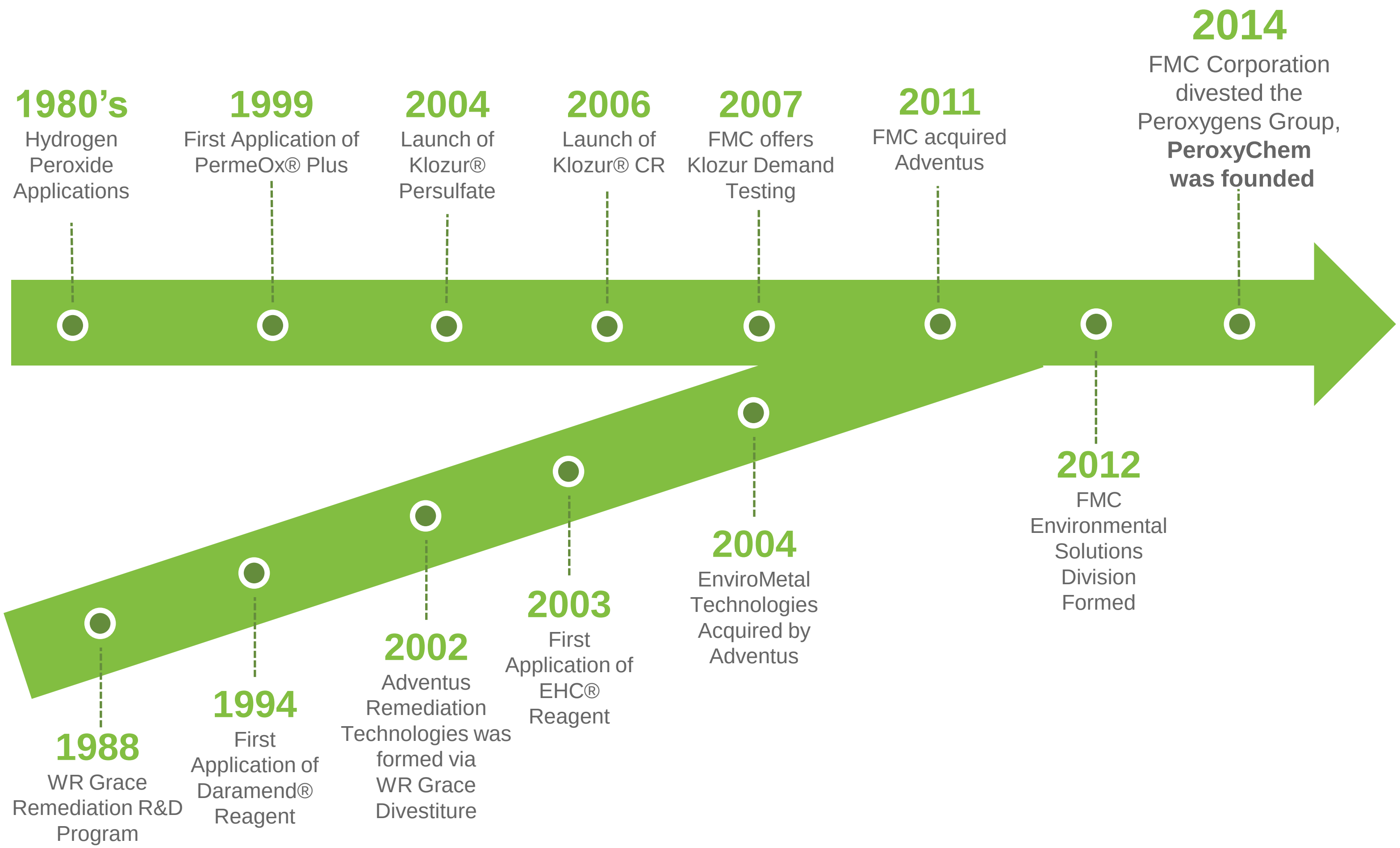
Successful Field Applications of Alkaline Activated Klozur® Persulfate

Brant A. Smith P.E., Ph.D.

October 29, 2014

Who We Were…

New Name.
Decades of Experience.



Who We Are…

Expert Technical Team
Field-Proven, Diverse Technologies
Field Support
PeroxyChem
Environmental Solutions
R&D and Treatability Laboratories
Technical and Design Support
Mixing and Handling Equipment

Environmental Solutions

PeroxyChem

Field-Proven Portfolio of Remediation Technologies Based on Sound Science

In Situ **Chemical Oxidation**

1. Klozur® persulfate
2. Klozur® CR

In Situ Chemical Reduction

3. EHC®
4. EHC® Liquid
5. Daramend®

Aerobic Bioremediation

6. Terramend®
7. PermeOx® Ultra

Immobilization/Stabilization

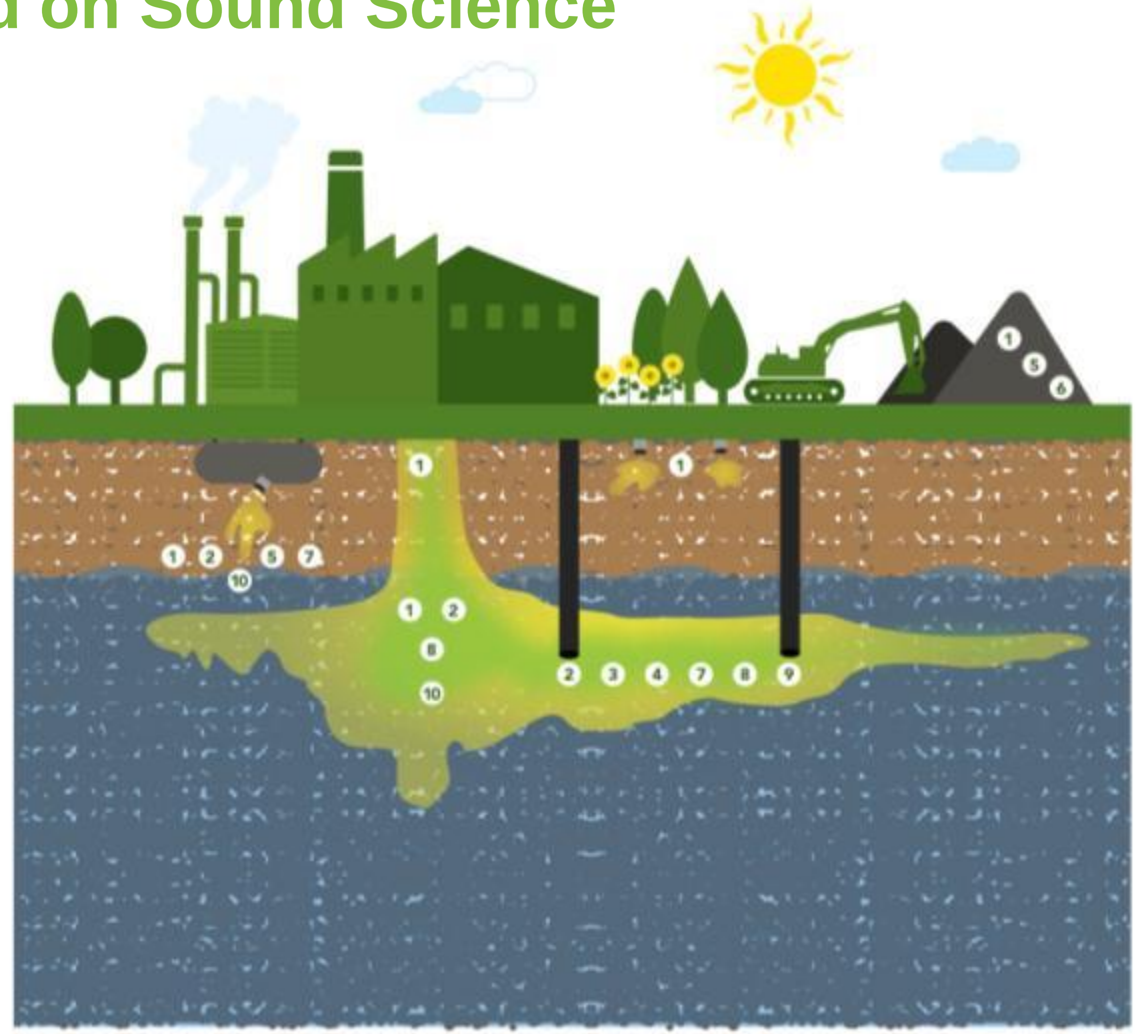
8. EHC® Metals and MetaFix™

Enhanced Reductive Dechlorination

9. ELS™

NAPL Stabilization/Mass Flux Reduction

10. ISGS™



ISCO

What is ISCO

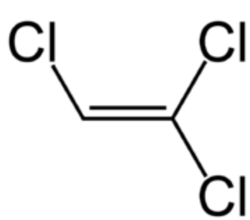
- In Situ Chemical Oxidation (ISCO)
- Addition of chemicals to the soil and groundwater that react with a wide variety of chemicals of concern (COCs) by taking electrons from, or oxidizing, those COCs
- Oxidative, reductive and nucleophilic pathways have also been shown to be effective under certain conditions

Introduction to Klozur® Persulfate

Examples of Contaminants Destroyed by Klozur Persulfate

Chlorinated Solvents
PCE, TCE, DCE
TCA, DCA
Vinyl chloride
Carbon tetrachloride
Chloroform
Chloroethane
Chloromethane
Dichloropropane
Trichloropropane
Methylene chloride

Others
Carbon disulfide
Aniline
PVA/ TNT / DNT



TPH
BTEX
GRO
DRO
ORO
creosote

Oxygenates
MTBE
TBA

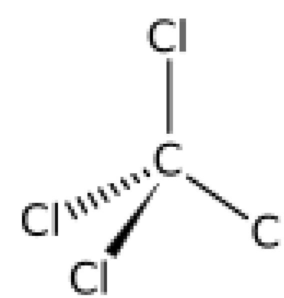
Perflourinated
Freon
PFOS
PFOA
PFBA

Chlorobenzenes
Chlorobenzene
Dichlorobenzene
trichlorobenzene

Phenols
phenol
Pentachlorophenol
nitrophenol

PAHs
Anthracene
Benzopyrene
Styrene
Naphthalene
Pyrene
Chrysene
trimethylbenzene

Pesticides
DDT
Chlordane
Heptachlor
Lindane
Toxaphene
MCPA
Bromoxynil



Why ISCO?

- Many in situ remediation technologies to choose from, why pick ISCO?
  - **Cost**: Often the lowest cost alternative
  - **Time**: Provides results quickly, usually within weeks to months of an application
  - **Effectiveness**: ISCO can treat a wide assortment of typical COCs
  - **Contaminant Mass**: ISCO can treat a wide variety of contaminant concentrations including heavily impacted areas that may inhibit bioremediation

KLOZUR® PERSULFATE

Introduction to Klozur® Persulfate

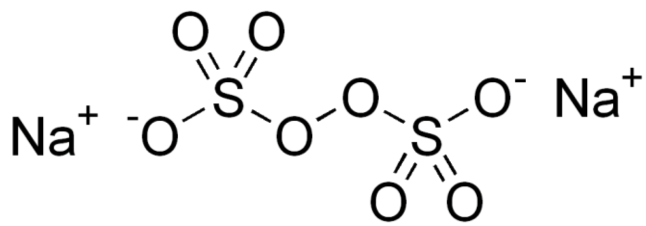
Klozur® Persulfate is:

- Based on the sodium persulfate molecule
- A strong oxidant used for the destruction of contaminants in soil and groundwater
- Aggressive and fast acting chemistry with extended subsurface lifetime (weeks to months) and little to no heat or gas evolution
- Applicable across a broad range of organic contaminants
- Highly soluble in water (significant oxidant mass is smaller volumes)

Field solubility of more than 500 g/L possible

Fundamental Chemistry

- Klozur® Activated Persulfate is based upon the persulfate anion:



- Persulfate is a peroxygen, and similar to hydrogen peroxide, it can be split at the O-O bond forming the sulfate radical:

$$^{-}O_3S\text{-}O\text{-}O\text{-}SO_3^{-} \rightarrow {}^{-}O_3S\text{-}O\bullet \quad \bullet O\text{-}SO_3^{-}$$

Fundamental Chemistry

- Common activation methods include:
  - Alkaline activation
    - ($OH\bullet$, $SO_4\bullet^-$, $O_2\bullet^-$)
  - Iron or iron chelate activation
    - ($SO_4\bullet^-$)
  - Heat activation
    - (Temperature dependent: $OH\bullet$, $SO_4\bullet^-$, $O_2\bullet^-$)
  - Hydrogen peroxide activation
    - ($OH\bullet$, $SO_4\bullet^-$, $O_2\bullet^-$)

Oxidant	Standard Reduction Potential (V)	Reference
Hydroxyl radical ($OH\bullet$)	2.59	Siegrist et al.
Sulfate radical ($SO_4\bullet^-$)	2.43	Siegrist et al.
Ozone	2.07	Siegrist et al.
Persulfate anion	2.01	Siegrist et al.
Hydrogen Peroxide	1.78	Siegrist et al.
Permanganate	1.68	Siegrist et al.
Chlorine (HOCl)	1.48	CRC (76th Ed)
Oxygen	1.23	CRC (76th Ed)
Oxygen	0.82	Eweis (1998)
Fe (III) reduction	0.77	CRC (76th Ed)
Nitrate reduction	0.36	Eweis (1998)
Sulfate reduction	-0.22	Eweis (1998)
Superoxide ($O_2\bullet^-$)	-0.33	Siegrist et al.
ZVI	-0.45	CRC (76th Ed)

Fundamental Chemistry

Persulfate anion kinetics are generally too slow for most contaminants.
As a result, you must activate persulfate to form the sulfate radical.

Activated Persulfate

- produces a radical which is more powerful and kinetically fast
- **PeroxyChem always recommends using an activator**
- proper activation method is based on contaminant, site lithology, and hydrogeology

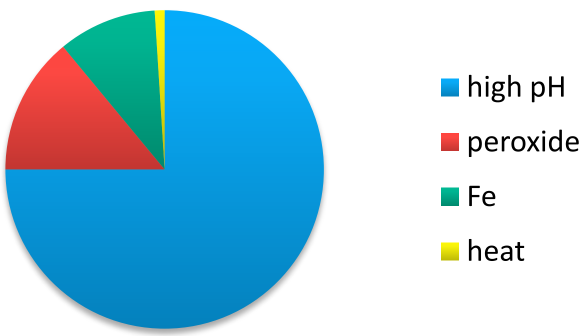
$$S_2O_8^{-2} + \text{activator} \rightarrow SO_4\bullet^{-} + (SO_4\bullet^{-} \text{ or } SO_4^{-2})$$

Heat   Iron H_2O_2 Alkaline

Purchase of PeroxyChem's Klozur® Persulfate includes rights to practice the inventions covered by global patents in the purchase price of the product.

Activator Selection

Estimated Activator Usage



- Alkaline Activated Persulfate
  - Premier activation method
  - Best suited for most applications
- Iron-Chelate Activated Persulfate
  - Chlorinated ethenes and hydrocarbons
  - Less contaminant mass
- Heat
  - Complex sites
  - Polishing step after thermal treatment
- Hydrogen Peroxide
  - Sites that benefit from vigorous reaction with both hydrogen peroxide and sodium persulfate

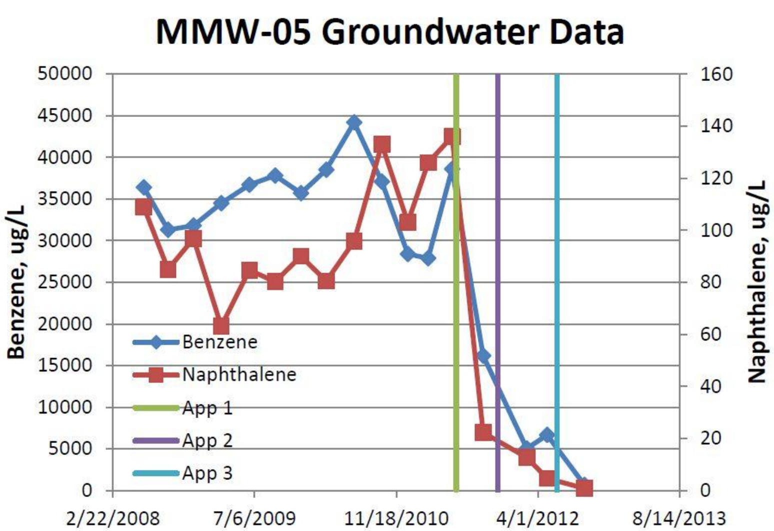
ALKALINE ACTIVATED PERSULFATE

Outline

- Two brief Case Studies
- Alkaline Activated Persulfate
- Two detailed Case Studies

MGP Site in Illinois

- Contaminant:
  - ~17,000 mg/Kg TPH
  - ~45,000 µg/L Benzene
  - ~140 µg/L Naphthalene
- Remedial goals:
  - TPH to less than 9,000 mg/Kg
  - Reduce benzene in groundwater by greater than 90 percent
- Applied 46,200 lbs of AAP to site over 3 applications
  - 32 g Klozur per Kg soil
- Results:
  - Less than 2,500 mg/Kg TPH
  - Benzene in groundwater reduced by greater than 98 percent
  - State of Illinois issue a ***No Further Action*** letter



Courtesy of XDD, LLC

Environmental Solutions

PeroxyChem

Active Industrial Site

- PCE, 1,1,1-TCA, and 1,4-dioxane (DNAPL source)
- AAP does not produce gas during treatment
- Treated with two applications totaling 31,000 Kg Klozur®
  - 25 g Klozur per Kg soil
- Remedial goal of less than 1 mg/L for each contaminant

Contaminants	Average Contaminant Concentrations (μg/L)			
	Baseline	Post 1st Application	Post 2nd Application	Total Percent Reduction
PCE	11,987	4,819	113	99.1
1,1,1-TCA	8,736	5,698	64	99.3
1,4-Dioxane	410	1,029	165	59.8

Courtesy of XDD, LLC

Alkaline Activation: Chemistry

- Sodium persulfate is activated when the solution is raised to pH > 10.5
- Alkaline Activation-*simple version*:

$$\text{pH} > 10.5 \qquad S_2O_8^{2-} \xrightarrow{OH^-} 2SO_4\bullet$$

- Alkaline Activation-*complex version* (Furman et al., 2010):

$$S_2O_8^{2-} + 2H_2O \rightarrow HO_2^- + 2SO_4^{2-} + 3\,H^+$$
$$HO_2^- + S_2O_8^{2-} \rightarrow SO_4\bullet^- + SO_4^{2-} + H^+ + O_2\bullet^-$$
$$SO_4\bullet^- + OH^- \rightarrow OH\bullet + SO_4^{2-}$$

(note: $H_2O_2 \leftrightarrow HO_2^- + H^+$ $pK_a = 11.7$)

- Complex version of the reaction results in the transient oxygen species of $SO_4\bullet^-$, $OH\bullet$, $O_2\bullet^-$, and HO_2^-
- Analogous to the chemistry that has been studied with catalyzed hydrogen peroxide (CHP)

Fundamental Chemistry

- Alkaline activation
  - ($OH\bullet$, $SO_4\bullet^-$, $O_2\bullet^-$)
- Has been shown to be reactive with:
  - Reduced organics (PAHs, BTEX, TPH, etc)
  - Chlorinated ethenes (PCE, TCE, DCE, and VC)
  - Chlorinated methanes or ethanes (1,1,1-TCA, CT, etc)
  - Oxygenates (MTBE, 1,4-Dioxane, etc)
  - Perfluorinated acids (PFOA, PFBA, etc)

Oxidant	Standard Reduction Potential (V)	Reference
Hydroxyl radical ($OH\bullet$)	2.59	Siegrist et al.
Sulfate radical ($SO_4\bullet^-$)	2.43	Siegrist et al.
Ozone	2.07	Siegrist et al.
Persulfate anion	2.01	Siegrist et al.
Hydrogen Peroxide	1.78	Siegrist et al.
Permanganate	1.68	Siegrist et al.
Chlorine (HOCl)	1.48	CRC (76th Ed)
Oxygen	1.23	CRC (76th Ed)
Oxygen	0.82	Eweis (1998)
Fe (III) reduction	0.77	CRC (76th Ed)
Nitrate reduction	0.36	Eweis (1998)
Sulfate reduction	-0.22	Eweis (1998)
Superoxide ($O_2\bullet^-$)	-0.33	Siegrist et al.
ZVI	-0.45	CRC (76th Ed)

Bench Scale Tests

Evaluate site specific geochemical impacts on ISCO process chemistry

- Purpose and benefits:
  - Can be used to refine cost estimates during a feasibility study
  - Develop engineering parameters for a field application
  - Evaluate potential failure mechanisms
  - Confirm treatment efficacy
- Specific engineering parameters for AAP typically derived from Bench Scale Tests
  - Base buffering capacity
  - Non-target demand (SOD, TOD, KDT, NOD, etc)
  - Degradation ratio/Persulfate efficiency number

Field Applications

ISCO requires establishing contact between a sufficient mass of oxidant with the contaminant mass in the subsurface

- Common steps following Bench Scale Tests:
  - Field Pilot Test
  - Full Scale Application
- Design and strategies for a field application are typically similar
  - Monitoring, objective and goals often different
- Cost of NaOH
  - Dependent upon volume/shipping container
  - Drums>Totes>>>Tankers
  - NaOH in tankers may be 30 percent cost of drums
  - AAP can be least expensive activator method

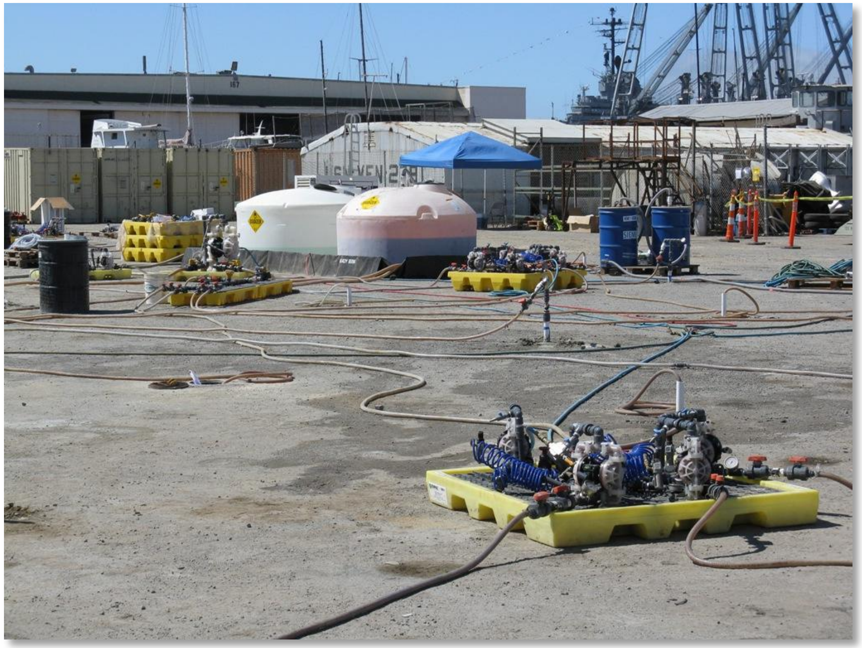
CASE STUDY: ACTIVE CONSTRUCTION SITE IN NEW YORK CITY

What People Think Sites Look Like

Environmental Solutions

PeroxyChem

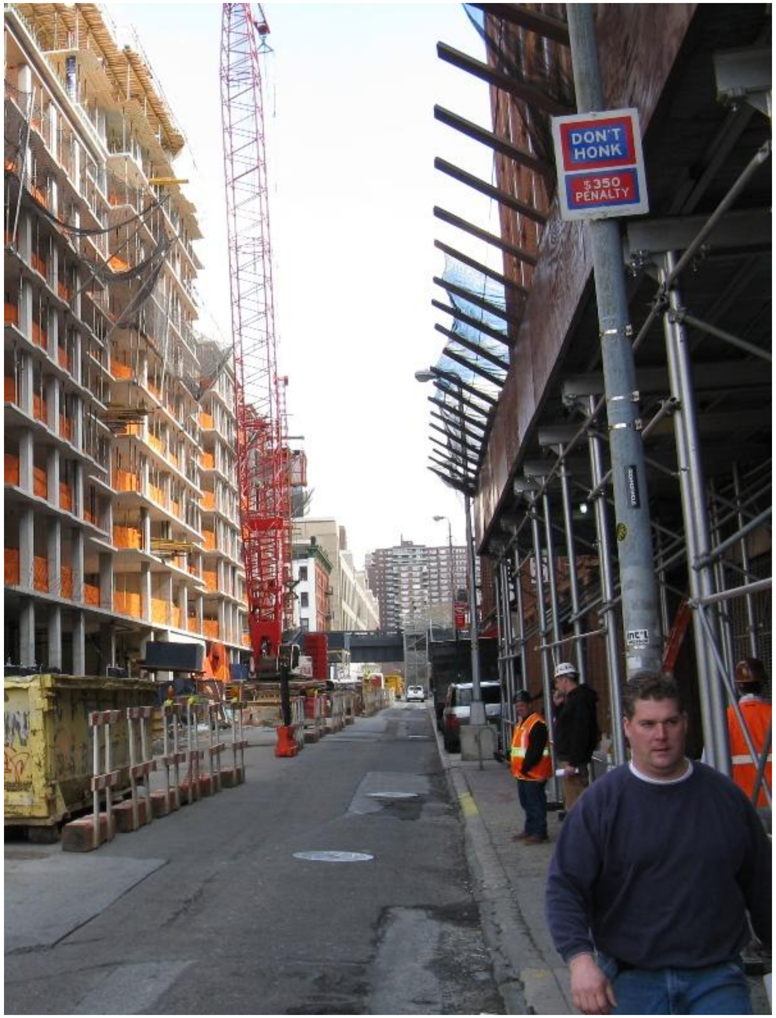
What Sites Usually Look Like



Environmental Solutions

PeroxyChem

What This Site Looked Like



Site Background

- Active construction of a 30+ story high rise building for retail and residential space

- Located 3 blocks from Penn Station in Manhattan (Chelsea)

Courtesy of XDD, LLC and Fleming-Lee Shue

Site Background

- Contamination (average baseline values):
  - BTEX (3,000 µg/L)
  - Naphthalene (140 µg/L)
  - GRO/DRO (1,400 mg/Kg)
  - Different signatures/fingerprints across site
- Contaminant Source:
  - Previous site uses include lumber yard, metal works facility, auto-repair facility, coal yard, piano manufacture, livery car service, and gasoline station
  - Leaking underground storage tanks

Bench Scale Tests: Phase 1

- Evaluated:
  - Catalyzed Hydrogen Peroxide
    - Acid buffering capacity: 6.0 -9.7 g H_2SO_4 per Kg soil
    - Stability: 1 hr (unstabilized) to 8 hr (stabilized) half life
  - Activated Persulfate
    - Base buffering capacity: 1.6 g NaOH / Kg Soil
    - SOD_{14}:

Treatment	Oxidant Test Concentration	Soil Oxidant Demand (grams oxidant / Kilogram dry soil)	Total Oxidant Demand (grams oxidant / Kilogram dry soil)
Unactivated Persulfate	50 g/L Persulfate	1.9	2.0
	200 g/L Persulfate	3.0	3.6
Iron Activated Persulfate	50 g/L Persulfate	2.5	2.7
	200 g/L Persulfate	5.2	15.1
Alkaline Activated Persulfate	50 g/L Persulfate	14.1	13.3
	200 g/L Persulfate	16.0	43.3

Courtesy of XDD, LLC and Fleming-Lee Shue

Bench Scale Tests: Phase 2

- Alkaline Activated Persulfate selected for Phase 2 Tests
  - Stability
  - Return pH to near neutral
  - Compatibility with construction materials

- Results
  - Soils
    - BTEX: 64 to 77 percent reduction
    - DRO: 21 to 33 percent reduction
  - Groundwater
    - Some treatment
    - Some increases
  - Overall ~50 percent treatment in 14 days with ~50 percent residual persulfate

Courtesy of XDD, LLC and Fleming-Lee Shue

Field Application Design

- Target Area: 6,500 ft^2
- Target Interval: ~6 ft
- Five injection wells
  - Large ROI-likely treated outside target area
- Design Mass:
  - 100,000 lbs to 180,000 lbs
- Application:
  - Kozur
    - 72,700 lbs (33 supersacks)
    - 17 g Klozur per Kg soil
  - NaOH
    - 60,300 lb 50 percent solution
- Injection Volume:
  - 35,000 gals
- Concentrations
  - Injection: 250 g/L
  - Formation: 55 g/L
- RemMetrik® Process
  - Wavefront Sidewinders
  - Pressure pulsed strategy
- 9 Day schedule
  - 3 days mobilize/demobilize
  - 6 days of injection
    - 5.5 supersacks per day
  - Construction activities limited

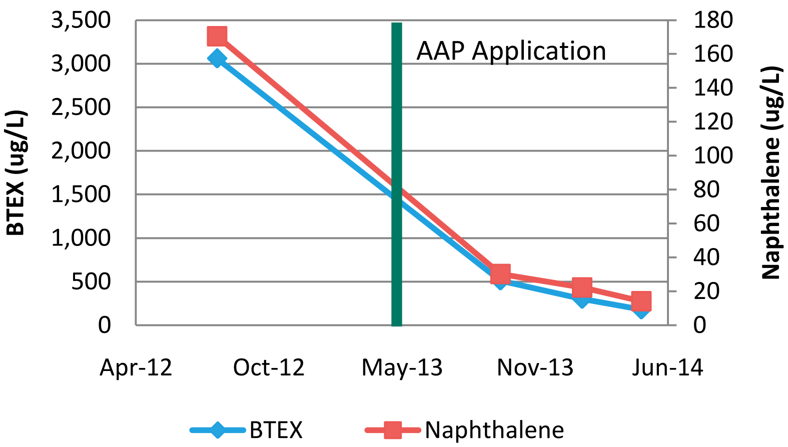
Courtesy of XDD, LLC and Fleming-Lee Shue

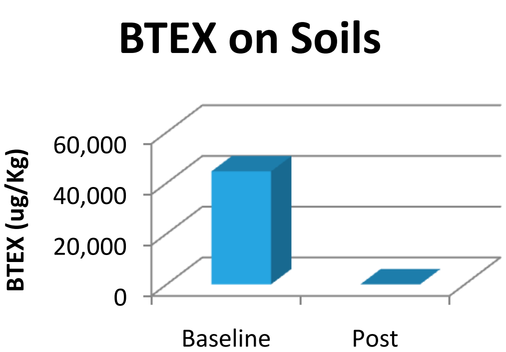
Environmental Solutions

PeroxyChem

Results

- Average groundwater
  - 92 to 95 percent treatment 9 months after treatment
- Average soil
  - 99.9 percent reduction of BTEX
  - 99.2 percent reduction of DRO + GRO
- **<u>Site closed by NY-DEC</u>**





Courtesy of XDD, LLC and Fleming-Lee Shue

CASE STUDY: INDIAN HEAD SITE 47

Site Background

- Geology:
  - Shallow confined aquifer
  - Silty sand lithology: 0 to 16-20 feet bgs
  - Silt/Clay layer starting at 18 – 20 feet bgs; thickness > 30 feet
  - Water table – between 5 and 6 feet bgs

Contaminants	Max. Concentration (µg/L)
CT	150,000
CF	61,000
PCE	2,200
TCE	420
Cis-1,2-DCE	480
Carbon disulfide	11,000

- Past releases – disposal of spent catalyst and inerting agent from 1957 – 1965

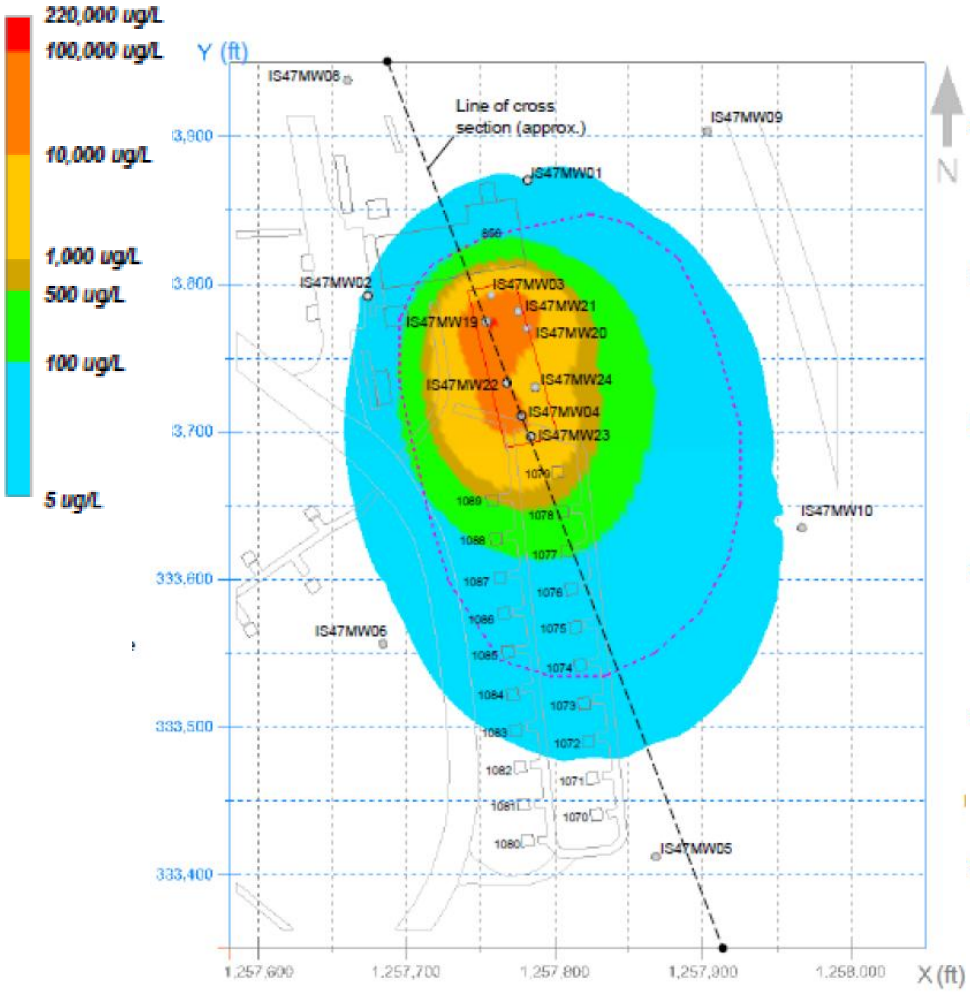
Courtesy of XDD, LLC , CH2M HILL, and US Navy

Bench Study

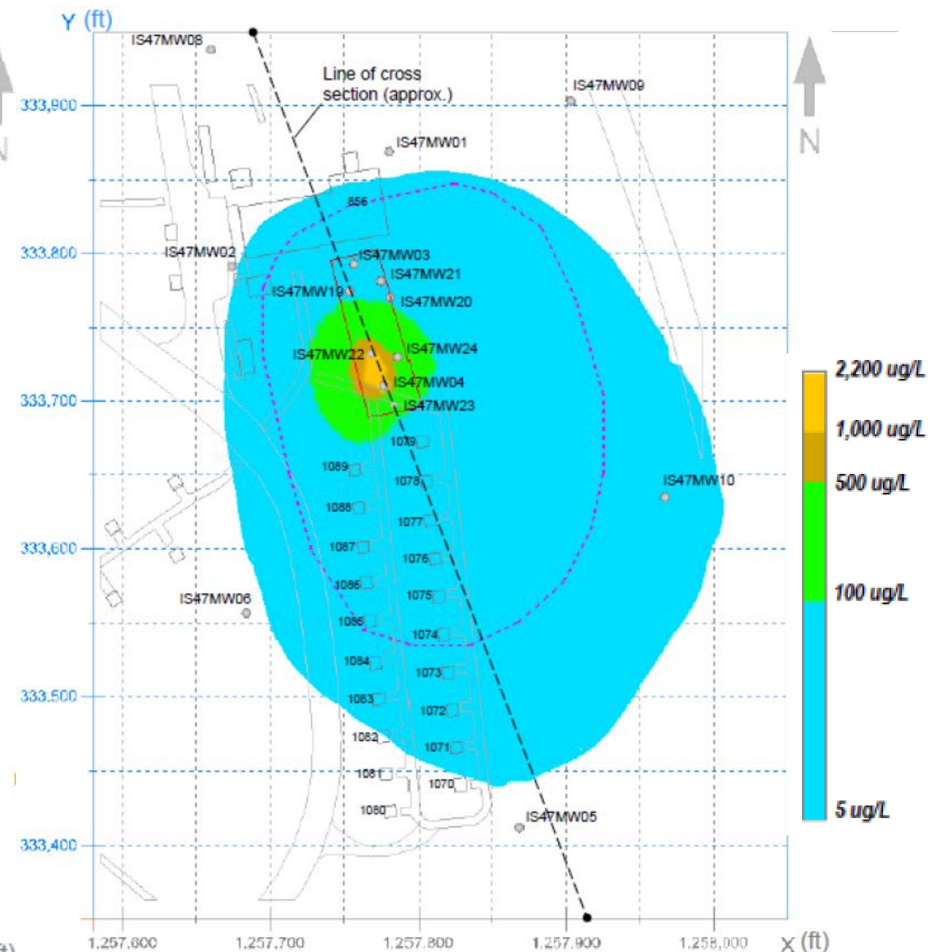
- Evaluated
  - Catalyzed Hydrogen Peroxide
  - Alkaline Activated Persulfate (AAP)
  - Micron scale
    - ZVI
    - Nickel catalyzed ZVI
  - Nano-scale ZVI
- AAP
  - 50 g/L
    - 75 percent CT in 1 application
    - >98 percent in 3 applications
  - 200 g/L
    - >99 percent after 1 and 3 applications
- CHP
  - Effective but concerned about gas evolution
- ZVI
  - Effective in treating CT, but persistent daughter products observed (chloroform and methylene chloride)

Courtesy of XDD, LLC , CH2M HILL, and US Navy

Pilot Test Baseline: CT and PCE Plumes



CT



PCE

Courtesy of XDD, LLC , CH2M HILL, and US Navy

Pilot Study

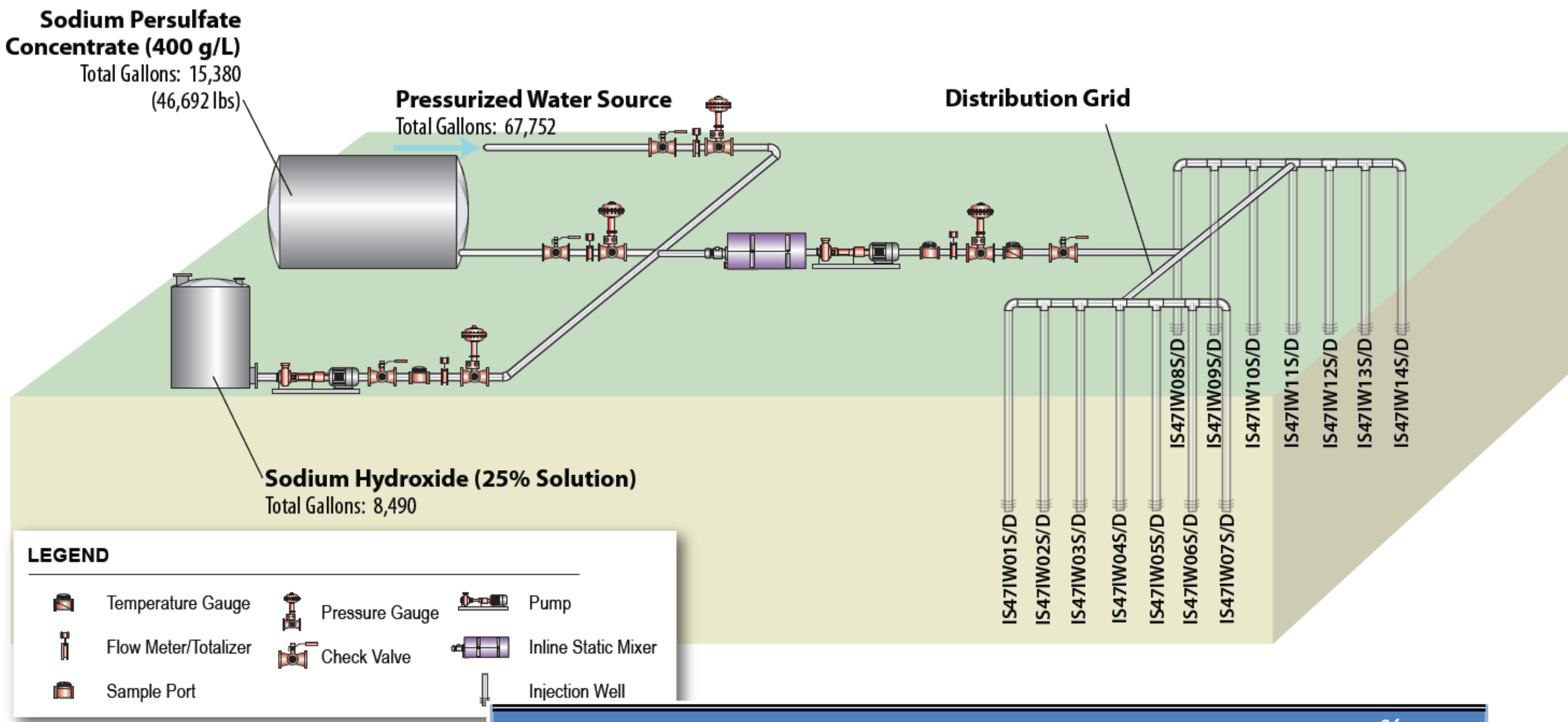
- Conducted Fall 2009
- Injected:
  - 46,700 lbs of sodium persulfate
    - 20 g Klozur per Kg Soil
  - 91,600 gals (55 g/L to 80 g/L)
  - 14 clusters of shallow/deep injection wells
- Plan for second injection after period of monitoring

Courtesy of XDD, LLC , CH2M HILL, and US Navy

Environmental Solutions

PeroxyChem

Actual vs. Design

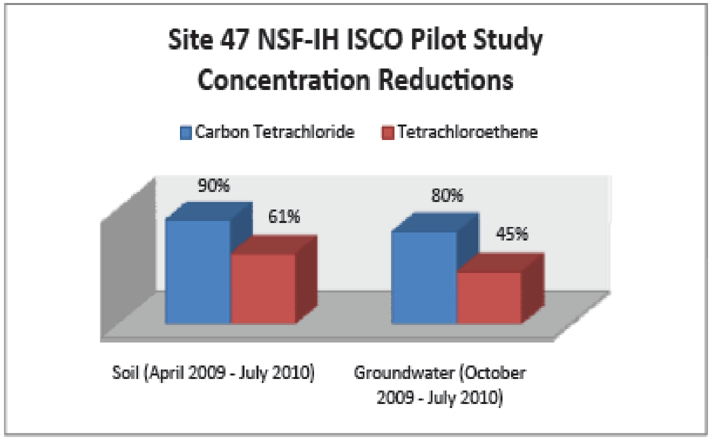


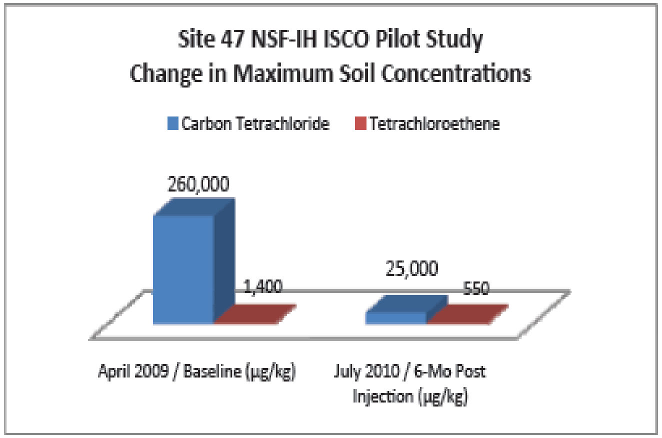
Parameter	Design	Actual	% Actual/Design
Mass of Persulfate (lbs)	46,200	46,692	101%
Volume of Persulfate (gallons)	102,004	91,622	90%
Mass Ratio in Shallow to Deep Wells	50% : 50%	42% : 58%	
Flow Rate/Well (GPM)	5	1.3 to 3.9	
Persulfate Concentrations (g/L)	55	55 to 80	

Courtesy of XDD, LLC , CH2M HILL, and US Navy

Pilot Test Conclusions

- Pilot Test deemed a success after a single application
  - ~80 percent reduction in contaminant mass
- Decision made to go full scale with AAP
- Well installation issues with significant underground utilities noted

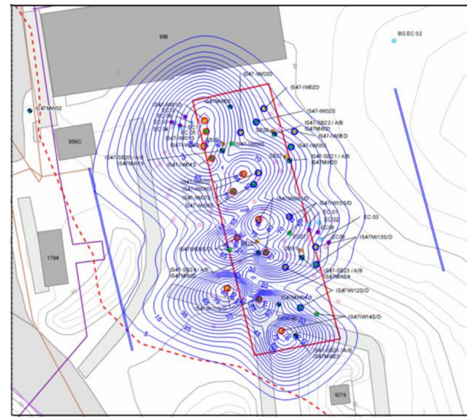




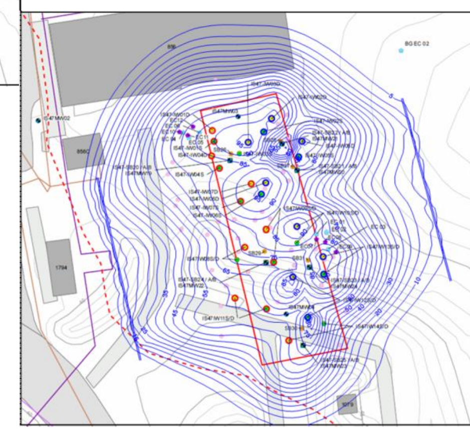
Courtesy of XDD, LLC , CH2M HILL, and US Navy

Full-Scale Pre-Design Activities

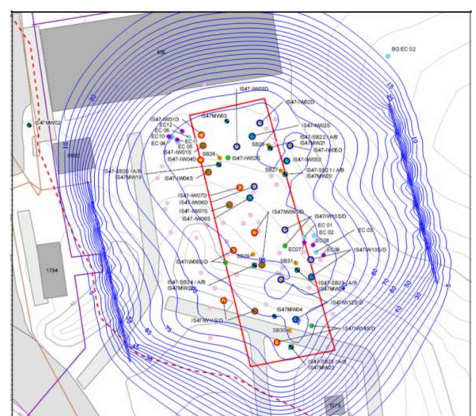
- Recirculation system considered as alternative to direct injection
  - Aquifer Performance Test
    - Refine hydraulic conductivity in anticipation of a recirculation system
  - Flow and Transport Model
    - Assessed flow paths, areas of influence, and particle transit times for recirculation system
- Data Gap Investigation
  - Refined target area (CT + PCE > 500 ug/L)



3 Days



6 Days



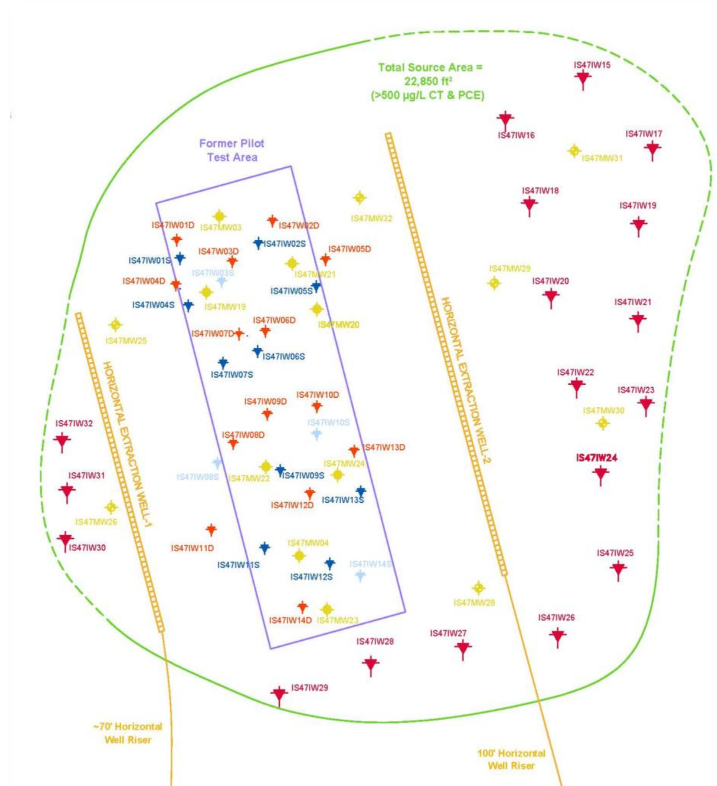
24 Days

Courtesy of XDD, LLC , CH2M HILL, and US Navy

Full-Scale Remedy

ISCO Recirculation Strategy

- Target area 22,850 ft^2
- 42 Injection wells
- 2 Horizontal extraction wells
- Rotation between 3 sets of 18 injection wells simultaneously



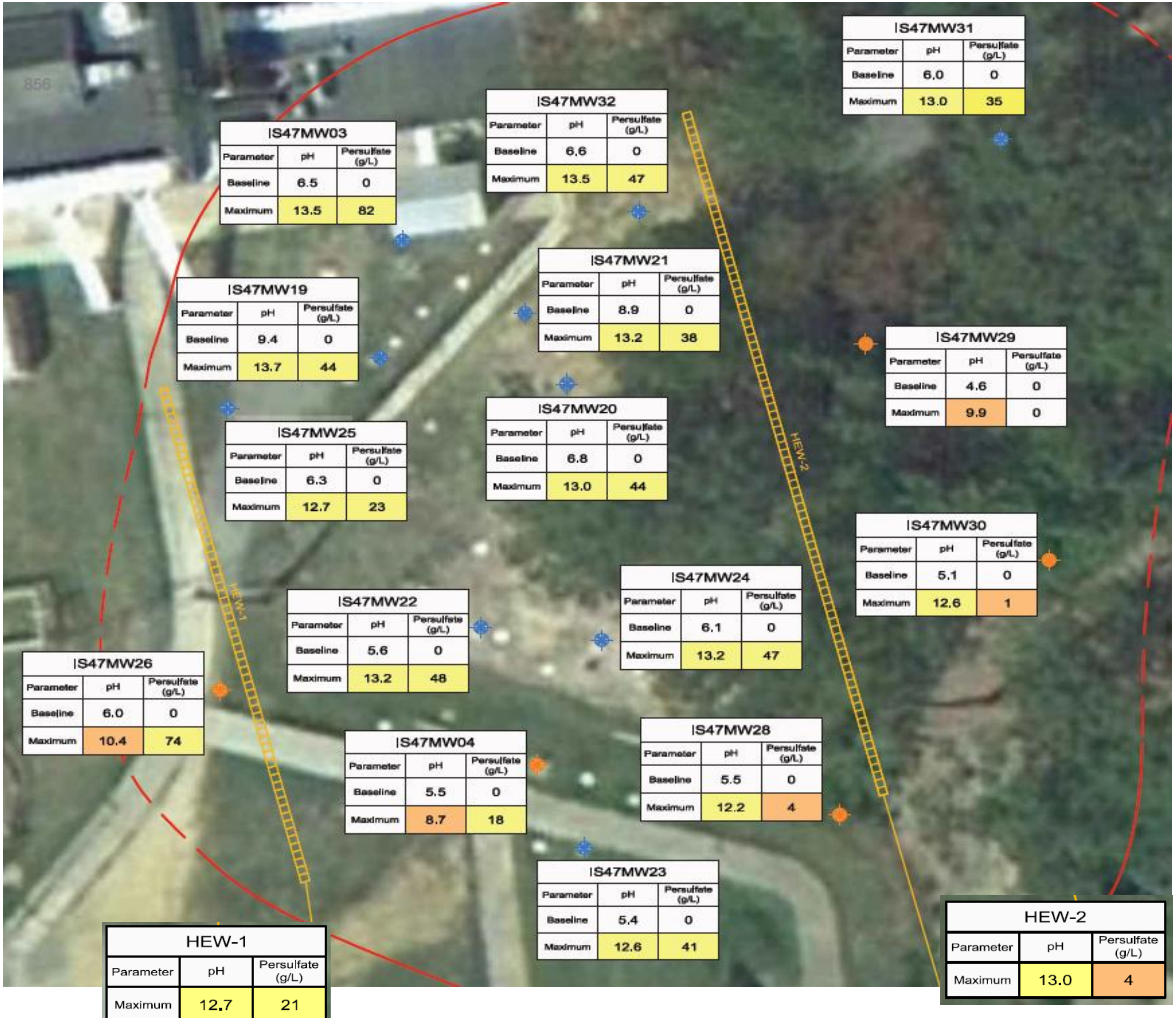
General Design

- 204,600 lbs of Klozur Persulfate
  - 36 g Klozur per g COCs
  - 19 g Klozur per Kg Soil
- 351,000 lbs of 25 percent NaOH
- Up to 477,800 gal of recirculated water

Courtesy of XDD, LLC , CH2M HILL, CB&I, and US Navy

Full-Scale Application

Parameter	Designed	Actual
Target persulfate concentration (g/L)	50	178
Sodium persulfate / NaOH-25%wt (lbs)	204,600 / 351,151	204,972 / 351,400
Injection volume (gals)	477,800	139,200
Total extraction rate (gpm)	38	5



IS47MW31		
Parameter	pH	Persulfate (g/L)
Baseline	6.0	0
Maximum	13.0	35

IS47MW32		
Parameter	pH	Persulfate (g/L)
Baseline	6.6	0
Maximum	13.5	47

IS47MW03		
Parameter	pH	Persulfate (g/L)
Baseline	6.5	0
Maximum	13.5	82

IS47MW21		
Parameter	pH	Persulfate (g/L)
Baseline	8.9	0
Maximum	13.2	38

IS47MW19		
Parameter	pH	Persulfate (g/L)
Baseline	9.4	0
Maximum	13.7	44

IS47MW29		
Parameter	pH	Persulfate (g/L)
Baseline	4.6	0
Maximum	9.9	0

IS47MW20		
Parameter	pH	Persulfate (g/L)
Baseline	6.8	0
Maximum	13.0	44

IS47MW25		
Parameter	pH	Persulfate (g/L)
Baseline	6.3	0
Maximum	12.7	23

IS47MW30		
Parameter	pH	Persulfate (g/L)
Baseline	5.1	0
Maximum	12.6	1

IS47MW24		
Parameter	pH	Persulfate (g/L)
Baseline	6.1	0
Maximum	13.2	47

IS47MW22		
Parameter	pH	Persulfate (g/L)
Baseline	5.6	0
Maximum	13.2	48

IS47MW26		
Parameter	pH	Persulfate (g/L)
Baseline	6.0	0
Maximum	10.4	74

IS47MW04		
Parameter	pH	Persulfate (g/L)
Baseline	5.5	0
Maximum	8.7	18

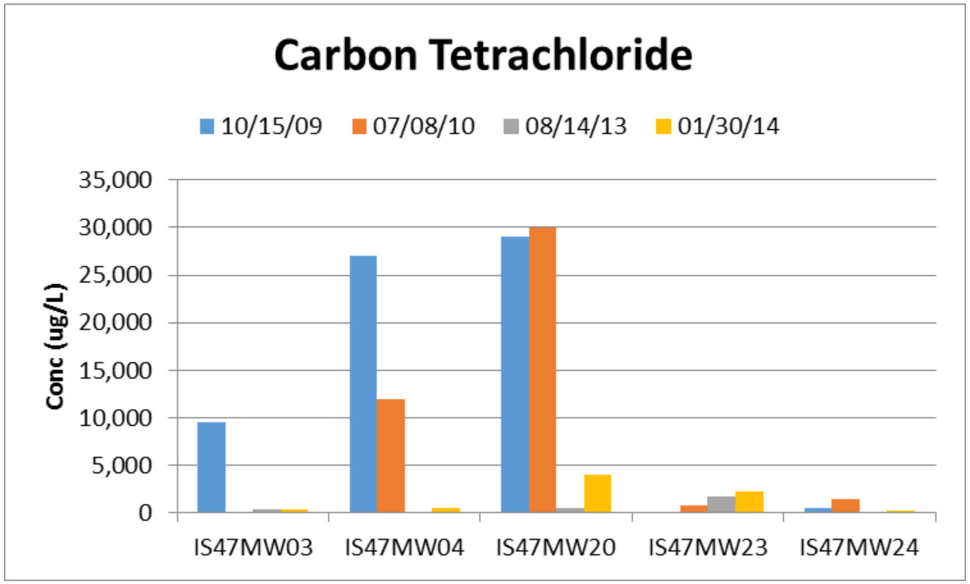
IS47MW28		
Parameter	pH	Persulfate (g/L)
Baseline	5.5	0
Maximum	12.2	4

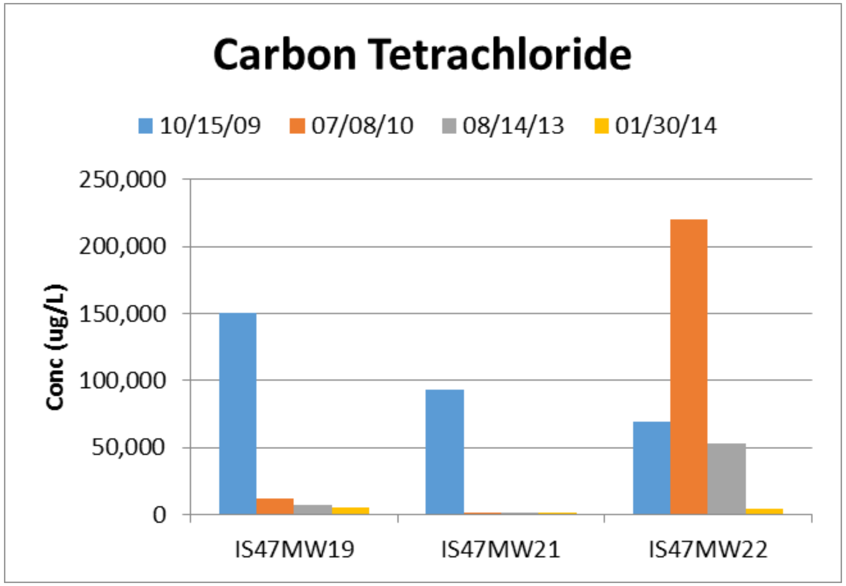
IS47MW23		
Parameter	pH	Persulfate (g/L)
Baseline	5.4	0
Maximum	12.6	41

HEW-1		
Parameter	pH	Persulfate (g/L)
Maximum	12.7	21

HEW-2		
Parameter	pH	Persulfate (g/L)
Maximum	13.0	4

Full-Scale Remedy: Results





Courtesy of XDD, LLC , CB&I, CH2M HILL, and US Navy

Full-Scale Remedy: Results

- Final soil and groundwater data yet to be collected
- Assessment of non-validated groundwater data:
  - CT: 83 to 96 percent reduction
  - PCE: 35 to 87 percent reduction

Courtesy of XDD, LLC and US Navy

Health and Safety

- No H&S issues on any of these events
- H&S requirements for alkaline material similar to those required for oxidants
  - Trained staff and proper equipment

Conclusion

- Alkaline Activated Persulfate is a potent in situ remedial technology
  - Oxidants
  - Reductants
- Can degrade chlorinated ethenes, ethanes, and hydrocarbons (among others)
- Can be safely and cost effectively implemented in the field
- Long history of successful field applications

Thanks to

- XDD, LLC
  - Mike Marley
  - Karen O'Shaughnessy
- Fleming-Lee Shue
  - Steve Panter
- U.S. Navy
  - Gunarti Coghlan
  - Joe Rail

Thank You

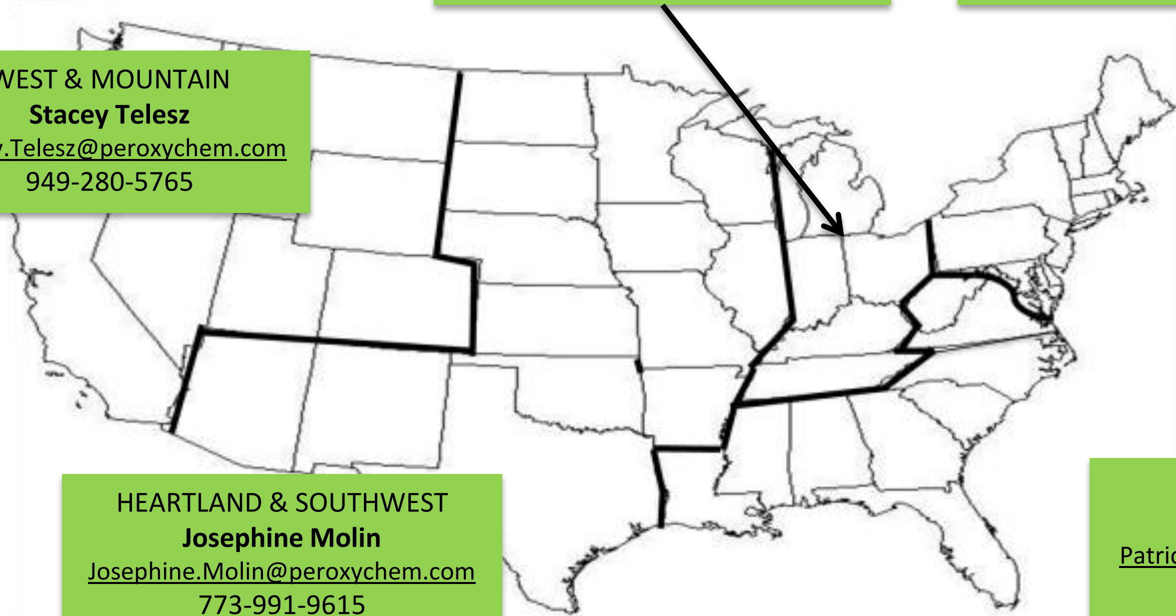
Environmental Solutions Team

MIDWEST
John Valkenburg
John.Valkenburg@peroxychem.com
517-669-5400

Laboratory
Brianna Desjardins
Brianna.Desjardins@peroxychem.com
716-263-5026

WEST & MOUNTAIN
Stacey Telesz
Stacey.Telesz@peroxychem.com
949-280-5765

NORTHEAST,
INCLUDING DC METRO
Ravi Srirangam, Ph.D.
Ravi.Srirangam@peroxychem.com
312-480-5250



HEARTLAND & SOUTHWEST
Josephine Molin
Josephine.Molin@peroxychem.com
773-991-9615

SOUTHEAST
Pat Hicks, Ph.D.
Patrick.Hicks@peroxychem.com
919-280-7962

Technical Application Managers
Subject matter experts and market segment focused

Dan Leigh P.G., C.Hg.
ERD and Federal Programs
Daniel.Leigh@peroxychem.com
925-984-9121

Alan Seech, Ph.D.
Metals, Laboratory, and ISCR
Alan.Seech@peroxychem.com
949-388-7065

Fayaz Lakhwala, Ph.D.
ISCR and Consultants
Fayaz.Lakhwala@peroxychem.com
908-688-8543

Brant Smith, Ph.D.
In Situ Chemical Oxidation
Brant.Smith@peroxychem.com
603-793-1291