Treatability Testing for In-Situ Chemical Oxidation

Jerry Cresap, PE
Regional Engineering Manager

knowledge. innovation. results.

Groundwater & Environmental Services, Inc.

Overview

- Definition of Treatability Testing
- Benefits and Limitations
- Types of Treatability Tests
- Case Study
- Summary

"The strongest arguments prove nothing so long as the conclusions are not verified by experience."

- Roger Bacon

What is Treatability Testing?

- Measurement of Treatment Under "Ideal" Conditions
- Controlled Tests Performed on Water and Soil Samples
- Proof of Concept
- Establish Parameters for Pilot / Full-Scale ISCO
- Common Objectives
  - Determine reactivity of soil
  - Select the optimum chemistry
  - Evaluate potential adverse reactions
  - Develop cost estimate

Will target compounds degrade to desired end products under site conditions.

Benefits of Treatability Testing

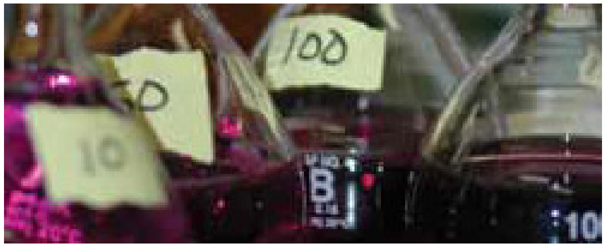
- Generates Site-Specific Data
- Allows Optimization Prior to Full-Scale Implementation
  - Refine chemistry
  - Incorporate efficiencies
  - Cost savings potential
- Enhances Pilot Testing / Full-Scale Implementation
  - Expected results guide next phase of work
  - Simplifies evaluation of field scale results

Limitations of Treatability Testing

- Linear Scale-Up Limitations
  - Difficult to simulate heterogeneity in test column
  - Small sample volume compared to site
  - Well-mixed static system
- Contact and Mixing
  - May favorably bias results
  - Not possible to evaluate delivery process
- Pilot Study Required (usually)

Types of Treatability Tests

- Laboratory Tests
  - > Simple, inexpensive tests
  - > Incorporate into RI
  - > SOD, peroxide reactivity
- Bench-Scale Study
  - > Proof of concept
  - > Basis of design
  - > Scale-up for pilot test
- Pilot Testing
  - > Discussed in next session
  - > Provides full-scale design parameters
  - > Requires extensive monitoring



Stoichiometric Evaluation

$$15Na_2S_2O_8 + \underset{benzene}{C_6H_6} + 12H_2O \rightarrow 6CO_2 + 30SO_4^{2-} + 30Na^+ + 30H^+ \qquad \text{Eqn. 1}$$

$$18Na_2S_2O_8 + \underset{toluene}{C_7H_8} + 14H_2O \rightarrow 6CO_2 + 36SO_4^{2-} + 36Na^+ + 36H^+ \qquad \text{Eqn. 2}$$

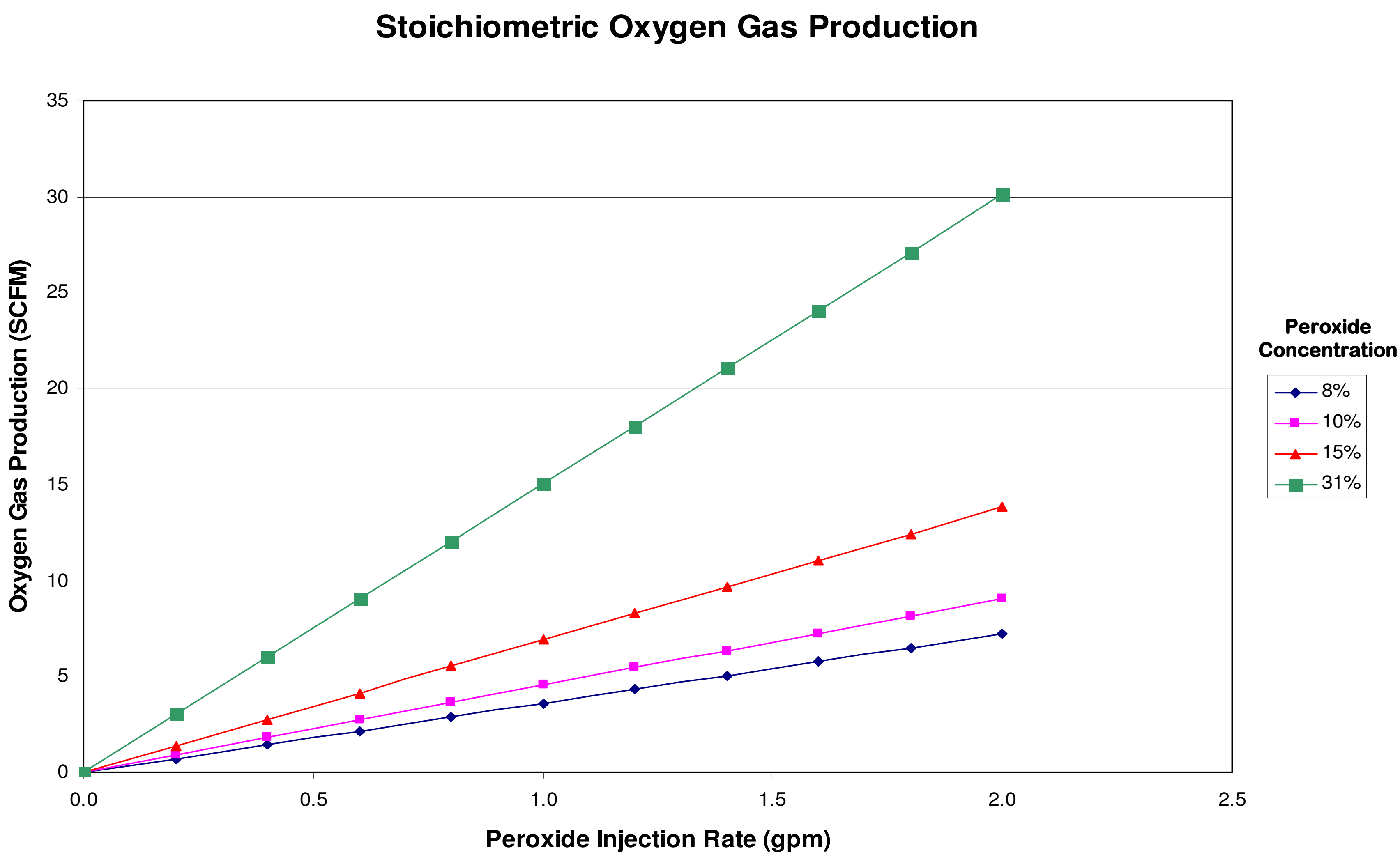
$$21Na_2S_2O_8 + \underset{ethylbenzene\ or\ xylenes}{C_8H_{10}} + 16H_2O \rightarrow 6CO_2 + 42SO_4^{2-} + 42Na^+ + 42H^+ \qquad \text{Eqn. 3}$$

$$25Na_2S_2O_8 + \underset{n\text{-}octane}{C_8H_{18}} + 16H_2O \rightarrow 8CO_2 + 50SO_4^{2-} + 50Na^+ + 50H^+ \qquad \text{Eqn. 4}$$

$$49Na_2S_2O_8 + \underset{n\text{-}hexadecane}{C_{16}H_{34}} + 32H_2O \rightarrow 16CO_2 + 98SO_4^{2-} + 98Na^+ + 98H^+ \qquad \text{Eqn. 5}$$

- Starting Point for All Treatability Tests
- Establish Baseline for Comparison
- Facilitates Oxidizer Selection
  - > Mass/volume requirements
  - > Reaction kinetics
  - > Catalyst requirements

Gas Evolution and Generation



Reference: 2011 *Pilot Test Work Plan*, GES

Soil Oxidant Demand

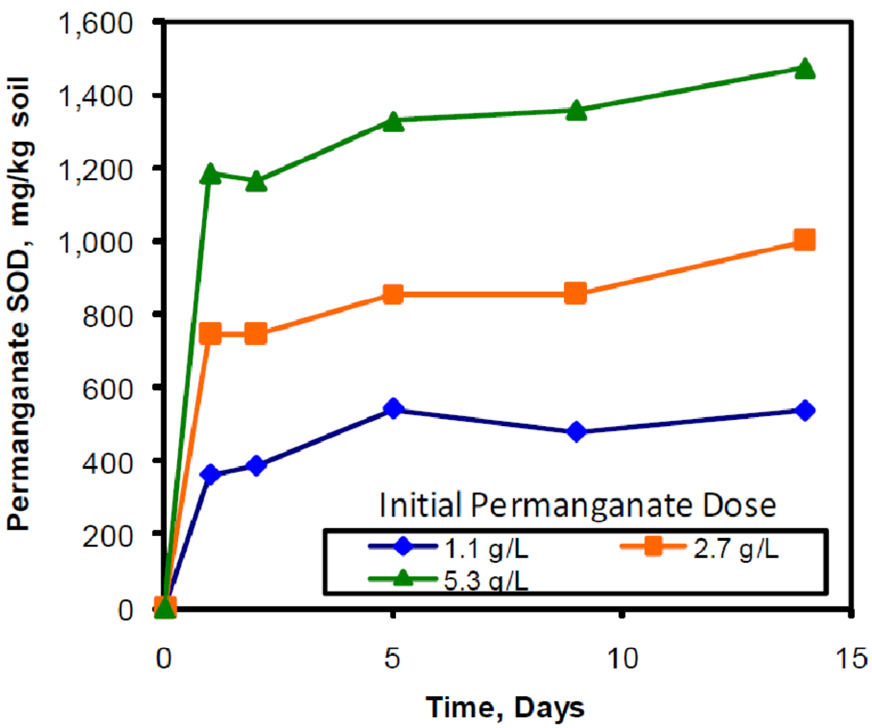
- Measure of Oxidant Depletion Over Time
  - Grams of oxidant per kilogram of soil (g/kg)
  - Range: 0.1 to 20 g/kg
- Standard Methods
  - Permanganate: USEPA Method – PSOD and ASTM D7262-10
  - Other oxidants: Varies
- Variables – Soil Related
  - Natural organic matter
  - Reduced solid species
  - Soil structure / mineralogy
- Variables – Process Related
  - Oxidant
  - Oxidant concentration
  - Time of measurement

Oxidant Demand – Primary Design Factor

- Soil Matrix is Generally Dominant
  - 2 to 3 orders of magnitude
  - Groundwater constituents relatively unimportant
- Matrix Demand May Exceed Contaminant Demand
- Interpreting the Results
  - Cost of full-scale implementation
  - Evaluate oxidant mass versus pore volume
  - SOD ignores relative reaction rates

Soil Oxidant Demand vs. Dose

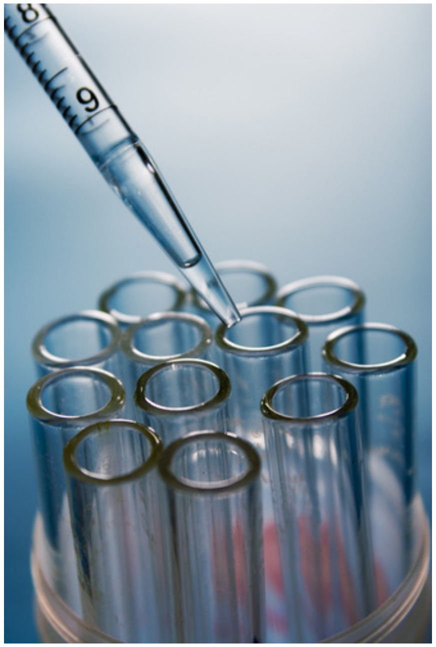
- Initial Oxidizer Concentration
- Activator / Catalyst
- Oxidant Dependent
- SOD Measurement Time
- Other Factors



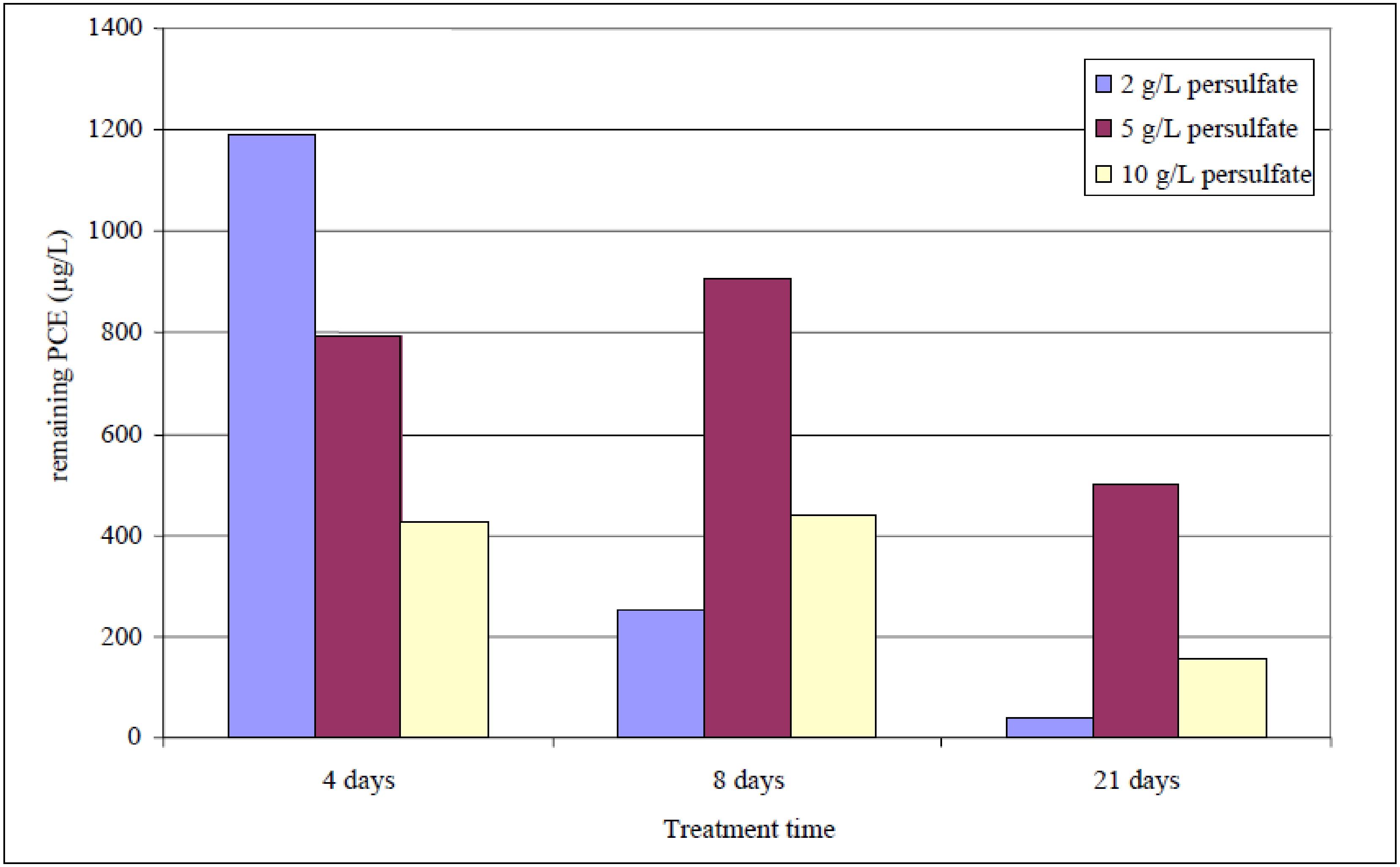
Reference: 2010 PRIMA Environmental, Inc.

Bench-scale Testing

- Establish Basis of Design
  - Oxidizer selection
  - Dose optimization
  - Oxidant/stabilizer concentration
  - Catalyst selection
  - Secondary considerations
- Address Concerns
  - Contaminant desorption
  - Metals mobilization
  - Cr(VI) formation
  - pH shift
  - By-product formation



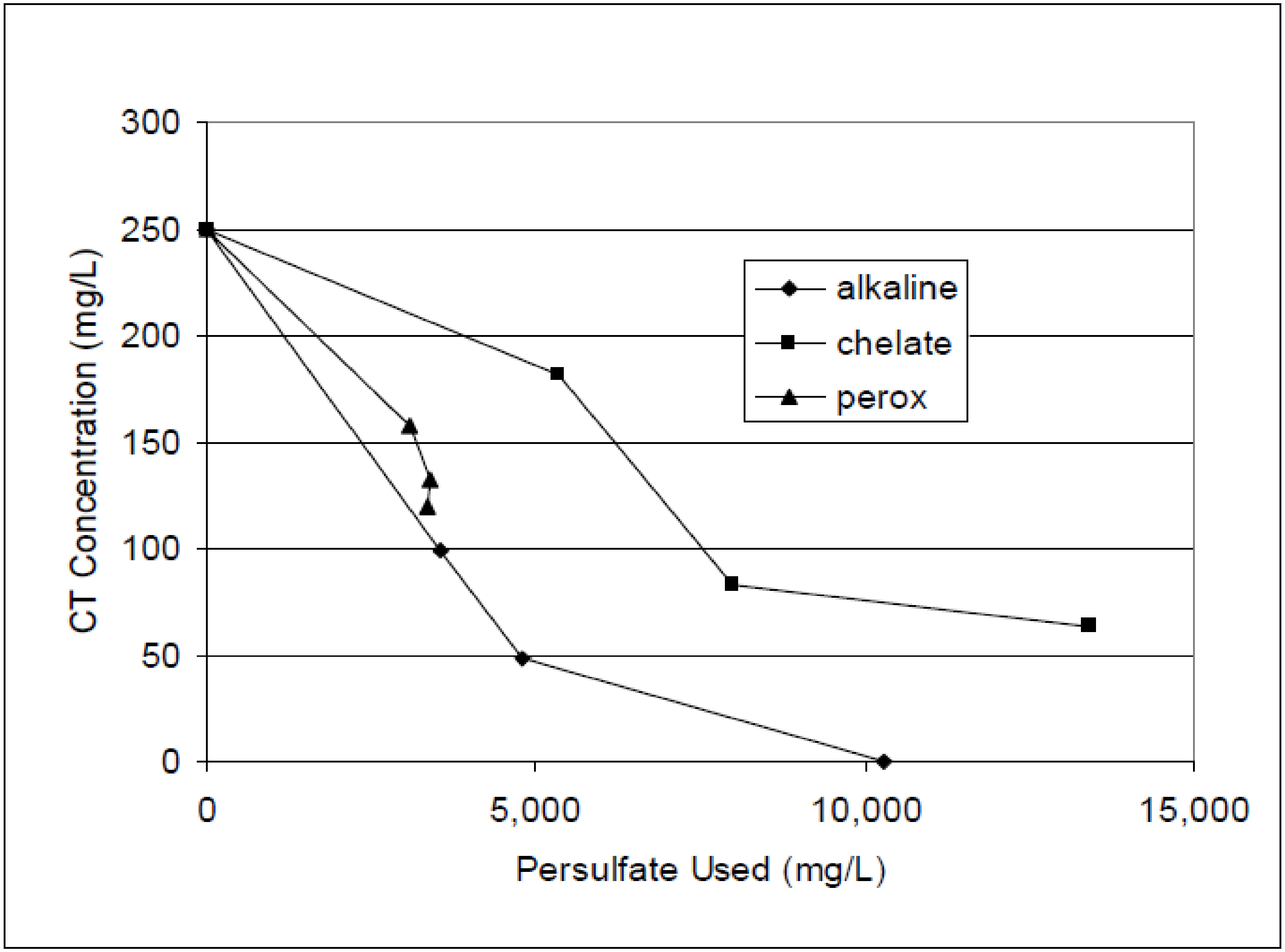
Dose Optimization



Metals Mobilization

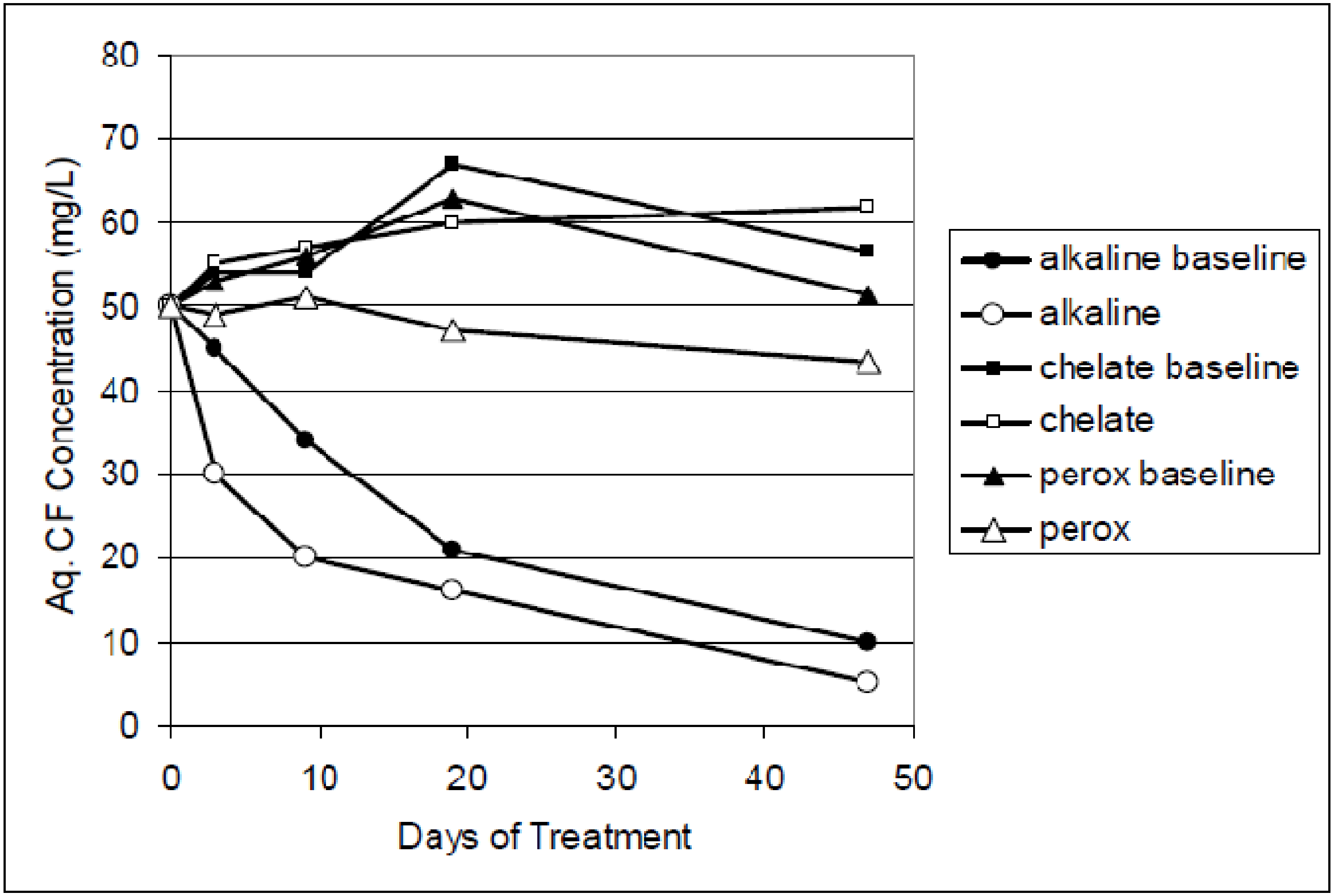
- Some metals can be mobilized by oxidizing conditions
- Redox sensitive metals must be considered
  - $Cr^{3+} \rightarrow Cr^{6+}$
- Bench-Scale and Pilot Test Important
  - Directly measure constituent concentrations
  - Evaluate "buffering" capacity of site

Catalyst Optimization



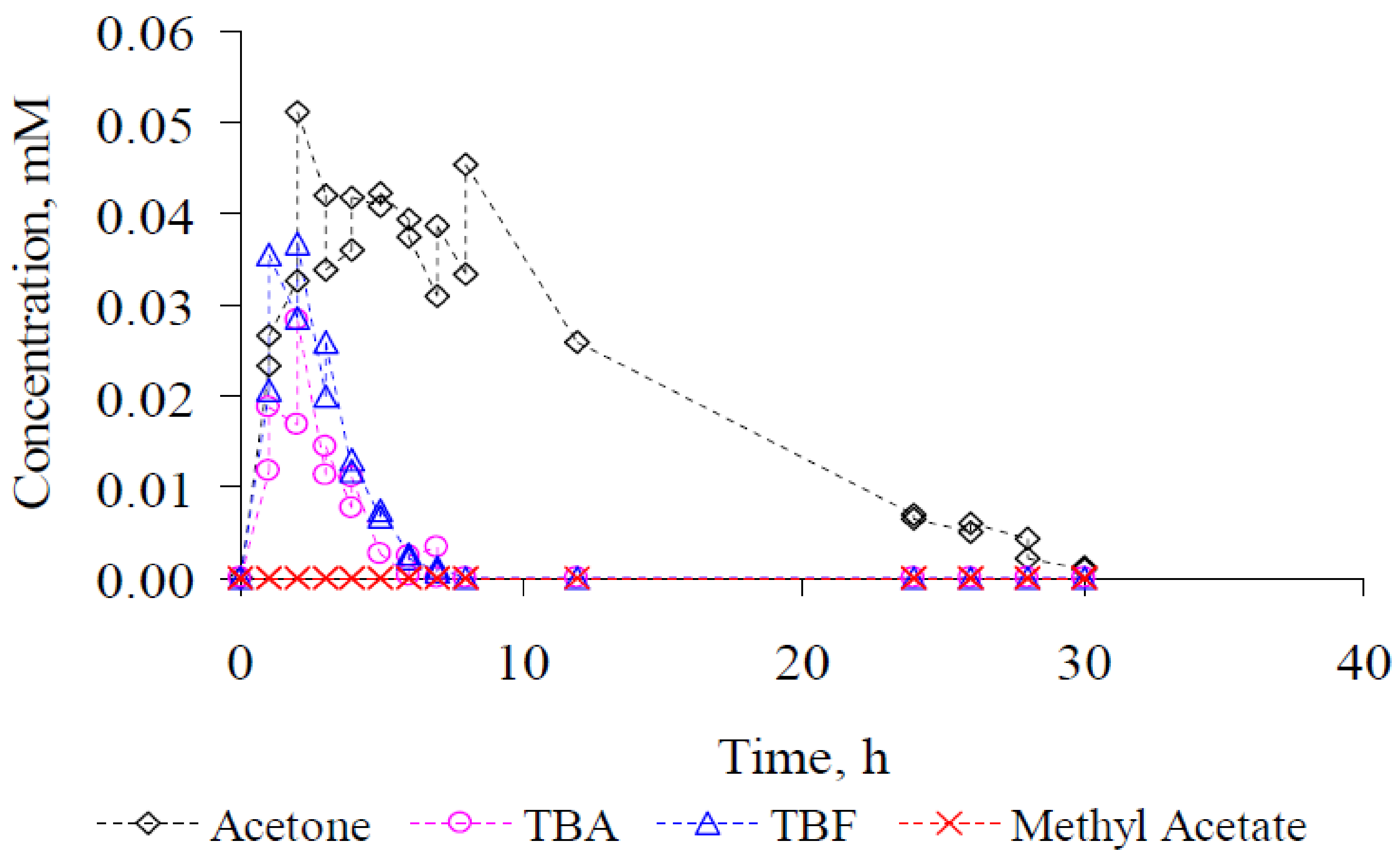
Reference: Proceedings of the First International Conference on Environmental Science and Technology (2005)

Activation Method Optimization



Reference: Proceedings of the First International Conference on Environmental Science and Technology (2005)

Intermediates in MTBE-Persulfate Reaction



Reference: *Optimization of In-Situ Chemical Oxidation Design Parameters*, Amine Dahmani, PhD, ERI

Pilot Tests

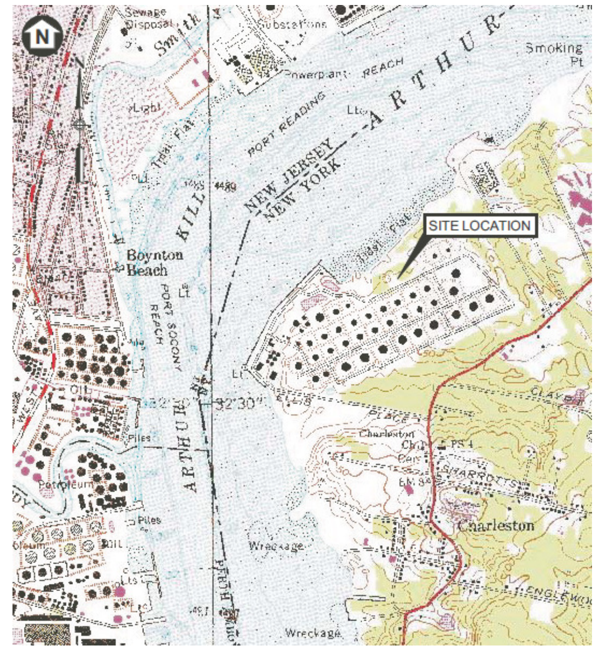
Pilot tests are performed on targeted area(s) of the site

- Common Objectives
  - Radius of influence
  - Rate of application
  - Field-scale inefficiencies
  - Field oxidant volume estimates
  - Evaluate injection design

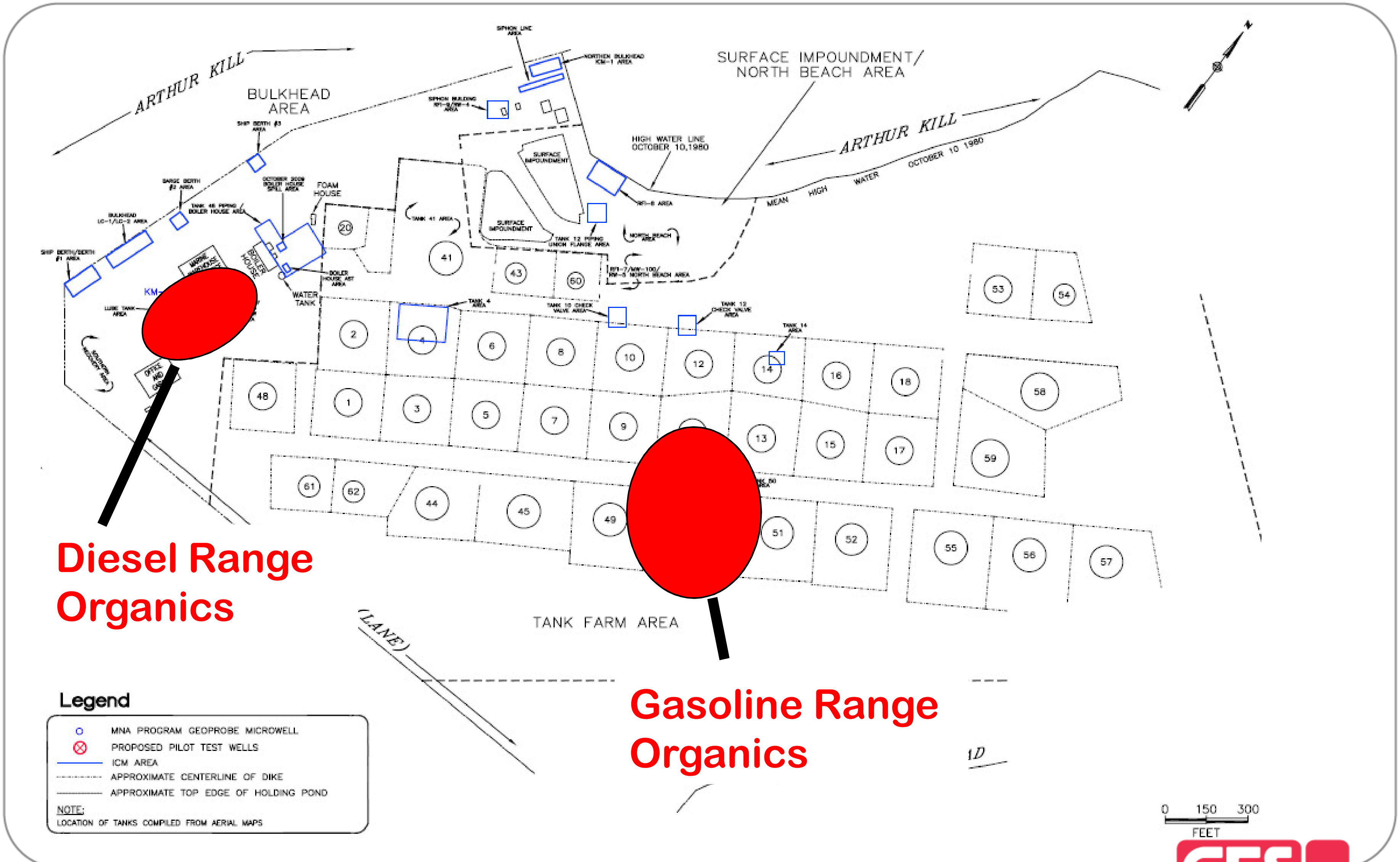
- Cost Estimate for Full-Scale Implementation
- Another Opportunity to Say "No"

Case Study: Bulk Storage Facility

- Background
  - Petroleum bulk storage facility
  - 125 million gallon storage capacity
  - 200 acres
  - COCs – gasoline, diesel, heavy fuel oil
- Geology
  - Heterogeneous deposits
  - Sand, silt, clay, some gravel
  - Clay unit underlies superficial water bearing unit
- Hydrogeology
  - Aquifer: 5 – 35 feet thick
  - DTW: 1 – 29 feet bgs
  - Hydraulic gradient: 0.04 ft/ft to 0.005 ft/ft
  - Hydraulic conductivity: 0.003 ft/min to 0.024 ft/min



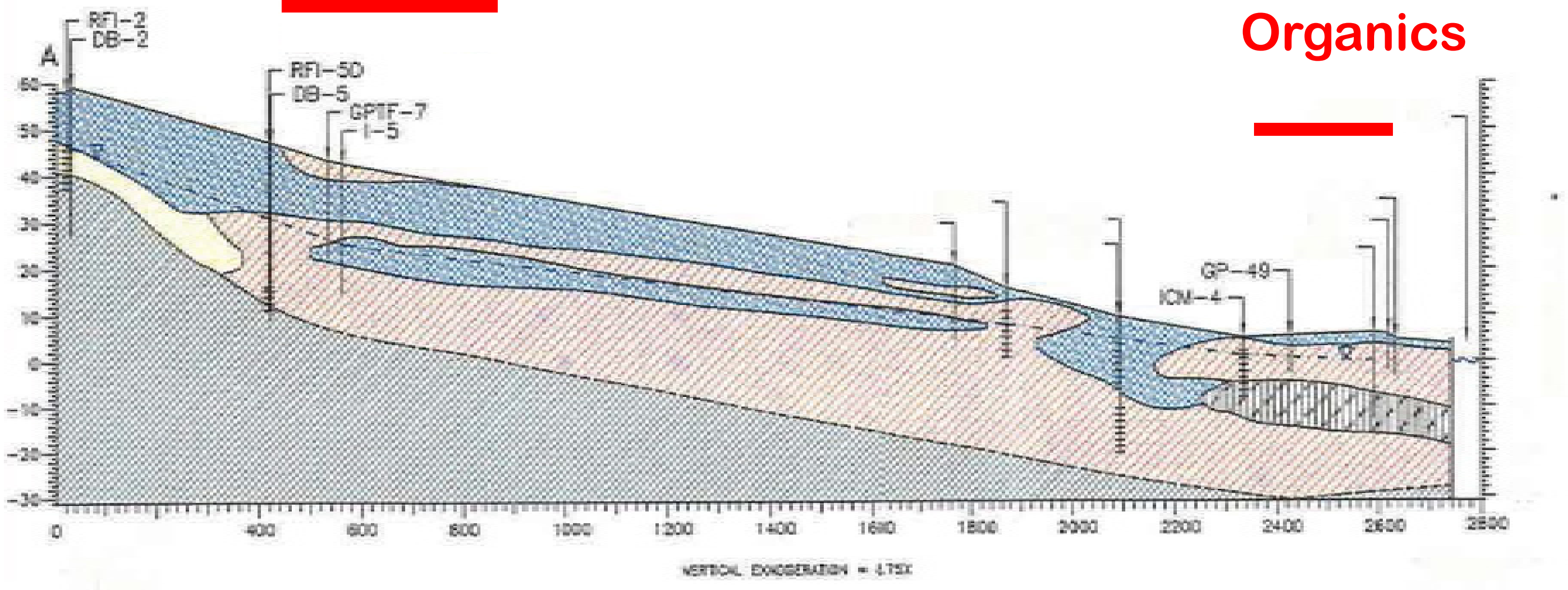
Case Study: ISCO Target Areas



Case Study: Geologic Cross-Section

Gasoline Range Organics

Diesel Range Organics



Case Study: Treatability Study Objectives

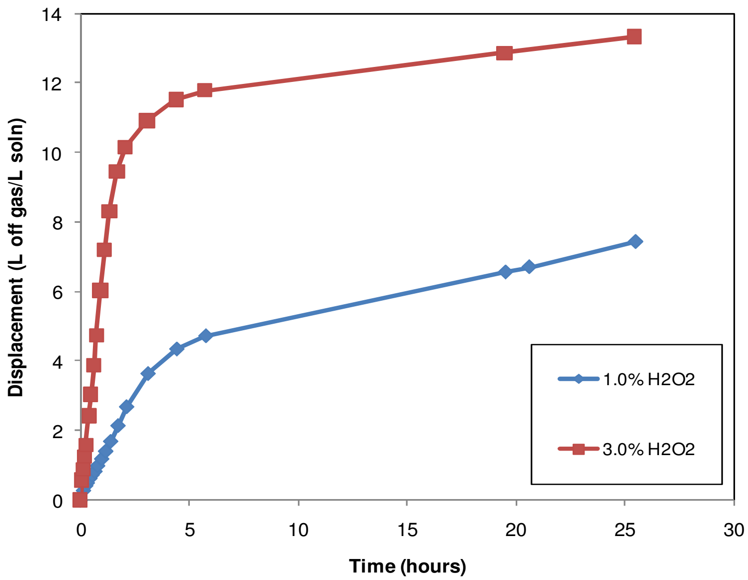
Process Variable Evaluation/Optimization

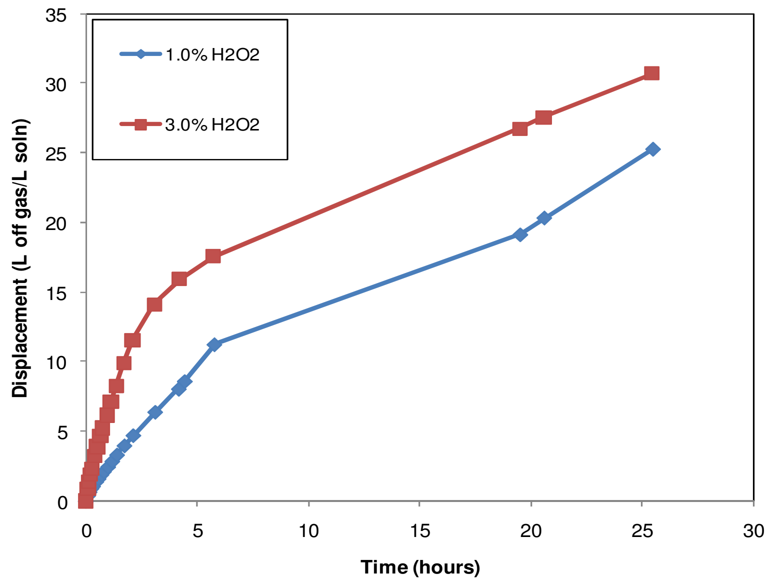
- Chemistry Optimization
- Oxidant Stability / Gas Evolution
- Soil Oxidant Demand
- Soil Buffering Capacity
- Optimize Reaction Chemistry
  - Oxidizer Dose
  - Oxidant Determination
- Address Concerns
  - pH reduction (persulfate)
  - Chromium VI

Case Study: Chemistry Optimization

- Sodium Persulfate / Hydrogen Peroxide Activation
  - > Activate with H_2O_2 / Persulfate
  - > Activate with EDTA-Iron
- Hydrogen Peroxide
  - > EDTA-Iron
  - > Stability of peroxide
- Catalyst Evaluation
  - > EDTA only
  - > Utilize “native” iron

Case Study: Oxidant Stability / Gas Evolution

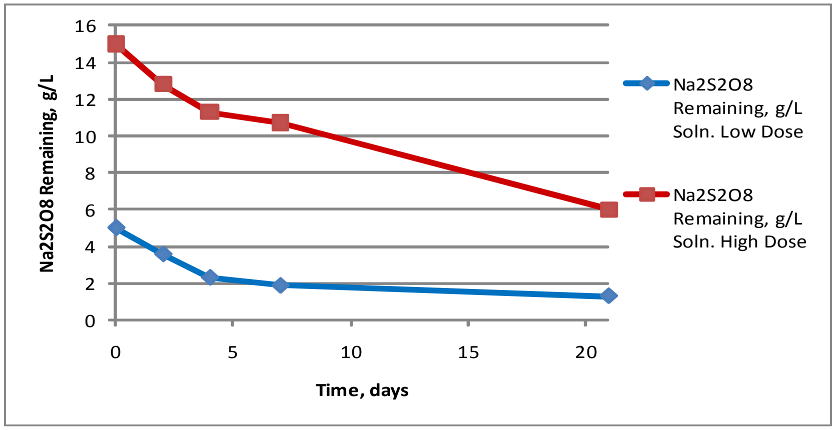


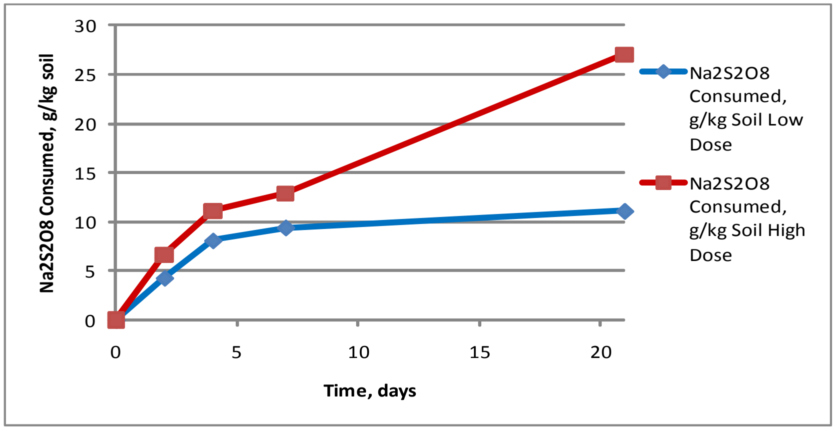


Hydrogen Peroxide Longevity Test

Case Study: SOD vs. Concentration

Time, Days	$Na_2S_2O_8$ Remaining, g/L Soln.		$Na_2S_2O_8$ Consumed, g/kg Soil	
	Low Dose	High Dose	Low Dose	High Dose
0	5	15	0	0
2	3.6	13	4.3	6.6
4	2.3	11	8.1	11
7	1.9	11	9.4	13
21	1.3	6.0	11	27





- Dose Optimization
- Higher Dose – Higher SOD

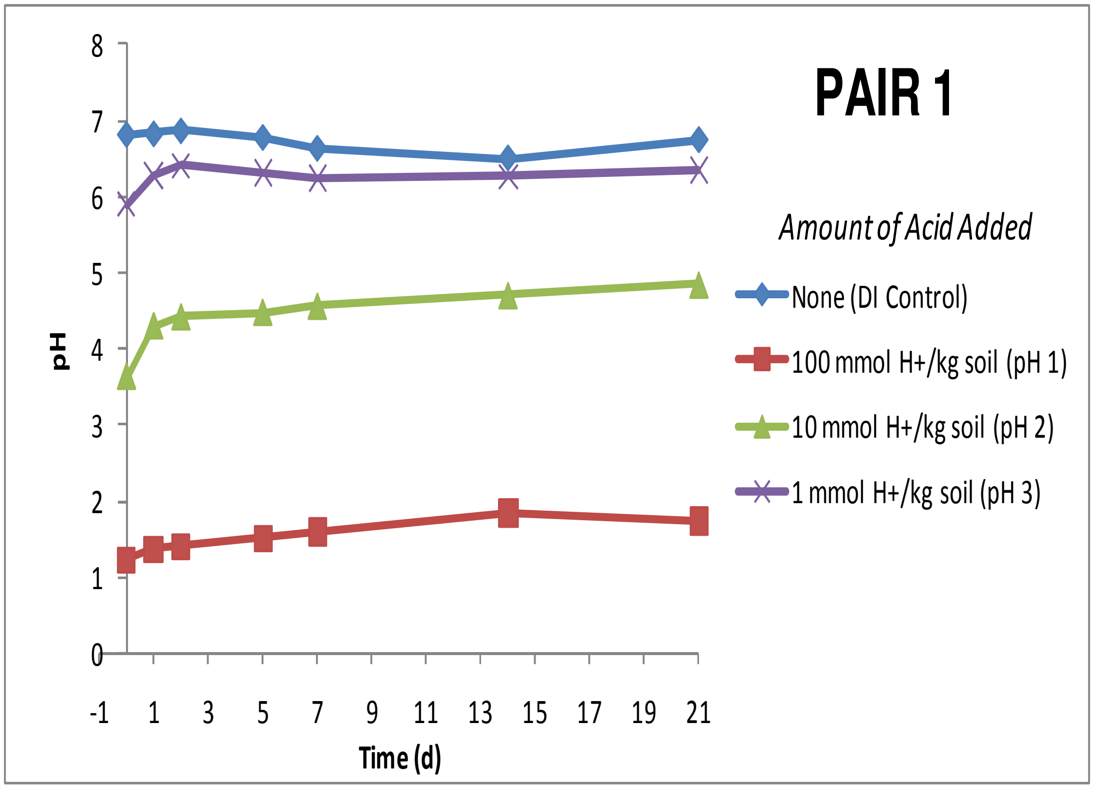
Low Dose

- Concentration: 5 g/L
- SOD: 11 g $Na_2S_2O_8$/kg

High Dose

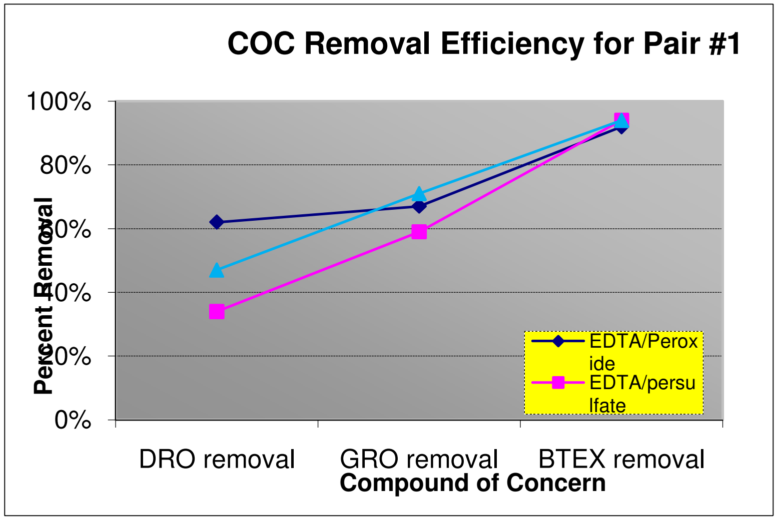
- Concentration: 15 g/L
- SOD: 27 g $Na_2S_2O_8$/kg

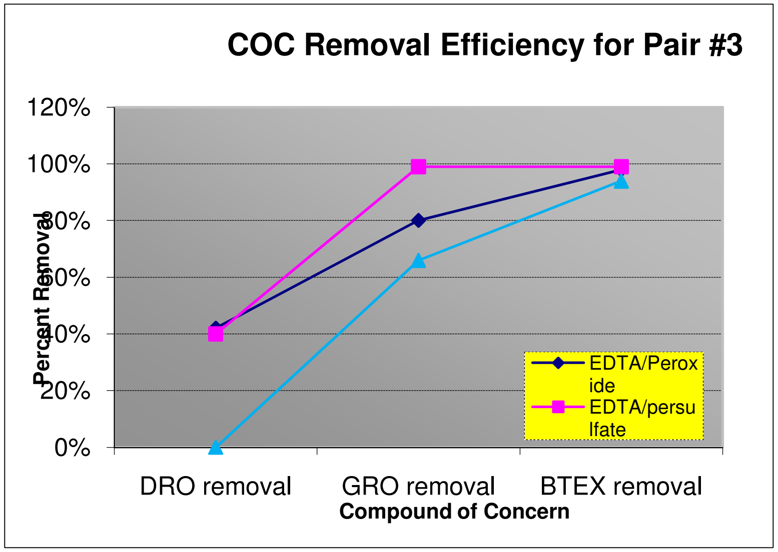
Case Study: Soil Buffering Capacity



- Assess pH drop following persulfate injection
- Mild buffering capacity of soil
- May require pH adjustment following persulfate injection
- All samples similar results

Case Study: Test Multiple Locations





- Oxidant/Catalyst Evaluation
- Multiple Samples per AOC
- Very Different Results

Pair #1 – GRO Optimized

- peroxide / persulfate – 70%
- EDTA-Fe / peroxide – 68%

Pair #3 – GRO Optimized

- EDTA-Fe / persulfate – 100%
- EDTA-Fe / peroxide – 80%

Case Study: Optimization Results

- EDTA-Iron Catalyst
  - > EDTA solution = 1,100 mg/L
  - > Chelated iron concentration = 150 mg/L
  - > EDTA : Iron = 10:1
- Persulfate – Peroxide
  - > H2O2 : Persulfate = 5 : 1
- Persulfate – EDTA-Iron
  - > EDTA : Persulfate = 1 : 4

Summary

- Treatability Testing is Valuable
  - > Process optimization
  - > Cost information
- Decision Making Enhanced
  - > Site-specific data
  - > Go / No-go earlier in design process
- Lessons Learned
  - > Optimize chemistry
  - > Develop contingencies for concerns
  - > Even “Simple Sites” benefit

”Happy is he who gets to know the reason for things.”

- Virgil

Treatability Testing for In-Situ Chemical Oxidation

Jerry Cresap, PE
Regional Engineering Manager

knowledge. innovation. results.

Groundwater & Environmental Services, Inc.