provectus
ENVIRONMENTAL PRODUCTS™

ISCO / ISCR – How to Decide in 2017?

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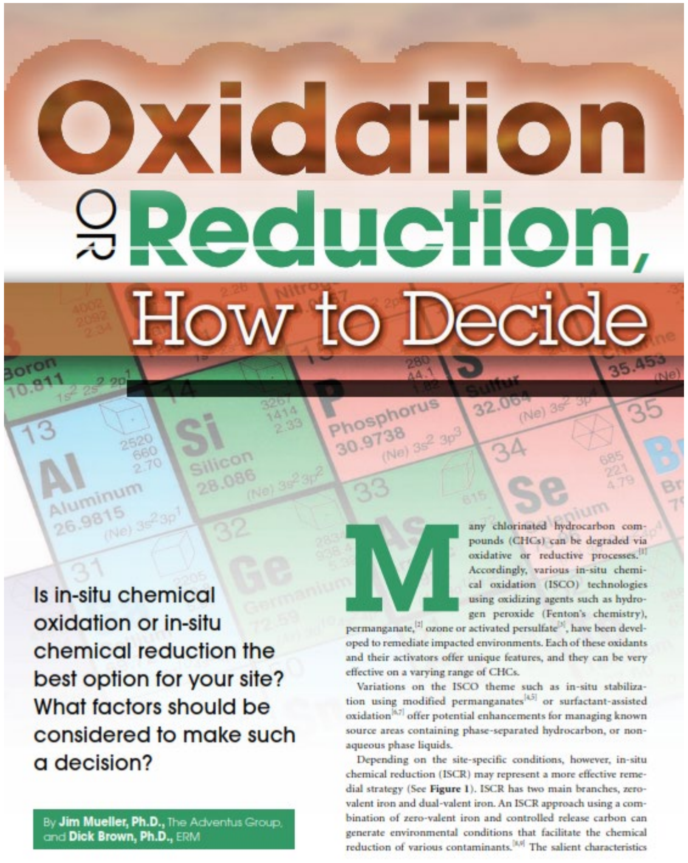
focusedremediationseminars

Focused Remediation Seminars
2017

10 year Update – References Cited

- Presentation is an update of past publications
- Not a complete analysis: a summary of factors that have been observed to affect technology selection, design and field performance



Oxidation OR Reduction, How to Decide

Is in-situ chemical oxidation or in-situ chemical reduction the best option for your site? What factors should be considered to make such a decision?

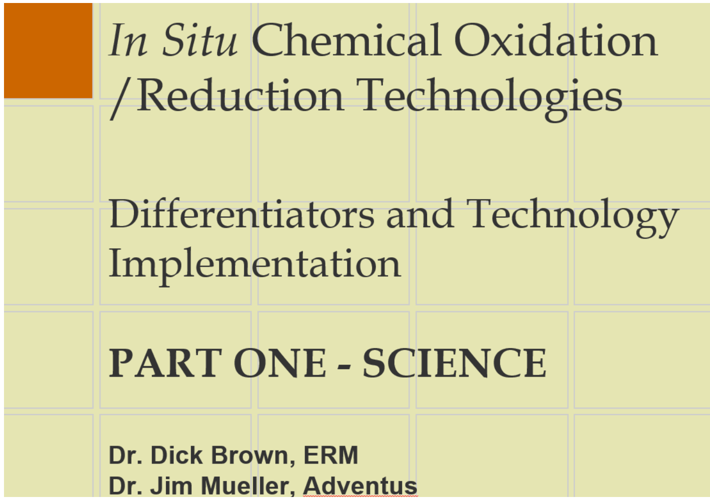
By **Jim Mueller, Ph.D.,** The Adventus Group, and **Dick Brown, Ph.D.,** ERM

Many chlorinated hydrocarbon compounds (CHCs) can be degraded via oxidative or reductive processes.[1] Accordingly, various in-situ chemical oxidation (ISCO) technologies using oxidizing agents such as hydrogen peroxide (Fenton's chemistry), permanganate,[2] ozone or activated persulfate[3], have been developed to remediate impacted environments. Each of these oxidants and their activators offer unique features, and they can be very effective on a varying range of CHCs.

Variations on the ISCO theme such as in-situ stabilization using modified permanganates[4,5] or surfactant-assisted oxidation[6,7] offer potential enhancements for managing known source areas containing phase-separated hydrocarbon, or non-aqueous phase liquids.

Depending on the site-specific conditions, however, in-situ chemical reduction (ISCR) may represent a more effective remedial strategy (See **Figure 1**). ISCR has two main branches, zero-valent iron and dual-valent iron. An ISCR approach using a combination of zero-valent iron and controlled release carbon can generate environmental conditions that facilitate the chemical reduction of various contaminants.[8,9] The salient characteristics

Mueller, J. and R. Brown. 2008. Oxidation or Reduction – How to Decide? Pollution Engineering News, April 2008, pages 51-54



In Situ Chemical Oxidation /Reduction Technologies

Differentiators and Technology Implementation

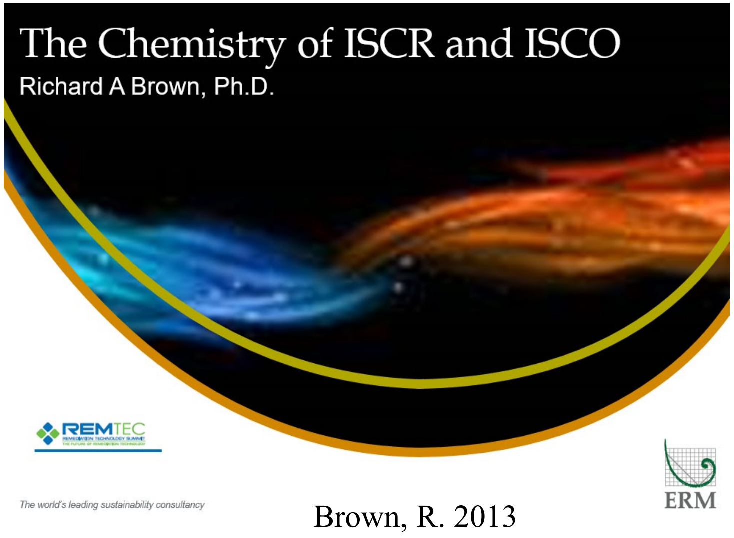
PART ONE - SCIENCE

Dr. Dick Brown, ERM
Dr. Jim Mueller, Adventus

Brown, R and J. Mueller. 2011. Oxidation or Reduction Technologies. to Decide? *Battelle Symposium on Bioremediation and Sustainable Environmental Technologies,* Reno, Nevada; June 27-30, 2011

All Public Documents and hereby fully credited and referenced

10 year Update – References Cited



The Chemistry of ISCR and ISCO

Richard A Brown, Ph.D.

Brown, R. 2013

FMC Environmental Solutions

Oxidation (ISCO) and/or Reduction (ISCR) ?

Jim Mueller Ph.D. and Ian Ross Ph.D. (FMC Environmental Solutions)
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SOIL & GROUNDWATER REMEDIATION

Introduction

Many chlorinated hydrocarbon compounds (CHCs) such as chlorinated ethenes, ethanes, and methanes can be degraded via oxidative or reductive processes. Technologies such as *in situ* chemical oxidation (ISCO) using Klozur® persulfate and *in situ* chemical reduction (ISCR) using use a combination of zero valent iron (ZVI) and controlled release carbohydrate (as with EHC® reductive chemistries) are both available and potentially appropriate. Each of these technologies offers differing features and can be very effective for *in situ* destruction of CHCs.

A number of other important factors should be considered when selecting between an ISCR or ISCO approach for a specific site. These include: targeted treatment area (source removal, plume control or both), contaminant characteristics, presence of free product, residuals or phase-separated hydrocarbons (*e.g.*, NAPL), desired clean-up time, degradation kinetics, and longevity of the added reagents in the subsurface.

Depending on the site-specific conditions, however, either ISCO with Klozur persulfate or *in situ* chemical reduction (ISCR) using EHC may represent a more effective remedial strategy, or a combination of these techniques is potentially viable. For example ISCO could be applied to high CHC concentration source areas, whereas ISCR could be placed in multiple lines to intercept the CHC plume. A description of these technologies is presented below.

Technology	Salient Features
In Situ Chemical Oxidation (ISCO) using Klozur®	• Thermodynamically powerful radical species are generated via activation of persulfate which can destroy a very wide range of aqueous phase organic compounds • The reaction kinetics can be controlled by varying the activation chemistry and concentrations of activator and persulfate to allow a tailored radius of influence from the point of injection • Versatility in being able to generate radicals which are oxidants or reductants • Safe reagent to use which does not break down generating heat or large volumes of gaseous by products.
In Situ Chemical Reduction (ISCR) using EHC®	• Synergistic chemical and microbiological reactions yield very low Eh conditions (e.g., <-500 mV) • These conditions yield thermodynamics that facilitate unique redox reactions that reduce catabolite accumulation • Persistent, oxidized compounds rapidly degrade under reduced Eh conditions • Includes surface catalyzed reactions on ZVI and other minerals • ZVI performs better than natural minerals and non-ferrous co-reductants

ISCO

ISCR

Figure 1. A conceptual plan where ISCO is combined with ISCR

Combining ISCO and ISCR

There are multiple benefits of combining the use of ISCO with Klozur persulfate and ISCR using EHC when these technologies are deployed in spatially distinct zones. For example, ISCO is more suited to rapid destruction of high concentrations of CHCs in source zones, whereas ISCR can be deployed to last for several years intercepting lower concentrations of CHCs in the plume.

The sulfate residual from use of Klozur persulfate will be significantly diluted before interaction with the reducing zone established using EHC. Alternatively the sulfate could be removed in the source area by addition of reagents such as ELS which will make the source area anaerobic and thus promote reductive dechlorination following oxidation. Within the ISCR zone, sulfate reducing bacteria will utilize residual sulfate and generate sulfide, thereby contributing to the formation of reactive iron sulfide minerals that support dehalogenation of CHCs.

In summary, ISCO for the source area combined with ISCR as a barrier to intercept groundwater flow offers a potentially attractive remedial solution.

General Applicability to COI Concentrations

In general, ISCO is employed for higher COI concentrations (source areas, residual concentrations) and ISCR is employed for lower COI concentrations (plumes), noting that there are well documented exceptions to this guideline.

So Which Technology May Be Best for a Specific Site?

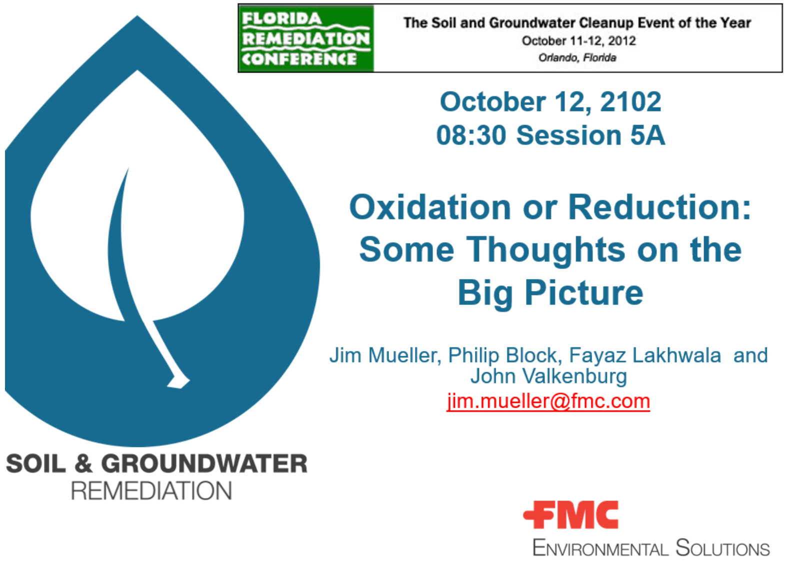
In general, if the targeted environment is in a reduced geochemical condition (low Eh; oxygen limited), it seems intuitive to employ an ISCR strategy; however, ISCO would also be potentially applicable in these environments.

Many releases of COIs to ground resulted from the disposal of waste degreasing solvents which comprised a combination of COIs and hydrocarbons, so the hydrocarbons can drive the conditions to be slightly anaerobic, meaning PCE and TCE are often converted to *cis*-DCE but the geochemistry is not driven to be increasingly reduced to allow further reductive dechlorination of *cis*-DCE as the hydrocarbon content in the waste solvent was not high enough. In these conditions the dissolved oxygen can be diminished, but the solubility of oxygen in water is only approximately 10 mg/L, so this parameter cannot be relied upon to indicate whether ISCO or ISCR is applicable. Then the redox potential is often driven by compounds present in water at mg/L concentrations, whereas when oxidants are added these are usually at g/L concentrations, so overcoming a low redox potential would not necessarily consume significant oxidant mass. The reductive poise of a site may be beneficial to activate persulfate to form radicals, which then cause destruction of COIs. Therefore, the dissolved oxygen concentration and redox potentials of a site groundwater are not reliable parameters to be used to determine if ISCO or ISCR are applicable.

The mass flux of combined terminal electron acceptors (oxygen, sulfate, nitrate) would be the logical parameter to consider when evaluating a site for either ISCO or ISCR, as the groundwater velocity in combination with the concentrations of the terminal electron acceptors will define whether a reducing environment can be maintained. The table below highlights some factors which may be pertinent for technology selection or combination.

1735 Market Street • Philadelphia, PA 19103 USA • Tel: +866 860 4760 • www.environmental.fmc.com

Mueller, J. and I. Ross. 2013. ISCO or ISCR: Battelle's Second International Symposium on Bioremediation and Sustainable Technologies, June 10-13, 2013 Jacksonville, Florida.



FLORIDA REMEDIATION CONFERENCE

The Soil and Groundwater Cleanup Event of the Year
October 11-12, 2012
Orlando, Florida

October 12, 2102
08:30 Session 5A

Oxidation or Reduction: Some Thoughts on the Big Picture

Jim Mueller, Philip Block, Fayaz Lakhwala and John Valkenburg
jim.mueller@fmc.com

SOIL & GROUNDWATER REMEDIATION

FMC ENVIRONMENTAL SOLUTIONS

Mueller, J., P. Block, F. Lakhwala and J. Valkenburg. 2012. Oxidation or Reduction: FRC October 11-12, 2012

All Public Documents and hereby fully credited and referenced

Presentation Outline

- Introduction to Provectus Environmental Products, Inc.
- Problem Statement
  - We Need ISCO & ISCR Technologies
- What is ISCO?
  - Mode of Action
  - Technologies Available
  - 2017 Recognized Limitations (partial oxidation, rebound, longevity, metals)
- What is ERD/ISCR?
  - Mode of Action
  - Technologies Available
  - 2017 Recognized Limitations (excessive CH4, heavy metals, ketones)
- Design and Selection Criteria – Lessons Learned
- Summary and Conclusions

Technical Background (Brown)

- B.S. Harvard - 1971
- M.Sc. Cornell - 1976
- Ph.D. Cornell - 1978
- FMC Corporation - 1978 to 1986
- Cambridge Analytical -1987 to 1988
- Groundwater Technologies → Fluor Daniel (1988 to 1998)
- ERM - 1988 to 2016 (retired)

- 21 Patents
- >1,000 publications
- Origins of ISCO and ISCR

Technical Background (Mueller)

- B.S., M.S. SIU Carbondale – 1983/1985
- Ph.D. Clemson University -1988
- Post Doctoral Studies US EPA GBERL (1988 – 1991)
- SBP Technologies, Inc.→ RF Weston (1991 to 1997)
- Dames & Moore → URS (1997 to 2002)
- Malcolm Pirnie, Inc. (2002 to 2003)
- WR Grace → Adventus Americas, Inc. → FMC Corporation → Peroxychem/JPM (2003 to April, 2014)
- Provectus Environmental Products – May, 2014 (acquired patents on CH4 inhibitors, ISCR and ISCO)

Overview of Provectus' Patent Estate (IET)

Application / Patent Number	Title	Filling Date	Issue Date
7,129,388 and 7,531,709	Method for Accelerated Dechlorination of Matter; Parts 1 and 2.		10/31/2006 and 05/12/2009
7,828,974	Method for the Treatment of Ground Water and Soils Using Dried Algae and Other Dried Mixtures		10/09/2010
8,147,694	Method for the Treatment of Ground Water and Soils Using Mixtures of Seaweed and Kelp		04/03/2012
8,766,030	Utilization of Ferric Ammonium Citrate for In-Situ Remediation of chlorinated Solvents		01/30/2014
9,221,699 B2	Method for Inhibition of methane production during anaerobic reductive dechlorination		12/29/2015
9,126,244	Use of encapsulated substrates to control the release rates of organic hydrogen donors		09/08/2015
9,126,245 B2	Chemical Oxidation and Biological Attenuation Process for the Treatment of Contaminated Media		09/08/2015
62/024,640	Method and Composition for Inhibiting Methanogenesis During *In Situ* Sediment Treatment	07/15/2014	
Filed	Inhibition of methane and hydrogen sulfide production in anaerobic digester animal farms, landfills, sediments and sewer systems	08/01/2014	
Filed	Method and Composition for Inhibiting Heavy Metal Methylation During *In Situ* Remedial Actions	10/15/2014	
62/220,389	Inhibition of Methanogenesis to Control Wood-Boring Insects and Pestilence	09/18/2015	
62/227,519	Inhibition of Methanogenesis during Environmental Applications (essential oils for controlling methanogens)	01/15/2016	

8 issued patents; 5 Pending Patents (as of January, 2016)

Provectus Environmental Products, Inc

OUR TECHNOLOGIES

Provect-IR® Solid, Antimethanogenic ISCR Reagent
As the prime developer of the original EHC® ISCR reagent, staff now at Provectus know that Provect-IR is a genuine improvement on the ISCR process and its older product formulations. Provect-IR uses carbon substrate more efficiently and therefore is more cost effective. Remedial designs can use less amendment and get expected results without excessive methane generation.

Provect-IRM® Solid Antimethanogenic ISCR / Metal Stabilization Reagent
More effective means of metal immobilization/ISCR that minimizes production of methylmetal(loids) for safer, more effective, long-term immobilization.

Provect-OX™ Self-Activating ISCO/ Enhanced Bioremediation Reagent
Persulfate-based ISCO reagent that is unique in terms of its safety (no extreme activators; no heat generated) and effectiveness, as it actively integrates ferrate chemistry and enhanced bioremediation as part of the overall treatment process – only ISCO reagent designed to manage rebound.

Provect-CH4® Methanogen Inhibitor and ERD/ISCR Supplement
Water-soluble amendment to effectively control methane production when combined with various ERD amendments (*e.g.*, [emulsified] oils, lecithin, lactates, molasses, sugars, etc.) or conventional ISCR reagents.

AquaGate+CH4™ Antimethanogenic Reactive Capping Technology
Developed in collaboration with AquaBlok, LTD subaqueous caps can be constructed more effectively by minimizing gas ebullition and contaminant methylation.

EZVI-CH4™ Antimethanogenic DNAPL Treatment
Unique reagent can be used for safe and effective treatment of chlorinated solvent DNAPL sources.

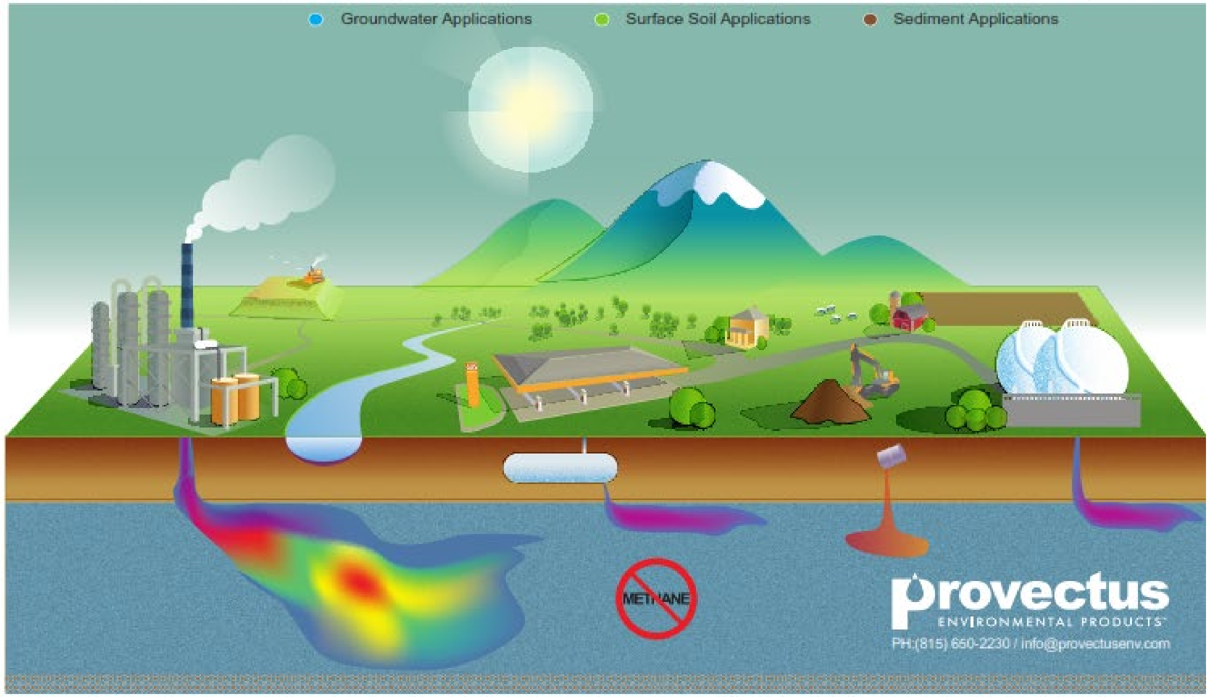
Provect-GS™ NAPL Immobilization Technology
A liquid reagent developed in collaboration with Beazer East, Inc. for *in situ* geophysicochemical immobilization (ISGI) of DNAPL sources.

ERD-CH4™ Liquid Antimethanogenic ISCR Reagent
Liquid, antimethanogenic ERD amendment that can be applied via screened systems. By inhibiting methanogenesis, this is a more efficient, longer-lived and safer ERD approach.

Provect-ABR Aerobic Bioremediation Reagent
Soil amendment for accelerated aerobic biodegradation of organic compounds.

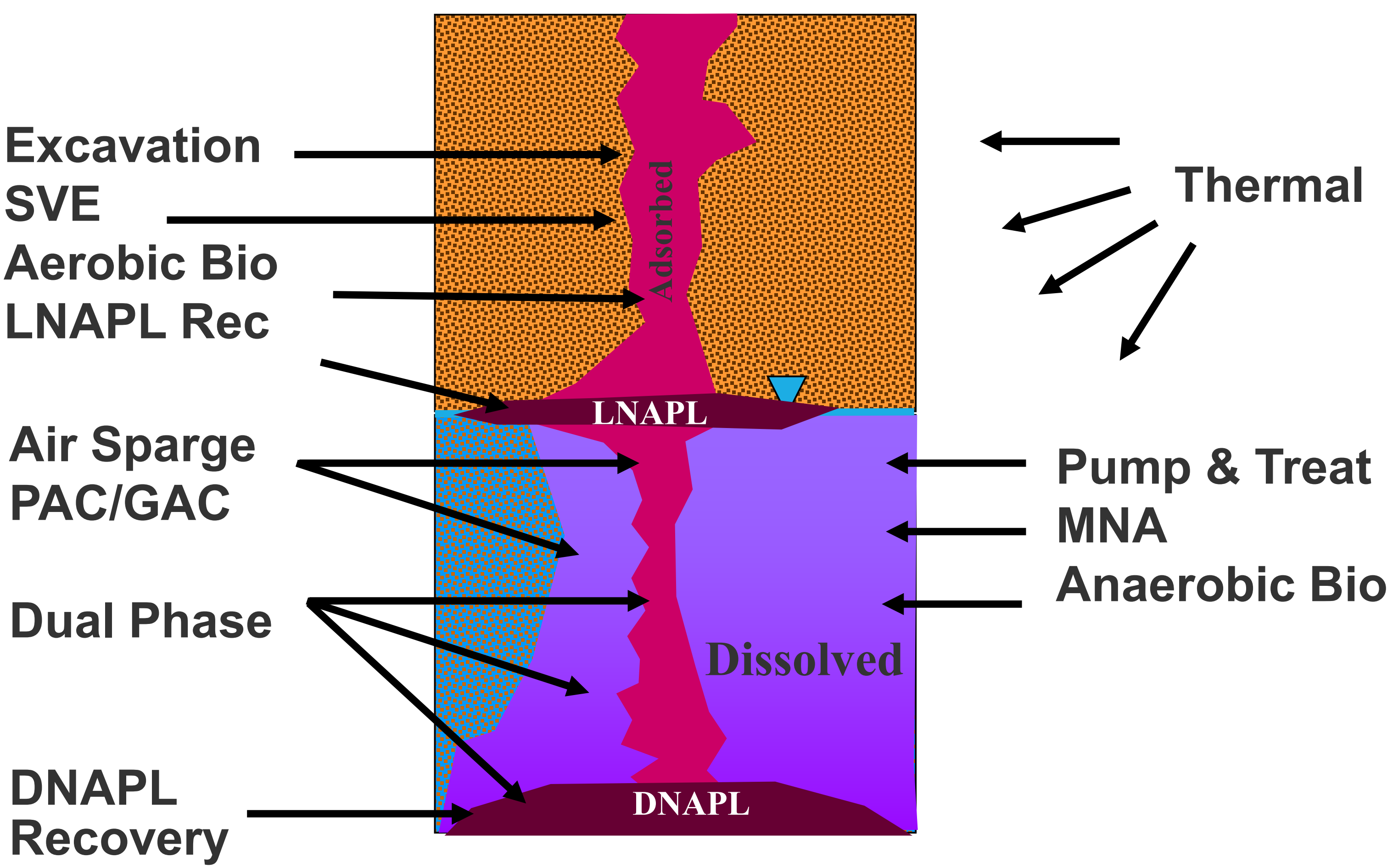
	PROVECTUS TECHNOLOGY								
	Provect-IR® 🔵 🟢	Provect-IRM® 🔵 🟢	Provect-OX® 🔵 🟢	Provect-CH4® 🔵	AquaGate +CH4™ 🟢 🟤	EZVI-CH4™ 🔵	Provect-GS™ 🔵	ERD-CH4™ 🔵	Provect-ABR 🟢
Halogenated Solvents	💧	💧	💧	💧	💧	💧	💧	💧	
Hydrocarbons			💧		💧		💧		💧
Heavy Metals		💧		💧	💧		💧	💧	
Pesticides	💧	💧	💧		💧		💧		💧
Fertilizers	💧	💧			💧				💧

🔵 Groundwater Applications 🟢 Surface Soil Applications 🟤 Sediment Applications



We Now Sell ZVI

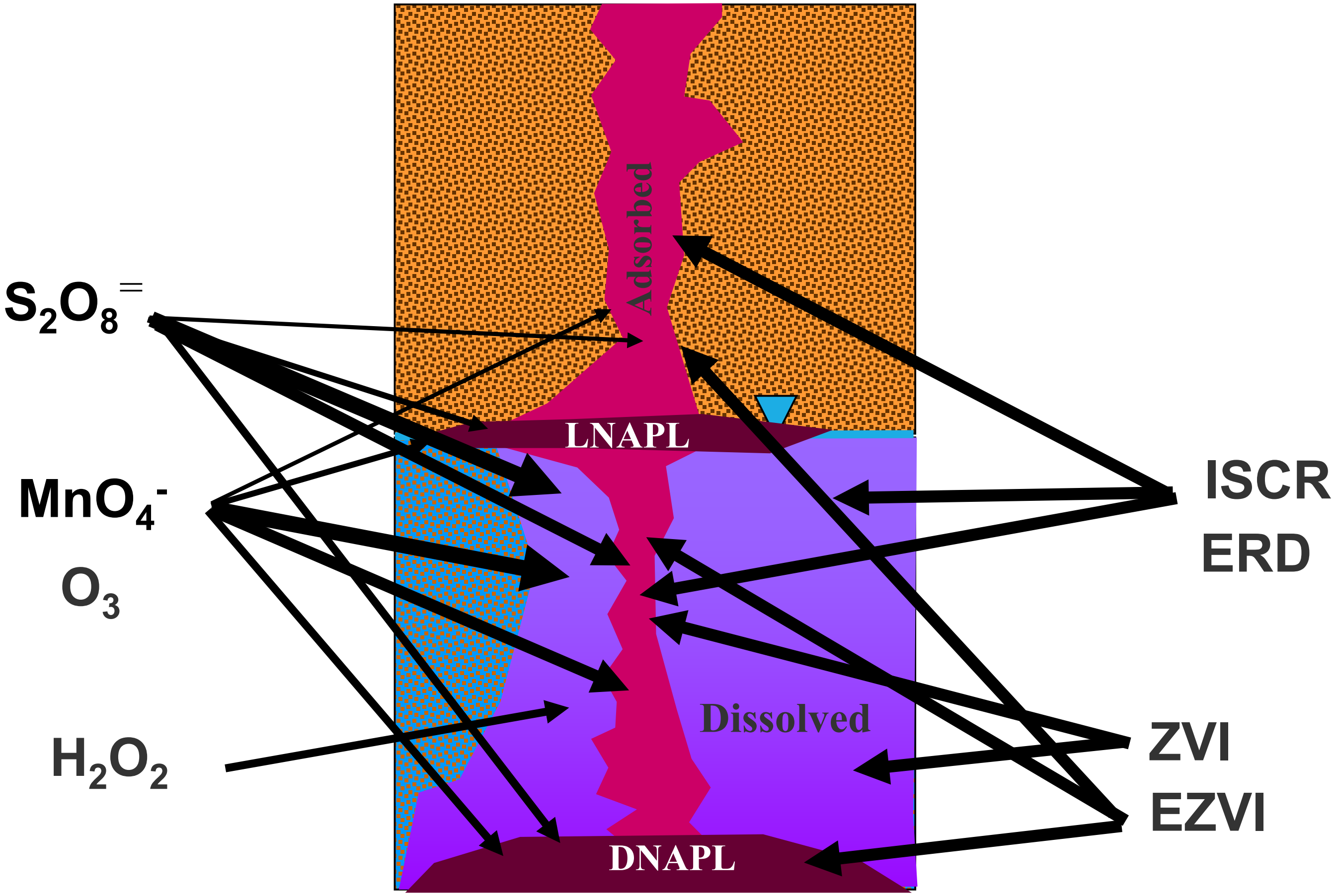
Conventional Remediation Technologies



Why Do We Need ISCO/ISCR?

- Speed
  - Many conventional technologies can take years to complete
  - Long term O&M
- Efficacy
  - Many cannot reach RAO / MCLs
  - Many require treatment / disposal of impacted media
  - Most are ineffective with DNAPLs
  - Ultimately, complete destruction of COI not always achieved
- Cost
  - Many have high O&M&M
  - Sustainability can be questionable

Applicability of ISCO/ISCR Technologies



$S_2O_8^{=}$

MnO_4^-

O_3

H_2O_2

ISCR

ERD

ZVI

EZVI

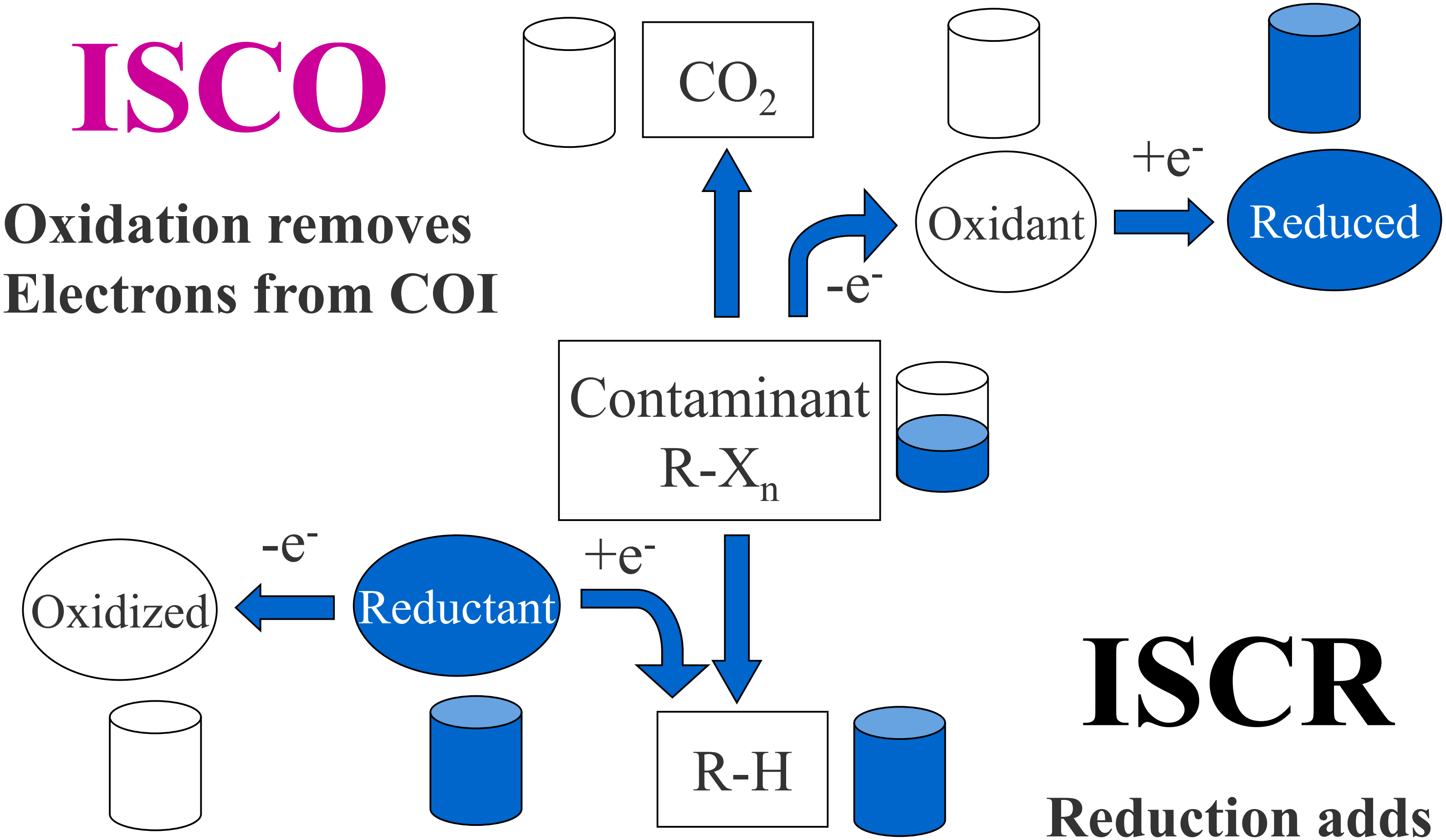
Fast, Effective (terminal destruction),

Cost Efficient and *In Situ*

Understanding ISCO/ISCR Reactions

ISCO

Oxidation removes Electrons from COI



CO_2

Oxidant

$+e^-$

Reduced

$-e^-$

Contaminant
R-X_n

Oxidized

$-e^-$

Reductant

$+e^-$

R-H

ISCR

Reduction adds Electrons to COI

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

Oxidation Potentials of Common ISCO

stronger oxidizer

Oxidation Potentials	Volts
Fluorine (F_2)	2.87
Hydroxyl radical ($OH\bullet$)	2.80
Persulfate radical ($SO_4\bullet$)	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

Higher oxidation potential = stronger the oxidizer

Reactivity of Various ISCO Reagents

Oxidant	Amenable VOC's	Reluctant VOCs	Recalcitrant VOCs	Limitations
Peroxide, Old Fenton's	PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA	DCA, CH_2Cl_2	TCA, CT, $CHCl_3$	Stability (25-95% decomp/hr), low pH
Peroxide, New Fenton's	PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA	DCA, CH_2Cl_2,TCA, CT, CHCl3		Stability (10-50% decomp/hr)
Potassium Permanganate	PCE, TCE, DCE, VC, TEX, PAH	MTBE, TBA	TCA, CT, B, $CHCl_3$, DCA, CB, CH_2Cl_2	Soil oxidant demand
Sodium Permanganate	PCE, TCE, DCE, VC, TEX, PAH	MTBE, TBA	TCA, CT, B, $CHCl_3$, DCA, CB, CH_2Cl_2	Soil oxidant demand
Sodium Persulfate, Fe	PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA	DCA, CH_2Cl_2, $CHCl_3$	TCA, CT	Stability (10-25% decomp/wk), low pH
Sodium Persulfate, Base	All VOCs			Stability (10-25% decomp/wk), NaOH costs
Sodium Persulfate, Heat	All VOCs			Stability (10-50% decomp/day), low pH, heating costs
Ozone	PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA		DCA, CH_2Cl_2, $CHCl_3$, TCA, CT	Mass Delivery, Volatilization

ISCO Issue 1: Non-Beneficial Consumption

$$[\text{Oxidant}]_{\text{Required}} = [\text{Stoichiometric Demand}]_{\text{Contaminant}} + \left. \begin{array}{l} [\textit{Soil Matrix Demand}] + \\ \quad [\textit{Metals}]_{\textit{Red}} \\ \quad [\textit{Organic Carbon}]_{\textit{Oxidizable}} \\ [\textit{Decomposition}]_{\textit{Oxidant}} \end{array} \right\} \text{Non-Beneficial Consumption}$$

	Peroxide	Persulfate	Permanganate	Ozone
Decomposition	XXXXX	XX	--	XX
SOD - Metals	XXXX	XXXX	XXXX	XX
SOD - Organics	---	✚ ----	XXXXX	---
Advection	X	X	X	XX

↑

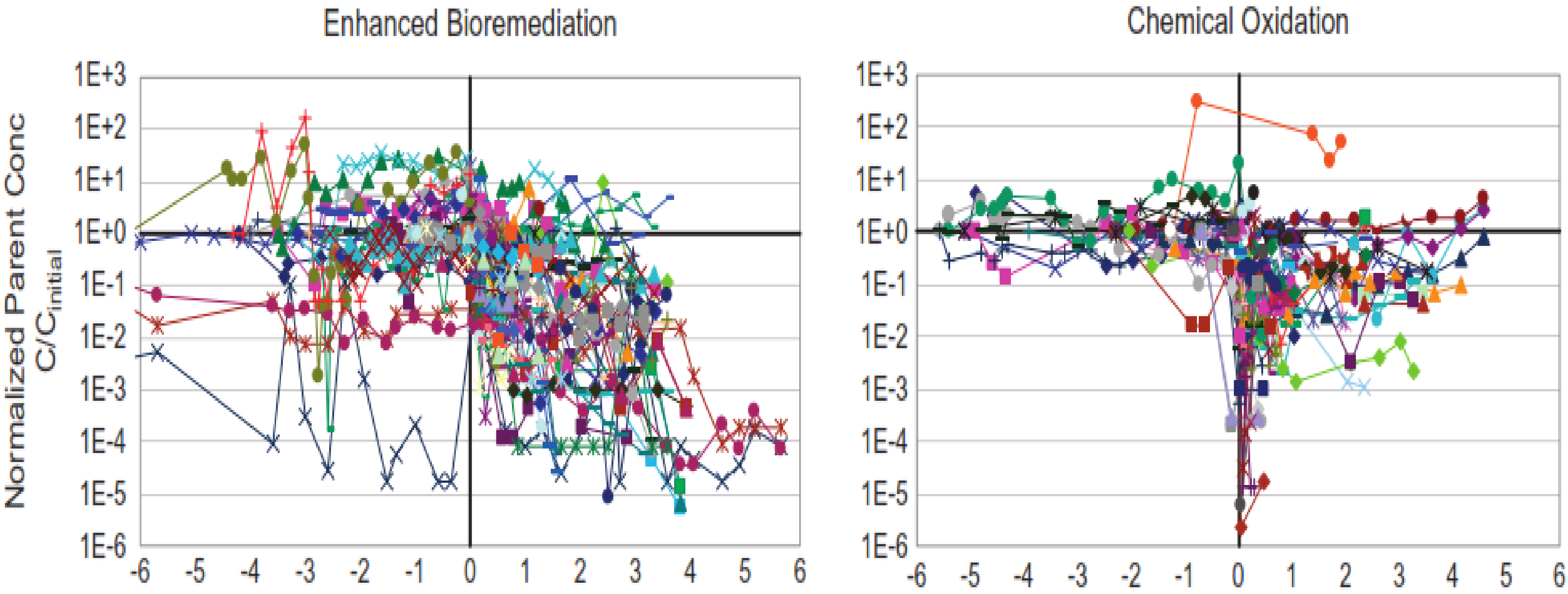
pSOD from non-impacted aquifer = less than accurate

✚ = slow to react

ISCO Issue 2: Contaminant Rebound

Figure 1. Temporal concentration records for wells at source depletion sites. Concentration is normalized by the initial measured concentration. Sampling time is normalized by the time of the initial source depletion treatment.

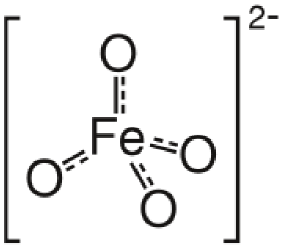
T.M. McGuire et al./ Ground Water Monitoring & Remediation 26, no. 1: 73–84 77

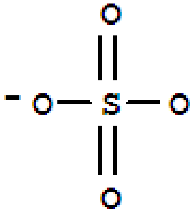


X-axis showing sampling time (years) relative to initial treatment (Time 0)

What is Provect-OX®?

- Sodium Persulfate + Ferric Oxide ISCO Reagent
  - Chemical Oxidation via Sulfate (SO4•) Radical
  - Chemical Oxidation via Ferrate (Fe6+•) Radical
- Enhances Biological Attenuation via Sulfate and Iron Reduction Processes
- Terminating Reaction Results in Pyrite: An Abiotic Reactive Particle with similar Kinetics to ZVI (BiRD / Pseudo-ISCR)
- Easily Transitions from Oxidation to Biological Attenuation to Abiotic Mineralization
- Safely Handled Catalyzed Process without the Hazards of Extreme Activators Caustics





Provect-OX Oxidation Potentials

Ferrate salts can easily be prepared from iron salts, hypochlorite and a base:

$$2\ Fe^{+3} + 3\ OCl^{-} + 4\ OH^{-} \rightarrow 2\ \mathbf{FeO_4^{-2}} + 3\ Cl^{-} + 2\ H_2O$$

$$S_2O_8^{-2} + \text{ACTIVATOR}\ [Fe^{+3}] \rightarrow SO_4\bullet^{-} + e^{-} \rightarrow SO_4\bullet^{-2}$$

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

Ferrate Chemistry is Complex…

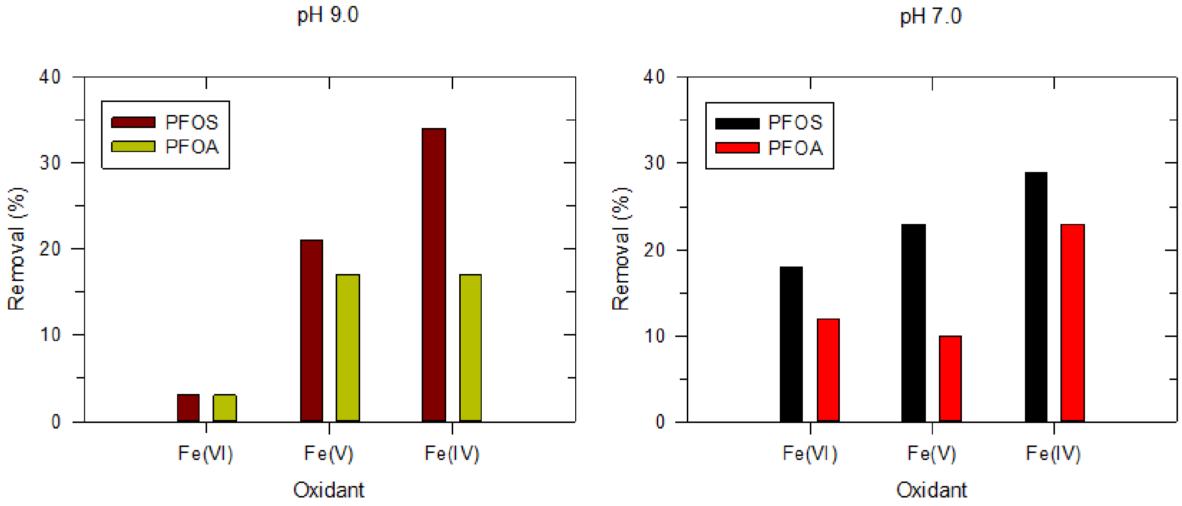
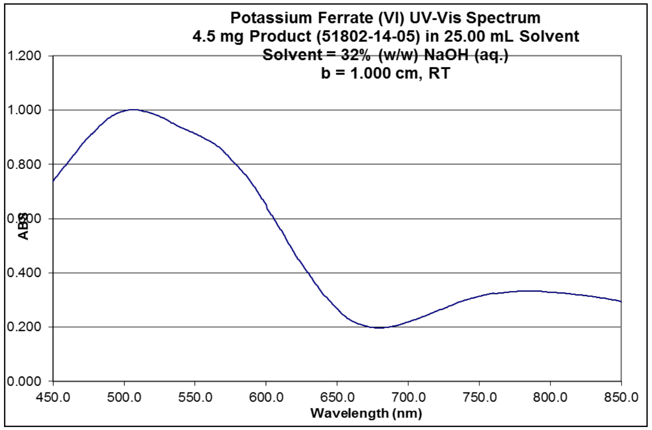


Figure 3. Oxidation of perfluorooctylsulfonate and perfluorooctanoic acid by one application of ferrates at pH 9.0 and 7.0 after five days.



Provect-OX® Coupled Oxidation w/ Sustained Bioremediation

- List \$1.95 / lb includes activator
- US Patent 9,126,245

- >\$1.35 / lb persulfate only

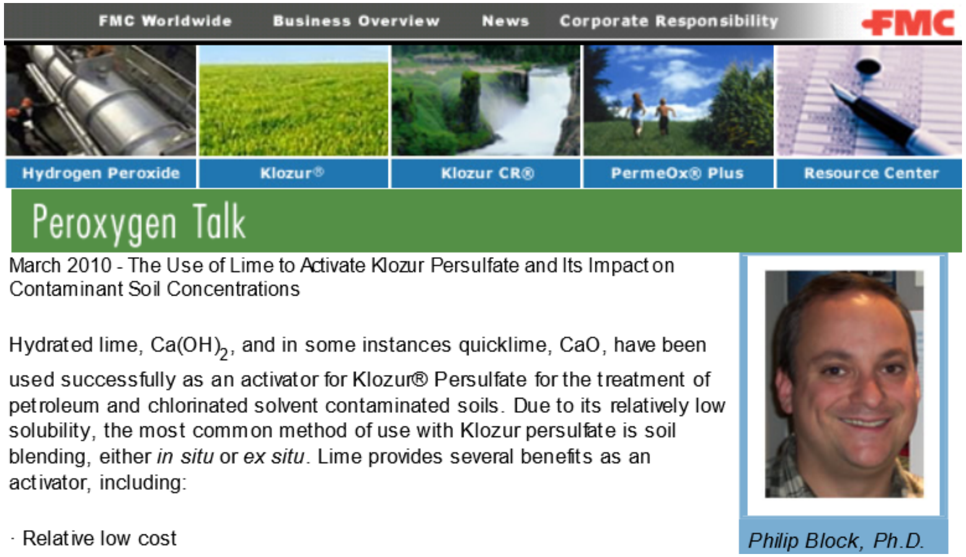
- Safely Handled
- All in one bag
- Uses Fe^{+3} as activator
- Conserves Oxidant
- Formation of Reactive Ferrate Species
- Enhances Bioattenuation Fe + SO_4
- Encourages the Formation of Pyrite
- Prevents H_2S Formation
- Minimizes Heavy metal mobilization
- No Heat generated = safer

- When Chelated Fe^{+2} used as activator EDTA Consumes the Oxidant
- When Caustic is used as activator
  - Short Lived Reaction
  - H_2S Formed
  - Secondary plumes / metals (Cr)
  - Can generate extreme heat
  - Handling and Safety issues

pH 10+ Does Not Promote Bio

Does Not Manage Rebound

Base-Activated Persulfate and Rebound



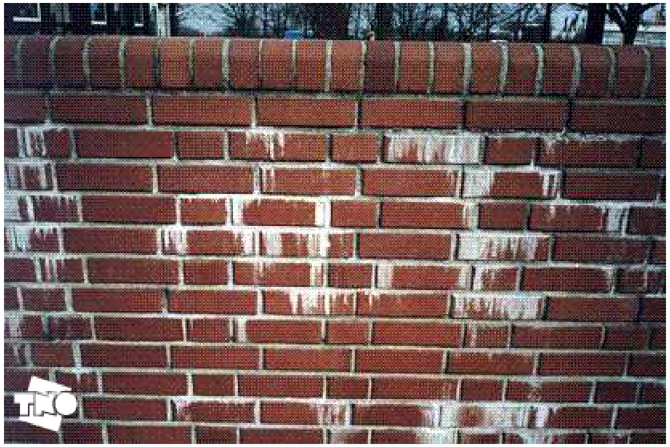
Peroxygen Talk

March 2010 - The Use of Lime to Activate Klozur Persulfate and Its Impact on Contaminant Soil Concentrations

Hydrated lime, $Ca(OH)_2$, and in some instances quicklime, CaO, have been used successfully as an activator for Klozur® Persulfate for the treatment of petroleum and chlorinated solvent contaminated soils. Due to its relatively low solubility, the most common method of use with Klozur persulfate is soil blending, either *in situ* or *ex situ*. Lime provides several benefits as an activator, including:

· Relative low cost

Philip Block, Ph.D.

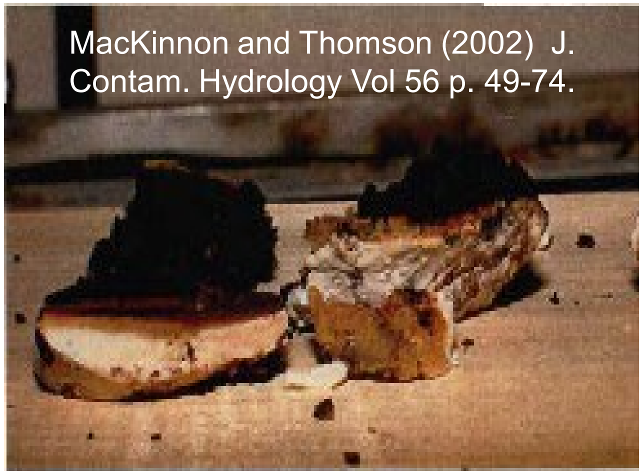


“In conclusion, it is evident that the standard EPA test method 3545 does not adequately account for reversible, lime encapsulation due to a lack of pH adjustment prior to extraction. This may lead to erroneous conclusions that lime application is adequate in remediating contaminated soils, and that it provides equivalent benefit to lime activated persulfate treatment. Adjusting the pH to circum-neutral levels prior to extraction will provide a more accurate estimation of the contaminant destruction that is capable with lime and lime activated persulfate”. FMC (now PeroxyChem) March, 2010.

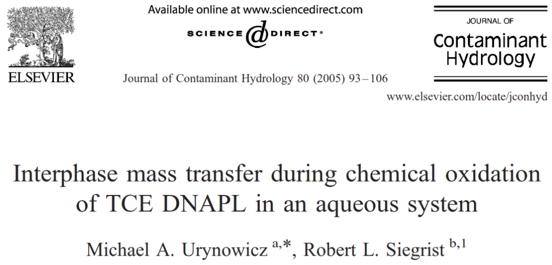
MnO_2 Potential Rebound

In the presence of an organic compound (R), MnO4 reactions yield an oxidized intermediate (Rox) or CO_2 ,… plus MnO_2

$R + MnO_4^- \rightarrow MnO_2 + CO_2$ or Rox



MacKinnon and Thomson (2002) J. Contam. Hydrology Vol 56 p. 49-74.



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JOURNAL OF Contaminant Hydrology
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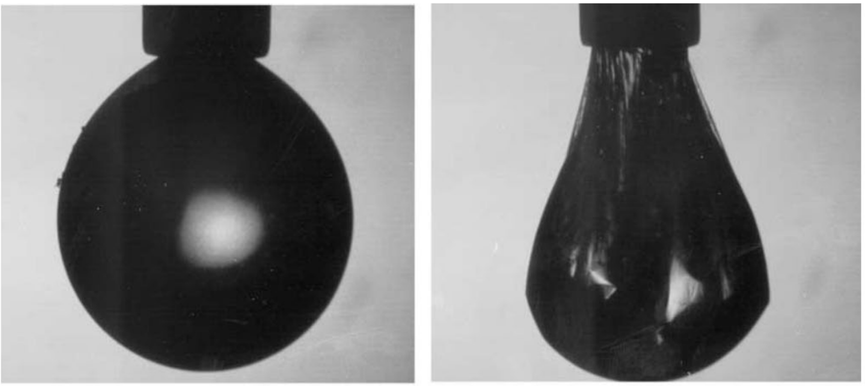
Interphase mass transfer during chemical oxidation of TCE DNAPL in an aqueous system

Michael A. Urynowicz [a,*], Robert L. Siegrist [b,1]



(a) (b)

Fig. 7. (a) Photograph of a TCE droplet suspended in phosphate buffered de-ionized water from the tip of a syringe needle prior to chemical oxidation with MnO_4^-. (b) Photograph of a TCE droplet following chemical oxidation with MnO_4^-. Needle diameter=0.8 mm.

ISCO Issue 3: Longevity of Reagents

Chemosphere

Volume 150, May 2016, Pages 239–247

A five-year performance review of field-scale, slow-release permanganate candles with recommendations for second-generation improvements

Mark Christenson[a, b], Ann Kambhu[c], James Reece[b], Steve Comfort[b], Laurie Brunner[d]

[a] AirLift Environmental, LLC, 5900 N. 58th, Suite 5, Lincoln, NE 68507, USA
[b] School of Natural Resources, University of Nebraska, Lincoln, NE 68583-0915, USA
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[d] Nebraska Department of Environmental Quality, Waste Management Division, Lincoln, NE 68509-8922, USA

Received 14 December 2015, Revised 26 January 2016, Accepted 31 January 2016, Available online 21 February 2016

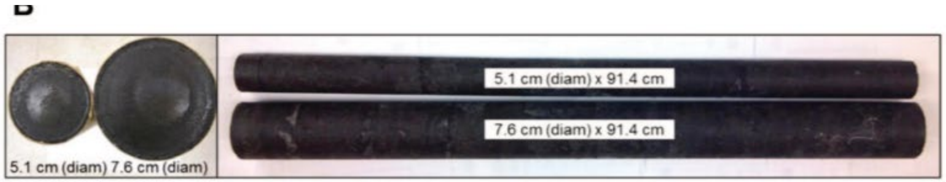
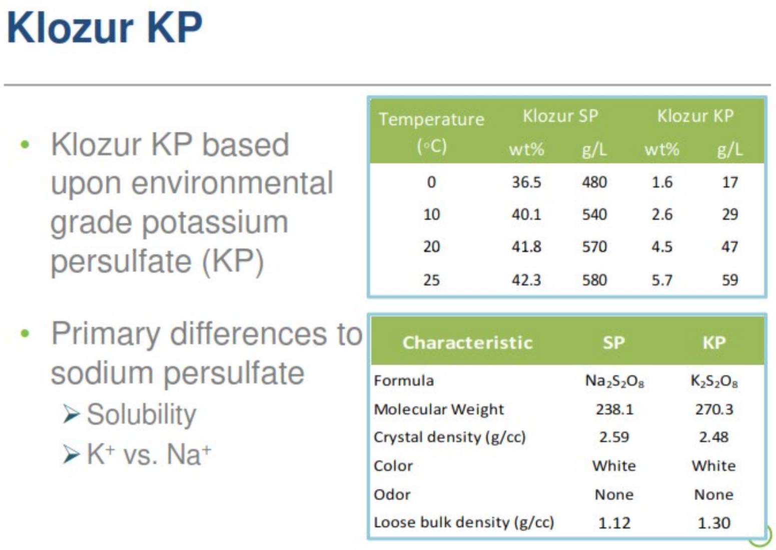


Figure 2. **(A)** Field plot of the permeable reactive barrier of SRPCs and monitoring wells; each SRPC location received five candles stack on top of each other; and **(B)** photograph of permanganate candles.

Longevity of ISCO Reagents – KP?

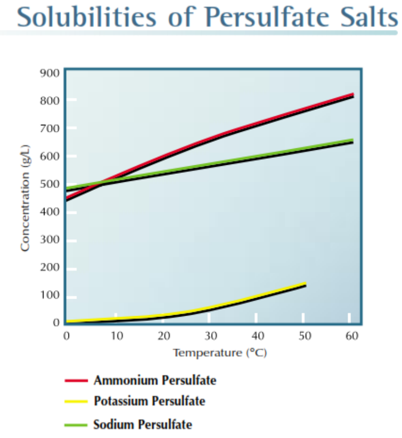


Klozur KP

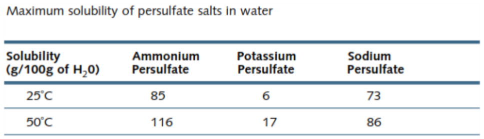
- Klozur KP based upon environmental grade potassium persulfate (KP)
- Primary differences to sodium persulfate
  - Solubility
  - K⁺ vs. Na⁺

Temperature (°C)	Klozur SP		Klozur KP	
	wt%	g/L	wt%	g/L
0	36.5	480	1.6	17
10	40.1	540	2.6	29
20	41.8	570	4.5	47
25	42.3	580	5.7	59

Characteristic	SP	KP
Formula	$Na_2S_2O_8$	$K_2S_2O_8$
Molecular Weight	238.1	270.3
Crystal density (g/cc)	2.59	2.48
Color	White	White
Odor	None	None
Loose bulk density (g/cc)	1.12	1.30



Solubilities of Persulfate Salts

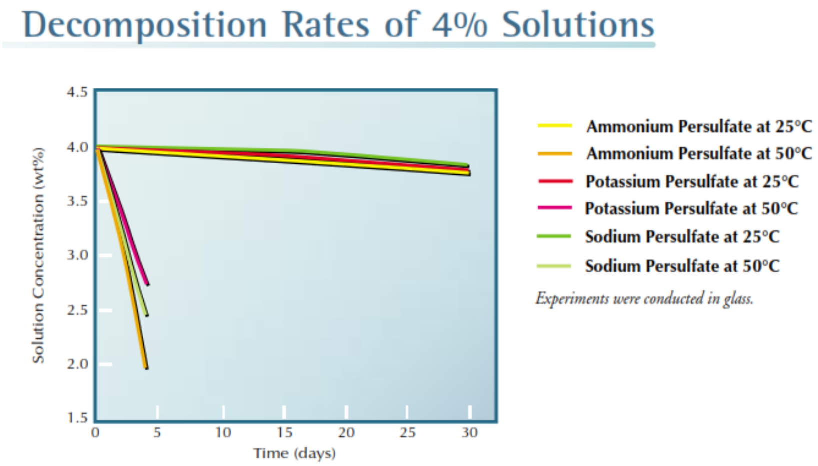


Maximum solubility of persulfate salts in water

Solubility ($g/100g$ of H_2O)	Ammonium Persulfate	Potassium Persulfate	Sodium Persulfate
25°C	85	6	73
50°C	116	17	86

Using Klozur® Potassium Persulfate as a Slow Release Oxidant and Permeable Reactive Barrier

Patrick Hicks, Brant Smith, Brianna Desjardins & Sandy Owen
PeroxyChem
IPEC Conference New Orleans, LA
November 9, 2016



Decomposition Rates of 4% Solutions

Experiments were conducted in glass.

- Potassium persulfate (Hoag, 1998) espoused for slow release ISCO
  - Solubility < 30,000 mg/L at average GW temp 11 C
  - Kinetics historically questioned

Kinetics of KP…

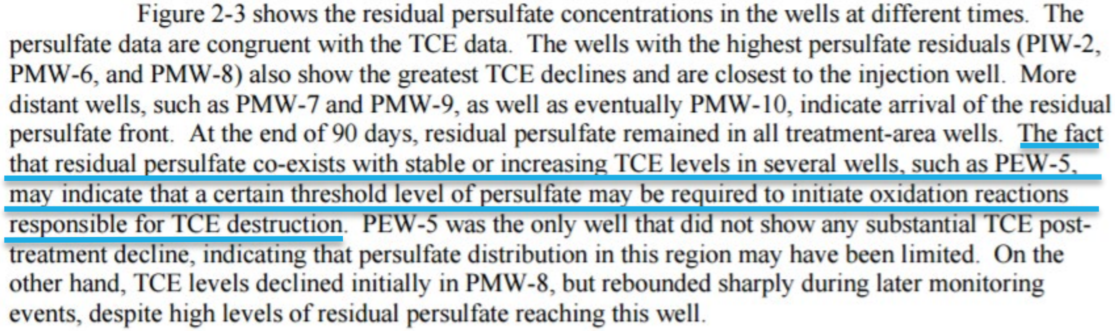
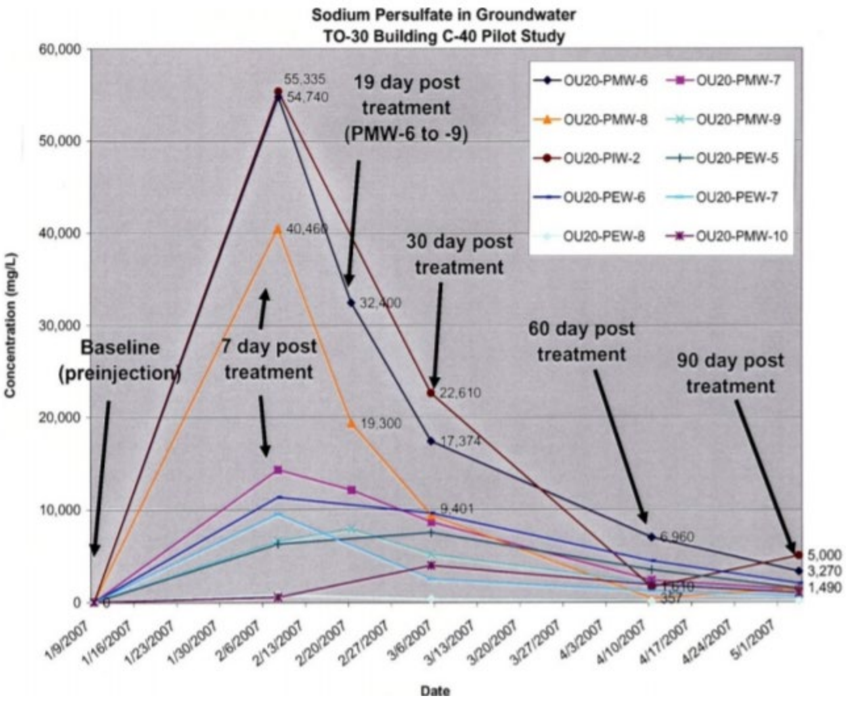
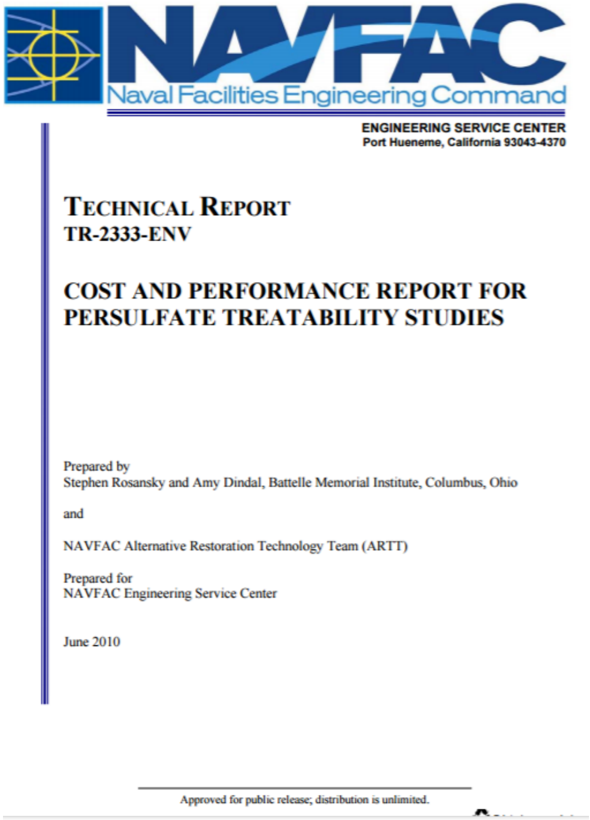


Figure 2-3 shows the residual persulfate concentrations in the wells at different times. The persulfate data are congruent with the TCE data. The wells with the highest persulfate residuals (PIW-2, PMW-6, and PMW-8) also show the greatest TCE declines and are closest to the injection well. More distant wells, such as PMW-7 and PMW-9, as well as eventually PMW-10, indicate arrival of the residual persulfate front. At the end of 90 days, residual persulfate remained in all treatment-area wells. The fact that residual persulfate co-exists with stable or increasing TCE levels in several wells, such as PEW-5, may indicate that a certain threshold level of persulfate may be required to initiate oxidation reactions responsible for TCE destruction. PEW-5 was the only well that did not show any substantial TCE post-treatment decline, indicating that persulfate distribution in this region may have been limited. On the other hand, TCE levels declined initially in PMW-8, but rebounded sharply during later monitoring events, despite high levels of residual persulfate reaching this well.



Sodium Persulfate in Groundwater
TO-30 Building C-40 Pilot Study



NAVFAC
Naval Facilities Engineering Command

ENGINEERING SERVICE CENTER
Port Hueneme, California 93043-4370

TECHNICAL REPORT
TR-2333-ENV

COST AND PERFORMANCE REPORT FOR
PERSULFATE TREATABILITY STUDIES

Prepared by
Stephen Rosansky and Amy Dindal, Battelle Memorial Institute, Columbus, Ohio

and

NAVFAC Alternative Restoration Technology Team (ARTT)

Prepared for
NAVFAC Engineering Service Center

June 2010

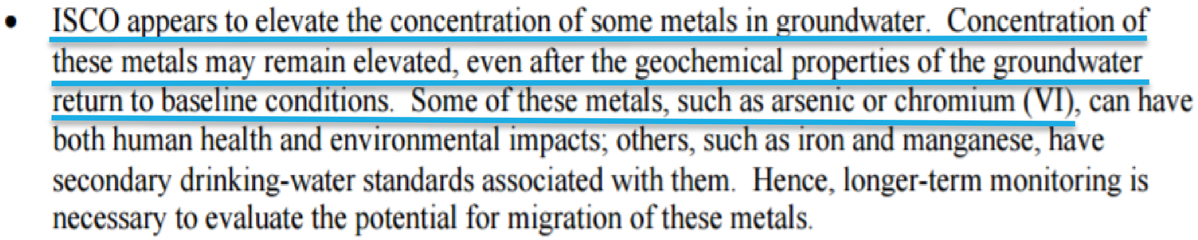
Approved for public release; distribution is unlimited.

Page 8 – North Island, CA

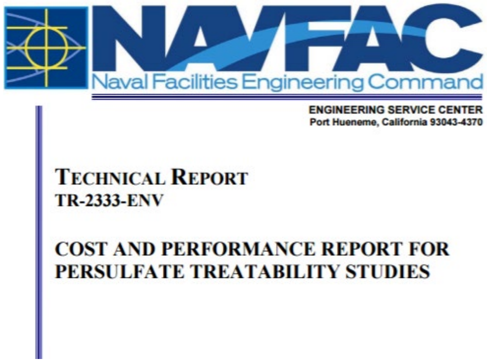
Ion Chromatography may be more accurate than the field test kits used

Issue 4: ISCO and Heavy Metals

Page iv – Executive Summary



- ISCO appears to elevate the concentration of some metals in groundwater. Concentration of these metals may remain elevated, even after the geochemical properties of the groundwater return to baseline conditions. Some of these metals, such as arsenic or chromium (VI), can have both human health and environmental impacts; others, such as iron and manganese, have secondary drinking-water standards associated with them. Hence, longer-term monitoring is necessary to evaluate the potential for migration of these metals.



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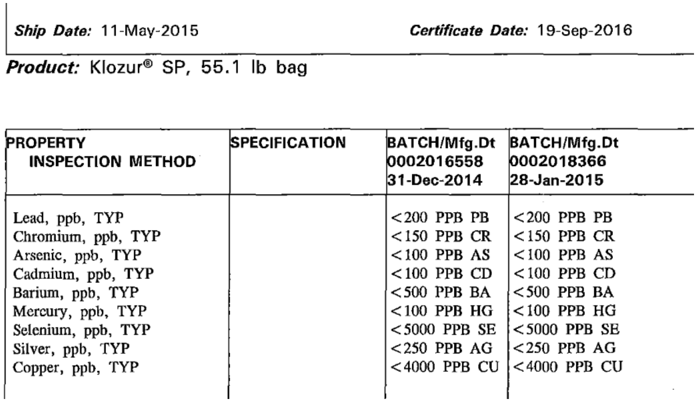
Naval Facilities Engineering Command
ENGINEERING SERVICE CENTER
Port Hueneme, California 93043-4370

TECHNICAL REPORT
TR-2333-ENV

COST AND PERFORMANCE REPORT FOR PERSULFATE TREATABILITY STUDIES



Ship Date: 11-May-2015 **Certificate Date:** 19-Sep-2016

Product: Klozur® SP, 55.1 lb bag

PROPERTY INSPECTION METHOD	SPECIFICATION	BATCH/Mfg.Dt 0002016558 31-Dec-2014	BATCH/Mfg.Dt 0002018366 28-Jan-2015
Lead, ppb, TYP		<200 PPB PB	<200 PPB PB
Chromium, ppb, TYP		<150 PPB CR	<150 PPB CR
Arsenic, ppb, TYP		<100 PPB AS	<100 PPB AS
Cadmium, ppb, TYP		<100 PPB CD	<100 PPB CD
Barium, ppb, TYP		<500 PPB BA	<500 PPB BA
Mercury, ppb, TYP		<100 PPB HG	<100 PPB HG
Selenium, ppb, TYP		<5000 PPB SE	<5000 PPB SE
Silver, ppb, TYP		<250 PPB AG	<250 PPB AG
Copper, ppb, TYP		<4000 PPB CU	<4000 PPB CU

A Certificate of Analysis for sodium persulfate obtained from PeroxyChem noted that there could be as much as 150 µg/kg of chromium in their product.

Drinking Water MCL = 100 µg/L Total Cr
CA Drinking Water =10 µg/L Cr^{6+}
IN risk-based groundwater remediation = 0.3 µg/L Cr^{6+}

Adding 10,000 kg of NPS to an aquifer can add up to 1,500,000 µg Cr that will most likely be oxidized to Cr VI >> State Guidelines if not immobilized.

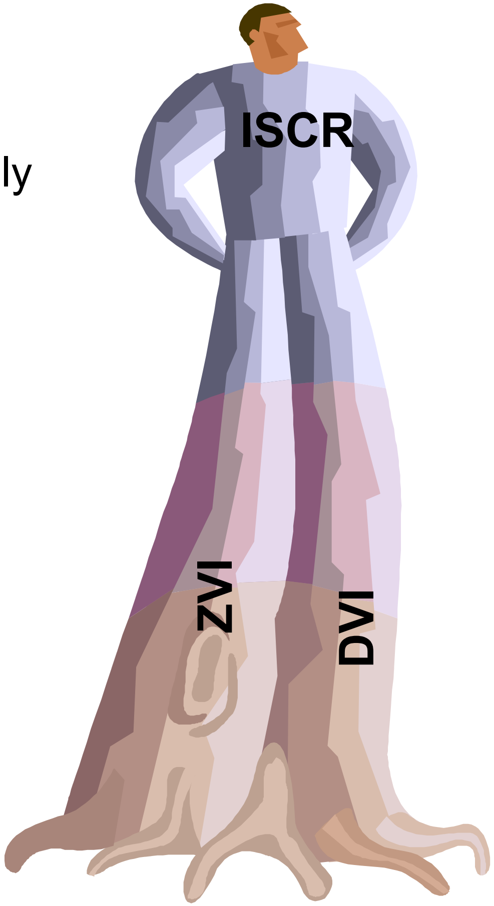
What is *In Situ* Chemical Reduction?

- In 2004, ISCR was defined as "a synergistic process that combines biotic + abiotic reactions and creates highly reducing, electron-rich conditions" (Mueller and Brown, 2004)
  - ISCR is **not** enhanced anaerobic bioremediation/ERD
  - ISCR is **not** ZVI only or BiRD or *et cetera*

Process	**Amendments**
Enhanced Anaerobic Degradation / ERD	**Molasses, (emulsified) vegetable oils / lecithins, sodium lactate, polylactic acid, whey, simple H release compounds**
***In Situ* Chemical Reduction / ISCR**	**Provect-IR™, ABC®+, EHC®, DARAMEND®**
Antimethanogenic ISCR Reagents	**Provect-IR®, Provect-IRM®, Aquablok®-CH4, and to some degree ABC-CH4™**

ISCR Builds on Decades of Knowledge

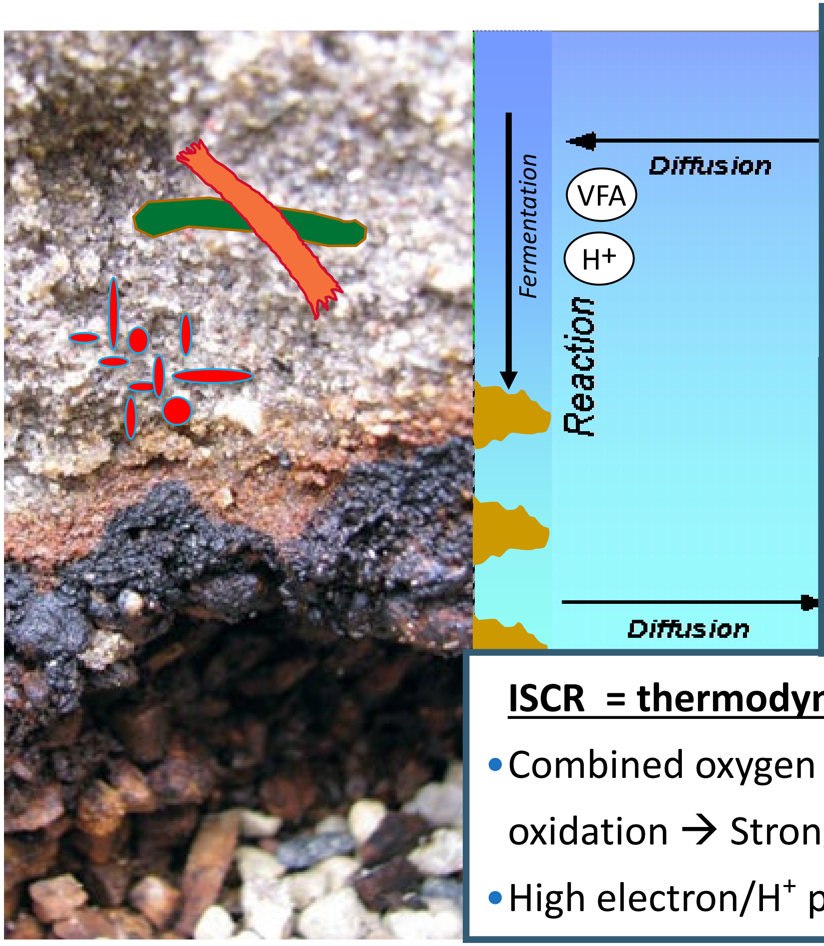
1. Biotic processes biodegrade COIs
2. Abiotic processes are based on reduced metals
3. Abiotic process are surface catalyzed
4. Abiotic pathways are different than biological pathways
5. Abiotic processes can be enhanced chemically or biologically



Makinawite FeS,
Pyrite FeS_2
Green Rust $[Fe^{2+}{}_6Fe^{3+}{}_2(OH)_{18}\cdot 4(H_2O)]$
Magnetite $Fe^{3+}{}_2Fe^{2+}O_4$
Glauconite $K_{0.6}Na_{0.05}Fe^{3+}{}_{1.3}Mg_{0.4}Fe^{2+}{}_{0.2}Al_{0.3}Si_{3.8}O_{10}(OH)_2$
Biotite $KMg_{2.5}Fe^{2+}{}_{0.5}AlSi_3O_{10}(OH)_{1.75}F_{0.25}$
Siderite $FeCO_3$
Artificially Created

- Steel Slag amended with Fe^{+2}
- Cement amended with Fe^{+2}
- Minerals treated with $Fe^{+2}{}_{(aq)}$
- Minerals treated with reductants

Carbon Fermentation + ZVI Corrosion = ISCR Multiple Reaction Mechanisms



Production of organic acids (VFAs): electron donors for reduction of COIs, O_2, NO_3, SO_4

- By preventing basification, reduces precipitate formation on ZVI surfaces to increase rate of iron corrosion /H_2 generation / reactivity

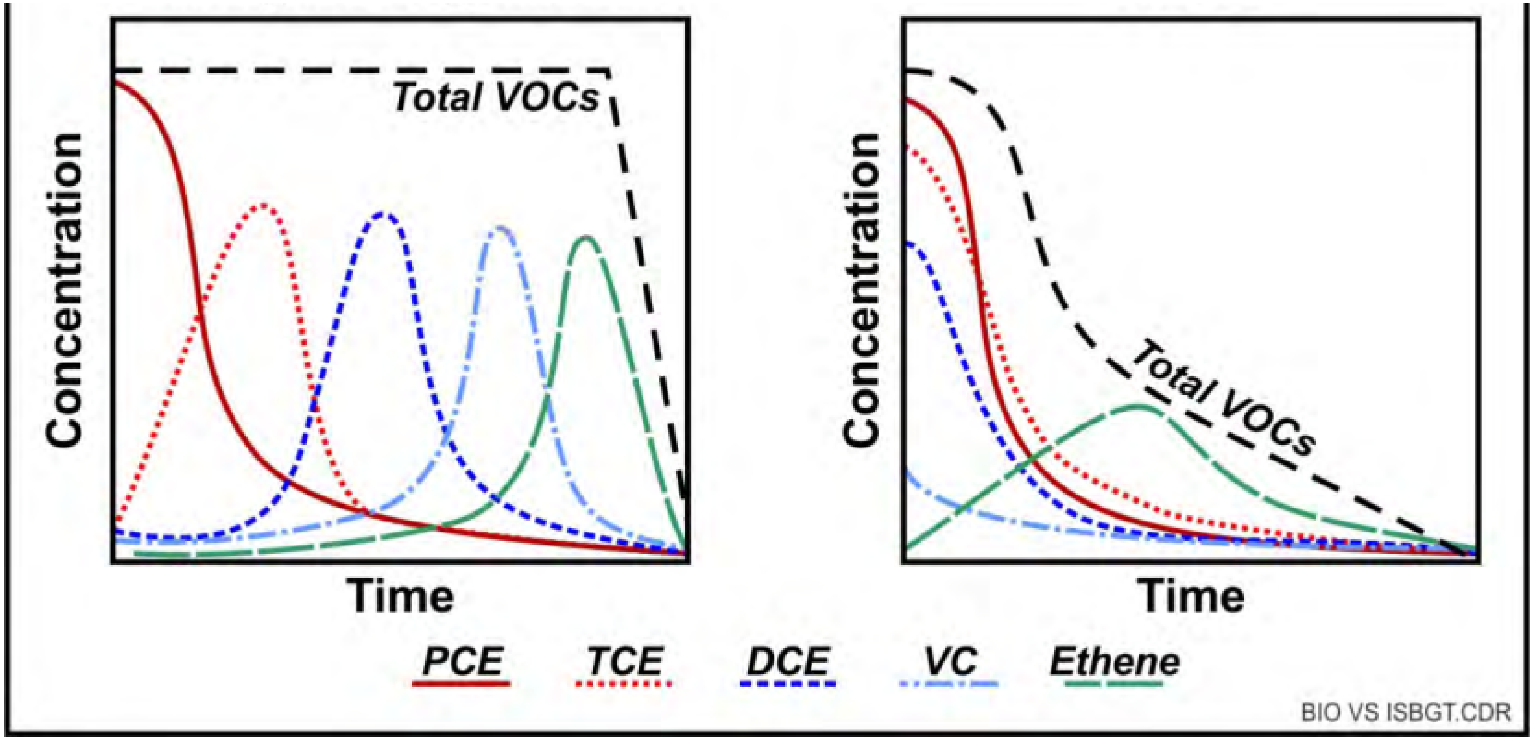
ZVI Reactions: H_2 and Fe^{+2} and generation

$$Fe^0 \rightarrow Fe^{2+} + 2e^-$$
$$2H_2O \rightarrow 2H^+ + 2OH^-$$
$$2H^+ + 2e^- \rightarrow H_{2(gas)}$$
$$R\text{-}Cl + H^+ + 2e^- \rightarrow R\text{-}H + Cl^-$$

ISCR = thermodynamic conditions for dechlorination:

- Combined oxygen consumption from carbon fermentation and iron oxidation → Strongly reduced environment (-250 to -500 mV)
- High electron/H^+ pressure

ERD v. ISCR



(Modified from Brown, 2009)

Figure 2. Abiotic versus Biological Degradation Pattern for Chlorinated Solvents

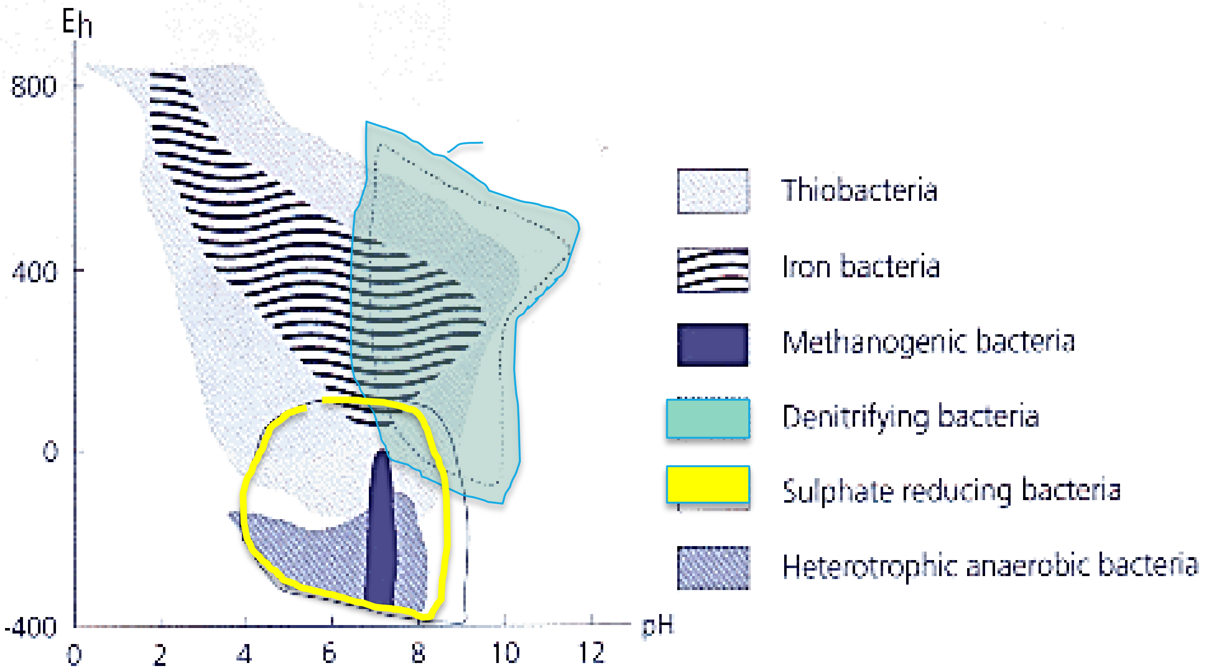
NAVFAC
Naval Facilities Engineering Command
ENGINEERING AND EXPEDITIONARY WARFARE CENTER

TECHNICAL REPORT
TR-NAVFAC EXWC-EV-1601

BIOGEOCHEMICAL TRANSFORMATION HANDBOOK

Idealized Eh pH Ranges for Microbial Growth

Microbe	Doubling Times
Dehalococcoides spp.	24 to 48 hours
Methanogens with cytochromes	10 hours
Methanogens without cytochromes	1 hour



Zajic, 1969. Sigma Aldrich

Why Add Carbon/ZVI to Reduce ORP?

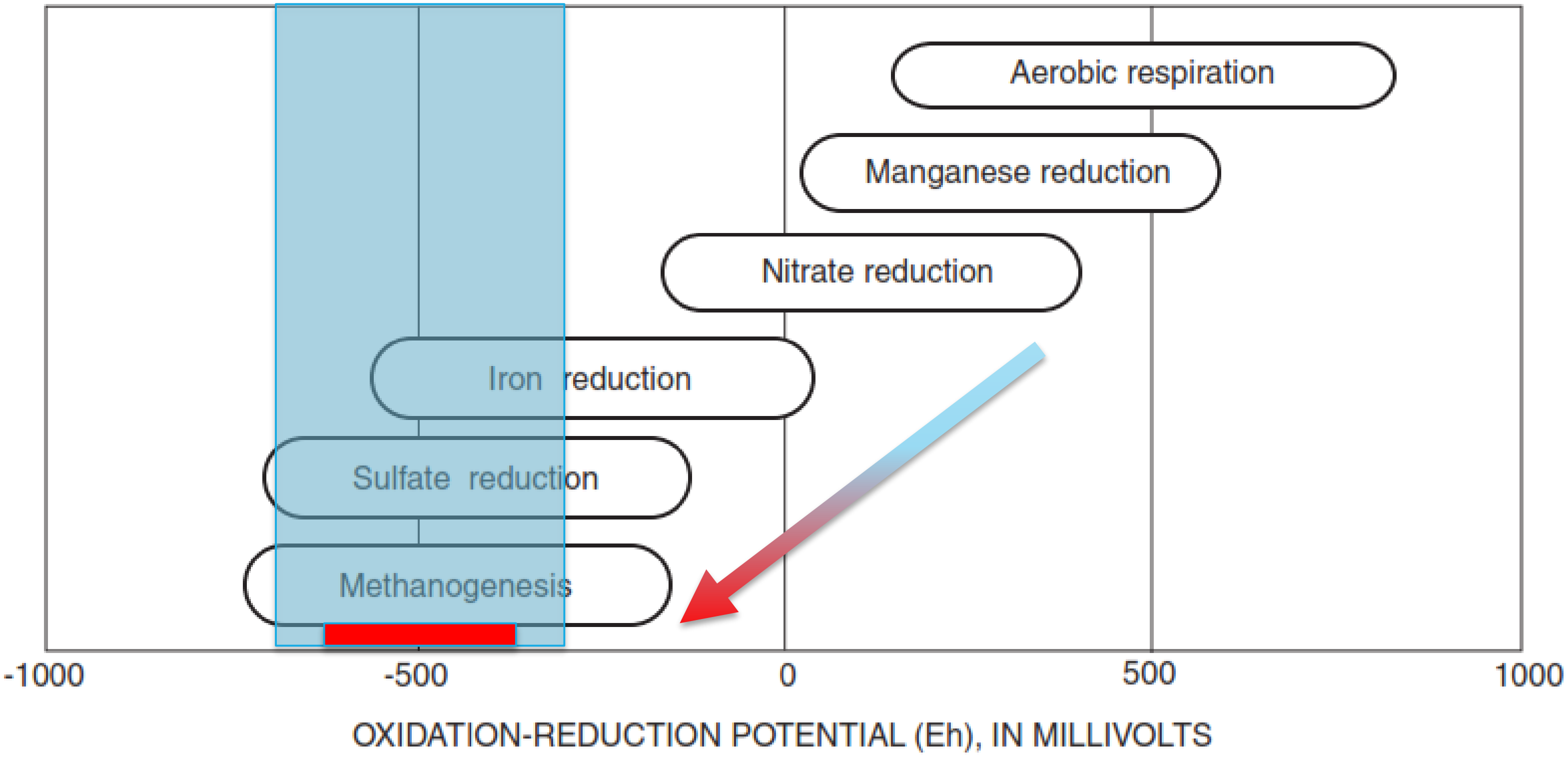
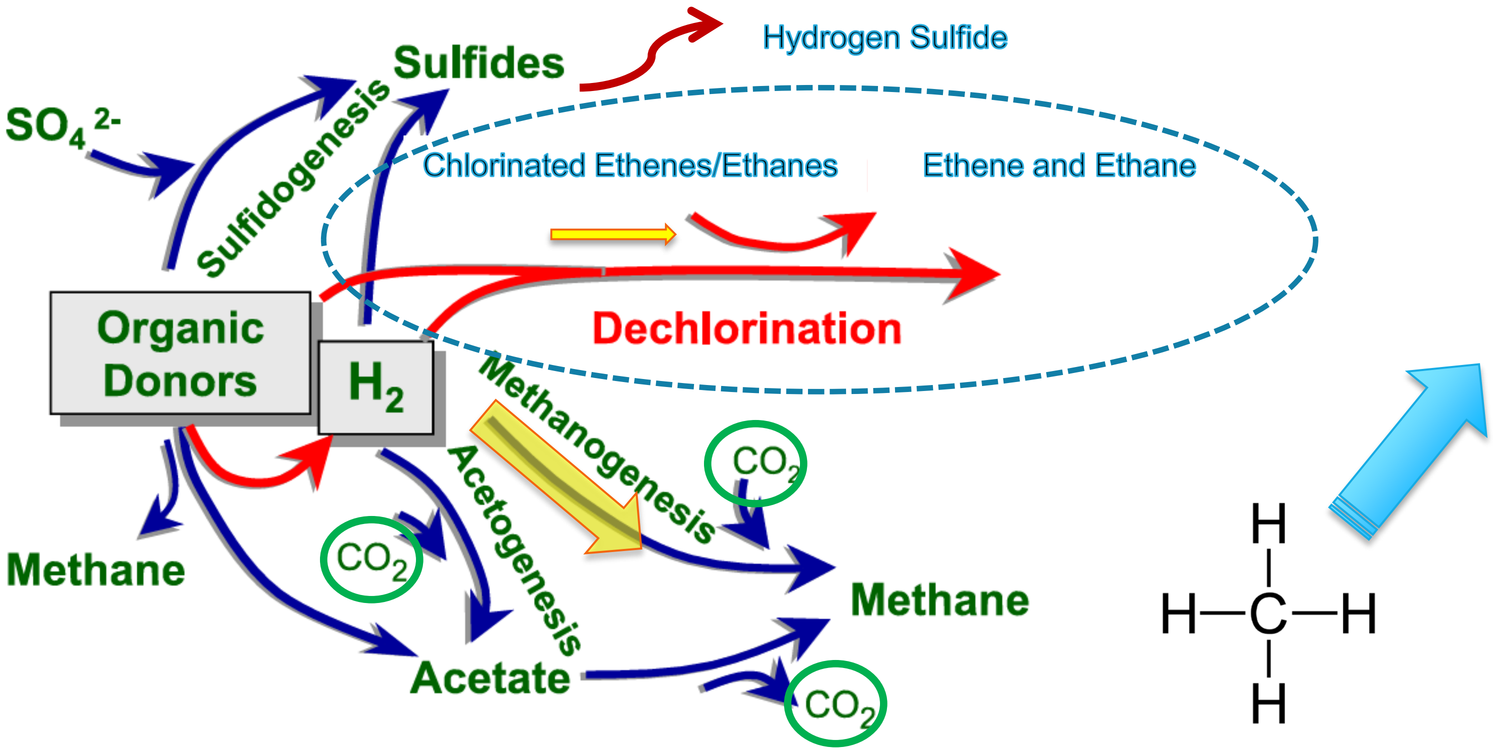


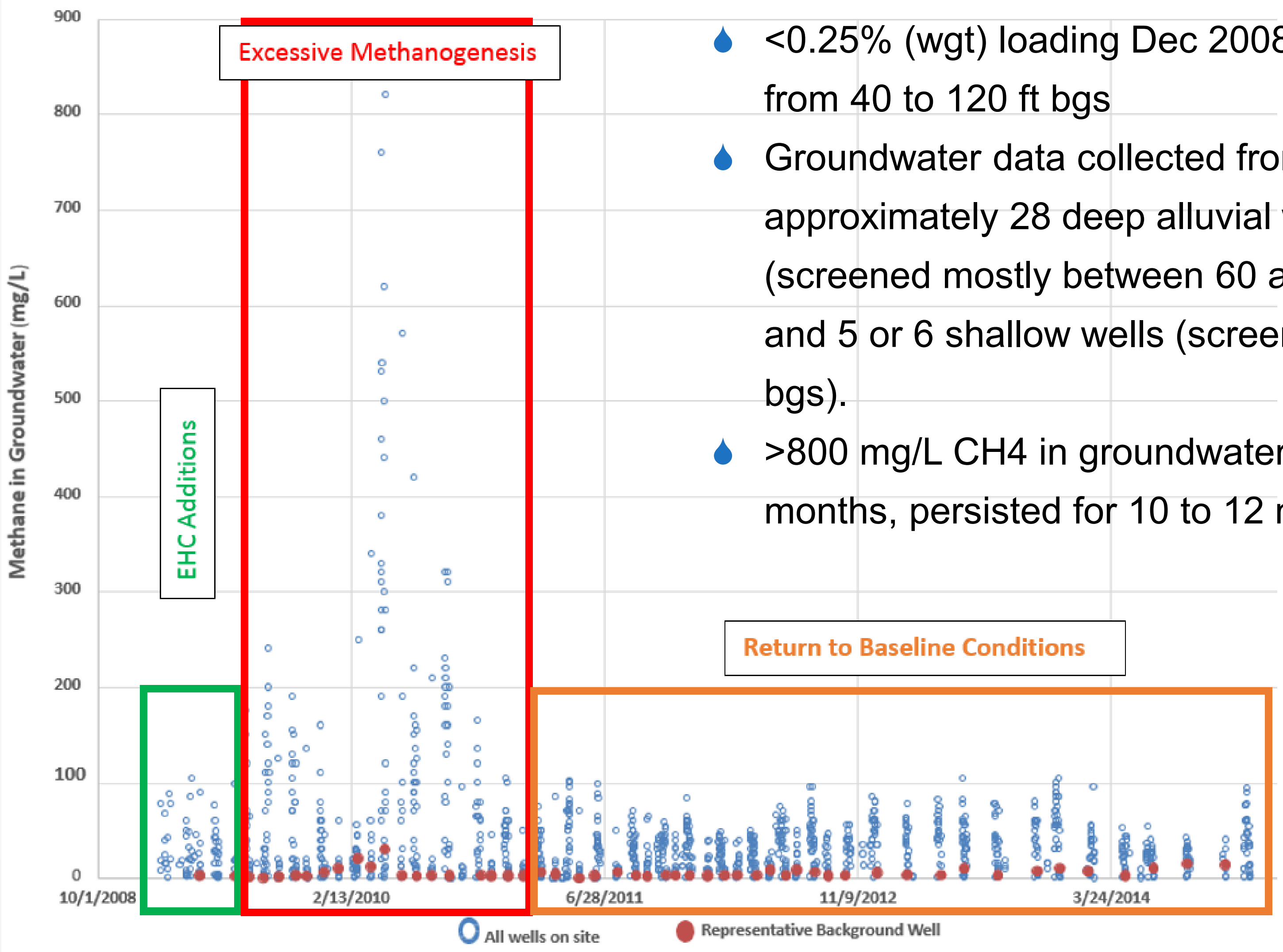
Figure 2. Oxidation-reduction potentials for selected microbial processes. (Modified from Stumm and Morgan, 1981.)

Hydrogen is the Currency

- **Where Does it Go? = Cost and Efficiency Issues**: Methanogens dominate anaerobic ecosystems and they can hinder dechlorination by competing for H_2 with dechlorinating bacteria (Yang and McCarty, 1998; yellow arrows modified by Provectus).



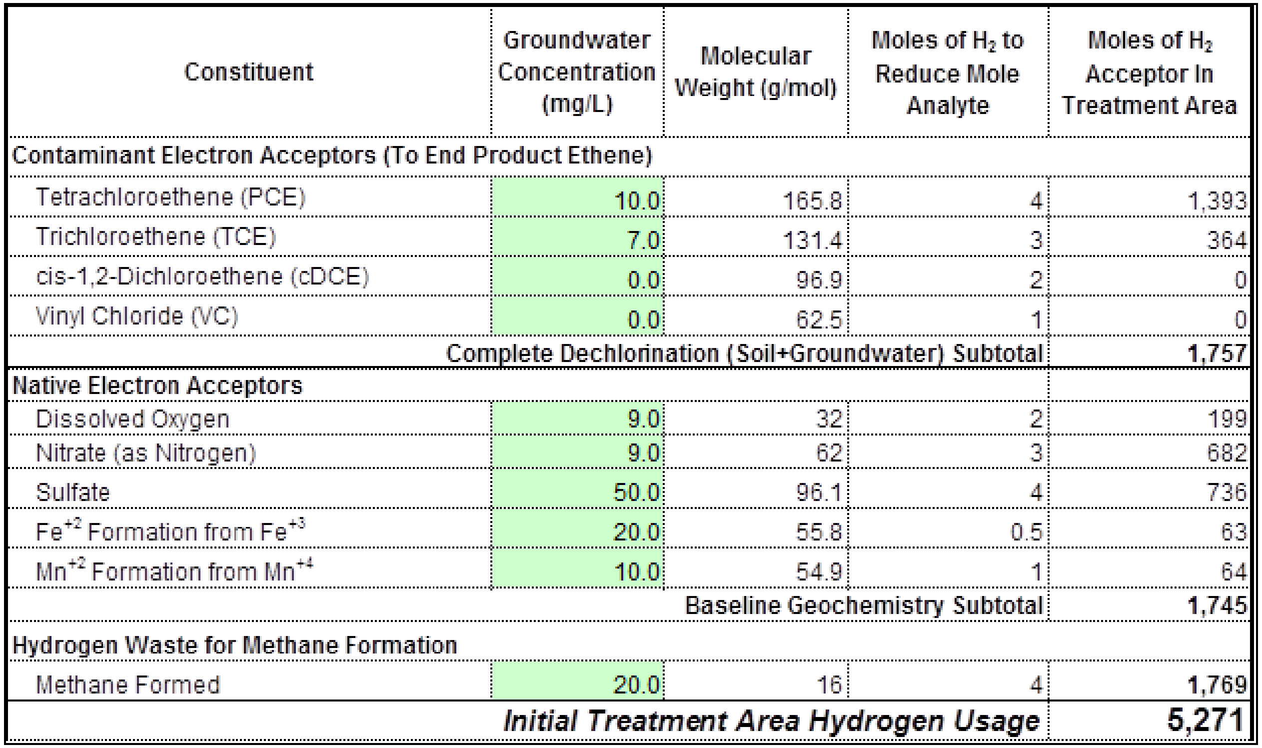
ISCR Issue 1: Excessive Methane



- <0.25% (wgt) loading Dec 2008-May, 2009 from 40 to 120 ft bgs
- Groundwater data collected from approximately 28 deep alluvial wells (screened mostly between 60 and 160 ft bgs) and 5 or 6 shallow wells (screened 25-35 ft bgs).
- >800 mg/L CH4 in groundwater after 6 months, persisted for 10 to 12 months

Cost and Efficiency

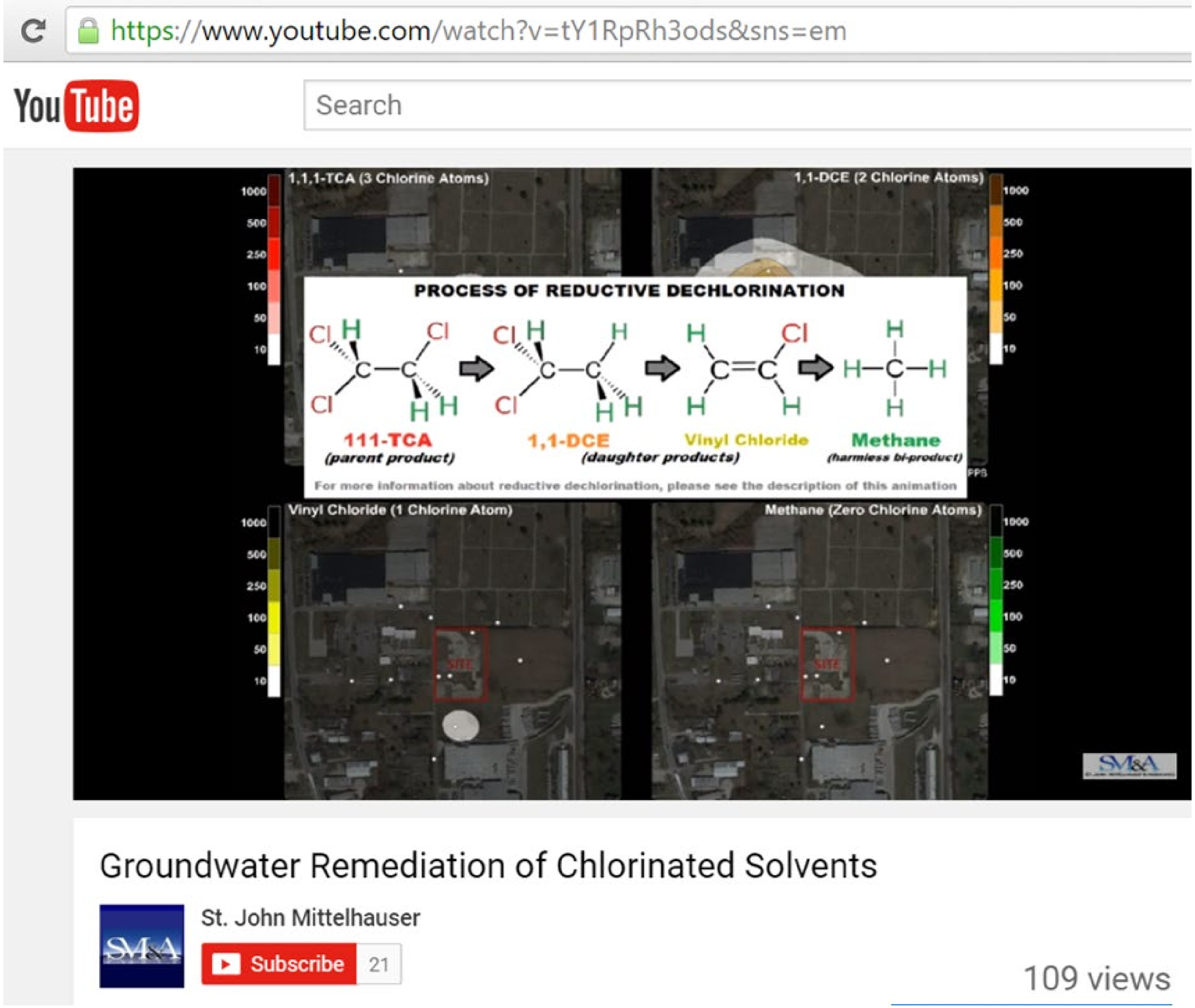
- Production of methane is a direct indication that hydrogen generated from the electron donor amendments was used by methanogens instead of the target microbes (*e.g., Dehalococcoides spp.*), substantially reducing application efficiency.



Constituent	Groundwater Concentration (mg/L)	Molecular Weight (g/mol)	Moles of H_2 to Reduce Mole Analyte	Moles of H_2 Acceptor In Treatment Area
Contaminant Electron Acceptors (To End Product Ethene)				
Tetrachloroethene (PCE)	10.0	165.8	4	1,393
Trichloroethene (TCE)	7.0	131.4	3	364
cis-1,2-Dichloroethene (cDCE)	0.0	96.9	2	0
Vinyl Chloride (VC)	0.0	62.5	1	0
			Complete Dechlorination (Soil+Groundwater) Subtotal	1,757
Native Electron Acceptors				
Dissolved Oxygen	9.0	32	2	199
Nitrate (as Nitrogen)	9.0	62	3	682
Sulfate	50.0	96.1	4	736
Fe^{+2} Formation from Fe^{+3}	20.0	55.8	0.5	63
Mn^{+2} Formation from Mn^{+4}	10.0	54.9	1	64
			Baseline Geochemistry Subtotal	1,745
Hydrogen Waste for Methane Formation				
Methane Formed	20.0	16	4	1,769
			Initial Treatment Area Hydrogen Usage	**5,271**

Even in a highly oxidized setting with relatively high total concentrations of PCE and TCE, generating just 20 mg/L of methane constitutes **greater than 33%** of the total amendment consumption based on moles of H_2.

Vapor Intrusion / H&S



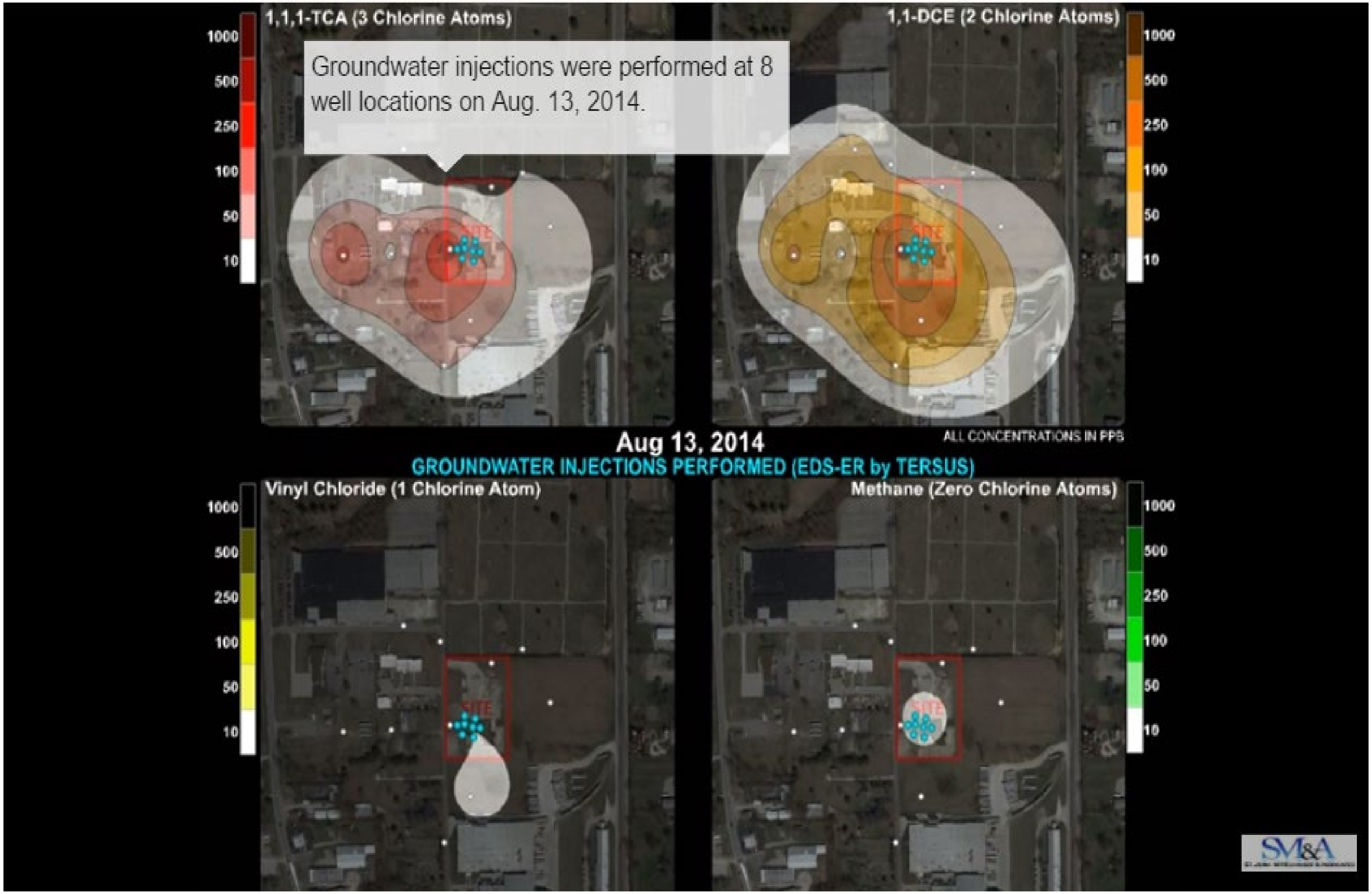
https://www.youtube.com/watch?v=tY1RpRh3ods&sns=em

Groundwater Remediation of Chlorinated Solvents

St. John Mittelhauser

109 views

EVO Case Study



1,1,1-TCA (3 Chlorine Atoms)

1,1-DCE (2 Chlorine Atoms)

Vinyl Chloride (1 Chlorine Atom)

Methane (Zero Chlorine Atoms)

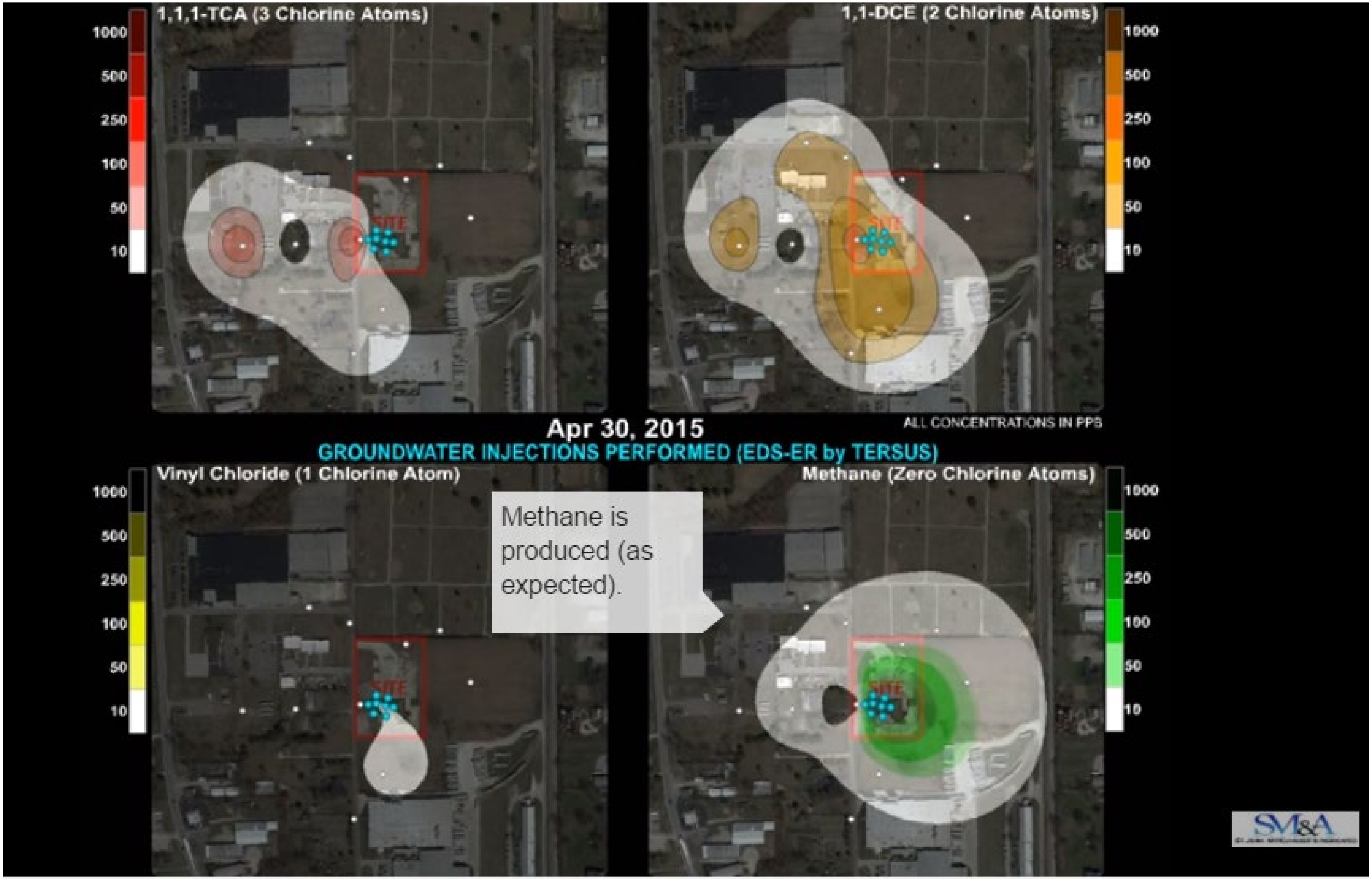
Groundwater injections were performed at 8 well locations on Aug. 13, 2014.

Aug 13, 2014

GROUNDWATER INJECTIONS PERFORMED (EDS-ER by TERSUS)

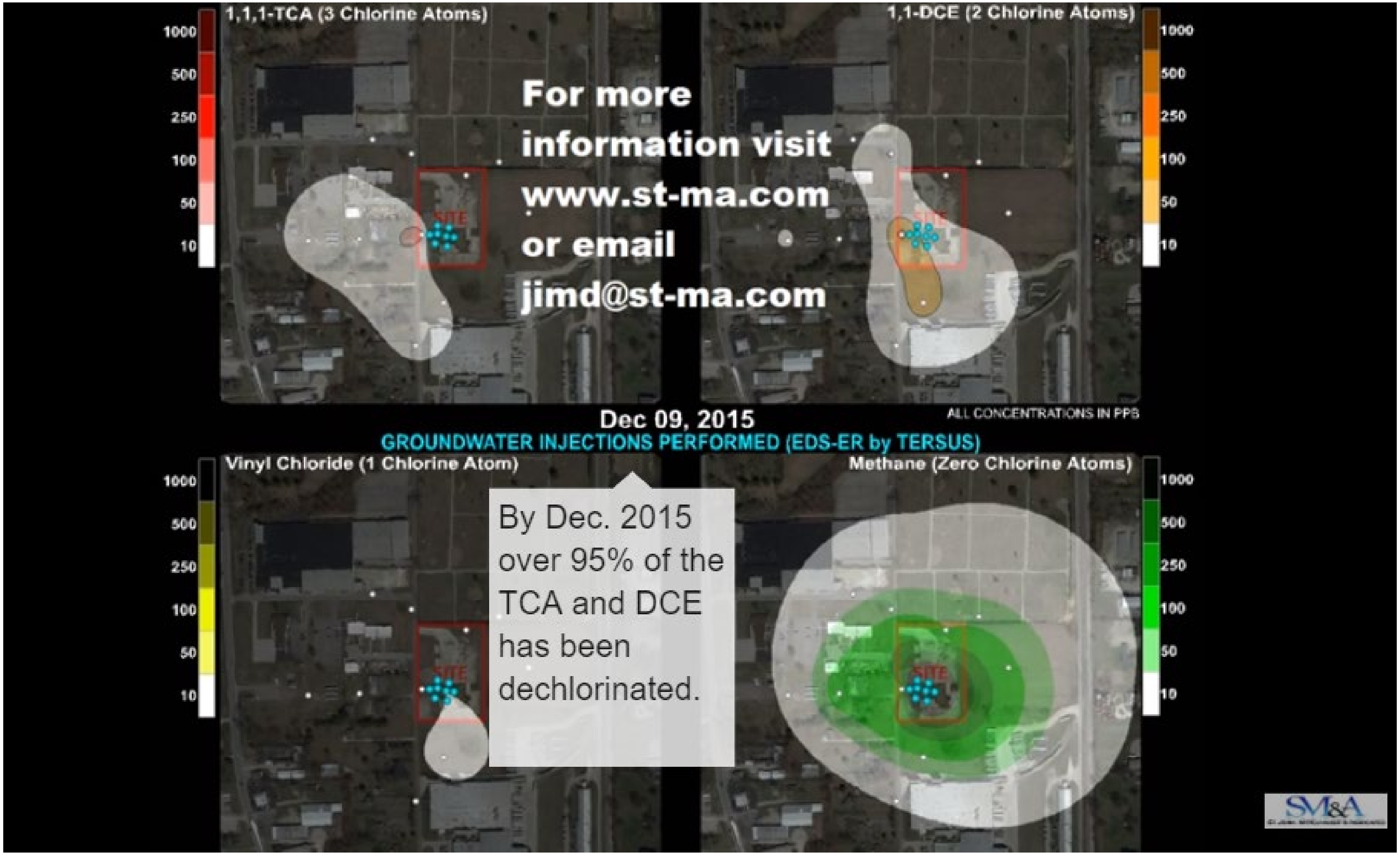
ALL CONCENTRATIONS IN PPB

EVO Case Study - 8 months



Methane is produced (as expected).

EVO Case Study - 16 months



For more information visit www.st-ma.com or email jimd@st-ma.com

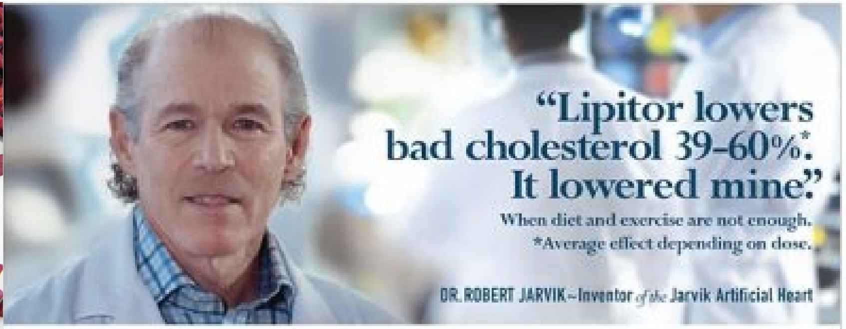
By Dec. 2015 over 95% of the TCA and DCE has been dechlorinated.

Excessive CH4 16 months post EVO

What is Red Yeast Rice (RYR) Extract?

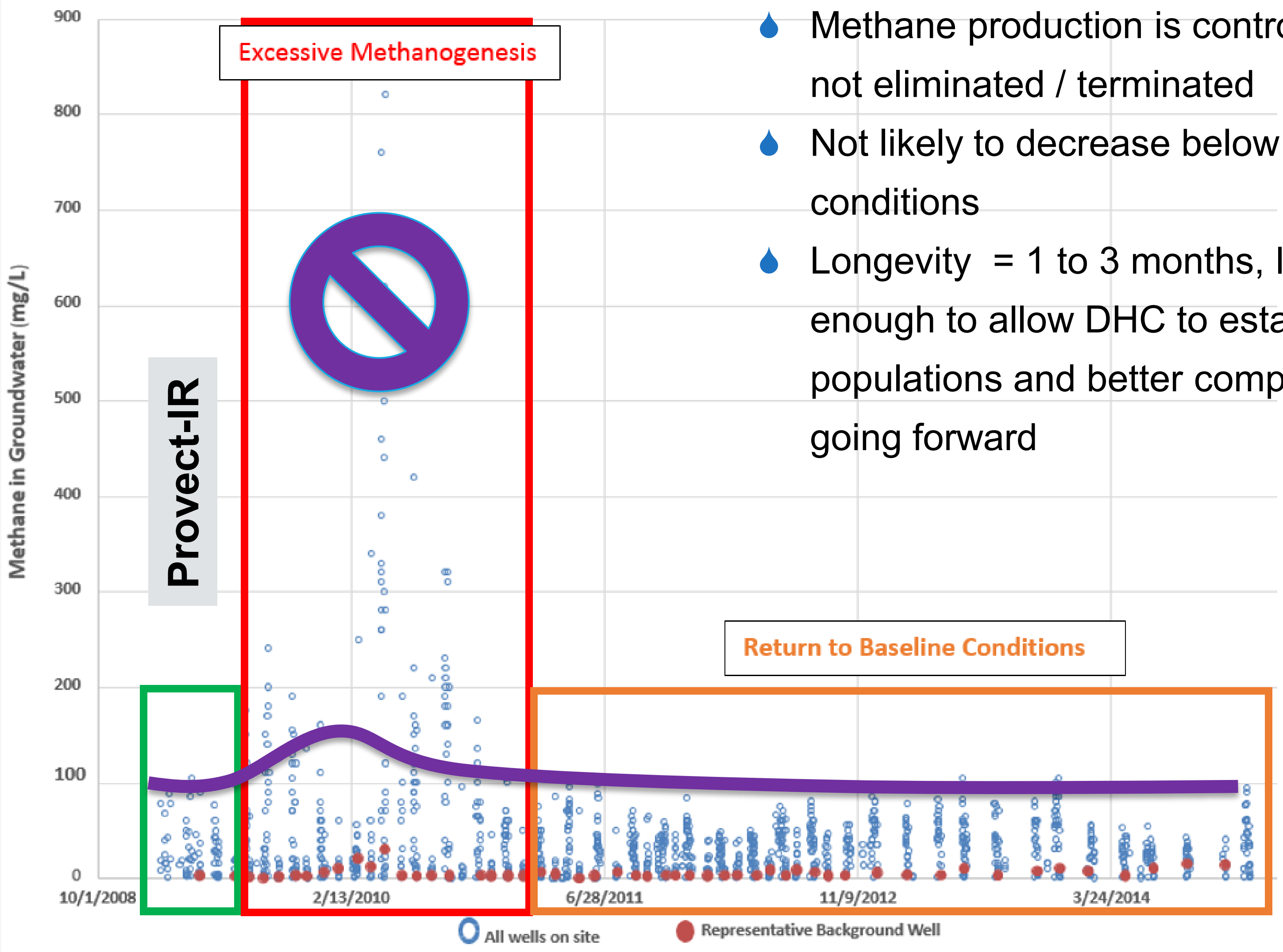
- RYR extract is a substance extracted from rice that has been fermented with a yeast called *Monascus purpureus*.
- RYR extract contains a number of natural statins - most importantly, Monacolin K - otherwise known as Lovastatin® / Lipitor® /etc.
- In addition to Monacolin K, RYR also contains 9 other statins, mono-unsaturated fatty acids, vitamins and other nutrients that will effectively stimulate anaerobic bacteria.
- RYR is used as a food coloring, food additive and preservative, and is widely consumed directly by humans.

[redacted]



Lovastatin is a registered trademark of Merck; Lipitor is a registered trademark of Pfizer

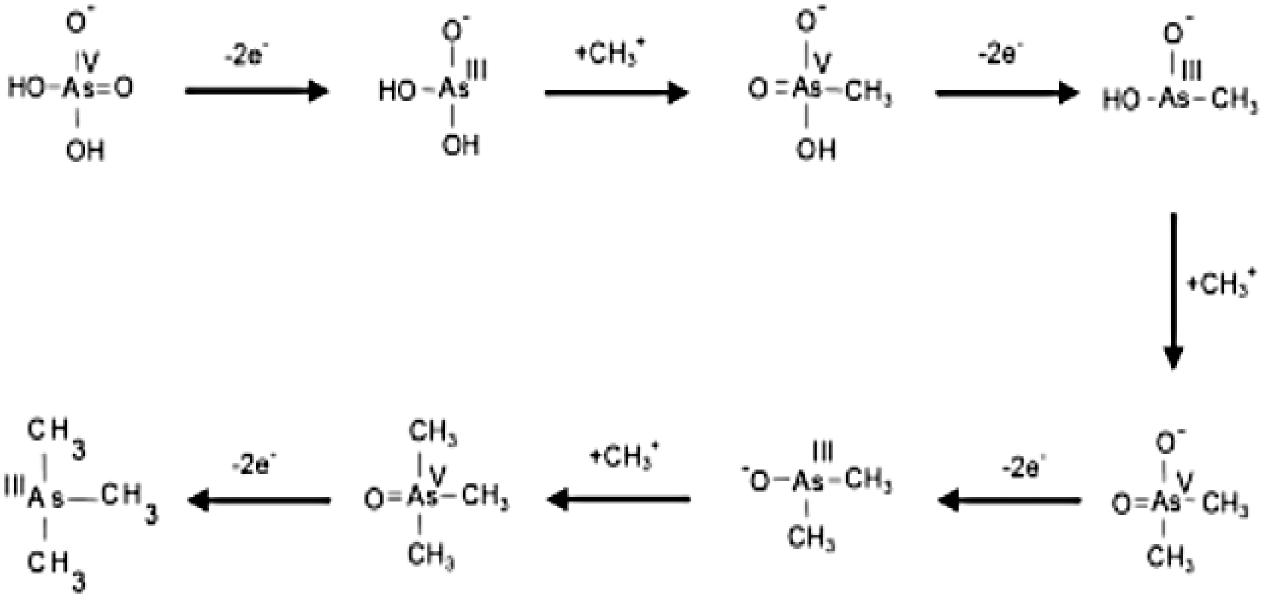
Controlled Methanogenesis



- Methane production is controlled, not eliminated / terminated
- Not likely to decrease below current conditions
- Longevity = 1 to 3 months, long enough to allow DHC to establish populations and better compete going forward

ISCR Issue 2: Arsenic Mobilization

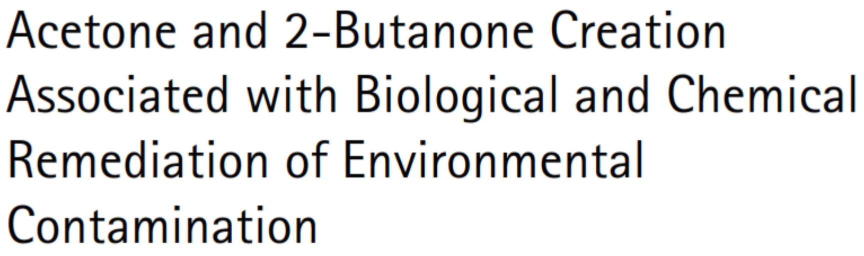
- Methanogens (and other organisms) methylate metals and they are not able to participate in precipitation reactions.
- Moreover, the overall toxicity of the site is not increased via the generation of methylmetal(loids) as a consequence of the treatment process (example – biomethylation of arsenate).



Challenger mechanisms for biosynthesis or Arsenate (Challenger, 1945)

ISCR Issue 3: Ketone Production

- **The occasional, transient production of acetone and/or MEK seems to mostly occur when alkanes are present along with high-organic carbon levels, in sub-oxic, especially methanogenic environments (Navylabs, 2005).**
- **The formation of these fermentation products is a recognized potential limitation of substrate addition for enhanced bioremediation (ESTCP, 2010).**
- **The accumulation seems to correlates with High TOC and low ORP but MEK/acetone production may occur before the system goes fully anaerobic, or soon after injection of a carbon source.**
- *** They do not migrate far (hydrogeologically dependent)**
- *** They are transient (persist between 10 and 180 days)**



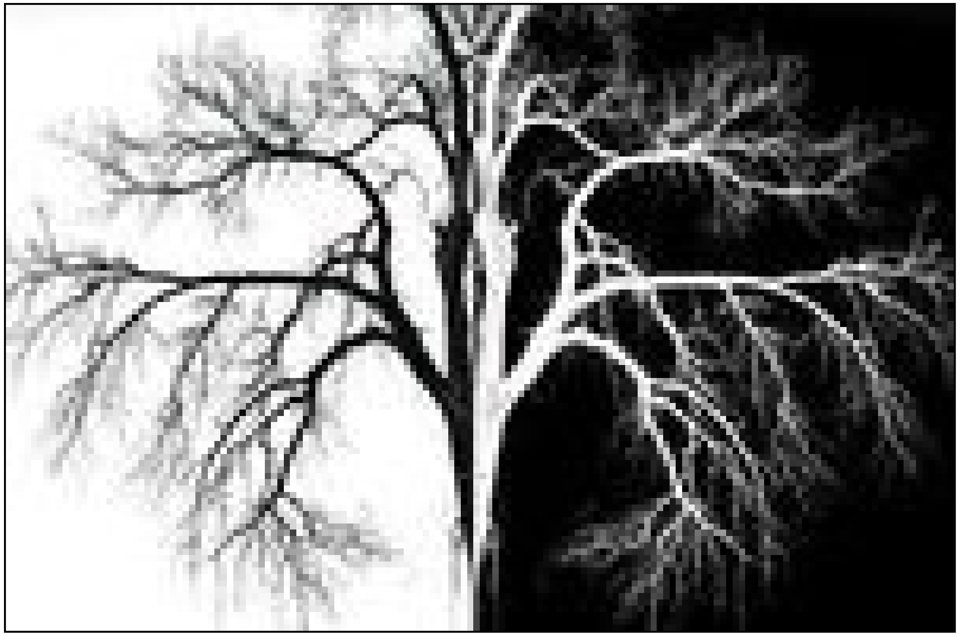
Acetone and 2-Butanone Creation Associated with Biological and Chemical Remediation of Environmental Contamination

Fowler, T., B. Thompson and J. Mueller. 2011. Acetone and 2-Butanone Creation Associated with Biological and Chemical Remediation of Environmental Contamination. Remediation Journal, Winter 2011, pages 9-28

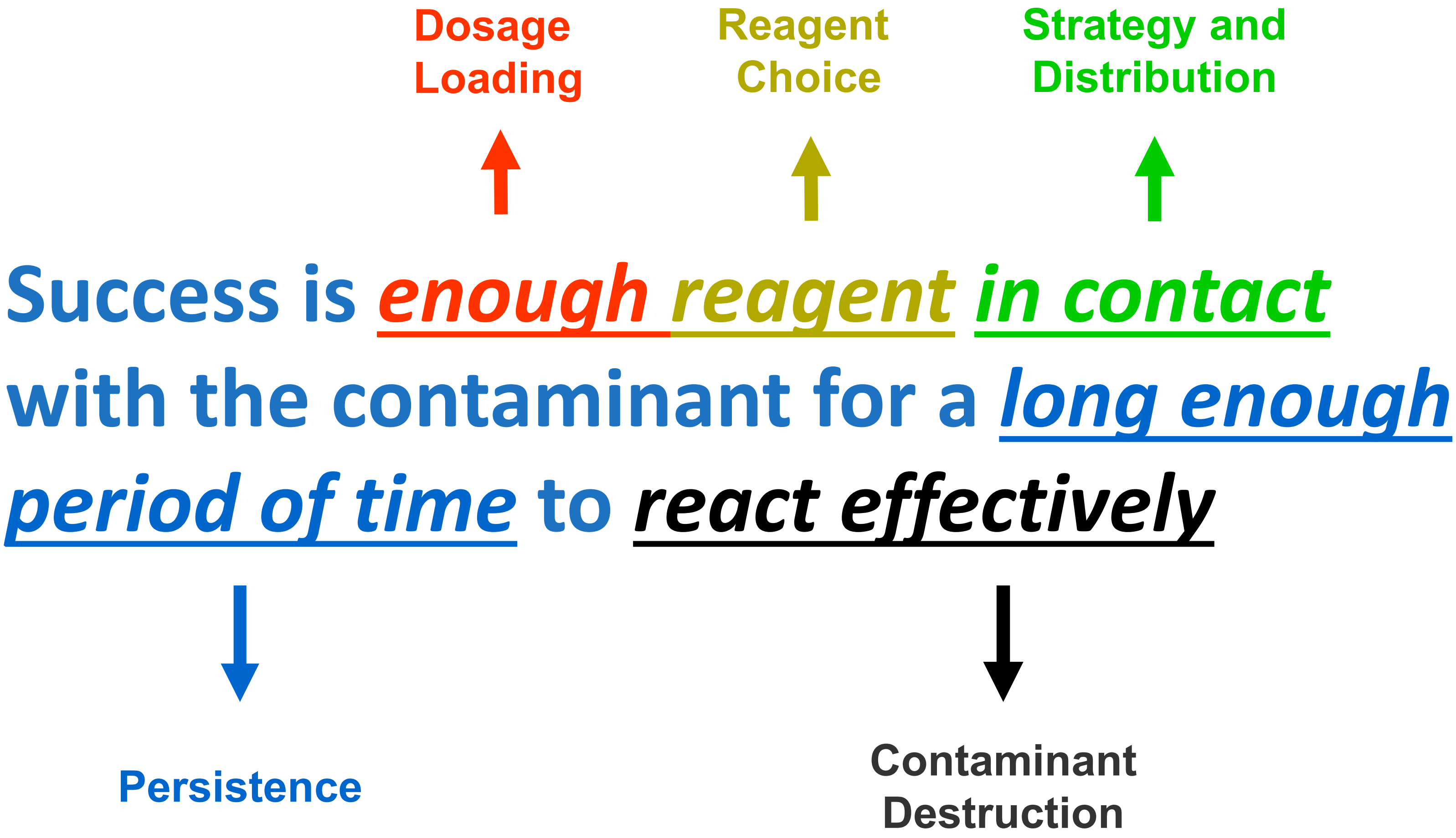
ISCO / ISCR – How to Decide in 2017?

ISCO and ISCR are electron transfer reactions. They are mirrors of each other. They can both be used for treating a number of contaminants, especially chlorinated solvents. However, for a given site, they may not be equally effective. Neither technology is universally applicable.

So - How does one determine which technology to apply?



ISCO or ISCR – Five Selection Criteria



Dosage Loading

Reagent Choice

Strategy and Distribution

Success is *enough reagent in contact* with the contaminant for a *long enough period of time* to *react effectively*

Persistence

Contaminant Destruction

Reagent Selection and Dosage

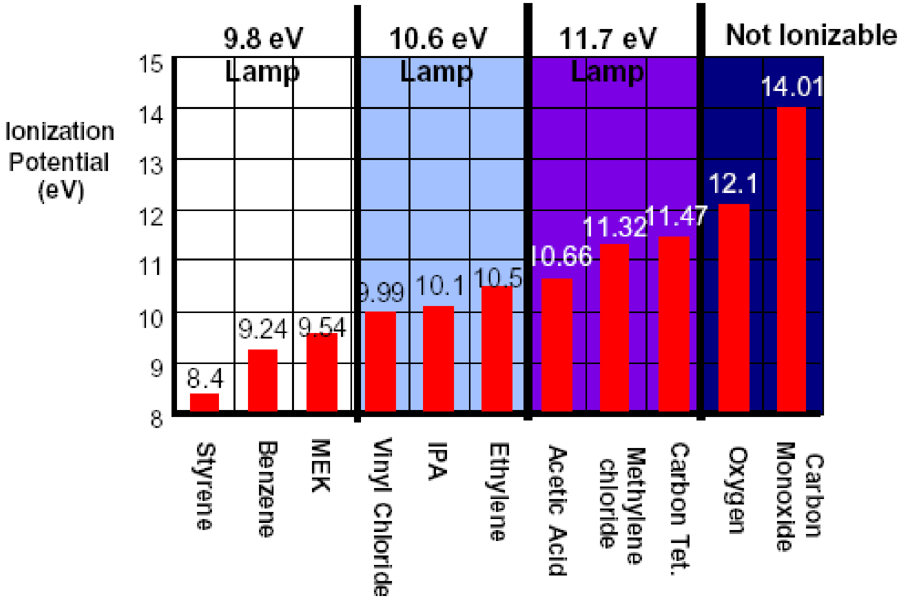
- Contaminant Type and Concentration
- Contaminant Distribution
- Aquifer Lithology / Hydrogeology / Biogeochemistry
  - DO/ORP
  - pH
  - TOC / SOD / COD
  - Nitrate / Sulfate
  - Reduced metals
- Performance Criteria
- Site Logistics
  - Health & Safety requirements
  - Constructability

What is ISCO?

- ISCO is the release of electrons from the contaminant
- COI to be oxidized must have transferable electrons
  - Aromatics
  - Double bonds
  - Few Chlorines!

$CCl_4 + 2H_2O \rightarrow CO_2 + 4H^+ + 4Cl^-$ No e^-

Some Ionization Potentials (IPs) for Common Chemicals



The more electrons available, the easier they are released

What is ISCR?

- **Reducible COI must be able to accept electrons**
  - Oxidized substrates (chloro- and nitro-organics; metals)
  - Electron rich (hydrocarbons) COIs do not reduce

“Reducible”

“Non-Reducible”

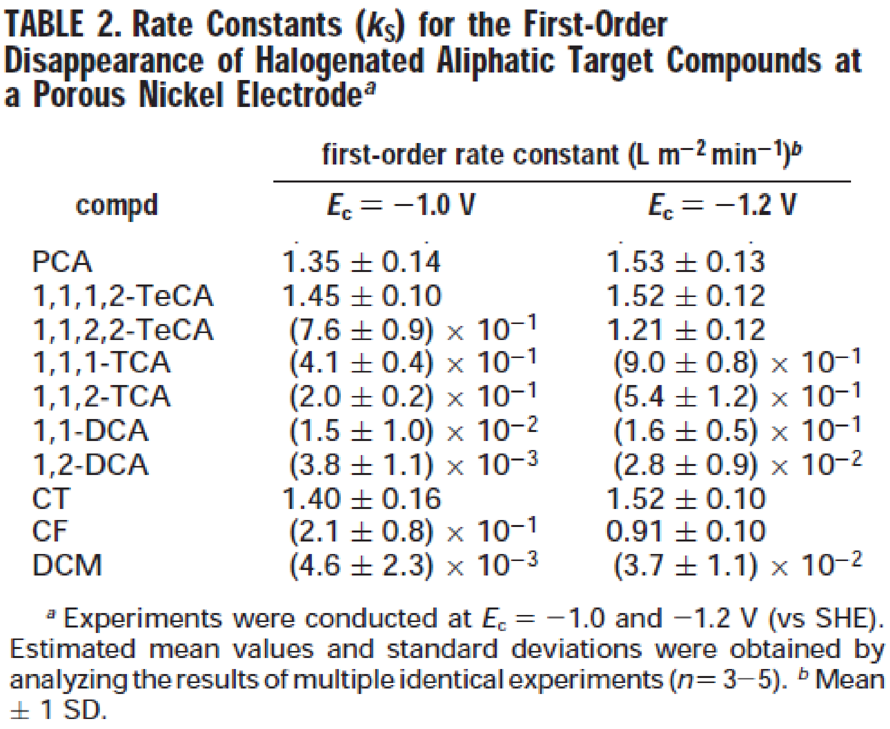


TABLE 2. Rate Constants (k_S) for the First-Order Disappearance of Halogenated Aliphatic Target Compounds at a Porous Nickel Electrode[a]

compd	first-order rate constant (L m^{-2} min^{-1})[b]	
	$E_c = -1.0$ V	$E_c = -1.2$ V
PCA	1.35 ± 0.14	1.53 ± 0.13
1,1,1,2-TeCA	1.45 ± 0.10	1.52 ± 0.12
1,1,2,2-TeCA	$(7.6 \pm 0.9) \times 10^{-1}$	1.21 ± 0.12
1,1,1-TCA	$(4.1 \pm 0.4) \times 10^{-1}$	$(9.0 \pm 0.8) \times 10^{-1}$
1,1,2-TCA	$(2.0 \pm 0.2) \times 10^{-1}$	$(5.4 \pm 1.2) \times 10^{-1}$
1,1-DCA	$(1.5 \pm 1.0) \times 10^{-2}$	$(1.6 \pm 0.5) \times 10^{-1}$
1,2-DCA	$(3.8 \pm 1.1) \times 10^{-3}$	$(2.8 \pm 0.9) \times 10^{-2}$
CT	1.40 ± 0.16	1.52 ± 0.10
CF	$(2.1 \pm 0.8) \times 10^{-1}$	0.91 ± 0.10
DCM	$(4.6 \pm 2.3) \times 10^{-3}$	$(3.7 \pm 1.1) \times 10^{-2}$

[a] Experiments were conducted at $E_c = -1.0$ and -1.2 V (vs SHE). Estimated mean values and standard deviations were obtained by analyzing the results of multiple identical experiments ($n = 3-5$). [b] Mean ± 1 SD.

Environ. Sci. Technol. **2000**, *34*, 804−811

Type of Contaminant

COIs	ISCO	ISCR
Chlorinated Ethenes	Yes	Yes
Chlorinated Ethanes and Chlorinated Methanes	Yes	Yes Except CA, DCM, CM
PCBs, OCPs	Potential	Potential
Organic Explosives	Yes	Yes
TPH GRO and DRO	Yes	No
Mixed CVOCs and TPH	Yes	No
Metals Cr, Pb, Cu, As, Zn, Ni	No Except As	Yes
Mixed CVOCs and Metals	Potential	Yes
Perchlorate	No	Yes
MTBE, TBA, Dioxane	Yes	No
Mixed TPH and Metals	Sequential Treatment	

Changes from 2008

Contaminant Concentration

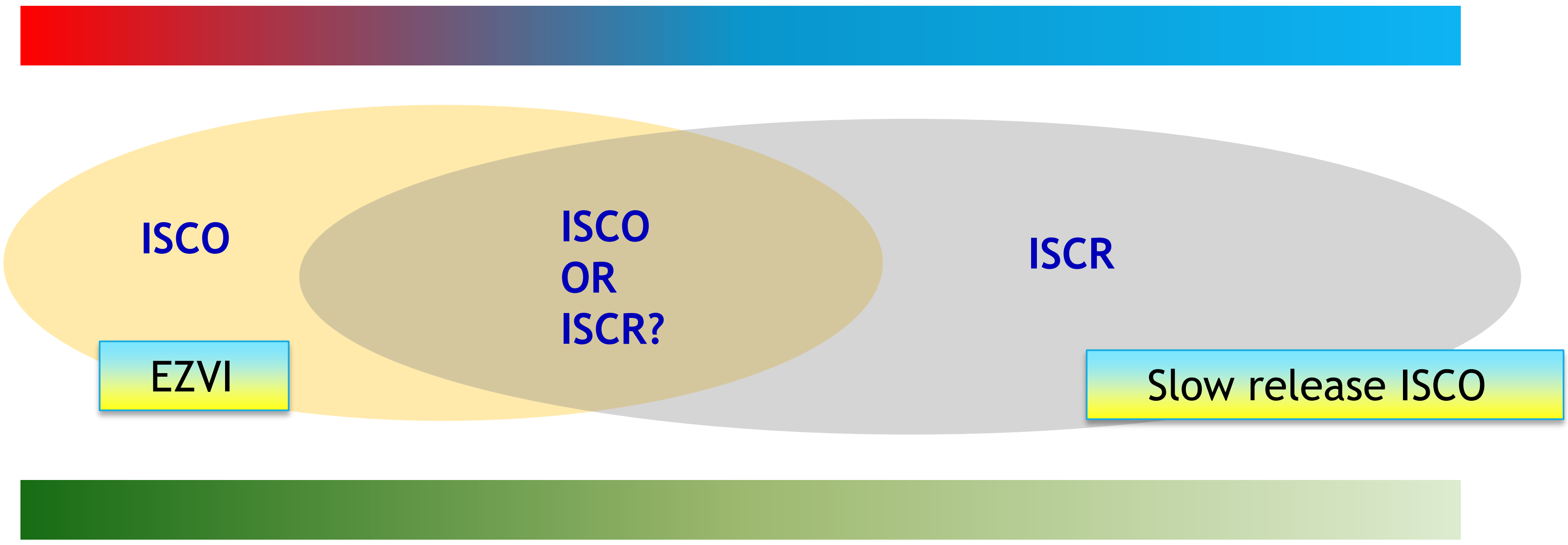
Media	COI Concentrations	ISCO	ISCR
Soil	Low Level Impacts Up to 10 mg/kg	Yes	Yes
	Mid Level Impacts > 10 mg/kg	Yes	**Yes**
	High Level Impacts NAPL	Yes	**EZVI**
Groundwater	Low Level Impact <1 ppm	No	Yes
	Mid Level Impacts 1 ppm to 100 ppm	Yes	Yes
	High Level Impacts >100 ppm	Yes	**EZVI**

Changes from 2008

Contaminant Distribution

Contaminant Concentration

> 100 ppm | 50 ppm | 10 ppm | 1 ppm | 500 ppb | 100 ppb | < 50 ppb



ISCO

ISCO
OR
ISCR?

ISCR

EZVI

Slow release ISCO

source | down gradient → | plume

Contaminant Source

Changes from 2008

Mueller *et al.*, 2009, 2010, 2011, 2012

Contaminant Distribution

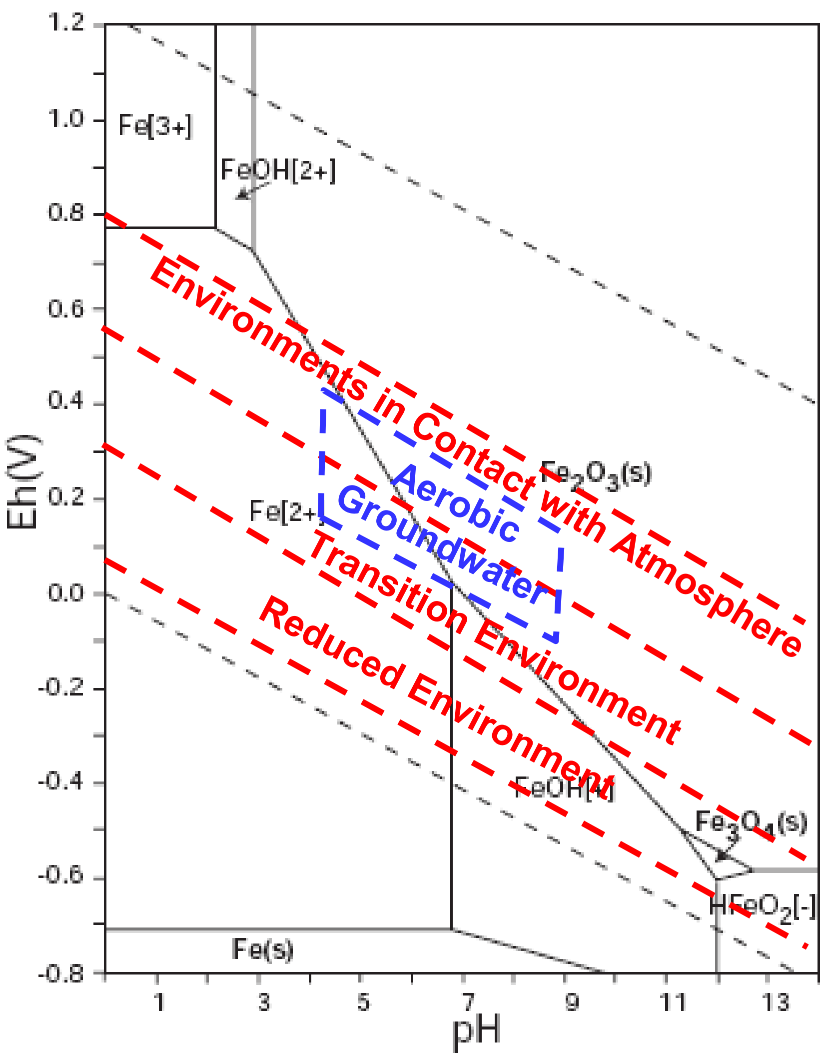
	ISCR	ZVI	ISCO
PRB Applicability	Yes (3 to >5 yrs)	Yes (>12 yrs)	Typically not applicable (short longevity)
Widespread Plume Treatment	More cost efficient at lower COI concentrations	Multiple PRBs possible	May not be cost effective at low concentrations
Hot Spot Treatment	Can apply to hot-spots	EZVI applicable to NAPL	Yes
Source with NAPL		Iron or iron/ clay can be mixed into NAPL zones	Typically not applicable due to cost

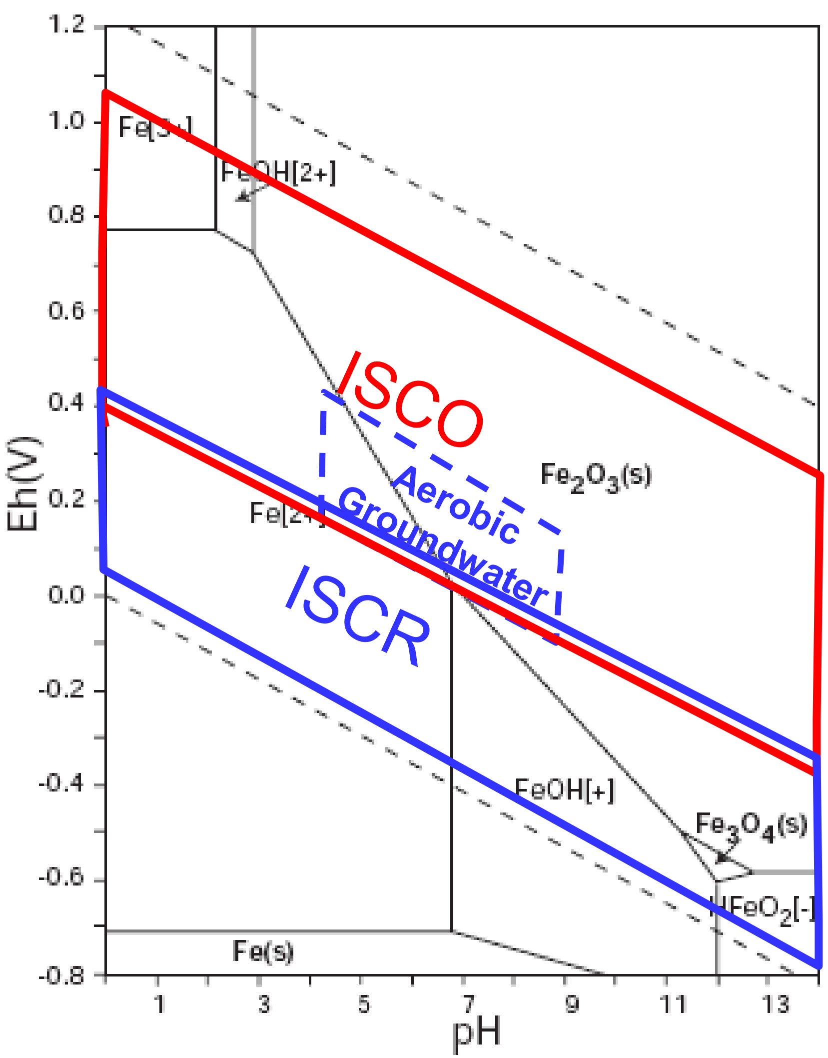
Changes from 2008

Aquifer Lithology

- Distribution Is Important = Both ISCR and ISCO can be less effective in low permeability environments
- Contact is Key = low permeability, fractured rock, and low porosity environments are generally less favorable for ISCO since oxidant half-lives are much shorter than ISCR
- Soil Blending of Reagents = mitigates the contact challenges
- Skilled Injection Contractors = can emplaced reagents into any lithology and help manage the contact challenges *in situ*
- High Velocity Aquifers = tend to favor ISCR since these (solid) reagents persist compared to water soluble oxidants
- Carbonate Rich Aquifers = generally not suitable for persulfate ISCO due to carbonate scavenging of free radicals (PersulfOx® seems to counter this position)

Aquifer pH and Redox Conditions





DO <1 mg/L and ORP <150 mV favors ISCR

Aquifer Biogeochemistry

- Geochemistry
  - high organic carbon favors ISCR
- Soil oxidant demand (SOD)
  - >10 mg/kg favors ISCR
- Competing electron acceptors (CEAs)
  - O_2 > Mn(IV) > NO_3^- > Fe(III) > SO_4^{2-} > CO_2
  - Sulfate > 100 mg/L favors ISCO
- Is there a concern from secondary plumes
  - sodium, sulfate, iron, purple color etc.

Factors that can be managed, but will increase cost

- Toxic intermediates and daughter products
  - Less likely with ISCO; more likely with ISCR
- Methane VI and other issues
  - Less likely with ISCO; more likely with Conventional ISCR

Regulatory Drivers

Implementation and Performance

Condition	Favors ISCO	Favors ISCR
Proximity to sensitive receptors	Varies	Varies
Sensitivity to Methane issue	X	Varies
Limited access for injections		X
Compatibility with sub-surface utilities		★
Health and Safety concerns (PPE, handling, storage, mixing and injecting)		★
Need for Speed	★	
Injection depths greater than 75 ft bgs	★	

Changes from 2008

Implementation and Performance

- Ease of Use
    - Injectability ISCO > ISCR (ferric iron solids)
    - Handling ISCR > ISCO (ferric iron self activated)
- Speed
    - ISCO faster than ISCR
    - Need to consider rebound potentials with ISCO
- Reagent Longevity
    - ISCR lasts longer than ISCO
    - Combined ISCO + multiple biological processes

Summary

ISCO

Multiple Oxidants Available

- ✓ Different reaction pathways
  - Non-Contaminant Specific
  - Oxidant Specific
  - Geochemical effects
- ✓ None naturally occurring

Limited Reagent Lifetime

- – Non-Beneficial Consumption
- – Rebound issue improved
- – Slow release reagents

Non-selective reactions

- – Partial oxidation
- – End products are CO_2, Water +
- – Sulfuric acid possible

ISCR

ZVI DVI (added, created or natural)

- ✓ Reaction pathways
  - β elimination primary reaction
  - Combination of electron reactions

Longer Reagent Lifetime

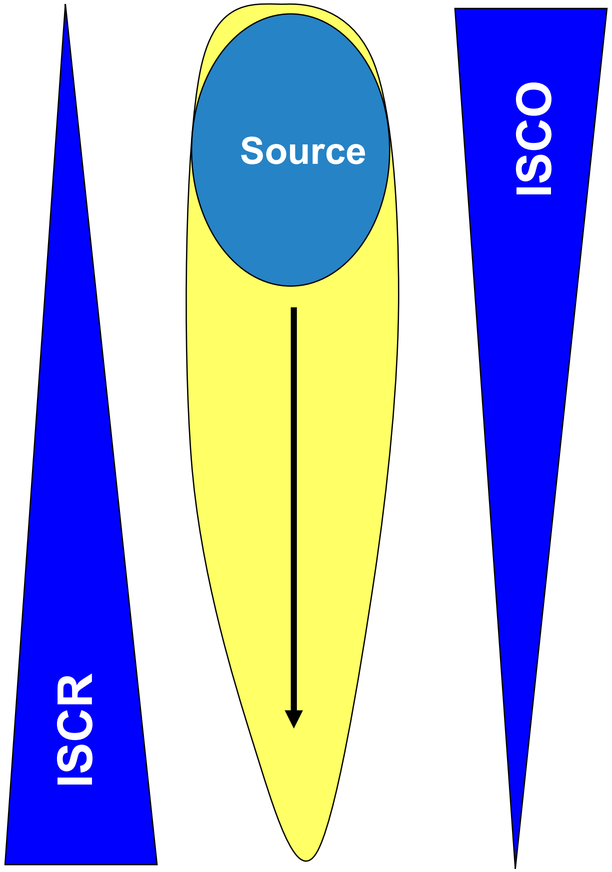
- – Minimal Non-Beneficial Consumption
- – DO and Nitrate

More selective reactions

- – Known catabolites
- – End products are dechlorinated organics +
- – CO, CO2, CH4

Summary

	ISCO	ISCR
LNAPL	Applicable; Direct injection and soil mixing.	Not Applicable to Hydrocarbons LNAPL
DNAPL - CVOC	Applicable; Direct injection and soil mixing.	EZVI - ZVI-Clay
DNAPL - PAHs	Applicable; Direct injection and soil mixing, Ozone injection	Not Applicable
Adsorbed	Applicable; Direct injection and soil mixing.	EZVI Direct injection and soil mixing; ZVI-Clay
Small GW Plume	Applicable Direct injection	Applicable Direct injection and soil mixing; ZVI-Clay
Large GW Plume with moderate to high Conc.	Generally not applicable except for ozone sparge barrier	Applicable PRB
Large dilute GW Plume	Not Applicable	Applicable Abiotic MNA, PRBs
Matrix Diffusion	Not Applicable - limited life time of oxidants; Repeted injections can work	Applicable - Ijection of Iron, PRBs, Abiotic MNA



Conclusions

Weight of Evidence Approach

- Selecting ISCO or ISCR requires site-specific evaluation
- Best choice usually has the fewest undesirable factors that can be overcome or managed most easily /cost effectively

2017 updates

- ISCO integrated with multiple biological processes = rebound
- Slow release ISCO reagents = longevity
- Antimethanogenic ERD ISCR technologies
- Sequestration technologies

Reminder:

– Presentation is an update of multiple past reports/publications

– Not a complete analysis, but a summary of factors that have been observed to affect technology selection, design and field performance

Provectus Environmental Products, Inc.

OUR TECHNOLOGIES

Provect-IR® Solid, Antimethanogenic ISCR Reagent
As the prime developer of the original EHC® ISCR reagent, staff now at Provectus know that Provect-IR is a genuine improvement on the ISCR process and its older product formulations. Provect-IR uses carbon substrate more efficiently and therefore is more cost effective. Remedial designs can use less amendment and get expected results without excessive methane generation.

Provect-IRM® Solid Antimethanogenic ISCR / Metal Stabilization Reagent
More effective means of metal immobilization/ISCR that minimizes production of methylmetal(loids) for safer, more effective, long-term immobilization.

Provect-OX™ Self-Activating ISCO/ Enhanced Bioremediation Reagent
Persulfate-based ISCO reagent that is unique in terms of its safety (no extreme activators; no heat generated) and effectiveness, as it actively integrates ferrate chemistry and enhanced bioremediation as part of the overall treatment process – only ISCO reagent designed to manage rebound.

Provect-CH4® Methanogen Inhibitor and ERD/ISCR Supplement
Water-soluble amendment to effectively control methane production when combined with various ERD amendments (*e.g.*, [emulsified] oils, lecithin, lactates, molasses, sugars, etc.) or conventional ISCR reagents.

AquaGate+CH4™ Antimethanogenic Reactive Capping Technology
Developed in collaboration with AquaBlok, LTD subaqueous caps can be constructed more effectively by minimizing gas ebullition and contaminant methylation.

EZVI-CH4™ Antimethanogenic DNAPL Treatment
Unique reagent can be used for safe and effective treatment of chlorinated solvent DNAPL sources.

Provect-GS™ NAPL Immobilization Technology
A liquid reagent developed in collaboration with Beazer East, Inc. for *in situ* geophysicochemical immobilization (ISGI) of DNAPL sources.

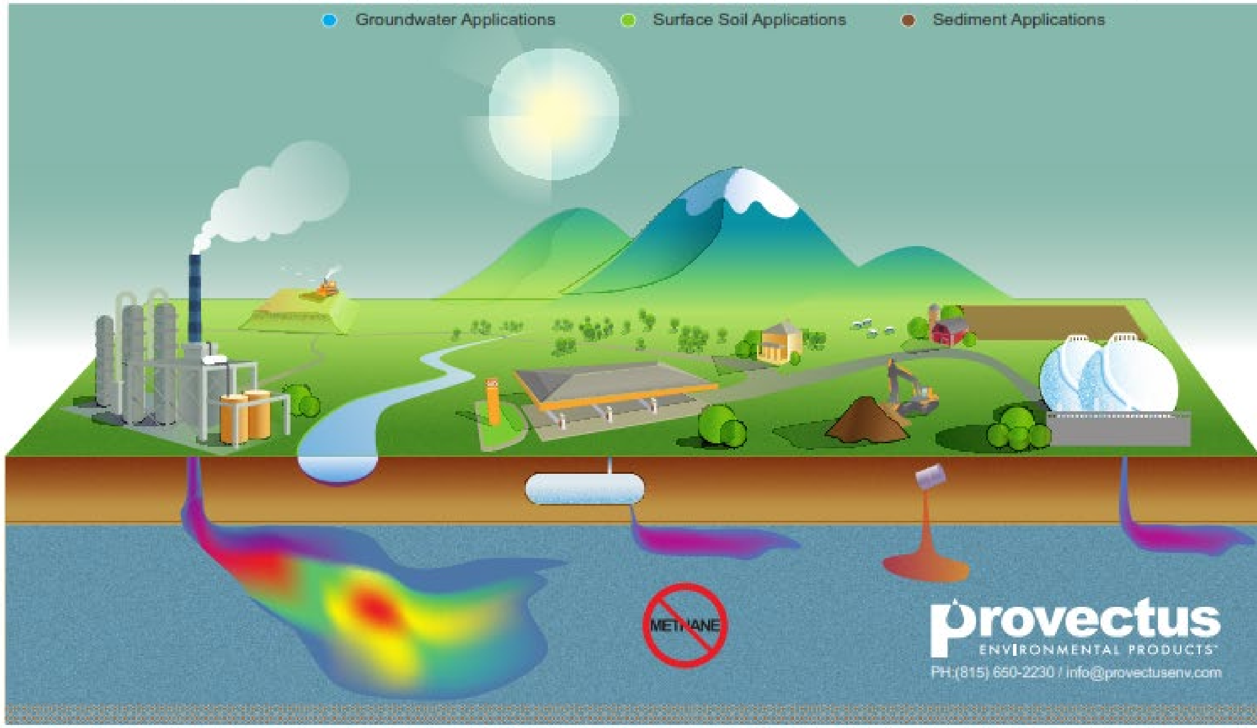
ERD-CH4™ Liquid Antimethanogenic ISCR Reagent
Liquid, antimethanogenic ERD amendment that can be applied via screened systems. By inhibiting methanogenesis, this is a more efficient, longer-lived and safer ERD approach.

Provect-ABR Aerobic Bioremediation Reagent
Soil amendment for accelerated aerobic biodegradation of organic compounds.

PROVECTUS TECHNOLOGY

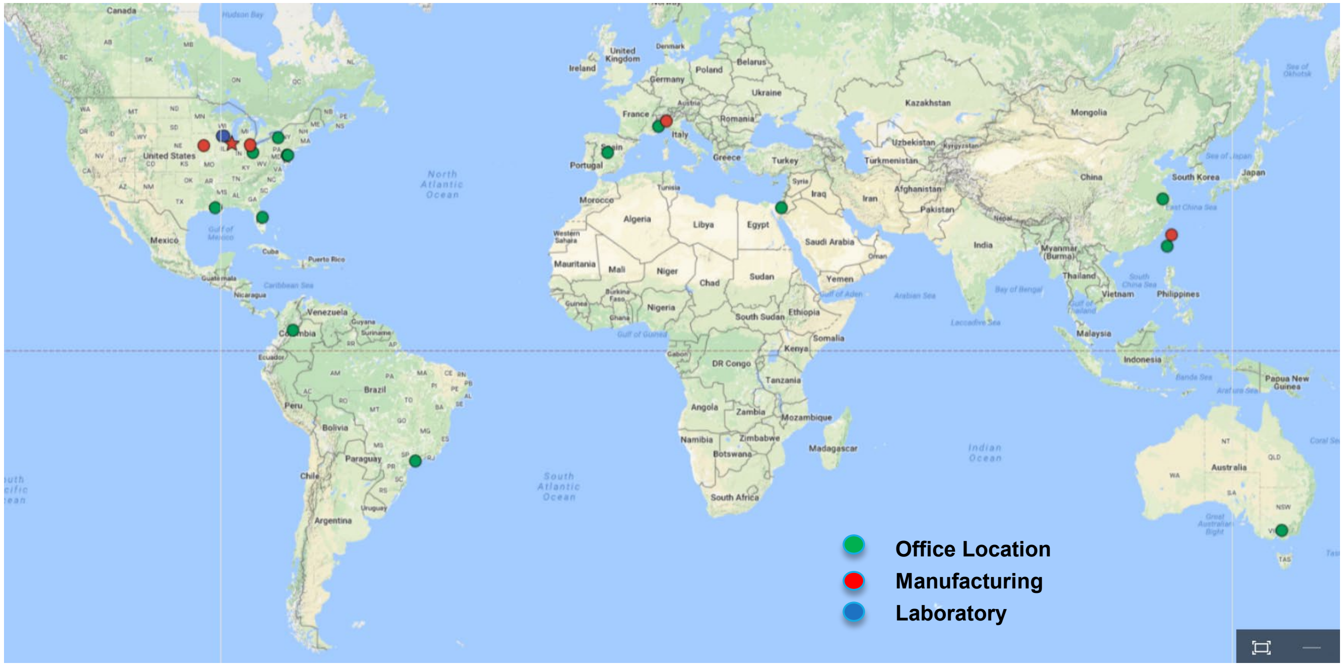
	Provect-IR® 🔵 🟢	Provect-IRM® 🔵 🟢	Provect-OX® 🔵 🟢	Provect-CH4® 🔵	AquaGate +CH4™ 🟢 🟤	EZVI-CH4™ 🔵	Provect-GS™ 🔵	ERD-CH4™ 🔵	Provect-ABR 🟢
Halogenated Solvents	💧	💧	💧	💧	💧	💧	💧	💧	
Hydrocarbons			💧		💧		💧		💧
Heavy Metals		💧		💧	💧		💧	💧	
Pesticides	💧	💧	💧		💧		💧		💧
Fertilizers	💧	💧			💧				💧

🔵 Groundwater Applications 🟢 Surface Soil Applications 🟤 Sediment Applications



Provectus Environmental Products

- Complimentary Site Evaluation
- Complimentary review of quarterly field performance data for 1 year with every project
- Laboratory Treatability Studies
- Turn-Key, Pay-for-Performance Contracting Options
- Project Specific Guarantees and Warranties



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