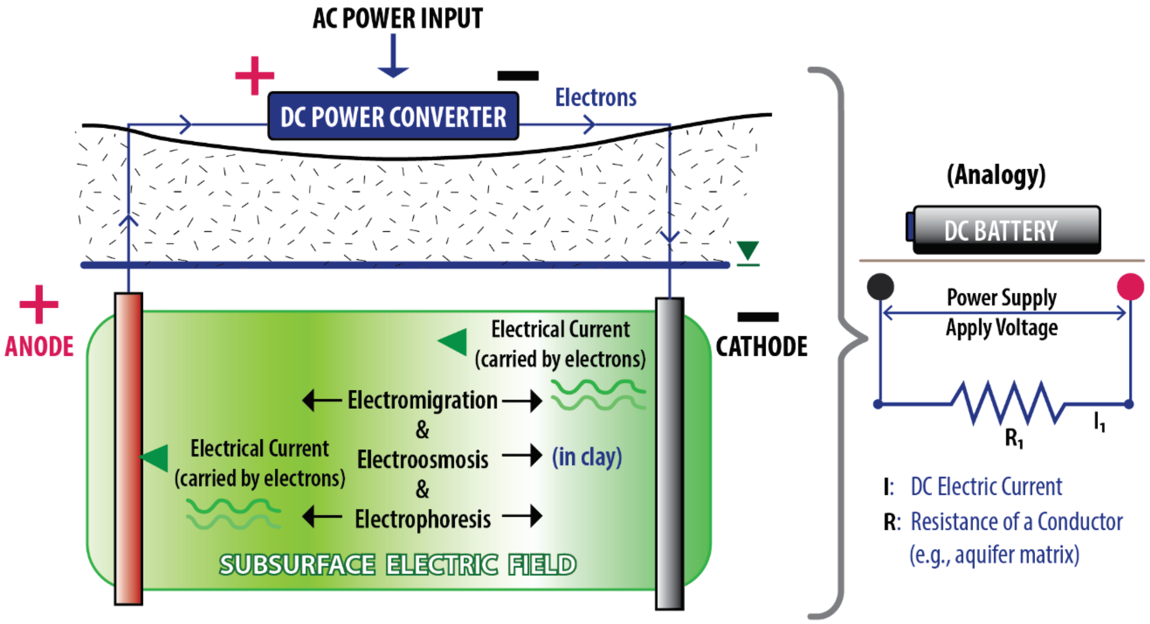


Figure ES-1. Concept: DC Battery-driven Electric Field in Subsurface

EK Transport Mechanism – Electromigration

Electromigration (also known as ion migration) is the movement of ions in the interstitial fluid within the aquifer matrix toward the electrode of opposite charge (**Figure ES-2**). Electromigration sustains the electrical current in a subsurface DC electric field. Charged ions in an aquifer carry the electric current driven by an applied voltage gradient between cathodes and anodes. The extent of electromigration of a given ion in an electric field within the subsurface depends on soil porosity, applied electric potential (voltage), and concentrations of the specific ion and other competitive ions. For *in situ* remediation considerations, electromigration is often the dominant EK transport mechanism for ionic metals, dissolved ions, and ionic micelles.

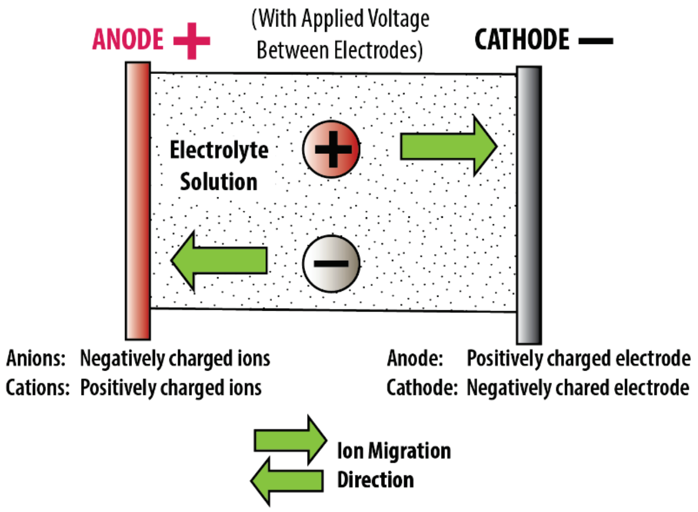


Figure ES-2. Electromigration (Ion Migration)

EK Transport Mechanism – Electroosmosis

Electroosmosis is the fluid movement relative to soil (in this case, clay) particle surface as a result of an applied voltage gradient. Electroosmosis is a complex mechanism that depends on the electrical characteristics of the solid surface, the properties of interstitial fluid, and the interactions between the solid surface and components in the interstitial fluid.

Discrete clay particles, due to their mineralogical compositions, typically have a negative surface charge. This net negative surface charge results in a corresponding positive charge zone with excess positive charge or exchangeable cations in the pore fluid immediately adjacent to the clay particle surface. With a layer of pore fluid adjacent to clay particles exhibiting a property of electrical charge (typically positively charged), a voltage gradient across a subsurface electric field induces the movement of pore fluid, sometimes referred to as electroosmotic flow.

EK Transport Mechanism – Electrophoresis

Electrophoresis is the transport of solid particles that exhibit a net surface charge in an electric field under an applied voltage gradient. The concept and fundamentals of electrophoresis are similar to those of electromigration related to the movement of ions in an electric field. However, given that electrophoresis is the movement of solid particles, this transport process in a subsurface is significantly affected by the soil matrices' physical properties. Relative to ion migration and electroosmosis, transport by electrophoresis in low-k aquifer materials is limited and highly dependent on the particle size relative to the formation's pore sizes.

EK-BIO Field-Scale Implementations

A pilot-scale demonstration of EK-BIO was completed at Naval Air Station Jacksonville in Jacksonville, Florida, targeting a tetrachloroethene (PCE) source area in a clay unit underlying a shallow sandy aquifer (ESTCP, 2018). The demonstration included a network of 9 electrode wells and 8 supply wells targeting an area of approximately 40 feet (ft) by 40 ft and a depth interval of approximately 17 to 25 ft below the ground surface (bgs). All the electrode wells, supply wells, and associated double-cased monitoring wells were screened in the targeted clay unit to allow assessments of treatment within the low-k materials. The remediation amendments included lactate, pH control reagents (potassium carbonate), and a dechlorinating microbial consortium (KB-1). The demonstration included two active EK operation stages, 5 months each, with a 6-month incubation period between the two active stages. The system was operated to supply electrical currents of approximately 1.5 amperes (amp; A) and 3 A to each cathode and anode, respectively, which required the DC power supply unit to apply approximately 18 to 29 volts (V) during Stage 1 and 12 to 20 V in Stage 2 operation. The total electrical energy consumption was 1,037 kilowatt-hours (kW-hr) during Stage 1 and 548 kW-hr during Stage 2. The power consumption by the EK system over the active operation period was equivalent to operating a single 100-watt (W) lightbulb for approximately 22 months. The overall monitoring data indicated that the project met the prescribed demonstration performance objectives. Average PCE concentrations were reduced by more than 60% in clay soil and groundwater within the treatment area, with corresponding and comparable increases in dechlorination intermediate and end products detected in the groundwater. Ethene was detected at all the groundwater monitoring wells and greater than a 10-fold increase of dechlorination microbes from baseline levels was observed in >60% of the samples of aquifer solids and groundwater collected from within the clay unit.

A full-scale EK-BIO remedy was completed at a former industrial facility in Skuldelev, Denmark, to remediate a PCE dense nonaqueous phase liquid (DNAPL) source zone in a low-k glacial clay unit (Riis et al., 2023). The full-scale EK-BIO remedy involved a network of 15 electrode wells and 10 amendment supply wells targeting a treatment area of 130 square meters (m^2) and a depth interval of 3 to 8 m bgs. The average spacing between electrodes was approximately 4.5 m, and each electrode well was installed with two vertically separated electrodes, each as a 1-m long titanium electrode with mixed-metal-oxide coating. The electrodes were powered at an average current of 1.7 to 3.3 A each. An initial voltage of 197 V was required to achieve the designed electrical current operation, and decreased with time to a steady level of 50 V. The performance monitoring over the 2-year remedy showed the level of a biomarker, vinyl chloride reductase functional gene (*vcrA*), increased by several orders of magnitude in the treatment area with significant PCE dechlorination end-product, ethene, observed at all treatment area wells. The project met the prescribed remediation goal for site aquifer solids with an estimated

285 kilograms (kg) of PCE (>98% of estimated pre-remedy total) in the treatment area biodegraded. Rebound testing 6 months after cessation of EK-BIO operation confirmed sustained microbial dechlorination activities and compliance with the remedial goals.

EK-ISCO Field Pilot Test

EPA Region 4 pilot tested EK-ISCO using permanganate to address a PCE source area at a former textile plant in North Carolina (Black & Veatch Special Projects Corp. and Geosyntec Consultants of NC, 2020). The target remediation zone resides in a saprolite unit extending from approximately 20 to 70 ft bgs. The saprolite at the site consists primarily of fine sand and silt with variable amounts of clay, representing a heterogeneous matrix. This limited-scale EK-ISCO pilot test included a pair of electrode wells (one cathode well and one anode well), a monitoring well network, an EK power supply unit, and associated amendment supply and operation control systems. Permanganate was supplied as the oxidant of choice. The system supplied DC between 0.7 and 0.9 A to each electrode and the required voltage was between 120 and 160 V. The pilot test operation and monitoring were performed over a period of 57 days. The pilot test monitoring data confirmed the distribution of permanganate within the target zone. The area of permanganate distribution was approximately 40 ft^2 consistent with the design estimate. Treatment of PCE and other chlorinated ethenes was apparent, with 74% to 90% concentration decreases at monitoring wells. This pilot test provided site-specific data supporting the design of a full-scale EK-ISCO remedy to be implemented in a phased approach.

Technical Considerations

Groundwater containing various ions is a conductor allowing for the completion of a direct electric circuit between electrodes. Consequently, a target treatment zone at or below the groundwater table is amenable to EK-enhanced amendment delivery for *in situ* remediation.

EK can be used as an amendment delivery technique deployed to deliver and enhance the transport of remediation amendments into a low-k zone. During remedy feasibility evaluation, the remediation amendments are selected based on the treatment mechanism (e.g., biodegradation, chemical oxidation, chemical reduction) given site-specific contaminants and geochemical conditions. Various ionic compounds can be effectively transported via electromigration, while both ionic and non-ionic compounds can be transported via electroosmosis. In most cases, electromigration is a more dominant transport mechanism relative to electroosmosis. Transport of solid particles (i.e., particulate amendments) via electrophoresis or electroosmosis is relatively limited in a low-k formation given the constraints related to the pore size.

Through effectively delivering treatment reagents into a low-k matrix, the EK approach has the potential to avoid rebounds of contamination, thus, shortening the overall remediation program timeframe. There are several technical considerations that require attention when planning for an EK-based *in situ* remedy:

- **Relative depth of target zone to the groundwater table.**
  Prior attempts to implement EK-enhanced amendment delivery for *in situ* remedy in partially saturated materials have not achieved consistent results. With the field experience to date, the technology should be considered mainly for fully saturated zones.
- **Targeted zones beneath buildings or other surface structures.**
  Current work with EK-based *in situ* remediation has used a network of vertical electrode wells with spacing between individual wells in the range of 15 to 25 ft. A target zone below large buildings and other structures may require the deployment of horizontal wells.

However, the use of horizontal EK systems is a concept that still needs additional technology development.

- **Contaminant hydrogeology.**
  Experiences with EK-enhanced *in situ* remediation to date show this technology merits consideration as a remedial alternative for zones with moderate contaminant strength in lower permeability matrices where back-diffusion may hamper the attainment of remedial goals.

  Particular care should be taken when considering EK applications in brackish-water environments where oxidation of excess chloride at anodes can produce chlorine gas and potentially form chloroform. The use of EK in brackish and highly saline waters should be avoided.

- **Remedy implementation duration.**
  The required remedy duration with EK-enhanced approach is controlled by several compositional and environmental variables that affect the overall process. It is prudent to conduct bench-scale and/or pilot tests for each case to develop an approach that will optimize the treatment process and reduce the remediation timeframe.

1 Introduction

The U.S. Environmental Protection Agency (EPA) Engineering Issue Papers (EIPs) are a series of technology transfer documents that summarize the latest information on selected waste treatment and site remediation technologies and related issues and present it in a conveniently accessible manner to the user community. EIPs are designed to help remedial project managers (RPMs), on-scene coordinators (OSCs), contractors, and other practitioners understand the type of data and site characteristics that are needed to evaluate a technology for a specific site, as well as ways to design and optimize a technology for a particular application.

This EIP summarizes the current knowledge on electrokinetic (EK)-enhanced *in situ* remediation technologies that are deployed for the purpose of treating contaminants in low-permeability (low-k) media. As a technical support document, it describes EK-enhanced remediation with a focus on remedial scoping needs based on direct experience with the development and deployment of the technology in the field. To remain concise, this EIP summarizes relevant information from peer-reviewed literature, government reports, and gray literature (e.g., websites, conference proceedings) and provides references for more in-depth information.

1.1 Background

Even after decades of intensive efforts and investments in restoring the nation's environment at sites impacted by past releases of contaminants, the scale of remaining challenges is tremendous. The National Research Council (NRC) reported "At least 126,000 sites across the country have been documented that have residual contamination at levels preventing them from reaching closure. A small percentage (about 12,000 or less than 10 percent) of the 126,000 sites are estimated by the Committee to be complex from a hydrogeological and contaminant perspective" (NRC, 2013).

The 2013 NRC report also stated "Although there is no formal definition of complexity, most remediation professionals agree that attributes include aerially extensive groundwater contamination, heterogeneous geology, large releases and/or source zones, multiple and/or recalcitrant contaminants, heterogeneous contaminant distribution in the subsurface, and long timeframes since releases occurred. ….. Thus, the more varied the geologic media or lithology, the more complex the flow patterns of contaminants and injected solutions are" (NRC, 2013).

It is generally recognized among remediation professionals that *in situ* remediation is often more cost-effective than *ex situ* approaches (ITRC, 2018). According to the EPA Superfund Remedy Report (USEPA, 2020), *in situ* treatment is selected as the most appropriate remedial approach in half of groundwater decision documents. At these sites, bioremediation and chemical treatment are also noted as the most frequently selected technologies (USEPA, 2020). However, challenging lithological conditions, such as those identified in the NRC report, often present significant obstacles to achieving desired remediation outcomes with the selected *in situ* remediation strategies.

Various *in situ* remediation technologies, such as enhanced *in situ* bioremediation (EISB), *in situ* chemical oxidation (ISCO), and *in situ* chemical reduction (ISCR), are well-established and demonstrated. In many cases, these technologies can be effective, when applied properly, to achieve remedial action objectives (RAOs). While these technologies have been able to achieve the treatment objectives in permeable sandy aquifers, they often face limitations in silt and clay materials, thus extending remediation timeframes and increasing costs.

In situ remedy implementation can be challenging at groundwater sites with low-k media (e.g., clay, silty clay) where diffusion, a much slower transport mechanism than advection, plays a more dominant role in reagent transport and increases the time required to achieve cleanup goals. Layered and heterogeneous deposits with varying permeabilities often result in higher levels of contamination just above low-k layers (Bradford et al., 1998; Kueper et al., 1989; Kueper and Frind, 1991; Schwille and Pankow, 1988). The accumulation of contaminants at the interface between high-k and low-k aquifer materials allows the contaminants to diffuse and penetrate the lower permeability zones directly, or through fingering formations (**Figure 1-1**) (Illangasekare et al., 1995a; Illangasekare et al., 1995b). Advances in the understanding of contaminant mass distributions in the subsurface have highlighted that in many cases most of the mass originally released from the source is held in storage in low-k materials, and that the release rate from the stored mass, via back-diffusion, into the dissolved plume is many times slower than the original rate of contaminant transport (Stroo et al., 2012). This contaminant transport via matrix diffusion, whereas the stored mass acts as a long-term source (often over decades), prevents the remedy from achieving RAOs within a reasonable timeframe. Therefore, an effective remediation program at a site with such long-term sources needs to address the contaminant mass present in low-k materials.

1.1.1 Amendment Delivery Techniques

A prominent underlying limitation of EISB, ISCO, and ISCR in low-k materials is the inability to effectively deliver the required remediation amendments to the targeted treatment zone using conventional hydraulics-based techniques. Depending on the designed approach, and particularly for ISCO and ISCR, the contact or proximity between treatment reagents and contaminant mass is critical to achieving effective treatment (Huling and Pivetz, 2007).

To ensure effective amendment distribution, the delivery technique must be compatible with the subsurface conditions (ITRC, 2020). Hydraulically-driven delivery of remediation amendments may potentially displace contaminated groundwater or mobilize dense nonaqueous phase liquid (DNAPL) in the source area, resulting in inefficient contacts between contaminants and treatment reagents. Laboratory studies on the removal of tetrachloroethene (PCE) contamination showed that a relatively simple layering of materials with less than an order of magnitude difference in permeability between layers leads to difficulty in remediation using hydraulic injection and flushing technologies (Hayden et al., 2006). Much greater volumes of flushing solutions are needed in heterogeneous environments to achieve target levels of flushing. This observation also extends to the injection of remedial reagents in less permeable lenses and

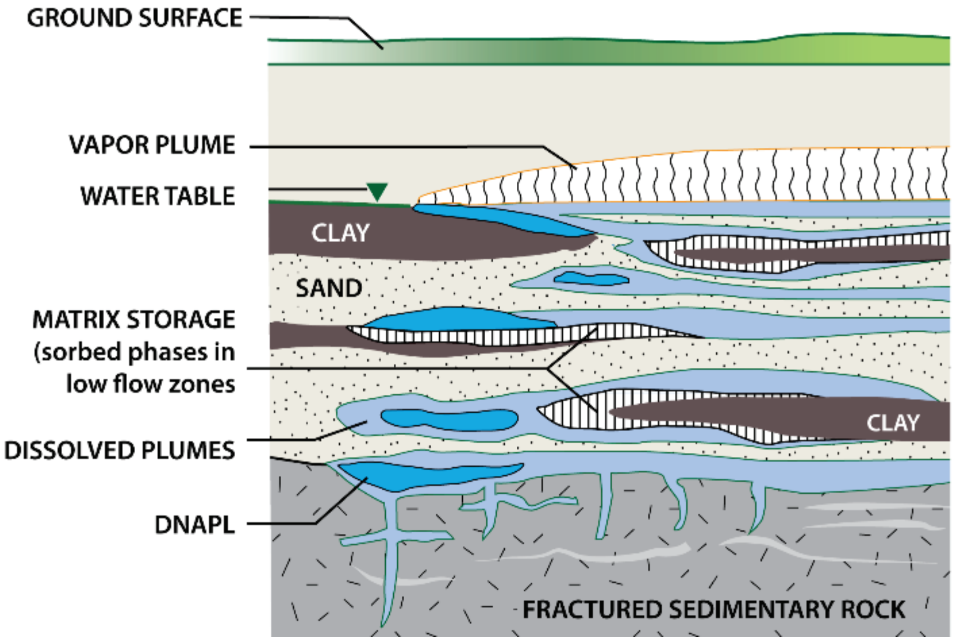


Figure 1-1. Contaminant Mass Storage at Sites with Complex Geology

layers (Hayden et al., 2006). When large volumes of fluids are injected to overcome the flushing inefficiency attributed to lithologic heterogeneities, mounding and mobilization of contaminants induced from increased hydraulic gradients may occur during injection events (ITRC, 2020).

Recirculation is one remedial strategy deployed to improve amendment distribution, but it may not address the contaminant mass stored within low-k materials. With recirculation, accomplished through the use of injection and extraction wells, amendment solution can be flushed through the preferential hydraulic pathways within a target recirculation zone. While recirculation can facilitate the advective transport of the amendments, it may not achieve sufficient penetration of the reagents into low-k materials given the contrast of permeabilities.

High-pressure injection techniques, such as fracturing or jet injection, are also alternative approaches to improving amendment distribution (Christiansen et al., 2010). Conceptually, the high-pressure techniques leverage the structural weakness within the aquifer formation to open and connect additional pores and pathways (i.e., cracks, fractures). Through this process, these techniques can facilitate the hydraulic flows of remediation reagents into more pores and pathways. These injection approaches require an adequate design for the density of pressure application locations and intervals in the subsurface. While these high-energy techniques may allow the delivery of injected reagents into an otherwise impermeable, or minimally permeable, formation, the resultant pathways may not be configured in a well-controlled or uniform pattern.

Additional technologies that do not rely on hydraulic delivery mechanisms have been developed for achieving *in situ* subsurface treatment. For example, large-diameter augers and rotating mixing heads on excavators can be used as part of a direct mixing approach to mechanically distribute amendments into the subsurface. In addition, various *in situ* thermal remediation technologies can be used to heat up soils and aquifer materials which in turn volatilizes and strips contaminants from the subsurface (USEPA, 2014). While these direct mixing and thermal technologies can be effective in targeting low-k materials, there are challenges and limitations at some sites. For example, potential limitations include current and future land use of the direct mixing zone, the presence of utilities, and current site activities within or close to the direct mixing or thermal treatment zone. Overall, it is evident that effective *in situ* remedial technologies for contaminated, low-k aquifer materials are critically needed.

1.1.2 EK-Enhanced Amendment Delivery

EK-enhanced amendment delivery is another technology that does not rely on hydraulic mechanisms to deliver the treatment reagents to a target zone in the subsurface. The overarching concept of this technology is to establish an electric field in the subsurface to provide an enhanced transport mechanism for the remediation reagents. Through this process, a more rapid and broader distribution of the reagents, relative to diffusive transport, in low-k materials can be achieved. EK-enhanced *in situ* remediation is implemented by applying an electrical current, typically low-voltage direct current (DC), to the individual electrodes installed in an aquifer. With an external power supply source delivering a direct electrical current and voltage to the electrodes, a DC electric field is created in the subsurface between cathodes and anodes (**Figure 1-2**). Conceptually, this is analogous to a DC battery-driven electrical circuit with the aquifer between electrodes acting as an electrical conducting unit. The DC electric field established in the low-k treatment zone and the resulting EK processes are used as the active mechanisms for remediation amendment delivery and distribution.

When a DC electric field is established in the subsurface via electrodes powered by an external power source, multiple reactions and processes, including EK-specific and other non-EK reactions, occur in that system (**Figure 1-3**). Several remediation technologies involve the use of DC-powered electrodes to take advantage of these different reactions and processes to achieve intended treatment outcomes. Major reactions and processes that occur within a subsurface electric field established by DC-powered electrodes are briefly introduced below and further discussed in detail in Section 2.1.

Engineering applications of EK-related techniques have a long history in the oil recovery industry and geotechnical fields (Lima et al., 2017). Electroosmosis has been applied since the 1930s for removing water from clays, silts, and fine sands (Monsanto Company, 1998). Applications of EK techniques for *in situ* contaminant remediation have also gone through several decades of development, with early experiences reviewed by EPA (Kovalick, 1995) and the Ground-Water Remediation Technologies Analysis Center (van Cauwenberghe, 1997). Further technology revisions and development have advanced EK-based technologies leading to more recent engineering applications for *in situ* remediation.

1.2 EK-Enhanced *In Situ* Remediation

More recent applications of introducing DC into the subsurface via electrodes for *in situ* remediation objectives can be grouped, based on the basic mechanisms and processes involved, as the following: (a) delivery of remediation reagents necessary for *in situ* treatment of contaminants;

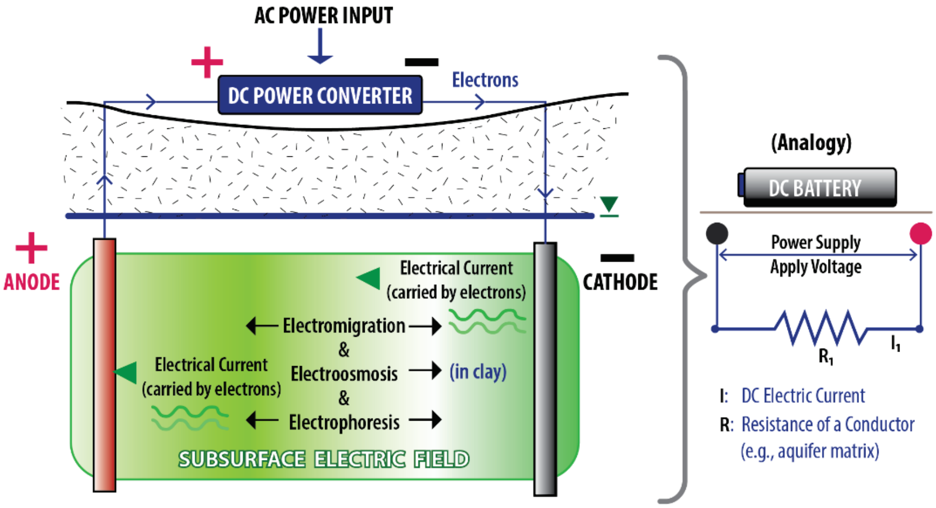


Figure 1-2. Concept: DC Battery-driven Electric Field in Subsurface

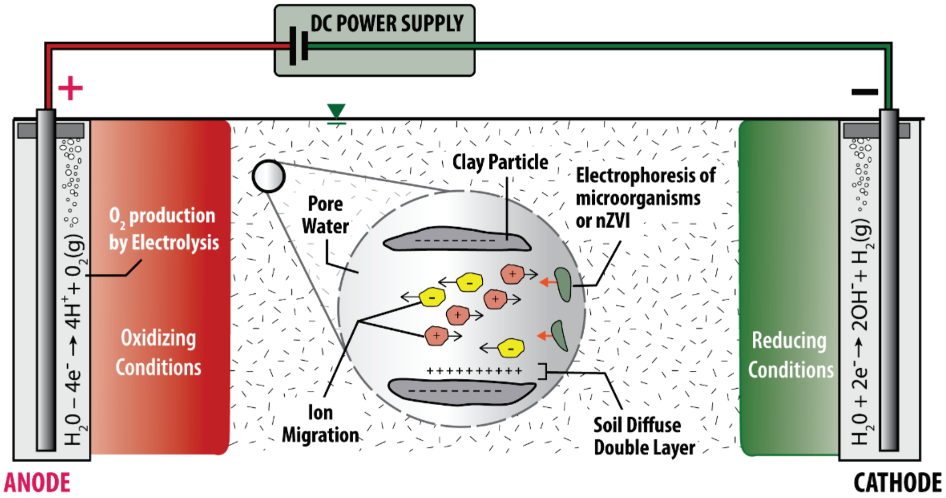


Figure 1-3. Processes in a Subsurface DC Electric Field

(b) transport of contaminants to target locations for extraction or treatment; (c) direct degradation of contaminants at electrode surfaces; and (d) induction of redox condition changes within a target zone in the subsurface.

While these different groups of technologies all involve the use of DC and electrodes installed in the subsurface, only the first two groups specifically employ EK mechanisms as the basis of the technologies. The other two groups of electrode-based technologies that do not employ EK mechanisms are only briefly introduced in Section 1.3 for awareness.

Table 1-1. Basic Processes and Reactions

EK processes within a DC electric field:

Electromigration—the movement of charged dissolved ions through an aqueous medium driven by an electric potential (voltage) gradient toward the electrode with a polarity opposite of the ion's charge.

Electroosmosis—the movement of pore fluid and, thus, dissolved constituents within a soil-water matrix induced by a voltage gradient between electrodes.

Electrophoresis—the movement of charged particles (solids) driven by a voltage gradient between electrodes, similar to the mechanism of electromigration.

Electrochemical reactions occurring at the electrodes:

Water Electrolysis—a process through which DC can drive an otherwise nonspontaneous oxidation-reduction (redox) reaction of water. When the voltages applied to electrodes exceed the decomposition voltage of water, water electrolysis occurs at the electrode surfaces (López-Vizcaíno et al., 2017).

Direct Oxidation/Reduction of Chemicals:

Depending on the applied voltage to the electrode, decomposition of certain organic chemicals through redox reactions can occur at the electrode surface. This phenomenon is sometimes referred to as **electrolytic or electrochemical degradation** of chemical compounds.

1.2.1 EK-Enhanced Delivery of Remediation Amendments

A recent remediation technological advancement is the use of EK to facilitate the distribution of selected remediation amendments into a target zone to achieve *in situ* remediation. This technology has been successfully demonstrated to distribute amendments required for ISCO (e.g., permanganate, persulfate), EISB (e.g., lactate, nitrate), and ISCR (e.g., nanoscale zero-valent iron [nZVI]).

With this technology, while the amendment distribution is still through the connected pores within aquifer materials, the transport is driven by EK processes (i.e., electromigration, electroosmosis, and electrophoresis), not hydraulic mechanisms, and, therefore, is not limited by the low-k barrier often encountered with conventional hydraulics-based delivery techniques. Section 2 provides more detailed information on individual EK-enhanced amendment delivery mechanisms, as well as reviews of the engineering applications of these EK mechanisms.

1.2.2 EK-Enhanced Extraction and Transport of Contaminants

EK-based *in situ* remediation was initially developed to facilitate the removal of metal contaminants through a process called EK extraction. EK extraction is performed by applying a direct electrical current across electrode pairs to effect electromigration of metal ions toward the electrodes, as well as electroosmosis of the pore water, which carries dissolved ions. The ionic (charged) metal contaminants present in the dissolved phase are transported toward respective electrodes depending on their charge. Ionic and non-ionic metal and nonmetal contaminants in the dissolved phase can also be transported by electroosmotic flow. The direction and rate of movement of ionic metal species depend upon the magnitude of the charge and the magnitude of the electroosmosis-induced flow velocity. The transported metal contaminants may then be isolated and contained by electroplating, precipitation, or coprecipitation at the electrode surface, or may be removed by extracting groundwater from near the electrode(s).

Bench and pilot tests were conducted to evaluate EK extraction of metal contaminants (Alshawabkeh et al., 1999). This technique was shown to successfully remove spiked lead from kaolinite (Acar and Alshawabkeh, 1996; Hamed et al., 1991); to remove cadmium, cobalt, nickel, and strontium from laboratory samples prepared from Georgia kaolinite, Na-montmorillonite, and sand-montmorillonite mixture (Pamukcu and Kenneth Wittle, 1992); and to remove cadmium from saturated kaolinite (Acar and Alshawabkeh, 1994). Further, a field study successfully demonstrated the removal of 600 grams (g) of chromium (VI) from soil beneath a chemical waste landfill after 2,700 hours of processing (Lindgren et al., 1998).

The Lasagna process is a representative technology utilizing electroosmosis to transport contaminants to target zones. Lasagna refers to the layered configurations of sequencing EK transport zones and capture and treatment zones (Ho et al., 1995, 1997, 1999a, b). Field applications of Lasagna technology have also been shown to remediate trichloroethene (TCE)–contaminated low-k soils through transporting dissolved-phase TCE into treatment zones containing activated carbon where TCE was immobilized (Ho et al., 1999b).

Lasagna technology was combined with a bioremediation process in a bench-scale study to address 2,4-dichlorophenoxyacetic acid (Jackman et al., 2001). Under a current density of 0.89 amperes (A) /meter^2 (m^2), the contaminant moved toward a microbiological (*Burkholderia* spp. RASC c2) treatment zone, where it was biodegraded.

1.3 Other Electrode-Based Applications for *In Situ* Remediation

There are other technologies involving the use of DC-powered electrodes installed in the subsurface. However, these technologies rely upon electrochemical processes and/or electrically induced redox conditions to degrade contaminants. These technologies are briefly introduced here for awareness. It is also noted that electrical resistance heating (ERH), an *in situ* thermal remediation technology, also involves the use of electrodes installed in the subsurface. However, ERH technology utilizes alternating current (AC) power to heat the subsurface media for thermal treatment. ERH does not employ any EK mechanisms and is not further discussed in this EIP.

Electro-oxidation, also known as anodic oxidation, electrolytic degradation, or electrochemical oxidation, is a process which has long been applied for wastewater treatment, mainly for industrial waste streams, and is considered a type of advanced oxidation process (AOP). Researchers demonstrated the potential utility of electrolytic degradation reactions using an electrolytic permeable reactive barrier (e-barrier). Sequential oxidation−reduction or reduction−oxidation transformations of aqueous phase energetic chemicals (hexahydro-1,3,5-trinitro-1,3,5-triazine and trinitrotoluene) were evaluated in flowthrough electrolytic reactors with titanium−mixed-metal-oxide electrodes (Gilbert and Sale, 2005). These researchers subsequently demonstrated an e-barrier at a field scale by installing panels of closely spaced permeable electrodes in a trench to treat a plume of TCE-contaminated groundwater (Sale et al., 2005). After operating the e-barrier with an applied voltage of 6.5 volts (V) for approximately 18 months, the monitoring of groundwater quality upgradient and downgradient of the barrier showed a 90% reduction of TCE flux.

There are ongoing research and development efforts to apply electrochemical degradation as an AOP for groundwater remediation, including degradation of emerging, highly recalcitrant contaminants, such as 1,4-dioxane (Blotevogel et al., 2018) and per- and polyfluoroalkyl substances (PFAS) (Fenti et al., 2022). However, other than the e-barrier approach, most other reports of electrochemical degradation are *ex situ*, reactor-based applications similar to industrial wastewater treatment engineering technologies.

There are also reported cases involving the use of DC-powered electrodes to affect subsurface redox conditions aimed to promote organic contaminant degradation. These are emerging technologies with relatively limited field experiences. One example is a technology called EBR® that has been tested at field-scale for the treatment of methyl tertiary-butyl ether (MTBE) (Lizer, 2022). The EBR system consists of subsurface electrodes, including sacrificial iron electrodes that corrode to supply iron, designed for high catalytic activity to promote O_2 generation, which in turn forms H_2O_2, a reactive oxidant. The EBR process is claimed to also support aerobic bioremediation given the production of O_2. However, based on the stated process, the produced O_2 likely only exists for a short period and does not affect a broader vicinity around the electrodes.

2 EK-Enhanced *In Situ* Remediation—Fundamentals and Applications

This section reviews the specific EK mechanisms, as well as their applications in remediation (i.e., EK-enhanced *in situ* bioremediation [EK-BIO], EK-enhanced *in situ* chemical oxidation [EK-ISCO], and EK-enhanced *in situ* chemical reduction [EK-ISCR]) that facilitate *in situ* treatment of contaminants in low-k materials.

2.1 Fundamental Mechanisms and Processes

The specific EK mechanisms contributing to enhanced amendment delivery in the subsurface include electromigration (Section 2.1.1), electroosmosis (Section 2.1.2), and electrophoresis (Section 2.1.3). Electrolysis is also discussed in this section (Section 2.1.4) as this process occurs as a concurrent process during EK system operations.

2.1.1 Electromigration (ion migration)

Electromigration, also known as ion migration, is the movement of ions in the interstitial fluid in an aquifer, induced by an electric field, toward the electrode of opposite charge (**Figure 2-1**). Electromigration sustains the electrical current in a subsurface DC electric field. Charged ions in an aquifer carry the electric current driven by an applied voltage gradient between cathodes and anodes. Cations (positively charged ions) move toward the cathode (negative electrode), and anions (negatively charged ions) move toward the anode (positive electrode). Ion migration in a solution-only system depends on the mass and charge of the ion as well as the strength of the electric field. The extent of electromigration of a given ion in a subsurface electric field depends on soil porosity, applied electric potential (voltage), soil moisture, and concentrations of the specific ion and other competitive ions. For *in situ* remediation considerations, electromigration is the major EK transport mechanism for ionic metals, dissolved ions, and ionic micelles.

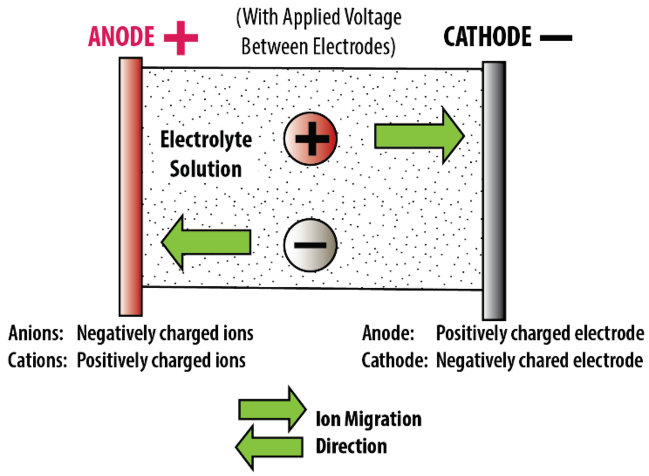


Figure 2-1. Electromigration (Ion Migration)

The rate of a particular ion transported in a subsurface environment via the electromigration mechanism can be described as:

$$J_i^m = c_i U_i^* i_e \qquad (1)$$

where J_i^m is the rate of mass transport (flux) of compound i by electromigration through a unit cross area (milligram/square centimeter/ second [$mg/cm^2/sec$ or $mg/(cm^2 \cdot sec)$]);

c_i is the dissolved concentration of compound i in the pore fluid (mg/cm^3);

U_i^* is the effective ionic mobility of compound i under one unit of voltage gradient (cm^2/V/sec or cm^2/(V·sec)); and

i_e is the voltage gradient applied (V/cm).

Ionic mobility is a measure of an ion's movement driven by a voltage gradient (i.e., electric field intensity), expressed as ion movement velocity (cm/sec) per unit voltage gradient (V/cm) within an electric field. The ionic mobility has a resulting unit of cm^2/(V·sec), which is a term of specific velocity normalized to unit voltage gradient. With infinite dilution in water, the ionic mobilities of common ions range from 10^{-3} to 10^{-4} cm^2/(V·sec) (Mitchell, 1993). The ionic mobilities of some cations and anions in an electrolyte solution are presented in **Table 2-1.**

In the subsurface, the effective velocity of an ion is lower than the velocity measured in a solution as the ion does not necessarily move toward electrodes by way of the shortest route. Effective ionic mobility reflects the effective soil porosity and tortuosity. As an example, heavy metal ionic mobilities in a dilute solution under an applied voltage gradient are in the range of 10^{-3} to 10^{-4} cm^2/(V·sec), while the measured effective ionic mobilities for those ions in clays are in the range of 10^{-4} to 10^{-5} cm^2/(V·sec) resulting in a transport rate in clays at several cm per day (cm/day) under an applied unit voltage gradient (1 V/cm).

Table 2-1. Ionic Mobility of Common Ions

Cation	U_i cm^2/(V·sec)	Anion	U_i cm^2/(V·sec)
Na^+	5.19×10^{-4}	HCO_3^-	4.61×10^{-4}
Mg^{+2}	5.5×10^{-4}	NO_3^-	7.4×10^{-4}
Ca^{+2}	6.17×10^{-4}	NO_2^-	7.4×10^{-4}
K^+	7.62×10^{-4}	CO_3^{-2}	7.46×10^{-4}
NH_4^+	7.62×10^{-4}	Cl^-	7.91×10^{-4}
H^+	36.3×10^{-4}	OH^-	20.6×10^{-4}

(modified from Vemulapalli, 1993)

Many studies conducted at both bench-scale and pilot-scale have shown the potential of EK-enhanced amendment transport of ionic remediation reagents (Gent et al., 2001a; Hodges et al., 2011; Mao et al., 2012; Reynolds et al., 2008; Wu et al., 2007). In a bench-scale study, acetate was effectively delivered through loess soil (K_h = 10^{-7} cm/s) and vertically deposited clay (K_h= 10^{-9} cm/s) at rates of 2.1 and 2.5 cm/day, respectively, with a voltage gradient near 0.5 V/cm (Gent et al., 2001a). An average lactate transport rate of 3.4 cm/day under a unit voltage gradient of 1 V/cm was achieved in a bench-scale study conducted using silty clay (K_h = 10^{-7} cm/s) (Gent et al., 2001b). As a generalized comparison, Gent et al. (2001b) reported that the observed EK-enhanced transport rate was more than 120 times higher than the hydraulic transport rate achievable in the same type of soil under one unit of hydraulic gradient.

2.1.2 Electroosmosis

Electroosmosis is the fluid movement relative to soil (clay) particle surfaces as a result of an applied electric potential (voltage) gradient (**Figure 2-2**).

Electroosmosis is a complex mechanism that depends on the electrical characteristics of the solid surface, the properties of interstitial fluid, and the interactions between solid surface and components in the interstitial fluid. Discrete clay particles, due to their mineralogical compositions, typically have a net negative surface charge. This net negative surface charge results in a corresponding positive charge zone attributed to exchangeable cations in the pore fluid immediately adjacent to the clay particle surface. In an aquifer matrix where particles with net negative surface charge, in conjunction with a layer of positively charged counterions in the aqueous phase, are subjected to a voltage gradient, the electric field induces the movement of pore fluid, also referred as electroosmotic flow.

In a contaminated aquifer with low-k (clayey) materials, electroosmotic flow due to a voltage gradient across a distance in the subsurface can

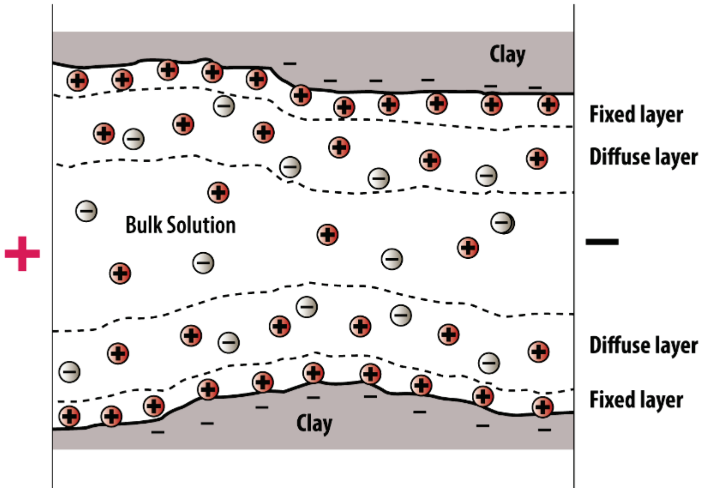


Figure 2-2. Electroosmosis in Subsurface

transport the dissolved compounds present in the pore fluid essentially via an advective mechanism (albeit the advective flow is induced by an EK mechanism). The advective contaminant transport due to electroosmosis can be described as:

$$J_i^e = c_i K_e i_e \qquad (2)$$

where J_i^e is the rate of mass transport (flux) of compound i by electroosmosis through a unit cross area (mg/cm^2/second or $mg/(cm^2 \cdot sec)$);

c_i is the dissolved concentration of compound i in the pore fluid (mg/cm^3);

K_e is the coefficient of electroosmotic permeability of the soil ($cm^2/V/sec$ or $cm^2/(V \cdot sec)$); and

i_e is the voltage gradient applied (V/cm).

The coefficient of electroosmotic permeability (K_e) is a measure of the fluid flux per unit area of soil per unit voltage gradient applied. This is a resultant function affected by the zeta potential of the soil-pore fluid interface (the electrostatic potential resulting from the soil particle surface charge), viscosity of the pore fluid, soil porosity, and soil electrical properties. Complex pore fluid properties (e.g., pH, ionic strength) can affect the zeta potential and, thus, electroosmotic permeability and the resultant electroosmotic flow in a soil-pore water matrix (Vane and Zang, 1997; West and Stewart, 1995). **Table 2-2** provides the coefficients of electroosmotic permeability of several types of low-k soils.

It is noted that the ionic mobilities discussed in Section 2.1.1 for common ions, which are ion-specific and not soil type-dependent, are approximately an order of magnitude higher than the coefficients of electroosmotic permeability for various low-k soils shown in **Table 2-2**, suggesting that in a given aquifer solid-pore fluid system under a same voltage gradient electromigration is likely a more dominant EK transport mechanism than electroosmosis for transporting an ionic compound in that system.

Table 2-3 shows the electroosmotic permeability (K_e) and hydraulic conductivity (K_h) for a few clayey materials (blue clay, kaolin, and clayey silt) and fine sand. The values illustrate that while K_h varies several orders of magnitude between sandy and clayey soils, K_e is in the same order of magnitude among these soil types. It is also important to note that, as discussed above, ionic mobility (related to ion migration) is ion-specific and not soil type-dependent. These electrical properties of soil and ions are the reasons why EK

Table 2-2. Coefficients of Electroosmotic Permeability (Ke) for Low-Permeability Soils

Soil Type	K_e (cm^2 / (V·sec))
Boston Blue Clay	5.1×10^{-5}
Clay Silt	5.0×10^{-5}
Kaolin	5.7×10^{-5}
London Clay	5.8×10^{-5}

(Modified from Asadi et al., 2013)

Table 2-3. Electroosmotic Permeability (K_e) and Hydraulic Conductivity (K_h) of Various Soils

Soil Type	K_e (10^{-5} cm^2/(V·sec))	Approximate K_h (cm/sec)
Boston Blue Clay	5.1	10^{-8}
Clayey Silt	5.0	10^{-6}
Fine Sand	4.1	10^{-4}
Kaolin	5.7	10^{-7}

(Modified from Mitchell, 1993)

can be a more effective transport mechanism compared to hydraulic methods in a heterogeneous geologic formation that includes low-k fractions.

Electroosmotic transport is more pronounced in aquifer matrices with more fine-grained clays due to clay's higher surface charges (Mikkola et al., 2008). Insignificant electroosmosis was measured in pure sand, whereas electroosmosis increased with increasing fractions of silt. The pH of an aquifer matrix may influence the surface charge of the soil particle and electroosmosis. Cherepy and Wildenschild (2003) reported the effect of limiting pH changes within clayey soil could achieve steady electroosmosis. Further, the electroosmotic velocity in their study was three orders of magnitude higher than the hydraulic velocity. Therefore, electroosmosis can be an important EK mechanism for transporting the dissolved constituents in the pore fluid within low-k materials.

2.1.3 Electrophoresis

Electrophoresis is the transport of particles that exhibit a net surface charge in an electric field created under the application of a voltage gradient. The concept and fundamentals of electrophoresis are similar to those of electromigration related to the movement of ions in an electric field. However, given that electrophoresis is the movement of solid particles, this transport process in a subsurface system is significantly affected by the physical properties of the soil matrices. DeFlaun and Condee (1997) found reduced rates of electrophoresis transport of bacteria in soils with silt and clay fractions compared to sand. This result alludes to the major effect of pore size on the mobility of particles. Relative to ion migration and electroosmosis, mass transport by electrophoresis in low-k soil systems is low and highly dependent on the particle size relative to the formation's pore sizes. Nonetheless, electrophoresis can be a contributing mechanism for the transport of colloids, such as nZVI, bacteria, and micelles, in a subsurface electric field.

Reddy et al. (2011) used dinitrotoluene (DNT)-spiked kaolin to test the ability of EK to effectively transport nanoscale iron particles into low-k soils for DNT degradation. Aluminum lactate was used to modify nano-iron particles to enhance the transport of nanoparticles. The application of a voltage gradient was able to transport both unmodified nano-iron and lactate-modified nano-iron in kaolin. Their study found that both electroosmotic flow and electrophoresis affected the extent of transport of unmodified and modified nano-iron, whereas improved delivery was achieved with lactate-modified nano-iron particles.

2.1.4 Electrolysis

Electrolysis is the passing of DC through an electrolyte (a solution containing mobile ions) causing chemical reactions at the electrodes that lead to the decomposition of certain chemical compounds. The key process of electrolysis is the removal or addition of electrons (i.e., oxidation or reduction reactions) driven by the applied electrical energy. The minimum voltage (or difference in electric potential) between the anode and cathode of an electrolytic cell that is needed for electrolysis to occur is referred to as decomposition potential or decomposition voltage.

At the electrodes powered by a DC power source, electrolysis can happen to water (water electrolysis), which is the electrolytic decomposition of water, and/or other chemicals in the electrolyte (electrolytic or electrochemical degradation). Electrolytic decomposition of water generates oxygen gas and hydrogen ions (H^+) at the anode due to the oxidation of water, and hydrogen gas and hydroxyl (OH^-) ions at the cathode due to the reduction of water (**Table 2-4**).

During water electrolysis, acid is produced at the anode and an alkaline condition is produced at the cathode. In addition, the aqueous environment surrounding the anode becomes more oxidizing, while a reducing condition develops around the cathode. Potentially, H^+ ions and the oxidizing

Table 2-4. Electrolytic Reactions at the Anode and Cathode

At the anode (oxidation of water):

$2\ H_2O \rightarrow 4\ e^- + 4H^+_{(aq)} + O_{2\ (gas)}$ $E^0 = -1.229$ V

At the cathode (reduction of water):

$4\ H_2O + 4\ e^- \rightarrow 2\ H_{2\ (gas)} + 4\ OH^-_{(aq)}$ $E^0 = -0.828$ V

(E^0: Standard Electrode Potential)

condition from the anode, as well as OH^- and the reducing condition from the cathode, can migrate from the electrodes into the surrounding aquifer material toward the electrodes of opposite polarities. Depending on the geochemistry of the aquifer matrix between the electrodes, the migration of these ions and redox conditions may not extend far beyond the electrodes. While pH and redox changes may be localized around the electrodes, certain remedial maintenance measures, such as adding buffering solutions to electrode wells, may be needed to control the pH around electrodes depending on the site geochemistry and the intended EK applications.

In addition to water electrolysis, electrochemical degradation of certain chemicals can occur at electrodes. As discussed in Section 1.3, the electrochemical degradation process (an AOP) can treat a variety of chemicals and has been applied primarily as an *ex situ* reactor-based technology or in an e-barrier application.

2.2 Applications of EK-Enhanced *In Situ* Remediation Technologies

Early applications of EK extraction of contaminants, while feasible, met with certain challenges in the field (Athmer, 2014). Over time, the technology evolved to emphasize the technical advantages of EK-enhanced amendment delivery for *in situ* remediation. Field-scale applications of EK-enhanced amendment delivery have been deployed for EK-BIO, EK-ISCO, and EK-ISCR, and the conceptual field application is illustrated in **Figure 2-3**.

It should be noted that while EK-enhanced amendment delivery provides an effective alternative for addressing contaminants in low-k materials, this technology can also be considered for sites that exhibit lithologic heterogeneity. It is common at sites where sandy and coarse materials account for a significant portion of the geology yet conventional hydraulic injections are still challenged by the abundance of low-k layers and preferential hydraulic pathways. EK-enhanced amendment delivery can be an alternative for considerations at those sites.

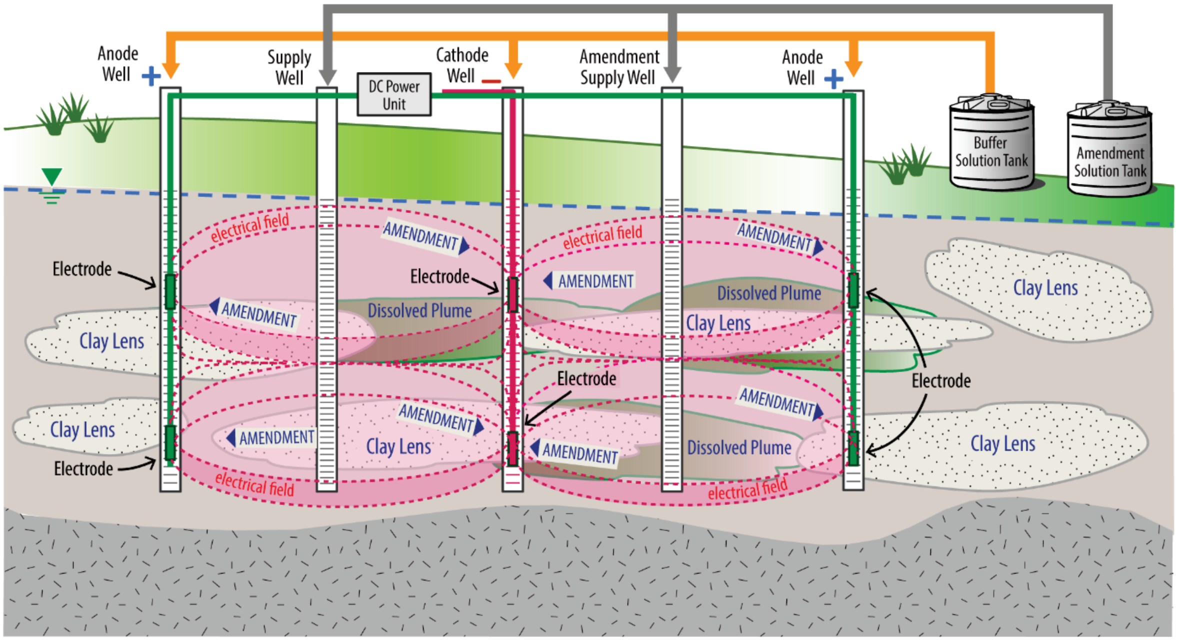


Figure 2-3. Concept: EK-Enhanced *In Situ* Remediation Technology
(Amendment can move toward cathode and/or anode via ion migration and electroosmosis)

2.2.1 EK-Enhanced In Situ Bioremediation (EK-BIO)

Successful *in situ* bioremediation requires close interactions between microorganisms, substrates, nutrients, and contaminants (Semple et al., 2004). EK transport processes have the ability to overcome site conditions (e.g., low soil permeability) that limit the effectiveness of conventional hydraulic delivery of bioremediation amendments.

2.2.1.1 EK for Biostimulation

Lactate is a common amendment that serves as an electron donor to promote reductive biodegradation (e.g., reductive dechlorination) of contaminants. Lactate, a negatively charged ion, can be transported by electromigration in a DC electric field toward an anode (Hansen et al., 2015; Mao et al., 2012; Wu et al., 2007). While Wu et al. (2007) observed electroosmotic flow in laboratory studies using clay samples, their results showed that electromigration was the governing transport mechanism for lactate. It is expected that during subsurface transport, lactate is potentially retarded by sorption to soil particles and consumed via microbial degradation. When the rate of EK-enhanced delivery exceeds the rate of amendment consumption, an effective transport and relatively uniform distribution through low-k materials is possible (Rabbi et al., 2000). Several studies reported the following net reactive transport rates for lactate obtained from bench-scale experiments:

- Natural clay: 4 $cm^2/(V·day)$ calculated from the observed migration rate of 3.2 cm/day at an average voltage gradient of 0.8 V/cm (Mao et al., 2012)
- Silty clay: 3.2 $cm^2/(V·day)$ (Wu et al., 2012)
- Clay: Lactate was detected 24 cm into clay toward the anode after 129 h at 0.5 V/cm (Wu et al., 2007), corresponding to 8.9 $cm^2/(V·day)$.

EK transport of nutrients (e.g., nitrogen, phosphorus) and electron acceptors (e.g., nitrate, sulfate) resulting in enhanced biodegradation activities in clayey soils has also been demonstrated repeatedly (Elektorowicz and Boeva, 1996; Lee et al., 2006; Lohner et al., 2008a, b; Schmidt et al., 2007; Xu et al., 2010). Electromigration was deemed the dominant transport mechanism for the ionic compounds tested in these studies.

No apparent negative impact of EK mechanisms on microbial activity was reported in various studies that applied relatively low electric currents (Lear et al., 2004; Shi et al., 2008). Jackman et al. (1999) showed that the application of a DC electric field density of 20 milliamps (mA)/cm^2 stimulated the activity of sulfur-oxidizing bacteria. Further, Wu et al. (2012) reported the transport of lactate by electromigration into a 40-cm-long column with silty clay spiked with PCE and a reductive dechlorination microbial culture. Complete dechlorination of PCE to ethene was reported, whereas the control experiment without electric current resulted in only limited PCE degradation. Overall, these results indicated that biodegradation by the reductive dechlorinating bacteria was enhanced by the EK transport of lactate.

2.2.1.2 EK for Bioaugmentation

Bioaugmentation of selected microbial suspensions can be a strategy when the target remediation area does not contain indigenous bacteria necessary to carry out the degradation of target contaminants. Electrophoresis transport of bacteria in solutions has been widely used in the field of micro-electrophoresis for characterizing bacteria (van der Wal et al., 1997). Studies have shown that bacteria can be transported by electrophoresis into sand (DeFlaun and Condee, 1997), sandy/silty loam (DeFlaun and Condee, 1997), field-sampled clay (Mao et al., 2012; Wick et al., 2004), and even bryozoan limestone (Hansen et al., 2015). Electrophoresis of bacteria depends on the physico-chemical properties of both the porous media (DeFlaun and Condee, 1997) and the surface properties of individual bacteria (Wick et al., 2007). Many bacterial strains carry a weak negatively charged cell surface in solutions of near neutral pH, and, thus, electrophoresis of these bacteria may be in the direction toward an anode.

Bacteria can also be transported by electroosmotic flow (Lee and Kisay, 2001; Mao et al., 2012). The electroosmotic transport rate of *Sphingomonas sp* L138 and *M. frederiksbergense* LB501TG was in the range of 3.4 to 6.7 $cm^2/(V \cdot day)$ in field-sampled clayey soil (Wick et al., 2004). In another study with field-sampled clayey soil, Mao et al. (2012) reported the transport of *Dehalococcoides* (Dhc) over 16 cm in 47 days (approximately 0.43 $cm^2/(V \cdot day)$) toward the cathode, primarily as a result of electroosmotic transport.

While EK transport of bacteria in soil can be via electrophoresis or electroosmosis, the dominant transport mechanism in porous media depends on the bacteria, soil characteristics, and soil solution chemistry. The transport of *Sphingomonas sp* L138 was estimated to be 80% to 90% via electroosmosis, as indicated by transport toward the cathode; and 10% to 20% via electrophoresis, as indicated by transport toward the anode (Wick et al., 2004). Mao et al. (2012) reported electroosmosis as the major transport mechanism for Dhc in their test with clayey soils. In contrast, Da Rocha et al. (2009) reported that electrophoresis was the main mechanism for the transport of endospores of *Bacillus subtilis* LBBMA 155 and nitrogen-starved cells of *Pseudomonas* sp. LBBMA 81 in clayey soil in their study.

2.2.1.3 EK-BIO Field-Scale Remedy Implementations (Skuldelev, Denmark)

Based on the results of a treatability test (Mao et al., 2012) and a subsequent pilot test, a full-scale EK-BIO remedy was completed at a former industrial facility in Skuldelev, Denmark, to remediate a PCE residual DNAPL source zone in a low-k glacial clay unit (**Appendix A**). The bench-scale EK treatability test estimated the transport rate of lactate through clay soil collected from the site at 3.2 cm/day, and subsequently promoted complete reductive dechlorination of the spiked PCE to ethene. The field pilot test utilized three sets of paired cathode and anode wells spaced at 1 m between electrodes of the same polarity and 3 m between paired anodes and cathodes. During the 65-day EK system operation, lactate was periodically dosed to the electrode wells. The pilot test area was bioaugmented with a dehalorespiring bacterial culture (KB-1 by SiREM, Guelph, Ontario, Canada) at the start of the pilot test. The pilot test monitoring data confirmed lactate migration at a rate of 2.5 to 5.0 cm/day, PCE dechlorination to ethene, and significant increases in the populations of Dhc and a biomarker, vinyl chloride reductase functional genes (*vcrA*), within the pilot test area.

The full-scale EK-BIO remedy involved a network of 15 electrode wells and 10 amendment supply wells targeting a treatment area of 130 m^2 and a depth interval of 3 to 8 m below ground surface (bgs) (Riis et al., 2023). The average spacing between electrode wells was approximately 4.5 m, and each electrode well was installed with two vertically separated electrodes, each as 1-m-long titanium electrode with mixed-metal-oxide coating. The electrodes were powered at an average current of 1.7 to 3.3 A each. An initial voltage of 197 V was required to achieve the designed electrical current operation and decreased with time to a steady level of 50 V. Bioaugmentation of KB-1 culture was included in the remedy. pH control at electrode wells was implemented through cross-circulation between pairs of anode and cathode wells, as well as additions of lactic acid to cathode wells and sodium hydroxide to anode wells. The EK system was operated in two one-year cycles.

The remedy performance monitoring showed the level of vinyl chloride reductase functional gene increased by several orders of magnitude in the treatment area wells, with significant levels of PCE dechlorination end-product, ethene, observed at all treatment area wells. The project met the prescribed PCE remediation goal for site soils of 10 mg/kg, with an estimated 285 kg of PCE (>98% of the estimated pre-remedy total) degraded in the treatment area. Rebound testing 6 months after cessation of EK-BIO operation confirmed sustained dechlorination activities and compliance with the remedial goals. The estimated total energy consumption for the 2-year EK operation was 43,000 kilowatt-hours (kW-hr), with an estimated electricity cost of $15,000.

2.2.1.4 EK-BIO Field-Scale Demonstration (Jacksonville, Florida)

A pilot-scale demonstration of EK-BIO was conducted at the Naval Air Station Jacksonville in Jacksonville, Florida, and targeted a PCE source area in a clay unit underlying a shallow sandy aquifer (**Appendix B**) (Cox et al., 2018). The demonstration included a network of 9 electrode wells and 8 supply wells targeting an area of approximately 40 ft by 40 ft and a depth interval of approximately 17 to 25 ft bgs. All the electrode wells, supply wells, and associated double-cased monitoring wells were screened in the targeted clay unit to assess the extent of treatment within the low-k materials. The remediation amendments included lactate, pH control reagents (potassium carbonate), and a dechlorinating microbial consortium (KB-1). pH control at the electrode wells also included engineering measures of cross-circulation between paired cathode and anode wells. The demonstration included two active EK operation stages, 5 months each, with a 6-month incubation period between the two active stages. The system was operated to supply electrical currents of approximately 1.5 and 3 A to each cathode and anode, respectively, which required the DC power supply unit to apply approximately 18 to 29 V in Stage 1 operation and 12 to 20 V in Stage 2 operation. The total electrical energy consumption was 1,037 kW-hr during Stage 1 and 548 kW-hr during Stage 2. The group estimated that the power consumption by the EK system over the active operation period was equivalent to operating a single 100-watt (W) lightbulb for approximately 22 months.

The overall monitoring data indicated that the project met the prescribed demonstration performance objectives (Cox et al., 2018). Average PCE concentrations were reduced by more than 60% in clay soil and groundwater within the treatment area, with corresponding and comparable increases of dechlorination intermediate and end products detected in the groundwater. Ethene was detected at all the groundwater monitoring wells and a greater than 10× increase of Dhc populations from the baseline level was observed in more than 60% of soil and groundwater samples collected from within the clay unit of the treatment area.

2.2.2 EK-Enhanced In Situ Chemical Oxidation (EK-ISCO)

ISCO is a feasible remediation option for a variety of organic contaminants. Common oxidants of choice include permanganate (MnO_4^-) and persulfate ($S_2O_8^{2-}$) or combinations of various oxidants (Huling and Pivetz, 2007). EK transport of permanganate or persulfate into a low-k zone to facilitate ISCO (EK-ISCO) has been demonstrated through bench-scale studies and field-scale tests.

2.2.2.1 EK-ISCO with Permanganate

Permanganate, provided as either $KMnO_4$ or $NaMnO_4$, is a common oxidant selected for ISCO due to its high redox potential, stability in aqueous solution, reactivity over a wide range of pH (3.5 to 12), and ability to achieve intended treatment without the need for an activator (Chowdhury et al., 2017a). EK transport of permanganate into homogeneous, uncontaminated soil has been extensively investigated (Hodges et al., 2013; Reynolds et al., 2008; Roach and Reddy, 2006). Reynolds et al. (2008) reported electromigration of MnO_4^- from a cathode reservoir into an anode reservoir through a 7-cm-long column packed with kaolinite. The concentration of MnO_4^- in the anolyte solution increased by 13 to 15% when applying 10 to 20 V between electrodes for 6.25 days. With an EK reactor setup in which the pH changes around electrodes were isolated from the soil, Hodges et al. (2013) reported electromigration transport of MnO_4^- through a 10-cm-long kaolinite core. After 5.2 days at 1.1 V/cm, MnO_4^- was detected in the anolyte solution, corresponding to a reactive transport velocity of 2.3 $cm^2/(V{\cdot}day)$.

Chowdhury et al. (2017a) conducted experiments in a two-dimensional (2-D) sandbox packed with sand and embedded layers of silt. The sand and silt were initially spiked with TCE. EK successfully delivered MnO_4^- into the silt layers, while in a control sandbox of identical setup but without EK, the MnO_4^- was observed only around the edges of the silt layers but not within the silt materials. The MnO_4^- delivery into the silt in the EK reactor was estimated to be 240% more than that in the control reactor. Furthermore, the treatment achieved in the EK reactor significantly reduced the back-diffusion of TCE from the contaminated silt.

2.2.2.2 EK-ISCO with Persulfate

Persulfate ($S_2O_8^{2-}$) is another common oxidant selected for ISCO remedy. Persulfate distribution in soil via EK transport has been demonstrated in bench-scale tests with uncontaminated soil (Mikkola et al., 2008), creosote-contaminated soil (Isosaari et al., 2007), and polychlorinated biphenyls (PCB)-contaminated soil (Fan et al., 2014; Yukselen-Aksoy and Reddy, 2012). Electromigration transport rate of persulfate in sand and silt was reported to be up to 19.8 $cm^2/(V{\cdot}day)$ (Mikkola et al., 2008). Chowdhury et al. (2017b) successfully delivered persulfate with electromigration throughout a 36-cm-long silt sample at voltages of 12 to 18 V in a system where pH at the electrodes was controlled with phosphate buffers. An average transport rate of 2 ± 0.7 cm/day was estimated based on the arrival times of 50% of the maximum persulfate concentration, corresponding to 3.1 ± 1.1 $cm^2/(V{\cdot}day)$.

While persulfate itself is a relatively strong oxidant (E_h 2.1 V for persulfate compared to E_h 1.7 V for permanganate), its activity can be significantly enhanced with an appropriate activator. Common persulfate activation methods include alkaline conditions (i.e., pH ≥10.5), iron, and thermal activation. In the EK transport of persulfate, ideally, the persulfate transport should occur prior to activation to maximize the persulfate delivery and distribution. Given this consideration, heat activation after reagent transport and delivery is the ideal sequence of events for EK-ISCO using persulfate.

Chowdhury et al. (2017b) demonstrated the ability of sequencing EK transport of persulfate followed by ERH heat activation of the persulfate anion ($S_2O_8^{2-}$) to achieve complete oxidation treatment of PCE. Monitoring of the column effluent during the ERH heating stage indicated increases in sulfate concentration with concurrent decreases in $S_2O_8^{2-}$ concentration, confirming activation of $S_2O_8^{2-}$. The study also showed that activation at 36°C was more efficient in degrading PCE than at higher temperatures (≥ 41°C). In another study, Yukselen-Aksoy and Reddy (2012) reported that 45°C was efficient for $S_2O_8^{2-}$ activation and PCB degradation after EK persulfate delivery.

2.2.2.3 EK-ISCO Field Pilot Test at Cristex Drum Superfund Site in North Carolina

An EK-ISCO pilot test was conducted using sodium permanganate to address a PCE source area at a former textile plant in North Carolina (Black & Veatch Special Projects Corp. and Geosyntec Consultants of NC, 2020) (**Appendix C**). The target remediation zone resided in a saprolite unit (20 to 70 ft bgs) consisting primarily of fine sand and silt with variable amounts of clay. A bench-scale treatability study using representative aquifer materials was used to measure the site-specific oxidant demand. The pilot test system included a pair of electrode wells (one cathode well and one anode well), a monitoring well network, an EK power supply unit, and associated amendment supply and operation control systems. Sodium permanganate was supplied as the oxidant, and a carbonate solution was used as the buffer reagent for pH control at electrode wells. The system supplied electric currents between 0.7 and 0.9 A to each electrode, and the required voltage was between 120 and 160 V. Pilot test operation and monitoring were performed over 57 days, followed by a post-test confirmatory sampling program that included collecting discrete aquifer solids and groundwater samples at various locations and depths to document the effectiveness of the pilot test.

The pilot test monitoring data confirmed the distribution of permanganate within the target zone, and the net permanganate transport rate was estimated to be in the range of 1.3 to 4.1 ft/month (Black & Veatch Special Projects Corp. and Geosyntec Consultants of NC, 2020). The area of permanganate distribution was approximately 40 ft^2, which was consistent with the estimate based on the quantity of permanganate supplied (136.5 kg) and the oxidant demand estimated from the bench-scale treatability study. Treatment of PCE and other chlorinated ethenes was apparent with 74% to 90% concentration decreases at monitoring wells, coupled with increases in groundwater redox potential. The overall electrical energy usage was relatively low at 152 kW-hr over the 57-day pilot test. This limited-scale pilot test provided site-specific estimates to support the remedial design of a full-scale EK-ISCO remedy to be implemented in a phased approach (**Appendix C**).

2.2.2.4 EK-ISCO Field-Scale Demonstration (Jacksonville, Florida)

Cox et al. (2021) conducted a pilot-scale technology demonstration of EK-ISCO using persulfate at the Naval Air Station Jacksonville in Jacksonville, Florida. The demonstration employed 3 electrode wells (two cathodes with one anode) arranged in a linear configuration with 4 supply wells located between individual electrode wells, all targeting a clay unit at approximately 19 to 23 ft bgs. During a 7-month operation, sodium persulfate was dosed to the supply wells while a DC electric field was established by supplying a constant current of 1.2 to 3 A to individual electrodes. The voltage required to sustain the target electric current through the system was generally between 40 and 50 V. The overall electricity usage over the 7-month test was approximately 425 kW-hr, which is equivalent to operating a single 100-W lightbulb for approximately 6 months.

The results indicated the transport of persulfate at an estimated net reactive transport rate ranging between 0.6 and 1.3 cm/day. Further analysis of site characterization data and the observed transport rate found that the site had a relatively high level of naturally occurring iron, which likely activated the persulfate as the oxidant being transported through the aquifer material and slowed the net transport rate. While the activated persulfate resulted in treatment of chlorinated ethenes in the target area, the lower-than-expected net transport rate highlighted the importance of understanding the geochemistry of the target area and how that may potentially affect the EK transport of the selected amendments.

2.2.3 *EK-Enhanced In Situ Chemical Reduction (EK-ISCR)*

Another application of EK-enhanced amendment transport for *in situ* remediation is to facilitate abiotic reduction by transporting nZVI via electrophoresis (Gomes et al., 2012; Jones et al., 2011; Pamukcu et al., 2008). It has long been recognized that the mobility of nZVI in the subsurface can be limited under various conditions, especially in low-k zones. nZVI has a strong tendency to aggregate, which quickly limits its movement through pores. Therefore, the surface of nZVI is often modified by various methods, such as coating with various polymers (Lefevre et al., 2016; Phenrat et al., 2008; Soukupova et al., 2015), or injecting the nZVI in an emulsified biodegradable oil (Comba et al., 2011) or natural gums (Padil et al., 2018). Reddy et al. (2011) reported EK transport via electromigration and electrophoresis of both unmodified nano-iron and lactate-modified nano-iron in kaolin, with enhanced delivery observed with lactate-modified nano-iron compared to unmodified nano-iron.

Well-documented field-scale applications of EK with nZVI for ISCR are relatively limited. Černíková et al. (2020) reported the long-term monitoring at a former industrial site in the Czech Republic where a DC electric field was used to enhance *in situ* remediation of chlorinated ethenes by nZVI. A network of 3 cathodes and 3 anodes was installed in a target area 2 years after an initial injection of nZVI. The electrodes were powered with a constant voltage to maintain a DC electric field for 4 years, during which 2 additional rounds of nZVI injections occurred. The field monitoring program was not designed to specifically assess the transport of nZVI by the DC electric field. Nonetheless, the monitoring results showed (a) no apparent rebound of chlorinated ethenes in the target zone during the years with DC electric field operations as opposed to chlorinated ethenes rebound observed in the years prior, and (b) significant pH and E_h changes, as expected of water electrolysis at the electrodes, in the vicinity of the electrodes but not at monitoring locations in the middle of the electric field away from the electrodes. Based on the overall long-term monitoring results, the group proposed that the DC electric field enhanced the reductive treatment of contaminants by nZVI near the cathodes while EK mechanisms improved the transport of nZVI between electrodes.

3 Engineering Applications of EK-Enhanced *In Situ* Remediation Technologies

This section discusses the stepwise processes for evaluating EK-enhanced *in situ* remediation technologies and applying the technologies for remedy implementation.

3.1 Technology Applicability and Screening Considerations

Per EPA (1988) guidance for remedial investigation (RI) and feasibility study (FS), to develop remedial alternatives for a given site, remedial technologies are first screened for their applicability to the conceptual site model (CSM) and RAOs. The initial technology screening also considers contaminant compositions and concentrations, site geology and hydrogeology, and various CSM elements (e.g., geochemistry, indigenous microbial populations). A technology may be carried forward for further evaluations in the FS if the screening process concludes that it is effective, implementable, and cost-effective (EPA, 1988). This screening evaluation may also include estimates related to the remediation timeframe and the sustainability of a given technology.

Initial screening considerations related to the effectiveness, implementability, and cost of EK-enhanced *in situ* remediation are discussed in the remainder of this section.

3.1.1 Effectiveness Considerations for EK-Enhanced In Situ Remediation

The effectiveness evaluation considers how well a technology can reduce the toxicity, mobility, volume of, or the exposure to, contamination. This evaluation should also take into account the ability of a remedial technology to meet the site remediation goals (RGs) identified in the RAOs (USEPA, 1988).

One of the first considerations for screening EK-enhanced *in situ* remedy effectiveness is the depths to the groundwater table and the target treatment zone. Groundwater containing ions is the electrical conductor allowing the completion of a DC electric circuit between electrodes in the subsurface. Field-scale testing of EK transport mechanisms in a vadose zone for *in situ* remediation purposes has not produced consistent outcomes. A treatment zone to be targeted by an EK-enhanced *in situ* remedy should be at or below the groundwater table for the technology to be effective. The initial technology screening for sites with significant groundwater table variations due to seasonal effects or other influences should consider this factor in the design, operation, and maintenance of the EK remedy.

The next technology screening criterion is whether EK-enhanced *in situ* remediation can effectively treat the target contaminants of concern (COCs) documented in the record of decision (ROD). EK is an amendment delivery technique applied to facilitate an intended treatment of target contaminants in a target zone. Therefore, the intended treatment mechanism (e.g., biodegradation, chemical oxidation or reduction) should meet the treatment effectiveness objective. Such a treatment technology selection process has

Table 3-1. Contaminant Applicability Rating for Treatment with EK-Enhanced Remediation (FRTR, 2022)

Non-Halogenated VOCs	Halogenated VOCs	Non-Halogenated SVOCs	Halogenated SVOCs	NAPL Fuels	Inorganics	Radionuclides	Munitions	Emerging Compounds
ID	DE	ID	DE	ND	LE	LE	LE	ID

Note: ID = insufficient data; DE = demonstrated effectiveness; ND = no demonstrated effectiveness; LE = limited effectiveness.

NAPL – non-aqueous phase liquid; SVOC – semi-volatile organic compounds

long been established and can be followed when screening the EK-enhanced remediation technology.

Once a treatment mechanism is identified, the consideration is whether the amendment(s) required for the remedy can be effectively delivered by EK mechanisms. Certain reagents commonly selected for *in situ* remediation (e.g., lactate, permanganate, persulfate) are present in ionic form and can be effectively transported via electromigration, while both ionic and nonionic compounds can be transported via electroosmosis. In most cases, electromigration is a more dominant transport mechanism relative to electroosmosis. Transport of solid particles (particulate amendments) via electrophoresis or electroosmosis, while feasible, is likely to be relatively limited in a low-k formation compared to the EK transport of dissolved compounds by electromigration. Electrophoresis cannot force particles through pores of sizes smaller than the particles. Therefore, if a particulate amendment (e.g., ZVI) is selected as the remediation amendment, the amendment particle size relative to the pore sizes of the target aquifer matrix should be carefully examined while determining whether EK transport is a feasible option.

EK-enhanced *in situ* remediation has been evaluated for a wide range of contaminants. **Table 3-1** identifies the types of contaminants that are amenable to EK-enhanced remediation based on the Federal Remediation Technologies Roundtable (FRTR) technology screening matrix (FRTR, 2022). The FRTR screening also includes EK extraction technologies, mainly for inorganics and radionuclides, and electrolytic degradation, mainly for various volatile organic compounds (VOCs), munitions, and emerging contaminants. EK-enhanced *in situ* remediation is still a developing technology. The screening matrix shown in **Table 3-1** will likely be updated as more studies and evaluations of this technology continue.

Another factor commonly considered during technology effectiveness screening is the duration required for the remedy to achieve the remediation objectives. The overall remedy timeframe for EK-BIO, EK-ISCO, or EK-ISCR should be incrementally improved over that of conventional hydraulic-based *in situ* remediation approaches when low-k materials are a key component of the target treatment zone. This is because, through delivering treatment reagents into low-k materials where residual contaminant mass resides, EK approaches can facilitate effective treatment of contaminant source, thus, minimizing rebounds caused by back diffusion.

EK-enhanced *in situ* remediation represents an effective remedial option for a source zone residing in challenging geology. At a large site, depending on the spatial and temporal coordination between various remedial actions, it is important to consider the compatibility between the selected remedies. There are many experiences and examples of treatment train integration and remedy optimization that combine various remedies to achieve RAOs. Those experiences can be applied in screening the effectiveness of EK-enhanced *in situ* remediation within a treatment train at a given site. Several guidance documents (e.g., NRC, 2013; ESTCP, 2011) provide additional information related to developing combined remedies and achieving remedy optimization.

3.1.2 Implementability Considerations for EK-Enhanced In Situ Remediation

The implementability evaluation reviews the relative level of efforts required to deploy the technology, and determines technology's feasibility based on site-specific conditions. Both technical and administrative feasibility of remedy implementation should be considered. Technical implementability is assessed during the initial screening process to eliminate technologies that are ineffective or unworkable at a site (USEPA, 1988).

EK-enhanced remedial approach represents an alternative at sites with fine-grained aquifer solids with variably permeable or low-k geology (FRTR, 2022). Site-specific CSM elements to be reviewed during the implementability evaluation of an EK-enhanced *in situ* remediation application are presented below in question (Q) – answer (A) format.

Q: Does the site have stored contaminant mass in low-k materials?

A: EK-enhanced *in situ* remedial approach likely presents the most advantages relative to other conventional hydraulics-based remedial approaches at sites with the source zone in low-k and/or relatively heterogeneous geology.

Another common challenging site condition is the presence of complex contaminant mixture. The implementability consideration related to this issue is whether an appropriate *in situ* treatment mechanism is selected and whether the remediation amendment(s) required is amenable to EK transport. An EK treatability study will be a good way to evaluate this aspect.

Q: How well are the hydrogeological/biogeochemical conditions of the target zone understood?

A: Major biogeochemical conditions, such as geochemistry (e.g., pH, anions, cations), competing electron acceptors (e.g., SO_4^{-2}, Fe^{+3}), soil organic contents (e.g., potential sorption retardation), total oxidant demand, and indigenous biodegradation capability (i.e., the microbial consortium and need for augmentation), are typically evaluated during the screening of *in situ* remedies (e.g., EISB/ISCO/ISCR). The implementability evaluation of EK-enhanced *in situ* remedies should consider the same, as well as whether the selected amendment(s) and/or bacteria can be delivered by EK through the targeted low-k matrix. Conceptually, the sites presenting challenges to the recirculation-based approach due to high retardation potential (sorption by soil organics, competing electron acceptors or oxidant demand) will also require EK-based approach to overcome these challenges. The implementability questions discussed herein can be best answered by a treatability test designed to evaluate these factors.

Q: Is the contaminant distribution in the target treatment zone well defined?

A: Similar to the considerations for other source area remedial alternatives, a well-defined, contiguous target zone presents fewer challenges than disbursed and disconnected zones requiring remediation. The reported electrode well spacing is in the range of approximately 15 to 25 ft. While an EK-enhanced remedy can be implemented to address various spatial configurations, the remediation system infrastructure, particularly the well network, and cost can be higher for a disbursed target zone.

One complexity is whether the target zone is underneath a building. Currently, the reported experiences have involved vertical electrode wells in EK technology deployment. The use of horizontal electrode wells may be considered, but such applications have not been demonstrated in the field with the EK-enhanced remedial approach.

The depth to a target zone is generally not a limitation for EK-based approaches. EK-enhanced *in situ* remedy can be implemented using regular polyvinyl chloride (PVC) wells. Typically, a well diameter larger than 2 inches (e.g., 4-inch dia.) is preferred to allow installation of electrodes and amendment supply tubing. Depending on the depth interval of a target zone, multiple vertically separated electrodes may be used in an electrode well.

Q: Is power available at the site? Are subsurface utilities present that could be adversely impacted?

A: The reported field experiences of EK-enhanced amendment delivery have not applied high levels of electrical energy, with the DC amperage and voltage generally in the range of tens of A and less than 300 V, respectively. The DC power source is typically supplied from an AC/DC transformer that generally operates with a commonly available AC electrical power source. While solar-based power is conceptually feasible based on the reported DC power usage of some EK-enhanced *in situ* remediation projects, such an application has not been fully demonstrated at a field scale. The availability of power is a consideration that should be a part of the implementability evaluation.

With respect to nearby subsurface utilities, several field-scale demonstrations reported no safety issues as the teams examined this aspect during their project performance. Nonetheless, a vertical separation of several feet between the top of the established DC electric field (or the top of groundwater table) and the subsurface utilities of concern should provide a level of safety for consideration. It is noted that cathodic protection of certain utilities and infrastructures is a standard practice for some industries with long-established protocols and available professionals with expertise that can be consulted.

3.1.3 Cost Considerations for EK-Enhanced In Situ Remediation

Cost is noted to play a limited role in the initial screening of technologies (USEPA, 1988). At the screening stage, remedial options are compared based on the relative total cost including both capital costs and operation and maintenance (O&M) costs. Relative rankings, such as very high, high, medium, and low, may be used in place of quantitative estimates.

When considering the costs of EK-enhanced *in situ* remediation, it is important to factor in the relative costs among the alternatives in terms of achieving defined RAOs. One key motivation for considering an EK-enhanced *in situ* remedial approach is when low-k materials represent a challenge to conventional hydraulics-based approaches. Depending on site-specific geological constraints and RAOs, conventional hydraulics-based approaches may require certain engineering measures (e.g., multiple rounds of applications, high-pressure fracturing) that can significantly affect the overall remedy costs, which should be captured in a comparative cost evaluation against EK-enhanced *in situ* remedial approaches.

Reports on two EK-technology field demonstration projects, funded by the Department of Defense (DoD) Environmental Security Technology Certification Program (ESTCP), provided comparative cost analysis between EK-based approaches and other select *in situ* remedial alternatives (Cox et al., 2018; 2021). The analysis suggests that EK-based remedial approaches are of low to medium cost relative to other alternatives for source remediation when the contaminant mass in low-k materials is factored in. Additional discussions related to project lifecycle cost considerations for EK-enhanced *in situ* remedies and comparable cost analysis are provided in Section 3.5.1.

3.2 Remedial Alternatives Analysis

The remedial alternatives considered to be implementable are analyzed in greater detail in the FS. EK-enhanced remediation can be considered as a standalone remedy or as a process option in combination with other technologies. For the purposes of this paper, we will review EK-enhanced *in situ* remediation as a standalone remedy to achieve a specific objective, and not in combination with other technologies that may be needed to address the entire site cleanup goal.

For the detailed analysis of remedial alternatives in the FS process, innovative technologies may need to be evaluated based on more limited data than conventional technologies. Treatability testing can be used to better evaluate an innovative technology for a given site (USEPA, 1988).

Table 3-2 summarizes the types of site-specific and project-specific information that will support the selection process for an EK-enhanced *in situ* remediation technology. To select a remedy (technology), the threshold criteria should be met to protect human health and the environment, while complying with federal and state laws. The balancing criteria help to compare the relative advantages and limitations of the various remedial technologies and alternatives in meeting the RAOs. The modifying criteria are used to determine remedial alternatives that are acceptable to regulatory and community stakeholders.

3.3 Treatability Studies

A treatability study can be performed to support the technology screening and remedy selection at a given site. Considering that EK-enhanced amendment delivery for *in situ* remediation is relatively innovative, a treatability study designed to provide site- and project-specific information is important for remedy screening and selection. It is noted that the discussions in this section are mainly for EK-BIO and EK-ISCO given that the practical experiences of EK-ISCR are still limited. **Appendix D** provides a case summary of a treatability study for evaluating EK-BIO approach for a chlorinated solvent source area within glacial geology.

Typical considerations for a treatability study evaluating EK-enhanced *in situ* remediation include the following factors.

3.3.1 Treatability Study Objective

The first thing to consider is whether the treatment method has been selected and confirmed. As EK is an amendment delivery technique, the treatability study design will depend on the treatment method to be evaluated. The selection of treatment method for a given site can be based on industry or practitioner experiences in considering site- and project-specific needs. Alternately, a two-stage treatability study may include evaluations of individual treatment methods (e.g., biodegradation, chemical oxidation) to confirm COC destruction and treatment effectiveness, followed by an evaluation of the efficacy of EK delivery of the selected remediation amendments.

The scope and scale of a treatability study depend on whether the study aims to only evaluate EK transport of selected amendment(s) or also the treatment effectiveness of the EK-transported amendment(s). With properly selected amendments, biodegradation and/or chemical oxidation of target contaminants under certain conditions is generally well-understood or may have already been evaluated for a site prior to an EK alternative being considered.

3.3.2 Scope and Test Design

- **Site materials for testing**

  Collection of the site aquifer materials for a treatability study should consider the study objective (e.g., target remediation zone), representative contaminant mixture, and contaminant strength. The sampling plan should be developed based on prior characterizations and CSM of the target remediation zone.

  Baseline field sampling, at least around the target zone, should be considered. The field-sampled aquifer materials should be subject to baseline analyses of chemical and geochemical parameters. The parameters of interest are the same as those for typical EISB or ISCO treatability studies, such as microbial populations for EISB and oxidant demand for ISCO studies.

- **Treatment selection and evaluation**

  This part of a treatability study, often conducted as microcosm tests, is the same as that for typical EISB or ISCO treatability studies, and will include amendment dosage requirements, need for bioaugmentation, and contaminant treatment effectiveness.

Table 3-2. Remedial Alternatives Analysis for EK-Enhanced *In Situ* Remediation

Criteria	EK-enhanced Remediation and Project-Specific Considerations
THRESHOLD CRITERIA	
Overall Protection of Human Health and the Environment	This criterion determines whether a remedial alternative eliminates, reduces, or controls threats to human health and the environment. By selecting an appropriate treatment option (i.e., EISB/ISCO/ISCR), EK-enhanced amendment delivery is anticipated to reduce and/or control threats through source zone treatment that ultimately reduces the potential exposure and/or the remedy timeframe to achieve RAOs. An important consideration is whether there is a clearly defined goal for what the EK-enhanced *in situ* remedy should achieve (e.g., source removal only in the saturated formation but not in the vadose zone).
Compliance with Applicable or Relevant and Appropriate Requirements (ARARs)	This criterion evaluates if a remedial alternative will meet applicable federal and state laws. *In situ* remedies (EISB/ISCO/ISCR) implemented via EK-enhanced amendment delivery should be able to meet ARARs just like remedies implemented via conventional methods. Except for the potential pH and redox changes localized around the electrodes, which can be controlled via proper engineering measures, EK-based remedial approaches can be designed and implemented to comply with ARARs.
BALANCING CRITERIA	
Long-Term Effectiveness and Permanence	This criterion considers the ability of an alternative to maintain protection of human health and the environment over time. EK-enhanced *in situ* remediation, by delivering the treatment capacity to the matrix where contaminant mass resides, should lead to favorable long-term effectiveness. The treatment mechanisms of EK-enhanced remedies (i.e., biodegradation or chemical degradation) are destructive mechanisms that should achieve the desired permanence of removing target contaminants.
Reduction of Toxicity, Mobility, or Volume through Treatment	This criterion evaluates the ability of a remedial alternative to reduce contamination and potential migration in the environment. As discussed above related to the overall protection of human health and the environment, EK-enhanced *in situ* remedies, by directly targeting contaminant mass for treatment, are expected to meet this criterion when properly designed and implemented. One aspect of EK transport for consideration is that, in addition to remediation amendments, contaminants may potentially be transported as well. However, the range of that transport is within the electric field between electrodes and is under controlled conditions for the purposes of contaminant treatment. A technical advantage of EK-enhanced delivery is that the "injection" volume is relatively small compared to conventional hydraulic injection methods. This is because the EK transport mechanisms act to transport the constituents within the amendment solution and not the solution itself. Therefore, the EK-based techniques may be more favorable than conventional injection techniques in terms of reducing contaminant mobility as a remediation outcome.
Short-Term Effectiveness	This criterion considers the effects of an alternative during the construction and implementation phase until remedial response objectives are met. The "effects" considered are effects on human health (including risks to workers and nearby residents) and the environment during the implementation of remedial action. *In situ* remedies (EISB/ISCO/ISCR) implemented via EK-enhanced amendment delivery should represent the similar short-term effectiveness as the same remedies implemented via conventional methods. A particular consideration is protection for remedial action workers related to electrical work. The safety considerations are fairly standard, and there are long-established standard protocols that should be followed.
Implementability	This criterion reviews the technical and administrative feasibility of implementing an alternative, including the overall availability of materials and services required during remedy implementation. The considerations related to implementability have been mostly discussed in Section 3.1.2. The equipment and components involved in the reported EK experiences are generally available, and the remedy installation techniques are common to most *in situ* remediation technologies. As a relatively innovative technology, there are fewer vendors with specific field experience in implementing EK-enhanced *in situ* remediation technology.
Cost	The cost criterion involves an evaluation of the capital costs, the annual O&M costs, and a present value estimate. At the FS phase, the cost estimates for each remedial alternative are order-of-magnitude level estimates. The net present value analysis also requires an estimate of the remedial timeframe to reach RAOs. Remediation construction costs for EK-enhanced *in situ* remediation are primarily dependent on the areal extent and depth of the target zone, which impacts well network construction. Other factors include power availability and the nature of contamination that drives the type of treatment method and, thus, the remediation reagents (FRTR, 2022). O&M costs are based on the number of electrodes, treatment duration, power requirements, utility rates, and other factors (FRTR, 2022). The ranges of cost are provided in **Table 3-3** in Section 3.5.1.
MODIFYING CRITERIA	
State Acceptance	Acceptance will be based on regulatory stakeholder review of the proposed plan during the required community involvement period. As a relatively innovative technology, there have not been broad applications where state acceptance was sought.
Community Acceptance	Acceptance will be based on community stakeholder review of the proposed plan during the required community involvement period.

Additional considerations specifically related to an EK-enhanced remedy include:

- Amendment for EK-BIO
  Lactate, an ionic compound, has been applied in multiple EK-BIO field projects. Lactate transport is primarily via electromigration, which is a relatively robust EK mechanism. The use of other bioremediation amendments (e.g., emulsified vegetable oil) in EK applications is relatively limited to date.
- Oxidant for EK-ISCO
  Both permanganate and persulfate are common oxidants for ISCO application. Both oxidants are anions that can be transported via electromigration. The selection of persulfate needs to include considerations of the levels of naturally occurring iron that may activate persulfate during EK transport and what the activation method for the EK-transported persulfate will be, if needed.

- **EK transport study**
  This part of a treatability study is typically conducted as column experiments or in a 2-D sandbox (see example photos in **Appendix D**). Preparations of column or sandbox reactors with site aquifer materials are the same as those for typical EISB or ISCO treatability studies. Depending on the study objectives and baseline analyses, the field-sampled materials may need to be spiked with contaminants during the reactor construction.

  The major components of an EK test reactor include electrode reservoirs and electrodes (often graphite plates or titanium-based rods), amendment supply units, DC power supply unit, interior sampling ports (optional), and electrolyte cross-circulation between electrode reservoirs (optional).

  Unless there are interior locations for amendment supply, which tends to significantly increase the scale of the reactor, the selected amendments will be provided in an electrode reservoir. Lactate, permanganate, and persulfate, all as anions, will be added to the cathode reservoir for transport toward the anode via electromigration. The pH of the cathode reservoir should be controlled (i.e., buffered) if persulfate is the selected oxidant to avoid localized alkaline activation of persulfate.

  The EK transport test can be conducted under a target constant current, or a target constant voltage, controlled by a DC power unit.

  Conceptually, EK operation under a constant current is to achieve a constant flux of electrical charges (ions), while a constant voltage is to apply a constant electric-field gradient. The cases reviewed in Sections 2.1 and 2.2 provide references for the typical ranges of EK conditions that have been tested.

- **EK-enhanced remedy effectiveness**
  If this evaluation is part of the treatability test, the site materials used for reactor setup need to contain adequate levels of contaminants at the start of the test. The overall considerations and design for this evaluation are the same as those in the treatability studies for typical EISB or ISCO.

  Particularly for EK-ISCO using persulfate, an evaluation of whether heat activation is needed to achieve an intended treatment by EK-transported persulfate will need to prepare two separate reactors, one for EK transport and one for EK transport with a subsequent heat activation phase, to assess the extents of treatment achieved by the transported persulfate with and without heat activation.

3.3.3 *Treatability Study Data Objectives*

While data objectives for a treatability study should be project-specific, some common data objectives for an EK treatability study include:

- Confirm EK delivery of selected amendment(s)
- Estimate the amendment demand required by the site aquifer materials

- Estimate the reactive (net) transport rate of the amendment(s)
- Confirm the achievable extent of contaminant treatment
- Confirm the transport or establishment of bioaugmented bacteria, if applicable
- Confirm the need and/or effectiveness of persulfate activation, if applicable.

3.3.4 Treatability Study Cost

The cost for a treatability study of an EK-enhanced *in situ* remedy depends on several key scope aspects of the study:

- **Sandbox reactor vs. column reactor**
  A 2-D sandbox reactor is of a larger scale than a soil column reactor and generally requires a longer test duration (e.g., 3 to 6 months for sandbox versus 1 to 2 months for column tests) to generate more data. Typical costs for an EK treatability study are likely in the range of $35,000 (column reactor) to $100,000 (sandbox reactor).

- **EK transport only vs. EK transport and contaminant treatment**
  An EK treatability study may be designed to evaluate only the transport of selected remediation amendment(s) or to also include an evaluation of treatment achieved by the EK-transported amendment(s). The latter will require a longer study duration and more sampling and analyses, resulting in a higher cost.

- **EK-BIO vs. EK-ISCO**
  If an evaluation of treatment effectiveness is part of the treatability study as discussed above, the cost for an EK-BIO treatability study can be higher than that for an EK-ISCO study due to the longer duration required for biological treatments (e.g., weeks to months) compared to that for chemical oxidation treatment (e.g., days to weeks), as well as the potentially more extensive analytical program associated with a biodegradation study than that for a bench-scale ISCO study.

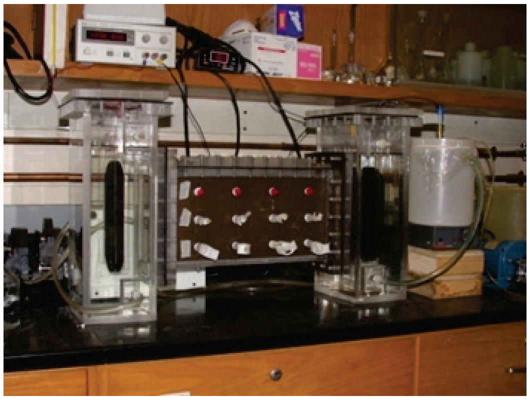


Photo: Example Bench-Scale EK Reactor Setup

3.4 Pilot-Scale Testing

Pilot-scale testing can be conducted to further the evaluations of EK-enhanced *in situ* remediation technology for a particular site. **Appendix B** and **Appendix C** provide project summaries of two EK pilot tests: one for EK-BIO and one for EK-ISCO. Typical considerations for planning and implementing a pilot test of EK-BIO or EK-ISCO include the factors described below.

3.4.1 Pilot Test Objectives

With the information collected prior to planning a pilot test, the pilot test objectives should be clearly defined. One common question related to an EK-enhanced remediation pilot test is whether there is a target extent of contaminant treatment to be achieved by the EK-transported amendment(s) or if the objective is only to demonstrate and assess the EK delivery of the selected amendment(s). This decision can affect the scope and scale and, thus, the cost of a pilot test, so this objective should be clearly defined at the onset of project planning.

Typically, a pilot test also aims to derive engineering design parameters to support subsequent remedial design. The major design parameters related to an EK-enhanced remedy include placement and well spacing of electrode wells and supply wells; amendment dosage requirements and dosing strategy; EK operational requirements; pH control needs at electrode wells;

and other O&M requirements. Selection of the equipment for a pilot test (such as electrodes, power supply capacity, pumps, and other mechanical components) should consider the option/feasibility of reusing the selected equipment for full-scale remedy implementation to achieve cost savings.

3.4.2 Pilot Test Elements of Work

- **Target pilot test zone**

  Selections of the areal and vertical extents of pilot test zone should be based on CSM elements related to hydrogeological, biogeochemical characterization, contaminant distribution, and remediation objectives.

- **Well network**

  The minimum number of electrode wells required is two: one cathode and one anode. Other options include using same number of cathodes and anodes for even pairings, or using uneven pairings between cathodes and anodes. Uneven pairings of electrodes will involve additional engineering measures for current and/or voltage distributions and pH controls. The configurations for an electrode well network generally include linearly parallel or grid patterns. The spacing between electrode wells has generally been in the range of 15 to 25 ft. The well spacing should take into account the estimated EK transport rate obtained from the site-specific treatability test as well as the pilot test duration and treatment target or other project-specific objectives. Electrode wells can be installed as typical PVC wells. An electrode does not require a large-diameter well, but depending on the design of pH control and/or amendment supply (discussed below), a well diameter larger than 2 inches provides better functionality.

  The EK-enhanced *in situ* remedy can target a low-k or heterogeneous formation. The amendment supply system and operation for an EK-enhanced remedy pilot test are the same as those for pilot testing of typical EISB or ISCO. One consideration is that the dosing strategy for an EK remedy is to maintain high amendment concentrations in the wells and not to supply large solution volumes. The concept is to have sufficient mass of amendment to be transported via EK mechanisms and not by hydraulic advective flow of the amendment solution. The dosing plan can be designed based on the reactive transport rate and the derived amendment consumption rate obtained from the treatability study.

  The amendment supply system should also include the function to control the pH at the electrode wells. This can include buffer supply and/or cross-circulation between cathode and anode wells.

- **EK power supply system**

  The power supply system typically uses an AC/DC converter that can receive AC power input and provide DC power output. As discussed above for the treatability study, the system is to either provide a constant current to individual electrodes or apply a constant voltage at individual electrodes. Findings from the treatability study can inform this design.

Photo: DC power supply unit and titanium-base electrodes

- **Operation, maintenance, & monitoring (OM&M)**

  General pilot test system OM&M tasks will be similar to those for a typical EISB or ISCO pilot test. The considerations specific to an EK pilot test are:

  - Power system operation monitoring—OM&M tasks will include checking the DC electrical supply to individual electrodes
  - Periodic cleaning of the cathode surface may be needed depending on the site

geochemistry (e.g., levels of calcium or iron)

  - Individual voltage probes may be installed within the target zone to allow periodic monitoring of the electric field
  - As applicable, check for potential stray currents at nearby surface features for safety.

The selected well screen interval should meet the pilot test objectives. If a long screen interval is needed for an electrode well (e.g., >25 ft), using multiple vertically spaced (e.g., 5–10 ft apart) electrodes in the well may provide better results.

Supply wells can be strategically located within the electrode well network for two purposes. One, this provides an option to introduce the selected amendment(s) while avoiding reactive loss at the electrode wells due to potential electrolytic reactions or pH interferences at electrodes. Second, this shortens the distance for EK transport, which reduces the reactive loss of the amendment(s) due to reactions with natural demands during transport. The number and location of the supply wells should be designed based on the transport rate and reactive consumption rate derived from the treatability study and balancing the pilot test cost/duration consideration.

- **Amendment supply**
  The pilot test performance monitoring program (e.g., groundwater/soil sampling frequency and analytes) for an EK-based remedy will be the same as that for a typical EISB or ISCO pilot test. Considering the heterogeneity within a target zone, a robust post-test sampling program (and/or one during the test) that includes discrete samples collected from within the target zone to provide adequate areal and vertical data coverage for pilot test assessment is important.

Picture courtesy Geosyntec Consultants

Photo: EK-ISCO pilot test setup at Cristex Drum Superfund Site (**Appendix C**)

3.4.3 Pilot Test Data Objectives

While data objectives for a pilot test should be project-specific, some common data objectives for an EK pilot test include:

- Confirm EK delivery of selected amendment(s)
- Estimate the amendment demand required by the target zone (aquifer materials and contaminants)
- Estimate the reactive (net) transport rate of the amendment(s)
- If included as an objective, confirm the achievable extent of contaminant treatment
- If included as an objective, confirm the transport and/or establishment of bioaugmented bacteria
- Confirm the need and/or effectiveness of persulfate activation, if applicable
- Develop and validate the EK system operation conditions.

3.4.4 Duration and Cost Ranges

The duration and costs for a pilot test of EK-enhanced *in situ* remedy depend on several key aspects related to the scope and objective as discussed above. Two DoD-funded ESTCP projects that demonstrated EK-BIO and EK-ISCO at Naval Air Station Jacksonville in Florida produced cost and performance reports following the completion of the demonstrations (Cox et al., 2018, 2021). Specific to the project objectives and site conditions of these two pilot-scale demonstration projects, the durations of active EK system operation were approximately 12.5 months for the EK-BIO project and approximately 7 months for the EK-ISCO project. The reported costs for remedy construction and system O&M, specific to the scope of these projects, were approximately $405,000 for the EK-BIO project and approximately $347,000 for the EK-ISCO project. It should be noted that the implementation of a pilot test will also require design, planning, permitting (as needed), and monitoring tasks, which are project- and site-specific and fairly common for all remediation pilot test projects.

3.5 Full-Scale Remedy Design and Implementation

The completion of a successful pilot test that confirms technical feasibility, evaluates the remedy's potential effectiveness, and derives engineering design parameters should lead to an informed decision for a full-scale implementation with well-defined remedial objectives (e.g., extent of source treatment, integration with other remedial measures) for the selected remedy. **Appendix A** provides the project summary of an EK-BIO full-scale remedy implemented for a chlorinated solvent source area present within a glacial till formation (site in Skuldelev, Denmark).

The major components of a remediation system for EK-BIO or EK-ISCO include EK-specific components (e.g., electrodes, DC power supply and distribution, pH controls at electrode wells) and amendment supply components. The amendment supply system for an EK-based *in situ* remedy is similar to that for a typical recirculation-based EISB or ISCO. The difference in amendment supply between an EK-based approach and a recirculation-based approach is the concept behind the dosing strategy as discussed in Section 3.4. The pilot test results should provide the basis for the dosing design of a full-scale EK-based remedy.

The EK-specific components of a full-scale system, including electrodes and electrode wells, DC power supply and distribution, and pH control measures for electrode wells, can be scaled up from the pilot test system. The first consideration during scaling up is the network arrangement of electrode wells and supply wells. As discussed for the pilot test, the pairing of electrode wells can be even (one cathode paired with one anode) or uneven (often two or three cathodes to one anode, or vice versa). While there is no limit to uneven pairings, the power distributions and pH controls at electrode wells can become complicated with a complex uneven pairing arrangement. General considerations for the number and locations of the supply wells are similar to those discussed above for the pilot test.

Given the demand of a full-scale system and the number of electrodes involved, more than one DC power supply unit may be required. The use of multiple DC power supply units also allows more flexible distributions and controls of the power supply to a network of electrodes.

One option to reduce the number of power supply systems required for a large target zone is to consider implementing the remedy in stages, with each stage addressing a portion of the overall target zone. Certain EK remediation system components (such as electrodes/power supply units) can be reused and redeployed in different stages of remediation operations representing a capital cost-saving opportunity. The phased-approach option is particularly suitable for EK-BIO when an active amendment transport stage is followed by an incubation period during which the subsurface microbial populations continue to utilize the distributed amendments to degrade target contaminants. A staged remedy implementation approach also allows the adjustment of subsequent stages, as needed, based on the performance monitoring of earlier stages.

The overall remediation construction, system OM&M, and monitoring program of a full-scale EK-based remedy are generally similar to those for a pilot test. The experience and observations from a pilot test provide the best site-specific information for the planning of a full-scale remedy.

3.5.1 Considerations of Overall Remedy Cost-Effectiveness

Table 3-3 presents a framework for considering the costs of developing and implementing an EK-enhanced *in situ* remedy at a given site. This framework was primarily developed by the project team that conducted the EK-BIO technology demonstration at Naval Air Station Jacksonville (Jacksonville, Florida) based mainly on the information derived from that project (Cox et al., 2018). The basis of the cost estimates is a hypothetical, generic chlorinated solvent source zone of 40 ft by 40 ft by 10 ft. The discussions of major cost drivers that follow **Table 3-3** provide additional insights to how to consider the information presented in the framework when estimating the costs for other sites.

3.5.1.1 Cost Driver Considerations

- **Target zone and contaminant mass**
  As for most remediation technologies, the size (areal and vertical) and volume of the target treatment zone, as well as the amount of contaminant mass requiring treatment, significantly affect the overall remediation costs. Particularly, the drilling and well installation costs for system wells (electrode wells and supply wells) vary based on the number and depth of these wells needed to adequately address the treatment zone. The spacing between electrode wells in the reported applications is approximately 15 to 25 ft. The number of supply wells located within the electrode well network can be adjusted based on the considerations of the EK transport rate and the desired remedy operation duration.

Table 3-3. Project Life Cycle Cost Framework for EK-enhanced Amendment Delivery for *In situ* Remediation

Project Phase	Task Summary	Approximate Cost Range
Bench-scale EK Treatability Test	• Laboratory batch tests—evaluate amendment's ability to treat target contaminant • Laboratory EK column tests—evaluate EK transport of select amendment • Laboratory EK column tests—evaluate contaminant treatment by EK-transported amendment	$35K–$100K
Pre-Design Data Collection (As Needed)	• Soil/groundwater sampling for geochemistry parameters related to EK evaluations • Better delineation and quantification estimate of contaminant distribution and mass within the target zone	As Needed
Remedial Design	• EK remediation system design • Associated plans for remediation construction, installation, operation, monitoring	$70K–$120K
Remediation Construction	• Well installation (assuming 15 electrode/supply wells; 6 monitoring wells) • EK system fabrication/electrodes • Site construction/system connection • System startup	$300K–$500K
Remediation System Operation & Maintenance	• Field O&M (assuming over 12 months of active operation) • Materials (for EK-BIO: lactate; for EK-ISCO: oxidant) • Materials (buffer and other chemicals) • Materials (system O&M parts and consumables) • Utilities	$85K–$250K
Remedy Performance Monitoring	• Typical groundwater (and soil) quality monitoring program for remedy performance evaluations	Project/Site-Specific

(Cost framework based on a target area measuring 40 ft by 40 ft by 10 ft thick)

When a target zone is relatively large, a multistage implementation approach, with each stage targeting a portion of the overall zone, should be considered. Electrodes, power systems, and amendment supply components can be reused in different stages to achieve cost efficiency.

However, the remedy O&M duration will be longer as a trade-off of using a staged approach. The overall duration of an EK remedy implementation will also depend on the contaminant mass present and the required mass reduction goal.

While there is no technical limit for applying EK technology in terms of target depth, the costs for well construction increase as the depth of the target treatment zone increases. The depth interval (thickness) of the target treatment zone may affect the number of electrodes installed within an electrode well and, thus, the overall number of electrodes needed. As a reference, the reported cost of an electrode for EK field implementations is in the range of approximately $500. Multiple electrodes can be installed and vertically separated in one single electrode well to target a thicker zone. Therefore, the overall well installation cost does not increase proportionally with the increase of target zone thickness. Generally, a zone of 15 to 20 ft thick can be readily addressed by deploying two electrodes in each electrode well.

- **Site geochemistry**
  Concentrations of iron and other major cations (e.g., calcium, magnesium) in groundwater are an important factor that can affect the cost of system O&M. While these geochemical parameters are an important factor for most *in situ* remediation technologies, they require special consideration when implementing an EK remedy because the electric field will result in, at least temporarily, concentrated iron and cations in cathode wells, which attract cations in groundwater. The EK system for sites with significantly elevated concentrations of these cations will need to be sized and equipped with adequate units for handling the anticipated amount of precipitates. More robust O&M programs and efforts will also need to be considered for such sites.

- **Utilities**
  As with any active remediation technologies, a power source is required for EK-based technology. Based on the electrical operation conditions (voltage and current) involved in the reported EK field projects, solar energy with battery units may be a feasible option.

  It is noted that the electricity cost is not a particular cost driver for EK-enhanced amendment delivery projects. Given the DC voltage (in the range of 100s V) and current (in the range of 10s A) ranges that have been reported in prior EK field projects, the overall electricity usage for EK processes is relatively low compared to other conventional active remediation technologies.

3.5.1.2 Comparative Cost-Effectiveness Considerations

When considering the costs of EK-enhanced *in situ* remediation, it is important to compare costs among the alternatives that are comparable in terms of achieving defined RAOs with particular considerations related to remediation in low-k or heterogeneous formations. The reports of two ESTCP EK field demonstration projects provided comparative cost considerations between the EK-based remedial approach and several conventional *in situ* remediation implementation approaches, including direct injection by direct push technology (DPT) with and without hydraulic fracturing and thermal remediation via ERH (Cox et al., 2018; 2021). The comparative cost analysis considered, for full-scale remediation of a generic contaminant source area of select dimensions and contaminant mass, the following elements:

- Remedial design and permitting,
- Remedial construction, and
- Remediation system O&M

These cost estimate exercises suggested that, under certain site conditions or constraints, the EK-based approaches could potentially be more cost favorable to an ERH remedy. The comparative cost-effectiveness between EK-based approaches and the DPT injection approach is highly dependent on whether DPT injection is technically feasible or effective at certain sites with low-k materials. When combined with fracturing techniques, the cost of the DPT injection approach may be comparable to that of EK-based approaches. Certain other site-specific constraints, such as sensitive subsurface utilities or thickness and strength of overburden materials above a target zone, may affect the implementability of fracturing techniques. Thorough evaluations and comparisons between remedial alternatives are critical to remedy selection for sites with challenging geology where EK-based approaches may provide a unique solution for considerations.

3.6 Limitations and Technology Development Prospects

As a relatively innovative technology, there are several technical aspects that require additional engineering development efforts to facilitate EK-based *in situ* remediation under certain conditions. These challenges include:

- **Target zone beneath buildings or other surface structures**

  Current experiences with EK-based *in situ* remediation have utilized networks of vertical electrode wells with spacing between individual wells in the range of 15 to 25 ft. While a larger well spacing is technically feasible, aboveground structures preventing the installation of vertical wells is a current limitation for this technology. While the concept of a horizontal electric field and its applications for *in situ* remediation are apparent, further engineering development is still needed to allow such field implementations.

- **Solar energy as the power source**

  The reported EK field projects to date suggest that solar power with batteries can potentially be the power source for this technology. However, the overall technology implementation also requires amendment supply and system control components that also have power requirements that need to be satisfied.

- **Engineering EK-ISCO for applications using thermally activated persulfate**

  One particular EK-ISCO application is to distribute persulfate (oxidant) through the target zone by EK mechanisms followed by thermal activation of the distributed persulfate. The idea is to use the same electrode network deployed for EK transport but apply AC power to achieve subsurface heating similar to the ERH process. While there has been field testing of this particular EK-ISCO approach using persulfate, additional engineering development related to electrode material and performance, as well as efficient electrode network arrangement, for both EK transport and subsurface heating processes is needed to achieve robustness of this combined remediation technology.

4 Summary

In situ remediation technologies face significant challenges when contaminant mass resides in low-k aquifer matrices comprised of clayey and silty materials. Conventional hydraulic delivery of remediation reagents relies primarily on advection. However, advection is limited in low-k aquifer materials and diffusion becomes the dominant transport mechanism. The diffusive movement of reagents into the low-k media, where residual contaminants often reside, is a slow transport process resulting in a lengthy remediation timeframe.

EK-enhanced *in situ* remediation technologies, currently under different stages of development, represent a remedial alternative in low-k subsurface environments where conventional hydraulic delivery technologies face limitations. EK transport may involve three mechanisms: electromigration, electroosmosis, and electrophoresis. Electromigration is the movement of charged dissolved ions through an aqueous medium driven by a voltage gradient toward the electrode with a polarity opposite of the ion's charge. Electroosmosis is the movement of pore fluid, and the dissolved constituents within a soil-water matrix, induced by a voltage gradient between electrodes. Electrophoresis is the transport of charged particles driven by a voltage gradient between electrodes. However, particle transport through electrophoresis is limited in low-k media of restricted pore sizes due to fundamental filtration mechanisms. The rate of transport attributed to these EK mechanisms in a typical aquifer system under a given voltage gradient generally occurs in the following decreasing order: electromigration > electroosmosis > electrophoresis.

EK-enhanced *in situ* remediation is implemented by applying an electrical current (or voltage) from an external power supply source, typically low-voltage DC, to individual electrodes installed in an aquifer. A DC electric field is then created in the subsurface between cathodes and anodes. Conceptually, this is analogous to a DC battery-driven electrical circuit with the aquifer materials between electrodes acting as an electrically conducting unit. The DC electric field established in a low-k treatment zone enables the EK transport of select remediation reagents to be supplied to the treatment zone.

The current state-of-practice of EK-enhanced remediation technologies primarily includes *in situ* bioremediation (EK-BIO) and *in situ* chemical oxidation (EK-ISCO). Bench-scale, pilot-scale, and full-scale applications of EK-BIO have reported the enhanced transport and delivery of nutrients (e.g., nitrogen, phosphorus), substrate (e.g., lactate), terminal electron acceptor (e.g., NO_3^-, SO_4^{2-}), and microbial amendments (e.g., Dhc). The enhanced transport of remedial reagents has been correlated with enhanced biodegradation. Similarly, the enhanced transport of chemical oxidants, such as permanganate (MnO_4^-) and persulfate ($S_2O_8^{2-}$), into low-k media resulting in contaminant treatment has been demonstrated. These EK-based technologies are applicable in saturated zones below the groundwater table where groundwater containing dissolved ions functions as the circuit between electrodes. Deployment of EK-based technologies in the unsaturated zone to date has not resulted in consistently effective outcomes.

EK has also been deployed in heterogeneous unconsolidated porous media involving layers of materials with highly variable permeabilities. Such formations contain hydraulic preferential pathways preventing conventional hydraulic injection techniques from achieving uniform distributions of remediation amendments. Applications of EK-enhanced amendment delivery techniques should achieve a more uniform and controlled delivery of remediation reagents in a relatively heterogeneous aquifer matrix.

The information reviewed in this EIP offers remediation practitioners valuable insights for evaluating the applicability and cost-effectiveness of this remedial approach to addressing the vexing challenges to *in situ* remediation presented by low-k geologic materials. EK-enhanced *in situ* remediation is an evolving technology. Practitioners should consider following a robust technology evaluation and testing framework, such as the one discussed in Section 3, to properly screen, select, design, and implement EK-enhanced *in situ* remediation in order to fully benefit from the specific technical advantages of this innovative technology.

5 References

Acar, Y. B. and Alshawabkeh, A. N. (1994). Modeling conduction phenomena in soils under an electric current. *International Conference on Soil Mechanics and Foundation Engineering*, 669–672.

Acar, Y. B. and Alshawabkeh, A. N. (1996). Electrokinetic remediation. I: Pilot-scale tests with lead-spiked kaolinite. *Journal of Geotechnical Engineering*, *122*(3), 173–185.

Alshawabkeh, A. N., Yeung, A. T., & Bricka, M. R. (1999). Practical aspects of in-situ electrokinetic extraction. *Journal of Environmental Engineering*, *125*(1), 27–35.

Asadi, A., K Huat, B. B., Nahazanan, H., & Keykhah, H. A. (2013). Theory of electroosmosis in soil. *International Journal of Electrochemical Science*, *8*(1), 1016–1025. www.electrochemsci.org

Athmer, C. J. (2014). Use of large-scale electrokinetic and ZVI treatment for chlorinated solvent remediation at an active industrial facility. *Remediation*, *24*(4), 41–51. https://doi.org/10.1002/rem.21403

Black & Veatch Special Projects Corp. and Geosyntec Consultants of NC, P. C. (2020). *Electrokinetic Enhanced In Situ Chemical Oxidation (EK-ISCO) Pilot Test Report Revision 1*.

Blotevogel, J., Pijls, C., Scheffer, B., de Waele, J.-P., Lee, A., van Poecke, R., van Belzen, N., & Staal, W. (2018). Pilot-scale electrochemical treatment of a 1, 4-dioxane source zone. *Groundwater Monitoring & Remediation*, *39*(1), 36–42. https://doi.org/10.1111/j.1745-6584.2010.00732.x

Bradford, S. A., Abriola, L. M., & Rathfelder, K. M. (1998). Flow and entrapment of dense nonaqueous phase liquids in physically and chemically heterogeneous aquifer formations. *Advances in Water Resources*, *22*(2), 117–132.

Černíková, M., Nosek, J., & Černík, M. (2020). Combination of nZVI and DC for the in-situ remediation of chlorinated ethenes: An environmental and economic case study. *Chemosphere*, *245*, 125576. https://doi.org/10.1016/j.chemosphere.2019.125576

Cherepy, N. J. and Wildenschild, D. (2003). Electrolyte management for effective long-term electro-osmotic transport in low-permeability soils. *Environmental Science & Technology*, *37*(13), 3024–3030. https://doi.org/10.1021/es026095h

Chowdhury, A. I. A., Gerhard, J. I., Reynolds, D., Sleep, B. E., & O'Carroll, D. M. (2017a). Electrokinetic-enhanced permanganate delivery and remediation of contaminated low permeability porous media. *Water Research*, *113*, 215–222. https://doi.org/10.1016/j.watres.2017.02.005

Chowdhury, A. I. A., Gerhard, J. I., Reynolds, D., & O'Carroll, D. M. (2017b). Low permeability zone remediation via oxidant delivered by electrokinetics and activated by electrical resistance heating: proof of concept. *Environmental Science & Technology*, *51*(22), 13295–13303. https://doi.org/10.1021/acs.est.7b02231

Christiansen, C. M., Damgaard, I., Broholm, M., Kessler, T., Klint, K. E., Nilsson, B., & Bjerg, P. L. (2010). Comparison of delivery methods for enhanced *in situ* remediation in clay till. *Groundwater Monitoring & Remediation*, 30(4), 107-122.

Comba, S., di Molfetta, A., & Sethi, R. (2011). A comparison between field applications of nano-, micro-, and millimetric zero-valent iron for the remediation of contaminated aquifers. *Water, Air, and Soil Pollution*, *215*(1), 595–607. https://doi.org/10.1007/s11270-010-0502-1

Cox, E., Wang, J., Reynolds, D., Gent, D., Singletary, M., & Wilson, A. (2018). *Electrokinetic-Enhanced (EK-Enhanced) Amendment Delivery for Remediation of Low Permeability and Heterogeneous Materials*. https://apps.dtic.mil/sti/pdfs/AD1064336.pdf

Cox, E., Watling, M., Gent, D., Singletary, M., & Wilson, A. (2021). *Electrokinetically-Delivered, Thermally-Activated Persulfate Oxidation (EK-TAP) for the Remediation of Chlorinated and Recalcitrant Compounds in Heterogeneous and Low Permeability Source Zones*. https://apps.dtic.mil/sti/pdfs/AD1154470.pdf

da Rocha, U. N., Tótola, M. R., Pessoa, D. M. M., Júnior, J. T. A., Neves, J. C. L., & Borges, A. C. (2009). Mobilisation of bacteria in a fine-grained residual soil by electrophoresis. *Journal of Hazardous Materials*, *161*(1), 485–491. https://doi.org/10.1016/j.jhazmat.2008.04.022

DeFlaun, M. F. and Condee, W. (1997). Electrokinetic transport of bacteria. *Journal of Hazardous Materials*, *55*(1–3), 263–277.

Elektorowicz, M. and Boeva, V. (1996). Electrokinetic supply of nutrients in soil bioremediation. *Environmental Technology*, *17*(12), 1339–1349.

ESTCP (2011). *Guide for Selecting Remedies for Subsurface Releases of Chlorinated Solvents*. https://www.clu-in.org/download/contaminantfocus/dnapl/treatment_technologies/dnapl-er-200530-dg.pdf

ESTCP (2018) Electrokinetic-Enhanced (EK-Enhanced) Amendment Delivery for Remediation of Low Permeability and Heterogeneous Materials, Environmental Security Technology Certification Program (ESTCP) Project ER-201325, 204 pp. https://serdp-estcp.org/projects/details/2a2e46b1-60c4-4469-8b9e-92526cf2bc86

Fan, G., Cang, L., Fang, G., Qin, W., Ge, L., & Zhou, D. (2014). Electrokinetic delivery of persulfate to remediate PCBs polluted soils: Effect of injection spot. *Chemosphere*, *117*, 410–418. https://doi.org/10.1016/j.chemosphere.2014.08.006

Fenti, A., Jin, Y., Rhoades, A. J. H., Dooley, G. P., Iovino, P., Salvestrini, S., Musmarra, D., Mahendra, S., Peaslee, G. F., & Blotevogel, J. (2022). Performance testing of mesh anodes for *in situ* electrochemical oxidation of PFAS. *Chemical Engineering Journal Advances*, *9*, 100205. https://doi.org/10.1016/j.ceja.2021.100205

FRTR. (2020, August 3). *Electrokinetic-Enhanced Remediation*. Federal Remediation Technologies Roundtable. https://frtr.gov/matrix/Electrokinetic-Enhanced-Remediation/

Gent, D., Bricka, R. M., Truax, D., & Zappi, M. (2001a). Electrokinetic movement of biological amendments through natural soils to enhance in-situ bioremediation. *Sixth International In Situ and On Site Bioremediation Symposium*, 241–248.

Gent, D., Larson, S. L., Marsh, C., Alshawabkeh, A., & Wu, X. (2001b). *In-situ remediation using electrokinetics mixing, injection, and transport*. https://serdp-estcp-storage.s3.us-gov-west-1.amazonaws.com/s3fs-public/project_documents/CU-1204-FR-01.pdf?VersionId=f0EiWdEBxX45DKmPZJE7zhRK62D73Rj_

Gilbert, D. M. and Sale, T. C. (2005). Sequential electrolytic oxidation and reduction of aqueous phase energetic compounds. *Environmental Science & Technology*, *39*(23), 9270–9277. https://doi.org/10.1021/es051452k

Gomes, H. I., Dias-Ferreira, C., Ribeiro, A. B., & Pamukcu, S. (2012). Electrokinetic enhanced transport of zero valent iron nanoparticles for chromium (VI) reduction in soils. *Chemical Engineering Transactions*, *28*, 139–144. https://doi.org/10.3303/CET1228024

Hamed, J., Acar, Y. B., & Gale, R. J. (1991). Pb (II) removal from kaolinite by electrokinetics. *Journal of Geotechnical Engineering*, *117*(2), 241–271.

Hansen, B. H., Nedergaard, L. W., Ottosen, L. M., Riis, C., & Broholm, M. M. (2015). Experimental design for assessment of electrokinetically enhanced delivery of lactate and bacteria in 1,2-cis-dichloroethylene contaminated limestone. *Environmental Technology & Innovation*, *4*, 73–81. https://doi.org/10.1016/j.eti.2015.04.006

Hayden, N., Diebold, J., Farrell, C., Laible, J., & Stacey, R. (2006). Characterization and removal of DNAPL from sand and clay layered media. *Journal of Contaminant Hydrology*, *86*(1–2), 53–71. https://doi.org/10.1016/j.jconhyd.2006.02.008

Ho, S. v, Athmer, C. J., Sheridan, P. W., & Shapiro, A. P. (1997). Scale-up aspects of the Lasagna™ process for *in situ* soil decontamination. *Journal of Hazardous Materials*, *55*(1–3), 39–60.

Ho, S. v, Athmer, C., Sheridan, P. W., Hughes, B. M., Orth, R., McKenzie, D., Brodsky, P. H., Shapiro, A. M., Sivavec, T. M., Salvo, J., Schultz, D., Landis, R., Griffith, R., & Shoemaker, S. (1999a). The Lasagna technology for *in situ* soil remediation. 2. Large field test. *Environmental Science & Technology*, *33*(7), 1092–1099. https://doi.org/10.1021/es980414g

Ho, S. v, Athmer, C., Sheridan, P. W., Hughes, B. M., Orth, R., McKenzie, D., Brodsky, P. H., Shapiro, A. M., Thornton, R., Salvo, J., Schultz, D., Landis, R., Griffith, R., & Shoemaker, S. (1999b). The Lasagna technology for *in situ* soil remediation. 1. Small field test. *Environmental Science & Technology*, *33*(7), 1086–1091. https://doi.org/10.1021/es980332s

Ho, S. v, Sheridan, P. W., Athmer, C. J., Heitkamp, M. A., Brackin, J. M., Weber, D., & Brodsky, P. H. (1995). Integrated *in situ* soil remediation technology: the Lasagna process. *Environmental Science & Technology*, *29*(10), 2528–2534. https://pubs.acs.org/sharingguidelines

Hodges, D., Fourie, A., Reynolds, D., & Thomas, D. (2011). Development of an apparatus for pH-isolated electrokinetic *in situ* chemical oxidation. *Journal of Environmental Engineering*, *137*(9), 809–816.

Hodges, D., Fourie, A., Thomas, D., & Reynolds, D. (2013). Overcoming permanganate stalling during electromigration. *Journal of Environmental Engineering*, *139*(5), 677–684. https://doi.org/10.1061/(asce)ee.1943-7870.0000660

Huling, S. G. and Pivetz, B. E. (2007). *Engineering Issue Paper: In Situ Chemical Oxidation.*

Illangasekare, T. H., Armbruster III, E. J., & Yates, D. N. (1995a). Non-aqueous-phase fluids in heterogeneous aquifers—experimental study. *Journal of Environmental Engineering*, *121*(8), 571–579.

Illangasekare, T. H., Ramsey Jr, J. L., Jensen, K. H., & Butts, M. B. (1995b). Experimental study of movement and distribution of dense organic contaminants in heterogeneous aquifers. *Journal of Contaminant Hydrology*, *20*(1–2), 1–25.

Isosaari, P., Piskonen, R., Ojala, P., Voipio, S., Eilola, K., Lehmus, E., & Itävaara, M. (2007). Integration of electrokinetics and chemical oxidation for the remediation of creosote-contaminated clay. *Journal of Hazardous Materials*, *144*(1–2), 538–548. https://doi.org/10.1016/j.jhazmat.2006.10.068

ITRC. (2018, February). *Optimizing In Situ Remediation Performance and Injection Strategies*. Interstate Technology Regulatory Council.

ITRC. (2020). *Optimizing Injection Strategies and In situ Remediation Performance*. https://ois-isrp-1.itrcweb.org/

Jackman, S. A., Maini, G., Sharman, A. K., & Knowles, C. J. (1999). The effects of direct electric current on the viability and metabolism of acidophilic bacteria. *Enzyme and Microbial Technology*, *24*(5–6), 316–324.

Jackman, S. A., Maini, G., Sharman, A. K., Sunderland, G., & Knowles, C. J. (2001). Electrokinetic movement and biodegradation of 2,4-dichlorophenoxyacetic acid in silt soil. *Biotechnology and Bioengineering*, *74*(1), 40–48. https://doi.org/10.1002/bit.1093

Jones, E. H., Reynolds, D. A., Wood, A. L., & Thomas, D. G. (2011). Use of electrophoresis for transporting nano-iron in porous media. *Ground Water*, *49*(2), 172–183. https://doi.org/10.1111/j.1745-6584.2010.00718.x

Kovalick, W. (1995). *In situ* remediation technology: Electrokinetics. *US Environmental Protection Agency, Office of Solid Waste and Emergency Response Technology Innovation Office, Washington.*

Kueper, B. H., Abbott, W., & Farquhar, G. (1989). Experimental observations of multiphase flow in heterogeneous porous media. *Journal of Contaminant Hydrology*, *5*(1), 83–95.

Kueper, B. H. and Frind, E. O. (1991). Two-phase flow in heterogeneous porous media: 2. Model application. *Water Resources Research*, *27*(6), 1059–1070. https://doi.org/10.1029/91WR00267

Lear, G., Harbottle, M. J., van der Gast, C. J., Jackman, S. A., Knowles, C. J., Sills, G., & Thompson, I. P. (2004). The effect of electrokinetics on soil microbial communities. *Soil Biology and Biochemistry*, *36*(11), 1751–1760. https://doi.org/10.1016/j.soilbio.2004.04.032

Lee, G., Ro, H., Lee, S., & Lee, S. (2006). Electrokinetically enhanced transport of organic and inorganic phosphorus in a low permeability soil transport. *Geosciences Journal*, *10*(1), 85–89.

Lee, H.-S. and Kisay, L. (2001). Bioremediation of diesel-contaminated soil by bacterial cells transported by electrokinetics. *Journal of Microbiology and Biotechnology*, *11*(6), 1038–1045.

Leeson, A. and Stroo, H. (2011). *SERDP and ESTCP Workshop on Investment Strategies to Optimize Research and Demonstration Impacts in Support of DoD Restoration Goals.* https://serdp-estcp-storage.s3.us-gov-west-1.amazonaws.com/s3fs-public/project_documents/Investment%2BStrategies%2BWorkshop%2BReport_October%2B2011.pdf?VersionId=Yhb5E45XPhTA06.f_GidDehhy0kKFhgq

Lefevre, E., Bossa, N., Wiesner, M. R., & Gunsch, C. K. (2016). A review of the environmental implications of *in situ* remediation by nanoscale zero valent iron (nZVI): Behavior, transport and impacts on microbial communities. *Science of the Total Environment*, *565*, 889–901. https://doi.org/10.1016/j.scitotenv.2016.02.003

Lima, A. T., Hofmann, A., Reynolds, D., Ptacek, C. J., van Cappellen, P., Ottosen, L. M., Pamukcu, S., Alshawabekh, A., O'Carroll, D. M., Riis, C., Cox, E., Gent, D. B., Landis, R., Wang, J., Chowdhury, A. I. A., Secord, E. L., & Sanchez-Hachair, A. (2017). Environmental electrokinetics for a sustainable subsurface. *Chemosphere*, *181*, 122–133. https://doi.org/10.1016/j.chemosphere.2017.03.143

Lindgren, E. R., Hankins, M. G., Mattson, E. D., & Duda, P. M. (1998). *Electrokinetic demonstration at the unlined chromic acid pit.* https://digital.library.unt.edu/ark:/67531/metadc698960/m2/1/high_res_d/576168.pdf

Lizer, T. (2022, May 22). New integrated biogeochemical/electrochemical method for remediation of contaminated groundwater. *Twelfth International Conference on Remediation of Chlorinated and Recalcitrant Compounds.*

Lohner, S. T., Katzoreck, D., & Tiehm, A. (2008a). Electromigration of microbial electron acceptors and nutrients:(I) transport in synthetic media. *Journal of Environmental Science and Health Part A*, *43*(8), 913–921.

Lohner, S. T., Katzoreck, D., & Tiehm, A. (2008b). Electromigration of microbial electron acceptors and nutrients:(II) Transport in groundwater. *Journal of Environmental Science and Health Part A*, *43*(8), 922–925.

López-Vizcaíno, R., Yustres, A., León, M. J., Saez, C., Cañizares, P., Rodrigo, M. A., & Navarro, V. (2017). Multiphysics implementation of electrokinetic remediation models for natural soils and porewaters. *Electrochimica Acta*, *225*, 93–104. https://doi.org/10.1016/j.electacta.2016.12.102

Mao, X., Wang, J., Ciblak, A., Cox, E. E., Riis, C., Terkelsen, M., Gent, D. B., & Alshawabkeh, A. N. (2012). Electrokinetic-enhanced bioaugmentation for remediation of chlorinated solvents contaminated clay. *Journal of Hazardous Materials*, *213–214*, 311–317. https://doi.org/10.1016/j.jhazmat.2012.02.001

Mikkola, H., Schmale, J. Y., Wesner, W., & Petkovska, S. (2008). Laboratory pre-assays for soil remediation by electro synthesis of oxidants and their electrokinetic distribution. *Journal of*

Environmental Science and Health Part A, *43*(8), 907–912.

Mitchell, J. (1993). *Fundamentals of soil behavior*. John Wiley & Sons.

Monsanto Company. (1998). *Rapid Commercialization Initiative (RCI) Final Report for an Integrated in-situ Remediation Technology (LasagnaTM).* https://www.researchgate.net/profile/Jay-Clausen/publication/265599281_Rapid_Commercialization_Initiative_RCI_Final_Report_for_an_Integrated_In-Situ_Remediation_Technology_Lasagna/links/5414d9d60cf2788c4b35aa74/Rapid-Commercialization-Initiative-RCI-Final-Report-for-an-Integrated-In-Situ-Remediation-Technology-Lasagna.pdf

National Research Council. (2013). *Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites*. National Academies Press.

Padil, V. V. T., Wacławek, S., Černík, M., & Varma, R. S. (2018). Tree gum-based renewable materials: Sustainable applications in nanotechnology, biomedical and environmental fields. *Biotechnology Advances*, *36*(7), 1984–2016. https://doi.org/10.1016/j.biotechadv.2018.08.008

Pamukcu, S., Hannum, L., & Wittle, J. K. (2008). Delivery and activation of nano-iron by DC electric field. *Journal of Environmental Science and Health Part A*, *43*(8), 934–944.

Pamukcu, S. and Kenneth Wittle, J. (1992). Electrokinetic removal of selected heavy metals from soil. *Environmental Progress*, *11*(3), 241–250.

Phenrat, T., Saleh, N., Sirk, K., Kim, H. J., Tilton, R. D., & Lowry, G. v. (2008). Stabilization of aqueous nanoscale zerovalent iron dispersions by anionic polyelectrolytes: Adsorbed anionic polyelectrolyte layer properties and their effect on aggregation and sedimentation. *Journal of Nanoparticle Research*, *10*(5), 795–814. https://doi.org/10.1007/s11051-007-9315-6

Rabbi, M. F., Clark, B., Gale, R. J., Ozsu-Acar, E., Pardue, J., & Jackson, A. (2000). *In situ* TCE bioremediation study using electrokinetic cometabolite injection. *Waste Management*, *20*(4), 279–286.

Reddy, K. R., Darko-Kagya, K., & Cameselle, C. (2011). Electrokinetic-enhanced transport of lactate-modified nanoscale iron particles for degradation of dinitrotoluene in clayey soils. *Separation and Purification Technology*, *79*(2), 230–237. https://doi.org/10.1016/j.seppur.2011.01.033

Reynolds, D. A., Jones, E. H., Gillen, M., Yusoff, I., & Thomas, D. G. (2008). Electrokinetic migration of permanganate through low-permeability media. *Ground Water*, *46*(4), 629–637. https://doi.org/10.1111/j.1745-6584.2008.00415.x

Riis, C., Cox, E. E., Wang, J., Gent, D., Bymose, M. B., & Pade, D. M. (2023). Remediating a PCE source area in clay using electrokinetically-enhanced *in situ* bioremediation. *Groundwater Monitoring & Remediation,* 43(3), 70-78. http://doi.org/10.1111/gwmr.12592

Roach, N. and Reddy, K. R. (2006). Electrokinetic delivery of permanganate into low-permeability soils. *International Journal of Environment and Waste Management*, *1*(1), 4–19.

Sale, T, Petersen, M., and Gilbert, D. (2005). Final Report, Electrically Induced Redox Barriers for Treatment of Groundwater. https://www.clu-in.org/download/contaminantfocus/dnapl/Treatment_Technologies/CU-0112-fr-01.pdf

Schmidt, C. A. B., Barbosa, M. C., & de Almeida, M. de S. S. (2007). A laboratory feasibility study on electrokinetic injection of nutrients on an organic, tropical, clayey soil. *Journal of Hazardous Materials*, *143*(3), 655–661. https://doi.org/10.1016/j.jhazmat.2007.01.009

Schwille, F. and Pankow, J. F. (1988). *Dense chlorinated solvents in porous and fractured media - Model experiments.* Lewis Publishers. https://www.osti.gov/biblio/6419077

Semple, K. T., Doick, K. J., Jones, K. C., Burauel, P., Craven, A., & Harms, H. (2004). Peer reviewed: Defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated. *Environmental Science & Technology, 38*(12), 228A-231A.

SERDP. (2006). *Expert Panel Workshop Report: Reducing the Uncertainty of DNAPL Source Zone Remediation.* ESTCP Arlington, VA, USA.

Shi, L., Müller, S., Harms, H., & Wick, L. Y. (2008). Effect of electrokinetic transport on the vulnerability of PAH-degrading bacteria in a model aquifer. *Environmental Geochemistry and Health*, *30*(2), 177–182. https://doi.org/10.1007/s10653-008-9146-0

Soukupova, J., Zboril, R., Medrik, I., Filip, J., Safarova, K., Ledl, R., Mashlan, M., Nosek, J., & Cernik, M. (2015). Highly concentrated, reactive, and stable dispersion of zero-valent iron nanoparticles: Direct surface and site application. *Chemical Engineering Journal*, *262*, 813–822. https://doi.org/10.1016/j.cej.2014.10.024

Stroo, H. F., Leeson, A., Marqusee, J. A., Johnson, P. C., Ward, C., H., Kavanaugh, M. C., Sale, T. C., Newell, C. J., Pennel, K. D., Lebrón, C. A., &

Unger M. (2012). Chlorinated ethene source remediation: lessons learned. *Environmental Science & Technology*, 46(12), 6438-6447.

USEPA. (1988). *Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA*. https://semspub.epa.gov/work/HQ/100001529.pdf

USEPA. (2014). Engineering Paper: *In Situ* Thermal Treatment Technologies: Lessons Learned. Office of Land and Emergency Management (5102G). EPA 542-R-14-012, May 2014. www.epa.gov/superfund.

USEPA. (2020). *Superfund Remedy Report 16th Edition*. https://www.epa.gov/sites/default/files/2020-07/documents/100002509.pdf

van Cauwenberghe, L. (1997). *Electrokinetics*. Ground-Water Remediation Technology Analysis Center. http://www.gwrtac.org

van der Wal, A., Minor, M., Norde, W., Zehnder, A. J. B., & Lyklema, J. (1997). Electrokinetic potential of bacterial cells. *Langmuir*, *13*(2), 165–171. https://pubs.acs.org/sharingguidelines

Vane, L. M. and Zang, G. M. (1997). Effect of aqueous phase properties on clay particle zeta potential and electro-osmotic permeability: Implications for electro-kinetic soil remediation processes. *Journal of Hazardous Materials*, *55*(1–3), 1–22.

Vemulapalli, G. (1993). *Physical Chemistry: Solutions Manual for Physical Chemistry: Selected Exercises and Problems*. Prentice Hall International.

West, L. J. and Stewart, D. I. (1995). Effect of zeta potential on soil electrokinesis. *Geoenvironment 2000: Characterization, Containment, Remediation, and Performance in Environmental Geotechnics*, 1535–1549.

Wick, L. Y., Mattle, P. A., Wattiau, P., & Harms, H. (2004). Electrokinetic transport of PAH-degrading bacteria in model aquifers and soil. *Environmental Science & Technology*, *38*(17), 4596–4602. https://doi.org/10.1021/es0354420

Wick, L. Y., Shi, L., & Harms, H. (2007). Electro-bioremediation of hydrophobic organic soil-contaminants: A review of fundamental interactions. *Electrochimica Acta*, *52*(10), 3441–3448. https://doi.org/10.1016/j.electacta.2006.03.117

Wu, X., Alshawabkeh, A. N., Gent, D. B., Larson, S. L., & Davis, J. L. (2007). Lactate transport in soil by DC fields. *Journal of Geotechnical and Geoenvironmental Engineering*, *133*(12), 1587–1596. https://doi.org/10.1061/(ASCE)1090-0241(2007)133:12(1587)

Wu, X., Gent, D. B., Davis, J. L., & Alshawabkeh, A. N. (2012). Lactate injection by electric currents for bioremediation of tetrachloroethylene in clay. *Electrochimica Acta*, *86*, 157–163. https://doi.org/10.1016/j.electacta.2012.06.046

Xu, W., Wang, C., Liu, H., Zhang, Z., & Sun, H. (2010). A laboratory feasibility study on a new electrokinetic nutrient injection pattern and bioremediation of phenanthrene in a clayey soil. *Journal of Hazardous Materials*, *184*(1–3), 798–804. https://doi.org/10.1016/j.jhazmat.2010.08.111

Yukselen-Aksoy, Y. and Reddy, K. R. (2012). Effect of soil composition on electrokinetically enhanced persulfate oxidation of polychlorobiphenyls. *Electrochimica Acta*, *86*, 164–169. https://doi.org/10.1016/j.electacta.2012.03.049

Appendix A. Case Study #1, EK-BIO Full-Scale Remedy in Skuldelev, Denmark

A.1 Background

Following a treatability study (**Appendix D**) and a subsequent pilot test, EK-BIO was selected for full-scale implementation at the Skuldelev site in Denmark.

A.1.1 Site Contaminants, Geology and Geochemistry

The primary contaminants included PCE, TCE, and cis-1,2-dichloroethene (cDCE). The contaminant source mass was present in a unit of low-k glacial clay till with interbedded stringers and lenses of medium-grained sand from depths of 3 to 8 meters below the ground surface (m bgs). The center of contamination was located at the depths between 3 and 7 m bgs as the observed PCE concentration within the clay was the highest.

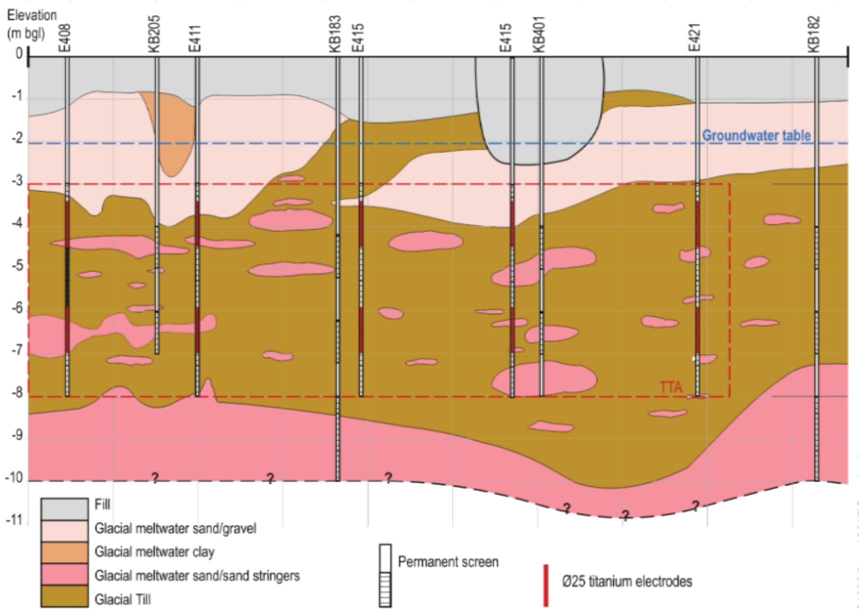


Figure A-1. Cross Section of Target Treatment Zone

Prior site characterization reported that the geochemical conditions in the source area groundwater were slightly reducing, with an average concentration of 1.7 milligrams (mg)/liter (L) dissolved oxygen (DO), 52 mg/L sulfate, 6 mg/L ferrous iron, and an average oxidation-reduction potential (ORP) of -69 millivolts (mV). The groundwater pH was relatively neutral (between 6.7 and 8.1). The site groundwater geochemistry generally suggested that bioremediation via reductive dechlorination would be a viable remedial alternative.

A.1.2 EK-BIO Pilot Test

A short-duration (4 months), small-scale pilot test was conducted at the site within the area identified as a PCE residual DNAPL source area. The pilot test consisted of six electrode wells (three cathodes and three anodes) and three amendment supply wells (each located generally in between a paired cathode and anode) to address a target pilot test zone of approximately 3 by 2 m and between 3 and 8 m bgs (**Figure A-1**). The electrode well spacing was 1 m between electrodes of the same polarity and 3 m between each paired anode and cathode. Lactate solution (electron donor source for microbial reductive dechlorination) was added to the electrode wells and supply wells for a period of 65 days. The pilot test area was bioaugmented one time with a dehalorespiring bacterial culture (KB-1) at the start of the pilot test. The bioaugmentation culture was injected directly into the electrode and amendment wells.

The results of the pilot test confirmed lactate migration at a rate of 2.5 to 5.0 cm/day, PCE dechlorination to ethene, and increases in the populations (gene copies/L) of *Dhc* and vinyl chloride reductase genes, *vcrA*, within the pilot test area. The results of the pilot test provided a basis for the full-scale EK-BIO remedy implementation at the site.

A.1.3 Target Area and Remediation Goals

The full-scale EK-BIO remedy targeted an area of approximately 130 m^2 (approximately 10 m by 12 m) at a depth of 3 to 8 m bgs, comprising a total volume of 665 m^3. The initial PCE mass within the target area was estimated to be 290 kg based on soil and groundwater data. Pre-remedy characterization showed the maximum concentrations of PCE and TCE in groundwater within the target area were 510 and 38 mg/L, respectively, while the maximum soil concentrations were 21,000 and 79 mg/kg, respectively. The remediation goal prescribed for the EK-BIO remedy was 10 mg/kg PCE (average) in soil.

A.2 Scope and Approach for Full-Scale EK-BIO Remedy

A.2.1. EK-BIO Well Layout and Operation

The full-scale EK-BIO system included a network of 15 electrode wells and 10 amendment supply wells. **Figure A-2** shows the well network in half (Treatment Area B) of the overall remediation zone. The spacing between electrode wells was approximately 4.5 m selected partially based on the lactate transport rate (5 cm/day) observed in the pilot test. The electrode well placement was designed to allow for maximum flexibility regarding electrode well configuration and optimization of the applied electric field. The overall remediation target area was divided into two subareas, which were treated in alternating stages, each stage of approximately 90 days of EK operation. The alternating-stage approach was designed to transport sufficient lactate during an active stage to facilitate continued degradation during the subsequent passive stage. Another advantage of the alternating stage approach was that the electric field direction was rotated by 90 degrees for each new active/passive operation cycle to optimize the lactate distribution.

Each electrode well was equipped with two 1-m long mixed-metal-oxide (IrO_2/Ta_2O_5)-coated titanium electrodes vertically separated within the well. Each electrode well functioned either as an anode well or a cathode well in an individual stage, depending on how the electrodes were connected at the DC power supply unit. The overall EK system was operated to achieve a constant target current supplying an average electrical current of 1.7 to 3.3 A to each electrode, resulting in current densities within the target area generally between

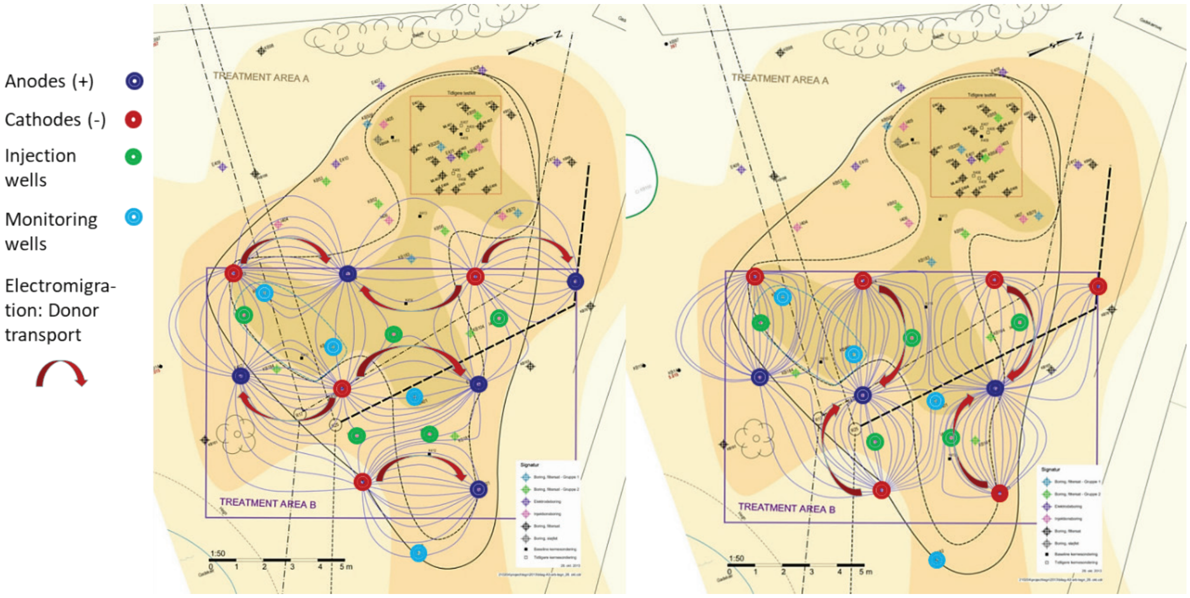


Figure A-2. EK-BIO Well Network and Electric Fields

Two electric field directions are shown, each was applied during a different stage of EK operation.

0.09 and 0.11 A/m^2. The applied voltage varied during the operation as the subsurface became more electrically conductive over time due to the supply of ionic remediation amendments. An initial voltage of 197 V decreased to a steady 50 V after two active/passive cycles and remained relatively steady through the end of remediation operation.

Lactate was used as an electron donor and supplied to all electrode and supply wells during each active operation stage. A total of 5,300 L of sodium lactate (60% w/w solution) was supplied to the target area over 2 years of active operation. Bioaugmentation using KB-1 culture (SiREM, Guelph, Ontario) was performed during the first active stage in each area. The remediation operation commenced in December 2012 and ended in August 2015.

Operation monitoring included current measurements of individual electrodes, voltage gradient measurements between select monitoring wells and cathode wells, and field measurements (conductivity, ORP, DO, pH, and temperature) at 30 monitoring wells. Voltage gradient monitoring and current measurements during operation showed a relatively consistent EK operation, with voltage gradients generally between 0.15 and 0.18 V/cm and current densities between 0.09 and 0.11 A/m^2. Control of pH in the electrode wells and within the target area was achieved. The energy consumption for operating the EK system varied between 4,300 and 6,300 kW-hr for each stage depending on duration and target current settings in individual stages. The estimated total energy consumption for the EK operation was 43,000 kW-hr, at an estimated total energy cost of US$15,000.

A.3 Remedy Performance

Groundwater samples were collected from 22 performance monitoring wells four times during each 90-day active operation stage. In addition, post-remedy monitoring was conducted 4 and 6 months after the end of the final remedy operation stage.

A.3.1 Electron Donor Amendment Distribution

Effective distribution of the electron donor throughout the target area was achieved, as evidenced by increases in non-volatile organic carbon (NVOC) (analogous to total organic carbon; TOC) in all monitoring wells located within the electric field (**Figure A-3**). NVOC concentrations at each monitoring well were several orders of magnitude higher than baseline in six of the nine monitoring wells after Stage 2. Maximum NVOC concentration detections exceeded 600 mg/L in several wells. The presence of elevated NVOC was relatively consistent in the target area over two cycles of active EK. The data indicated that the EK system operation effectively distributed the electron donor at concentrations that could promote and sustain the dechlorination of PCE.

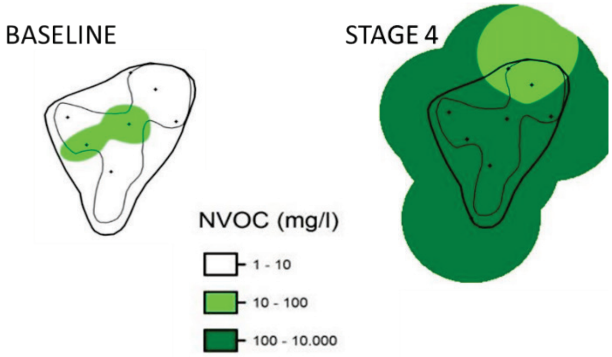


Figure A-3. Electron Donor in Target Area

A.3.2 Microbial Dechlorination Enhancement

Baseline *vcrA* data showed relatively high baseline *vcrA* levels (>1E+06 gene copies per liter) in five of the nine monitoring wells (selected as representative wells for monitoring data discussion purposes), but non-detect (below 3E+03 to 1E+04 gene copies per liter) in two of the nine wells, indicating some variability in existing *Dhc* and *vcrA* in the target area. It is possible that the baseline *vcrA* levels in several of the monitoring wells were affected (elevated) by the prior pilot test, which included bioaugmentation. Despite the relatively high baseline levels, *vcrA* gene copy counts further increased in all nine monitoring wells, from a baseline average of 7E+07 to an average of 2E+08 gene copies per liter at the end of active EK operation. Interestingly, *vcrA* counts continued to increase in multiple wells in the 6 months following cessation of active EK to an average of 3E+09 gene copies per liter, indicating that dechlorination likely sustained months after cessation of active EK given the electron donor that had been delivered by the EK-BIO remedy.

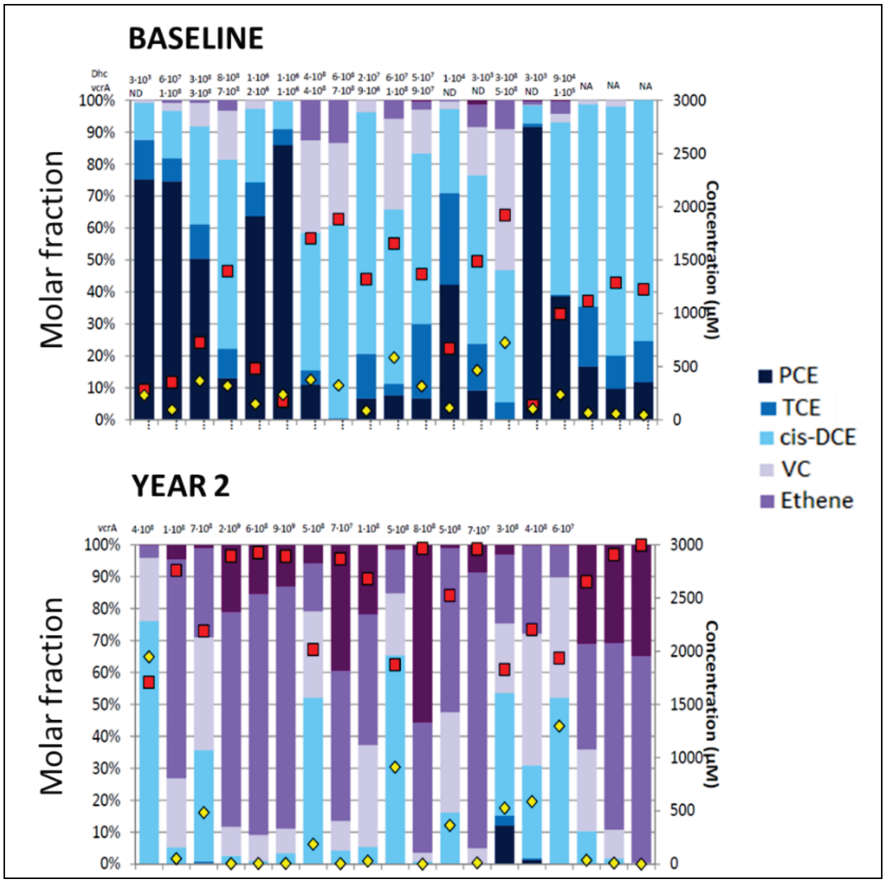


Figure A-4. Groundwater Monitoring

Red square: degree of dechlorination (%);
Yellow diamond: sum of PCE + TCE + cDCE + vinyl chloride (VC) + ethene + ethane.

At the outset of the EK application, all nine monitoring wells contained PCE at concentrations ranging from 1 to 34 mg/L (average baseline PCE of 12 mg/L), and at each well, the sum of PCE + TCE + cDCE represented upwards of 60% of the (chlorinated ethenes + ethene) mass in the groundwater (**Figure A-4**). At each monitoring well, substantial PCE dechlorination was observed within the first 180 days, with PCE below detection in six of the nine wells by the end of Stage 2 operation. Low levels of ethene and/or ethane were detected in baseline groundwater samples in three of the nine monitoring wells, possibly a remnant of prior pilot test activities. By the end of Stage 2 (180 days), ethene and/or ethane were detected in eight of the nine monitoring wells, and ethene concentrations at these wells continued to increase through the end of active EK and even during the 6-month period following the cessation of active EK.

The average degree of dechlorination, calculated using the equation below and molar concentrations of individual compounds, prior to active EK was about 32%. The degree of dechlorination increased in all nine monitoring wells averaging 81% at the end of active EK operation, and further increased to 87% 6 months after cessation of active EK.

$$\begin{aligned} &\mathit{Degree\ of\ Dechlorination}\ (\%) \\ &= \frac{TCE + 2 \cdot cDCE + 3 \cdot VC + 4 \cdot Ethene + 4 \cdot Ethane}{4 \cdot (PCE + TCE + cDCE + VC + Ethene + Ethane)} \cdot 100 \end{aligned}$$

Monitoring well KB182 is located in the downgradient periphery of the target treatment area and represents groundwater flowing from the remediation area. At the start of the EK-BIO application, the chlorinated volatile organic compound (CVOC) composition at this well consisted of a mixture of PCE, TCE, and cDCE, with a total concentration of ~65 micromoles (µM) (~7,500 µg/L). At the end of the EK-BIO application, the total concentration of PCE, TCE, and cDCE at this well had decreased to less than 4.2 µM (280 µg/L), and ethene and ethane represented 94% of the CVOC + ethene mass at this location. The monitoring data at this downgradient well provided an indication of the effectiveness of the source area remediation in substantially reducing the flux of CVOCs from the source area, with little to no rebound 6 months after cessation of active EK.

A.3.3. Contaminant Mass Reduction

Soil sampling was conducted at four clusters during baseline, post-Stage 4, and 6 months after cessation of EK operation. The baseline soil CVOCs consisted primarily of PCE, TCE, and cDCE. At the end of Stage 4 and 6 months following EK operation, the soil cores from all cluster locations and depths showed substantial dechlorination. Supporting this trend, the degree of dechlorination increased at almost every soil cluster and depth from baseline to the final sampling event. Based on the soil data collected 6 months after cessation of active EK treatment, a 98.75% reduction in PCE equivalent (PCE and its dechlorination products) soil concentration was observed in the target treatment area. Most importantly, the average soil PCE concentration across the target area declined from the baseline of approximately 533 mg/kg to 3.8 mg/kg following treatment, thus meeting the prescribed remediation goal of <10 mg/kg average soil PCE concentration.

This EK-BIO remedy implementation successfully remediated a PCE residual DNAPL source area. The reduction of source mass and subsequently the contaminant mass flux to the downgradient area supported the transition of the groundwater remedy to a monitored natural attenuation-based approach.

Appendix B. Case Study #2, EK-BIO Pilot Demonstration at Naval Air Station Jacksonville, Jacksonville, Florida

B.1 Background

The DoD Environmental Security Technology Certification Program (ESTCP) funded a pilot-scale technology demonstration of electrokinetic-enhanced delivery for *in situ* bioremediation (EK-BIO) at Naval Air Station (NAS) Jacksonville in Jacksonville, Florida. The selected target treatment area for the demonstration is located within the Operable Unit 3 (OU3) at NAS Jacksonville.

Part of the former Building 106 in OU3 was the station's drycleaning facility where occasional PCE leaks and spills occurred, resulting in contamination of the shallow aquifer (5 to 16.5 ft bgs). A low-permeability (low-k) clay layer (approximately 16.5 to 24 ft bgs) was present beneath the shallow sand aquifer. Underneath the clay unit is another aquifer consisting of fine sand and silty materials.

Chlorinated volatile organic compounds (CVOCs), such as PCE, TCE, cDCE, and vinyl chloride (VC) were detected in both shallow (CVOCs concentration > 10,000 µg/L) and the underlying formations (CVOCs concentration from 1,000 to 10,000 µg/L). The vertical distribution of CVOCs in soil and groundwater at depths above, within, and below the clay unit depicts a classic PCE diffusion profile, with PCE penetration into approximately the upper 5 ft of the clay unit (**Figure B-1**). Pore-water PCE concentrations detected at various depths across the clay unit ranged from 15,000 to 40,000 µg/L indicating the presence of contaminant source mass in the clay materials.

B.2 Field Demonstration and Data Collection

A preliminary characterization of aquifer materials from the target area was performed to support the design of the EK system. A soil core was obtained from the vicinity of the target area for mineralogical analysis of the soil. A bench-scale EK column test with a conservative bromide tracer was conducted to demonstrate the bromide (an anion) transport rate in the site soil was at least 3.3 cm/day.

The target area for the EK-BIO demonstration was approximately 40 ft by 40 ft. A network of nine electrode wells and eight supply wells was installed to deliver the remediation amendments (**Figure B-2**). In addition, 11 monitoring wells (7 within the target area) were used to monitor the progress of remediation. Monitoring wells were specifically screened within the clay unit to allow assessments of the conditions in that low-k unit.

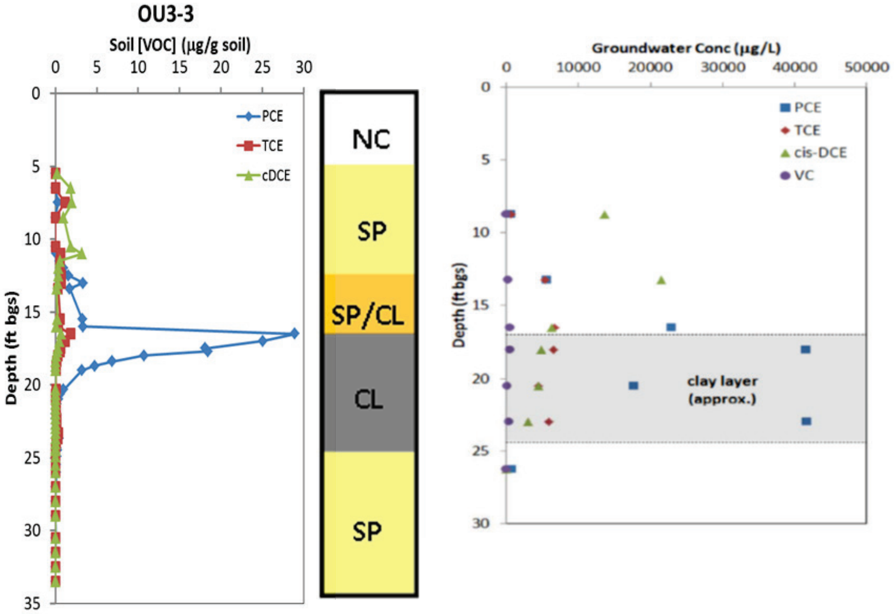


Figure B-1. Soil and Groundwater CVOC Concentration Profiles

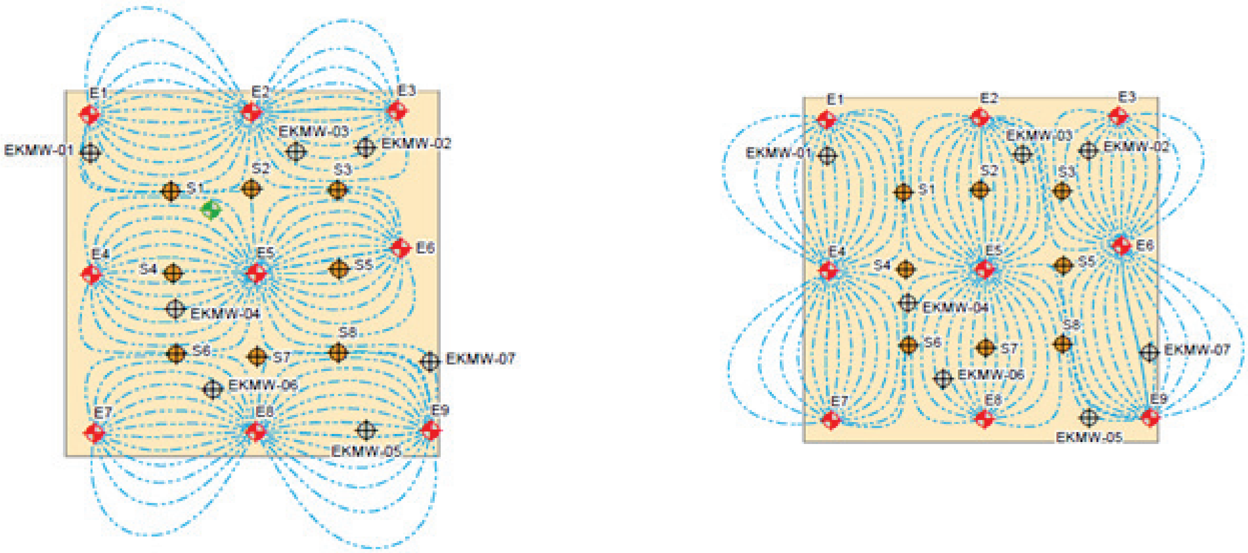


Figure B-2. Well Network for EK-BIO Demonstration

E-series: electrode wells. S-series: supply wells. EKMW-series: monitoring wells. Blue dashed lines: conceptual electrified fields between paired cathode-anode. Two different electric field orientations established in two separate operation stages.

Electrode wells, supply wells, and monitoring wells were all screened across the clay unit at depths between 19 and 23 ft bgs. The EK system was powered by a DC power supply unit that outputs up to 250 V and up to 24 A. During a given stage of operation, six of the nine electrode wells were used as cathodes and the other three as anodes. Each electrode was a titanium rod (¾-inch diameter; 4-ft long) with mixed-metal-oxide coating and connected by an electrical cable from the electrode well to the DC power unit. The amendment solution (lactate) was supplied to the wells in short-duration pulses using feed pumps.

The overall demonstration operation consisted of several phases: (1) system setup and initial field conditioning (2 months); (2) Stage 1 EK operation (5 months); (3) post-Stage 1 incubation (no electricity; 6 months); (4) Stage 2 EK operation (6 months); and (5) post-Stage 2 incubation (no electricity; 3 months). As illustrated in **Figure B-2**, individual electrode wells were used as cathodes or anodes in Stage 1 and Stage 2, resulting in electric fields of different orientations in different stages of operation.

The demonstration included bioaugmentation of the target area with dechlorination microbial culture containing *Dhc*. After 75 days of system operation during Stage 1, the system was stopped to add KB-1 culture to each supply well and electrode well to complete bioaugmentation.

The two active EK operation stages together delivered a total of 555 kg of lactate via 2,548 gallons of solution to the target area (or 23 kg lactate in 112 gallons to each supply well and 41 kg lactate in 184 gallons to each electrode well).

B.3 Data Evaluation and Discussion

The EK-BIO system operation monitoring results are shown in **Figure B-3** for voltage, current, and power usage during the two stages of operation.

The power supply unit's voltage output was generally steady between 18V and 28V during Stage 1, and 12V and 20V during Stage 2. The cumulative power consumption was calculated as 985 kW-hr for Stage 1 and 548 kW-hr for Stage 2. The overall electrical power consumption throughout the demonstration was approximately 1,585 kW-hr, which is equivalent to operating two 100-W lightbulbs over the same duration, reflecting the low-energy demand of the EK-BIO approach.

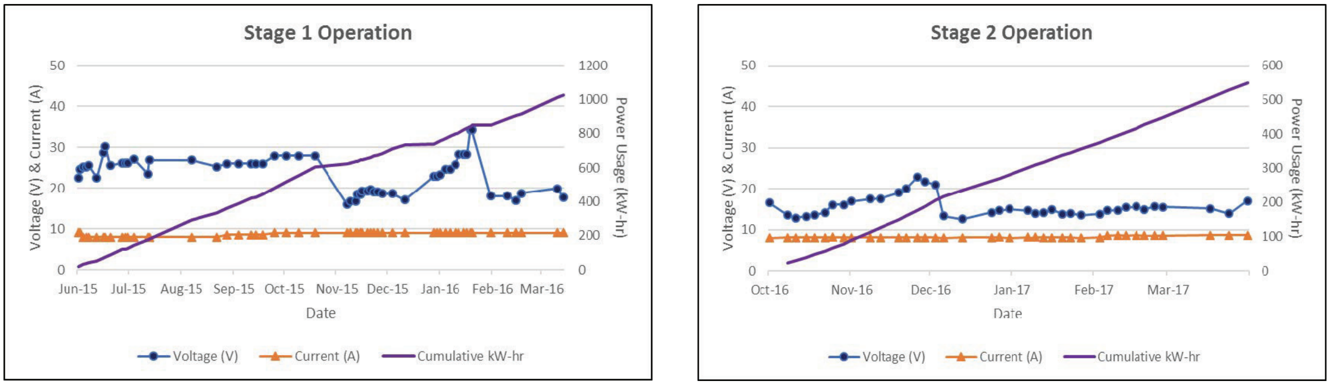


Figure B-3. EK-BIO System Operation Monitoring

B.3.1 Amendment Delivery

Groundwater TOC and volatile fatty acid (VFA) monitoring results provided an assessment of amendment distribution across the target area, particularly in the clay units within the target area. While lactate was provided as the bioremediation amendment, it was expected that lactate would biodegrade quickly when it was transported in the subsurface. Therefore, total VFAs were considered as an appropriate indicator of amendment distribution. The groundwater TOC and VFA monitoring results are summarized in **Table B-1**.

The data showed substantial increases (generally >8×) in TOC and VFA concentrations across the target area compared to the low levels that remained at the two monitoring wells (EKMW-09 and -10) located outside the target area.

B.3.2 Contaminant Degradation

The CVOC transformation and concentration change monitoring results and the microbial population monitoring results for all monitoring wells are shown in **Figure B-4**. The five sampling events as shown correspond to the five milestones: (1) baseline event in October 2014; (2) end of Stage 1 EK operation in March 2016; (3) end of post-Stage 1 incubation in September 2016; (4) end of Stage 2 EK operation in March 2017; and (5) end of post-Stage 2 incubation in June 2017.

Two monitoring wells, EKMW-09 and -10, were located upgradient and downgradient outside of the target area, respectively. At EKMW-09, throughout

Table B-1. Groundwater TOC and VFA Summary (mg/L; baseline vs. maximum during Stage1 or Stage 2)

	Well ID	TOC (baseline)	TOC (max)	VFA* (baseline)	VFA* (max)
Within Target Area#	EKMW-01	2.5	20.1	3.2	60.7
	EKMW-02	2.5	36.2	1.6	141
	EKMW-03	2.5	57.9	1.2	233
	EKMW-04	3.6	6.70	1.9	18.3
	EKMW-05	1.7	15.9	1.8	6.6
	EKMW-07	6.8	57.0	2.2	204.7
Outside Target Area	EKMW-09	1.6	1.90	2.3	1.4
	EKMW-10	1.9	10.1	2.1	1.4

One monitoring well (EKMW-06) was determined to have blockage and not included in the monitoring program.
*VFA = total of lactate, acetate, propionate, formate, butyrate, and pyruvate....

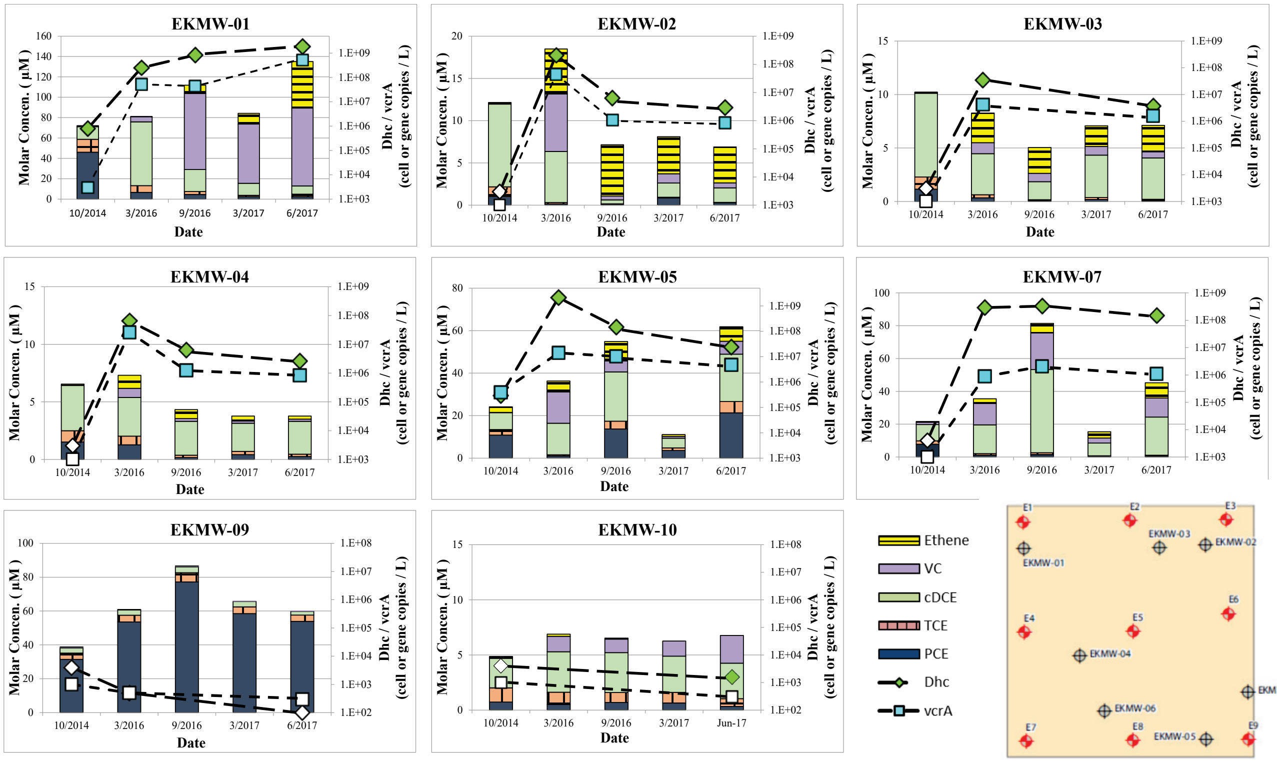


Figure B-4. Groundwater Monitoring of CVOCs and Biomarkers
EKMW-09 and -10 are located outside the target area.

the demonstration, the PCE concentration remained above the baseline with no apparent degradation or detectable biomarkers (*Dhc* and *vcrA*). The monitoring data of a downgradient well, EKMW-10, did not show significant decreases in PCE concentration or increases in degradation intermediates. Overall, the EKMW-10 monitoring results appeared to suggest a slight influence from the operation in the target area.

In contrast to the data from the two background monitoring wells, the CVOC concentrations and compositions (i.e., the relative presence of PCE versus dechlorination daughter products and end-product ethene), as well as the detections of two specific biomarkers at the monitoring wells within the target area, collectively indicated apparent microbial dechlorination activities. Decreases of PCE contractions observed at these monitoring wells were generally between 70% and 95% from the baseline levels, coupled with increases of ethene generally greater than 10-fold from the baselines. Every monitoring well within the target area also showed significant increases (several orders of magnitude) of *Dhc* and *vcrA*. It should be noted that all the monitoring wells were screened only in the clay unit. These data indicated that biodegradation of target CVOCs actually occurred within the low-k materials in the target area.

B.4 Performance and Cost Assessments

The overall performance monitoring results indicated apparent microbial growth and reductive dechlorination activities within the low-k clay unit. The overall PCE mass reduction during the demonstration was estimated to be more than 60% in the clay layer with the detection of ethene indicating the complete dichlorination of PCE to ethene.

The project cost tracking reported that the overall field demonstration and system operations and maintenance (excluding field sampling, laboratory analyses, and reporting) was approximately $405,000. Based on the demonstration project, the project team identified the major cost drivers for EK-BIO, including target treatment zone and contaminant mass, utilities and infrastructure availability or interference, and site geochemistry. These cost drivers are the common cost drivers for the implementation of most other *in situ* remediation technologies.

The project team conducted a cost comparison between EK-BIO, conventional direct-injection bioremediation, and electrical resistance heating (ERH) for a generic CVOC source area residing in low-k materials. The cost analysis was conducted as a high-level (feasibility study) cost estimate exercise. The analysis suggested that EK-BIO may potentially be more cost favorable than ERH and comparable to direct-injection (multiple rounds) bioremediation, assuming direct injection is even feasible in a low-k environment.

Appendix C. Case Study #3, EK-ISCO Pilot Test at Cristex Drum Superfund Site, Oxford, North Carolina

C.1 Background

The U.S. EPA issued a record of decision (ROD) in September 2017 for the Cristex Drum Superfund Site in Oxford, North Carolina. The site is a former textile plant with a former drum storage and cleaning pad where past practices resulted in soil and groundwater contamination. The remedial investigation (RI) identified chlorinated volatile organic compounds (CVOCs) as the primary contaminants, with tetrachloroethene (PCE) as the most prevalent contaminant.

The site geology is composed of surficial fill material and natural deposits to approximately 20 ft bgs. The fill material generally consists of clayey sand and is underlain by saprolite extending to a depth of approximately 70 ft bgs. The saprolite consists primarily of fine sand and silt containing variable amounts of clay representing a complex heterogeneous matrix. The saprolite is underlain by a transition zone generally consisting of coarser sand and weathered rock fragments. This transition zone represents a relatively high flux hydrogeologic unit underlain by a competent bedrock.

The RI identified a PCE source area adjacent to the former Cristex building. A dissolved plume of CVOC has extended vertically from the saprolite into the underlying transition zone and fractured bedrock. The remedial strategy for the site, which utilizes an adaptive management approach, includes: (1) aggressive remediation of source contamination (e.g., soil and groundwater with high concentrations of contaminants or DNAPL); and (2) phased active remediation of groundwater in the greater dilute plume. The saturated source zone (SSZ) was identified as an approximately 70 ft-thick zone (generally from 20 to 90 ft bgs) of saturated materials within the saprolite and transition zones above the bedrock. The 2017 ROD selected EK-ISCO, potentially to be coupled with biobarriers, as a remedy for the SSZ.

An EK-ISCO treatability study using site-specific saprolite materials was completed to evaluate the feasibility of applying this technology. The site-specific natural oxidant demand (NOD) for persulfate (unactivated) and permanganate were comparable and relatively low (28-day NOD of 1.15 to 3.73 g oxidant per kg soil), supporting the selection of an ISCO-based remediation approach. An EK column test was also conducted with persulfate to evaluate the EK transport of an anionic oxidant through the site's aquifer solids. The bench test results confirmed the EK transport of the anionic oxidant, at approximately 2.5 to 3.3 ft per month, through saprolite materials and the feasibility of an EK-ISCO approach for the site.

C.2 Pilot Test Scope and Data Collection

The objectives of the EK-ISCO pilot test were to:

- Evaluate the technology deployment (e.g., equipment requirements) for distributing the selected oxidant (permanganate, MnO_4^-) within the target zone, but not the full extent of CVOC treatment because the contaminant mass within the test area may be at a level that requires a significantly extended pilot test duration
- Evaluate potential changes in geochemistry (e.g., pH, ORP) within the pilot test area under EK operation conditions
- Evaluate engineering parameters including oxidant transport/supply rate, injection well spacing, and electrical current and voltage needed, to support the design of a full-scale EK-ISCO remedy at the site.

The EK-ISCO pilot test area was in the vicinity of an existing monitoring well (MW-3I) located near the former drum storage pad (**Figure C-1**). The pilot test area was approximately 40 ft^2. The previously reported PCE concentrations in the area have ranged from 730 to 2,400 µg/L in the depth interval of approximately 20 to 50 ft bgs targeted by the pilot test. The water table in the pilot test area was at approximately 20 ft bgs.

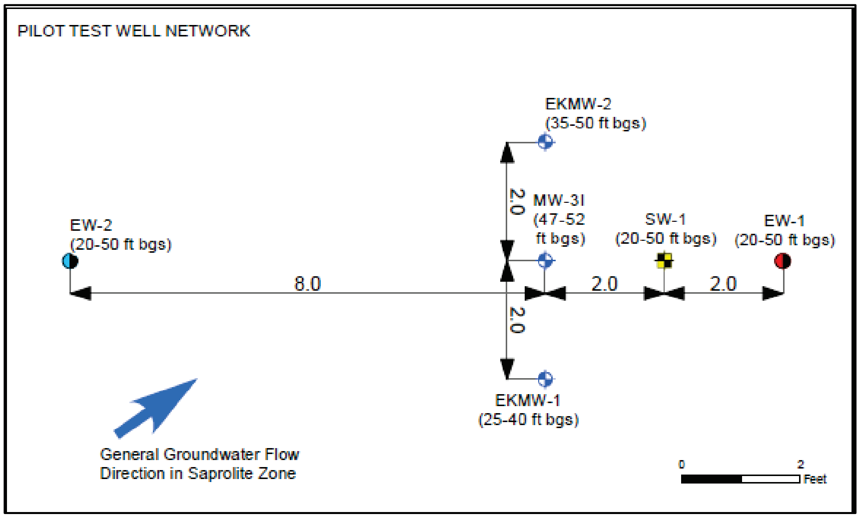


Figure C-1. Pilot Test Well Network

The pilot test well network included two electrode wells (EW-1 and -2), three monitoring wells, and a supply well (SW-1). The two electrode wells and the supply well were constructed as 4-inch diameter PVC wells screened within the saprolite unit. The three monitoring wells were screened at various depths within the saprolite unit.

A direct current (DC) power supply unit was employed to power the EK pilot test system. Two 2-ft long titanium-based electrodes were suspended in each electrode well, one at 25 ft bgs and the other at 40 ft bgs. The sodium permanganate solution (approximately 80.1 g $NaMnO_4$ per liter) was added to the supply well and the pH buffer solution (sodium bicarbonate) was added into the electrode wells, all as short-duration pulses controlled by a timer.

A baseline groundwater sampling event was conducted after the installation of pilot test wells and before the pilot test system operation. Subsequently, the pilot test system was operated for 57 days between February and April 2020. During the pilot test, the system operational parameters (voltage, current, power consumption, injection volume, etc.) were monitored and two groundwater monitoring events were conducted. Following the completion of the 57-day EK operation, a post-test sampling event was performed to complete the pilot test monitoring program.

C.3 Data Evaluation and Discussion

During the pilot test, the DC power unit was set to supply constant current to the electrodes, and the associated voltage requirement varied, corresponding to the overall electrical conductance changes in the subsurface. The supplied electric currents were between 0.7 and 0.9 A to each electrode with the observed required voltage between 120 and 160 V (**Figure C-2A**). The electrical current readings at each wellhead for EW-1 and EW-2 showed the current was relatively stable (**Figure C-2B**). No apparent loss of current from the power supply unit to the electrodes was observed in the electrode wells, confirming the overall stability of the system operation throughout the pilot test duration.

Over the 57-day test, a total of 535 gallons of sodium permanganate solution (~80.1 g $NaMnO_4$/L) was added to the supply well (SW-1). The overall quantity of permanganate added to SW-1 was approximately 136.5 kg or 300 lbs as MnO_4^-. The total volume of $NaMnO_4$ solution supplied was equivalent to the pore volume within an area of approximately 1.47 ft radius surrounding SW-1, assuming a 30-ft depth interval and 35% total porosity. It is noticed that the distances between SW-1 and monitoring wells are 2 to 2.8 ft, and the general direction of groundwater flow in the saprolite within the pilot test

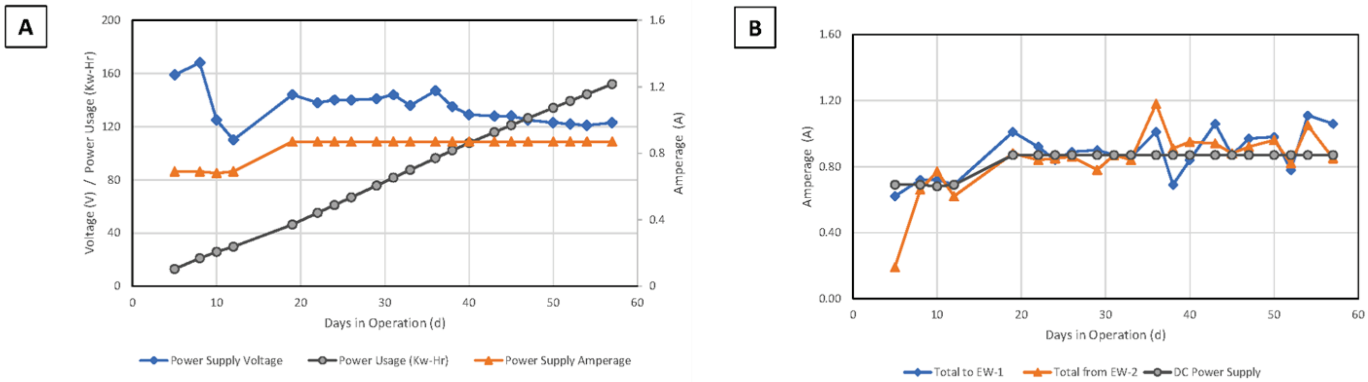


Figure C-2. EK System Operation Monitoring

area is northeast while the monitoring wells are located to the west (upgradient) of SW-1. The rate of supplying 535 gallons of $NaMnO_4$ solution to SW-1 over the 57-day operation was equivalent to 0.0065 gallons per minute (gpm). At such a low volumetric amendment supply rate and with the considerations of soil-pore volume and groundwater flow direction in the pilot test area, it is expected that EK transport would be the primary mechanism for the appearance of permanganate at performance monitoring wells.

Additionally, approximately 212 kg (467 lbs) of sodium bicarbonate was supplied to the electrode wells in the form of sodium bicarbonate buffer solution (1,530 gallons in volume). The pH values measured in the monitoring wells were relatively stable (between 6.3 and 6.9) throughout the pilot test.

With permanganate being supplied into the subsurface, groundwater ORP in the pilot test area is expected to increase. The data in **Figure C-3** show groundwater ORP at the three pilot test monitoring wells clearly increased from the baseline level (between -145.1 and 97.8 mV) to the post-test event (between 634 and 727 mV).

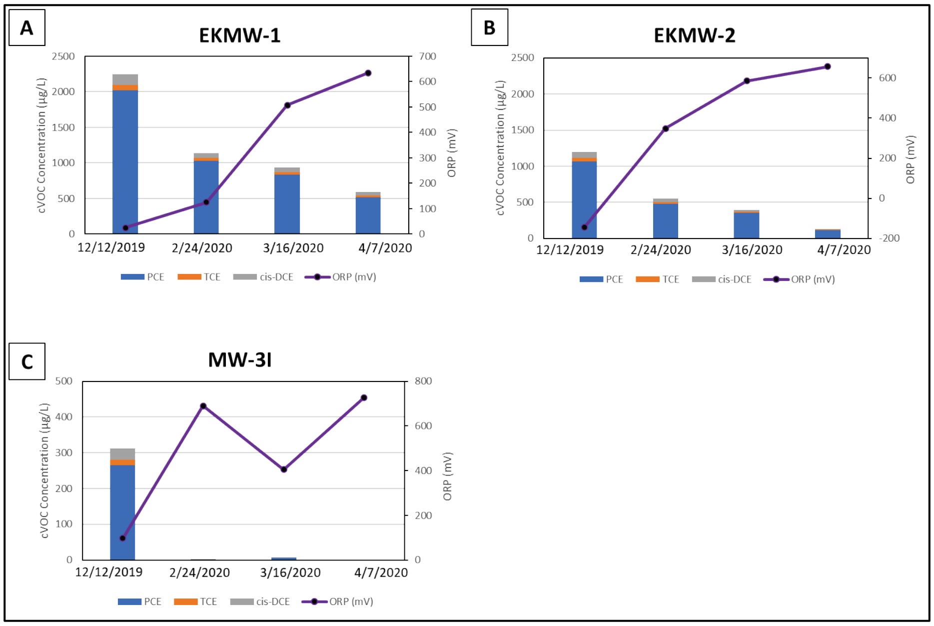


Figure C-3. Pilot Test Groundwater Monitoring

As presented in **Figure C-3**, the CVOC concentrations (PCE, TCE, and cDCE) at the three pilot test monitoring wells clearly decreased while the ORP increased. The concurrent CVOC concentration decreases and ORP increases provided evidence of the effect of permanganate being transported from the supply well (SW-1) towards the monitoring wells and the oxidation of CVOCs by the transported permanganate during the pilot test.

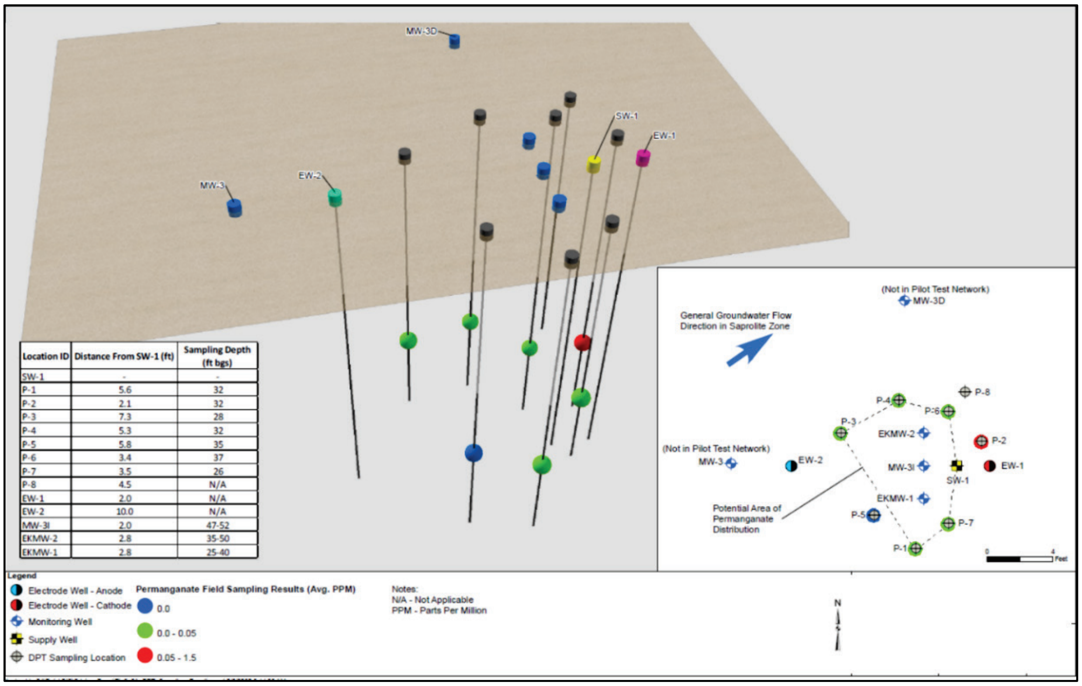
Detection of permanganate in the groundwater at a monitoring well would indicate the presence of residual permanganate still available to react with contaminants in the vicinity. The estimated permanganate transport rate was 1.5 and

2.3 cm/day, based on the detection of permanganate in the EKMW-1 and EKMW-2 wells on Days 58 and 36, respectively. However, the observed changes in groundwater ORP and CVOC concentrations suggest that oxidation treatment of CVOCs likely already occurred in the vicinity of EKMW-1 and EKMW-2 as early as Day 15 or Day 36. When factoring in the observed changes in groundwater ORP and CVOC concentrations and the potential volumetric displacement of the amendment solution added to the subsurface, the net (effective) EK transport rate for permanganate is estimated to be at 1.4 cm/day to 4.2 cm/day (approximately 1.4 to 4.1 ft per month), generally within the range estimated by the treatability test.

The total permanganate supplied (136.5 kg) could theoretically satisfy the soil NOD within an area of 25.4 to 36 ft^2 for the 30-foot injection interval with assumed 35% porosity. Given the distance from SW-1 to EKMW-1 and EKMW-2 at approximately 2.8 ft, a radial area centered at SW-1 and encompassing EKMW-1 and EKMW-2 would be approximately 24.6 ft^2. The detection of available permanganate at these monitoring wells was consistent with a potential treatment zone anticipated based on stoichiometric oxidant demand. While the observed CVOC concentration decrease was 74% to 90%, with the residual permanganate still observed in the monitoring wells, additional treatment of CVOC after the pilot test cessation likely continued.

The post-test sampling also included discrete-point sampling using direct push technology to confirm the transport of permanganate within the target zone (**Figure C-4**). The sampling results confirmed permanganate distribution laterally within the pilot test area and vertically between 26 and 37 ft bgs. The potential area of EK-facilitated permanganate distribution was estimated to be approximately 38.4 to 41.3 ft^2.

In summary, the pilot test results showed that EK-ISCO effectively distributed permanganate through the site saprolite materials at the quantity that met the oxidant demand and treated CVOCs. The pilot test also demonstrated the potential of scaling up the technology to a full-scale remedy and supported the subsequent remedial design.



Location ID	Distance From SW-1 (ft)	Sampling Depth (ft bgs)
SW-1	-	-
P-1	5.6	32
P-2	2.1	32
P-3	7.3	28
P-4	5.3	32
P-5	5.8	35
P-6	3.4	37
P-7	3.5	26
P-8	4.5	N/A
EW-1	2.0	N/A
EW-2	10.0	N/A
MW-3I	2.0	47-52
EKMW-2	2.8	35-50
EKMW-1	2.8	25-40

Notes:
N/A - Not Applicable
PPM - Parts Per Million

Figure C-4. Post-test Groundwater Monitoring

Appendix D. Case Study #4, EK-BIO Treatability Study for a PCE Source in a Low-Permeability Formation

D.1 Background

This bench-scale treatability study was designed to evaluate the potential application of EK-BIO to remediate a source area at a former industrial facility site in Skuldelev, Denmark, where past releases of tetrachloroethene (PCE) have impacted the subsurface. The site geology generally consists of topsoil and sand, overlying a thick sequence of clay till containing frequent, discontinuous, lenses and stringers of sand. Prior site characterization identified presences of localized PCE dense non-aqueous phase liquid (DNAPL) in the clay till formation.

Given the challenging geology and contaminant distributions, EK-BIO was considered as a remedial alternative for PCE source area remediation. The objective of the bench-scale treatability study was to evaluate the feasibility of applying EK to transport and distribute bioremediation amendments and, thus, facilitate and enhance microbial reductive dechlorination activities within site-specific low-permeability (low-k) materials.

D.1.1 Site Contaminants, Geology, and Geochemistry

The primary contaminants included PCE, trichloroethene (TCE), and cis-1,2-dichloroethene (cDCE). The contaminant source mass was present in a unit of low-k glacial clay till with interbedded stringers and lenses of medium-grained sand from depths of 3 to 8 meters below ground surface (m bgs). The contaminant distribution profile along a cross-section of the target source remediation area is shown in **Figure D-1**. The center of contamination was located at depths between 3 and 7 m bgs as the observed PCE concentration within the clay was the highest.

Prior site characterization reported that the geochemical conditions in the source area groundwater were slightly reducing, with an average concentration of 1.7 milligrams (mg)/liter (L) dissolved oxygen (DO), 52 mg/L sulfate, 6 mg/L ferrous iron, and an average oxidation-reduction potential (ORP) of -69 millivolts (mV). The groundwater pH was relatively neutral (between 6.7 and 8.1). The site groundwater geochemistry generally suggested that

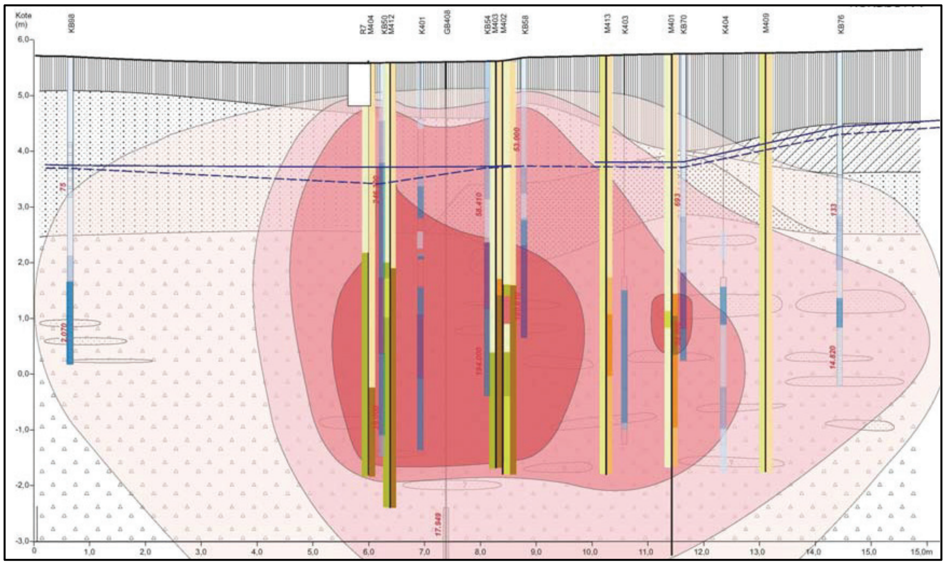


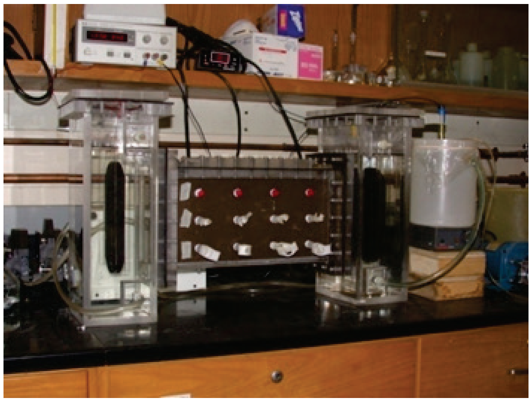
Figure D-1. Cross-Section of Contaminant Distribution in Target Source Area bioremediation via reductive dechlorination would be a viable remedial alternative.

D.2 Laboratory Test and Data Collection

A bench-scale treatability test was conducted to evaluate the feasibility of employing EK processes for promoting and enhancing reductive dichlorination of PCE by *Dehalococcoides* (*Dhc*) in site-specific low-k glacial clay materials. A commercial microbial culture (KB-1) was the source of *Dhc* for its ability to complete PCE dechlorination to the end-product, ethene. Using clayey soil collected from the target remediation area, the treatability test evaluated the potential migration and biodegradation activities of *Dhc* under EK conditions, the electrical conductivity of the site soil, and the EK delivery rate of lactate (as electron donor).

The EK acrylic-made reactors consisted of a central soil cell and two electrode compartments (**Figure D-2**).

The overall test reactor was airtight. The central rectangular soil cell was 15 cm (height) by 40 cm (length) by 5 cm (width) and packed with site-specific soil samples. A sand boring (1 cm in diameter and approximately 12 cm in depth) within the packed soil was installed in the center of the soil cell to simulate a supply well configuration for field application. Two sealed 5-L acrylic electrode compartments, which stored electrolyte (including 10 g/L of sodium lactate maintained throughout the test) and supported the graphite plate electrodes, bookended the soil cell. Two high-density polyethylene (HDPE) porous panels (80 µm pore size) separated the soil cell and the electrode compartments. The soil cell had four ports (V1 to V4) for voltage measurements and eight ports (Port-1 to Port-8) for collecting pore-water samples.



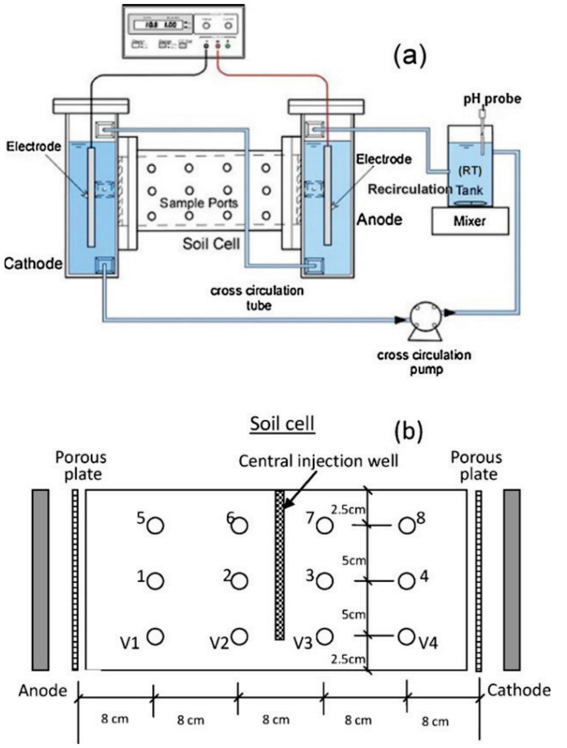


Figure D-2. Bench-Scale EK Reactor
(a) Schematic of the EK apparatus, and (b) Locations of the sampling ports (Port-1 to -8) and voltage measurement ports (Port-V1 to -V4).

A total of three test reactors were constructed for this treatability study and the experimental design for each reactor is shown in **Table D-1**.

Table D-1. Reactor Conditions and Objectives

Reactor ID	Conditions	Objective
A	Site soil (with confirmed PCE); with electrical field	EK-BIO treatment (duplicate #1)
B	Site soil (with confirmed PCE); with electrical field	EK-BIO treatment (duplicate #2)
C	Site soil (with confirmed PCE); without electrical field	Control for EK-BIO treatment

The tests for reactors A and B include four stages of operations: (1) delivery of lactate under EK for 20 days; (2) bioaugmentation of KB-1 culture and subsequent acclimation period for 2 days without electric field; (3) second stages of EK application with lactate for 60 days (EK conditions similar to the first stage); and (4) post-EK incubation (no EK conditions; 12 days for reactor A and 78 days for reactor B).

A constant current of 38 mA was applied during the active EK operation stages. Voltage was monitored with a voltage meter at each of the four voltage monitoring ports (V1 to V2 in **Figure D-2**). Port water samples from Port 1 through Port 8 were collected periodically for lactate concentration, chlorinated volatile organic compounds (CVOCs), and dissolved hydrocarbon gases (DHG, including ethene, ethane, and methane). Pore-water samples and final post-test soil samples were also analyzed for microbial (i.e., *Dhc*) quantity.

D.3 Data Evaluations and Discussions

The power supply was set to apply a constant DC to each EK reactor during the test. The voltage required to maintain the target current reflected the electrical conductivity of the soil matrix within the reactor. After 82 days of EK operation, the required voltage decreased from more than 50 V to less than 20 V, reflecting an increase of apparent electrical conductivity of the soil matrix by threefold from approximately 4E-4 to 14E-4 Siemens/cm in both Reactors A and B. The increase in electrical conductivity was likely due to, to an extent, the increases of ionic compounds within the system associated with the transported lactate.

EK operation was monitored routinely for pH and ORP with the liquid samples from the pore-water sampling ports. Pore-water pH was in the range of 7.6 to 8.3, indicating neither acidic nor alkaline condition build-up in the soil. Pore-water ORP in the EK reactors was below 100 mV compared to the positive ORP observed in the control reactor (**Figure D-3**) indicating that reducing conditions conducive to reductive dechlorination developed within the EK reactors.

By the end of Stage 3 EK operation (82 days under EK operation), pore-water lactate concentrations in Reactors A and B were significantly higher than those in the control reactor (**Figure D-3**). The lactate ion migration rate was estimated at 3.2 cm/day (4.0 cm^2/(V·day) net specific migration rate).

The final pore-water lactate concentrations in Reactor A before the EK operation stopped were equivalent to 9-20% of the boundary lactate ion concentration in the electrolyte compartment. During Stage 4 (post-EK incubation), pore-water lactate concentration decreased due to continuing microbial metabolic consumption.

Pore-water CVOC and DHG concentrations were assessed at three sampling events: 67 days since EK

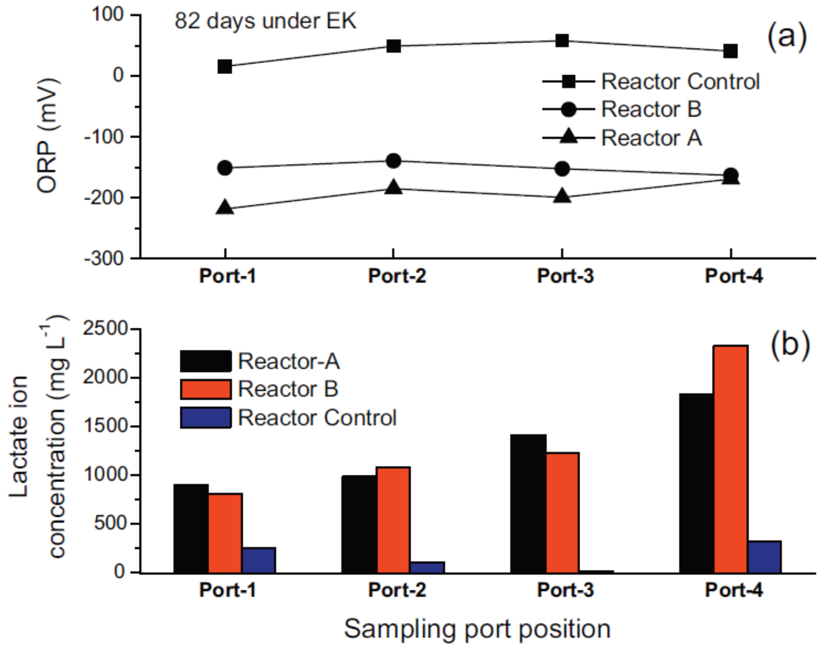


Figure D-3. Monitoring of ORP and Lactate within EK Reactors
Port 1 was closest to the anode compartment.

Table D-2. Pore-water CVOC Concentrations in Reactor B

Sampling Port	PCE (mg/L)			TCE (mg/L)			cDCE (mg/L)			Vinyl Chloride (mg/L)		
	End of EK Op.	75 D Post	% ↓	End of EK Op.	75 D Post	% ↓	End of EK Op.	75 D Post	% ↓	End of EK Op.	75 D Post	% ↓
Port 1	<0.06	<0.01	NA	<0.06	<0.01	NA	4.3	0.1	98%	1.8	<0.01	>99%
Port 2	55.1	0.4	99%	4.8	0.2	96%	50.7	0.7	99%	1.5	0.2	87%
Port 3	2.3	<0.01	>99%	1	<0.01	99%	15.8	2.3	85%	5.9	0.3	95%
Port 4	114	6.5	94%	14.6	1.3	91%	58.9	11	81%	3.7	1.1	70%

operation, 82 days since EK operation, and 12 days post-EK incubation. While lactate was distributed through the soil reactor in 82 days, biodegradation of target CVOCs required additional incubation time. A final pore-water sampling event was conducted with Reactor B after 75 days of incubation (following the termination of EK operation). The final concentrations of target CVOCs generally showed >85% decrease from the concentrations at the end of the EK operation (**Table D-2**), indicating the conditions in the soil matrix supported the continuing degradation of CVOCs by the reductive dechlorination bacteria.

The DHG data in Reactors A/B versus the control reactor indicated that the EK-BIO process effectively promoted microbial reductive dechlorination of CVOCs to ethene within the soils. The detections and subsequent increases of ethene concentrations in Reactors A and B (**Figure D-4**), and no apparent ethene concentration in the control reactor, were clear indications of *Dhc* activity. These ethene data suggested that the conditions for complete CVOC dechlorination were established in the reactor.

Complete reductive dechlorination of CVOCs to ethene requires the *Dhc* with a functional gene (*vcrA*) enabling the bacteria to produce a specific enzyme (vinyl chloride reductase) for degrading vinyl chloride. The baseline site soil analysis showed the number of *vcrA* gene copies was 2x10^4 copies per gram of wet soil, suggesting that *Dhc* were either absent (potential false positive analytical results) or present at a very low level. The post-test soil analysis showed the *vcrA* gene levels in EK Reactor A in the range of 10^6 to 10^7 gene copies per gram of soil (**Table D-3**), which were two to three orders of magnitude higher than those in the baseline.

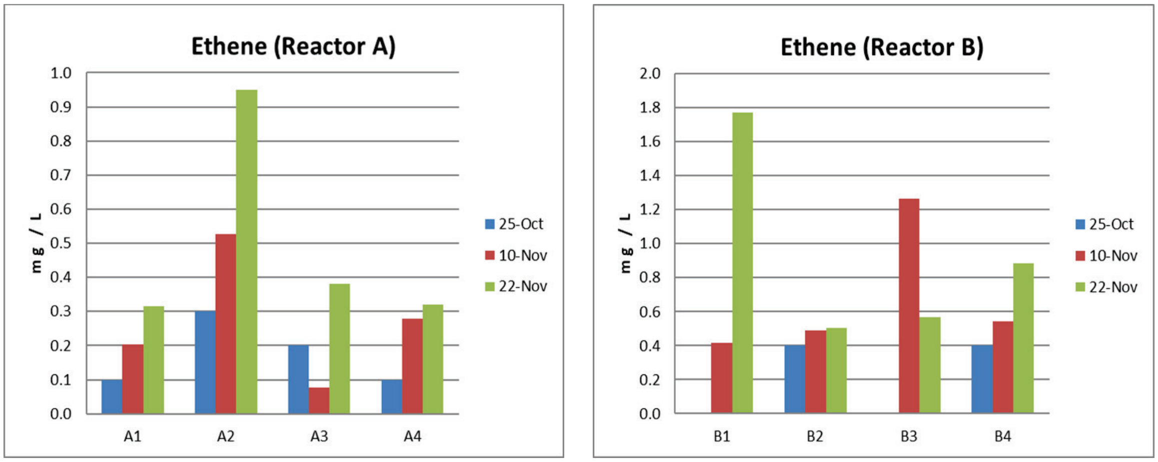


Figure D-4. Ethene Concentrations in Reactors A and B (A1 through A4 and B1 through B4 are the sampling port ID)

Table D-3. EK Reactor #1 Post-test Soil Analysis (12 days after the end of EK operation)

	Sampling Position			
Analyte	**Port 1**	**Port 2**	**Port 3**	**Port 4**
PCE (mg/kg)	2.5	30	1.7	51
TCE (mg/kg)	0.2	2.5	0.1	6.6
cDCE (mg/kg)	7.5	9.3	14	22
Vinyl Chloride (mg/kg)	0.7	0.3	0.3	<0.8
vcrA (gene copies/g)	3×10^7	6×10^7	2×10^7	3×10^6

All the volatile organic compound (VOC) concentrations are reported by dry soil. The *vcrA* copy number is reported by wet soil.

D.4 Summary

This study demonstrated that EK transport effectively distributed lactate and *Dhc* in low-k clay soil samples. The governing transport mechanism for lactate ions was ion migration and the lactate transport rate was estimated as 3.2 cm/day. The bioaugmentation of KB-1 was successful and the PCE degradation was sustainable during the EK operation. Complete dechlorination of PCE was achieved based on the observed ethene production. The treatability study results suggested that EK-BIO could be considered a feasible *in situ* remedial option for the PCE DNAPL source area in low-k zones at the site. A subsequent pilot test was designed and implemented following this treatability study and led to the full-scale EK-BIO remedy completed at this site (see **Appendix A**).

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