Provect-EBR® Integrated Biogeochemical / Electrochemical Method for Remediation of Contaminated Groundwater

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REMTECH Europe

Groundwater Remediation Session 7

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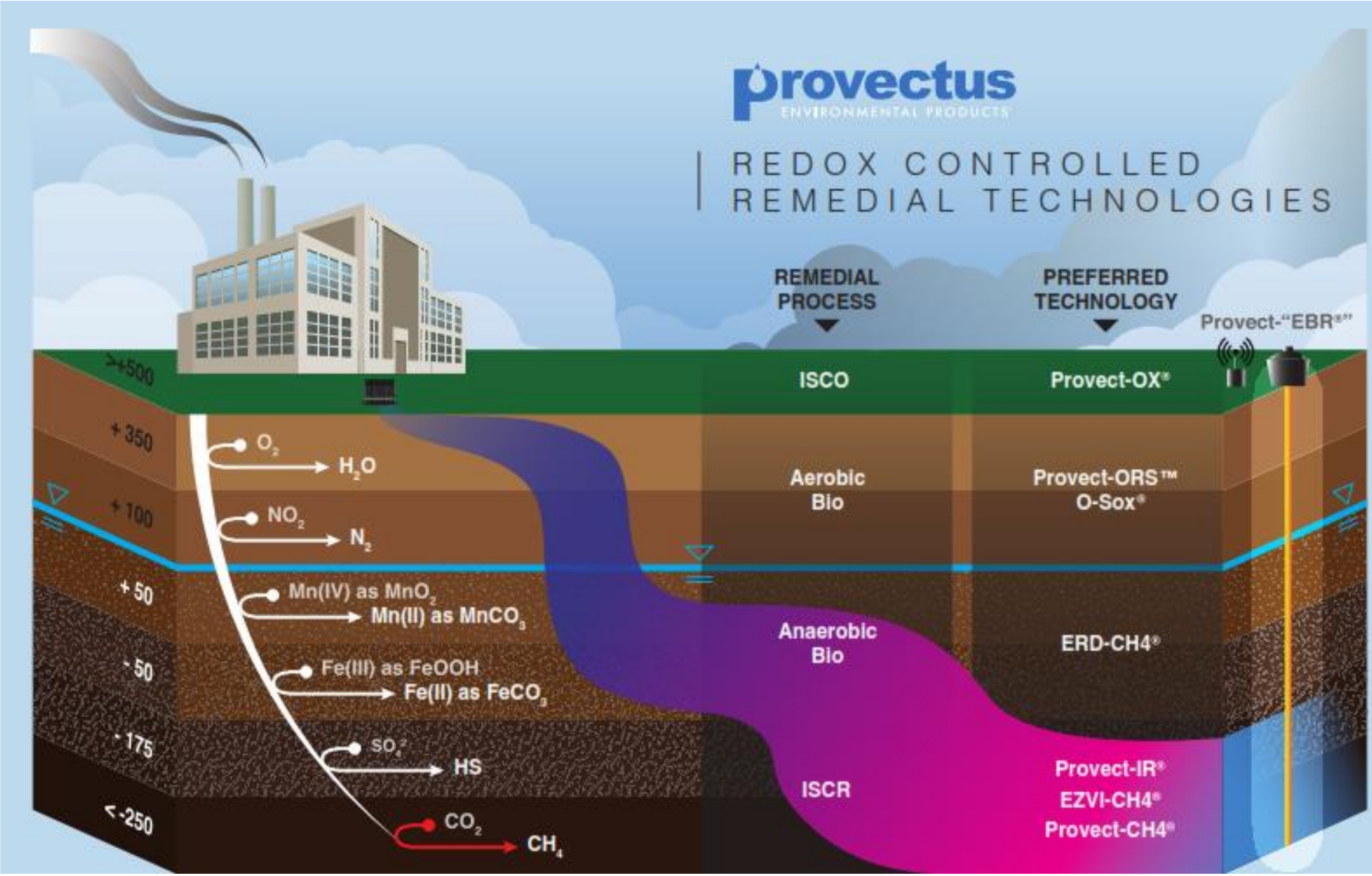
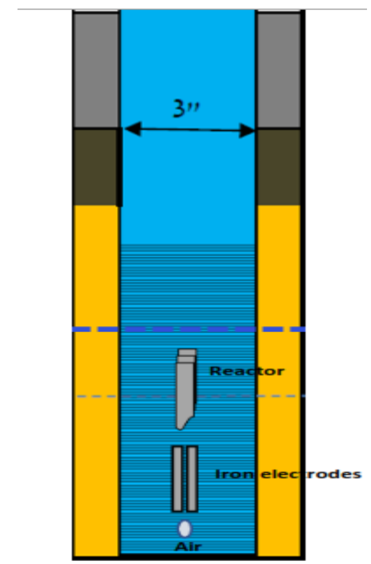


provectus
ENVIRONMENTAL PRODUCTS
REDOX CONTROLLED
REMEDIAL TECHNOLOGIES
REMEDIAL PROCESS
PREFERRED TECHNOLOGY
Provect-"EBR®"
>+500
+350
+100
+50
-50
-175
<-250
O_2
H_2O
NO_2
N_2
Mn(IV) as MnO_2
Mn(II) as $MnCO_3$
Fe(III) as FeOOH
Fe(II) as $FeCO_3$
SO_4^{2}
HS
CO_2
CH_4
ISCO
Provect-OX®
Aerobic Bio
Provect-ORS™
O-Sox®
Anaerobic Bio
ERD-CH4®
ISCR
Provect-IR®
EZVI-CH4®
Provect-CH4®

Presentation Outline

- Problem Statement
  - Summary of ISCO Technologies
  - Why Do We Need Another?
- What is Provect-"EBR®"?
  - What is Provect-EBR?
  - How does it Work / Mode of Action?
  - Remote System Control and Real-Time Monitoring
  - Applications to Date
- Case Studies
  - CHCs: Confidential military site
  - B/MTBE: Neve Tzedik Site (Israeli Water Authority and Ben-Gurion Univ.)
  - Future R&D
- Summary and Conclusions



ISCO = Breaking Chemical Bonds

- Oxidant must be able to accept electrons
  - Capacity = Equivalent weight (MW / No. electrons)
- Ultimate end point is mineralization
  - Partial oxidation is common

Bond Type	Volts (eV)
Carbon-Carbon (single) Long chain hydrocarbons PAHs, DRO, GRO	2.5
Carbon-Carbon (one and a half) Aromatic Type - BTEX and PCP	2.0
Carbon-Carbon (double) HVOCs, PCE, TCE, DCE, VC	1.5
Carbon-Hydrogen (Alkanes)	1.0

Summary of ISCO Technologies

stronger oxidizer

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
https://sites.google.com/site/ecpreparation/ferrate-vi	

Fenton's
- Treats wide range of contaminants
- Short subsurface lifetime
- Difficult to apply in reactive soils

Persulfate
- Treats wide range of contaminants
- Sulfate radical forms slower than the hydroxyl radical, allowing a larger radius of influence

Provect-OX
- Generates Ferrate (Fe IV, V, VI possible)
- Treats wide range of contaminants
- Extended *in situ* lifetime w/ continual production
- Avoids Rebound

Ozone
- Treats wide range of contaminants
- Short subsurface lifetime
- Limited use in saturated zone

Permanganate –
- Treats limited range of contaminants
- Partial oxidation of TPHs, etc
- Long subsurface lifetime
- Potential effects on hydrogeology

Reactive Oxidant Species (ROS)

Higher oxidation potential = stronger the oxidizer

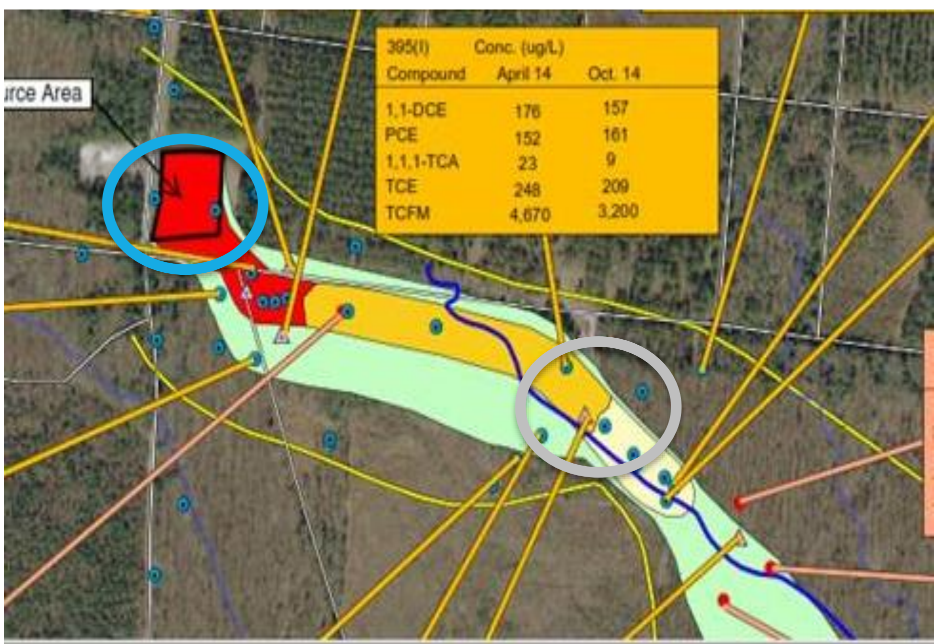
Why We Need A New ISCO Technology

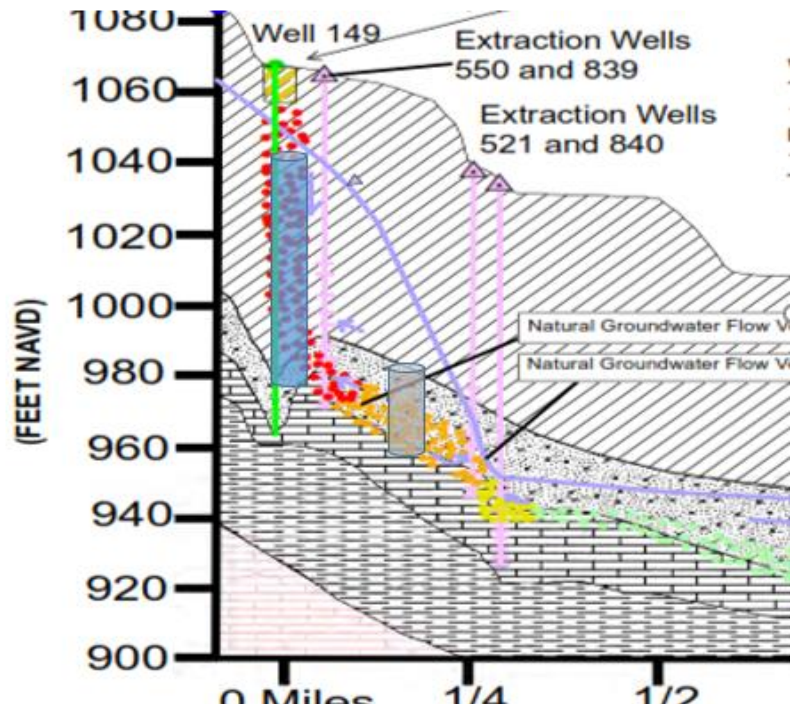
- **Longevity**: Conventional ISCO amendments and means of generating ROS are limited by distribution, kinetics, and short environmental half-lives ($10E^{-9}$ to $10E^{-6}$ seconds) = need to be continuously generated / applied.
- **ISCO PRBs**: PRB applications using existing ISCO (candles, KPS, etc) are limited
- **Sustained, *In Situ* Production of ROS could yield effective PRBs, especially for:**
  - COIs not conducive to ISCR/ZVI such as 1,4-dioxane, MTBE/TBA, perchlorate, (PFAS) plumes.
  - Deep aquifers
  - Challenging lithologies (fractured rock, etc)

ISCO PRB Can Save Money

APPENDIX A. Comparative Analysis of Various Options for an Example PRB @ 50 m long x 5 m deep (4 to 9 m bgs) x 3 m wide.

Technology	Process	Benefits	Detriments	Materials	Example Construction O&M&M costs (USD)
Provect-EBR	*In situ* ISCO (Fenton's) generator	Longevity 5 to >7 years; Treats COIs without intermediates; Remote monitoring control panel and software included	Limited application outside Israel; Mostly used to date for MTBE and refined petroleum products	8 EBR wells spaced 5.5 m apart	8-well EBR system, installed = $125K 8x, 4-inch diam wells = $24K Engineering/startup = $30K Annual OMM = $30/yr TOTAL = $209

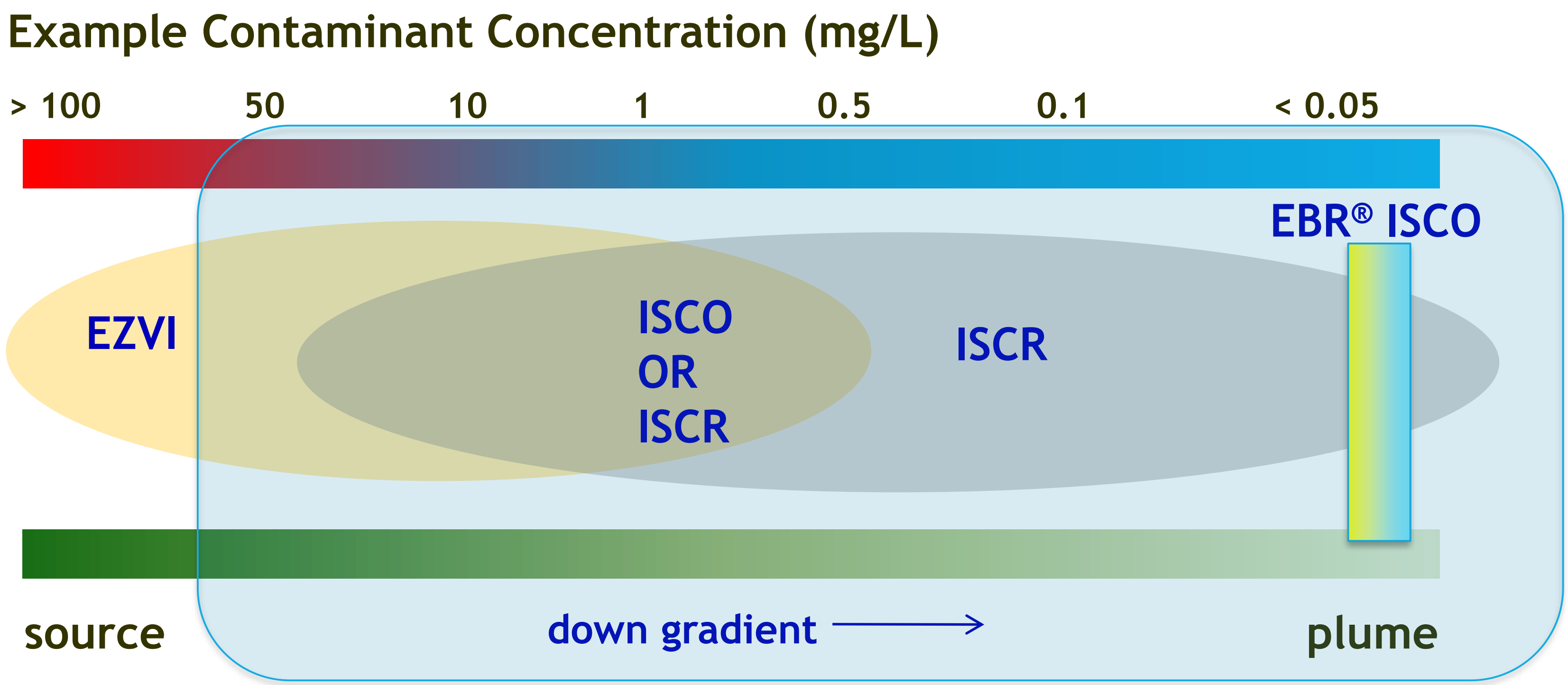




Provect-"EBR®" ISCO PRB

***In Situ* ISCO Generator** to continuously produce Fenton's type ROS yields an effective PRB technology for:

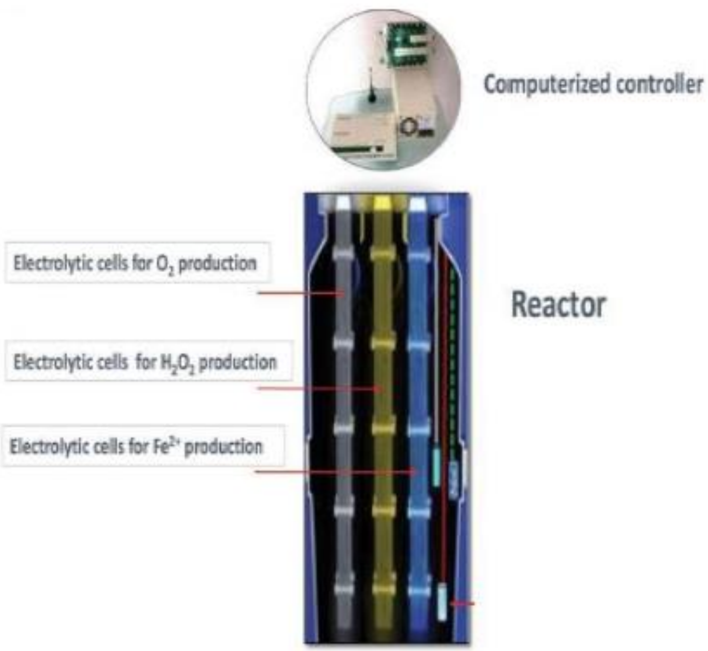
- Challenging lithologies (deep aquifers, clayey soils, fractured rock)
- Situations where sorption/sequestration is not considered an effective response
- Alternatives to hydraulic containment (long term O&M&M)



What is Provect-"EBR®"

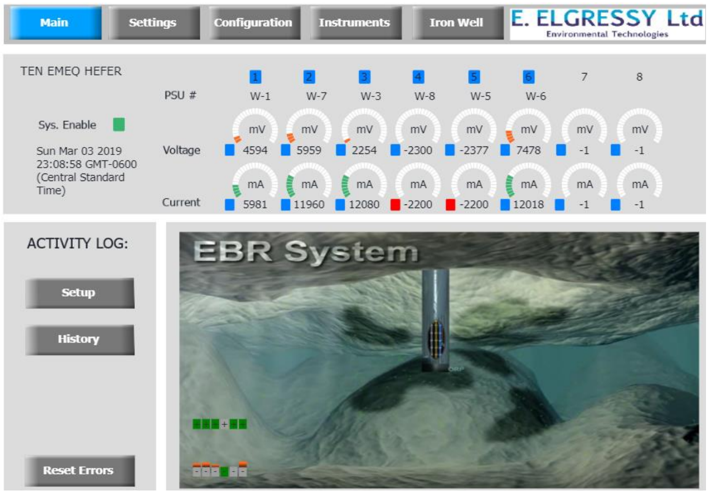
Electro Bioremediation (EBR) well(s) contain an air sparge plus 3 electrodes:

- H_2O_2 production
- Fe^{2+} release
- O_2 production



US Patent No. 9,975,156 B2

Computerized control panels for remote system / adjustment and real-time performance monitoring



US and EPC Patents

EPC 15 885 303.7-1014

Europäisches Patentamt
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21 MAY 2019

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Application No.	Ref	Date
15 885 307.7 - 1014	17763P/EP	16.05.2019
Applicant: Elgressy, Elie		

Communication under Rule 71(3) EPC

1. Intention to grant

You are informed that the examining division intends to grant a European patent on the basis of the above application, with the text and drawings and the related bibliographic data as indicated below.

A copy of the relevant documents is enclosed.

1.1 In the text for the Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

US Patent No. 9,975,156 B2

US009975156B2

(12) **United States Patent**
Elgressy

(10) **Patent No.: US 9,975,156 B2**
(45) **Date of Patent: May 22, 2018**

(54) **BREAKDOWN OF FUEL COMPONENTS AND SOLVENTS IN GROUNDWATER AND CONTAMINATED SOIL**

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(72) Inventor: **Elie Elgressy**, Netanya (IL)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days. days.

(21) Appl. No.: **15/559,053**

(22) PCT Filed: **Dec. 3, 2015**

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§ 371 (c)(1),
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(87) PCT Pub. No.: **WO2016/147168**
PCT Pub. Date: **Sep. 22, 2016**

(65) **Prior Publication Data**
US 2018/0071800 A1 Mar. 15, 2018

(56) **References Cited**

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(Continued)

Primary Examiner — Benjamin F Fiorello
(74) *Attorney, Agent, or Firm* — Ted Whitlock

(57) **ABSTRACT**

A system and method for remediation of polluted sites,

Provectus is the Exclusive Provider in North America and Italy

How Does EBR Work?

The EBR Well Generates Reactive Oxidant Species (ROS) in a manner similar to other Electro-Fenton's (EF) type systems (Nazari *et al*., 2019; Rosales, *et.al,* 2012; Sires *et al*., 2014; Yuan et al., 2013):

Production of O_2: electrolytic reduction of water on a catalytic electrode yields molecular oxygen, O_2

Production of H_2O_2: two-electron reduction of oxygen on a cathode surface generates H_2O_2

Release of Iron: H_2O_2 interacts with ferrous iron (Fe^{2+}) released from a third cell to yield hydroperoxyl ($HO_2\cdot$)/superoxide ($O_2\cdot$) and hydroxyl radicals ($OH\cdot$), and likely ferrates

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

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

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

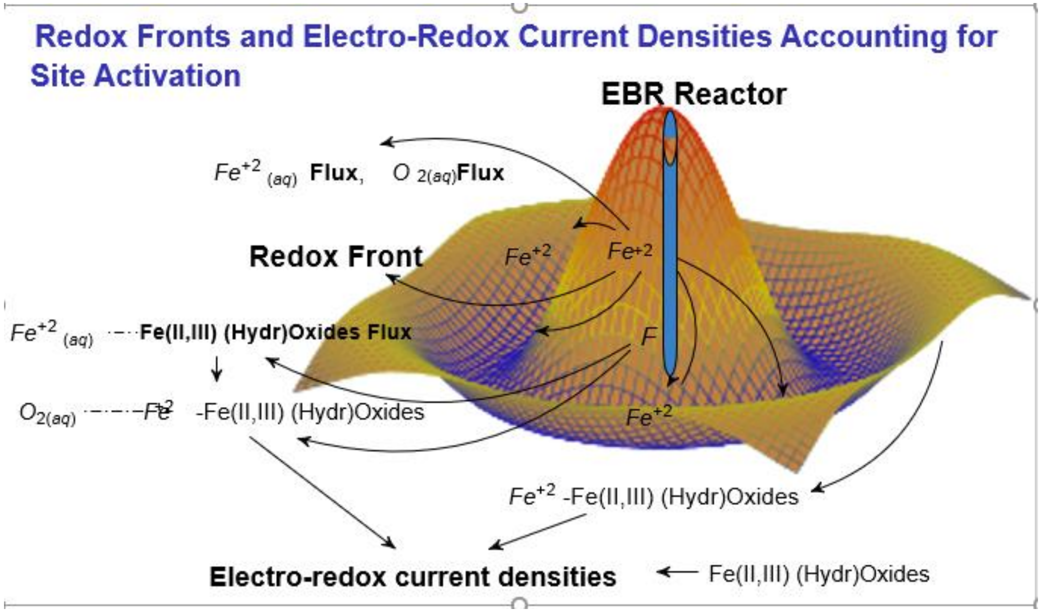
$$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + O_2 + H^+$$

How Does EBR Differ From EF?

$Fe^{2+/3+}$ Nanoclusters: At neutral pH EBR uniquely generates "low" Fermi Level (highly oxidized) FeII/III oxyhydroxide nanoclusters (2 nM) as the sacrificial Fe source corrodes within the well (Ai *et al.*, 2013; Elgressy 2019).

Subsurface distribution of Fe nanoclusters throughout aquifer is driven by:

- Equilibration of differences in Fermi level energies
  self-generated
  self-propagated
- Induced redox fronts
- Electro-redox
  current densities
- Electroosmosis
- Electrophoresis
- Dynamic coupling
  between EBR wells



https://www.provectusenvironmental.com/p-ebr/P-EBR_SIMULATION_VIDEO_M-720.mp4

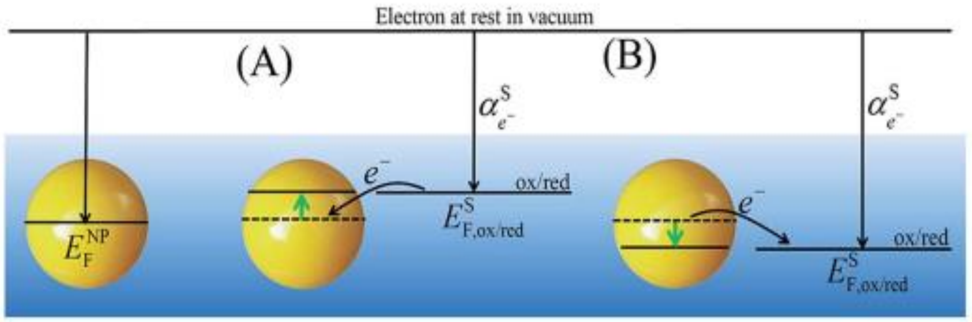
How Does EBR Differ From EF?

$Fe^{2+/3+}$ Nanoclusters: A critical and unique feature of the EBR is use of geophysical mechanisms to enhance subsurface distribution of low Fermi level Fe nanoclusters and propagate catalysis *in situ* to continuously generate reactive oxidants throughout its effective ROI.

Electrochemical Potential of an e- is the difference in potential between the oxidized and reduced species (Peljo *et al.*, 2017; Scanlon *et al.*, 2015)

Fermi Level is a thermodynamic “value” to define the electrochemical potential of an electron in a redox couple in solution

At +850mV (“low” Fermi Level electrochemical potential) electrons are essentially freely transferred from Fe^{3+} to Fe^{2+}



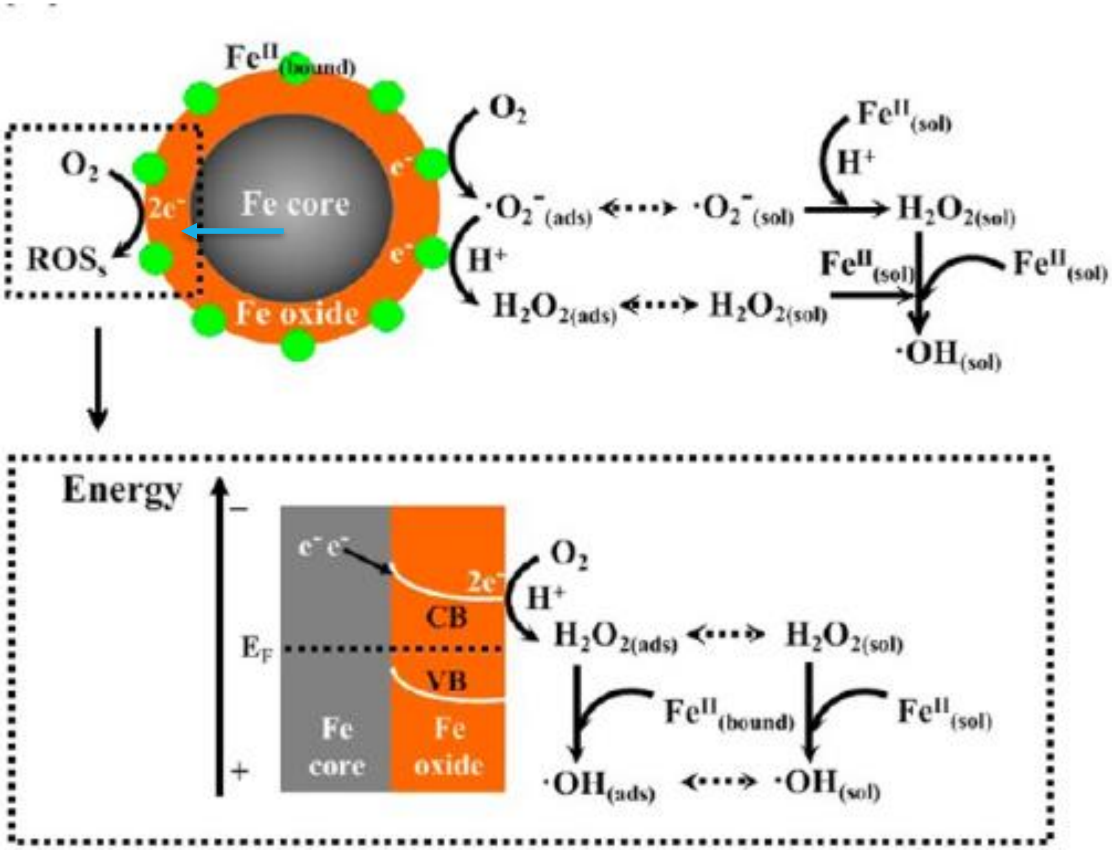
Scheme 3 Redox equilibria for metallic NPs in solution showing the capabilities of metallic NPs to be (A) charged and (B) discharged upon Fermi level equilibration with an excess of a single dominant redox couple in solution.

In Situ Generation of ROS

As Fe (hydro)oxides within the aquifer ROI equilibrate their Fermi level electrochemical potentials they continuously catalyze *in situ* generation of new ROS from dissolved molecular O_2 via two kinds of molecular oxygen activation pathways (Ai *et al*., 2013):

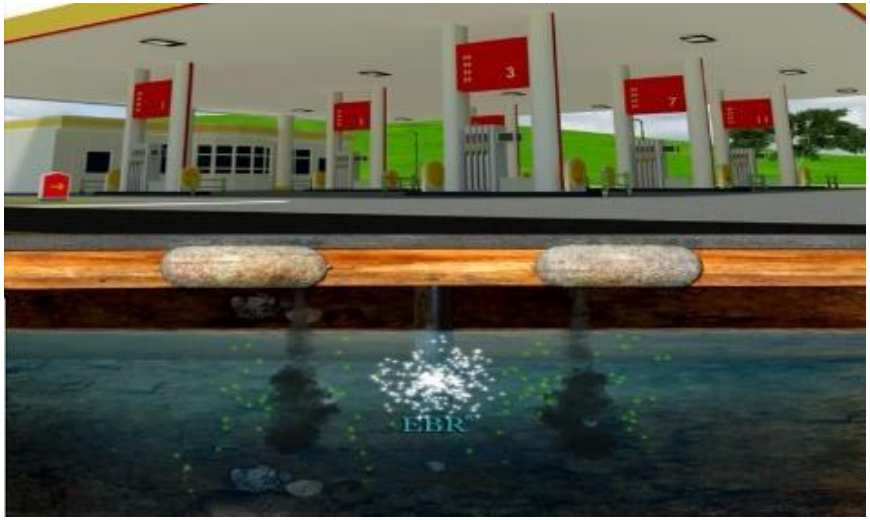
- On the Fe core via rapid two-electron-reduction molecular oxygen activation (may eventually be blocked by the formation of iron oxide coatings), then

- Surface bound ferrous ions catalyze the single-electron-reduction molecular oxygen activation pathway



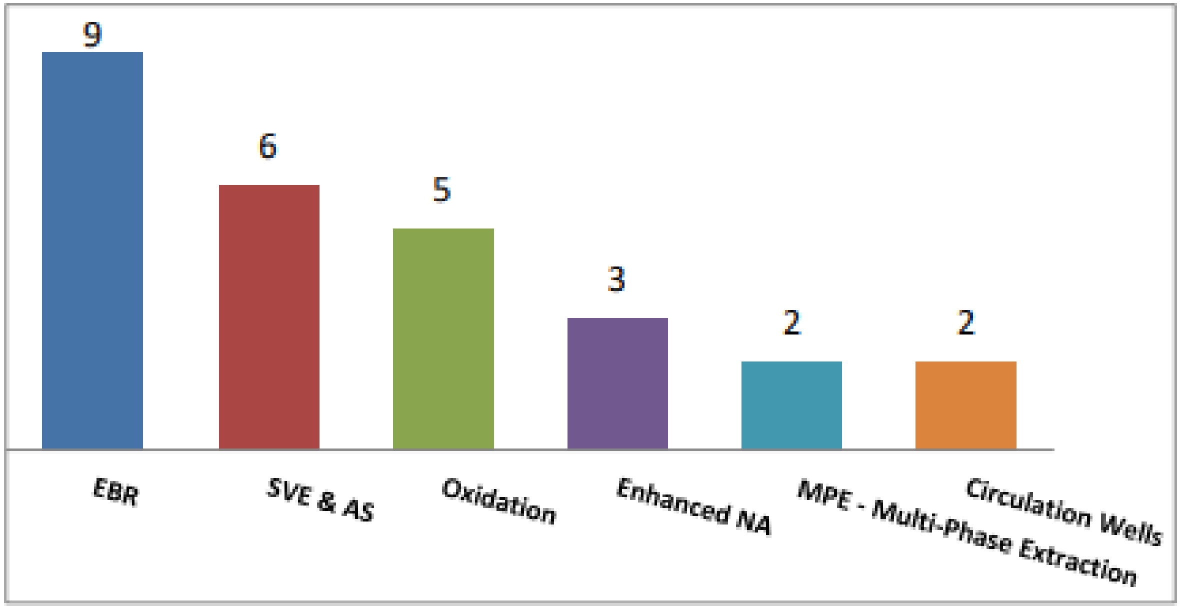
Summary of EBR Reactions

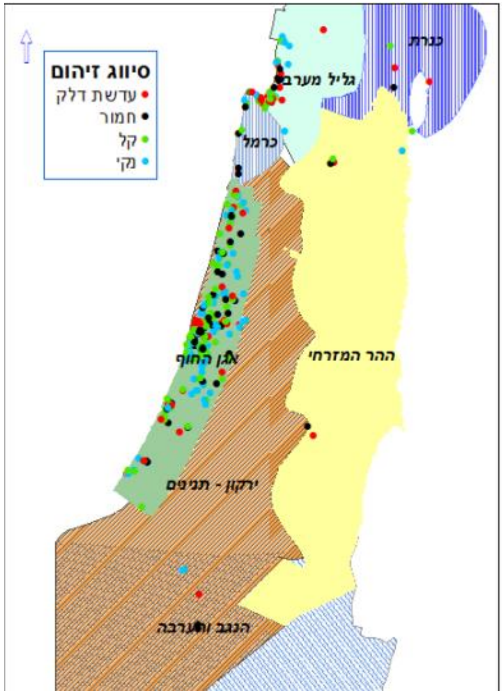
- Generation of H_2O_2
- Release of Fe^{2+}
- H_2O_2 interacts Fe^{2+} to yield ROS $HO_2\cdot/O_2\cdot$ and $OH\cdot$ (ferrate?)
- Release of O_2 and low Fermi Level Fe^{2+}/Fe^{3+} nanoclusters
- Self-propagation throughout ROI (less confined by lithology)
- Continuous *in situ* production of ROS catalyzed by O_2 activation from equilibration of Fermi levels of Fe
  - Transition from ISCO to bioremediation (using oxygen and iron as electron acceptors) and RNA using abiotic transformations.
  - Process controlled remotely with real-time monitoring



Where has it been Used?

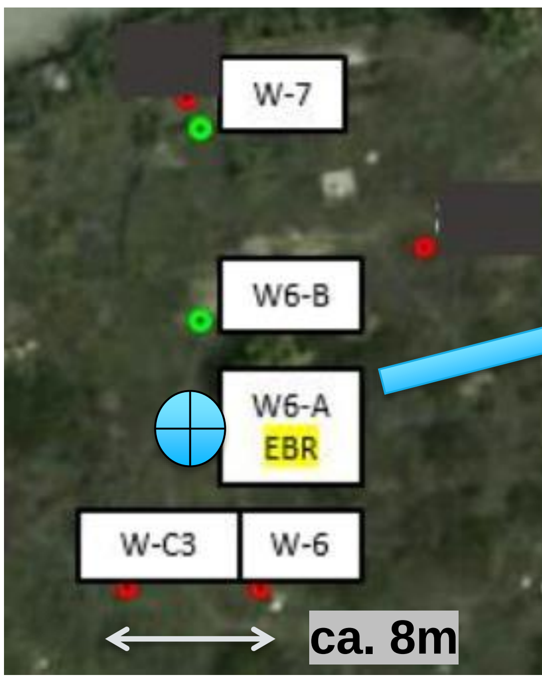
- In 2017 , Israel had 27 gas stations undergoing active remediation
- EBR technology was employed at 9 (33%) + 2 chlorinated solvent sites
- Today, 7 sites are in clean-closure monitoring after 1 year of operation
- EBR is ISO-certified and approved by the Israeli Water Authority and is now the preferred technology for BTEX/MTBE sites.
- No PRB Applications. No USA applications.

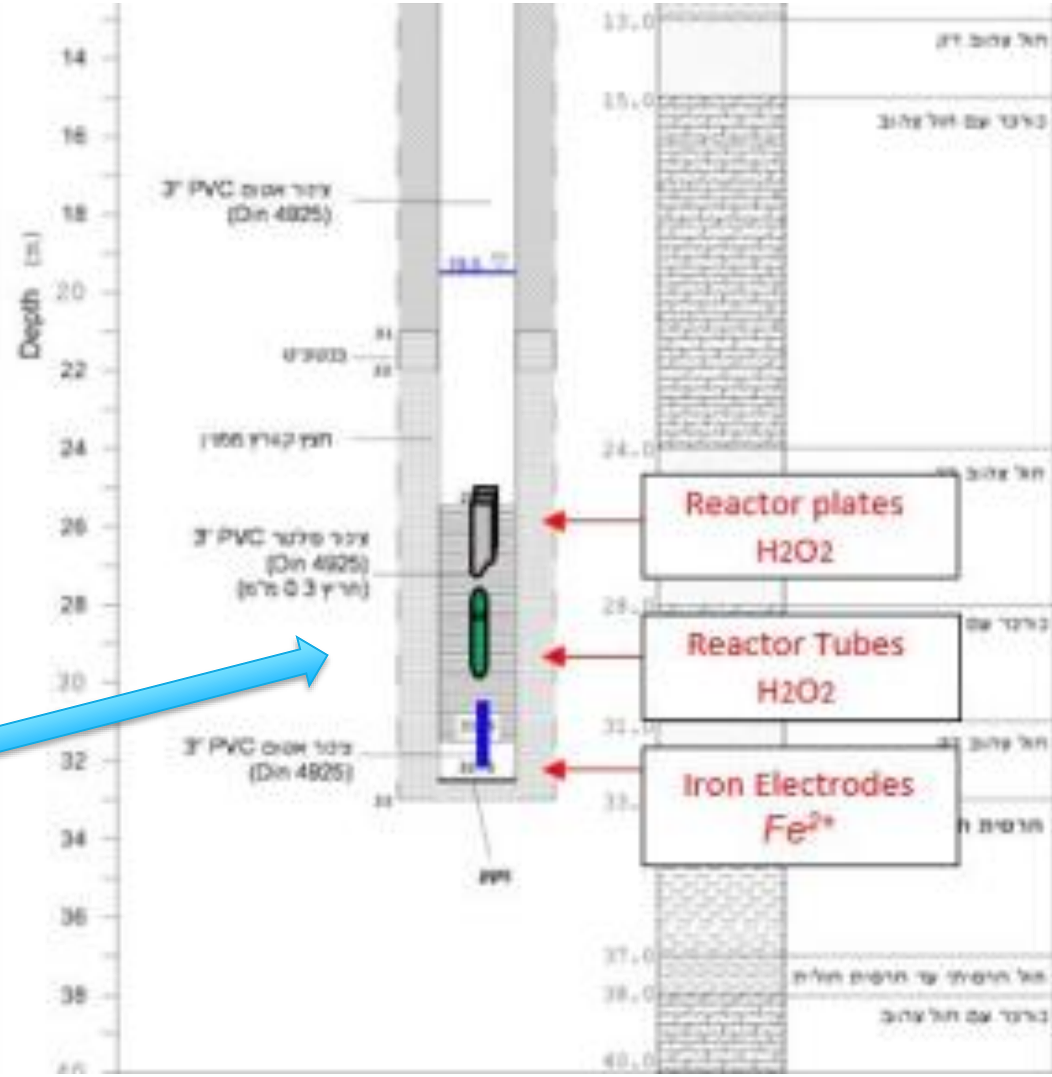




Case Study - Solvent Site

- DTW 19.5 m bgs
- Sandy aquifer impacts
  - PCE max. 257 ug/L
  - TCE max. 25,146 ug/L
  - DCE max. 47 ug/L





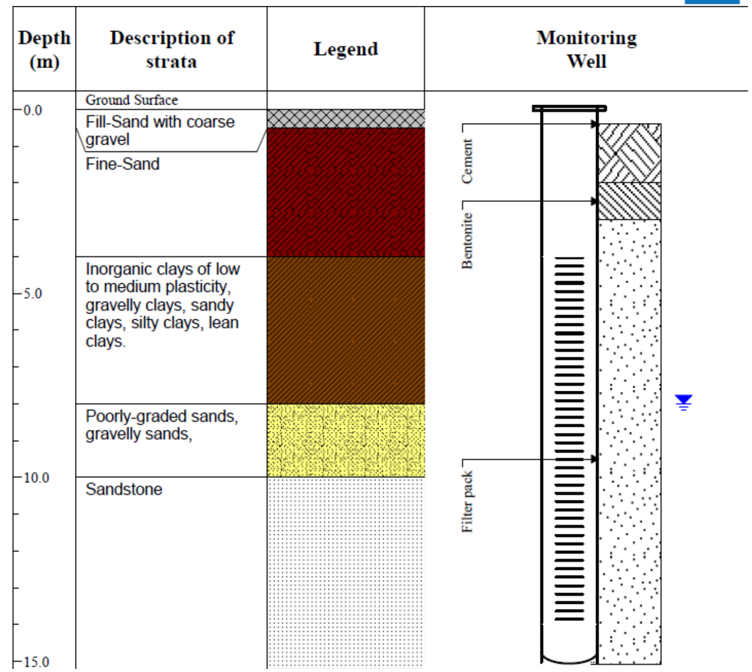
CVOC Removal (60 days)

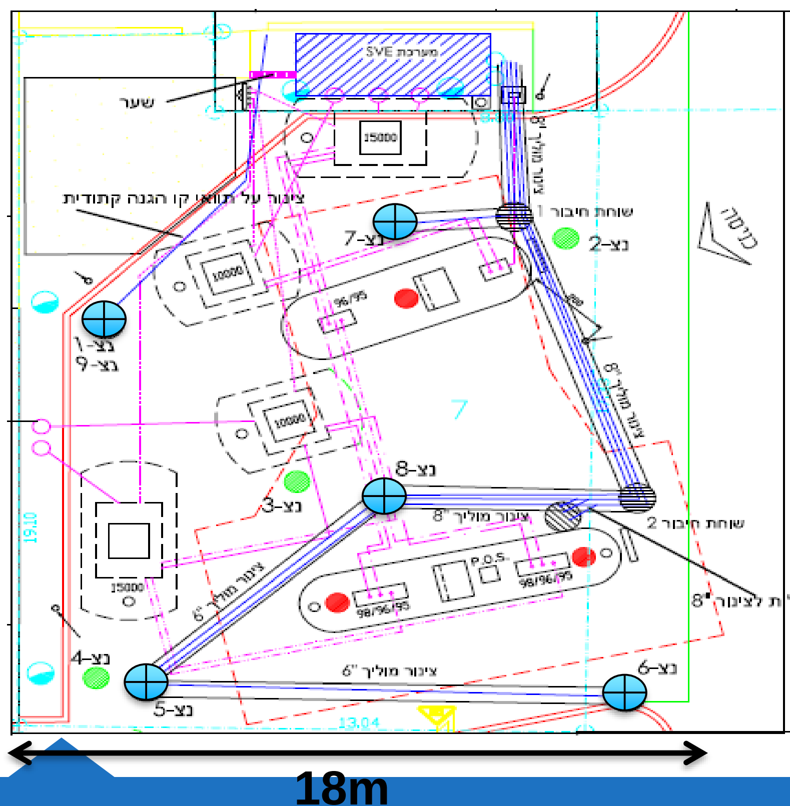
CVOC (ug/L)	Time (Days)	Well 6 (10 m up)	Well 6a EBR Well	Well 6b (5 m down)	Well 7 (20 m down)
PCE	0	8.7	257	<2	<2
	30	2.4	<2	<2	<2
	60	<2	5	<2	<2
TCE	0	752	25,146	74	24
	30	201	<2	6	14
	60	37	15	4	<2
DCE	0	14	47	<1	<1
	30	2.6	<1	<1	<1
	60	1.6	8	<1	<1

- Single EBR Well + Control Panel and remote monitoring < $45K installed
- ROI observed 20 m downgradient within 30 to 60 days.
- >99% CVOC removal within 30 days

Case Study – Neve Tzedik Site

- Operating Gasoline Station
  - Groundwater at 7 m bgs
  - Sandy aquifer with si cl lenses
  - MTBE >50 mg/L; TPH >100 mg/L
  - 242 m^2 impacted area



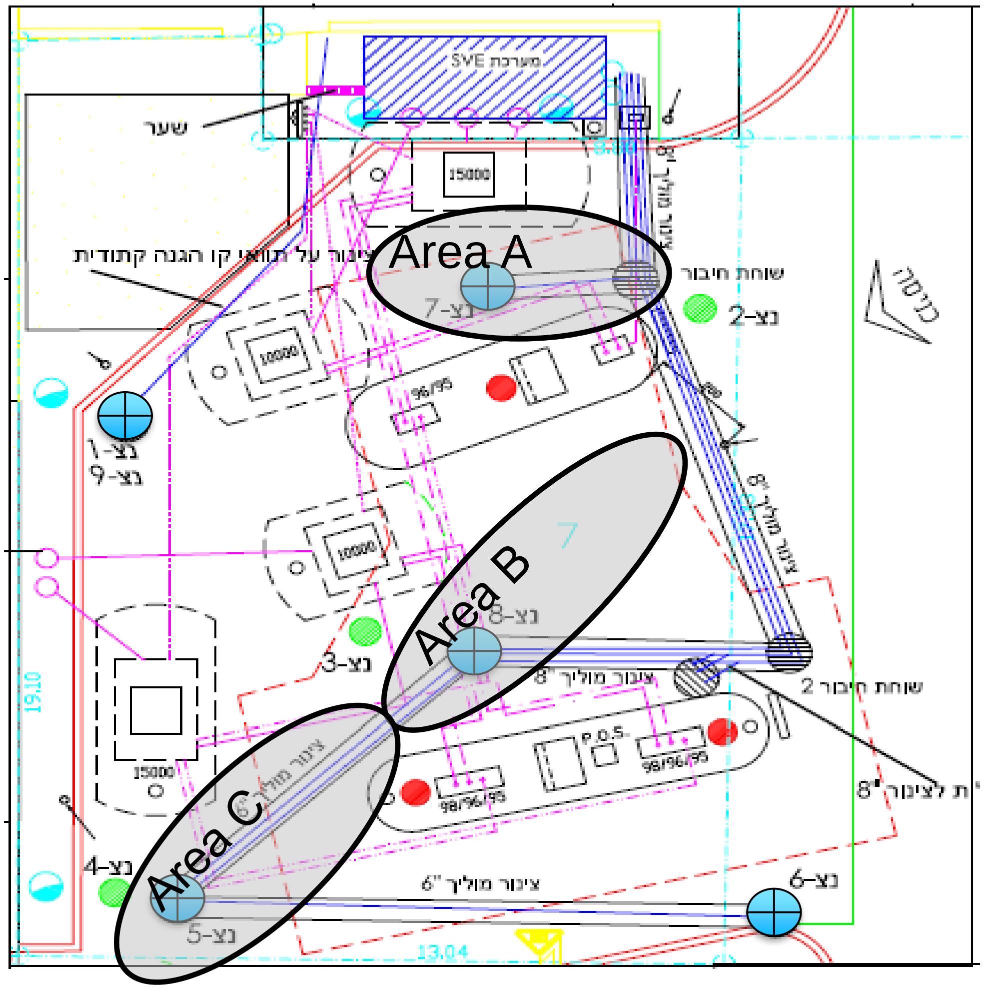


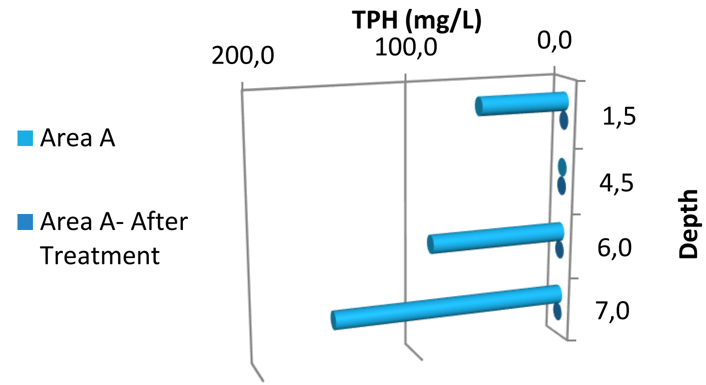
5 EBR/SVE Systems (2017)

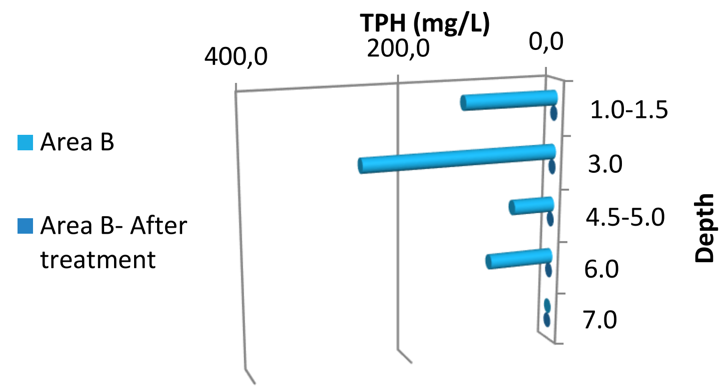
Monitoring wells

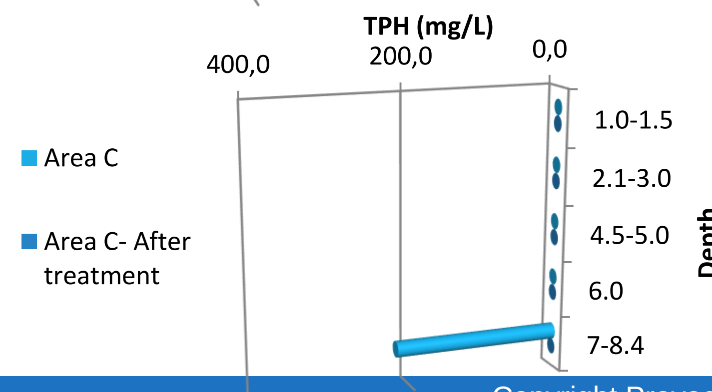
Soil / Groundwater TPH (18 mo)

TPH from >100,000 to <5 ppb (RAO <400 ppb)



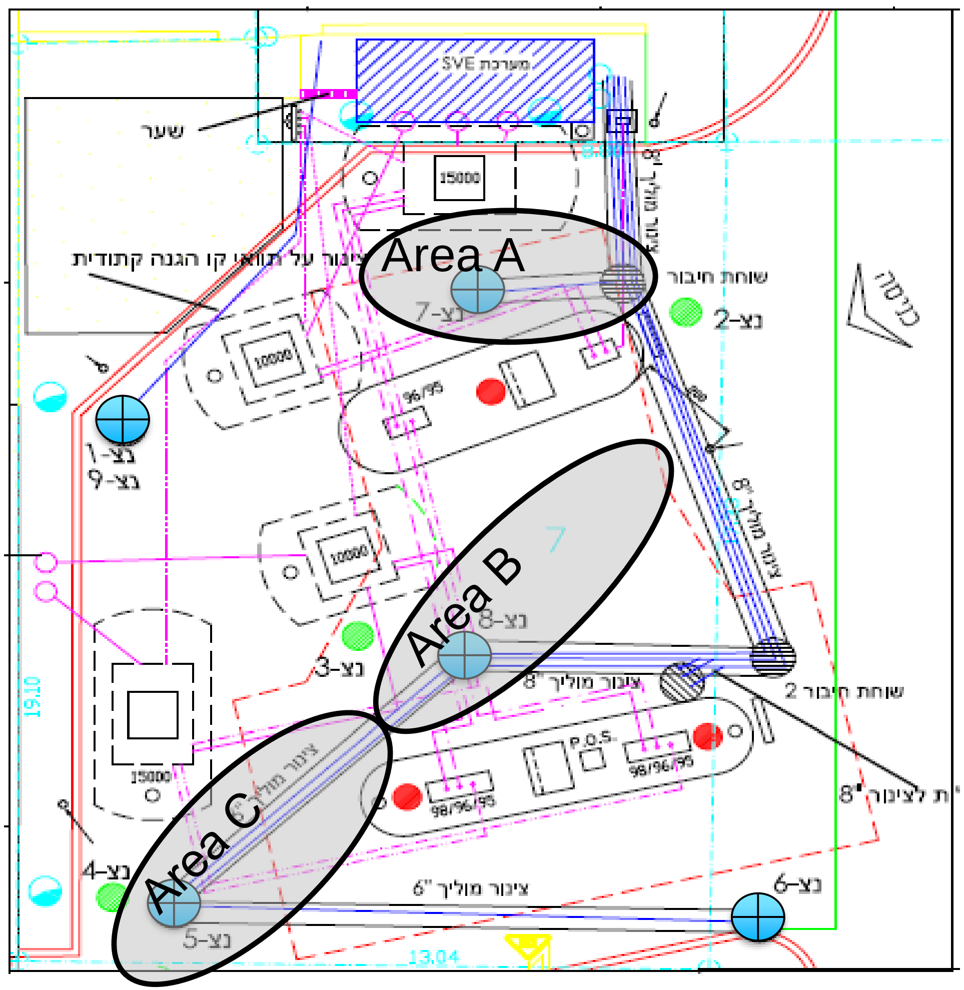


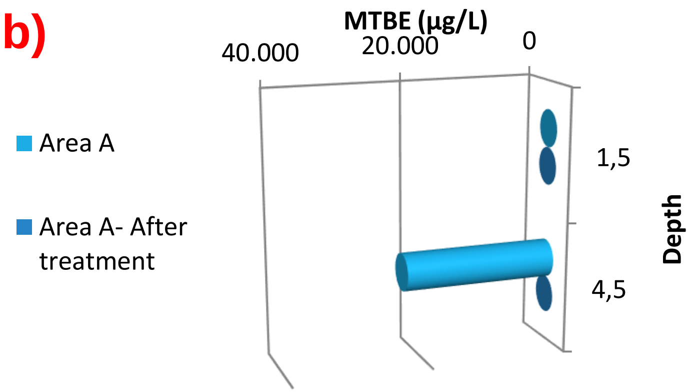


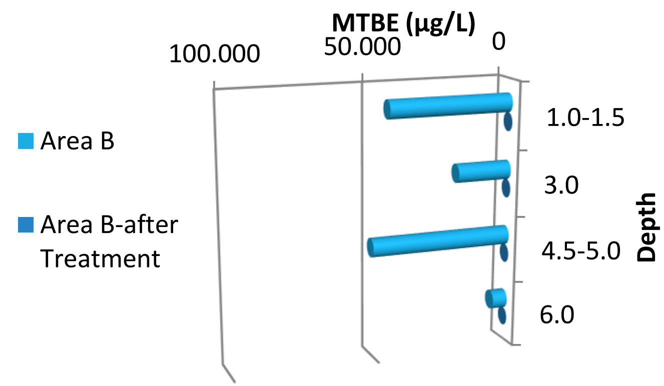


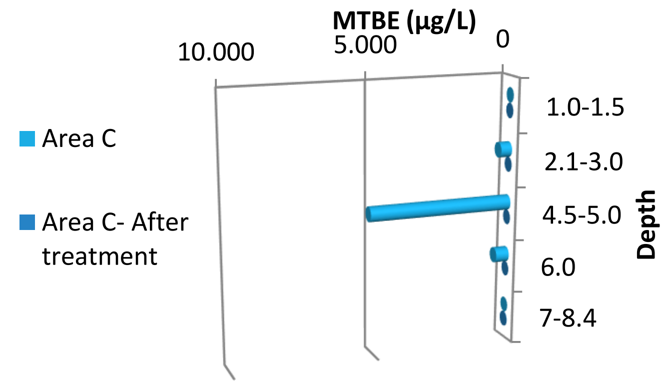
Soil / Groundwater MTBE (18 mo)

MTBE from >50,000 to <50 ppb (RAO <1,600 ppb)









- 5 EBR Wells, Control Panel, O&M < $150K

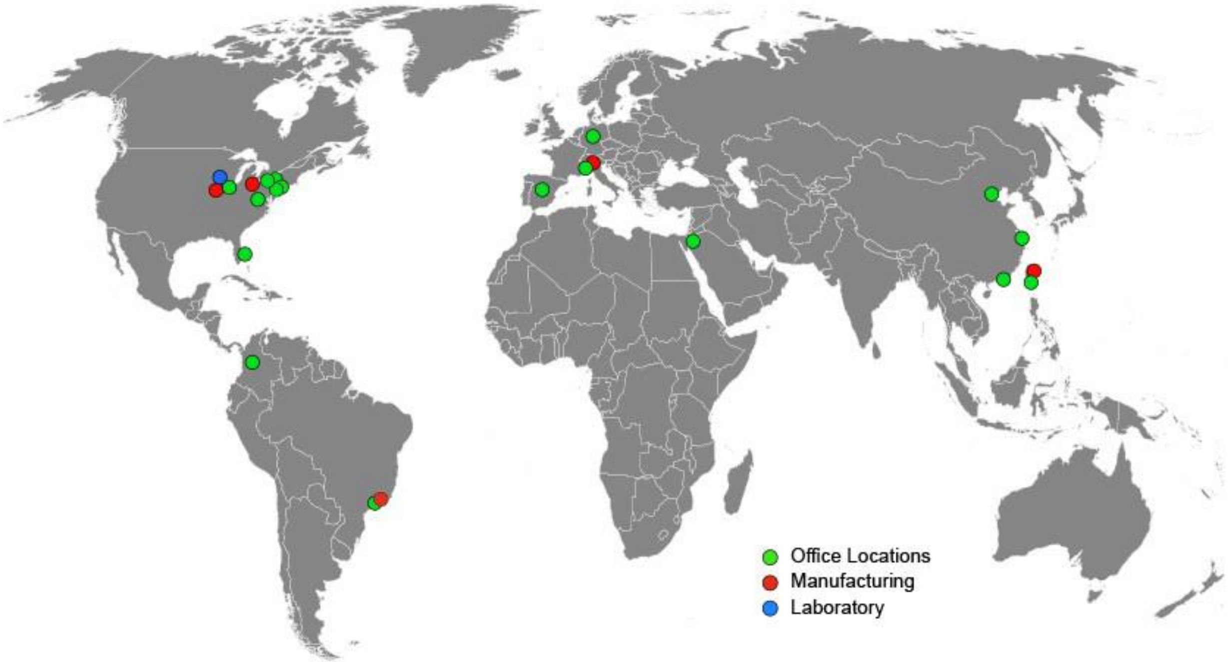
Future R&D / Continued Studies

Validate ROI and Effective Propagation Time, Vertically and Horizontally
(RSC, USEPA,USACE, DOW, AECOM,GEOSYNTEC, TETRATECH, others)

- ORP / Measurements (indirect)
- COI Reductions (indirect)
- Fe2+/Fe3+ measurements: Particle size (BEM) and mineralogy (XRD patterns, TEM micrographs, XPS spectra and high-resolution scan); possible using variations of Bradley and Tratnyek (2019).
- Self-Potential Method (direct): passive geophysical analysis based on the natural occurrence of electrical fields resulting from the existence of source currents in the conductive subsurface (Fachin *et al*., 2012)
- Electrical Resistivity Tomography (direct): measures variations in electrical conductivity associated with changes in pore water ionic strength or water phase saturation.
- Lab-fabricated oxygen microprobes/sensors (direct): validate the distribution of ROS.
- Simple and Predictive Models: facilitate PRB design and implementation

Provectus Environmental Products

- Complimentary Site Evaluation
- Complimentary review of quarterly field performance data with every project
- Laboratory Treatability Studies
- Turn-Key, Pay-for-Performance Contracting Options
- Project Specific Guarantees and Warranties



- USA (Illinois, New Jersey, Ohio, Pennsylvania)
- Australia, Brazil, China, Colombia, Germany, Israel, Italy, Spain and Taiwan

THANKS FOR THE ATTENTION,

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