PeroxyChem

Environmental Solutions

Treatment of Contaminated Sites with In Situ Chemical Oxidation

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Technical Applications Manager: ISCO

PeroxyChem

Presentation Overview

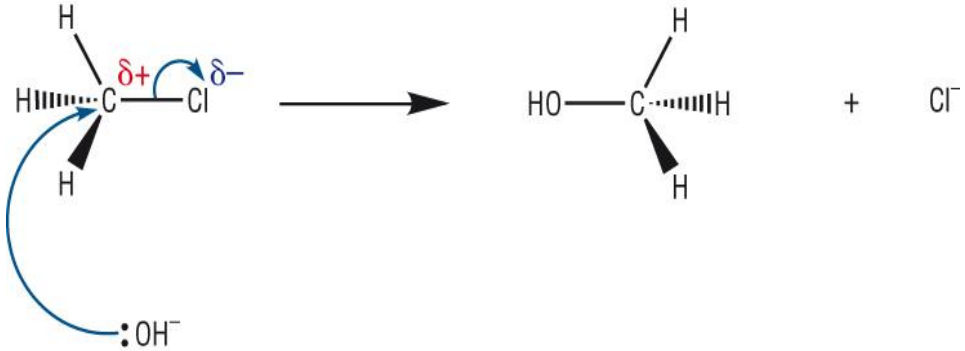
- Principles of Remediation
- Concepts of Chemical Oxidation
- Primary Chemical Oxidation Technologies
  - Catalyzed Hydrogen Peroxide (Fenton's Reagent)
  - Permanganate
  - Klozur® Persulfate
- Potential Issues
- Conclusions

Principles of Remediation

- Remediation methods work to exploit a characteristic of the contamination
  - Vapor pressure
    - Air Sparging/Soil Vapor Extraction (AS-SVE)
  - Boiling point/vapor pressure:
    - Thermally enhanced SVE
  - Chemical transformations
    - Bioremediation
    - Chemical oxidation
    - Nucleophilic transformation
    - Chemical reduction
    - Chemical precipitation/Metals stabilization
- Remediation methods often selected based on chemical characteristics and site conditions that favor a particular method

Reaction Pathways

- Oxidative
  - Electrons are taken from contaminants → CO_2
- Reductive
  - Electrons are donated to the contaminants → CH_4
- Nucleophilic
  - Substitution reaction (electron neutral)



IN SITU CHEMICAL OXIDATION: OVERVIEW

What is ISCO

- In Situ Chemical Oxidation (ISCO)
  - Transform/degrade contamination in place in the subsurface

Massive supply of thermodynamically powerful electron acceptors

- Addition of chemicals that take electrons from, or oxidizing, contaminants of concern (COCs)

- Reductive (electron donating) and nucleophilic pathways are also present with certain technologies
  - Allows for treatment of multiple types of contaminants
  - Technology and activation method specific

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

Compounds Degraded by ISCO

Examples of Contaminants Destroyed by Klozur Persulfate

(not all ISCO reagents treat all compounds listed)

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

Others
Carbon disulfide
Aniline
1,4-Dioxane

TPH
BTEX
GRO
DRO
ORO
creosote

Oxygenates
MTBE
TBA

Perflourinated
Freon
PFOS
PFOA
PFBA

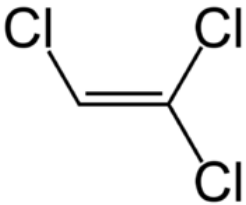
Chlorobenzenes
Chlorobenzene
Dichlorobenzene
Trichlorobenzene

Phenols
Phenol
Chlorophenols
Nitrophenols

PAHs
Anthracene
Benzopyrene
Styrene
Naphthalene
Pyrene
Chrysene
Trimethylbenzene

Pesticides
DDT
Chlordane
Heptachlor
Lindane
Toxaphene
MCPA
Bromoxynil

Energetics
Trinitrotoluene (TNT)
Dinitrotoluene (DNT)
RDX



Where is ISCO Applied?

- ISCO is a mass reduction technology usually used to target low mg/Kg to greater than 10,000 mg/Kg contamination
  - GW concentrations depend upon solubility
- ISCO can be used to target
  - Source area (typical)
  - Plume (often depends on contaminant concentration)
- To treat both oxidized and reduced contamination

Key to Success for Field Applications

- Reactions are known to take place on the laboratory scale
  - 100% contact between ISCO and contamination

ISCO works by establishing contact between a sufficient mass of activated oxidant with the contaminant mass in the subsurface

Field Applications

Sufficient Mass of Oxidant

1. Target demand
   1. Contaminant type and mass
2. Non-target demand
3. Uncertainties and variability
   1. Target Demand
   2. Non-target demand
   3. Contaminant distribution

- Remedial goals

Establishing Contact

- Site Geology
- Contaminant distribution
- Reagent distribution
- Injection network
- Injection strategy
- Injection volume
- Contact time
- Groundwater velocity

Progression to a Field Application

Typical Path

- Path
  - Bench scale tests
  - Design Optimization (Pilot scale tests)
  - Full scale applications
  - Achievement of goals or transition to another technology as part of a treatment train approach

Bench Scale Tests

- Evaluate potential interactions between the site geochemistry and the ISCO process chemistry
- Objectives include:
  - Developing design parameters
  - Confirm treatment efficacy
  - Satisfy regulatory concerns
- Specific tests will vary for each ISCO technology

Design Optimization (Pilot Scale Test)

- Target Area
  - Typically a subset of the full scale area
  - For a small area, may be the first application in the entire area
- Objective
  - Older Objective: Proof of concept for new and emerging technologies
  - **Current Objective:** Confirming site specific performance and design parameters
- Critical Field Parameters
  - Treatment efficacy
  - Injection rate
  - Injection pressure
  - Distribution of reagents
    - Active oxidant
    - Inactive oxidant
  - Potential issues
- Monitoring program
  - Typically more extensive than full scale
  - Intended to monitor treatment efficacy and field parameters

Full Scale Applications

Full Scale Application

- Objective
  - Progress toward remedial goals
- Monitoring Program
  - Monitor progress toward remedial goals
  - Monitor effect of each ISCO application
    - Mass reduction not always represented by groundwater concentrations

Expectations

- Is 99 percent reduction a success?
- Mass reduction
  - Will depend upon
    - Dosage/ability to contact contamination
    - Initial concentrations
- Typically 80 to 99 percent per successful application
- Multiple applications and, potentially, multiple technologies are typically necessary for greater than 1 to 2 order of magnitude reductions

Combined Remedies/Treatment Train

- ISCO can be used as a mass reduction technology and be followed by:
  - Monitored natural attenuation
  - In situ bioremediation
  - In situ biogeochemical remediation
- ISCO used following:
  - Thermal technologies
  - Surfactant/solvent enhanced extraction
  - Extraction systems (dual phase extraction)
- Treatment train approach works to maximize the strengths of different technologies to reflect the changing site situation
  - ISCO: Mass reduction (fast acting, large quantities of oxidant in injection solution) when contact can be established
  - ISB/ISCR/etc: Persistence
    - 6 months to 1 year following ISCO

Monitoring Programs

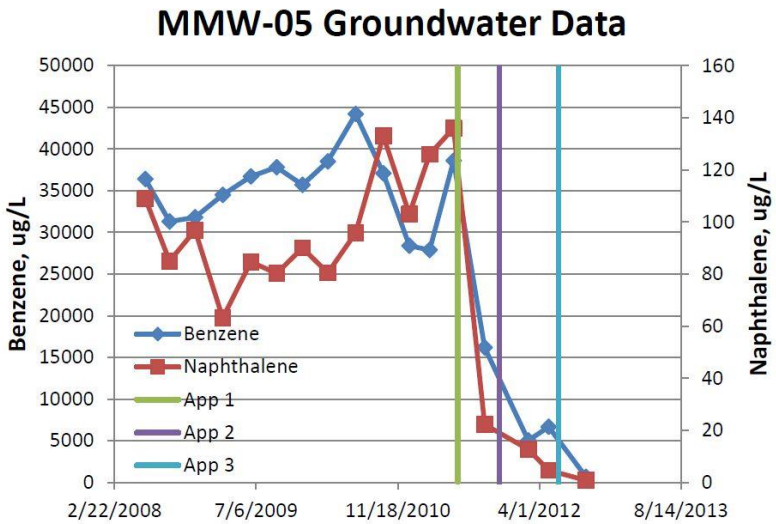
- Critical aspect to ISCO design
- Objectives
  - Progress toward remedial goals
  - Assessing effectiveness of ISCO application
- Monitoring Phase
  - Soil and groundwater typical
  - Phase monitored may be different for each objective
  - Progress of ISCO best measured by total mass reduced (GW mass plus Soil mass)
- Soil
  - Discrete/grab
  - Composite
- Frequency
  - Allow time:
    - ISCO to react
    - Groundwater, soil and NAPL re-equilibrate
    - Can have biotic activity following ISCO
  - Minimum 2-3 months post application recommended
  - Multiple monitoring events recommended
- Parameters
  - Contaminant
  - Residual oxidant
  - Geochemical parameters
    - DO, temperature, conductivity, pH, ORP
  - Others, as needed

IN SITU CHEMICAL OXIDATION: TECHNOLOGIES

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

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

Primary ISCO Oxidants

- Hydrogen Peroxide (aka Fenton's reagent, catalyzed hydrogen peroxide)

- Permanganate

- Persulfate (activated)
  - Alkaline
  - Iron
  - Heat
  - Hydrogen Peroxide

Hydrogen Peroxide (Fenton's Reagent)

- Hydrogen Peroxide is catalyzed by transition metals to form the hydroxyl radical

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^-$$
$$OH\bullet + H_2O_2 \rightarrow HO_2\bullet + OH^- + H^+$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\bullet + H^+$$
$$HO_2\bullet \leftrightarrow O_2\bullet^- + H^+ \quad (pKa\ 4.8)$$

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

- Forms:
  - Hydroxyl radical: Powerful oxidant (2.6 V)
  - Superoxide radical: Reductant (-0.33 V) and nucleophile
  - Hydroperoxide: Nucleophile

Hydrogen Peroxide: Key Characteristics

- Characteristics
  - Capable of degrading most types of contamination
  - Relatively inexpensive
  - Forms oxidants, reductants, and nucleophiles
  - Decomposes to water and oxygen

- Common Issues
  - Sensitive to subsurface conditions (can decompose in minutes or persist for days)
    - If an issue, can impede successful distribution
    - Stabilization agents
  - Gas and heat evolution
  - Hydroxyl radical can be scavenged by naturally occurring carbonates

Hydrogen Peroxide: Bench Tests

- Acid buffering capacity of soils
  - Look for presence of carbonates (pKa 6.1)
- Stability (half life) in presence of site soils
  - Stabilized
  - Unstabilized
  - Activated
- Gas and heat evolution
- Treatment efficacy
- Degradation ratio
  - Mass oxidant consumed per mass of contaminant degraded

Permanganate

- Sodium or potassium permanganate

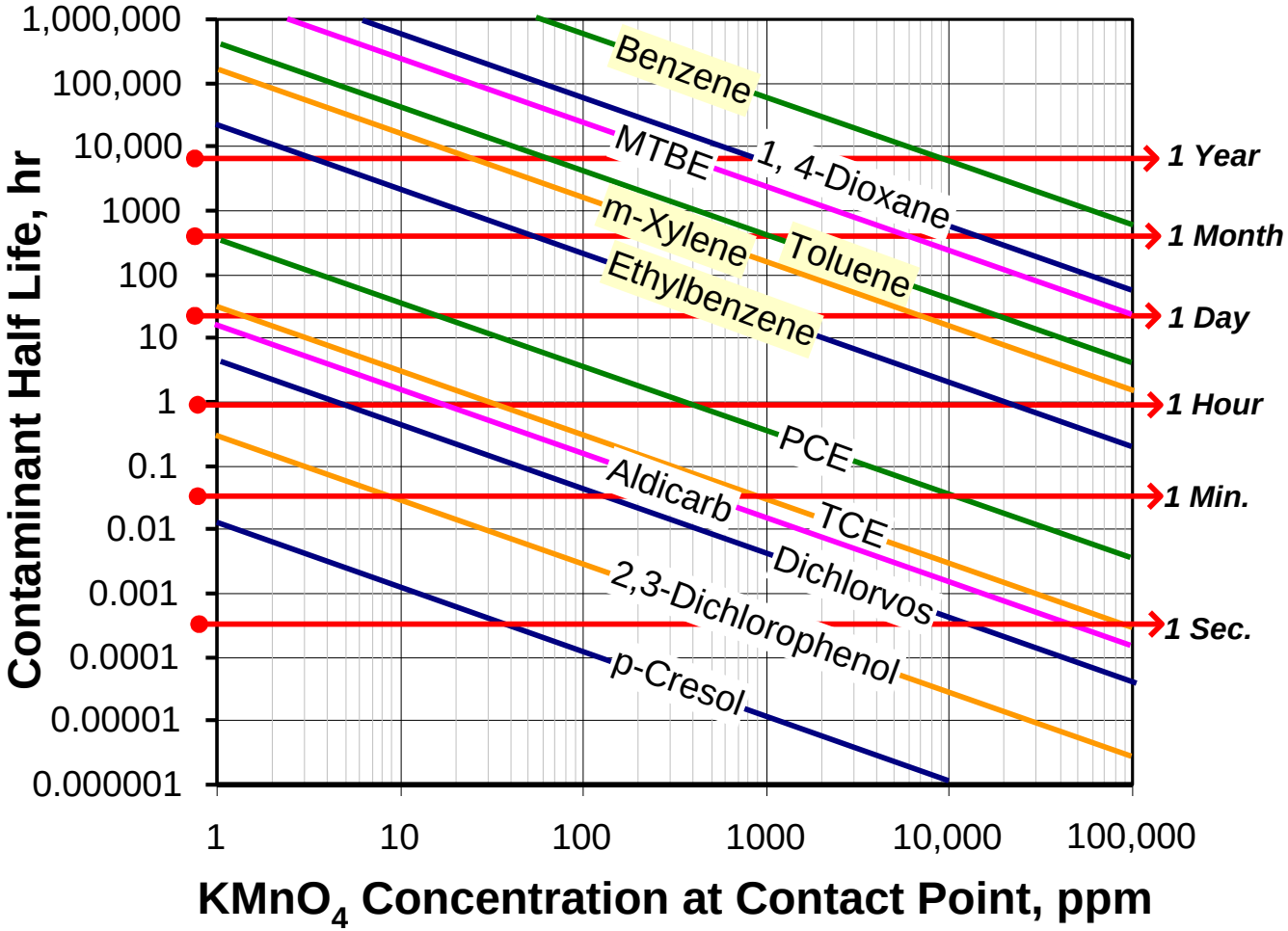
$$KMnO_4 \text{ or } NaMnO_4 \rightarrow \mathbf{MnO_4^-}$$
$$\mathbf{MnO_4^-} \rightarrow MnO_2\ (s)$$

- **Dark purple at >0.5 g/L and pink even at 1 mg/L**
- Permanganate has a redox potential of 1.7 V
- Primarily used for chloroethenes (TCE and PCE)

Permanganate Characteristics

- Characteristics and Common Issues
  - Direct oxidative pathway
  - Reactive with:
    - Chlorinated ethenes (TCE, PCE, etc), some PAHs, etc
    - Little to no reaction with many other compounds (chloromethanes, chloroethanes, benzene, MTBE, etc)
  - Kinetically aggressive reactions
  - Field solubility:
    - Potassium permanganate ~30 g/L
    - Sodium permanganate >400 g/L (typical application < 200 g/L)
  - Very stable, can persist for months to years, if oxidant demand is met

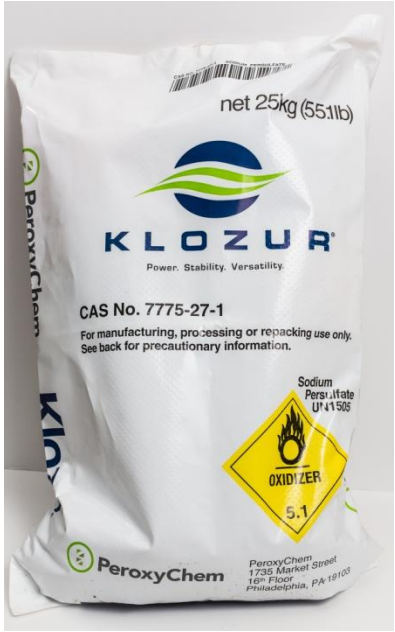
Permanganate Reactivity



Activated 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

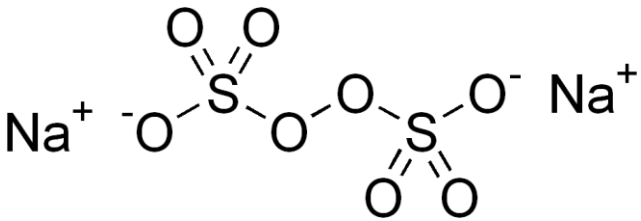
Why Activate?

Persulfate Anion

- Relatively stable
- Kinetically slow
  - Persistence of weeks to months
  - May not be kinetically aggressive with targeted contaminants
- Oxidative pathway
  - May not react with all contaminants

Radicals

- Kinetically aggressive
- Oxidative, reductive and nucleophilic pathways
  - Reacts with wide assortment of common contaminants of concern:
  - Oxidants more powerful than persulfate anion



Radical Formation

- Common activation methods include:
  - Alkaline activation
    - ($OH\bullet$, $SO_4\bullet^-$, $O_2\bullet^-$)
  - Nascent iron, 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)

Compounds Degraded by 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
1,4-Dioxane

TPH
BTEX
GRO
DRO
ORO
creosote

Oxygenates
MTBE
TBA

Perflourinated
Freon
PFOS
PFOA
PFBA

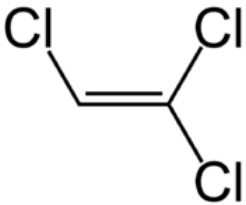
Chlorobenzenes
Chlorobenzene
Dichlorobenzene
Trichlorobenzene

Phenols
Phenol
Chlorophenols
Nitrophenols

PAHs
Anthracene
Benzopyrene
Styrene
Naphthalene
Pyrene
Chrysene
trimethylbenzene

Pesticides
DDT
Chlordane
Heptachlor
Lindane
Toxaphene
MCPA
Bromoxynil

Energetics
Trinitrotoluene (TNT)
Dinitrotoluene (DNT)
RDX



Activated Persulfate

- Key Design Characteristics
  - Dosing persulfate in excess of contaminant and non-target demand
  - Accounting for site uncertainties (safety factor)
  - Radicals and reaction pathways formed depend upon activation method
    - Depending upon activation method, can react with most common contaminants of concern
  - Highly soluble
    - Field > 500 g/L
    - Injection concentration of 200 g/L or more
  - High stability in the subsurface (weeks to months) if oxidant demand is met
    - Slow reaction with water
  - Acid formation during decomposition
    - If needed, can be neutralized (alkaline activated persulfate)

Persulfate: Bench Scale Tests

- Key Bench Scale Tests:
  - Base buffering capacity -pH > 10.5-Alkaline activation only
  - Non target demand
  - Treatment efficacy
  - Degradation ratio

General Oxidant Niches

- Permanganate
  - Mostly chlorinated ethenes
  - Cost effective injection concentrations and number of applications
  - 10-30 g/L potassium permanganate
  - High concentrations of sodium permanganate at small sites
- Hydrogen peroxide
  - Most contaminants
  - Suitable soils (persistence/gas evolution)
  - 4-10 percent stabilized hydrogen peroxide
- Activated persulfate
  - Applicable at most sites
  - Most contaminants and masses
  - 50-250 g/L Klozur Persulfate
  - Activator pulsed or inline injected

At this time, the distribution issues due to the stability of hydrogen peroxide has severely limited its wide scale use.

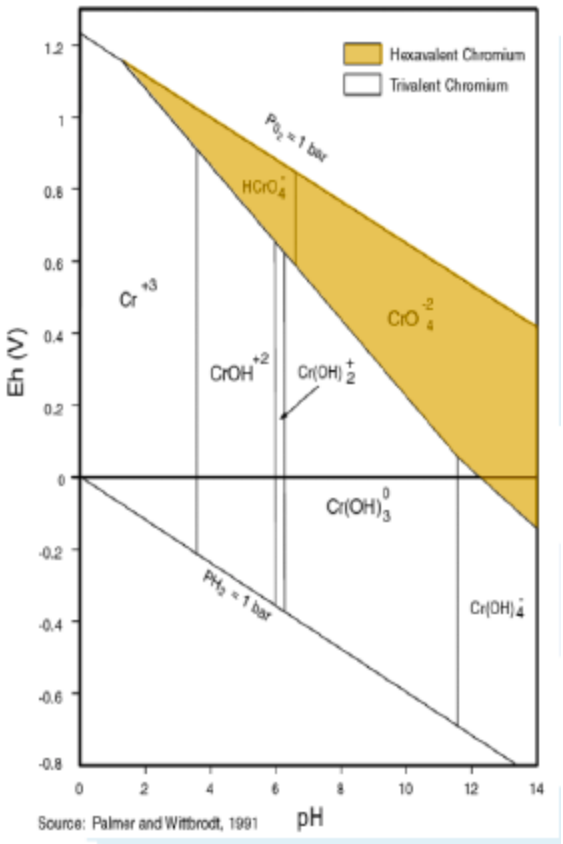
POTENTIAL ISSUES

Secondary MCLs

- Sulfate (250 mg/L)
  - Has not typically been an issue
  - Several fate mechanisms for sulfate depending upon site geochemical conditions
    - Persistence
    - Precipitation as a sulfate such as $CaSO_4$
    - Reduction and potential precipitation as metallic sulfide (FeS)
- Manganese (0.05 mg/L)
  - Under neutral pH, permanganate becomes solid $Mn0_4$
  - Under acidic conditions, reaction can result in Mn (II)

Metals Mobilization

- Metals solubility tends to follow pe-pH diagrams
- As geochemical conditions return to baseline, metal concentrations should also return
  - Will conditions return to baseline?
- If concerned, could be evaluated in the bench or design optimization phases
  - If bench, may need to mimic site returning to baseline conditions
  - If field, monitor long enough for geochemical conditions to recover
- Combined remedial
  - Reduction technology (ISB/ISCR) could mitigate metals mobilization, if present



Source: Palmer and Wittbrodt, 1991

Summary

- ISCO consists of a series of technologies with decades of history of successfully remediating a wide variety of common contaminants of concern
- Each technology has unique characteristics that should be considered in the selection and design phases
- Common keys to success: Establishing contact of sufficient activated oxidant mass with the contamination
- Bench tests can be used to determine key design parameters

ISCO Resources

- SERDP-ESTCP (ER-0623-Siegrist, Crimi, and Simpkin)
  - Video Short Course/Workshop
  - Design Tool
  - **Monograph: Siegrist et al (2011)"In Situ Chemical Oxidation for Groundwater Remediation" SERDP-ESTCP Monograph Series, Springer (ISBN: 978-1-4419-7825-7)**

- Huling & Pivetz (2006) "In-Situ Chemical Oxidation-Engineering Issue" (EPA/600/R-06/072)

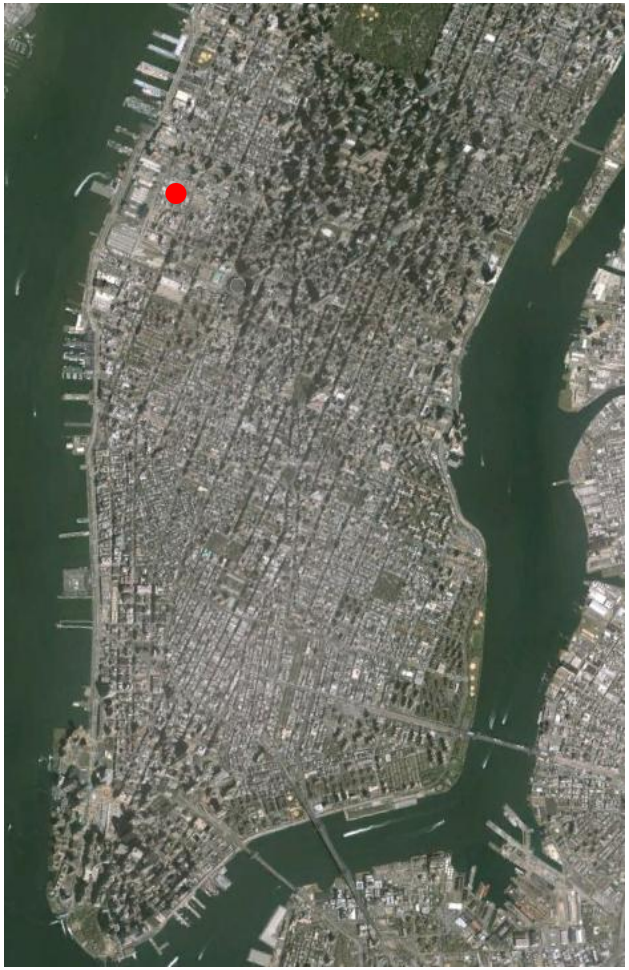
- Watts & Teel (2006) "Treatment of Contaminated Soils and Groundwater Using ISCO" J. Environ. Eng (10) 2-9

CASE STUDY

Background

- Located in the Chelsea neighborhood of New York City.
- Site uses included lumber yard, metal works facility, auto-repair facility, coal yard, piano manufacture, livery car service, and gasoline station.
- Leaking underground storage tanks observed at site.

Contractor: XDD, LLC
Consultant: Fleming-Lee Shue



Target Area

- Approximately 6,500 ft^2 (185 ft x 35 ft).
- Treatment Interval of 9 to 14 ft bgs.
- Sandy and silty-sandy material.

Contaminants of Concern

- Average Concentration of Petroleum Hydrocarbons:
  - 3,000 μg/L BTEX
  - 140 μg/L Naphthalene
  - 1,400 mg/kg GRO + DRO

- DRO and GRO up to 3,760 and 4,180 mg/kg, respectively.
- Variable GRO to DRO distribution indicated possible multiple releases.

Bench-Scale Tests

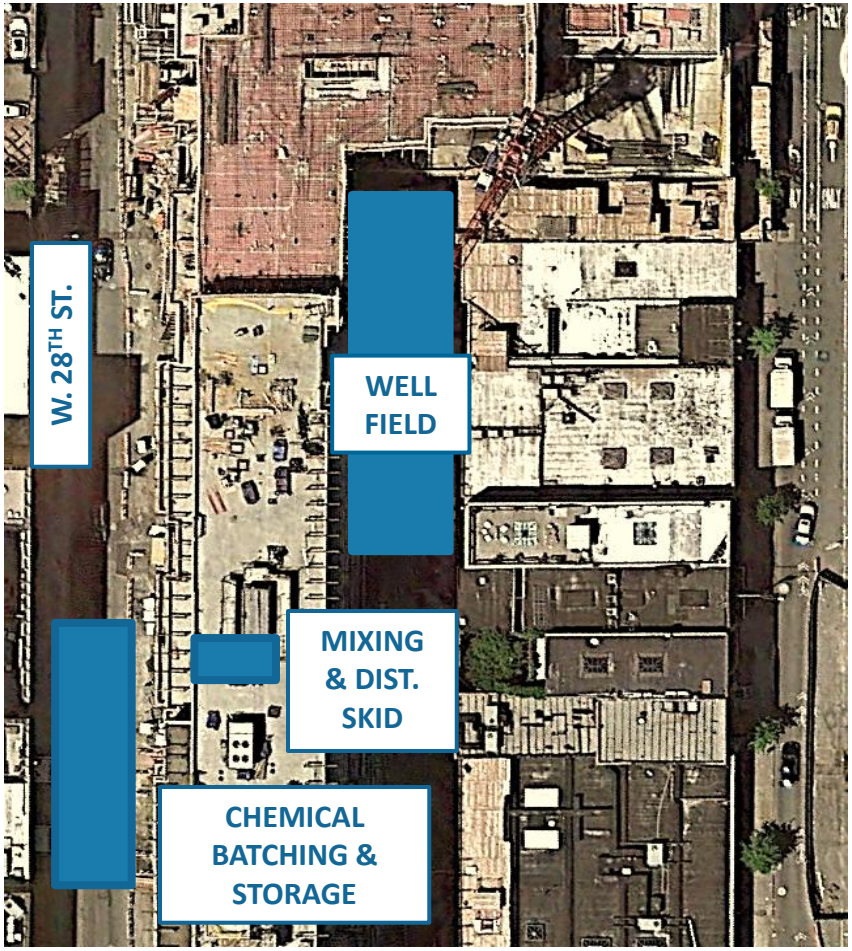
- Evaluated catalyzed hydrogen peroxide (CHP) and alkaline activated persulfate (AAP).
- CHP eliminated as peroxide decomposed rapidly even with stabilizing reagents, likely limiting subsurface distribution and resulting in rapid release of gas.
- Alkaline activated persulfate selected for effectiveness and chemical compatibility.
  - Reduced BTEX by 64-77%.
  - Reduced total TPH by 50%, with 50% percent of persulfate mass remaining.

Field Application Design

- Designed based on multiple applications with emphasis on achieving remedial goals in single application.
- Injection wells installed to be accessible upon completion.
- Design called for 100,000 to 180,000 lbs of persulfate.
  - 72,700 lbs in first application
  - 60,300 lbs of 50% sodium hydroxide
  - Approximately 35,000 gallons of reagent solution (250 g/L persulfate)
- Design incorporated the RemMetrik process utilizing Wavefront technology.

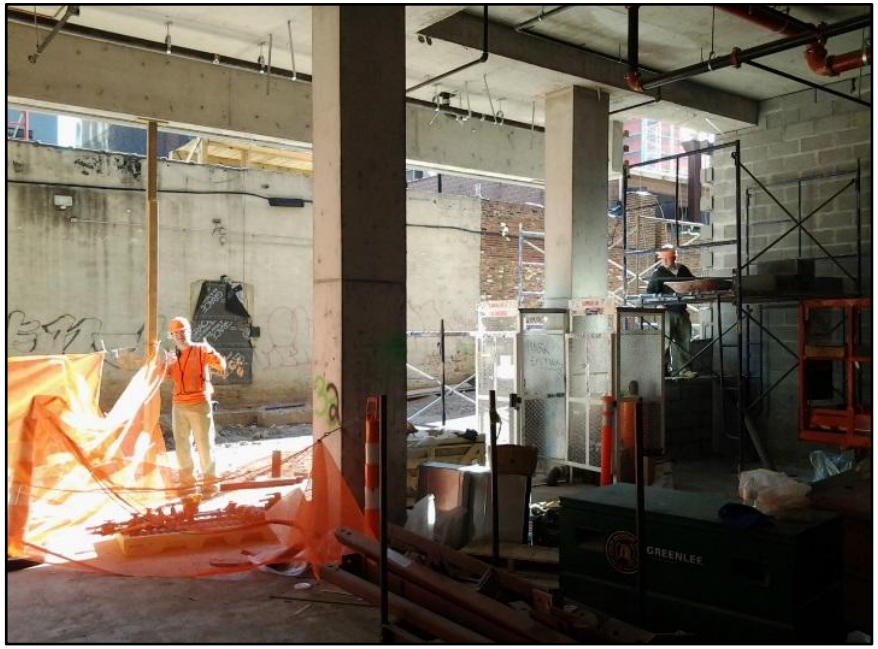
Field Application Logistics

- Difficult spatial constraints from construction activities
- Temporarily closed lane of W. 28th St. each day for batching. Road was open during injection.
- Over 400 daily construction personnel
- Total access window of 9 days.

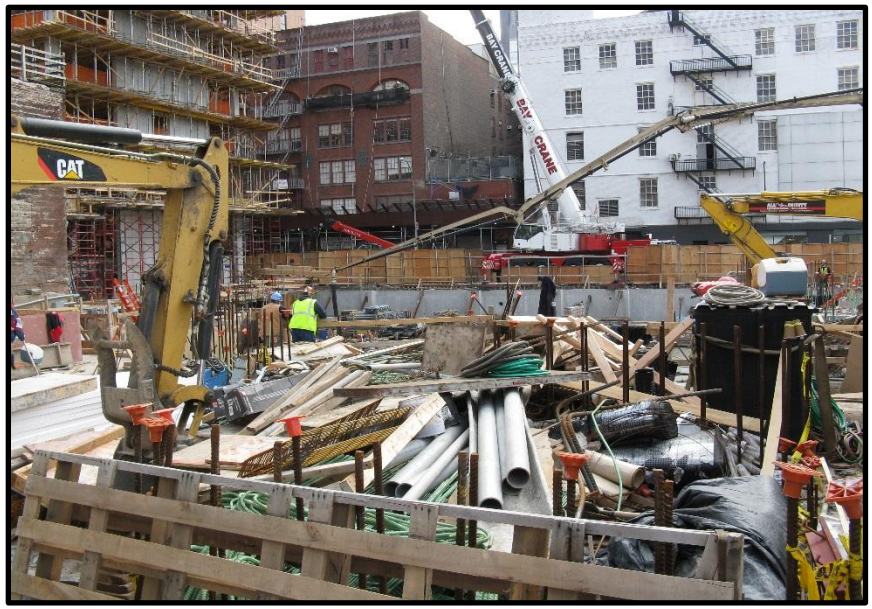


Batching

Mixing and Distribution Areas



Well Field



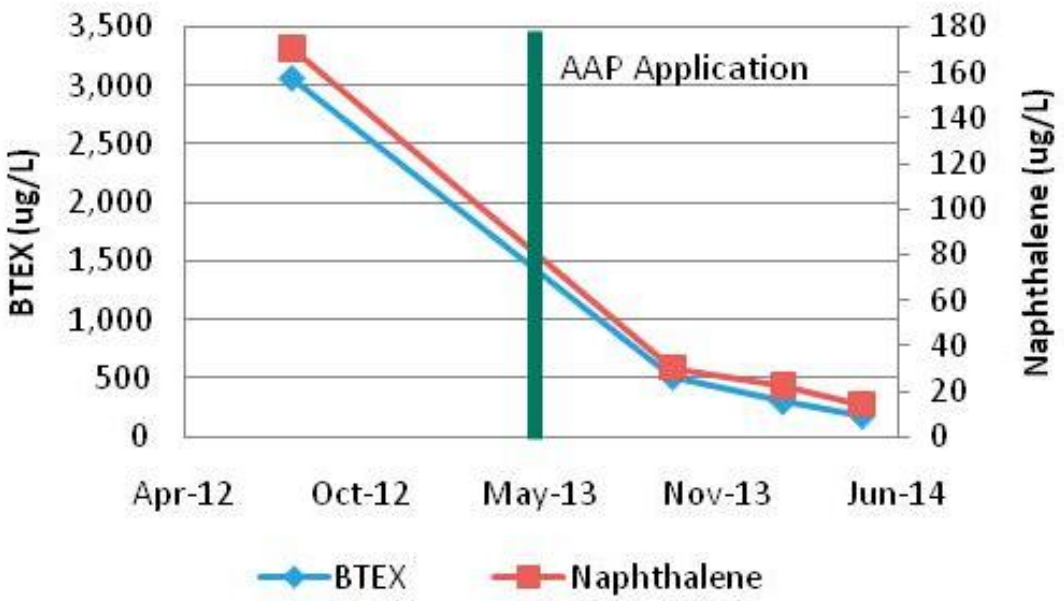
Field Application

- Occurred May 7 to 17, 2013
- Performed by XDD in cooperation with ZEBRA Environmental and Fleming-Lee Shue.
- 72,372 lbs of alkaline activated Klozur persulfate injected in 35,432 gallons of solution.
- Completed on schedule and within budget, with no impact to construction activities.

Groundwater Results

- Monitoring conducted approximately 5 months after the application in three quarterly events.
- BTEX and naphthalene GW concentrations decreased by 92 to 95%.

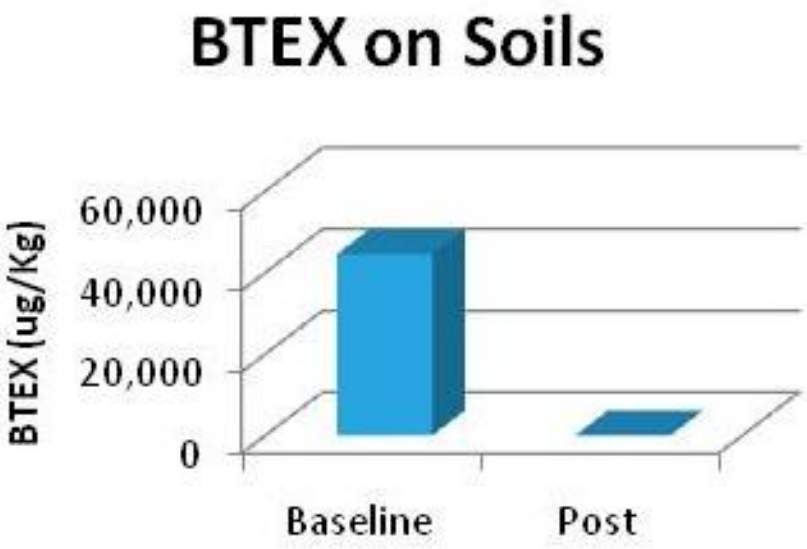
Rebound was Not Observed



Soil Results

- Soil sampled approximately 5 months after the application.
- BTEX concentrations reduced by 99.9%.

DRO/GRO Soil Concentrations were reduced by an Average of 99.2 percent



Conclusions

- Single application of alkaline activated persulfate effectively treated BTEX, DRO and GRO
  - Up to 4,000 mg/Kg DRO and GRO
- No rebound observed after 3 quarterly monitoring events.
- Site closed by NY-DEC

Questions

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