NEW DEVELOPMENTS IN CATALYZED PERSULFATE TECHNOLOGY

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REGENESIS
18 October 2013

IN SITU CHEMICAL OXIDATION (ISCO):

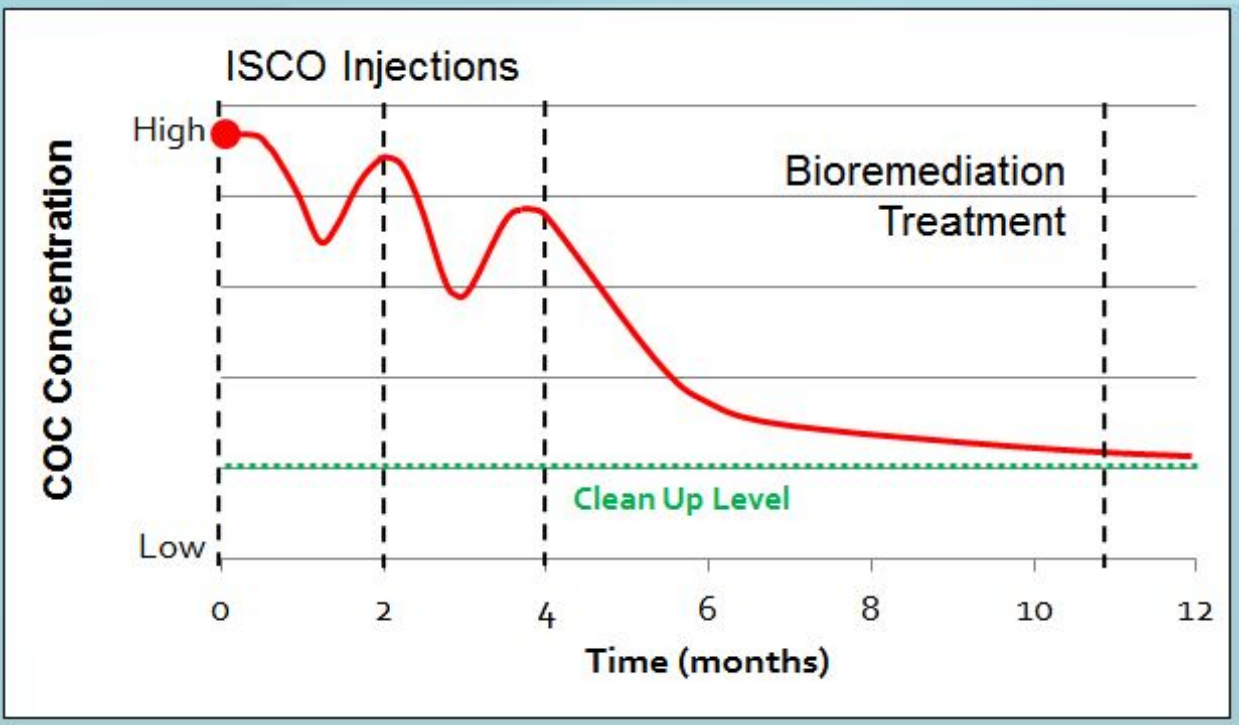
- Use of chemical oxidants at a site for destruction of soil and groundwater contaminants, including:
  - Petroleum hydrocarbons (BTEX, F1-F4, etc.)
  - Fuel oxygenates (napthalene, 1-4 dioxane, etc.)
  - Halogenated/Chlorinated hydrocarbons (PCE, TCE, DCA,TCA, etc.)

- Typically applied using subsurface injection or direct mixing of reagent into impacted media (treats up to thousands of ppm)

- CONTACT, CONTACT, CONTACT!!!

ACCELERATE MASS REDUCTION WITH ISCO

Contaminant Reduction Trends



Advantages

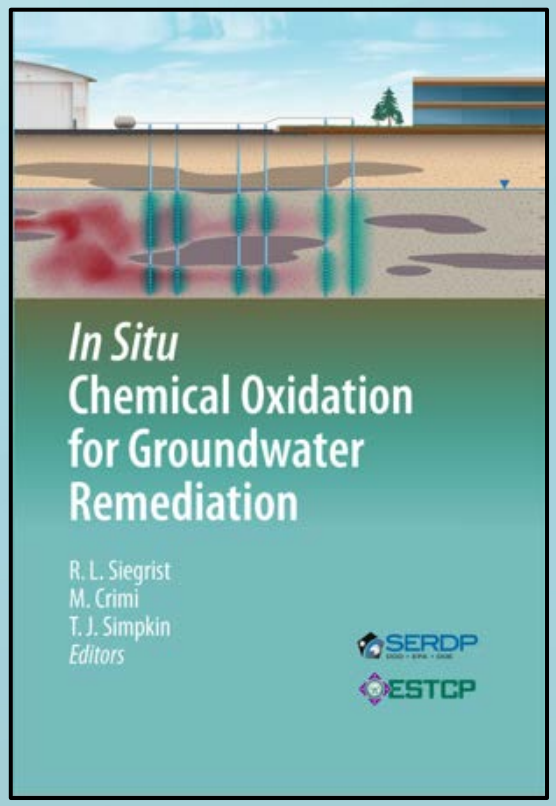
- Fast acting (weeks to months)
- High concentrations
- Wide-range of difficult contaminants
- Powerful oxidation for mass reduction
- **Easily coupled with bioremediation**

Considerations-

*Health and Safety, Efficacy, Ease of use, residuals

ISCO AGENTS

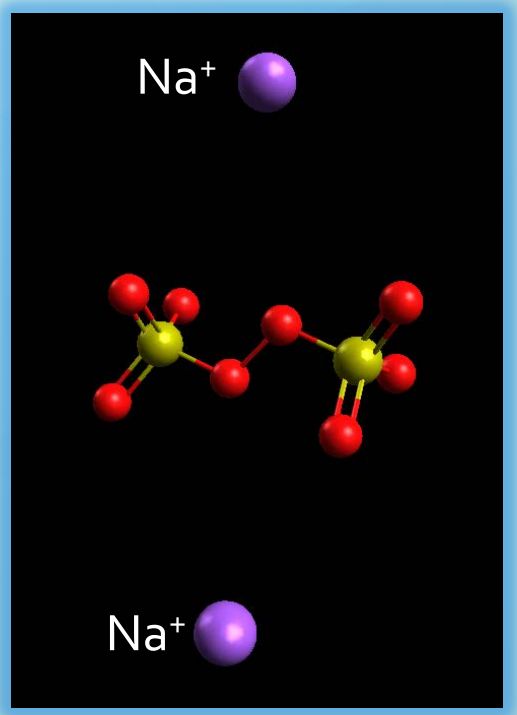
- Ozone gas
- Permanganates
- Hydrogen Peroxide
  - Percarbonate
- Persulfates
  - Stability
  - Solubility
  - Broad reactivity (with proper activation)



"In Situ Chemical Oxidation for Groundwater Remediation" Siegrist, R.L.; Crimi, M.; Simpkin, T. J., eds. 2011, Springer, SERDP/ESTCP monograph Series.

MORE ON SODIUM PERSULFATE….

- Formula $Na_2S_2O_8$
- Strong oxidizer
  - E_0 = 2.07 eV
- Active Oxygen 6.7% w/w
- Colorless crystalline solid typically applied in two-parts (persulfate oxidant + an activator)



WHY ACTIVATION?

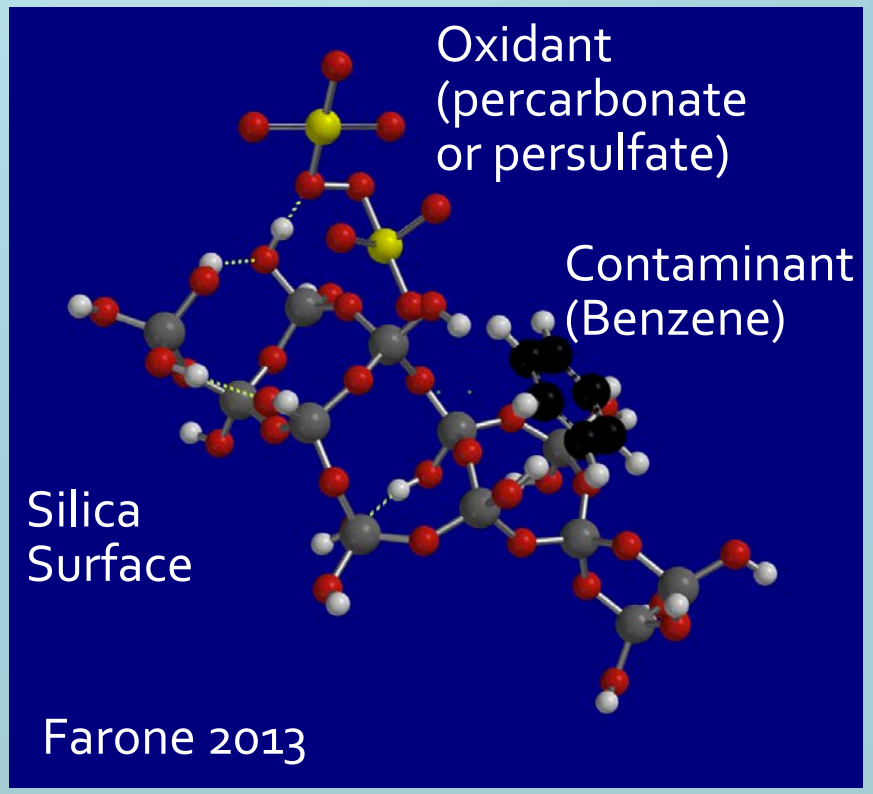
- Sodium Persulfate ($Na_2S_2O_8$)
  - Directly oxidizes organic compounds
    - Generally too slow for most contaminant remediation applications
  - Forms radicals *upon activation* that are much more effective in rapidly oxidizing contaminants
    - Sulfate radical - $SO_4^{\bullet-}$
    - Hydroxyl radical - $OH^{\bullet}$
    - Organic/inorganic radicals (result of continued radical propagation)

CONVENTIONAL PERSULFATE ACTIVATION

Persulfate + (Activator)	Issues
Chelated Metals (i.e. Iron)	Efficacy- limited compounds, expensive, corrosivity
Thermal/Heat	Expensive, can increase oxidant demand
Hydrogen Peroxide	Health and safety- exothermic/corrosive, multiple injections= costly
Alkaline/Base (25% caustic, pH > 10)	Health and safety-exothermic/corrosive, multiple injections= costly, alkalinity quickly buffered out

SURFACE MEDIATED OXIDATION

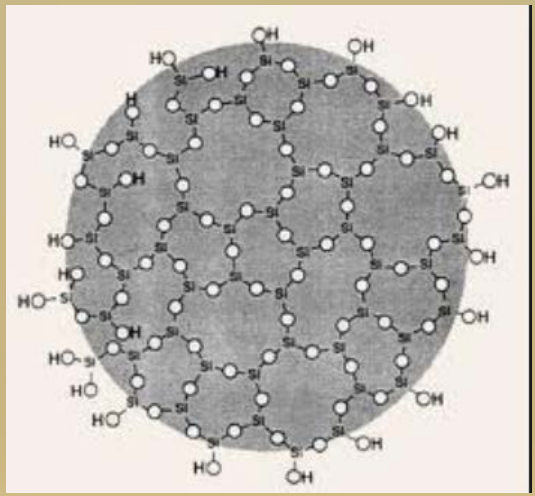
- Patented heterogeneous catalyst technology
  - Microscale amorphous silica
    - High surface area
  - Sorption of both oxidants and contaminants
    - Increased contact
  - Wide-range of oxidants

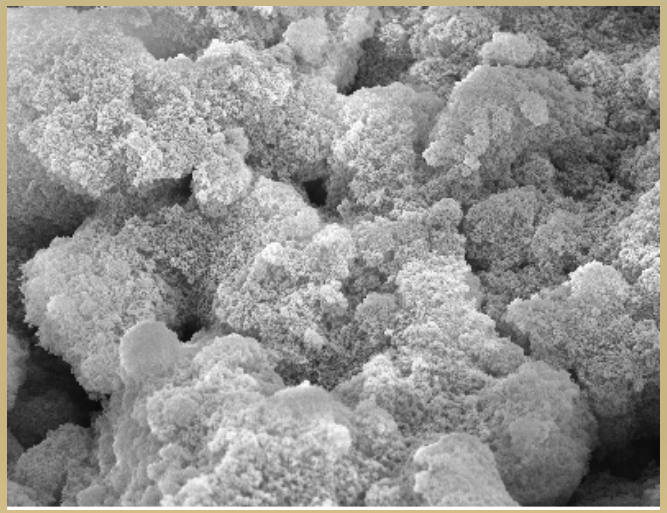


Molecular mechanics, geometry optimization

CATALYST ACTIVATION THEORY

- Plausible mechanisms include
  - Colloidal structures sorb contaminants from water
  - Surface brings together contaminant and oxidant which catalyzes direct oxidation
  - Silanol groups (OH groups) activate radical formation
  - Co-precipitated metals activate formation of radicals





REGENESIS ISCO TECHNOLOGIES

- Started in 2005 with RegenOx®
  - Sodium percarbonate-based oxidant
    - Applied on > 1,000 sites
    - Effective on hydrocarbon and chlorinated contaminants
    - Compatible with underground infrastructure, bioremediation, and H&S
    - Typically applied as 4 to 6% solution

NEW PRODUCT : PERSULFOX

- Catalyzed sodium persulfate $Na_2S_2O_8$
- All-in-one powder- built-in-activation
- Surface Mediated Oxidation- silica catalyst precipitates as pH drops below 10 and persists
- Formulation
  - 100% soluble: 90% sodium persulfate, 10% silicates
  - 15% solution (opaque)
  - pH 12 (alkaline activation)

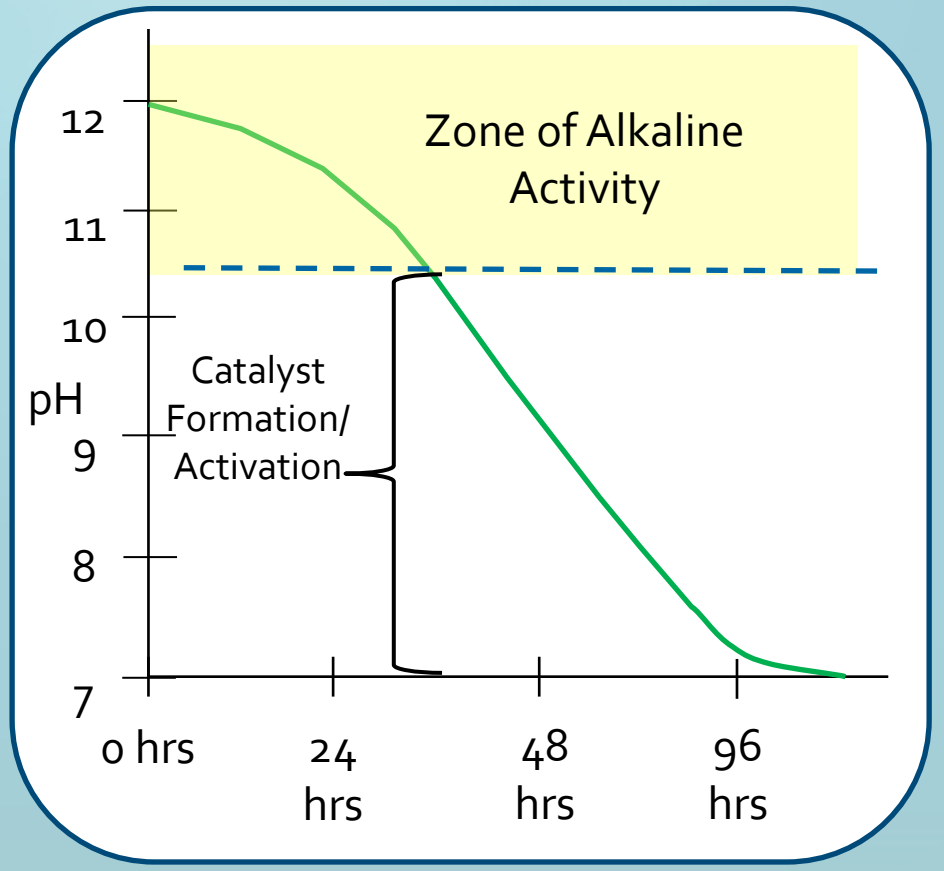
PersulfOx™

CATALYZED PERSULFATE

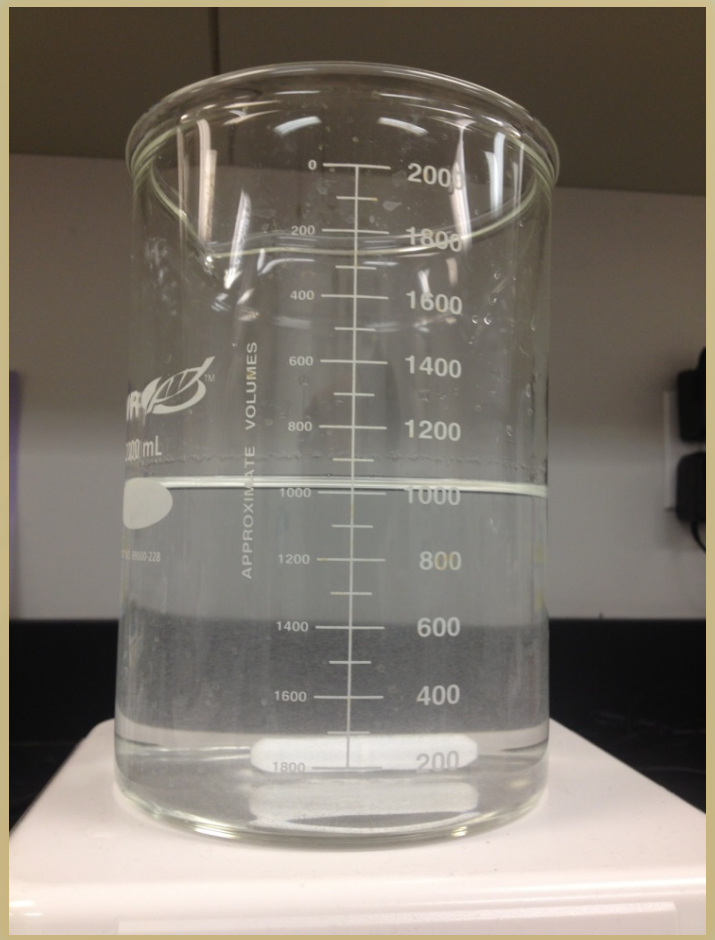
PERSULFOX TECHNOLOGY

- Dual Activation Mechanism
- Self-activates in water
  - Initial Alkaline Activation

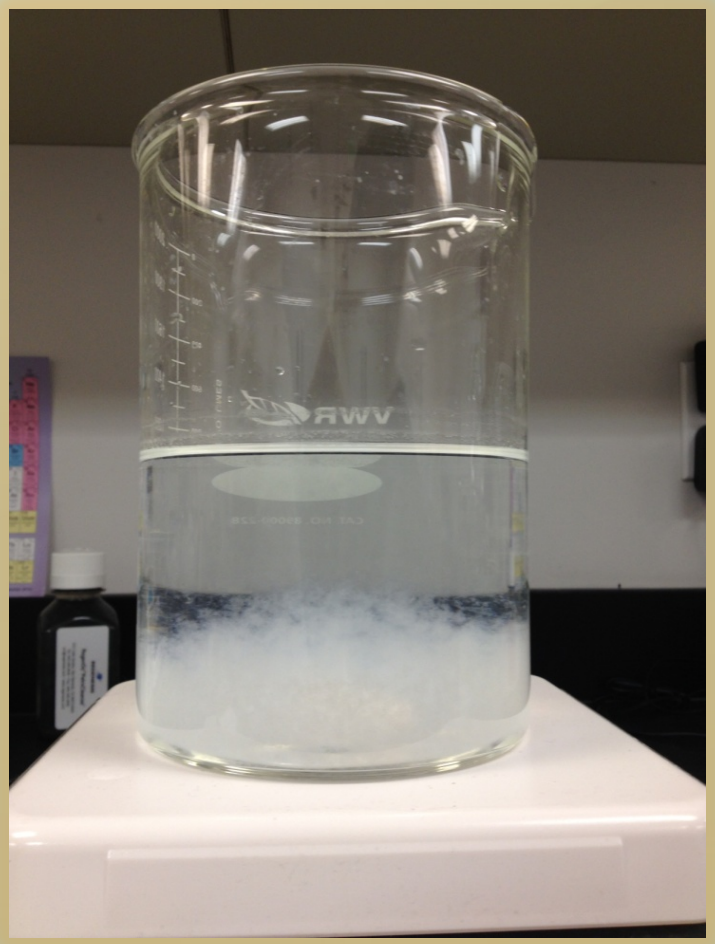
    But then as pH drops…….
- Catalyst forms *in situ*
  - As pH drops <10 catalyst begins to form
  - Continues activation at lower pH range



CATALYST FORMATION



pH 12 (DI water)



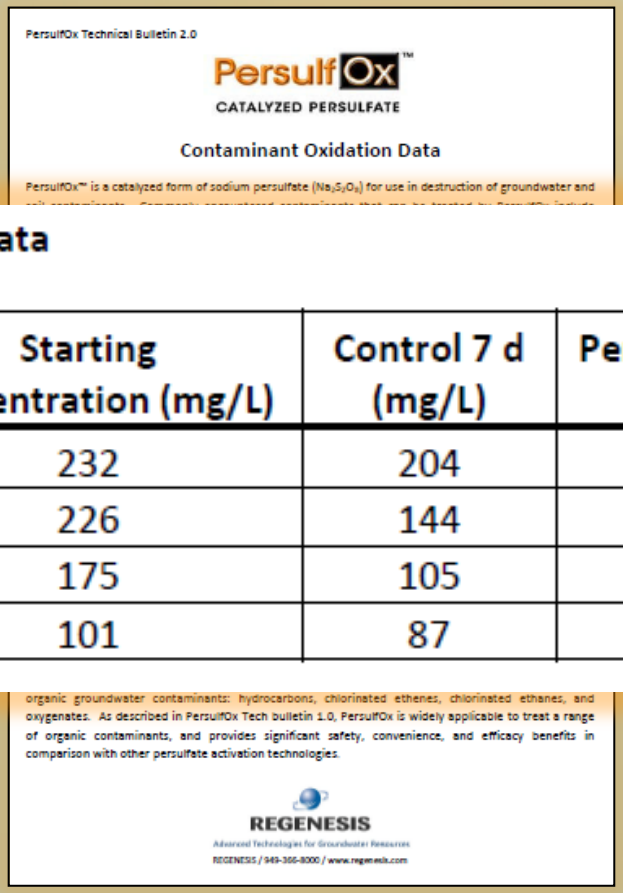
Adjusted- pH 7

EASE OF USE AND HANDLING

Application Methods:

-Direct Push
-Injection Wells
-Excavation
-Soil Mixing

EFFICACY- LAB TESTING


PersulfOx Technical Bulletin 2.0

PersulfOx™
CATALYZED PERSULFATE

Contaminant Oxidation Data

PersulfOx™ is a catalyzed form of sodium persulfate ($Na_2S_2O_8$) for use in destruction of groundwater and

Table 1. Contaminant Oxidation Data

Contaminant	Starting Concentration (mg/L)	Control 7 d (mg/L)	PersulfOx 7 d (mg/L)	% Oxidized vs. Control
BTEX	232	204	7	96%
trichloroethene (TCE)	226	144	< 1	> 99%
1,4-dioxane[1]	175	105	< 1	> 99%
1,2-dichloroethane (DCA)	101	87	< 10	> 88%

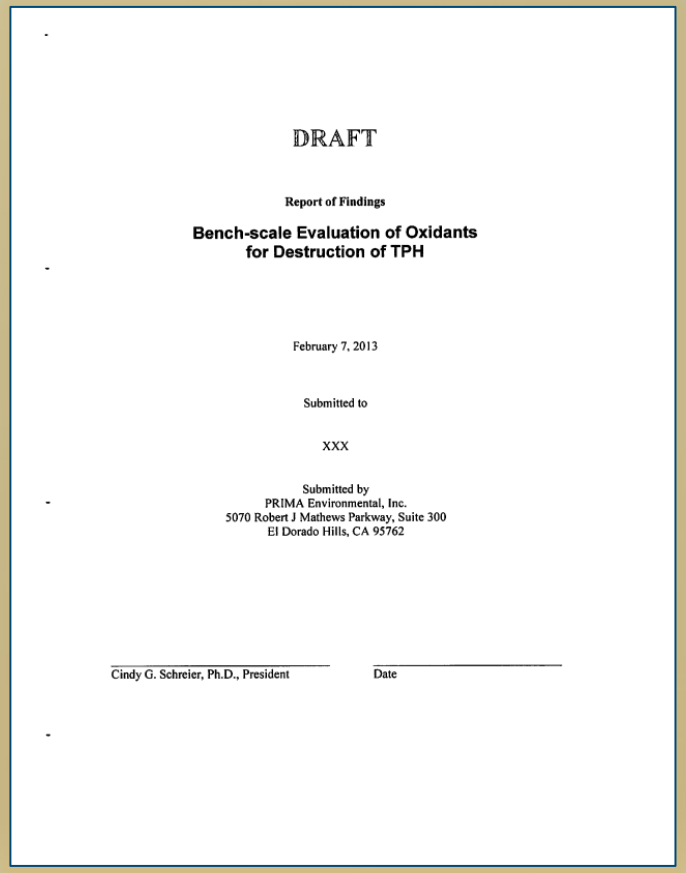
organic groundwater contaminants: hydrocarbons, chlorinated ethenes, chlorinated ethanes, and oxygenates. As described in PersulfOx Tech bulletin 1.0, PersulfOx is widely applicable to treat a range of organic contaminants, and provides significant safety, convenience, and efficacy benefits in comparison with other persulfate activation technologies.

REGENESIS
Advanced Technologies for Groundwater Resources
REGENESIS / 949-366-8000 / www.regenesis.com

Reference: PersulfOx Tech Bulletin 2.0 available at persulfox.com

EFFICACY- LAB TESTING

- Third party remediation treatability laboratory testing*
  - Direct comparison:
    - Persulfate activated with NaOH
    - PersulfOx
  - Actual site groundwater and soil
  - Petroleum hydrocarbons



DRAFT

Report of Findings

Bench-scale Evaluation of Oxidants for Destruction of TPH

February 7, 2013

Submitted to

XXX

Submitted by
PRIMA Environmental, Inc.
5070 Robert J Mathews Parkway, Suite 300
El Dorado Hills, CA 95762

Cindy G. Schreier, Ph.D., President

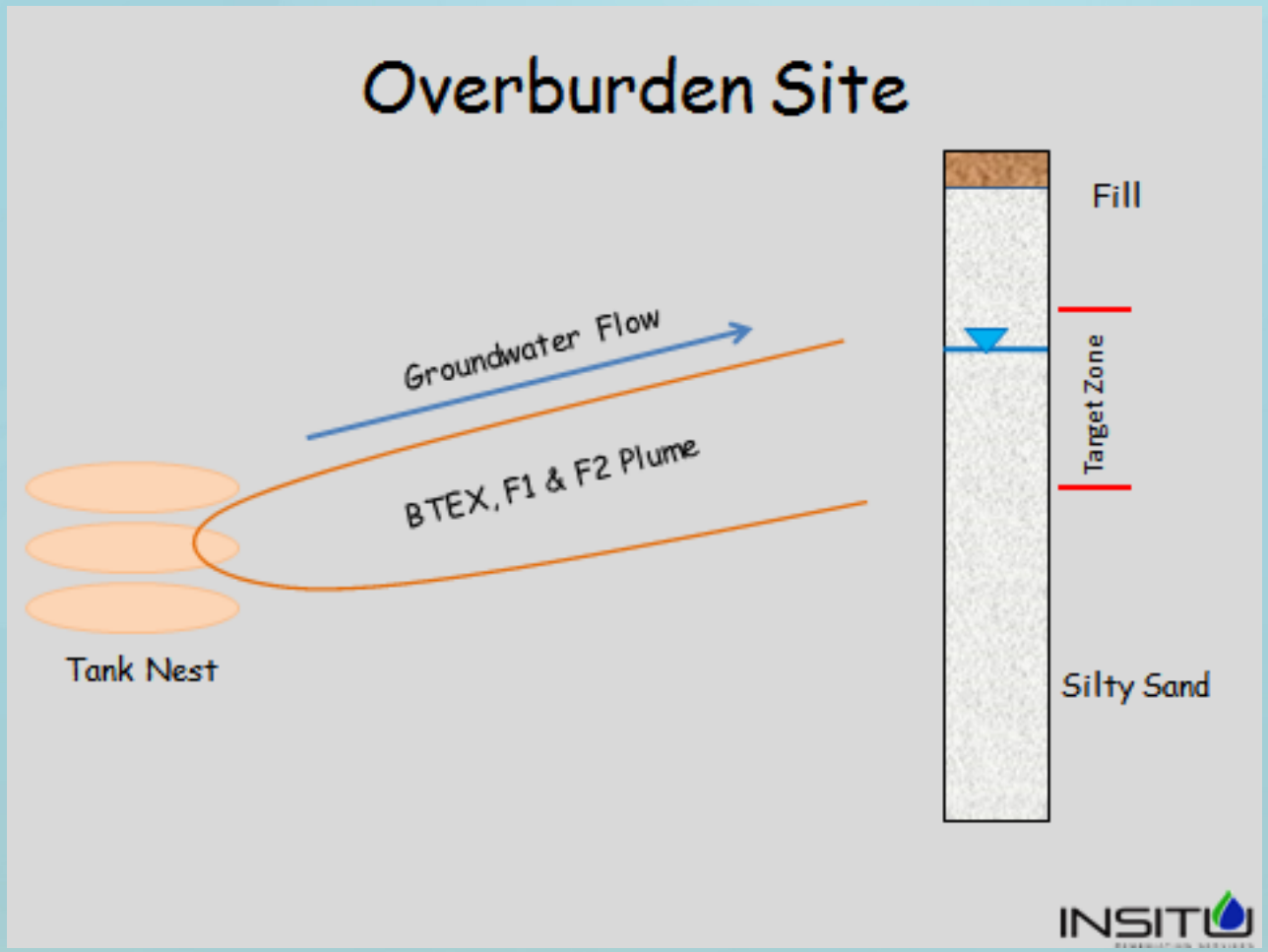
Date

* PRIMA Environmental Inc. El Dorado Hills, CA

FIELD PERFORMANCE/CASE STUDIES

- Remediation Field Studies Evaluating the Effectiveness of Catalyzed Persulfate (PersulfOx) vs. Base-Activated Persulfate- Ontario, Canada
- PersulfOx® Treats High PCE, TCE Soil Concentrations at Former Printing Site- Southeastern US
- PersulfOx® Treats Groundwater at Gasoline Tanker Truck Spill Site- Midwestern US

PROJECT OVERVIEW



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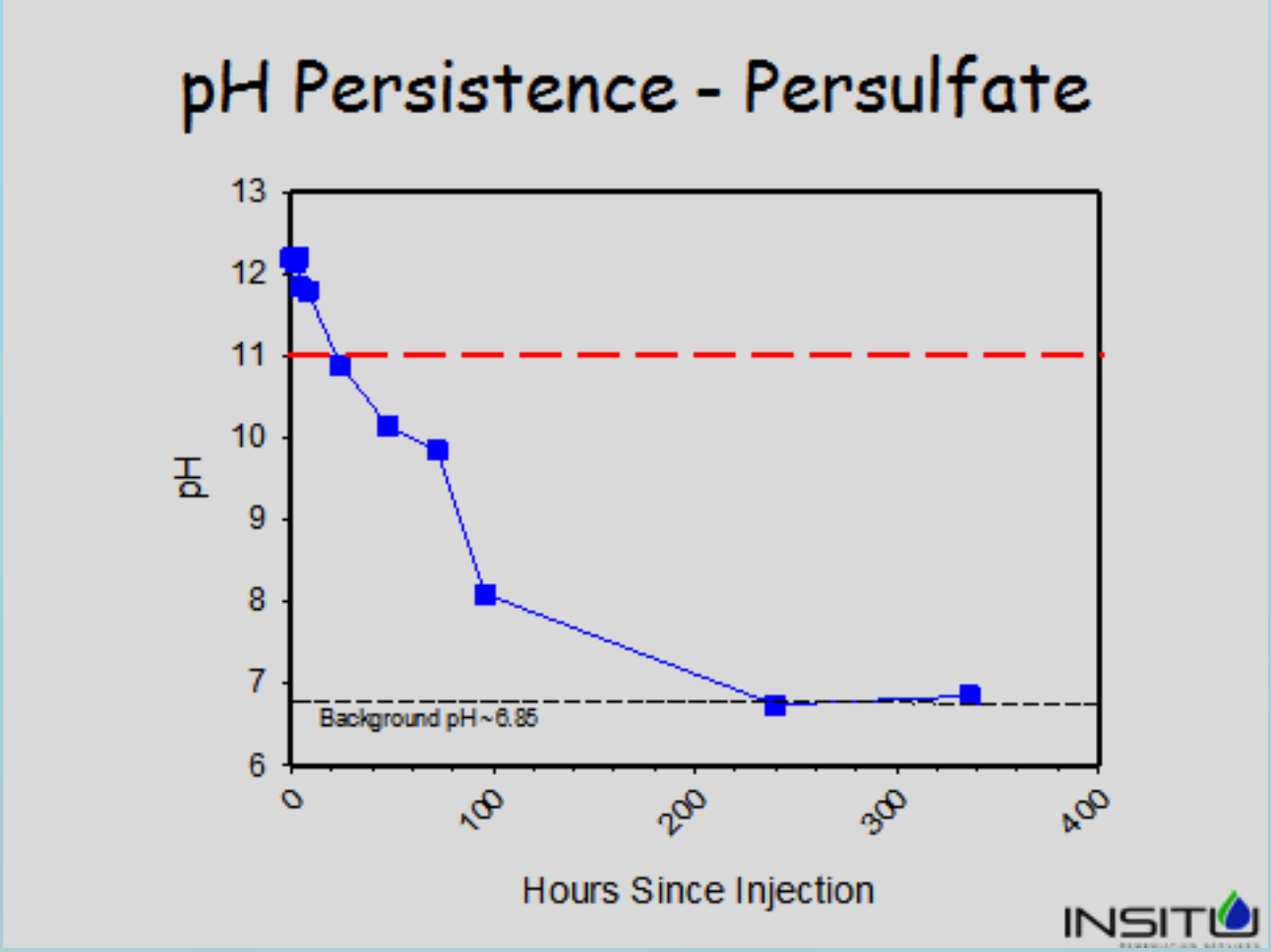
BACKGROUND INFORMATION



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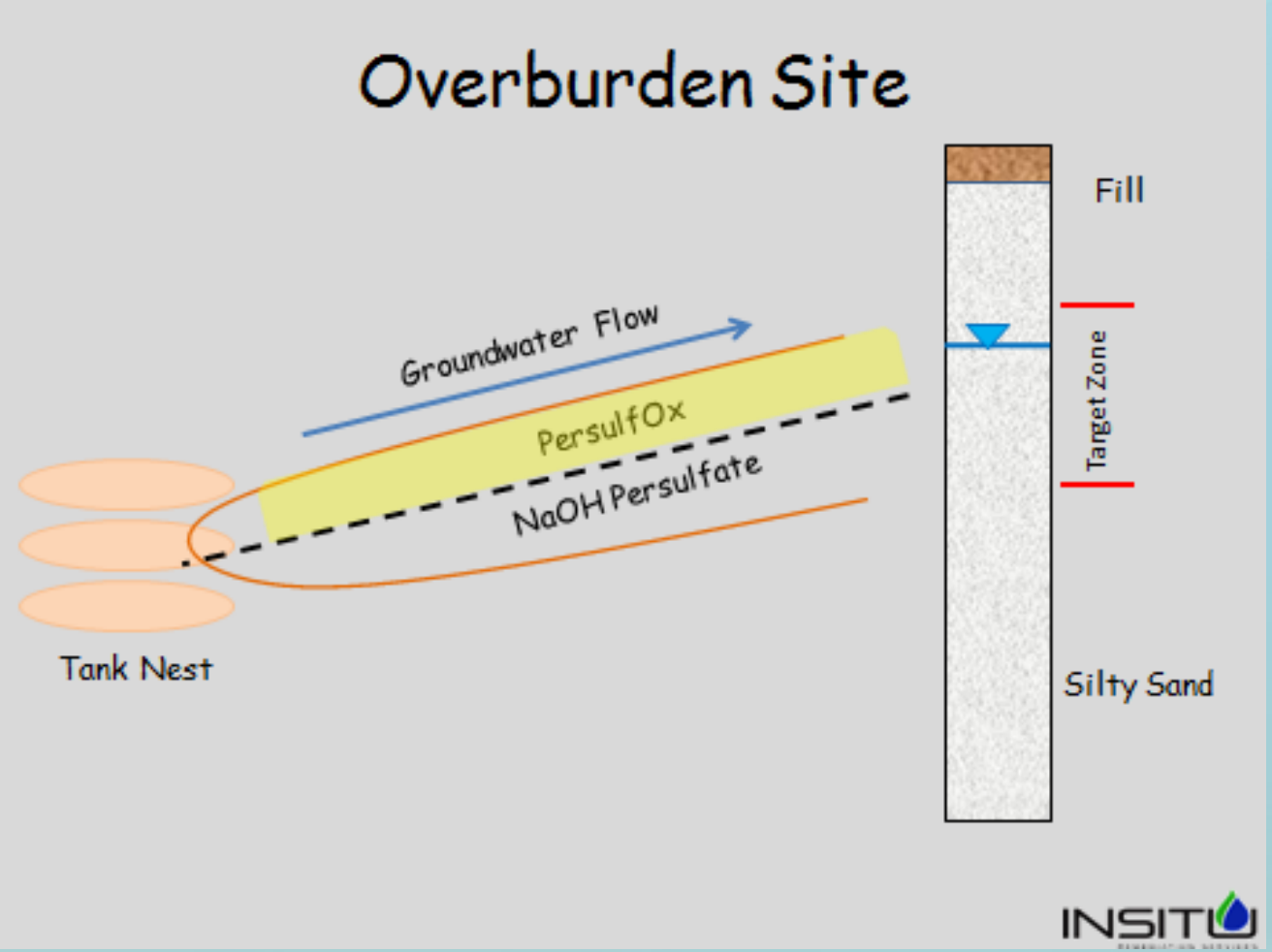
TREATMENT AREA



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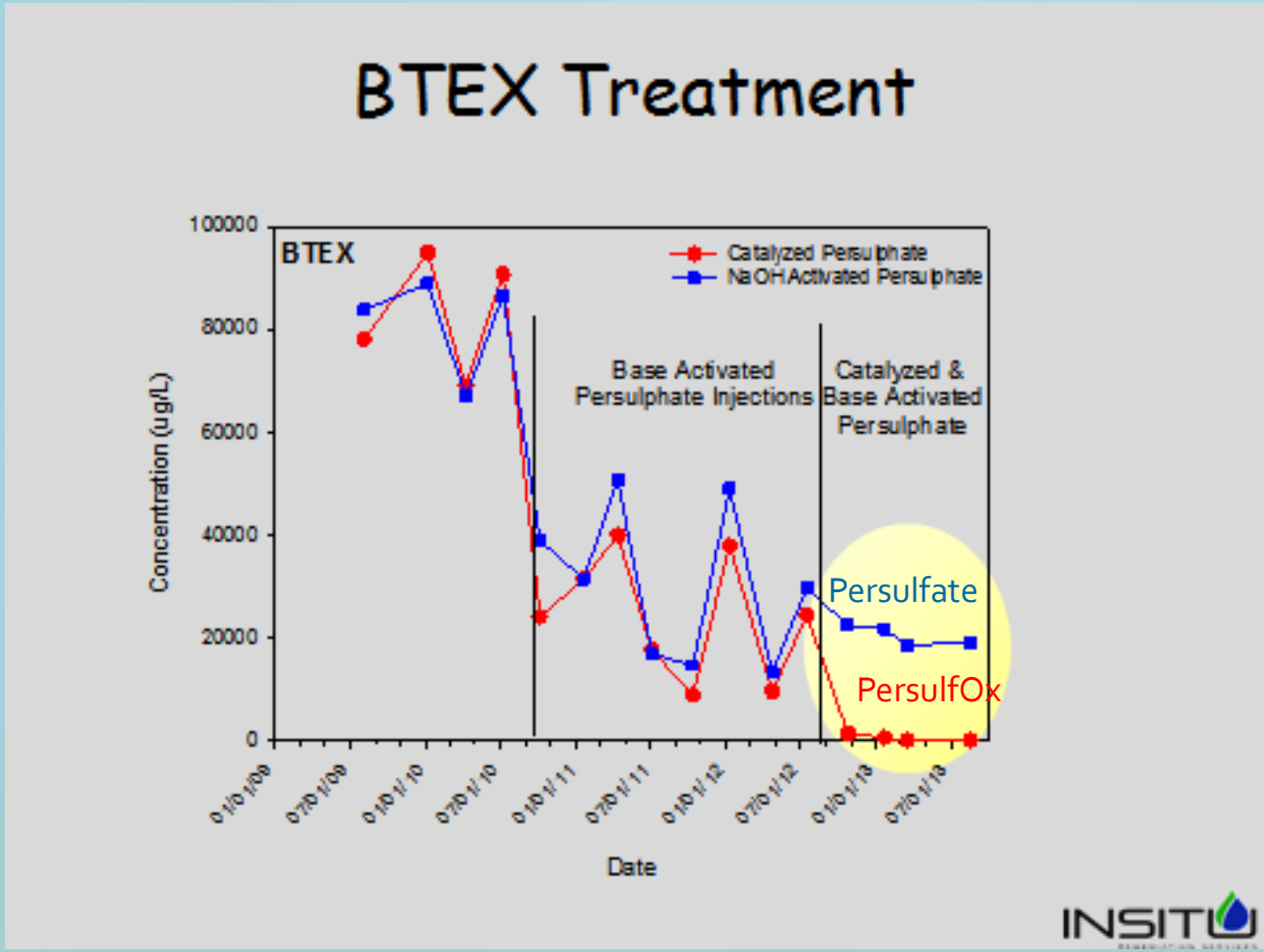
RESULTS



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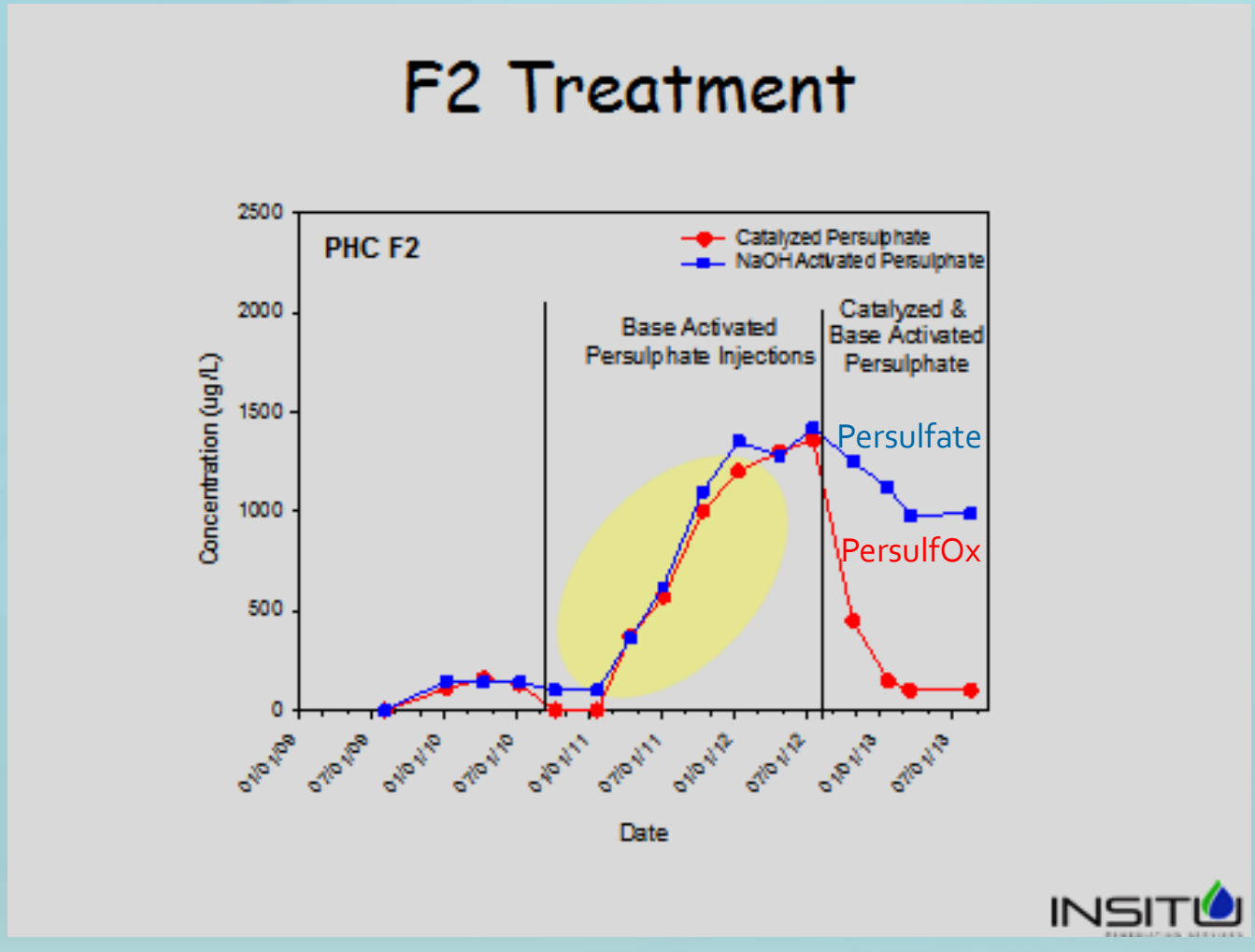
RESULTS



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CONCLUSIONS

Conclusions

- NaOH-activated and PersulfOx both showed good treatment of PHCs including:
  - BTEX,
  - F1, F2 and F3 fractions
- Similar lateral and vertical distributions
- PersulfOx persistence was good
- NaOH-activated persulphate had issues with maintaining pH greater than 10

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PROJECT OVERVIEW

PersulfOx® Treats High PCE, TCE Soil Concentrations at Former Printing Site

Aerial View of Project Site

Location: Southeastern U.S.; EPA Region IV

Former commercial printing and lithography operation which used chlorinated solvents

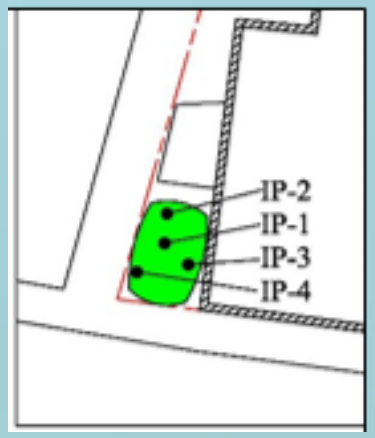
Half-acre lot with 12,136-square-foot building

APPLICATION SPECIFICS

- Treatment - two injection events of PersulfOx into soils occurring two months apart

- 20 % Solution of PersulfOx

- Application - 165 pounds (100 gallons) of PersulfOx per each injection event



Injection Locations Map

TREATMENT AREA

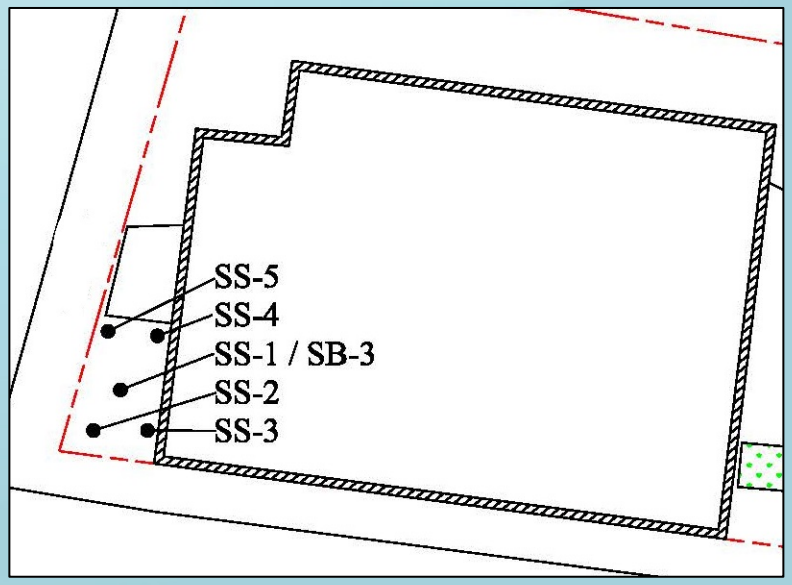
Contamination Area: 200 Square Feet

Target treatment depth = 15-20 feet bgs

Total VOC peak concentrations:
Total- 3700 ug/kg

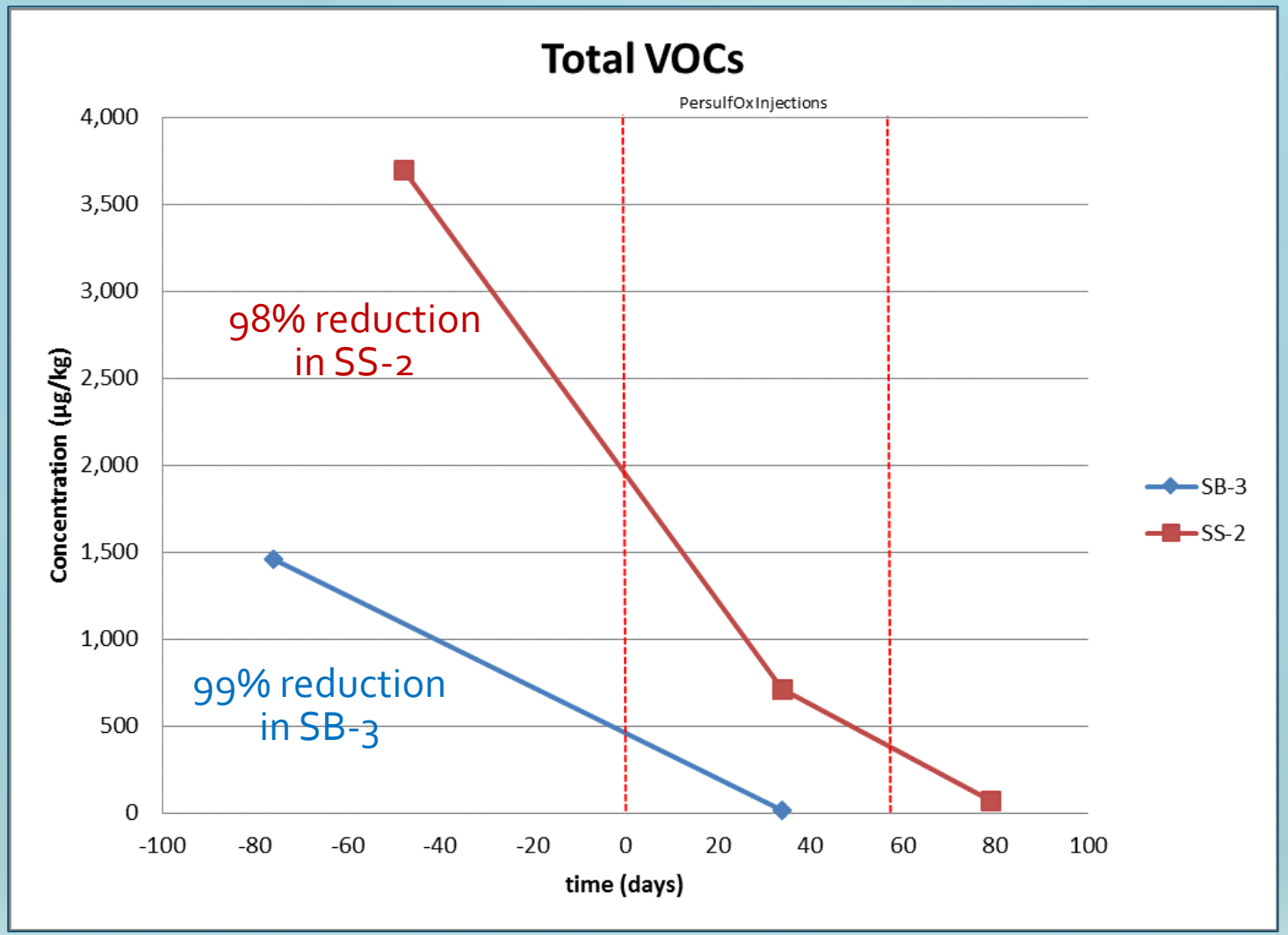
PCE- 325 ug/kg

TCE- 3700 ug/kg



Site Plan and Treatment Area with Soil Sample Locations

RESULTS - TOTAL VOC REDUCTION

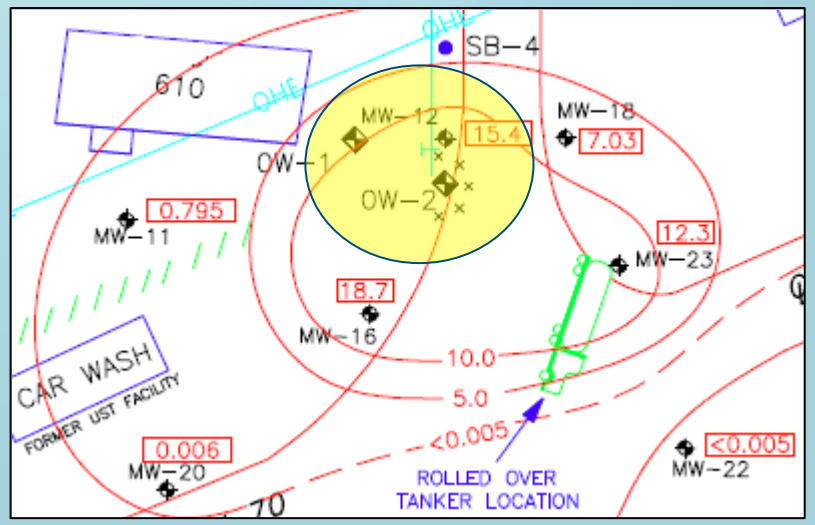


PROJECT OVERVIEW

PersulfOx® Treats Groundwater at Gasoline Tanker Truck Spill Site

Location: Southwest, U.S. ; EPA Region VI

Gasoline tanker truck spill with impacts to soil and groundwater



Site Plan and Treatment Area

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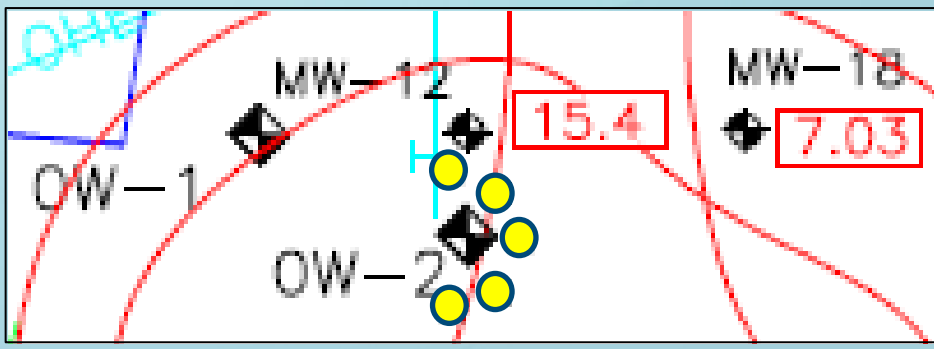
PersulfOx™ CATALYZED PERSULFATE

APPLICATION SPECIFICS

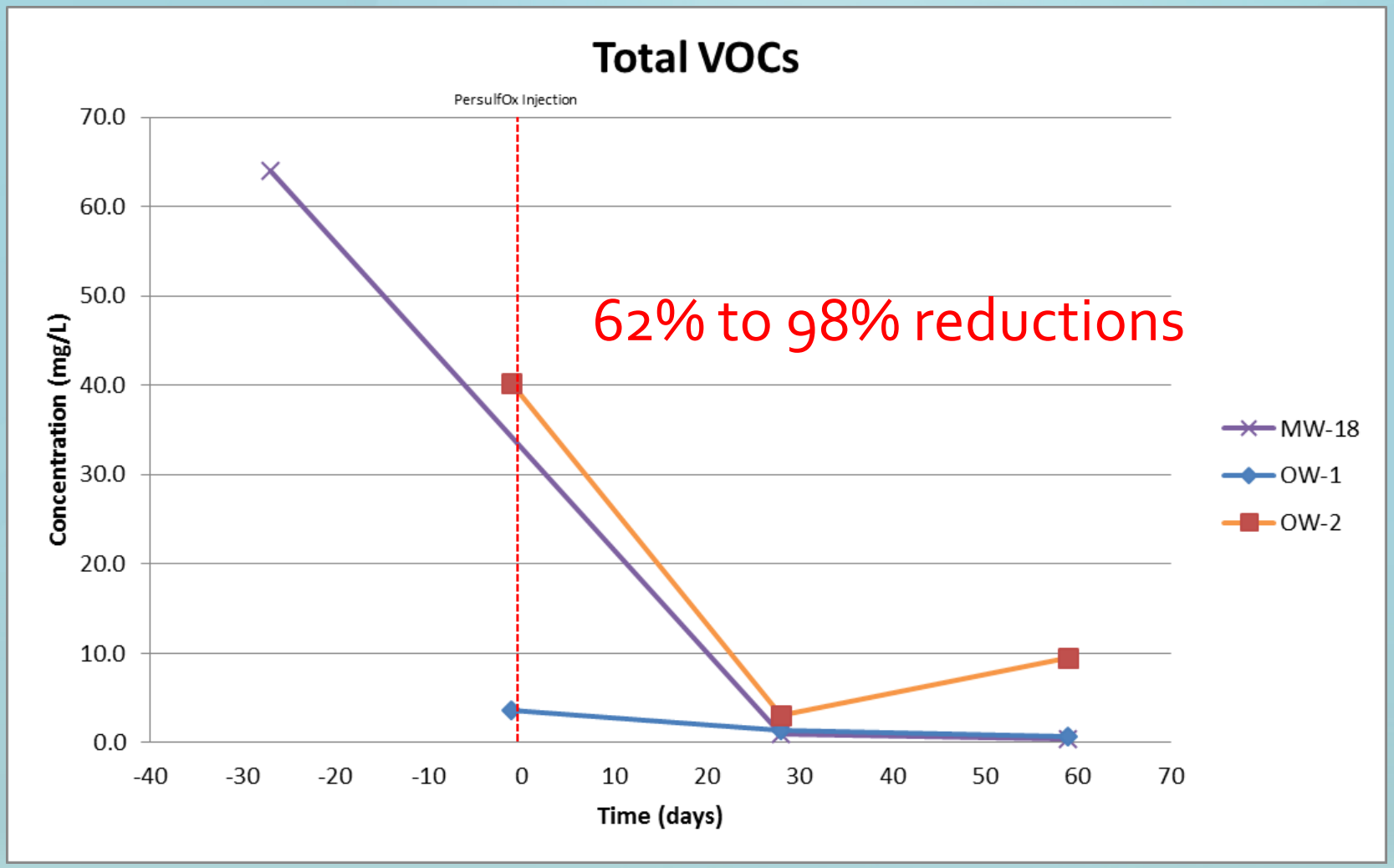
- Area- 1 well
- Soil Type- silty clay overlying siltstone
- Target injection depth = 5 feet to 10 feet bgs in 1 foot intervals
- Total VOC concentration peak: 64.1 mg/L (~26 mg/L Benzene)
  - Including TPH-GRO and BTEX
- Single injection event- 5 injection points (20 % solution , 570 lbs PersulfOx, 300 gallons)



Injection Location Map

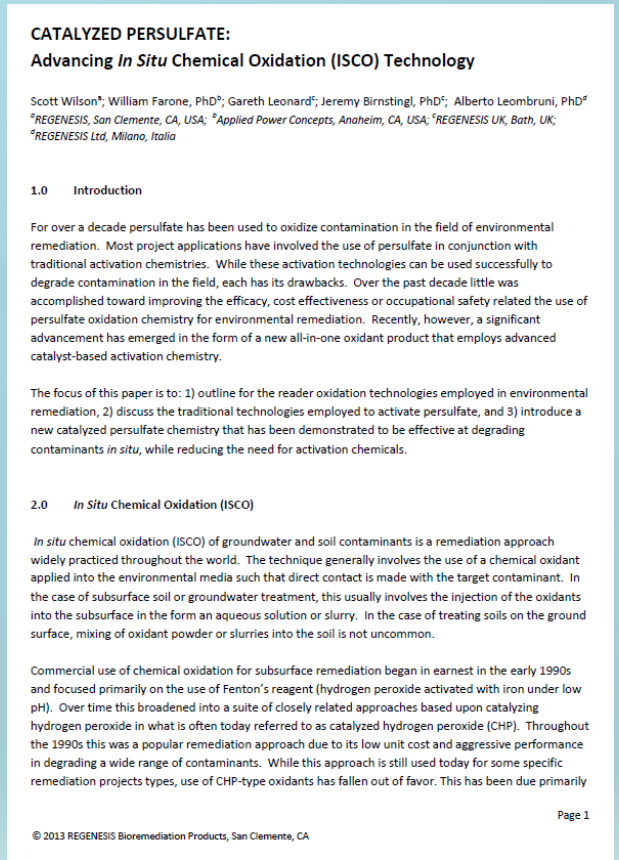
Injection Point

RESULTS - TOTAL VOC REDUCTIONS IN GW



MORE DETAILS AND INFORMATION

- White Paper: Catalyzed Persulfate: Advancing *In Situ* Chemical Oxidation (ISCO) Technology
- 16 pages of detailed information
- Full references and citations
- Copies are available at our exhibit or at www.persulfox.com



CATALYZED PERSULFATE:
Advancing *In Situ* Chemical Oxidation (ISCO) Technology

Scott Wilson[a]; William Farone, PhD[b]; Gareth Leonard[c]; Jeremy Birnstingl, PhD[c]; Alberto Leombruni, PhD[d]
[a]REGENESIS, San Clemente, CA, USA; [b]Applied Power Concepts, Anaheim, CA, USA; [c]REGENESIS UK, Bath, UK; [d]REGENESIS Ltd, Milano, Italia

1.0 Introduction

For over a decade persulfate has been used to oxidize contamination in the field of environmental remediation. Most project applications have involved the use of persulfate in conjunction with traditional activation chemistries. While these activation technologies can be used successfully to degrade contamination in the field, each has its drawbacks. Over the past decade little was accomplished toward improving the efficacy, cost effectiveness or occupational safety related the use of persulfate oxidation chemistry for environmental remediation. Recently, however, a significant advancement has emerged in the form of a new all-in-one oxidant product that employs advanced catalyst-based activation chemistry.

The focus of this paper is to: 1) outline for the reader oxidation technologies employed in environmental remediation, 2) discuss the traditional technologies employed to activate persulfate, and 3) introduce a new catalyzed persulfate chemistry that has been demonstrated to be effective at degrading contaminants *in situ*, while reducing the need for activation chemicals.

2.0 *In Situ* Chemical Oxidation (ISCO)

In situ chemical oxidation (ISCO) of groundwater and soil contaminants is a remediation approach widely practiced throughout the world. The technique generally involves the use of a chemical oxidant applied into the environmental media such that direct contact is made with the target contaminant. In the case of subsurface soil or groundwater treatment, this usually involves the injection of the oxidants into the subsurface in the form an aqueous solution or slurry. In the case of treating soils on the ground surface, mixing of oxidant powder or slurries into the soil is not uncommon.

Commercial use of chemical oxidation for subsurface remediation began in earnest in the early 1990s and focused primarily on the use of Fenton's reagent (hydrogen peroxide activated with iron under low pH). Over time this broadened into a suite of closely related approaches based upon catalyzing hydrogen peroxide in what is often today referred to as catalyzed hydrogen peroxide (CHP). Throughout the 1990s this was a popular remediation approach due to its low unit cost and aggressive performance in degrading a wide range of contaminants. While this approach is still used today for some specific remediation projects types, use of CHP-type oxidants has fallen out of favor. This has been due primarily

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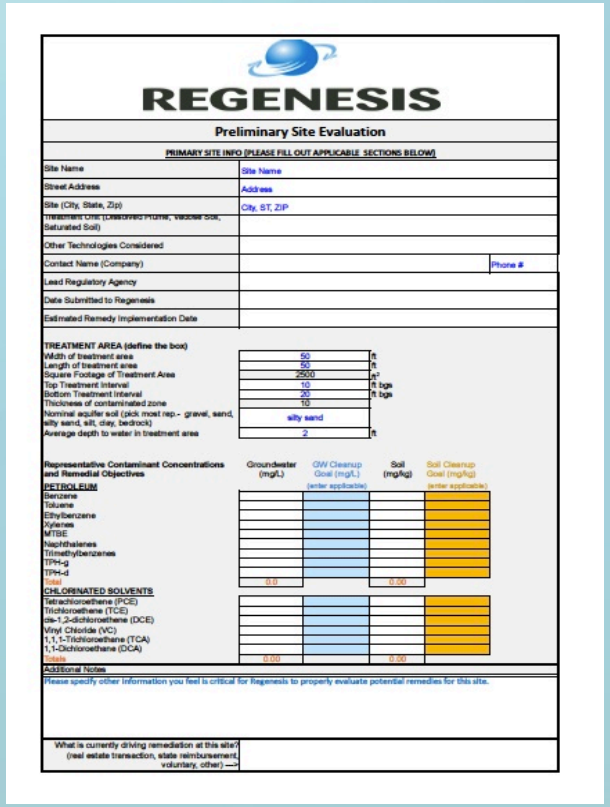
PersulfOx™ CATALYZED PERSULFATE

RESOURCES FOR YOUR BENEFIT…

PersulfOx™
CATALYZED PERSULFATE

- Free site evaluation/consultation/cost estimates and post-application project review and support
- Qualified staff of remediation professionals- engineers, scientists, geologists, etc.
- Since 1994 - 19 Years of remediation industry experience, we see over 1000 sites a year
- Extensive Library of Contaminant-Specific Information, Case Studies and Application Instructions



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Preliminary Site Evaluation

PRIMARY SITE INFO [PLEASE FILL OUT APPLICABLE SECTIONS BELOW]

Site Name	Site Name
Street Address	Address
Site (City, State, Zip)	City, ST, ZIP
Treatment Unit (Dissolved Plume, Vadose Soil, Saturated Soil)	
Other Technologies Considered	
Contact Name (Company)	Phone #
Lead Regulatory Agency	
Date Submitted to Regenesis	
Estimated Remedy Implementation Date	

TREATMENT AREA (define the box)

Width of treatment area	50	ft
Length of treatment area	50	ft
Square Footage of Treatment Area	2500	ft²
Top Treatment Interval	10	ft bgs
Bottom Treatment Interval	20	ft bgs
Thickness of contaminated zone	10	
Nominal aquifer soil (pick most rep.- gravel, sand, silty sand, silt, clay, bedrock)	silty sand	
Average depth to water in treatment area	2	ft

Representative Contaminant Concentrations and Remedial Objectives	Groundwater (mg/L)	GW Cleanup Goal (mg/L) (enter applicable)	Soil (mg/kg)	Soil Cleanup Goal (mg/kg) (enter applicable)
PETROLEUM				
Benzene				
Toluene				
Ethylbenzene				
Xylenes				
MTBE				
Naphthalenes				
Trimethylbenzenes				
TPH-g				
TPH-d				
Total	0.0		0.00	
CHLORINATED SOLVENTS				
Tetrachloroethene (PCE)				
Trichloroethene (TCE)				
cis-1,2-dichloroethene (DCE)				
Vinyl Chloride (VC)				
1,1,1-Trichloroethene (TCA)				
1,1-Dichloroethane (DCA)				
Totals	0.00		0.00	

Additional Notes

Please specify other information you feel is critical for Regenesis to properly evaluate potential remedies for this site.

What is currently driving remediation at this site? (real estate transaction, state reimbursement, voluntary, other) —>

Thank you for your attention!

REGENESIS

THANK YOU!

ASHLEY CEDZO
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