Final

**In-Situ Electrokinetic Remediation
of Metal Contaminated Soils
Technology Status Report**

**US Army Environmental Center
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Acknowledgements

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I. Introduction

Electrokinetic remediation is an in-situ process in which an electrical field is created in a soil matrix by applying a low-voltage direct current (DC) to electrodes placed in the soil. As a result of the application of this electric field, heavy metal contaminants may be mobilized, concentrated at the electrodes, and extracted from the soil. Many vendors have marketed the potential of electrokinetic remediation for metals contaminated soils; however, no large-scale field demonstrations had been conducted. Issues such as control of contaminant movement, ability to achieve cleanup goals, byproduct formation, treatment effects on the soil matrix, etc. had not been addressed. Interest in electrokinetic remediation has been driven by the demand for technologies that are cost effective and will eliminate the long-term liability that is incurred by landfilling of contaminants.

This report provides an overview of the current developmental status of electrokinetic remediation for metals contaminated soils. Concerns with its in situ application and issues that require further investigation are identified. The results of a field demonstration conducted at Naval Air Weapons Station (NAWS) Point Mugu are presented to illustrate the concerns with the in situ application of this technology at its current stage of development.

II. Technology Description

Electrokinetic remediation is an in-situ process in which an electrical field is created in a soil matrix by applying a low-voltage direct current (DC) to electrodes placed in the soil (Figure 1). The current density is generally on the order of milliamperes per square centimeter (mA/cm^2) or an electric potential difference on the order of a few volts per centimeter across electrodes placed in the ground.
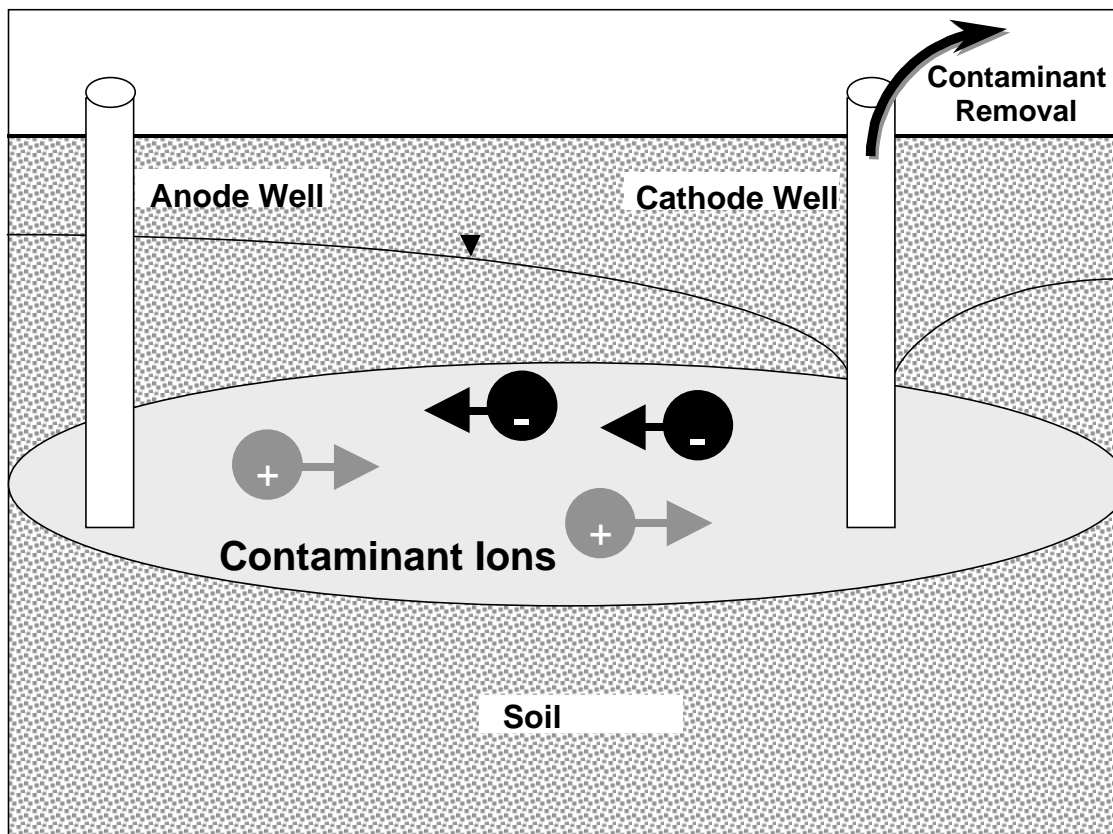
Figure 1: General Schematic of Electrokinetic Remediation

The electrodes can be placed in either a vertical or horizontal array. When DC current is applied to the electrodes, an electrical field develops between the anodes and cathodes. The application of the electric field has several effects on the soil, water, and contaminants. These effects include electromigration, electroosmosis, changes in pH, and electrophoresis.

Electromigration refers to the movement of cations and anions under the influence of the electrical field. Cations (positively charged ions) tend to migrate towards the negatively charged cathode, and anions (negatively charged ions) migrate towards the positively charged anode. These ions concentrate in the solutions near the electrodes or may undergo reactions at the electrodes, which may plate the metals onto the electrodes or liberate gaseous compounds.

pH changes occur under the influence of the current as a result of electrolysis reactions at the electrodes. Oxidation of water occurs at the anode and generates hydrogen (H^+) ions (Equation 1). H^+ ions generate an acid front, which migrates to the cathode. In contrast, reduction of water occurs at the cathode and generates hydroxyl (OH^-) ions (Equation 2), which migrate as a base front towards the anode (Acar, et al. 1988).

$$2H_2O - 4e^- \longrightarrow O_2 + 4H^+ \qquad \text{(Equation 1)}$$
$$4H_2O + 4e^- \longrightarrow 2H_2 + 4OH^- \qquad \text{(Equation 2)}$$
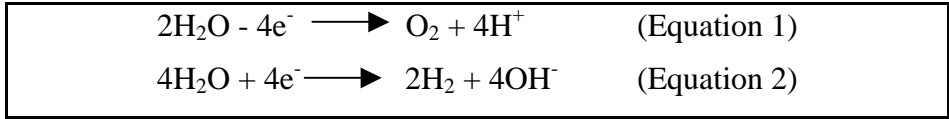
The transport of the H^+ ions is approximately two times faster than the OH^- ions. Thus, the acid front moves at a greater rate than the base front (Acar and Alshawabkeh 1993). Unless the transport of the proton (H^+ ion) is retarded by the soil buffering capacity, the soil between the electrodes will be acidified. This acidification results in solubilization of contaminants due to desorption and dissolution of species from soil. Once contaminants are present in ionic form in the soil pore fluid, they migrate to the electrode opposite in polarity under the applied electric field and/or via electroosmosis, leading to their extraction from the soil at the electrodes.

Electroosmosis is a bulk transport of water, which flows through the soil as a result of the applied electrical field. Electrophoresis refers to the movement of charged particles under the influence of the electric field.

Of these electrokinetic phenomena, the application of electrokinetic remediation to mobilize the metals in the soil is expected to be predominately influenced by the formation of a pH front between the electrodes and electromigration of the mobile contaminants to the electrode wells. Extraction and removal of the contaminants may be accomplished by electrodeposition, precipitation or co-precipitation at the electrode, or removal and treatment of water containing the mobile contaminant species from the electrode wells.

III. Technology Issues and Concerns

Electrokinetic remediation heavy metal extraction rate and efficiency is dependent upon many subsurface characteristics such as soil type and grain size, contaminant concentration, ionic mobility, total ionic concentration, types of contaminant species and their solubility, etc. Additional complications with the application of electrokinetic remediation can arise from the presence of organic contaminants and possibly the organic material in the soil. The soil's physical, chemical, and biological characteristics can individually and cumulatively impact the extraction rate and efficiency of the technology. As a result of the numerous factors affecting performance, the following technology application issues and performance concerns have been identified:

- There is a lack of understanding of the technology's effects on naturally occurring ions and how these effects impact mobilization and removal of the target contaminants. The field demonstration at NAWS Point Mugu identified many discrepancies between the laboratory testing and the performance observed in the field test. The retarding effects created by the naturally occurring ions cannot be accurately quantified in the laboratory tests and their effects on the type of metal species formed under the electric field influence cannot be accurately predicted. The metals species observed in the laboratory testing differed from those observed in the field. The species development will affect migration rate and extraction efficiency.

- The presence of naturally occurring ions and organic material as well as organic contaminants can result in the development of potentially hazardous by-products (i.e. chlorine, trihalomethanes, acetone, etc.) when an electric field is applied to the soil. The addition of ions to the soil as a result of the amendment addition to the cathode well may also result in the formation of hazardous by-products during operation of the technology. Laboratory treatability testing as currently designed cannot identify the potential for by-product production.

- The ability of the electric field to control the movement of mobilized contaminant ions in treatment zones affected by groundwater flow or tidal influences has not been validated.

- The soil chemical and biological factors that may limit the application of electrokinetic remediation have yet to be adequately quantified. As a result, site screening using readily measurable soil characteristics cannot be performed. Also as previously stated, laboratory treatability testing may give a false indication of the applicability of electrokinetic remediation to a specific site.

- The impact that electrokinetic extraction will have on the soil's physical, chemical, and biological characteristics has not been addressed. Application of an electric field has not produced any measurable adverse impacts; however, changes to the soil (and their potential ecological impacts) after cleanup target levels have been reached have not been assessed.

- There is a lack of understanding of the impact that electrode shape and electrode placement will have on the electric field shape and intensity formed within the soil matrix. The electric field shape and intensity will effect the formation of and movement

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of mobile heavy metal species. If complete coverage of the treatment area is not achieved, then all of the contaminants may not be extracted.

- Determination of the appropriate current density to the treatment area appears to be more of an art than a science. Current density or voltage application to the treatment area cannot be correlated to any specific measurable site parameter(s). Considering that electric field intensity can effect the types of contaminant species developed as well as impact the soil physical, chemical, and biological properties, this parameter and the effects that varying this parameter has requires investigation and quantification.

- Those marketing the technology have not accurately represented the cost of applying electrokinetic remediation for heavy metals extraction. Typically only power and chemical costs are referred to, thus giving the impression that this is a low-cost technology. Equipment costs, installation, maintenance, removal, and contaminant disposal significantly increase the turnkey cost of applying electrokinetic remediation.

Full-scale application of this technology for remediation of metals contaminated soil is limited at best until the issues and concerns stated above can be resolved.

IV. Technology Costs

Electrokinetic vendor literature typically quote costs only in terms of power and chemical amendments used. The capital costs and operation and maintenance (O&M) costs have not been available in the past. Table 1 documents the capital and O&M cost associated with the use of electrokinetic remediation at NAWS Point Mugu. These costs reflect full-scale costs extrapolated from the costs incurred on the demonstration-scale project. Also, these costs do not reflect turnkey costs because effective treatment was not achieved during the demonstration. Although an accurate treatment cost associated with electrokinetic remediation cannot be derived from the available information, the costs presented here will shed some light on the true potential cost range for the in situ use of the technology at its current stage of development.

Table 1: Electrokinetic Remediation Unit Costs

Cost Category/Element	Cost ($)	Cost for Calculating Unit Cost
Capital Cost for Technology		
Technology mobilization, setup, and demobilization	278,081	
Planning and preparation (regulatory permitting)	19,774	
Site work (utility installation)	10,908	
Equipment and appurtenances (Process equipment and appurtenance/construction)	470,019	
Startup and testing	50,000	
Other (Pre-deployment treatability testing)	62,206	
Total Capital Costs		**890,988**
O&M for Technology		
Labor	206,390	
Materials	5,979	
Utilities and fuel	4,429	
Equipment ownership, rental, or lease	1000	
Performance testing and analysis	84,264	
Other		
Total O&M Costs		**302,062**
Other Technology-Specific Costs		
Compliance testing and analysis	0	
Soil, sludge, and debris excavation, collection, and control	0	
Disposal of residues	0	
Total cost		
Total cost for calculating unit cost		**1,193,050**
Quantity treated (cubic yards)		**1,000**
Calculated unit cost ($/cubic yard)		**1,193**

V. Case Study

The US Army Environmental Center (USAEC) and the Engineer Research and Development Center (ERDC) conducted a field demonstration of electrokinetic remediation to assess the performance and cost of the technology. This demonstration, sponsored by the Environmental Security Technology Certification Program (ESTCP) and the Southwest Division, Naval Facilities Engineering Command, was conducted at a metals contaminated site at NAWS Point Mugu, California (USAEC, 2000). Electrokinetic remediation was investigated for this ecologically sensitive area because of its potential to be a less invasive technology.

A.   Background

Located in Ventura County, California, the site at NAWS Point Mugu selected for demonstration of electrokinetic remediation was Site 5, the Old Area 6 Shops. Site 5 is a large area where electroplating and metal finishing operations were conducted. The area of study was approximately ½ acre in and around two former waste lagoons located in the center of Site 5. The lagoons are unlined and were used between 1947 and 1978 to receive wastewater discharge from electroplating and metal finishing activities. The largest waste generator was a plating shop that discharged approximately 95 million gallons of plating rinse solution into the lagoons. Additionally, up to 60,000 gallons of waste photographic fixer solution and small quantities of organic solvents and rocket fuel were disposed of in the lagoons. Following a 1994 emergency removal action, surface sampling within the lagoons indicated that levels of chromium and cadmium (up to 25,100 mg/kg and 1,810 mg/kg, respectively) exceeded allowable limits for California (22 CCR 66261.24 < 2,500 mg/kg and 100 mg/kg, respectively>).

Prior to the field demonstration, extensive laboratory testing was conducted to assess the potential effectiveness of electrokinetic extraction at NAWS Point Mugu. Testing included determining the contaminant and soil characteristics, such as contaminant types and concentrations, particle size assay, pH, total organic carbon (TOC), toxicity characteristic leaching procedure (TCLP), hydraulic conductivity, cation exchange capacity (CEC), and a total charge balance. The characteristics of the soil matrix are listed in Table 2. These analyses were followed with a series of treatability studies that were expected to determine electrolyte-conditioning requirements, migration of contaminants and competing ions, effects of brackish water, electrode placement, time versus treatment analysis, removal efficiency, and process

Table 2: Matrix Characteristics

Parameter	Value
Soil type	<sand> soil and sediment
Particle size distribution	85% sand, 7% gravel, 6% silt, 1% clay
pH	5.84
TOC	6390
TCLP	10.5 mg/L cadmium, non-detect (ND) chromium
Hydraulic conductivity	0.045 cm/sec
CEC	3.9
Maximum or range of contaminant concentrations	ND to 1,810 mg/kg cadmium ND to 25,100 mg/kg chromium

power/operating requirements.

ERDC initially conducted laboratory studies using soil samples collected from the proposed demonstration site at NAWS Point Mugu (Bricka, 1998). The laboratory treatability studies were conducted in cylindrical cells constructed of a non-conducting Plexiglas material. The middle section of the cell contained the soil within the 10 cm diameter X 10 cm long cylinder. A cylindrical carbon electrode was installed at each end of the test cell to serve as the anode and cathode. The electrolyte used during the initial treatability tests was deionized water. The treatability tests were operated for a period of approximately two months during which significant chromium and cadmium movement and removal was observed. Also, pH across the soil samples was lowered to below 3.2. Early in each test run the formation of chlorine gas in the anode was detected, however, as the chloride ions within the sample were depleted, chlorine gas formation ceased. As noted in the field data and subsequent lab tests, the chloride content of the surrounding soil and the site water resulted in the continuous production of chlorine gas and is believed to have been a retarding factor in the formation of the pH front between the electrodes and in the movement of the metal contaminant ions. The laboratory treatability tests initially did not adequately assess the effects of site water and conditions on the performance of electrokinetic remediation. Also, during laboratory testing, monitoring for the formation of undesirable byproducts was not conducted. As observed in the field and in subsequent lab testing, trihalomethane and acetone contaminants were generated in the pore fluid as a result of the application of the electric field and the introduction of the citrate ions from the cathode amendment. Had this monitoring been conducted, appropriate steps could have been taken to mitigate these effects on the system's performance. Subsequent treatability testing conducted by Lynntech, Inc. (the technology contractor performing the field demonstration) prior to conducting the field demonstration also did not identify the issues stated above that resulted in inadequate field performance of the technology.

The initial laboratory studies conducted by ERDC and Lynntech, Inc. indicated that electrokinetic extraction could successfully be applied to the demonstration site at NAWS Point Mugu. The treatability studies indicated that the majority of the metal contaminants would be solubilized in the pore water as a result of the pH front generated by the application of electrokinetic extraction. The major phenomena contributing to electrokinetic transport of the contaminants at NAWS Point Mugu was expected to be electromigration of these solubilized metals.

B.   System Description

The electrokinetic remediation system basically consists of an array of electrodes, a power distribution and control system, automated process monitoring equipment, and process piping to distribute chemical amendments to the electrode wells and to extract contaminants from the electrode wells. Other equipment necessary to support system operations due to the site conditions at NAWS Point Mugu included off-gas extraction and treatment equipment to treat the gases that were generated in the electrode wells during system operation.

The electrode array consists of a series of anodes and cathodes housed in wells. Figure 2 illustrates the array of anodes and cathodes that were installed within the test area at NAWS Point Mugu. The spacing between the electrode wells was established by Lynntech based on the voltage gradients observed during a preliminary field test conducted in October 1997. Based on these tests the optimum distance between the anodes and cathodes was determined to be 14 feet. The optimum distance between the each anode well in the anode well rows (as well as each cathode well in each cathode well row) was determined to be 6 ½ feet (Hodko et al 1999).
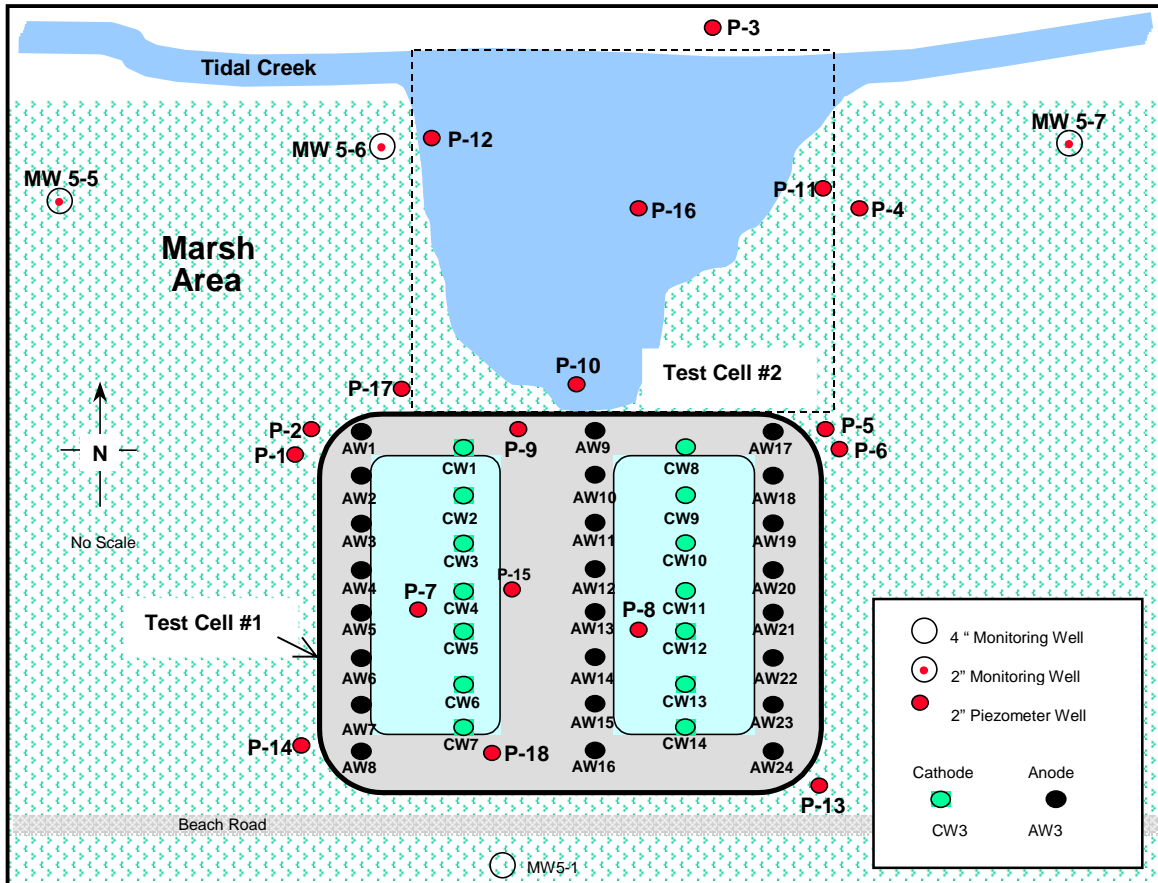

Figure 2: Schematic Showing Electrode Well Placement

The electrode wells contain either anodes (positive electrodes) or cathodes (negative electrodes) (Figure 3). The anode electrode wells are 4-inch diameter slotted polyvinyl chloride (PVC) well casings. The anode well casings were wrapped in a tightly woven linen fabric. The well packing was a kaolinite and sand mixture. The cathode wells are 3-inch diameter porous ceramic well casings with a kaolinite and sand packing mixture. The specific well designs are considered proprietary Lynntech designs. Lynntech believed the well construction and packing mixes would enhance contaminant transport into the wells. This had not been validated in field trials.

The electrode materials used in the anode and cathode well were selected based on their ability to withstand the corrosive processes created by the application of the electric field. The anode electrode, which operates under highly corrosive conditions, was a rod shaped electrode constructed of titanium with an iridium oxide coating. The cathode electrode was constructed from approximately 2-inch wide strips of stainless steel mesh.
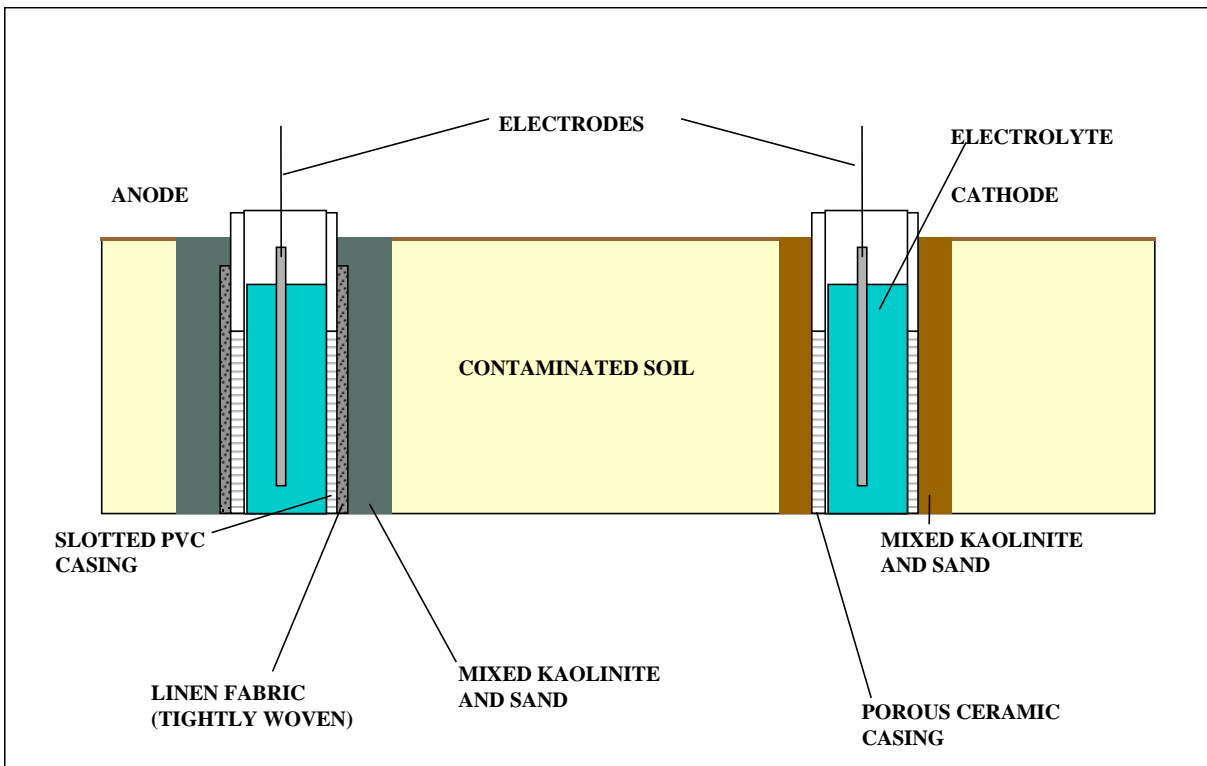
Figure 3: Electrode Well Construction

Electrical power is applied to the electrode array via three 10-kilowatt (kW) power supplies. Each of these power supplies is capable of delivering up to 30 volts (V) at up to 333 amps (A). The power supplies were hooked in series to deliver up to 90 V at up to 333 A. Application of the electric power to the electrode array was controlled by an on-site computer system with customized LabView 4.0 software. The control system applied a pulsed 45 V power supply to the electrode array. The applied current fluctuated with the varying resistivity of the soil in the treatment area. The resistivity varies due to heterogeneities in the soil, varying of the soil volume treated, and with time as the ion load in the soil is changed by the electrochemical reactions that occur during the electrokinetic system operation. The control system also monitored temperature in the soil and electrode wells and the applied voltage gradient to control the electric power supplied to the electrode array. Excessive temperature increases in the soil and electrode wells would indicate that too much power was being supplied to the treatment area and being wasted to heat generation. An increase in voltage gradient would indicate that the resistivity of the treated soil was increasing and higher current density is required to maintain the mobility of the contaminant ions. The power supply current and the current applied to each individual well were logged by the computer system.

The electronic system was designed to provide for multi-signal monitoring of the system process. Each well had sensors that monitored solution temperature, voltage, pH, and current. All operating data were logged by the computer system. Computer monitoring and control was accessed remotely via modem hookup. In addition to monitoring the data stated above and regulating the power input to the electrode array, the computer system also was designed to monitor fluid level sensors and alarms for fluid levels. The computer control system provided for the remote operation of the pumps in the process piping system to transfer the fluids from the

electrode wells to the holding tanks and to add amendments to the cathode wells (Hodko et al 1999).

Amendments are used to control the formation of the pH front in the treatment area. Factors in selecting an amendment include cost, hazardous characteristics of the amendment, and the desired reaction. The desired reaction not only involves the mitigation of OH^- or H^+ ion production at the cathode and anode wells but also involves the amendments' reaction with the contaminants of concern. As found during the field demonstration at NAWS Point Mugu, the amendments' potential effect on other naturally occurring organic and inorganic species as well as its effect on biological activity may also be of concern.

As a result of initial public and regulatory concerns with the use of mineral acids, nitric and sulfuric acids were not proposed for use during the demonstration. Of the organic acids tested in laboratory trials, citric acid provided the best contaminant mobility and removal results. All of the acids were able to prevent the migration of OH^- ions into the soil; however, citric acid resulted in the formation of soluble metal citrates that were capable of electromigrating to the electrodes. The citric acid was readily available, relatively inexpensive, and environmentally benign.

The system for the storage and distribution of the citric acid amendment to the cathode wells is depicted in the system schematic in Figure 4. Bags of dry citric acid are mixed with water in a 1,000-gallon double walled tank at a 13-wt% concentration. The citric acid solution is transferred from the tank to the cathode wells via a low-noise pump. Solenoid valves control the delivery of the citric acid amendment to each cathode well. The volume delivered to each cathode well is monitored and controlled via a flowmeter. All equipment, pump, solenoid valves, and flowmeter, are continuously monitored and controlled by the central computer control system.

In the anode well H^+ ions are produced that depresses the pH in the anode wells and is transported through the soil towards the cathode wells. The acid front solubilizes metal ions on the soil surface. This is required to support transport of the metal ions toward the wells. As a result of this pH front, the soil was expected to decrease to a pH of approximately 4. Experience had indicated that a pH lower than 2.5 was unlikely to be attained because of normal soil buffering capacity. By monitoring the soil pH through frequent core sampling and sampling soil pore fluid using piezometers, any depression of pH below the 2.0 level could be detected and controlled by electrical current adjustment to the wells or the addition of a base chemical to the anode wells. Provisions were incorporated into the system design to provide for base chemical amendment addition to the anode wells in the event that the pH level could not be controlled. This system is described below. No amendment additions were needed in the anode wells during the technology demonstration.

C.   Contaminant Recovery and Disposal System

The electrokinetic remediation system was designed to extract the metal contaminants via electromigration of the contaminant ions and concentration of the ions in the electrode wells. The majority of these contaminants were expected to remain in solution with only minimal plating occurring on the electrodes. Once metal contaminant concentrations had built up in the electrode well, processing of the electrolyte fluid would be conducted to extract the metal contaminants and return the processed electrolyte fluid back to the wells for continued use. This would have minimized the volume of waste generated by the process and resulted in the
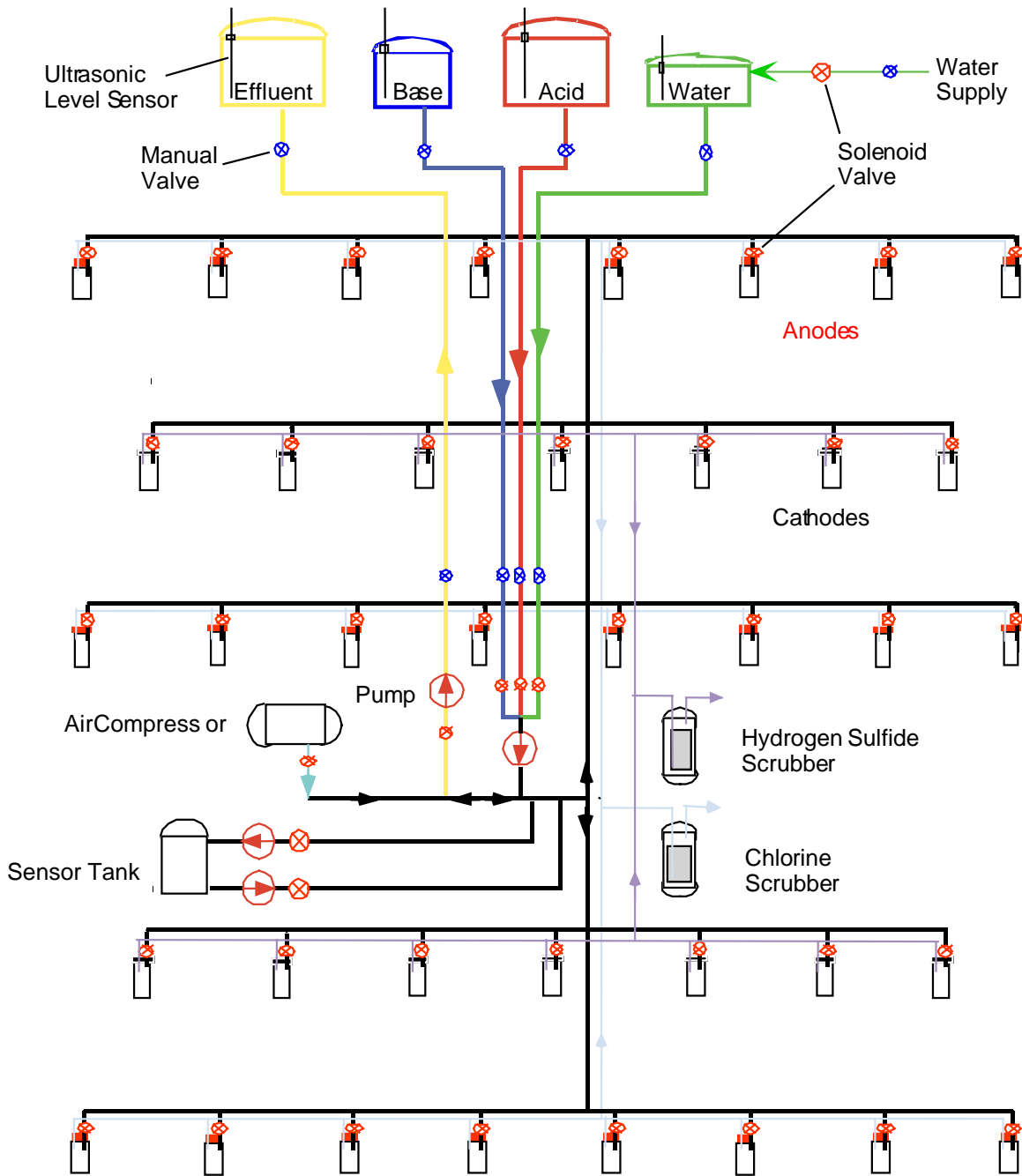
Figure 4: Electrokinetic Fluid System Schematic.

production of a potentially recyclable material. Processing of the fluid consisted of periodically pumping the fluid from the wells to a 1,000-gallon double walled effluent tank (Figure 4). The frequency of extracting the contaminated electrolyte from the wells would be determined based on the concentration of the metals in the electrolyte and the observed effects the metals contaminated electrolyte was having to the electrokinetic system's removal efficiency. Once contaminated electrolyte fluid had been collected in the effluent tank, circulating the fluid through an electrodialysis reversal (EDR) unit would process the fluid. Any waste sludge resulting from the process was to be stored on-site for analysis, classification, and disposal or recycle (if possible). The recovery and disposal system was not operated because no contaminants were removed during the field demonstration.

D.   Off-Gas Extraction and Treatment

As a result of the electrolysis reactions at the electrodes, oxygen gas is formed at the anode and hydrogen gas is formed at the cathode. These gases are usually allowed to vent to the atmosphere. However, due to the presence of sodium chloride in the soil and groundwater, chlorine gas was produced in the anode wells along with the oxygen. This was detected during the laboratory trials and off-gas extraction and treatment for the anode wells was incorporated into the system design. During the conduct of the field demonstration, the formation of hydrogen sulfide gas in the cathode wells was detected. A field modification was performed to extract and treat the off-gas from the cathode wells. The off-gas extraction and treatment system for the anode and cathode wells consisted of capping the wells with PVC couplings for easy removal and installing a vent system to vent the gases produced during system operation to a scrubber unit prior to release to the atmosphere. Passing the gases through a column of sodium hydroxide solution (5.0 molar) stripped the chlorine and hydrogen sulfide gases. The chlorine gas produced at the anode and the processing reaction of the chlorine gas within the scrubber is shown in Equations 3 through 6.

Generation at anode	$2\ Cl^- \rightarrow Cl_2 + 2\ e^-$	Equation 3
Scrubber Step 1	$Cl_2 + H_2O + \rightarrow HOCl + H^+ + Cl^-$	Equation 4
Scrubber Step 2	$HOCl + NaOH \rightarrow NaOCl + H_2O$	Equation 5
Scrubber Step 3	$H^+ + Cl^- + NaOH \rightarrow NaCl + H_2O$	Equation 6

The discovery of the hydrogen sulfide evolution in the cathode wells was attributed to metal sulfides in the soil. Equation 7 shows how the H_2S may have been generated as the hydrogen ion front solubilized iron sulfides in the soil as it moved from the anode to the cathode array. Similar reactions would occur with other metal sulfides in the soil. Once generated, the hydrogen sulfide moved to the cathode wells. The gas was treated in the scubber where it was reacted with sodium hydroxide (NaOH) as shown in Equation 8.

$2Fe_2S_3 + 12H^+ \rightarrow 6H_2S_{(g)} + 4Fe^{+2}$	Equation 7
$H_2S + 2\ NaOH \rightarrow 2\ H_2O + Na_2S$	Equation 8

The vent system was modified during the demonstration to increase efficiency of gas extraction from the well fluid. Initially, the headspaces of the wells were evacuated with a vacuum pump with the pump discharge being routed through the scrubber prior to release to the atmosphere. To increase the efficiency of chlorine gas removal from the anode wells, an air sparging system

was installed to accelerate gas extraction as it was produced on the anode electrode. This was used in tandem with the existing headspace evacuation system.

E. Demonstration Design and Operation

The objective of the field demonstration was to evaluate electrokinetic extraction of heavy metal contaminants from impacted soil and sediment. The demonstration was designed to identify, collect, and verify the economic, operational, and performance data that would be used to validate and transfer this technology to potential users. The following evaluation points were to be addressed by the field demonstration:

- Validation of the ERDC treatability study predictions of electrokinetic extraction performance.

- Assessment of electrokinetic extraction's ability to achieve site cleanup target levels.

- Assessment of the ability to control the effects of electrokinetic extraction in both an artificially confined and an unconfined treatment area.

- Identification of off-gas emissions resulting from electrokinetic extraction.

- Monitoring the effects of electrokinetic extraction on organic contaminants in the soil.

- Identification of site-specific characteristics affecting the performance of electrokinetic extraction.

- Identification of site-specific characteristics affecting electrokinetic extraction costs.

- Assessment of potential health hazards to site workers and the public resulting from fugitive emissions (i.e., H_2, O_2, and Cl_2) from electrokinetic extraction.

- Quantification of the costs (capital costs and operation and maintenance costs) associated with the use of the electrokinetic extraction.

USAEC demonstrated the electrokinetic remediation technology in an approximately 1/2 acre area in and around two former waste lagoons. Two test cells (one confined by a nonconductive barrier wall and one unconfined) were established for conducting the demonstration (Figure 5). Two test cells were constructed in order to assess the ability of the electrokinetic technology to limit its effects within a defined area and control contaminant movement within that same area. Initial operations were conducted in test cell #1. This test cell contained the two former waste lagoons and the surrounding berms. Contaminants were characterized to a depth of 11 feet. An electrically non-conductive sheet pile barrier wall was installed to a depth of 20 feet around test cell #1 to prevent uncontrolled movement of metal ions and contaminants outside of the test cell and to mitigate the effects of groundwater flow and tidal effects within the test cell. Once positive control of the effects produced by the technology had been proven via monitoring of process effects in 2" piezometer wells located within and around the test cell, system operations in the unconfined test cell (test cell #2) were the begin. Operations within test cell #2 were never initiated due to the performance problems observed in test cell #1.

The electrokinetic remediation system was installed in test cell #1 and ready for operation by 15 March 1998. The system was designed to operate for nine months or until the contaminant levels were reduced to below regulatory action levels for metals concentration and toxicity criteria.
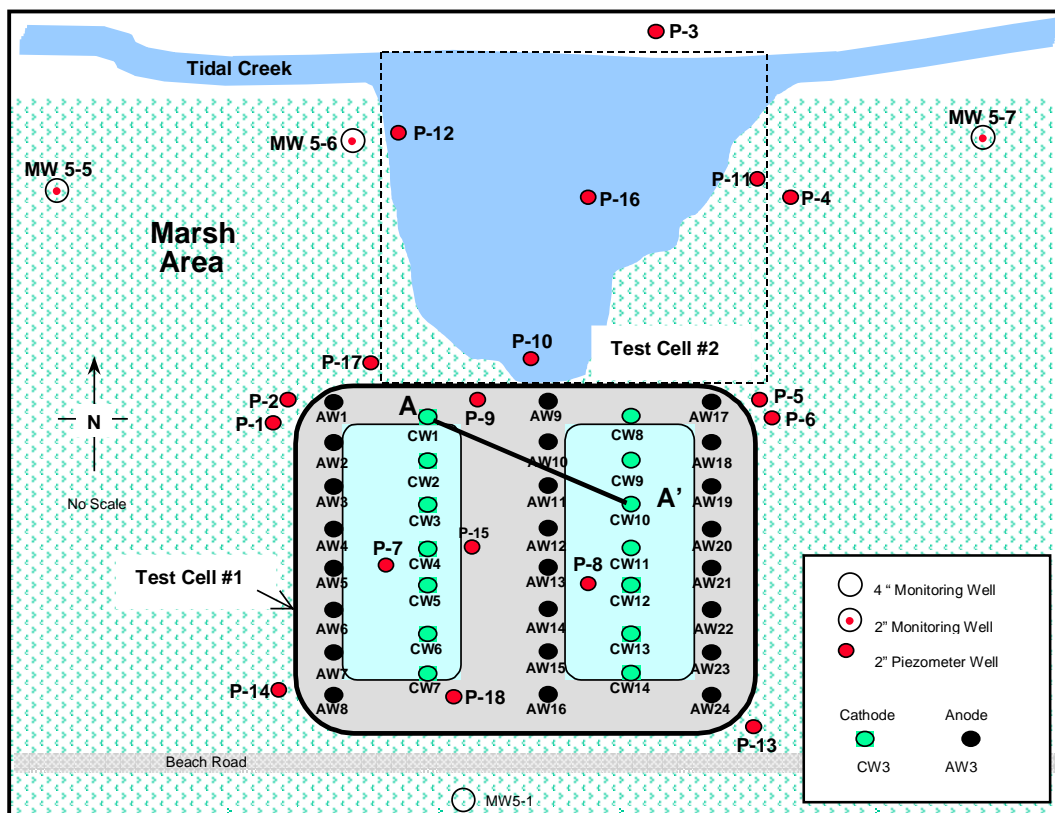
Figure 5: Test Cell Layout and Electrode Well Locations

Operation and monitoring of test cell #1 was initiated in March 1998 and continued until October 1998 with a temporary shutdown for 6 weeks from the end of June through mid-August due to contractual issues with Lynntech, Inc. In May 1998, a 3-month progress review was held. It was determined that electrokinetic extraction was progressing much slower than originally expected. There was no contaminant movement, and the pH front in the soil had not developed. The pH front had been expected to be observed based on the laboratory trials conducted at ERDC and Lynntech. The program review revealed that the current densities used in the bench scale studies (0.5 mA/cm^2 [ERDC] and 2.3 mA/cm^2 [Lynntech]) were much higher than those used in the field demonstration (initially 0.1 mA/cm^2 and increased to approximately 0.2 mA/cm^2). The current density was changed from to 0.1 mA/cm^2 to 0.2 mA/cm^2 two weeks prior to the 3-month progress review. In an effort to increase the rate of contaminant movement, the power applied to test cell #1 was increased further. To achieve a power increase with the existing equipment, the treatment area within test cell #1 was reduced by approximately one half so that treatment was applied to only the east waste lagoon. The current density was increased from 0.2 mA/cm^2 to more than 0.33 mA/cm^2 in the reduced test area. The reduced electrokinetic extraction system was operated for an additional 10 weeks.

In total, the system operated for 22 weeks. At the end of this 22-week period, the pH front was just beginning to appear and low contaminant concentrations were detected in some of the electrode wells. Another progress review was conducted at this point, and it was determined that unknown factors (either system design or site soil characteristics, or both) were retarding the

performance and that the technology required further investigation and development prior to full-scale implementation. On 7 October 1998, the field demonstration at Site 5 was suspended. The treatment timeline for the demonstration is summarized in Table 3.

Table 3: Treatment Timeline for Test Cell #1

Activity	Time Period	Comment
Operations and maintenance begun	March 1998 to end-June 1998	Initial operations (1/8 acre, 0.1 - 0.2 mA/cm^2)
Three-month progress review	May 1998	- No contaminant movement and pH front had not developed - Increased current density and reduced treatment area (1/16 acre, 0.33 mA/cm^2)
Temporary shutdown	end-June 1998 to mid-August 1998	Shut down due to contractual issues with Lynntech, Inc.
Operations and maintenance resumed	mid-August 1998 to October 1998	pH front just beginning to develop. Low contaminant concentrations detected in some electrode wells.
Progress review	October 1998	Unknown factors were retarding performance. Determined that the technology required further investigation.

In January 1999, ERDC resumed operation of the electrokinetic extraction system in test cell #1 to attempt to identify the factors that may be retarding the performance of the technology and to improve design and operational parameters. At this point, the technology's potential for use at the NAWS Point Mugu site was still considered possible if the factors retarding the process could be identified and addressed. This was based on the limited performance that had been observed prior to system shutdown in October 1998. To reduce operational costs, the treatment area was again reduced, consisting of six anode electrodes and three cathode electrodes (Figure 6). The electrokinetic extraction system was restarted and was operated through mid-June 1999. The current density was increased from 0.33 mA/cm^2 to 1.0 mA/cm^2 in the reduced test area.

F.   Technology Performance

The cleanup goals for the field demonstration were:

1.   To reduce metal contaminant concentrations in soil to below federal regulatory action levels for metals concentrations and toxicity criteria.
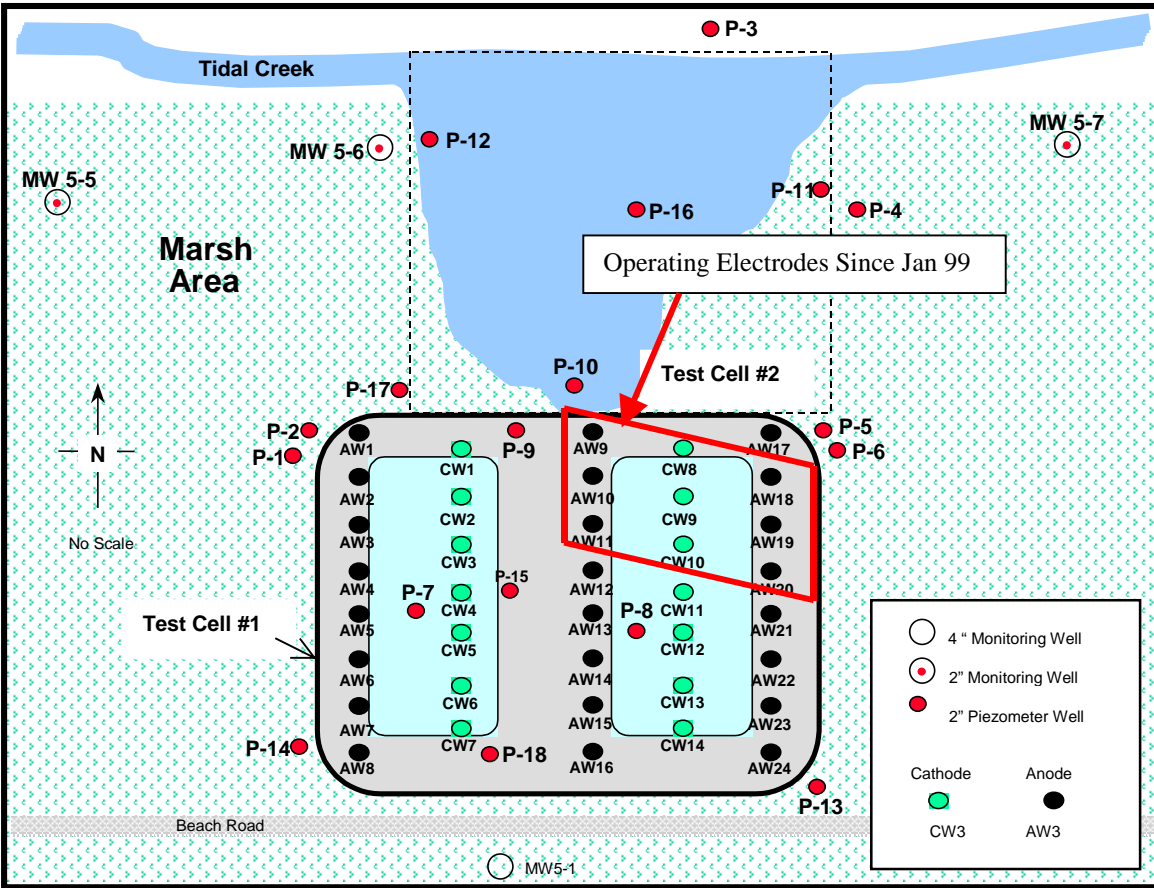
Figure 6: Electrode Wells Operated by ERDC

2. To reduce contaminant concentrations to modified USEPA Region IX Preliminary Remediation Goals (PRGs) that are based on human health risk assessments and established site background levels.

The field demonstration was monitored to verify control and containment of the electric field effects and control of contaminant migration and emissions. Process dynamics were assessed using surface water, groundwater, and soil contaminant levels measured prior to, during, and after system operation.

Prior to initiation of the electrokinetic remediation system operation, process control zones were established between select pairs of electrode wells to monitor the progress of the metals movement. The area between AW-10 and CW-09 was used as a control zone (Figure 7). This zone was baseline characterized by a soil sampling in February 1998 and was monitored consistently throughout the entire period of operation. To monitor pore fluid, piezometer wells were inserted into the control zone. The pore fluid was sampled monthly and was analyzed for pH, chromium, and cadmium. The analytical results of the multiple soil and pore fluid samples were used to track the movement of the heavy metals over time. Table 4 summarizes the results of the monitoring.
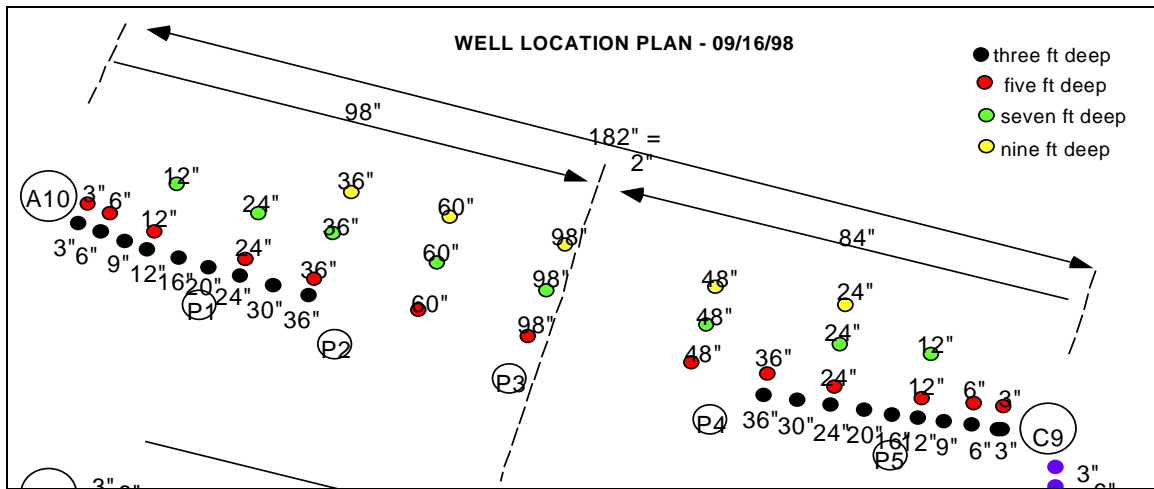
Figure 7: Process Control Zone Sampling Points

Table 4: Monitoring Results of Control Zone Profile

Sampling Event	pH Front	Cadmium Movement	Chromium Movement
February 1998	pH front had not developed	Peak concentration (50 mg/kg) 2 ft from cathode	Peak concentration (3000 mg/kg) approximately 5 ft from cathode
October 1998	pH front was just beginning to develop	Peak concentration (50 mg/kg) midway between anode and cathode, approximately 8 ft from cathode	Concentrations increasing/migrating toward cathode Peak concentrations (5000 - 5500 mg/kg) 2 ft and 6 ft from cathode
June 1999	pH front had almost traversed control zone profile	Concentrations increasing/migrating toward cathode Peak concentrations (55 - 60 mg/kg) 2 ft from cathode	Concentrations increasing/migrating toward cathode Peak concentration (6500 - 7000 mg/kg) 1 ft from cathode

The development of a pH front was considered a precursor to contaminant mobilization. After three months of operation, the pH effects in the pore fluid were primarily concentrated within one foot of the anode well. Continued operation for ten weeks at a higher current density resulted in the development of a pH front that extended approximately three feet from the anode well at the seven-foot depth. Also, during this period, the chromium concentrations in the anode well appeared to increase by an order of magnitude. Even though there was an increase in

contaminant concentrations in the wells, sampling in the process control zone did not indicate a significant trend of contaminant migration towards the electrodes. As a result, full-scale operation to the system was suspended.

ERDC, with NAWS Point Mugu support, continued the investigation and development of the technology for its potential use at Site 5. ERDC conducted additional bench scale testing to assess the impact of the competing ions in the soil and water present at the site on the technology's performance. Also, bench testing was conducted on the fundamental aspects of the technology, electrode shape and electrode array configuration, to assess the potential impacts that the fielded systems' design and operation may have had on overall performance. The bench testing, using site water in lieu of de-ionized water, resulted in the conclusion that the electrokinetic effects will mobilize the contaminants. However, as a result of the competing ions present at the site, the preferential electrochemical effects on the competing ions will retard the technology's effects on the target contaminants.

The bench studies investigating electrode shape and array configuration indicated that the system design installed by Lynntech might not provide optimum performance. The electrode shape used in the anode well, cylindrical rods, generated an electric field that primarily emanated as a point source from the end of the rod. This explained the primary pH front development at the 7 to 9 foot depths while minimal pH effects were observed in the shallow soils. The bulk of the treatment effects were occurring near the bottom of the wells. The distance between the electrode wells and the staggering of the anode/cathode arrays at Site 5 were also believed to reduce the efficiency of the technology's performance. Bench die tests indicated that improved electric field coverage in the treatment area could be obtained with uniform rows of anodes and cathodes. Installing the rows closer together (approx. 6 foot spacing) would also reduce the time required to treat the area by reducing the distance the contaminant ions would have to travel. Other suspected system characteristics that may have impeded the performance was the well design and the pulsing of the electricity. Field measurements of the voltage gradient between the electrodes conducted by ERDC indicated that the bulk of the gradient occurred across the well packing material. The packing material may be inhibiting ion transport into the electrode wells. The pulsing of the electricity was not believed to have any positive effect as claimed by Lynntech. It was believed to have actually slowed the production of the pH front.

Though the fielded system may not have provided the optimum performance, the main effect from these design deficiencies would be to extend the time required for cleanup at the site. In January 1999, ERDC resumed operation of the electrokinetic extraction system in test cell #1. At this point, the technology's potential for use at the NAWS Point Mugu site was still considered possible if the factors retarding the process could be addressed. The existing system was slightly modified to address the issues identified in the laboratory studies. The electrodes were raised in the wells to ensure treatment occurred in the shallow soils where the highest concentrations of contaminants are found. Also, the pulsing of the electricity was stopped. A constant voltage was applied to the electrode array. The current density was increased from 0.33 mA/cm^2 to 1.0 mA/cm^2 in the reduced test area. The electrokinetic extraction system was restarted and was operated through mid-June 1999.

The pore fluid sampling conducted in June 1999 measure a pH profile between the electrodes (Figure 8). The pH front had traversed the entire distance between the anode and cathode wells. With the establishment of this pH front, contaminant movement and concentration in the wells was expected to become readily observable.
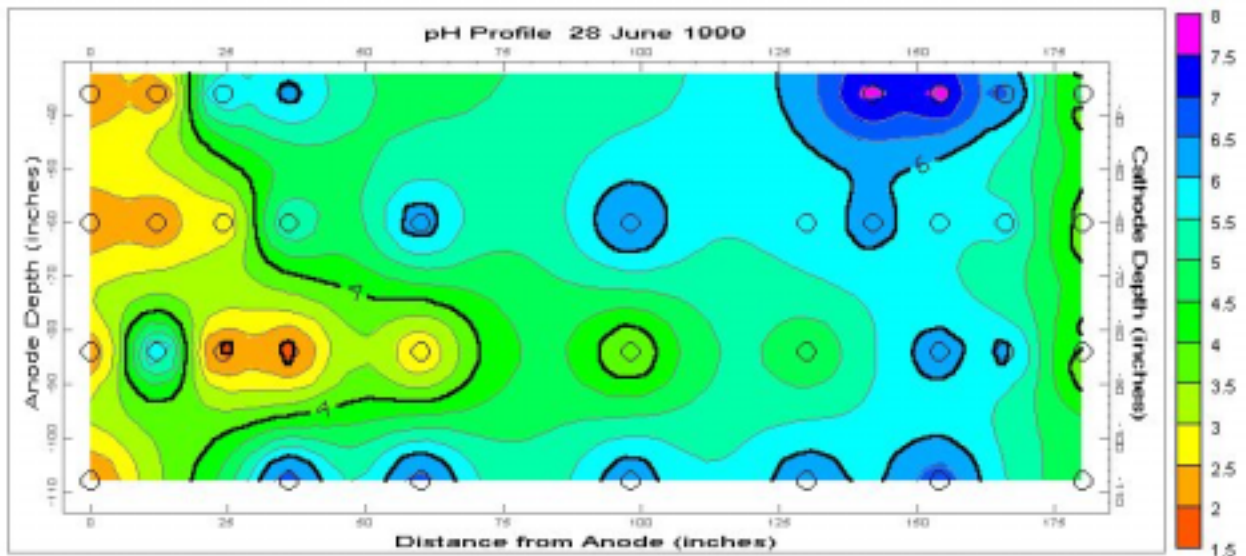
Figure 8: pH Profile (June 1999)

The results of the baseline characterization in February 1998 showed that cadmium was seen throughout the control zone profile primarily in the upper layer of soil (0 to 5 ft deep). The peak cadmium concentration was 50 mg/kg approximately two feet from cathode CW-09. The results of the October 1998 soil sampling showed that cadmium had been removed from both the anode and cathode regions and were predominantly in the center of the profile. Again, the peak cadmium concentration was approximately 50 mg/kg in the upper layer of soil. The results of the June 1999 soil sampling implied that the cadmium was moving toward the surface and towards the cathode region, with concentrations increasing toward the cathode (Figure 9).

The results of the February 1998 soil sampling showed that chromium, like cadmium, was initially in the upper soil layer, approximately in the middle of the control zone profile, with concentrations up to 3,000 mg/kg. The results of the October 1998 soil sampling indicated that chromium was migrating towards the cathode. The results of the June 1999 soil sampling showed a definite trend of chromium movement toward the cathode region, with concentrations increasing toward the cathode (Figure 10).

Throughout the operation of the electrokinetic system, monthly sampling was conducted to monitor for the release of the inorganic contaminants outside of the defined treatment zone. The electrokinetic process effects on the existing organic contaminants were believed to be inconsequential and only quarterly monitoring were conducted to track process effects on VOCs. Routine sampling began showing indications of trihalomethane accumulation in the shallow (3 to 5 foot) piezometer wells inside and outside of the defined treatment area. Subsequent sampling revealed that trihalomethanes (with chloroform being the primary trihalomethane constituent) were accumulating in the shallow breakout wells outside of the barrier wall at the site (Figure 11). Upon the discovery of trihalomethane contaminants, the sampling plan was modified to include the monthly monitoring of VOC's (EPA Method 8260) and chlorine residual. Sampling of the electrode wells in the treatment area showed elevated levels of trihalomethanes and free chlorine in the electrolyte solution thus indicating the electrokinetic system was the source of the
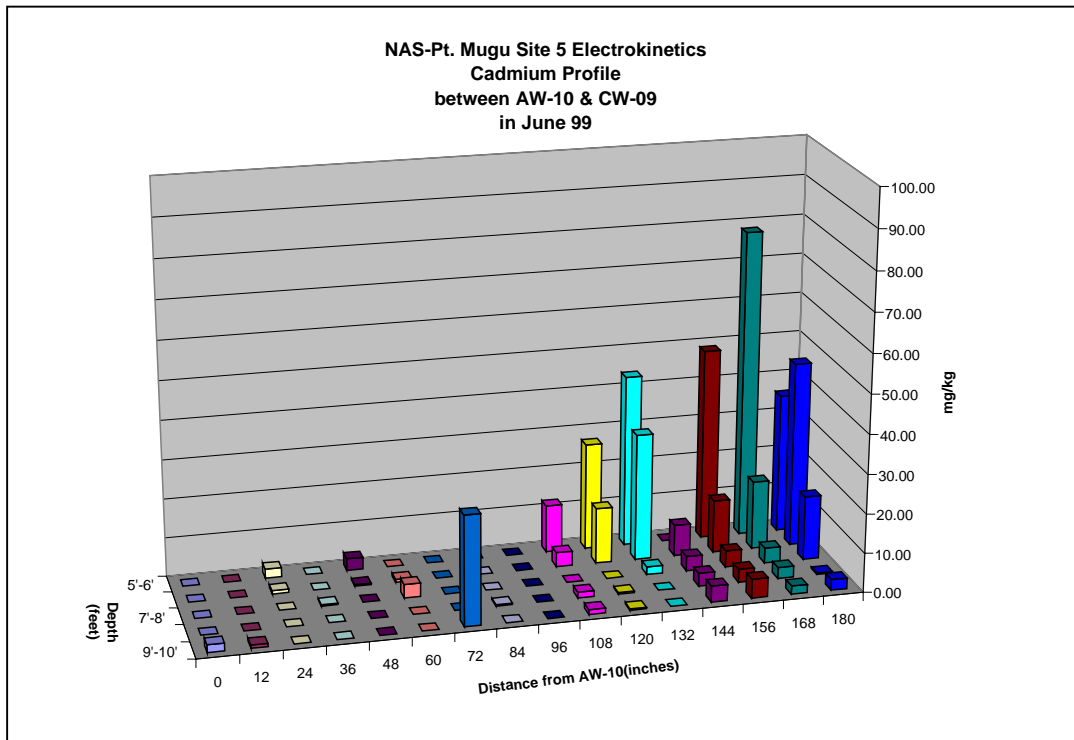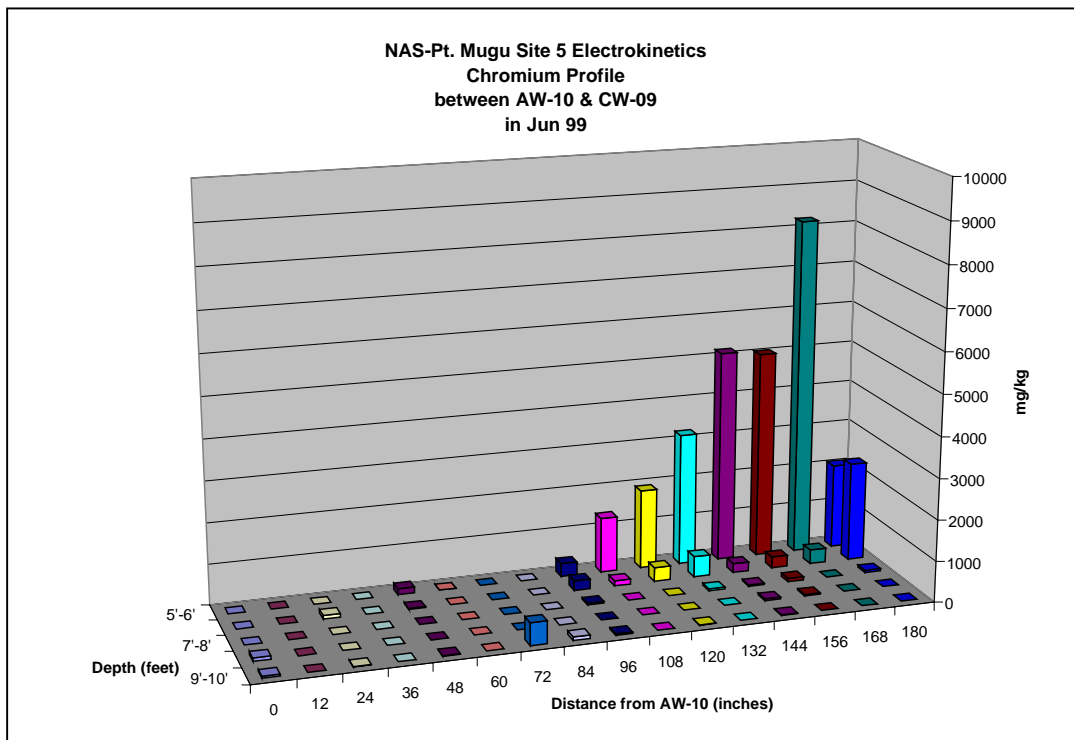
Figure 9: Cadmium Profile (June 1999)

Figure 10: Chromium Profile (June 1999)

trihalomethane production (Figure 12). This was verified in a laboratory bench test cell operated at ERDC. The naturally occurring chlorides present at the site are being electrochemically transformed into free chlorine at the anode well electrodes. This chlorine is saturating the pore fluid and reacting with the naturally occurring organic material in the shallow soil layer. This reaction is believed to be forming the trihalomethane compounds detected at the site. Mitigation steps taken to control the trihalomethane release included periodically pumping down the electrode wells and improving anode well air sparging to remove the free chlorine generated on the electrode. Subsequent sampling showed a corresponding reduction in chloroform levels in the anode wells and piezometer wells resulting from these actions. As a result of the trihalomethane production, operation of the electrokinetic system was again suspended until appropriate controls could be established to prevent trihalomethane production and regulatory approval was received to resume operations.

The VOC data also indicated that there was an increase in the vinyl chloride concentrations in some of the wells. While PCE and TCE were commonly used solvents that would be expected to be found in the lagoons due to past dumping practices, vinyl chloride would not have been used as a solvent due to its high vapor pressure and reactivity. The increase in the vinyl chloride concentration (Figure 13) is indicative of a dehalogenation process occurring at an accelerated rate during the time the electrokinetic remediation system was operating.

G.   Conclusions

Following is an assessment of each of the evaluation issues.

- The bench tests did not accurately reflect the effects that site conditions would have on the technology, specifically the retarding effects that competing ions would have on pH front development and contaminant mobility. Contaminant mobility and pH effects were ultimately observed in the field, however, the duration required for treatment in the field will be much longer than anticipated by the bench tests. Also, the bench tests did not reflect the by-product formation that was encountered in the field, specifically the hydrogen sulfide gas and trihalomethane formation. As currently designed, the bench tests do not provide an adequate means of predicting performance, duration, and efficiency or the formation of potentially hazardous by-products as a result of the technology's reaction with site-specific constituents. At best it provided an indication that contaminants would ultimately be mobilized when the technology is applied.

- The performance goal for the technology was to reduce contaminant levels to California State TTLC and STLC levels as well as to established Modified Region 9 PRGs. No contaminants were extracted during the demonstration period. Post treatment soil samples were not taken because of the poor performance. The contaminant reduction goals for the technology were not met. The contaminant reduction efficiency should be re-evaluated upon completion of ERDC's follow on fieldwork.

- Control of the electrokinetically mobilized contaminants within the confined and unconfined treatment areas could not be assessed due to the poor performance of the technology during the demonstration period. The process control zone monitoring indicates that metal contaminants were mobilized during the later stages of the system's operation. Piezometer well monitoring did not detect any pH effect or mobilized metal contaminants from the artificially confined treatment area (test cell #1) during this period. Although mobilized metals were not detected, an accurate assessment of contaminant

Pt. Mugu Site 5
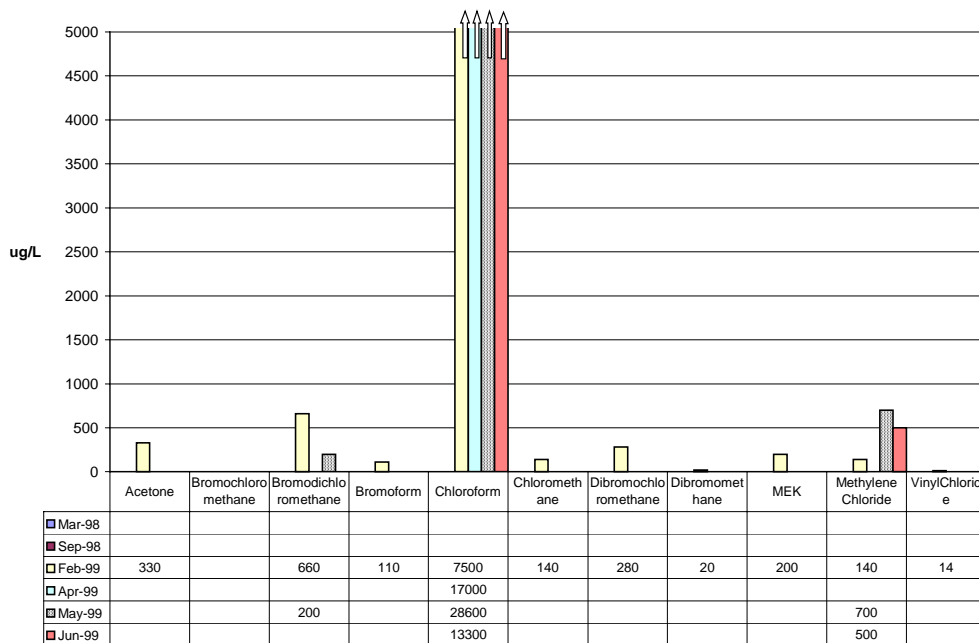**Piezometer Well (P-6)**
Data for all Rounds Tested

	Acetone	Bromochloromethane	Bromodichloromethane	Bromoform	Chloroform	Chloromethane	Dibromochloromethane	Dibromomethane	MEK	Methylene Chloride	VinylChloride
Mar-98											
Sep-98											
Feb-99	330		660	110	7500	140	280	20	200	140	14
Apr-99					17000						
May-99			200		28600					700	
Jun-99					13300					500	

Figure 11: Piezometer Well (P-6) VOC Data

Pt. Mugu Site 5
Electrode Well Data
for AW-19 for all Rounds Tested

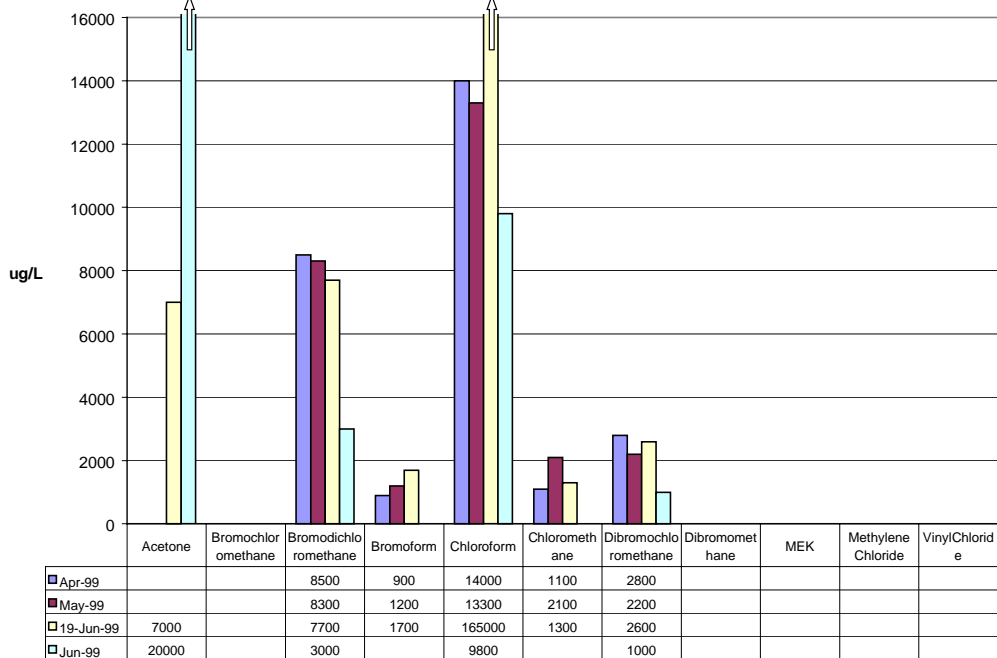|	Acetone	Bromochloromethane	Bromodichloromethane	Bromoform	Chloroform	Chloromethane	Dibromochloromethane	Dibromomethane	MEK	Methylene Chloride	VinylChloride
Apr-99			8500	900	14000	1100	2800				
May-99			8300	1200	13300	2100	2200				
19-Jun-99	7000		7700	1700	165000	1300	2600				
Jun-99	20000			3000	9800		1000				

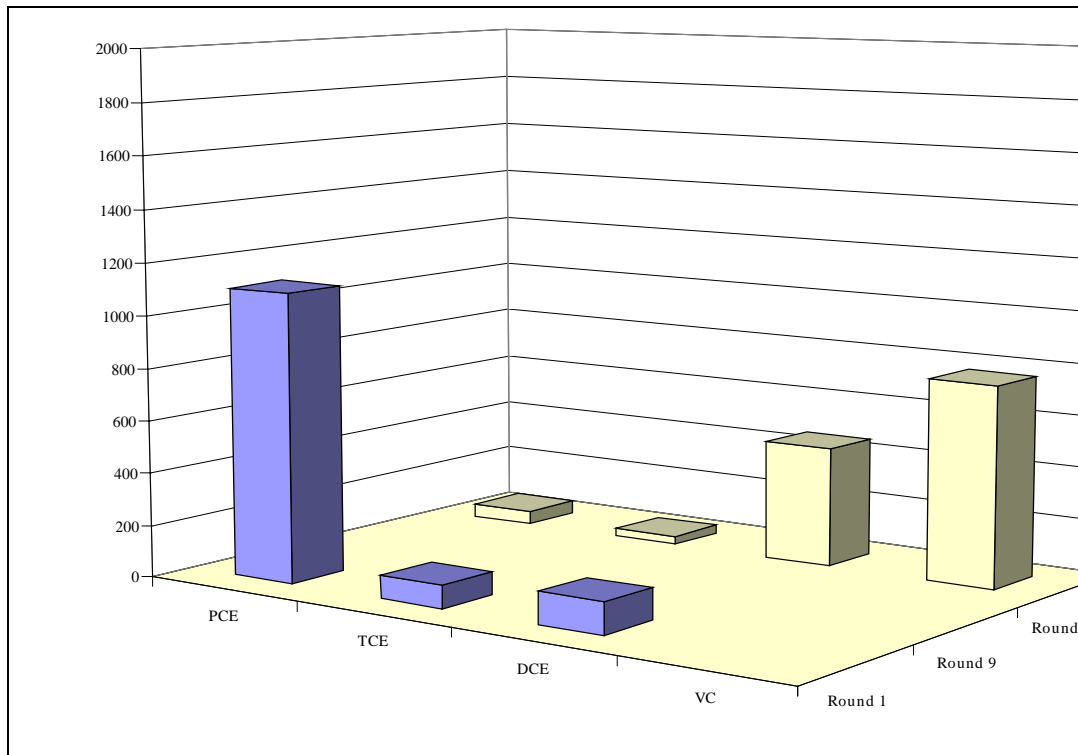**Figure 12: Anode Well (AW-19) VOC Data**

Figure 13: PCE-to-Vinyl Chloride Reduction – Piezometer P-16

mobility control cannot be made until significant treatment has occurred. No data was collected to assess the technology's ability to control contaminant movement in the uncontrolled treatment area (test cell #2) because this test cell was never activated.

- Gas emissions produced at the anode and cathode wells were chlorine, oxygen, hydrogen, and hydrogen sulfide. The gases were evacuated from the headspace of the wells and passed through a scrubber prior to release to the atmosphere. Monitoring of the scrubber discharge showed no indication of chlorine or hydrogen sulfide release.

- The technology had an impact on organic contaminants at the site. An increase in organic contaminants was detected. This was primarily a result of the trihalomethane production resulting from the chlorine buildup in the anode wells. The VOC data also indicated that there was an increase in the vinyl chloride concentrations in some of the wells. The increase in the vinyl chloride concentration is attributed to acceleration of the naturally occurring dehalogenation of PCE and TCE as a result of the electrokinetic remediation system operation.

- The site characteristic that most affected the treatment performance was the high chloride concentration of the groundwater. The chloride reactions at the anode act to retard the development of the pH front, which in turn lengthens the time required to extract the contaminants from the soil.

VI. References

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