

E-REDOX[®] TECHNOLOGY FOR REMEDIATION OF PERCHLORATE IN GROUNDWATER

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HIGHLIGHTS

- E-Redox[®] is a newly developed technology that works on the core mechanism of reductive reactions by supplying electrons directly to compounds of higher redox potentials, including perchlorate and chlorinated contaminants.
- The electrochemical reactions sustained by E-Redox[®] are independent of matrix permeability and favored by clay formation for its higher electrical conductivity.
- Both laboratory and field studies demonstrate effective reduction of perchlorate in groundwater.
- E-Redox[®] has a field ROI > 14 feet.

1. Background

1.1 *Perchlorate-contaminated Groundwater and Remediation*

Perchlorate, which tends to persist in the environment, is an anion that is highly soluble (200 g/L) and mobile in groundwater systems due to its low adsorption affinity for soil and sediments. These characteristics of perchlorate in the environment limit the type of methods and technologies that can be used for large-scale remediation of perchlorate-contaminated groundwater.

Ex situ methods for remediation of perchlorate-contaminated groundwater mostly consist of pump-and-treat systems, where perchlorate is removed from groundwater by sorbents or ion-exchange resins. Aquifer permeability limits the rate of groundwater transport, which in turn limits the rate of groundwater treatment; therefore, pump-and-treat methods are limited to sites with proper permeable groundwater lithology. Other challenges common to pump-and-treat methods include the replacement and regeneration of sorbents/resins and the occurrence of contaminant rebound.

In situ methods for the remediation of perchlorate-contaminated groundwater are chemical injections that enhance abiotic or biotic (or both) reduction of perchlorate. Some types of bacteria that exist in groundwater that can reduce perchlorate by using it as a terminal electron acceptor. In order to enhance microbial reduction of perchlorate, readily degradable electron donor compounds may be injected into the contaminant zone. Abiotic reduction may occur by manipulating subsurface oxidation-reduction (redox) properties of minerals to reduce perchlorate by using injections of sodium dithionite (or other strong chemical reductants) or zero-valent iron (ZVI) that directly reduces perchlorate. *In situ* passive treatments such as permeable reactive barriers (PRBs) often utilizes ZVI to reduce perchlorate; however, passivation of ZVI is common occurrence, which decreases the effectiveness and longevity of ZVI treatments. Contaminant zone material permeability is also a major issue that limits the distribution of injectates, both for enhancing microbial reduction or chemical reductions, and treatment effectiveness decreases with low permeable groundwater systems.

1.2 *E-Redox[®] Remediation Technology*

Electrochemical remediation technologies, such as electrokinetic remediation technologies, have been developed for overcoming the distribution issues in low permeable matrices (e.g., clay aquifers) that chemical technologies encounter. Electroremediation systems consist of at least two opposite poled electrodes (i.e., an anode and a cathode) that are inserted into a saturated matrix at a selected distance apart and a direct current is applied to generate an electric field (voltage

gradient). This electric field (as illustrated in Figure 1) extends out beyond the cross-sectional area between the electrodes; therefore, the influence of the electroremediation system may have a higher range than other remedial technologies depending on the resistivity and distance between the electrodes. Electrokinetic (EK) remediation technologies require high voltage gradients (or current densities) to induce ionic movement that occurs in a water-saturated matrix where cations migrate toward the cathode and anions migrate toward the anode. For EK remediation technologies, redox potential is often ignored since contaminants are often transported through treatment zones (subsurface zones with sorbents) or are degraded/transformed at the electrodes (often avoided due to fouling). Overall, EK remediation is limited to areas with low permeability and is energy intensive due to the high electrical power requirements; however, a lower intensity electroremediation method, namely E-Redox[®], has recently been developed and applied to enhance reduction redox reactions for contaminant reduction in the matrix within an electric field.

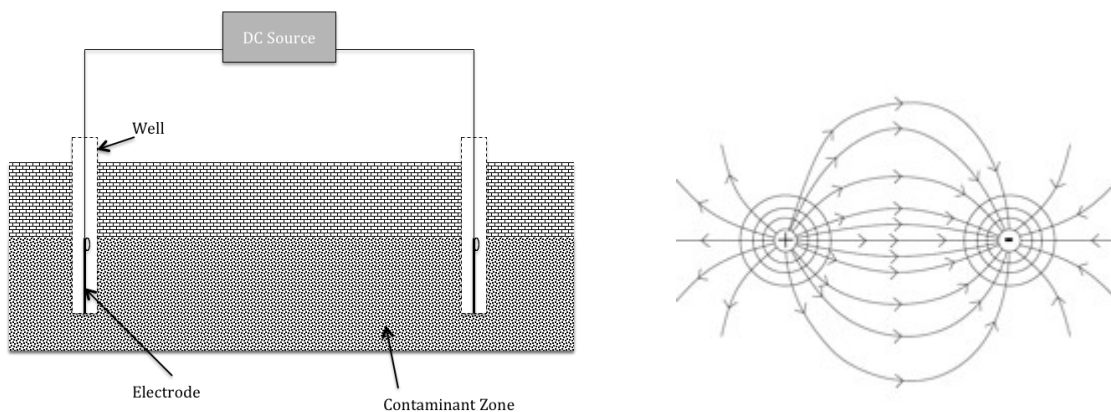


Figure 1. Example electrodes installation for *in situ* electrochemical redox manipulation (left) and a top view of the illustrative electric field (right)

Advanced Environmental Technologies, LLC (AET) has developed an electroremediation technology and service package known as E-Redox[®] that is distinguishable from other similar technologies. E-Redox[®] utilizes voltage gradients (<12 V/m) that are substantially less than EK systems and does not initiate observable ionic or contaminants movements. Redox reactions are generated by an E-Redox[®] system and occurs *in situ* within the electric field. This is where soil/sediment particles and certain compounds such as humic acids may become “micro-electrodes” and electron shuttles within the induced electric field (Rahner et al., 2002). Soil/sediment particles within the electric field may act as capacitors and continuously charge and discharge electrons where redox reactions occur at the particle surface (Figure 3). Depending on the orientation of

a neighboring particle or contaminant, it is likely that the discharging of electrons would favor reduction reactions; therefore, reducing conditions are produced within the low-potential gradient electric field and results in decreasing redox potential. E-Redox[®] technology has been tested in the laboratory and field for treating soils and groundwater impacted by different types of contaminants. For example, application of a low-voltage/low-current electric field in groundwater sediments for enhancing nitrate reduction was tested by members of the AET team (Luo et al., 2010). The test demonstrated that nitrate reduction could occur abiotically; however, the electrochemical enhancement of denitrifying bacteria substantially increased the rate of nitrate reduction. The same bacteria associated with nitrate reduction could also reduce perchlorate (Bardiya and Bae, 2011); therefore, it is likely that the application of E-Redox technology would enhance the microbial reduction of perchlorate at a contaminated site. Sections 2 and 4 present laboratory test results and field pilot test results, respectively, for enhanced perchlorate reduction in groundwater by E-Redox[®].

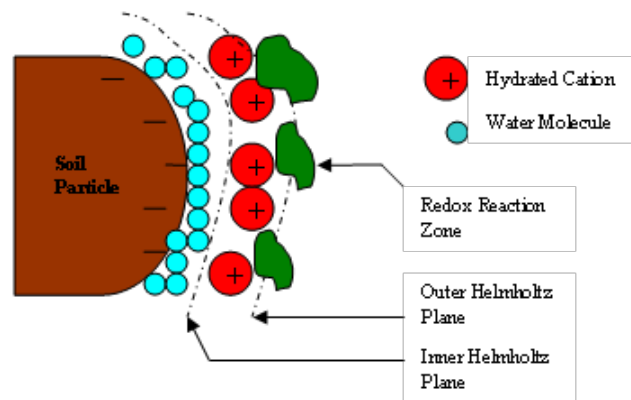


Figure 2. Redox reactions at a soil particle surface within an electric field (derived from Jin and Fallgren, 2010)

2. Laboratory E-Redox[®] Technology Tests

AET conducted two separate sets of laboratory E-Redox[®] tests to confirm that the E-Redox[®] technology can promote abiotic reduction of perchlorate in groundwater. The first set of laboratory E-Redox[®] tests were conducted by using sterile artificial groundwater spiked with sodium perchlorate. The test units shown in Figure 3 (left) utilized electrodes that were processed using the AET proprietary treatment. Direct current (DC) and alternating current (AC) sources

provided the electrical requirements for the E-Redox[®] electric field. The E-Redox[®] units were connected to the electrical sources as follows:

- 5 VDC: electrodes connected to DC power supply set at 5 volts
- 12 VDC: electrodes connected to DC power supply set at 12 volts
- 12 VAC: electrodes connected to AC power supply set at 12 volts
- 0 V: No electrical connection

Abiotic perchlorate reduction rate was the highest under the highest DC current (Figure 3, right); however, nitrate and sulfate that are present in groundwater “compete” for electrons. It is expected that when nitrate and sulfate concentrations decrease to trace levels, perchlorate reduction will dominate and the rate will increase. *This was also the first demonstration of sulfate reduction by E-Redox[®].*

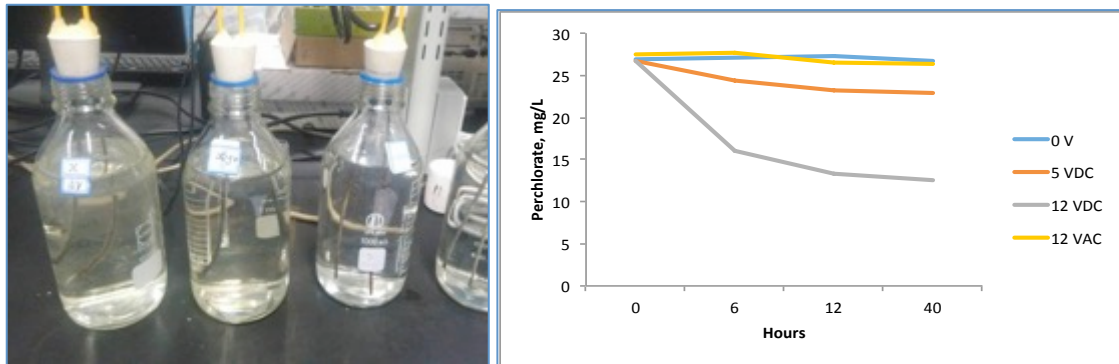


Figure 3. Laboratory E-Redox[®] system reactors and perchlorate data

3. Field Applications of E-Redox[®]

3.1 E-Redox[®] as a Passive Treatment

The E-Redox[®] technology may be applied as passive or an *in situ* barrier type treatment for plumes. Figure 4 presents a general layout of an E-Redox[®] barrier treatment of a contaminant plume that maximizes the cathodic influence, favoring reduction reactions. In this layout, the proprietary E-Redox[®] electrodes are installed into the groundwater aquifer typically at the same screening levels as the contaminant zone. Each E-Redox[®] electrode set includes two cathodes and one anode where the cathodes first intercept the contaminant plume. The induced electric fields extend out and overlap where the contaminant plume

passes and is treated through these electric fields, reducing contaminants. E-Redox[®] electrodes are connected to a DC power supply within a shelter where the electric field intensity is controlled. The actual layout and number of E-Redox[®] sets depends on site specific factors such as power accessibility, site accessibility and barriers, available wells and feasibility of installation of new wells, contaminant plume size, groundwater flow direction and velocity, and groundwater water matrix conductivity.

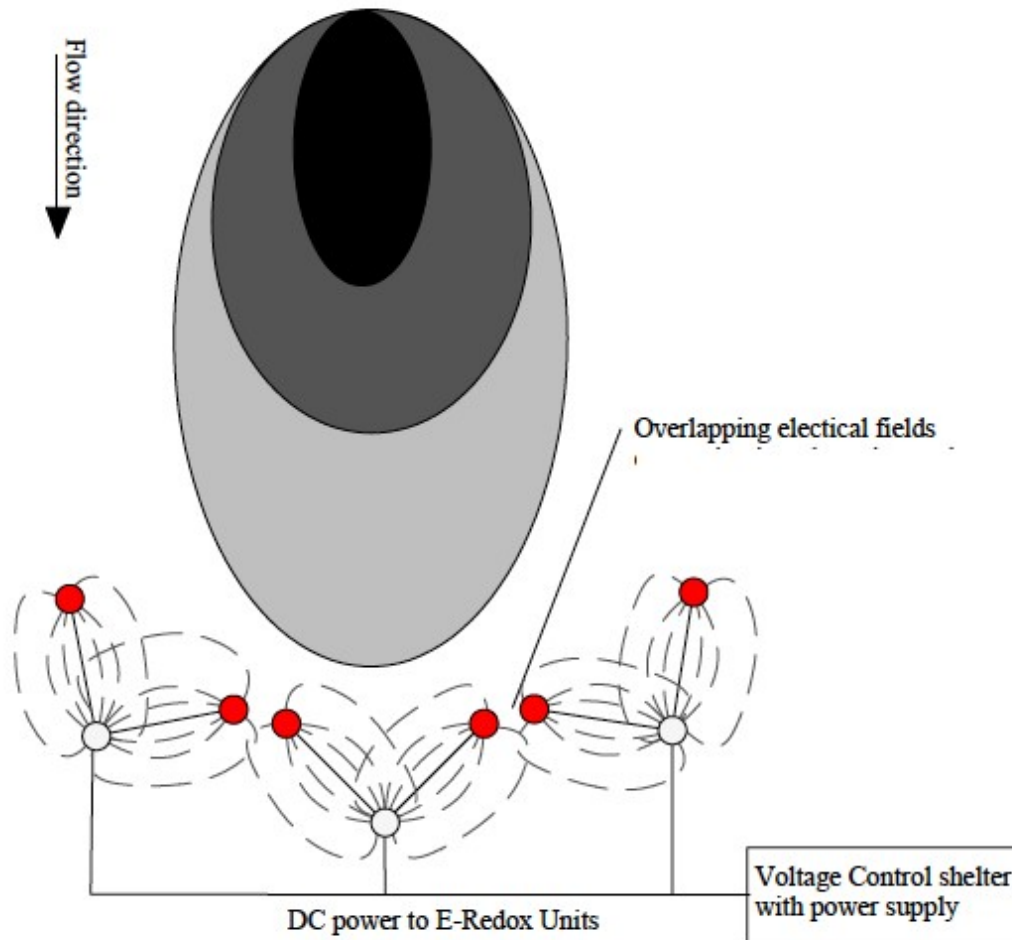


Figure 4. E-Redox[®] system layout for treatment of a contaminant plume

3.2 E-Redox[®] as a Source Treatment

E-Redox[®] technology may be applied as a source area treatment. Figure 5 presents a general layout for an E-Redox[®] system treating a contaminant source

area, which maximizes the cathodic influence that favors reduction reactions within the source area. In this layout, the proprietary E-Redox[®] electrodes are installed into the groundwater aquifer at the same screening levels as the contaminant zone. Each E-Redox[®] electrode set includes two cathodes and one anode: the cathodes are inserted into the source area and anodes outside the source area. The induced electric fields extend out and overlap, “covering” the contaminant source area where contaminants are reduced. E-Redox[®] electrodes are connected to a DC power supply within a shelter where the electric field intensity is controlled. The actual layout and number of E-Redox[®] sets depends on site specific factors such as power accessibility, site accessibility and barriers, available wells and feasibility of installation of new wells, contaminant plume size, groundwater flow direction and velocity, and groundwater water matrix conductivity.

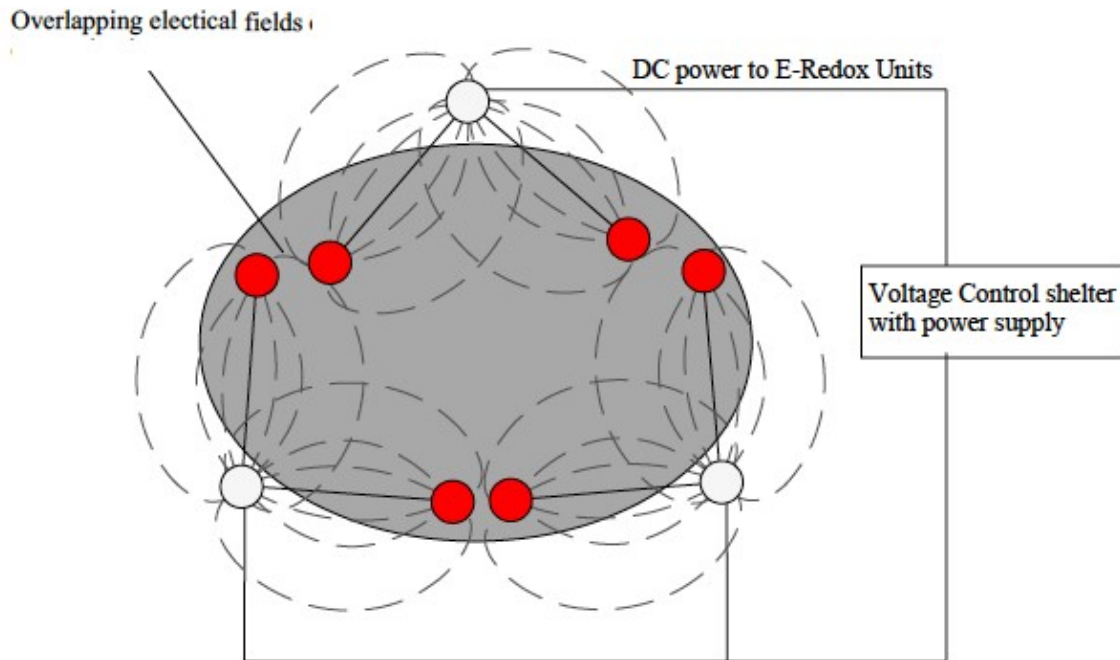


Figure 5. E-Redox[®] system layout for source area treatment

3.3 Integration of E-Redox[®] with Other Remediation Technologies

E-Redox[®] may be utilized as a stand-alone remedy for treating contaminated matrices; however, E-Redox[®] can also be easily integrated with other treatment

technologies (Note: see the conflicts of interest statement in section 3.5 concerning integration of E-Redox[®] with other technologies). Developmental work on E-Redox[®] technology has demonstrated that it can simultaneously enhance contaminant reduction and restore passivated ZVI (Chen et al., 2012; Luo et al., 2010; Zhang et al., 2016); therefore, E-Redox[®] technology can be integrated with most PRB technologies. Since low-intensity electric fields can enhance microbial activity (Thrash and Coates, 2008; Jin and Fallgren, 2014), which E-Redox[®] has demonstrated through the enhancement of microbial reduction of oxyanionic contaminants, it can be applied in conjunction with *in situ* bioremediation or bio-barrier technologies to enhance both abiotic and biotic reduction of contaminants.

Activated carbon injectates are adsorption-based *in situ* remediation technologies that have recently been applied to contaminated sites. Activated carbon injectate technologies immobilize contaminants *in situ* and it is expected that contaminants may be degraded or reduced to innocuous compounds or ions, resulting in the regeneration of adsorption sites. However, contaminant reduction tends to be too slow and contaminant breakthrough occurs. E-Redox[®] technology may be used in conjunction with activated carbon injectates to enhance their regeneration by enhancing adsorbed contaminant reduction.

3.4 Pilot Tests/Demonstrations

Prior to a full-scale implementation of E-Redox[®] technology, it is recommended that pilot-scale tests be conducted. A typical E-Redox[®] pilot test or demonstration utilizes two to four existing wells (or new wells if necessary) and is conducted in a source area or down-plume. The pilot test/demonstration can be conducted for three to six months. Results from the pilot tests provide the basis to appropriately expand to a full-scale implementation of E-Redox[®] technology.

3.5 Conflicts of Interest Statement

E-Redox[®] technologies are patented, trademarked, and fully-owned by Advanced Environmental Technologies, LLC (AET); therefore, when conducted or supervised by AET, there are no conflicts of interest for the sole application of E-Redox[®] technology and service for enhancing groundwater remediation. If E-Redox[®] is to be integrated or used in conjunction with other technologies, the project owner is responsible for determining any conflicts of interest.

4. Case Study: E-Redox[®] Field Pilot Test

4.1 Site Background

The E-Redox[®] field pilot test was conducted at a confidential location in Riverside County, California. The site is a former industrial testing area for propellants and explosives, where early soil and groundwater analyses indicated the presence of contaminants associated with propellants and explosives such as perchlorate. The groundwater aquifer material is primarily composed of sandstone with mudstone lenses. Perchlorate (and other contaminants) have persisted in the groundwater at the site, where past remediation efforts failed to reduce contaminant concentrations due to the low-permeability of the aquifer material. The E-Redox[®] pilot test system was installed within a high-contaminant concentration plume.

4.2 E-Redox[®] Pilot System Implementation

The E-Redox[®] pilot test site was conducted in a remote location without access to the power grid; therefore, solar power was utilized as the electrical source. The pilot test area consisted of four wells of interest (see Figure 6), where two wells were selected as electrode wells (I and IV) and the other two wells were selected as monitoring wells (II and III). The electrode wells were selected based on spacing, well diameter, casing material (PVC), and screening levels. The spacing between electrode wells I and IV was measured to be 29.5 feet. After the installation of the E-Redox electrodes, six solar panels were mounted and raised over 6 feet above the ground surface and were connected to deep-cycle batteries for recharging (Figure 7). The electrodes were connected to the batteries, where well I was initially the anode well and well IV was initially the cathode well. Electrical parameters were measured at the electrode wells utilizing a multi-meter.

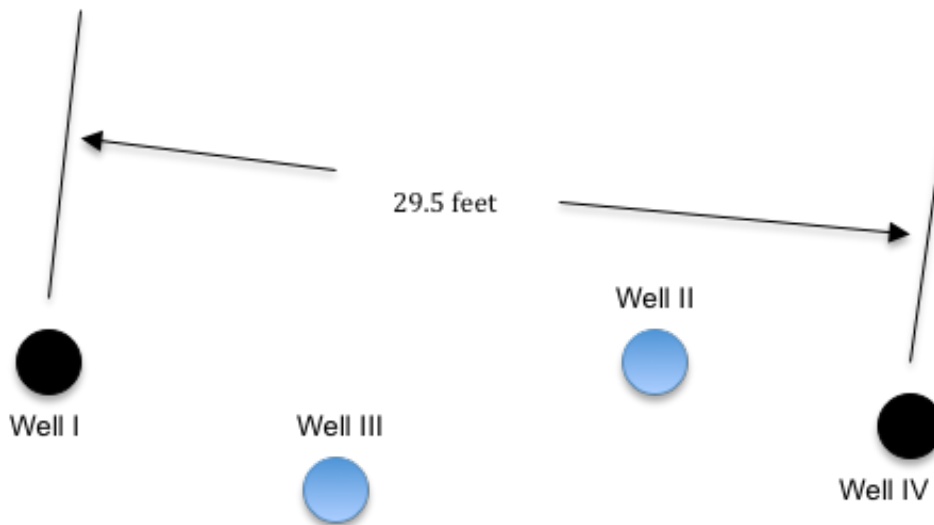


Figure 6. E-Redox[®] pilot test site layout



Figure 7. Solar panels as power source for E-Redox[®] pilot system and monitoring of electrical parameters

4.3 E-Redox[®] Pilot Test Results

The first month of operation was conducted under unstable electric field intensities due to issues with solar panels and control equipment. This resulted in no decrease in perchlorate concentrations in any of the pilot test area wells. After switching polarities (i.e., well I was switched to being the cathode well and well IV was switched to being the anode well) and partial equipment repair, a stable low-intensity electric field was maintained for 98 days. No decrease in perchlorate concentration was observed at the anode well IV and the closest monitoring well II; however, as shown in Figure 8, perchlorate concentrations decreased substantially in the cathode well I and the adjacent monitoring well III (14.3 feet from the well I). The perchlorate reduction rates were determined to be 1245 and 174 $\mu\text{g/L/day}$ in wells I (cathode well) and III, respectively.

The polarities of the electrodes were switched back after 98 days (i.e., well I was switched back to being the anode well and well IV was switched back to being the cathode well). E-Redox[®] was allowed run an additional 36 days before completion of the pilot test. As with the previous 98-day run, the final 36-day run showed that the wells under cathodic influence (i.e., wells IV and II) resulted in decreases in substantial perchlorate reduction while no decreases were observed in wells under anodic influence (see Figure 9). The cathode well IV yielded a 1247 $\mu\text{g/L/day}$ perchlorate reduction rate and the adjacent monitoring well II (7.1 feet from well IV) yielded a reduction rate of 755 $\mu\text{g/L/day}$. Overall, the results indicated that E-Redox[®] technology can enhance *in situ* perchlorate reduction while inducing a stable low-intensity electric field within the influence of the cathode.

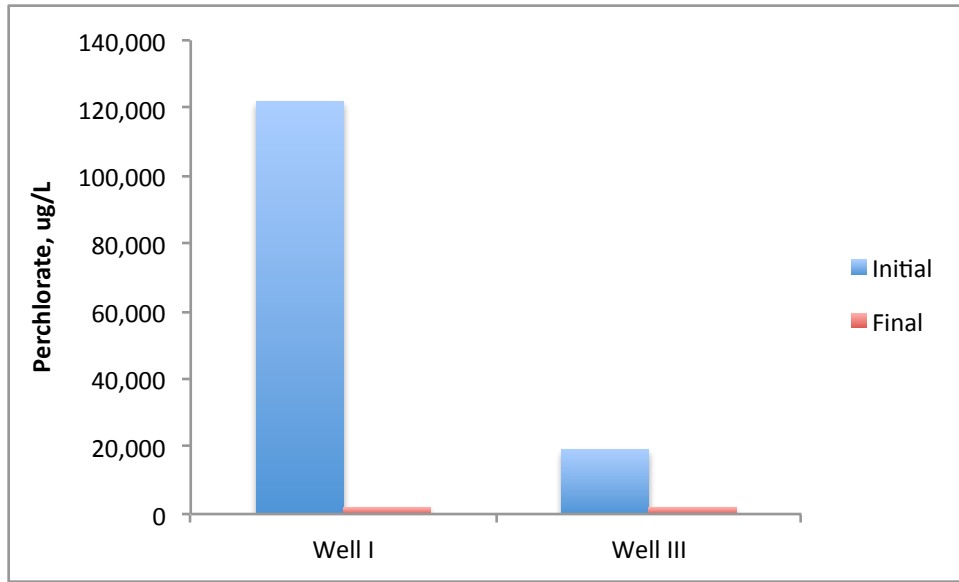


Figure 8. Perchlorate concentrations after 98 days within the cathodic ROI (Well I was the cathodic well)

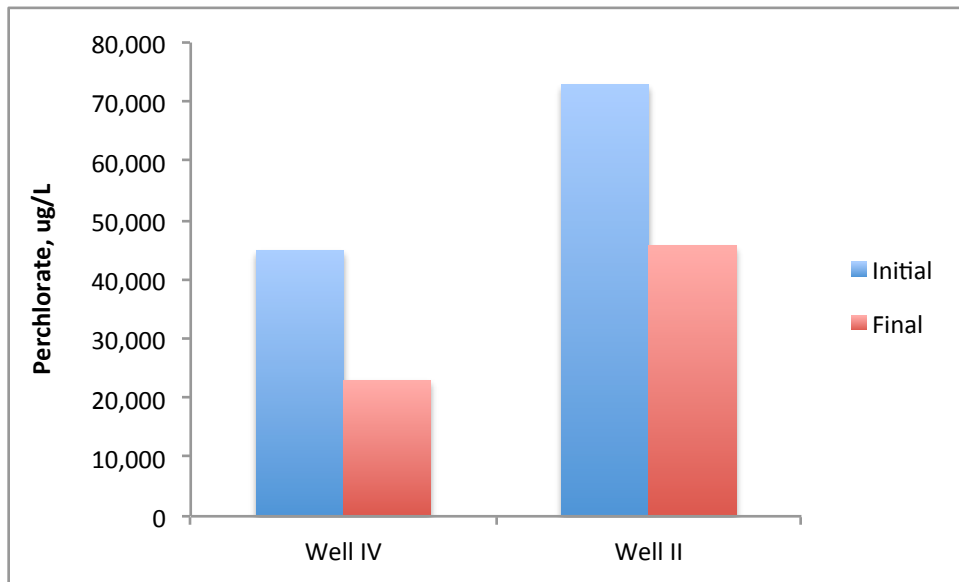


Figure 9. Perchlorate concentrations after 36 days within the cathodic ROI (Well IV was the cathodic well)

4.4 E-Redox[®] Pilot Test Conclusions

- Enhanced perchlorate reduction sustained during the pilot period within a stable low-intensity electric fields. This reaction is independent of matrix permeability and favored by clay formations
- Higher perchlorate reduction rates occur in areas surrounding the cathode (i.e., within the cathode radius of influence of > 14 feet)
- E-Redox[®] implementation includes a package of hardware and installation. The operation of E-Redox[®] systems requires minimum O&M and the monitoring electrical parameters are non-intrusive and convenient

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