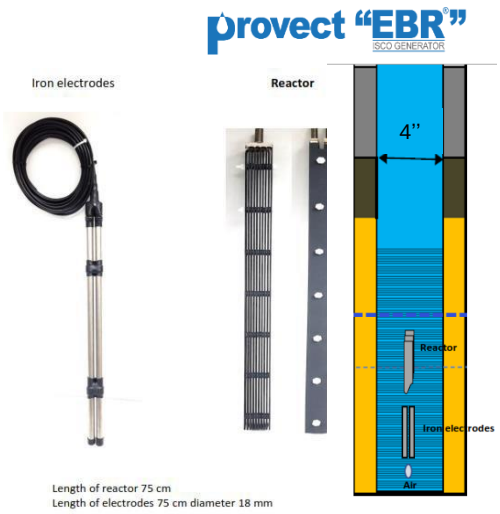
# PROVECT-"EBR®"
# *IN SITU* GENERATOR OF REACTIVE OXIDANTS

## TECHNOLOGY DESCRIPTION

EBR® (US patent 9,975,156 B2) is a subsurface, electrokinetic system that continually generates within a reactor well (see inset) Fenton's-like reagents and dissolved oxygen in a controlled manner, at neutral pH, and without the addition of exogenous chemicals. These colloidal (nanoscale) catalytic and reactive reagents are uniquely propagated via multiple mechanisms outside of the reactor wells (spaced *ca*. 4 to 8 m apart) into the aquifer. Provect-"EBR®" is a field-proven system that effectively integrates ISCO, microbiological, and geophysical mechanisms to treated contaminated aquifers.



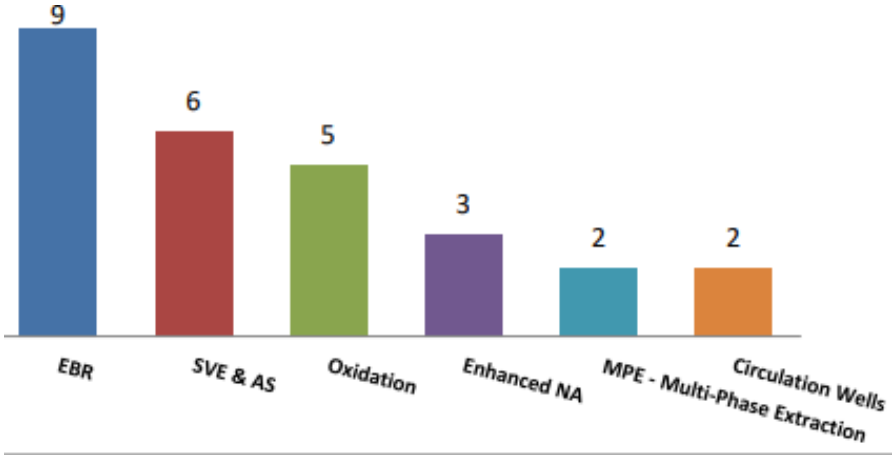

Targeted constituents of interest (COIs) are destroyed via multiple oxidation reactions and accelerated biodegradation using oxygen and iron as the preferred electron acceptors. Accordingly, the technology has been used to rapidly mineralize chlorinated solvents, petroleum hydrocarbons and MTBE. It has near-future applications for perchlorate, 1,4-dioxane, pharmaceuticals and - potentially - other challenging contaminants such as fluorinated compounds.

The treatment systems are monitored real-time and controlled/adjusted remotely via a dashboard interface. The software will also compile data, generate reports, and issue programmed alarms. As such, the technology is a cost-effective, low-profile full remediation system for the rapid mineralization of various organic COIs present in aquifer media.

## TECHNOLOGY APPLICATIONS

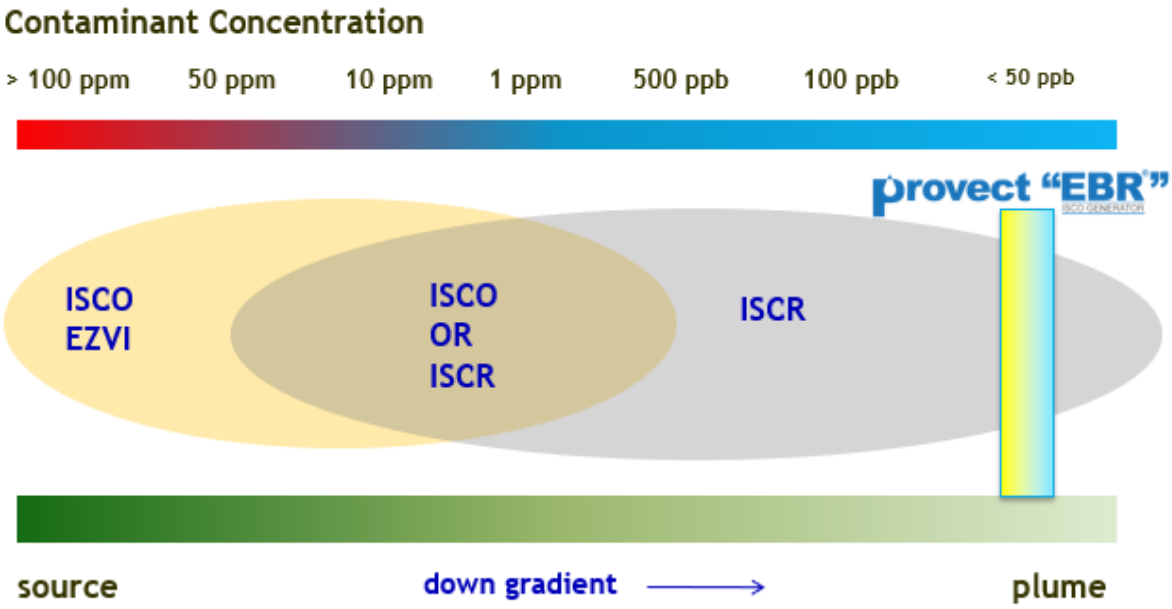
**Source Treatment**. The Provect-"EBR®" technology has been successfully used at multiple sites to treat chlorinated solvents (PCE, TCE, DCE, VC), gasoline (BTEX) and MTBE. It is presently the fastest growing and most commonly used remedial technology in Israel having been applied to 9 of the 27 active remediation projects in 2017 (**Figure 1**). Many of these sites have entered post-treatment monitoring (2 years) and several have received clean closure certification.

**Figure 1:** EBR® is the Most Commonly Used *In Situ* Remediation Technology in Israel




**<u>ISCO PRB technology</u>**. The Provect-"EBR®" technology is an ISO-certified (certificate no. 98261) *in situ* soil and groundwater remediation system that operates continuously over a long term (many years) and can be sustainable (low energy requirements; potentially solar). It therefore represents an **effective ISCO Permeable Reactive Barrier (PRB) technology** (**Figure 2**). As such it can address (via destruction and not just transient sorption to GAC, biochars, etc.) a variety of COIs commonly found in large dilute plumes of chlorinated solvents, MTBE, TBA, 1,4-dioxane, perchlorate, etc.

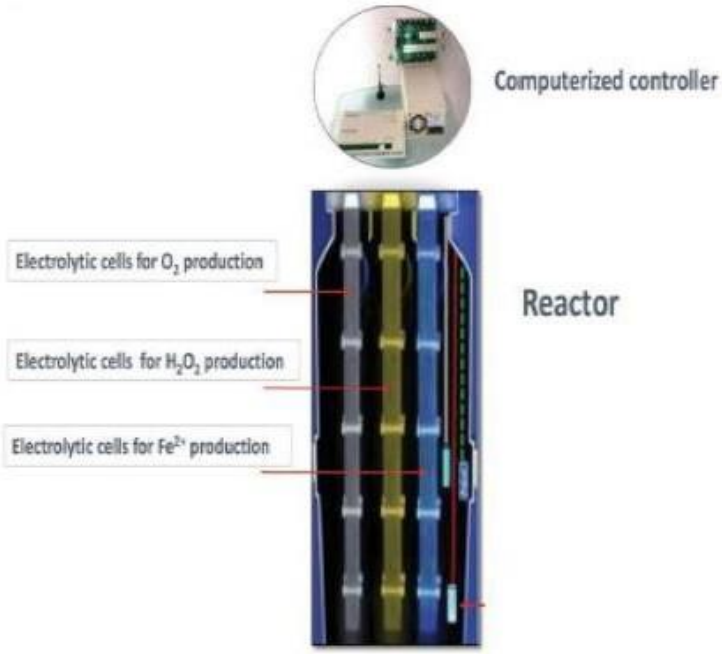
**Figure 2:** Conceptualized Application of Provect-"EBR®" technology as an Effective ISCO PRB



## EBR® MODE OF ACTION

In the simplest terms, EBR® is an *in situ* ISCO generator. Under variable electrical fields the system employs catalytic electrodes to continuously generate molecular oxygen from water while releasing iron cations via forced corrosion of neighboring installed iron electrodes. This creates reactive oxidant species (ROS) such as hydrogen peroxide ($H_2O_2$), superoxide ($O_2\cdot$), hydroxyl radicals (OH·), ferrate ($Fe^{4+}$, $Fe^{5+}$ and/or $Fe^{6+}$) along with low Fermi Level (oxidized) ferrous oxyhydroxides (**Figure 3**). Multiple forces described below induce subsurface movement of these oxidants along with colloidal (nanoscale) ferrous oxyhydroxides (elevated Fermi level energy level) particles to distribute these reactants throughout the effective ROI. As these reactants migrate throughout the formation and the ferrous (hydro)oxides within the aquifer they equilibrate their Fermi level electrochemical potentials to continuously catalyze *in situ* generation of new oxidizing species which subsequently destroy contaminants via chemical oxidation. Residual oxygen and iron serve as electron acceptors to sustain enhanced biodegradation of COI residuals.

**Figure 3:** Conceptualized Provect-"EBR®" ISCO Generator Reactor Well




| Oxidation Potentials | Volts |
|---|---|
| Fluorine ($F_2$) | 2.87 |
| Hydroxyl radical (OH•) | 2.80 |
| Persulfate radical ($SO_4$•) | 2.60 |
| Ferrate ($Fe^{+6}$) | 2.20 |
| Ozone ($O_3$) | 2.08 |
| Persulfate ($S_2O_8^{-2}$) | 2.01 |
| Hydrogen peroxide ($H_2O_2$) | 1.78 |
| Permanganate ($MnO_4^-$) | 1.68 |
| Chlorine ($Cl_2$) | 1.49 |

**Overview of Conventional Electrokinetic Technologies.**

The EBR® technology has potential to completely mineralize a wide range of COIs and differs from other electrokinetic systems or electrochemical systems as follows (see Zhang *et al.,* 2018):

- Conventional electrokinetic (EK) approaches use an oxidizing anode (Equation 1) and a reducing cathode (Equation 2) to apply direct current to subsurface media and induce COI migration via electroosmosis, electromigration and electrophoresis, but it has limited direct effect on actual COI destruction (US DOE, 1996).

  (Acidic) Oxidation Reaction at Anode: $H_2O + 4\,e \text{---->} O_2 + 4H^+$ (Eg 1)
  (Basic) Reduction Reaction at Cathode: $H_2O + 4\,e \text{---->} H_2 + OH^-$ (Eg 2)

- Conventional electrochemical remediation systems are usually limited to electrochemical degradation mechanisms within a well and COIs are primarily degraded on the interface of the electrochemical reactor. Here, direct electrochemical reduction involves the direct transfer of an electron from the cathode to a COI on the cathode surface yielding dehalogenated intermediates, while indirect electrochemical reduction results from dehydrohalogenation reactions catalyzed by reductive atomic hydrogen generated by the cathode. Conversely, direct electrochemical oxidation involves the exchange of electrons between the anode and the COI on the anode surface: while indirect oxidation of COIs results from their interaction with oxygen and ROS generated (Acar *et al.,* 1993).

- Electrokinetic bioremediation systems can generate hydrogen via water electrolysis and organic carbon electron donors via $CO_2$ reduction and perhaps other sources to help drive anaerobic bioremediation processes. But as such the "e-barriers" are limited to enhanced reductive bioremediation processes, and performance can be influenced by microbiological variables (Gill *et al.,* 2014; Hassan *et al.,* 2016; US EPA, 2007).

- Electro-Fenton's (EF) systems (Rosales, *et.al,* 2012; Sires *et al*., 2014) generate molecular oxygen with one electrochemical cell while another drives two-electron reduction of oxygen on the cathode surface to generate $H_2O_2$ which interacts with ferrous iron ($Fe^{2+}$) released from a third cell to yield reactive oxidants including $OH^{\cdot}$ and $O_2^{\cdot}$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^-$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+$$

**How is EBR Different from Other EK Technologies?**

The EBR reactor has significant differences when compared to conventional EF and other EK technologies.

- EBR Generates Oxidants at Neutral pH: Conventional EF systems employ Fenton's chemistry, which is strongly pH dependent reactions. Accordingly, for oxidants to be generated spontaneously (in thermodynamic representation) at some reasonable rate within an aquifer, an acidic environment (pH <3) is required throughout. This is a main obstacle (rate limiting factor) in applying EF (and conventional Fenton's chemistries) for *in situ* groundwater remediation. The EBR system overcomes this energetic obstacle (by using physics of Fermi level equilibrium as discussed next) to generate Fenton-like reactions in a neutral aqueous medium, at effective rates.

- EBR Generates Reactive Ferrate: When $Fe^{3+}$ ions colloid with $OH^{\cdot}$ (and perhaps $O_2^{\cdot}$) radicals they yield reactive ferrates (Equation 3), along with the low Fermi level Fe-cluster nanoparticles. These are additional oxidants that can help degrade COIs.

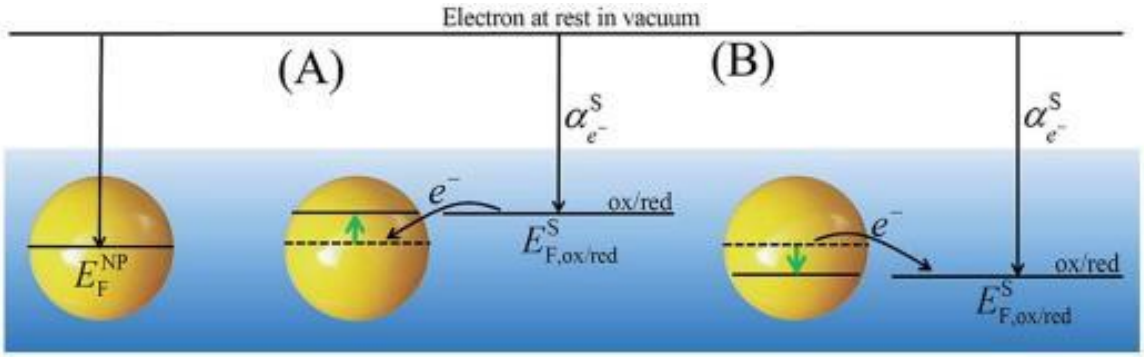
$$OH\bullet + Fe^{+3} \text{ ---> } Fe^{(+4 \text{ to} +6)} + OH^{-} \qquad \text{(Eq. 3)}$$

- EBR Continuously Generates Oxidants *In Situ*: Hydrogen peroxide ($H_2O_2$), superoxide ($O_2^{\cdot}$), hydroxyl radicals ($OH^{\cdot}$) have very limited environmental half-lives (10E-9 to 10E-6 seconds). Hence, they need to be continuously generated throughout the treated aquifer for targeted COIs to be oxidized / mineralized within an effective PRB system. The EBR accomplishes this via activation of molecular oxygen on the Fe-cluster nanoparticles catalyzed by Fermi level equilibration of their electrochemical potentials.

- EBR Drives Fermi Level Equilibration which is Self-Propagating: As $Fe^{2+}$ ions are continuously released from an iron core (iron electrodes installed within EBR well) in the presence of powerful oxidants including $H_2O_2$, $O_2^{\cdot}$ and $OH^{\cdot}$ the Fermi level equilibrium of these oxidized particles is lowered (Ai, 2013). Within the EBR well, air is introduced to facilitate formation of nanoparticles that are then released into the formation. The difference between the Fermi level energies of Fe colloids (> 2 nm particle size) within the well and those in the aquifer creates an inducing flux that drives the oxidized, higher energy, lower Fermi level particles away from the EBR well as they seek equilibrium with neighboring particles (Scanlon *et al.,* 2015). Multiple forces (described below) induce subsurface movement of these oxidants along with colloidal (nanoscale) ferrous oxyhydroxides ("high energy", low Fermi level) particles to distribute these reactants throughout the effective ROI [point of reference, at Oxidation-Reduction Potential (ORP) +850mV - meaning lowering Fermi levels - there is a very high availability of free electrons]. As these reactants migrate throughout the formation and the ferrous

(hydro)oxides within the aquifer equilibrate their Fermi level electrochemical potentials (as summarized in **Figure 4**) they continuously catalyze *in situ* generation of new oxidizing species which subsequently destroy contaminants via chemical oxidation (Peljo, *et al*., 2017).

**Figure 4:** Fermi Level Equilibration of Electrochemical Potentials (Scanlon et al., 2015)




**Scheme 3** Redox equilibria for metallic NPs in solution showing the capabilities of metallic NPs to be (A) charged and (B) discharged upon Fermi level equilibration with an excess of a single dominant redox couple in solution.

In other words, the EBR emanates ferrous (hydro)oxides colloids/nanoparticles with lower Fermi Levels that allows exceptional reducing abilities that get distributed throughout the aquifer system to catalyze the continuous, *in situ* generation of Fenton's oxidants within the aquifer itself via two kinds of molecular oxygen activation pathways (Ai *et al*., 2013). One, this can occur on the Fe core where the more rapid two-electron-reduction molecular oxygen activation process may eventually be blocked by the formation of iron oxide coatings. But then the surface bound ferrous ions will also catalyze the single-electron-reduction molecular oxygen activation pathway to continuously generate reactive oxidants. These same activation processes are driven by the Fermi level equilibrium energy exchanges between the distributed ferrous (hydro)oxides colloids and directly by high redox potential in the aqueous medium. Hence, The EBR system overcomes the energetic obstacle (by using physics of Fermi level equilibrium as reviewed by Ai *et al,* 2013; Peljo *et al*., 2017) to generate Fenton-like reactions, throughout the aquifer, in a pH-neutral aqueous medium, and at effective rates.

***In situ* propagation of ROS is an important differentiator between EBR technology/ISCO PRB concept and other related (bio)electrochemical / electro-Fenton's technologies**. Lowered Fermi level and surface activation of oxygen due to induced ORP of the aqueous medium, and $Fe^{+2}$ adsorption mechanism on the interfaces is a well-known activation mechanism. Available solid matrix electrons participate in these electrochemical reactions on the adsorptive surfaces and electronic conduction along the interfaces all take place within the aqueous medium itself, enforcing oxygen activation mechanisms within the aquifer for sustained production of ROS. And self-induced electro-redox current densities (multiple induced constant redox fronts) account for the electrochemical reactions of oxygen activation.

**How Does EBR Enhance Subsurface Reactions between COI and Oxidants?**

Having generated multiple oxidants and catalytic, high-Fermi level Fe-cluster nanoparticles within the EBR well the challenges now become: i) subsurface distribution of reagents, both vertically and horizontally, and ii) longevity, or managing the reactivity of short-lived oxidants.

Subsurface Distribution of Reagents: In addition to the natural dispersion and advection forces, conventional EK and Electro-Fenton's systems rely on electroosmosis, electromigration and electrophoresis to induce subsurface movement of COIs, reagents, nutrients and microorganisms. Hence, the effective radius of influence (ROI) is often limited, and the ISCO reactions *per se* are not actively propagated throughout the aquifer (Acar *et al.,* 1993; Hassan*, et al*., 2016).

- With the EBR system electroosmosis between coupled EBR wells induces groundwater flow yielding a larger treatment zone. This is especially apparent in fine-grained, low-permeability materials that typically harbor sorbed residuals because electrokinetics enhances the mobilization and therefore the availability of the contaminants.

- With the EBR system the ROI is increased by imposing an effective constant flux across the well interface due to boundary condition effects and high chemical potential. Here, the reactor wells continuously generate Fenton's-like reagents *in situ* within a reactor well for an extended period (years). This creates a redox front that drives subsurface distribution away from the well itself (Revil *et al.,* 2009).

- Coupled electrokinetic force is generated by applying voltage or current density between EBR wells. The ferrous (hydro)oxides generated by the EBR and introduced into the water are the electronic conductors / nanowires within the aqueous medium (Ai *et al.,* 2013) along with "biogeobattery" agglomerates (Revil *et al.,* 2010).

- However, electrokinetic coupling alone does not account for the redox fronts (Revil *et al*., 2009). Rather, excess (dominant) redox couples (*i.e.,* constant generation of high energy,

Fermi-level ferrous (hydro)oxide nanoparticles) introduced by the EBR into the aqueous medium generates the driving force redox fronts.

***Hence, ability to manage electronic conductivity within the aqueous medium and redox fronts are critical, unique features of the EBR system (US Patent Office, 2018)*.**

Managing Longevity of Reactive Agents: Once introduced into a groundwater environment, active oxidants such as $H_2O_2$, $O_2^{\cdot}$ and $OH^{\cdot}$ do not persist long (half-lives 10E-9 to 10E-6 sec). As such, under conventional conditions these reactive oxidants do not emanate far beyond their source of production (which is a significant limitation to convention EF technologies and conventional ISCO technologies that rely on Fenton' chemistries). Therefore, a critical and unique feature of the EBR system centers around its ability to propagate these reactions and continuously generate reactive oxidants throughout its effective ROI. This is accomplished by various mechanism including induced redox fronts, electro-redox current densities, and equilibration of differences in Fermi level energies, the latter being self-generated and self-propagated.

- Electrokinetic coupling as discussed above aids in reactant distribution, but it also facilitates molecular oxygen activation reactions on the ferrous (hydro)oxides interfaces of nanoparticles distributed throughout the aquifer. This can be a supplementary site activation mechanism that should only be employed in situations where sensitive infrastructure is not present (and in consultation with a cathodic protection engineer**).**

- More importantly, ferrous (hydro)oxides generated by the EBR and introduced into the water serve as electronic conductors / nanowires within the aqueous medium that can continuously activate molecular oxygen via one- and two-electron reduction reactions (Ai *et al.,* 2013).

- The subsurface distribution of high energy Fermi level ferrous (hydro)oxides colloids and nanoparticles throughout the aquifer system catalyze the continuous, *in situ* generation of Fenton's oxidants are generated within the aquifer itself via two kinds of molecular oxygen activation pathways. These can occur on the Fe core (Ai, 2013), where the more rapid two-electron reduction molecular oxygen activation process my eventually be blocked by the formation of iron oxide coatings. But then the surface bound ferrous ions will catalyze the single-electron reduction molecular oxygen activation pathway to continuously generate reactive oxidants. These same activation processes are driven by the Fermi level equilibrium energy exchanges between the distributed ferrous (hydro)oxides colloids and directly by high redox potential in the aqueous medium (US Patent 2018).

**Effective Radius of Influence / EBR Well Spacing:**

In summary, the effective, cross-gradient ROI of an EBR well will be influenced by site specific lithology and hydrogeology but will typically range between 2 and 4 meters. As such, EBR wells are typically spaced between 4 and 8 m apart. In the field, effective ROI can be validated by measurement of multiple field parameters in (nested) piezometers or monitoring wells located at defined distances from an EBR system (**Table 1**).

**Table 1.** Measurement of Groundwater Field Parameters to Validate Effective ROI.

| Parameter | Expected Result within ROI |
|---|---|
| DO | Elevated readings, can be as high as 8 mg/L |
| ORP | Elevated readings, can be as high as +1000 mV |
| Turbidity | Elevated from baseline due to presence of Fe particles |
| pH | Slightly elevated from baseline, depending on buffering |
| Conductivity | Elevated from baseline due to presence of suspended particles |
| Fe | Elevated from baseline due to presence of suspended particles |

**SECONDARY ATTENUATION PROCESS (Biologically Mediated):**

The EBR technology enhances secondary bioremediation processes to manage COI rebound. Here, bacterial distribution throughout an aquifer is often overlooked. But soil bacteria are like a colloid - with a surface charge – and are therefore also subjected to dynamics influenced by the effect of an applied electric field.

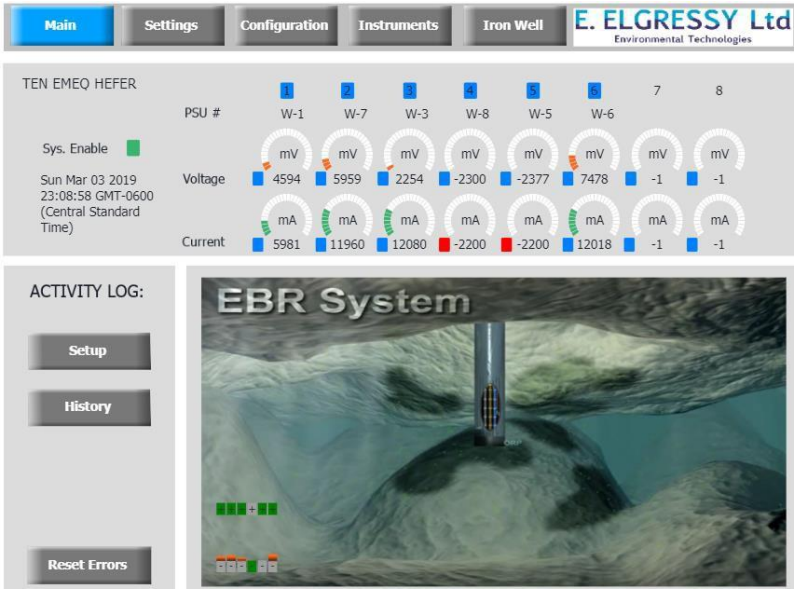
1) Oxygen: Throughout the aquifer, reduction of dissolved superoxide $O_2^{\cdot}$ by oxidized ferric Fe(3+) colloids and floating (nano)particles yields oxygen and hydrogen. Oxygen is a preferred electron acceptor for the rapid biodegradation of many organic compounds. Stoichiometrically, the basic reactions for the mineralization of benzene are:

$$C_6H_6 + 7.5\ O_2 + 3\ H_2O \text{ --> } 6\ H^+ + 6\ HCO_3^- \quad \text{yields -3173 kJ/mol}$$

2) Ferric Iron: Ferric iron is also used as an electron acceptor for the biodegradation of many contaminants, sometimes in conjunction with sulfate. During this process, ferric iron is reduced to ferrous iron, which is soluble in water. Degradation intermediates generated during pollutant oxidation may act as electron shuttles, allowing the reduction of Fe(III) to Fe(II) in the redox cycling of iron and continued activation. As an example, Stoichiometrically, the degradation of 1 mg/L of BTEX results in the average consumption of approximately 22 mg/L of ferric iron (or "production" of ferrous iron) as shown below.

$$C_6H_6 + 18\ H_2O + 30\ Fe^{3+} \text{ --> } 6\ HCO_3^- + 30\ Fe^{2+} + 36\ H^+ \quad \text{yields -30703 kJ/mol}$$

## INTEGRATED REAL-TIME MONITORING AND REMOTE SYSEM OPERATIONS




A computerized controller with proprietary software regulates the operation of the three electrochemical cells within each EBR reactor to allow dynamic control over the integrated processes *e.g.*, ISCO generator and distribution of reagents for enhanced bioremediation (US Patent Office, 2018). The system begins by collecting data on groundwater ORP, current density, conductivity, pH and temperature. Once established, molecular oxygen and H2O2 are produced electrocatalytically which react with dissolved iron ions. Dissolved air is introduced to agglomerate the nanoparticles. The data are measured continuously and distributed via wireless communication to a secure server were data can be reviewed and the reactor system operations can be adjusted (see inset).

## SUMMARY OF FEATURES:

The combination of ISCO generator and secondary bioremediation with subsurface distribution provides for long-term oxidant release that may represents a more practical ISCO PRB strategy. Other potential benefits and attributes are summarized below:

- Rapid Contaminant Destruction: ISCO reactions rapidly mineralize targeted COIs, as opposed to simply sequestering them on sorptive media.

- Effective: Promotes multiple oxidation reactions and bioremediation of a wide-range of organic contaminants for an extended time s. Also provides a unique microbiological component for multiple accelerated attenuation processes.
- Cost Efficient: Low capital cost, small footprint, minimal energy consumption (solar), low density current, low maintenance and no external chemical requirements.
- Sustained Secondary Bioremediation: Enhanced bioremediation processes use oxygen and iron as electron acceptors (Fe remains in place active for many years to manage COI rebound).
- Ease of Use: Control panel and specialized software supports secure, real-time monitoring and remote system operations.
- Improved Performance: Electrokinetics aid in the release of COIs bound in lower permeability lithologies to rebound, which is often seen in other oxidation processes. Presence of residual iron clusters maximizes the inherent geochemistry of a "post-oxidation" environment for biologically based attenuation.
- Patented Technology: Exclusive license to US Patent No. 9,975,156 protects you and your clients from patent infringement claims.
- Broad Applicability: Can be effectively employed in deep aquifers and mixed lithologies to manage large, dilute plumes often in remote areas.
- Safe for Subsurface Infrastructure The catalytic electrodes are placed in the subsurface aquifer hence there is no negative impact on piping or other equipment present in the overlying vadose soil (i.e., safe implementation at operating gas stations, facilities, etc).
- Flexible Operations: Integrated monitoring and control panel allows for alteration of electric current, voltage, and polarity to control pH, enhance COI desorption, and aid subsurface distribution of ISCO reagents.

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