

Bench- and Full-Scale Applications of Stabilized Hydrogen Peroxide

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Remediation of Chlorinated and Recalcitrant
Compounds**

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Presentation Outline

- Resources and Credit
- Overview of Hydrogen Peroxide based Remediation
- Evolution of Fenton's Reagent to CHP
- Stabilized Hydrogen Peroxide Chemistry
- Case Studies



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Technical Resource

- Iron (II)-Chelate, dilute (0.01%) hydrogen peroxide
 - Sun, Y.; and Pignatello, J.; (1992) "Chemical Treatment of Pesticide Wastes. Evaluation of Fe(III) Chelates for Catalytic Hydrogen Peroxide Oxidation of 2,4-D at Circumneutral pH," J. Agric. Food Chem., 40 322-327
- Chelate with soils, 2% hydrogen peroxide
 - Watts, R.; Finn, D.; Cutler, L.; Schmidt, J.; and Teel, A.; (2007) "Enhanced Stability of Hydrogen Peroxide in the Presence of Subsurface Solids," J. Contam. Hydro., 91, 312-326



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Fenton's Reagent

- Fundamental Fenton's reaction



- Dilute hydrogen peroxide
 - Excess iron (II)
 - Exclusively generates hydroxyl radical
- Hydroxyl radical (2.8 V) is reactive with many environmental contaminants of concern at near diffusion limited rates



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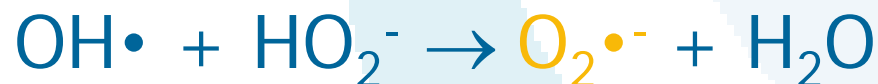
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Additional (Propagation) Reactions

Perhydroxyl Radical



Superoxide



Hydroperoxide



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Reaction with Compounds

- Fenton's Reagent was found to degrade compounds such as:
 - Hexachloroethane
 - Carbon Tetrachloride
- Multiple transient oxidant species
 - Perhydroxyl radical
 - Superoxide radical anion
 - Hydroperoxide
- Solvent effect



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What is in a Name?

- Commonly referred to as:
 - Fenton's reagent
 - Modified Fenton's reagent
 - Acidified Fenton's reagent
 - Catalyzed Modified Fenton's reagent
- More recent names:
 - CHP:
 - Catalyzed H₂O₂ Propagations; or,
 - Catalyzed Hydrogen Peroxide
 - Stabilized hydrogen peroxide
- More recent names based on greater understanding of chemistry and recognition that CHP is much more than classic Fenton's reagent



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Evolution of Application

- Grand Daddy of ISCO
 - Early applications of hydrogen peroxide had great successes and unexplained failures
- General Injection Strategies:
 - Catalyzed (Early):
 - Hydrogen Peroxide and Iron
 - Injection of Hydrogen Peroxide with Chelated Iron
 - Un-Catalyzed (More Recent):
 - Injection of Hydrogen Peroxide
 - Injection of Hydrogen Peroxide with stabilization agent



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Stabilization Chemistry

- Several Factors can influence the stability of Hydrogen Peroxide:
 - pH
 - Temperature
 - Activator-transition metals
 - Reactions with organics
 - Soil type/surface area
- Stability of Hydrogen Peroxide will be site specific
- Transition metals in the mineralogy are a common problem that can be addressed



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Why Stabilized Hydrogen Peroxide

- More stable hydrogen peroxide:
 - Allows for greater areas of influence
 - Longer contact time and dissolution time
 - Has been shown to react at rates greater than natural dissolution (Smith et. al, 2006)



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Control of Transition Metals

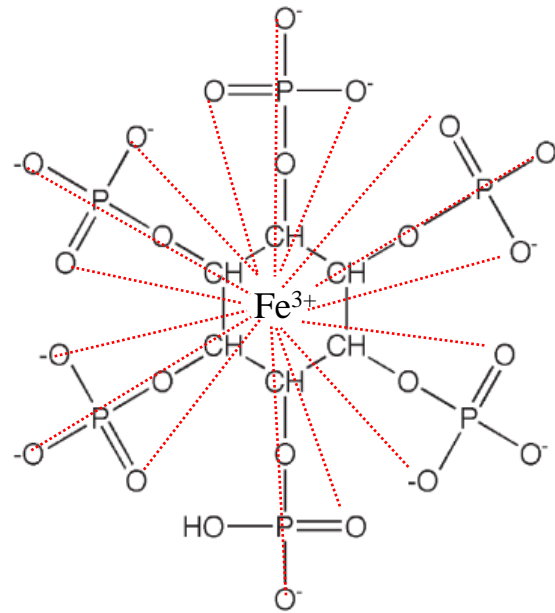
- Coordination chemistry
 - Premise is to bind up transition metals with chelates to make them less reactive with hydrogen peroxide
 - Results in a new aqueous species with it's own properties



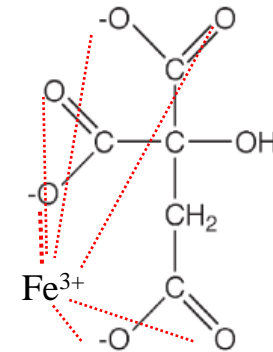
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Stabilized Hydrogen Peroxide



Phytate



Citrate

(Watts et al, 2007)



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Stablized Hydrogen Peroxide

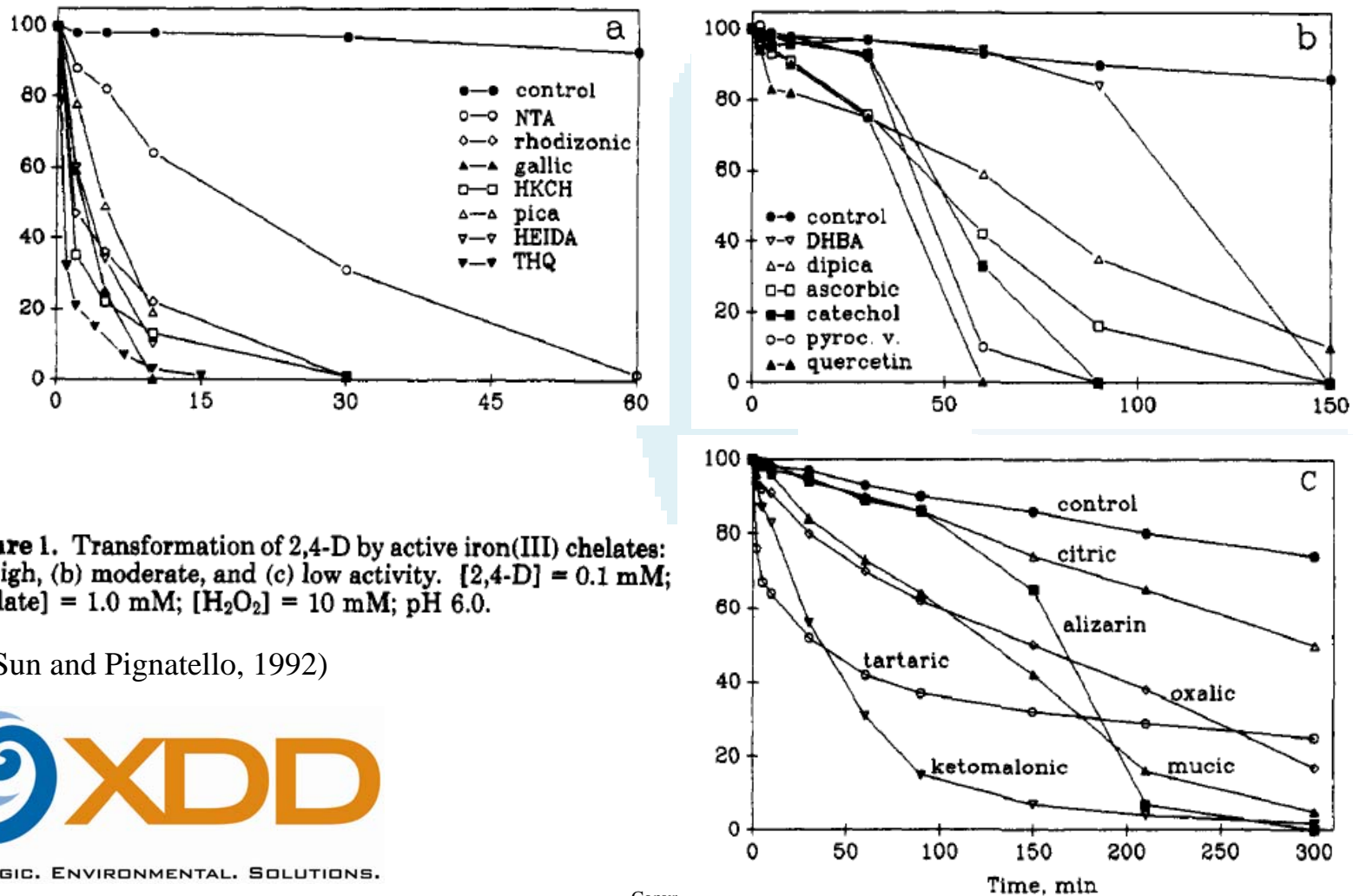


Figure 1. Transformation of 2,4-D by active iron(III) chelates: (a) high, (b) moderate, and (c) low activity. [2,4-D] = 0.1 mM; [chelate] = 1.0 mM; [H₂O₂] = 10 mM; pH 6.0.

(Sun and Pignatello, 1992)



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Stability Constants

- Different for every metal and chelate



Metal	Citrate
Al	11.7
Ba	2.3
Ca	3.5
Co	4.4
Cu	6.1
Fe(II)	3.2
Fe(III)	11.9
Mn	3.2

Treatment	Half Life (hrs)
Soil Only	26
10 mM Citric Acid	23
50 mM Citric Acid	21
0.1 mM Phytic Acid	25
10 mM Phytic Acid	37

Treatment	Half-life (hrs)
Soil only	7
10 mM Citric Acid	15.2
20 mM Citric Acid	13.3
50 mM Citric Acid	20
0.1 mM Phytic Acid	13.9
1 mM Phytic Acid	19
10 mM Phytic Acid	93.7



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Dark Side of Stabilized Hydrogen Peroxide

- Metals Mobilization
- Gas Evolution
- Non-target demand

Table II. Stability of Active Fe(III) Chelates in 10 mM H₂O₂ at pH 6

chelate	color change	precipitation within
NTA	yellow ^a	2-3 h
HEIDA	yellow ^a	3-4 h
mucic acid	yellow ^a	3 days
malonic acid	yellow ^a	1 days
malic acid	yellow ^a	3 days
ketomalonic acid	yellow ^a	1 days
tartaric acid	yellow ^a	3 days
oxalic acid	yellow ^a	1 days
pica	orange to yellow ^b	7 days
dipica	yellow ^a	>7 days
catechol	dark brown to yellow ^b	3 days
DHBA	dark blue to yellow	7 days
ascorbic acid	yellow ^a	<16 h
gallic acid	dark blue to yellow	7 days
rhodizonic acid	brown to yellow	5 days
HKCH	yellow ^b	3 days
THQ	brown to yellow	5 days
quercetin	dark brown to yellow	>7 days
pyrocatechol violet	dark brown to yellow	>7 days
alizarin red	dark brown to yellow	7 days
citric acid	yellow ^a	>7 days

^a No color change on addition of hydrogen peroxide; however, precipitation indicates eventual oxidation. ^b UV spectral changes were observed.

(Sun and Pignatello, 1992)



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Case Study 1: Eastland Woolen Mills Superfund Site

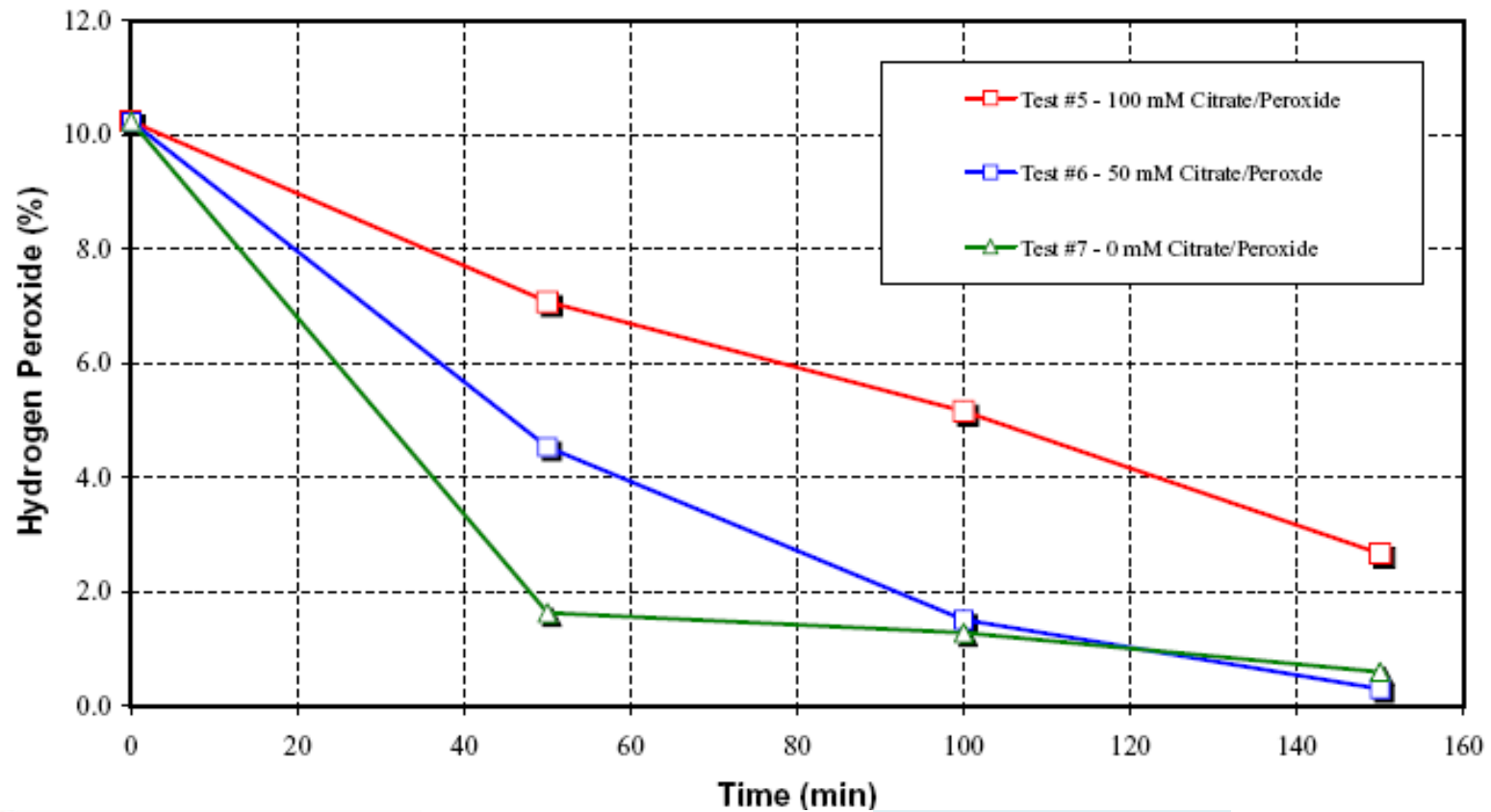
- Former Textile Mill located in Corinna, ME
- Contaminant: Aqueous, residual, and DNAPL phase Chlorobenzene(s)
- Soils: Overburden-Glacial till with high transition metals content



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Case Study 1: Continued



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Case Study 1: Continued

- Increased stability by ~3 times with chelate
- Despite success, half life is still too short for Hydrogen Peroxide
- Site is currently being successfully treated with Activated Persulfate

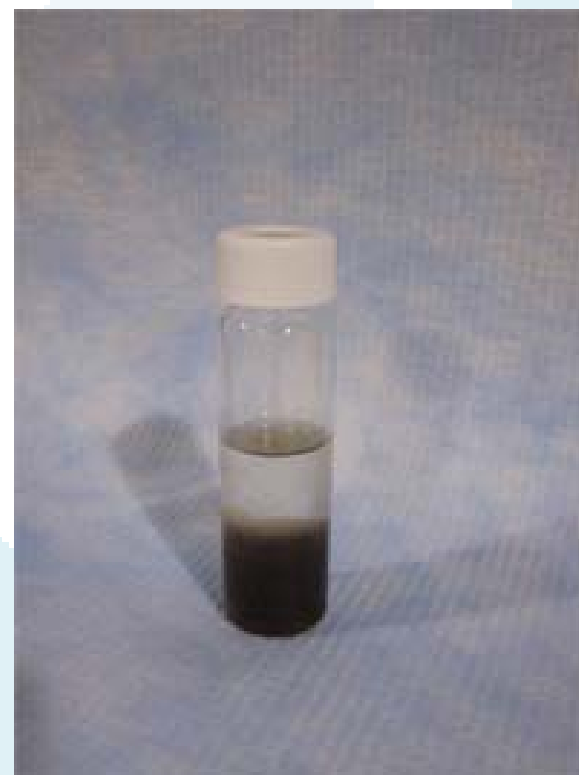
Citrate added to Peroxide	Peroxide Half Life
(mM)	(minutes)
100	84.5
50	31.9
0	29.0



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Case Study 2: Anonymous 1,1,1-TCA DNAPL Site

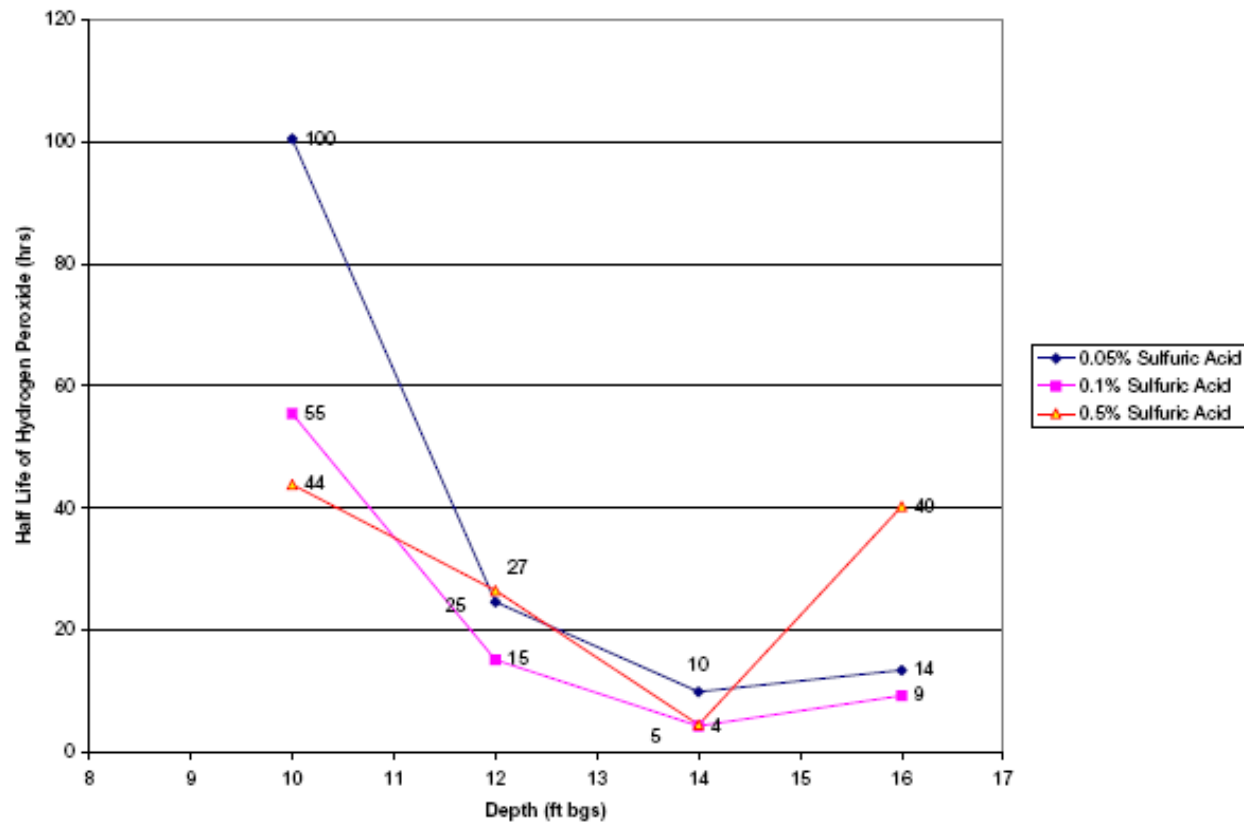
- Site contains mixed DNAPL (mostly 1,1,1-trichloroethane)
- Based on reactivities, CHP was selected for bench-scale and full-scale treatment



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Case Study 2: Bench Testing



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Case Study 2: Continued

- Bench tests indicate the significance of pH and stabilization agent
- 20 mM Citric Acid was selected to stabilize the Hydrogen Peroxide

Treatment	Half life (hrs)	Estimated % H ₂ O ₂ after 10 hrs (initial conc 7%)
0 mM	4.6	1.5
20 mM	15.6	4.7
50 mM	17.4	4.5



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Case Study 2: Field Results

- Stabilized Hydrogen Peroxide applied on the full-scale in multiple applications
- Average decrease of 83 percent of TCA and total VOCs in groundwater samples (high: 99 percent)
- Average decrease of VOCs and TCA concentration in soil of 90 percent in the target area (high: 99.5 percent)



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Conclusions

- Scientific advances in understanding of hydrogen peroxide based treatment have resulted in an evolution of the technology
 - New names
- Stabilized hydrogen peroxide can increase the stability of hydrogen peroxide in the subsurface allowing for better distribution
- Stability will vary depending upon metal, chelate and other site conditions
- Limitations should be considered in the design phase



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Questions?

