

**In-Situ Treatment of Groundwater  
with Non-aqueous Phase Liquids**  
December 10-12, 2002, Chicago, IL

**Scott G. Huling, Ph.D., P.E.**  
USEPA Robert S. Kerr Environmental  
Research Center, Ada OK

**In-Situ Fenton Oxidation: A Critical Analysis**  
Fundamental Chemistry  
Bench-scale Treatability Studies  
Field-scale Applications (pilot- or full-scale)  
Fate and Transport Issues



## Fenton and Related Reactions



### *Scavenging reactions*



### *Nonproductive reactions*



*Miscellaneous* optimum pH 3-4; metals mobility;  
exothermic; stabilizers

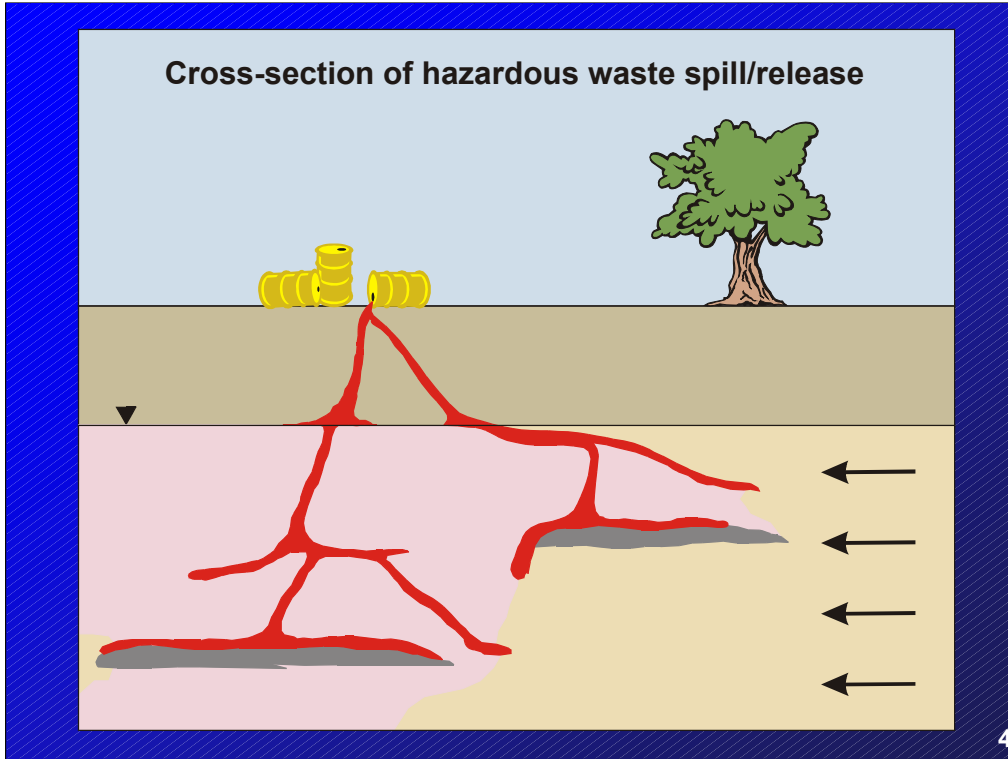
2

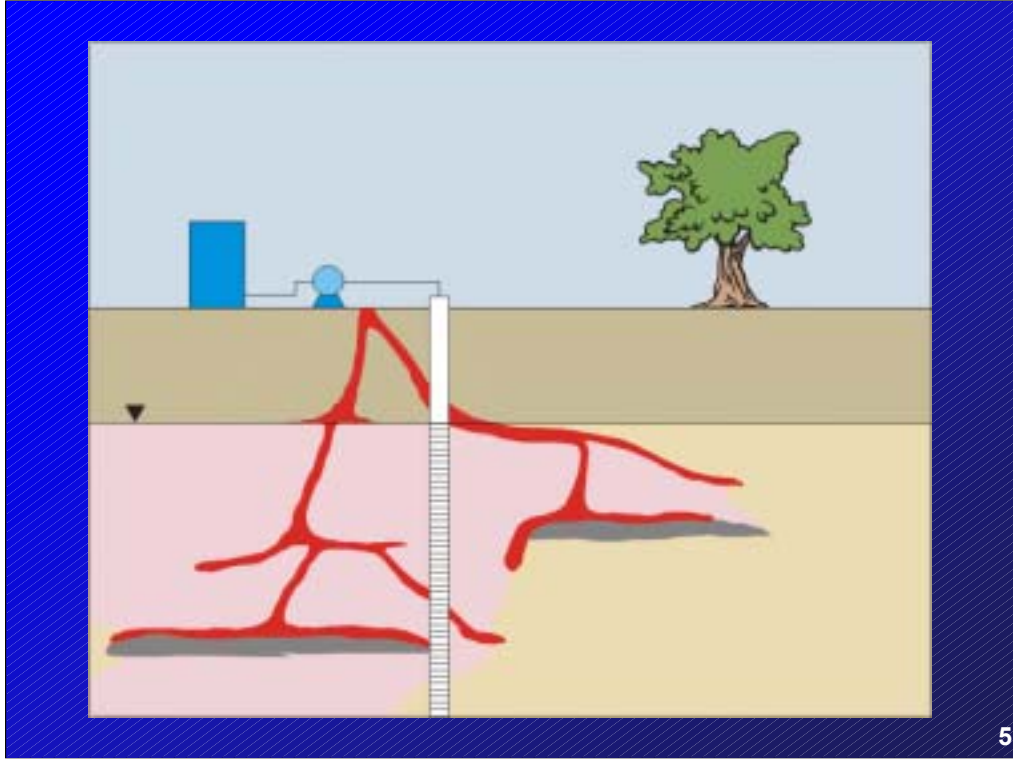
## Potential Limitations of Fenton Oxidation

1. Non-productive reactions
2. Scavenging
3. Low reaction rates
4. Insufficient Fe
5. pH adjustment
6. Oxidant, iron, acid, stabilizer transport
7. O<sub>2</sub>(g) production
8. Undesirable reaction byproducts
9. Enhanced volatilization and transport
10. Unreactive target compounds



3





# Bench-scale Treatability Study Objectives

## High Priority

1. Proof of concept – quantify extent of oxidation given potential limitations
2. Determine reaction byproducts
3. Metals mobility



## Bench-scale Study Guidelines



1. Components: soil, ground water, reagents
2. Capture and quantify losses from the reactor
3. pH change
4. Monitoring parameters: target, byproducts, metals
5. Control
6. Establish pre-, post-oxidation concentrations
7. Perform pre-, post-oxidation mass balance

## Field-Scale Application Guidelines

1. Injectate volume vs. pore volume target area
2.  $\text{H}_2\text{O}_2$  concentration
3. pH adjustment
4. Pulse injection of Fe(II) and  $\text{H}_2\text{O}_2$
5. Injection strategy



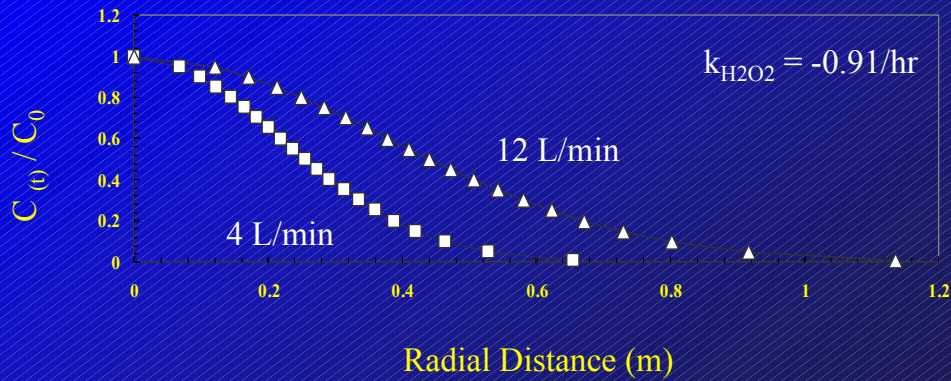


## H<sub>2</sub>O<sub>2</sub> Reaction, Subsurface Transport

$$[\text{H}_2\text{O}_2]_{(t)} / [\text{H}_2\text{O}_2]_0 = \exp(-K_{\text{H}_2\text{O}_2} R^2 \pi Z \eta / Q)$$

(After, Clayton, 1998)

Flow, well spacing, pH



9

## Other Chemical Reagents



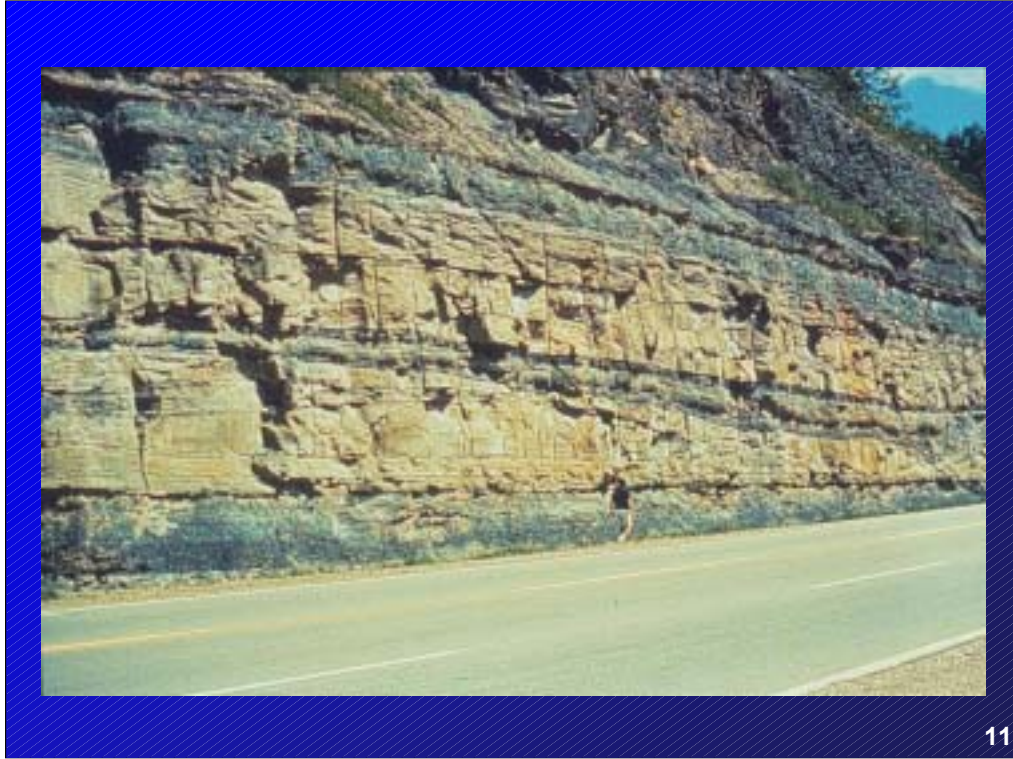
Reactions/interactions

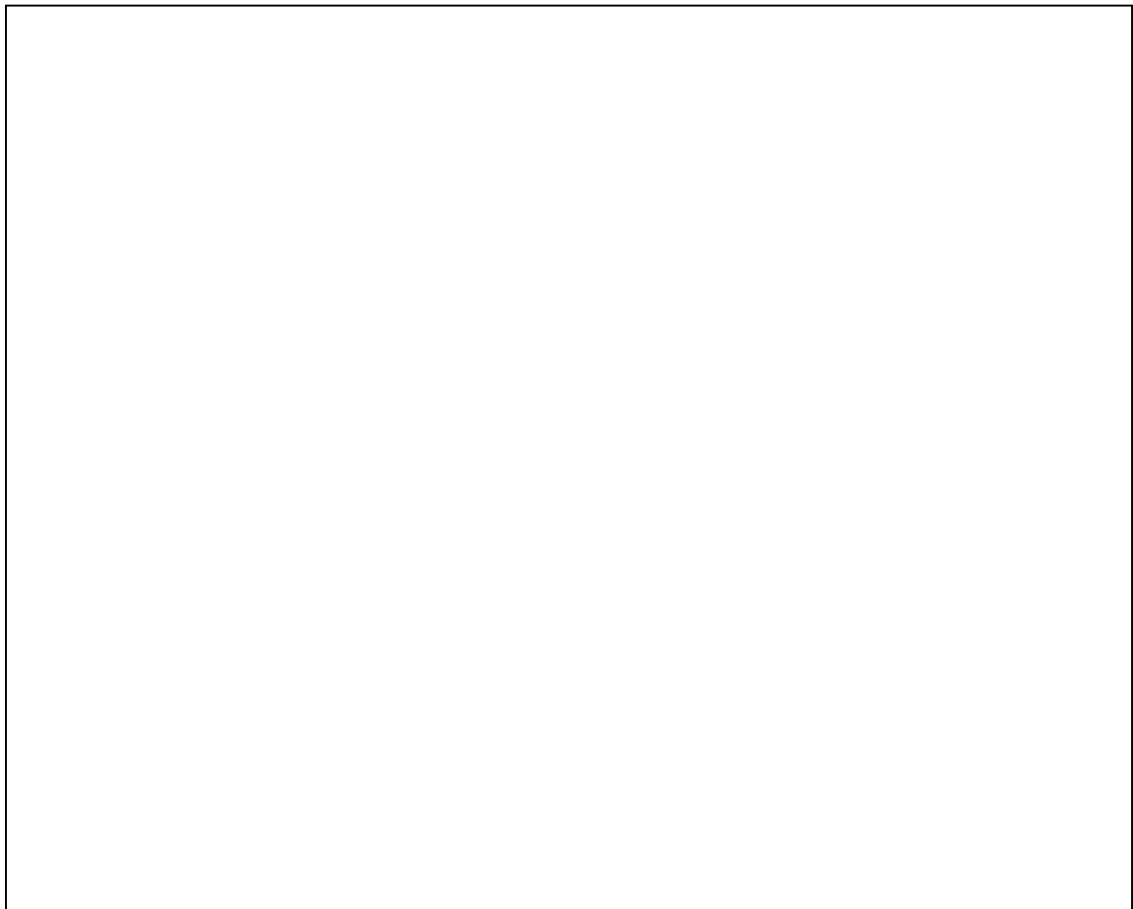
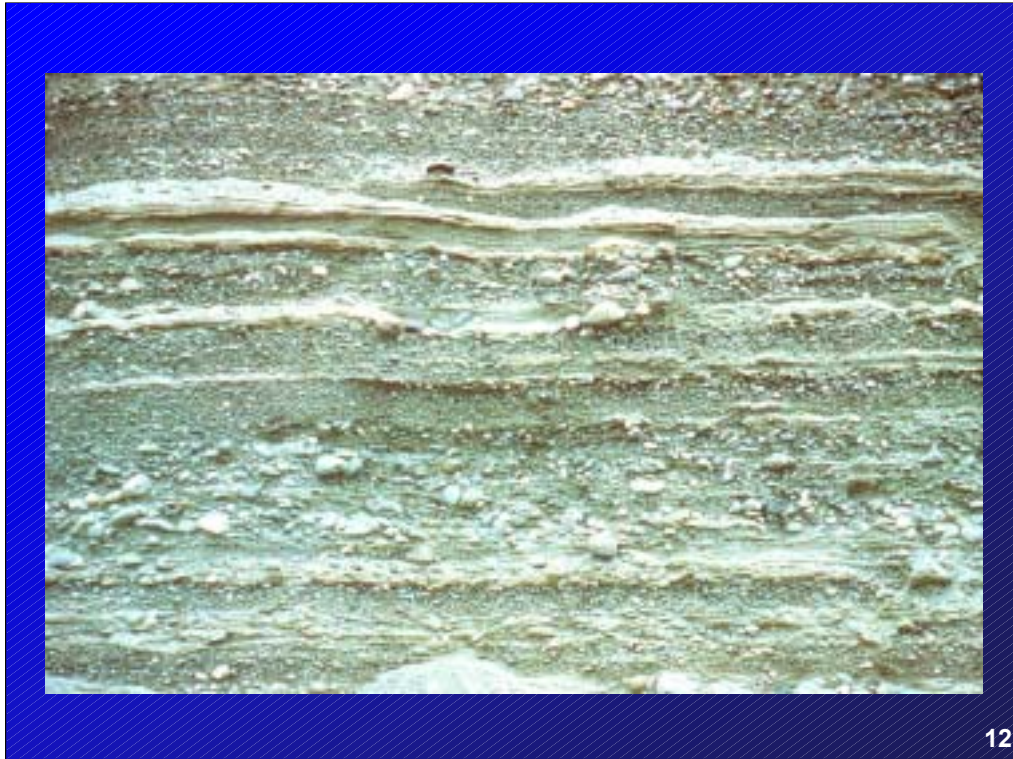
**Fe(II)** - precipitation, complexation, oxidation

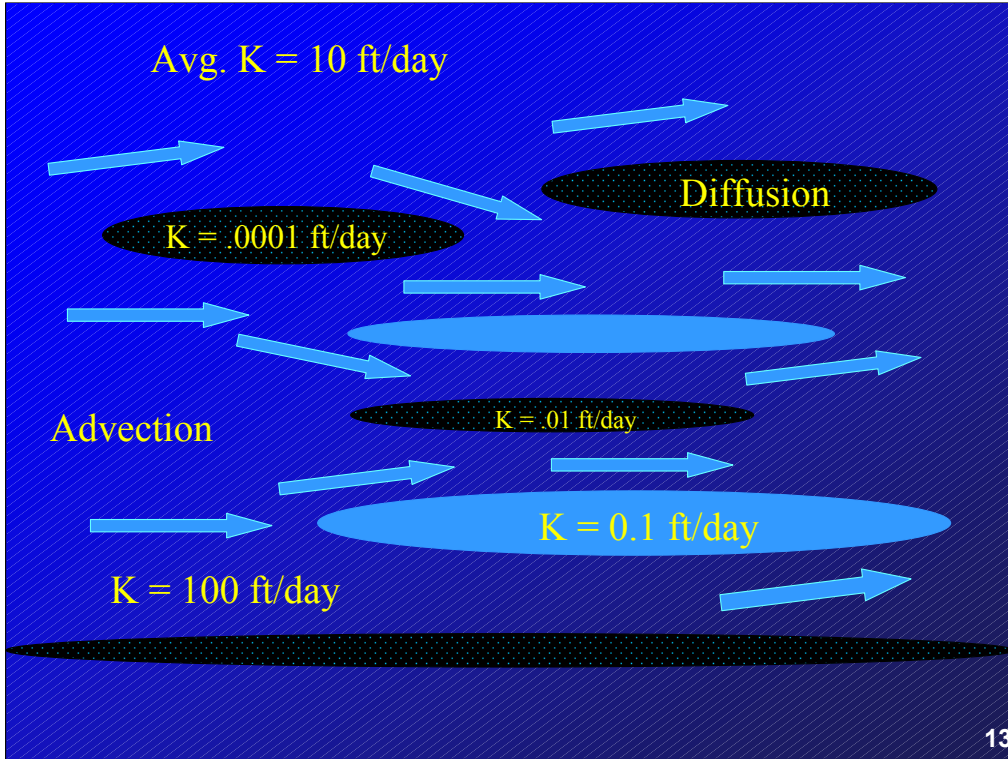
**Acid** - consumed by acid neutralizing capacity

**Stabilizers (H<sub>2</sub>O<sub>2</sub>, Fe(II))** - precipitation,  
complexation, oxidation

10







## Non-ideal Conditions Need to be Considered

Preferential pathways - greater rate of transport  
and oxidant delivery occurs through high  
conductive zones

Lower permeability zones - diffusion  
dominated transport  $\ll$   $\text{H}_2\text{O}_2$  reaction

Multiple applications



## Transport Issues



Representative volume

Heat and  $O_2(g)$  released - impact

Pneumatic transport of ground water

Decreased DNAPL visc., increased mobility

DNAPL evaporation

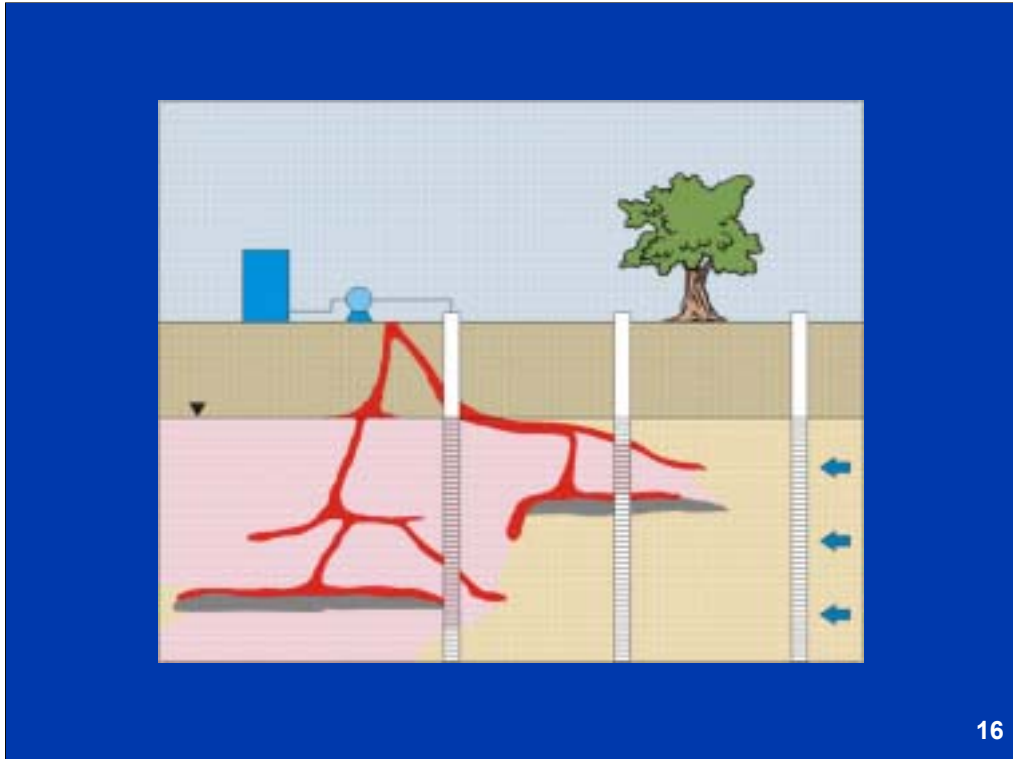
Volatilization of DNAPL components

Thermal desorption from the solid phase

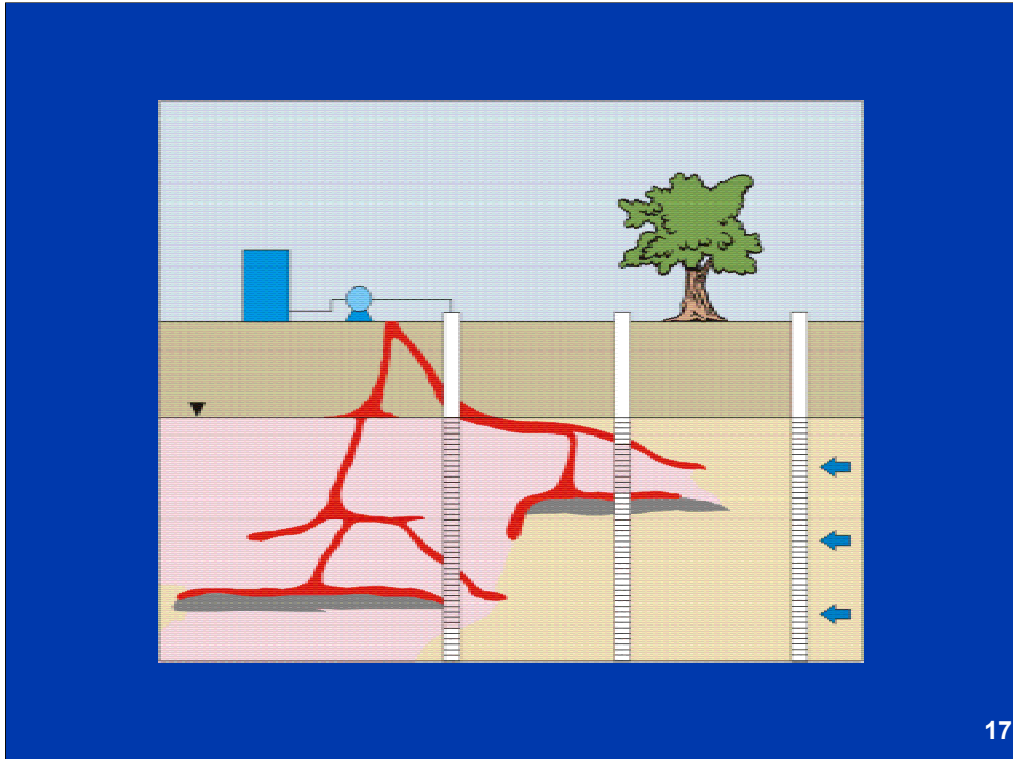
Enhanced  $H_2O_2$  decomposition

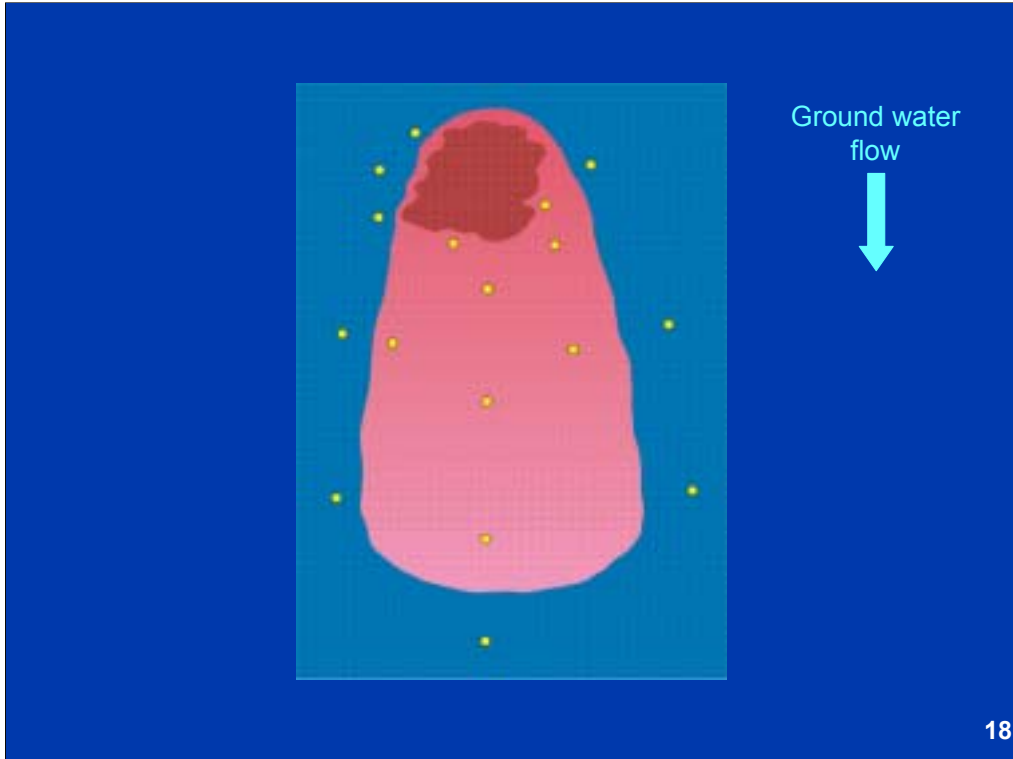
15

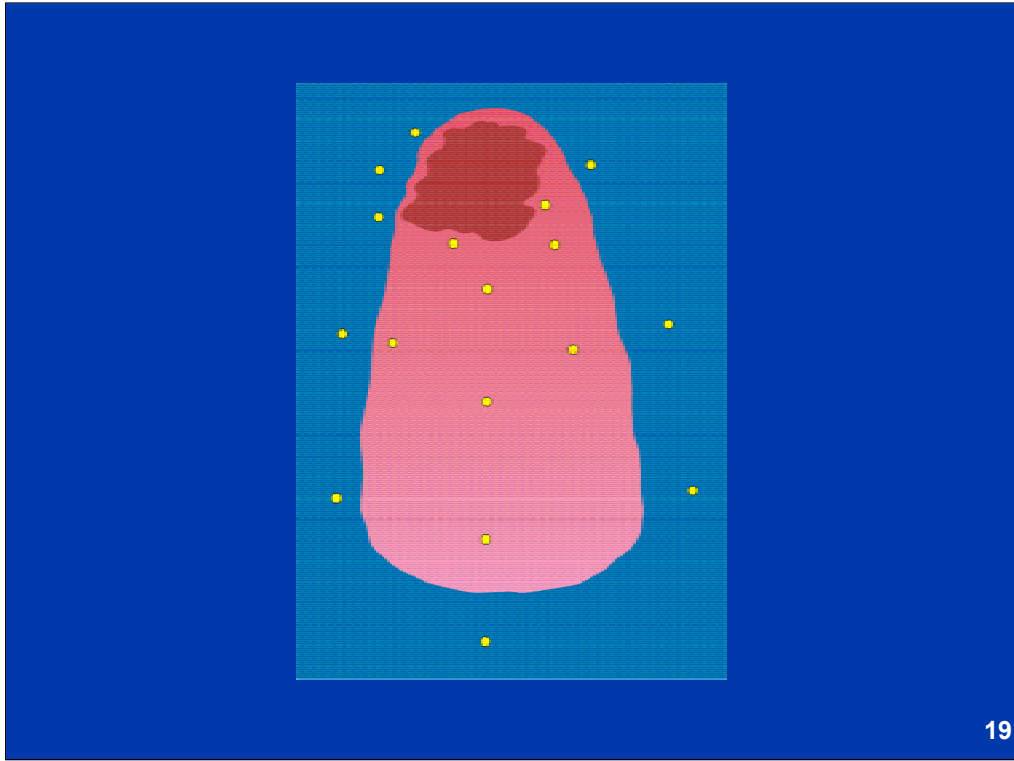












## SVE is a Complimentary Technology to Fenton Oxidation

Capture/treat/dispose volatiles

SVE may already be part of the remedy

Minimize the transport/uncontrolled loss

Minimize potential exposure pathways

Vent wells for deeper systems



## Performance Monitoring



Preferred monitoring parameters:

target compound - aqueous (rebound: long term vs. immediate), solid

reaction byproducts - aqueous

Metals - aqueous

H<sub>2</sub>O<sub>2</sub> - aqueous

Off-gas, soil gas samples

Establish sentry wells



## ... performance monitoring

### Ground water monitoring

Low priority - limited value for performance evaluation

CO<sub>2</sub>

DO

TOC

COD

Conductivity

ORP

Temperature



## Effects of ISFO on Natural Attenuation?

1.  $H_2O_2$  - antiseptic, heat
2. Heterogeneity - microniches, preferential pathways
3. Improvement in post-oxidation biodegradation
4. Microbial sensitivity
5. Population changes
6. Toxicity response



## Health and Safety

Heat released

O<sub>2</sub>(g) released + Flammable vapors

Enhanced volatilization

Accumulation of vapors (buildings, utilities)



24





## Conclusions



Hydroxyl radical – strong oxidant

Potential limitations

Numerous parameters influence success/failure

Monitoring parameters/approach – key to successful performance evaluation

Enhanced transport processes

Recognize/capture volatile emissions



25

## Scavenging Analysis

Target contaminant oxidation reaction:



Scavenger oxidation reaction:



Reaction rate equations:

$$D[\text{C}]/dt = k \cdot\text{OH} [\text{C}]$$

$$D[\text{S}_i]/dt = \sum_i k_i \cdot\text{OH} [\text{S}_i]$$



26

A simplified scavenging analysis has been included for your review to illustrate the rate of oxidation of the target compound relative to other potential scavengers that may be present in the ground water. Reactions between  $\cdot\text{OH}$  and the target contaminants (C) and scavengers ( $\text{S}_i$ ) and the associated reaction rate equations can be used to assess the role of scavengers.

## Relative Reaction Rates

Relative rate of reaction ( $R_R$ ) between  $\cdot\text{OH}$  and  $S_i$ ,  
and  $\cdot\text{OH}$  and C

$$R_R = (\sum_i k_i [\cdot\text{OH}] [S_i]) / (k [\cdot\text{OH}] [C])$$



27

The rate of reaction between  $\cdot\text{OH}$  and scavenger relative to  $\cdot\text{OH}$  and the target can be calculated using this equation.

Sources of reaction rate constants:

Buxton, G.V., Greenstock, C., Hellman, W.P. and Ross, A.B. (1988) "Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms, and Hydroxyl Radicals ( $\cdot\text{OH}/\cdot\text{O}^-$ ) in Aqueous Solution." *Journal of Physical Chemical Reference Data*. (17)2,513-886.

Dorfman, L.M. and Adams, G.E. (1973) "Reactivity of the Hydroxyl Radical." *National Bureau of Standards*, Report No. NSRDS-NBS-46.

Haag, W.R. and Yao, C.C.D. (1992) "Rate Constants for Reaction of Hydroxyl Radicals with Several Drinking Water Contaminants." *Environ. Sci. Technol.* (26)5, 1005-1013.

## Example 1

[TCE] = 450  $\mu\text{g/L}$  ( $3.42 \times 10^{-6}$  M);  $k = 4.2 \times 10^9$  L/mol-s  
[Cl<sup>-</sup>] = 1250 mg/L ( $3.52 \times 10^{-2}$  M);  $k = 4.3 \times 10^9$  L/mol-s  
[CO<sub>3</sub><sup>2-</sup>] = 150 mg/L ( $2.5 \times 10^{-3}$  M);  $k = 3.9 \times 10^8$  L/mol-s  
[·OH] assume  $10^{-15}$  M

$$R_R = 10,600$$



28

*Example 1 considers the role of background ground water quality in radical scavenging:*

You are reviewing a remediation proposal that a company has submitted involving the use of Fenton oxidation. As you read through the document and other reference materials, you compile the ground water data and information presented above. (Note: the [Cl<sup>-</sup>] was high at this site as a result of agricultural practices in an arid region. This can also occur in brine-affected areas and areas with salt water intrusion. Typically, [Cl<sup>-</sup>] is much lower than in the example used here).

Given these values, and the relative reaction rate equation in the previous slide, you estimate that the relative rate of ·OH reaction with TCE is 10,600× slower than the scavenging rate by CO<sub>3</sub><sup>2-</sup> and Cl<sup>-</sup>. This does not include the effects of other potential scavengers present in the ground water (including H<sub>2</sub>O<sub>2</sub>) which would decrease TCE oxidation efficiency even greater. If the initial concentration of TCE is lower in some areas, the relative rate of scavenging increases and the rate of TCE oxidation declines.

Based on these results, one may conclude that oxidation mechanisms involving the hydroxyl radical will be significantly inefficient. Assuming poor efficiency, multiple applications of H<sub>2</sub>O<sub>2</sub> would be needed and costs may increase significantly over a single application scenario. This does not take into consideration other potential sources of inefficiency.

One additional issue is that the amount of carbonate suggests the pH and buffer capacity are high leading to pH adjustment (acidification) problems, rapid H<sub>2</sub>O<sub>2</sub> decomposition and H<sub>2</sub>O<sub>2</sub> delivery problems, contributing to poor oxidation efficiency. In this case, technical limitations appear significant and you may choose not to move forward, or at a minimum, a bench-scale treatability study could be conducted to gain additional insight, i.e., establish proof of concept before pilot- or field-scale application is considered further.

## Example 2

[PCE] = 4.15 mg/L ( $2.5 \times 10^{-5}$ M);  $k = 2.6 \times 10^9$  L/mol-s

[Cl<sup>-</sup>] = 45 mg/L ( $1.27 \times 10^{-3}$ M);  $k = 4.3 \times 10^9$  L/mol-s

[H<sub>2</sub>O<sub>2</sub>] = 50% , 500,000 mg/L ( $1.47 \times 10^1$ M);

$k = 2.7 \times 10^7$  L/mol-s

[·OH] assume  $10^{-15}$  mol/L

$$R_R = 6,180$$



29

*Example 2 considers the role of H<sub>2</sub>O<sub>2</sub> as a radical scavenger:*

Reading through another remediation proposal and associated reference materials, you compile the data and information presented above.

Given these values, the relative rate of ·OH reaction with PCE is 6180× slower than the scavenging rate by H<sub>2</sub>O<sub>2</sub> and Cl<sup>-</sup>. This condition is transient - as [PCE] and [H<sub>2</sub>O<sub>2</sub>] decrease, the rate of radical scavenging will vary. The effects of other scavengers present in the ground water would further increase PCE oxidation inefficiency. Lower initial concentrations of PCE at some site locations will yield greater scavenging rates and a lower rate of PCE oxidation. This does not take into consideration other potential sources of inefficiency. Based on these results, one may conclude that oxidation efficiency will be limited and multiple applications of H<sub>2</sub>O<sub>2</sub> may be needed. The associated costs may increase significantly.

Process optimization could include a decrease in [H<sub>2</sub>O<sub>2</sub>] to 5% to minimize scavenging by H<sub>2</sub>O<sub>2</sub> and use of smaller spacing between injection wells. Assuming the same mass of H<sub>2</sub>O<sub>2</sub> is applied, this could reduce the relative rate of scavenging from 6180 to 690, and increase the volume of aquifer contacted by oxidant. Here, a bench-scale treatability study could provide additional insight before pilot- or field-scale application is considered.