In-Situ Treatment of Groundwater with Non-aqueous Phase Liquids

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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

$H_2O_2 + Fe^{+2} \rightarrow Fe^{+3} + OH^- + \cdot OH$ (1)

$H_2O_2 + Fe^{+3} \rightarrow Fe^{+2} + \cdot O_2^- + 2\,H^+$ (2)

$\cdot O_2^- + Fe^{+3} \rightarrow Fe^{+2} + O_2$ (3)

$\cdot OH$ + Contaminant → Products (CO_2, Cl^-, etc.) (4)

Scavenging reactions

$\cdot OH + \Sigma^n_{i=1} S_i \xrightarrow{\Sigma^n_{i=1} k_i}$ products of scavenging rxn (5)

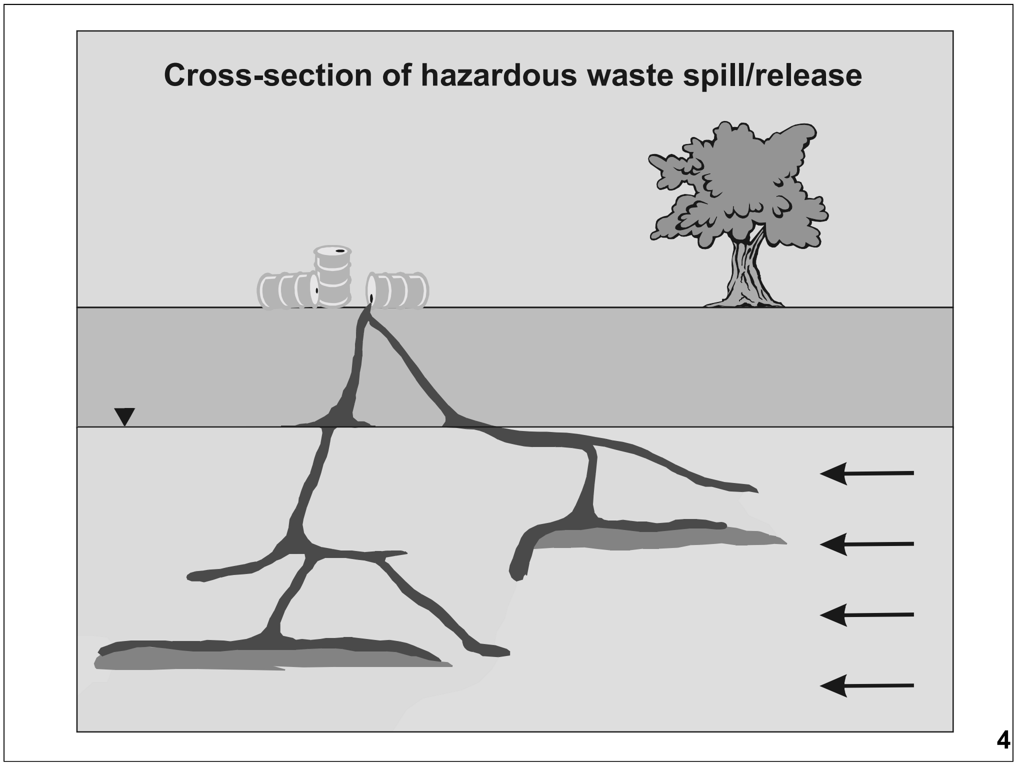
Nonproductive reactions

$2\,H_2O_2$ + reactants $\rightarrow O_2 + 2\,H_2O$ (6)

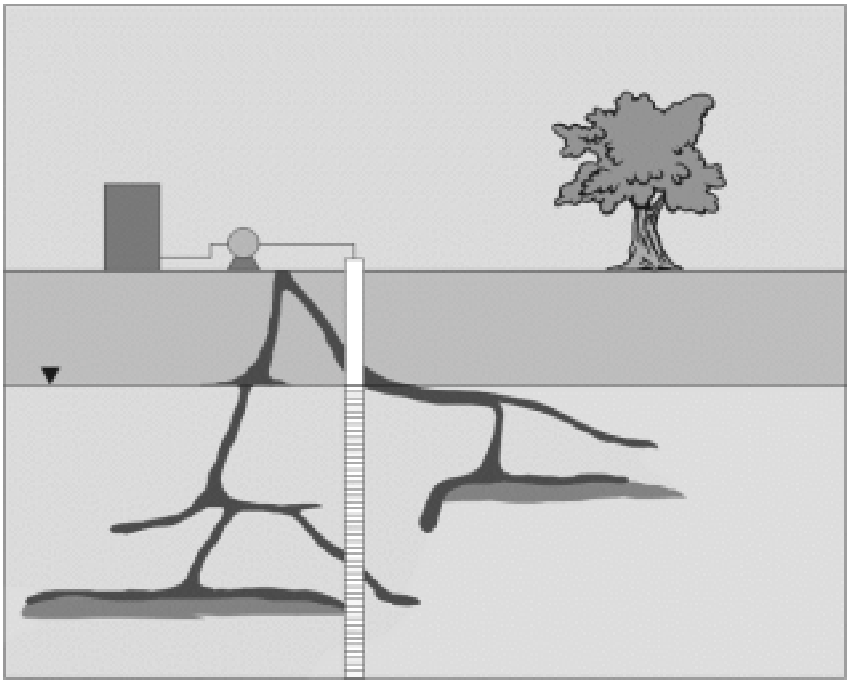
Miscellaneous optimum pH 3-4; metals mobility; exothermic; stabilizers

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. $O_2(g)$ production
8. Undesirable reaction byproducts
9. Enhanced volatilization and transport
10. Unreactive target compounds



Cross-section of hazardous waste spill/release



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

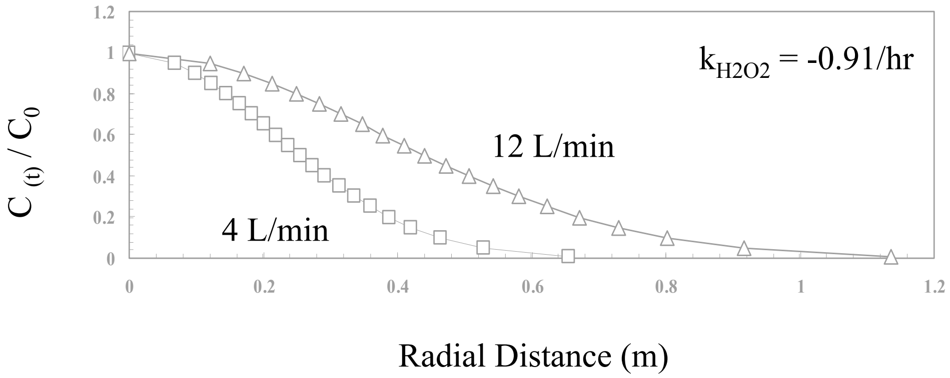
1. Injectate volume vs. pore volume target area
2. H_2O_2 concentration
3. pH adjustment
4. Pulse injection of Fe(II) and H_2O_2
5. Injection strategy

H_2O_2 Reaction, Subsurface Transport

$$[H_2O_{2(t)}] / [H_2O_2]_O = \exp(-K_{H2O2}\, R^2\, \pi\, Z\, \eta / Q)$$

(After, Clayton, 1998)

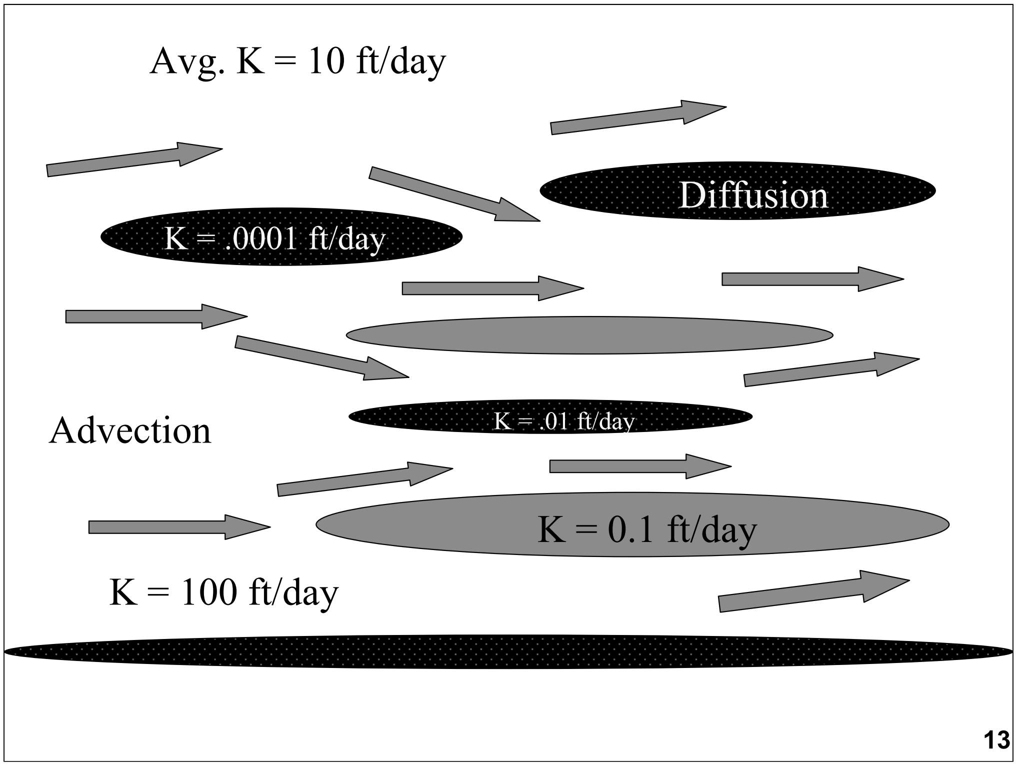
Flow, well spacing, pH



Other Chemical Reagents

Reactions/interactions

Fe(II) - precipitation, complexation, oxidation
Acid - consumed by acid neutralizing capacity
Stabilizers (H_2O_2, Fe(II)) - precipitation, complexation, oxidation



Avg. K = 10 ft/day

Diffusion

K = .0001 ft/day

Advection

K = .01 ft/day

K = 0.1 ft/day

K = 100 ft/day

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 << H_2O_2 reaction

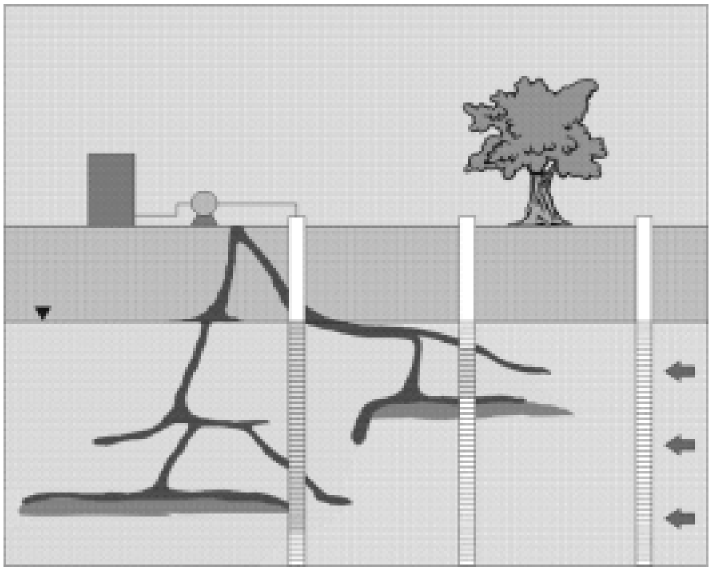
Multiple applications

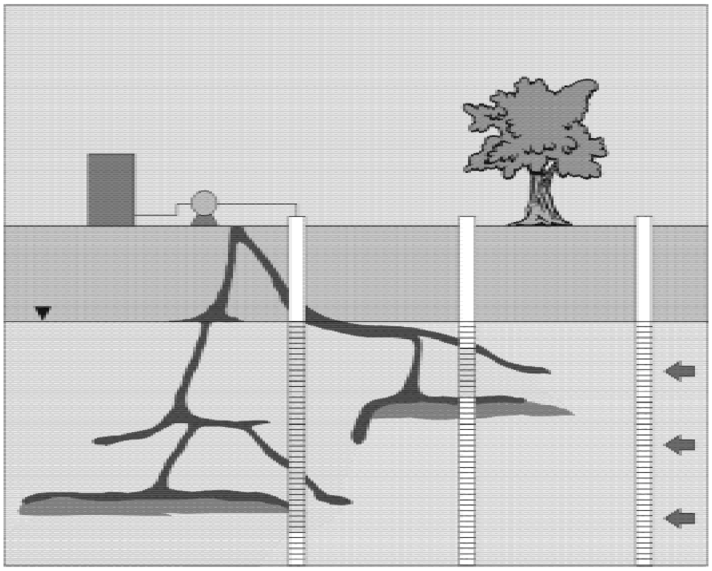
Transport Issues

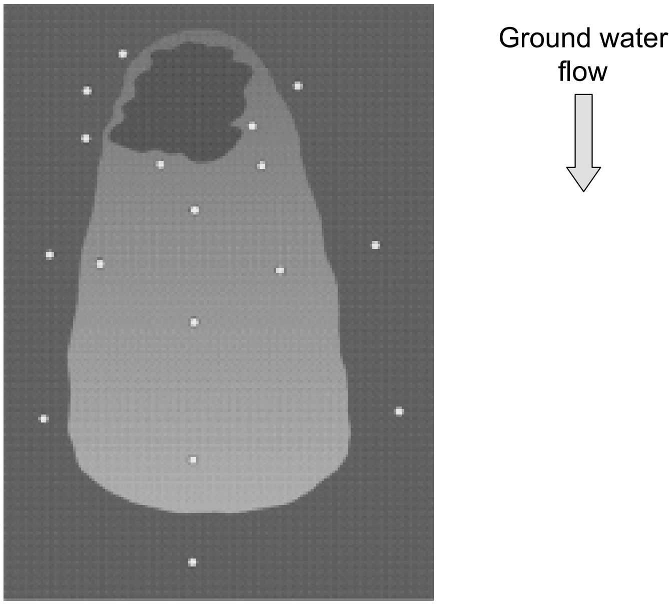
Representative volume

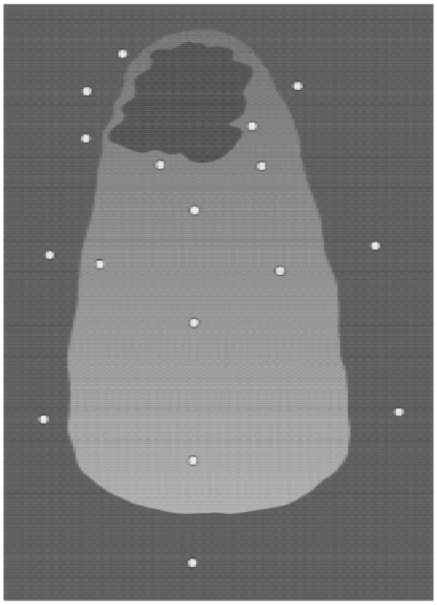
Heat and O_2(g) released - impact

- 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






Ground water flow



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_2O_2 - aqueous

Off-gas, soil gas samples

Establish sentry wells

… performance monitoring

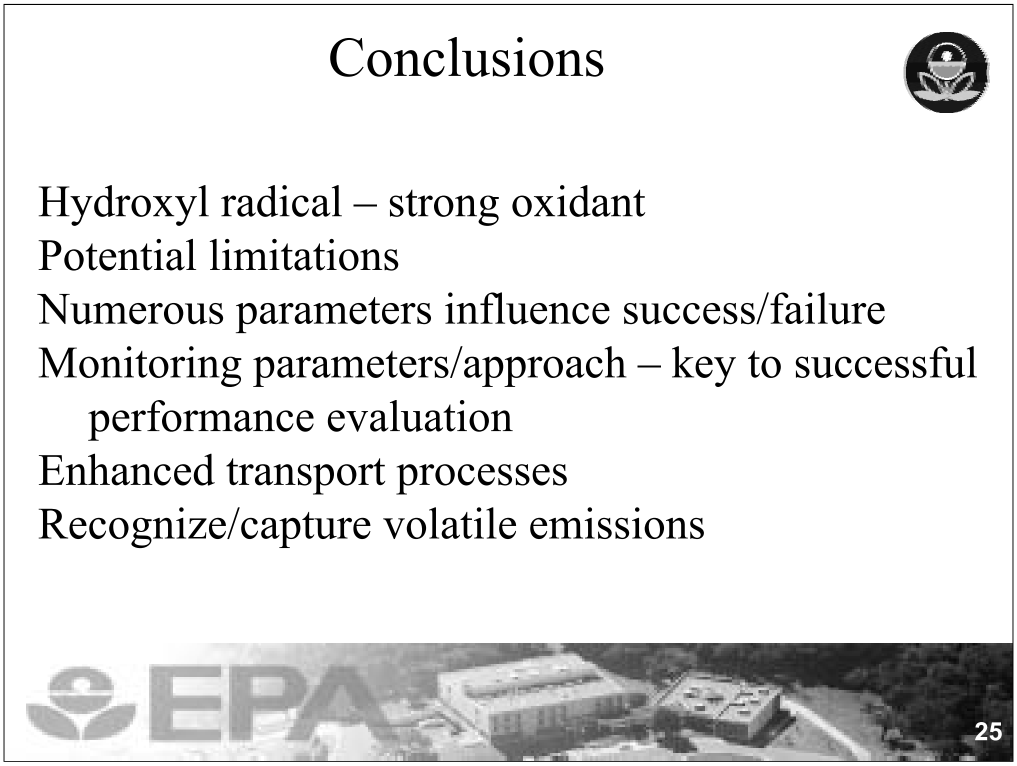
- Ground water monitoring
  - Low priority - limited value for performance evaluation
    - CO_2
    - DO
    - TOC
    - COD
    - Conductivity
    - ORP
    - Temperature

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

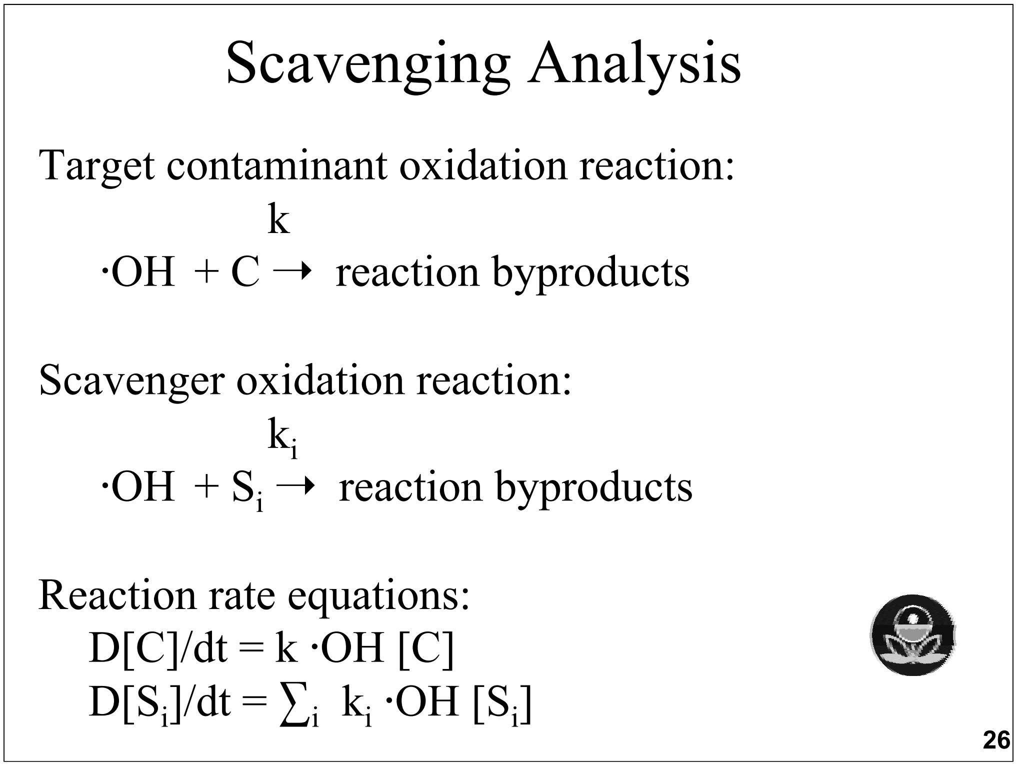
Health and Safety

Heat released
$O_2(g)$ released + Flammable vapors
Enhanced volatilization
Accumulation of vapors (buildings, utilities)



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



Scavenging Analysis

Target contaminant oxidation reaction:

$$\cdot OH + C \xrightarrow{k} \text{reaction byproducts}$$

Scavenger oxidation reaction:

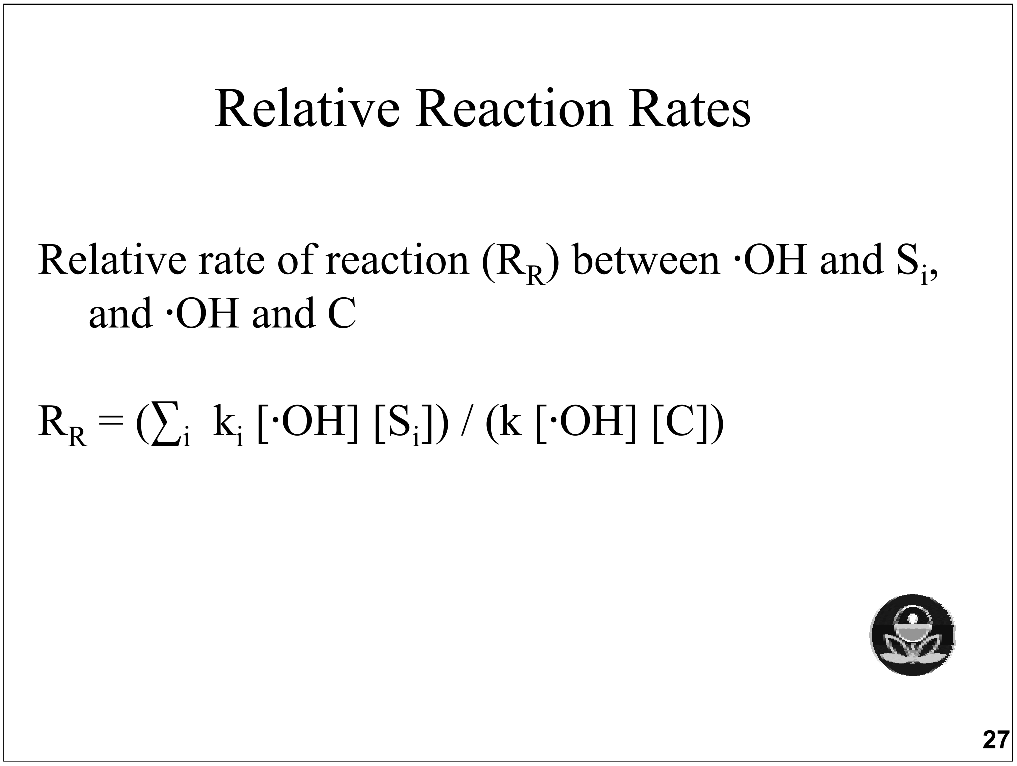
$$\cdot OH + S_i \xrightarrow{k_i} \text{reaction byproducts}$$

Reaction rate equations:

$$D[C]/dt = k \cdot OH\,[C]$$

$$D[S_i]/dt = \sum_i k_i \cdot OH\,[S_i]$$

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 ·OH and the target contaminants (C) and scavengers (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 ·OH and S_i, and ·OH and C

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

The rate of reaction between ·OH and scavenger relative to ·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 ($\cdot OH/ \cdot O^-$) 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

$[TCE] = 450\ \mu g/L\ (3.42\times10^{-6}\ M)$; $k = 4.2\times10^{9}$ L/mol-s
$[Cl^-] = 1250$ mg/L $(3.52\times10^{-2}\ M)$; $k = 4.3\times10^{9}$ L/mol-s
$[CO_3^{2-}] = 150$ mg/L $(2.5\times10^{-3}\ M)$; $k = 3.9\times10^{8}$ L/mol-s
$[\cdot OH]$ assume 10^{-15} M

$R_R = 10,600$

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 $[Cl^-]$ 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, $[Cl^-]$ 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_3^{2-} and Cl^-. This does not include the effects of other potential scavengers present in the ground water (including H_2O_2) 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_2O_2 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_2O_2 decomposition and H_2O_2 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 (2.5×10^{-5}M); k = 2.6×10^{9} L/mol-s
[Cl^-] = 45 mg/L (1.27×10^{-3}M); k = 4.3×10^{9} L/mol-s
[H_2O_2]= 50% , 500,000 mg/L (1.47×10^{1}M);
k = 2.7×10^{7} L/mol-s
[·OH] assume 10^{-15} mol/L

R_R = 6,180

Example 2 considers the role of H_2O_2 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_2O_2 and Cl^-. This condition is transient - as [PCE] and [H_2O_2] 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_2O_2 may be needed. The associated costs may increase significantly.

Process optimization could include a decrease in [H_2O_2] to 5% to minimize scavenging by H_2O_2 and use of smaller spacing between injection wells. Assuming the same mass of H_2O_2 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.