# In-Situ Chemical Oxidation
## (Basics, Theory, Design, & Application)


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**Aquifer Solutions, Inc.**


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Toxic Substances Control

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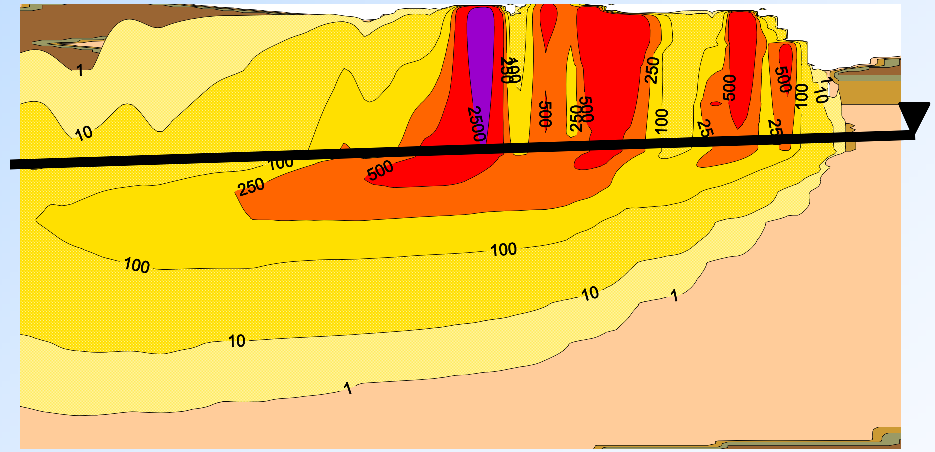
# Outline of This Presentation

- ISCO Basics – Overview
- ISCO Chemistry and Oxidant Alternatives
- ISCO Design Considerations
  - ISCO Application Configuration Alternatives
  - ISCO Dose Design Approaches
  - Oxidant Reactive Transport – Delivery Issues
- Lessons Learned from Industry Case Studies
- ISCO Safety

# ISCO Technology Primer

- In Situ Chemical Oxidation (ISCO)
- Injection of oxidant chemicals to degrade Organic COCs
  - Chlorinated Organics, Hydrocarbons, PAHs, Pesticides, Explosives, others
- Involves Destroying molecular bonds of COCs
  - Oxidation = removal of electrons
- Requires The Following:
  - Favorable Contaminant Chemical Treatability
  - Appropriately Aggressive Design and Application
    - Adequate Oxidant Dose
    - Effective Contact with Contaminants
    - Often Involves Multiple Injection Events

# The Technical Goals of ISCO Can Be Varied




- Source Zone Treatment
  - NAPL Treatment
  - Soil Treatment
  - Mass Reduction
  - Flux Reduction
  - Numerical Concentration Goal
  - Vadose Zone vs. Saturated Zone
- Groundwater Plume Treatment
  - Groundwater Attenuation After Source Zone Oxidation
  - Direct Plume Treatment
  - Barrier Configurations

# Advantages and Disadvantages of ISCO

- Advantages
  - Fast Treatment (weeks to months)
  - Temporary Facilities
  - Treatment to Low Levels (ND in some cases)
  - Effective on Some Hard-to-Treat Compounds
- Disadvantages
  - Requires Spending “Today’s” Money to Get Fast Cleanup
  - Limitations of Fast-Reacting Chemistry
  - Can Be Geochemical Side-Effects (not unique to ISCO)

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# Primary Challenges for Effective ISCO Design & Application

- Proper Oxidant Dosage
  - Not Stoichiometric With Contaminants
  - Soil Oxidant Demand Based for Some Oxidants
  - Kinetic-Based Oxidant Consumption for Others
- Subsurface Oxidant Transport and Delivery
  - Hydro & Geologic Limitations
  - Oxidant Reaction Kinetic Limitations
- Oxidant Persistence
  - Oxidant Reaction Rates vs. Contaminant Reaction Rates
  - Need for Multiple Injection Events

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# Some Common Questions About ISCO?

- Is the Oxidation Reaction Complete, Are By-Products Present and What Is Their Fate?
- How Much Oxidant Do I Need?

Not Dealt With Herein:

- Will I Oxidize/Mobilize Metals?
- Will Oxidation Kill-Off Subsurface Microbes and Halt Natural Attenuation Processes?
- Cost

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# ISCO Theory

- Oxidant Alternatives
- Reaction Chemistry
  - Oxidant Reactions
  - Contaminant Destruction Reactions
- Reaction Rates and Kinetics
- Subsurface Delivery

# Oxidant Alternatives

| Oxidant Formulation | Two-Part Formula? | Advanced Oxidation (radical formation) | Direct Oxidation | General Considerations | Interesting Developments |
|---|---|---|---|---|---|
| Permanganate $KMnO_4$ or $NaMnO_4$ | No | No | Yes | Favorable Longevity<br>Solids Formation | Extensively researched via SERDP, others |
| Catalyzed Hydrogen Peroxide | Yes | Yes | No | Complex Chemistry<br>Off gas generation | Peroxide Stabilizers |
| Activated Persulfate | Yes | Yes | No | Complex Chemistry<br>persistent un-activated | New Activators |
| Ozone | No | Yes | Yes | Gaseous Delivery<br>Short Half-Life | Vadose Zone Sources |
| Solid Peroxygens $MgO_2$ or $CaO_2$ | No | No | No | Decomposes to release hydrogen peroxide and oxygen | Application as persulfate activator |

# Permanganate Summary

- Potassium Permanganate ($KMnO_4$)
- Sodium Permanganate ($NaMnO_4$)
- $MnO_4^-$ ion is the active oxidant

<u>Characteristics</u>

- Longevity
- Not Advanced Oxidation, so doesn't all recalcitrant organics
- Manganese oxide solids
  - recirc solids handling
  - Pure phase DNAPL coating

# Permanganate Chemistry "Direct Oxidation"

Balanced Reaction (simplified):

$$2KMnO_4 + C_2HCl_3 \rightarrow 2CO_2 + 2MnO_2 + 2K^+ + 3Cl^- + H^+$$

$$2MnO_4^- + 6e^- \rightarrow 2MnO_2$$

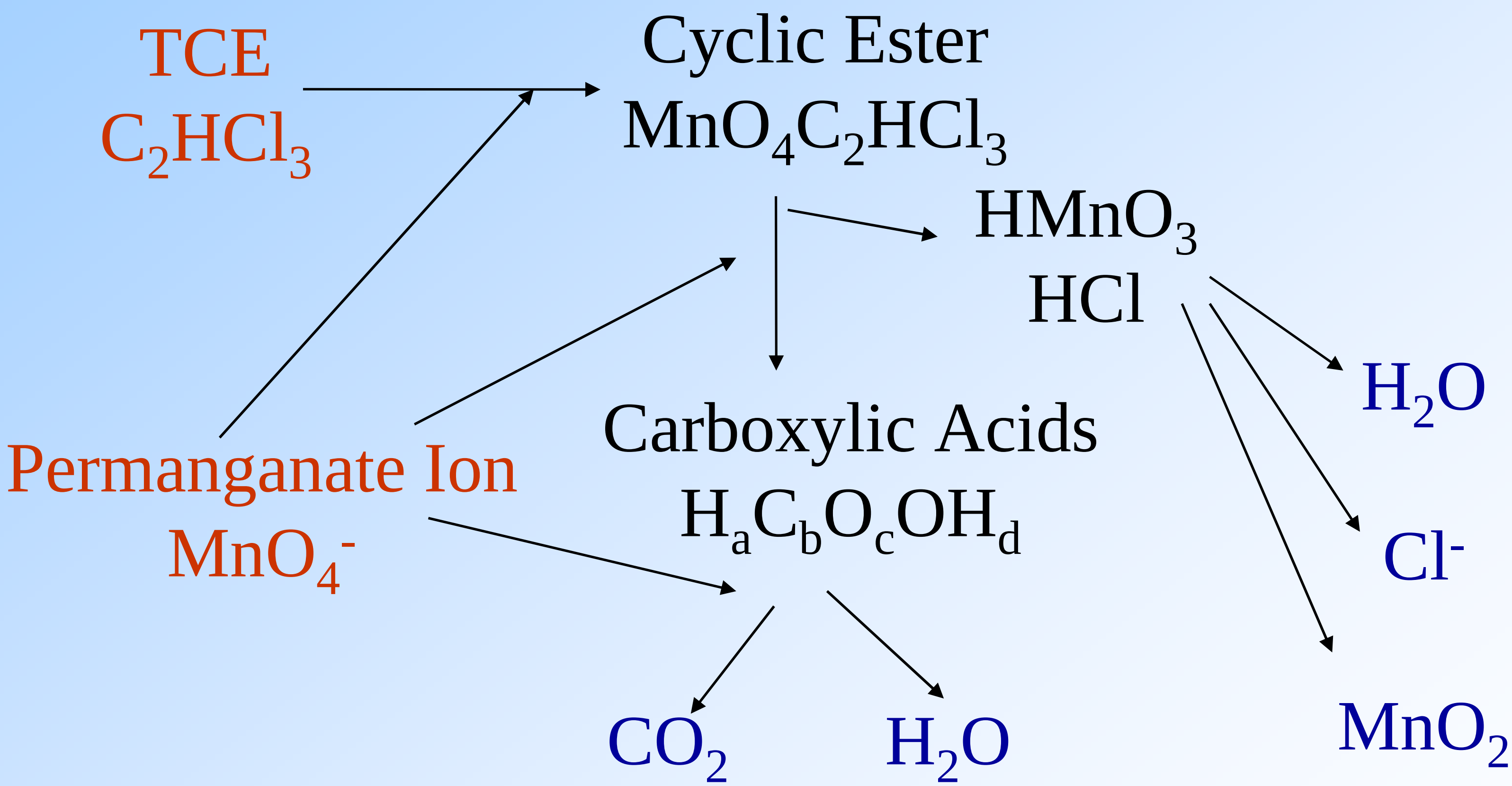
Permanganate Reduction (adding electrons)

*electron transfer*

$$CH_2Cl_3H \rightarrow 6e- + 2CO_2 + 3Cl- + H^+$$

TCE Oxidation (removing electrons)

# Permanganate – TCE Reaction Pathways




**Source: Yan and Schwartz (1998)**

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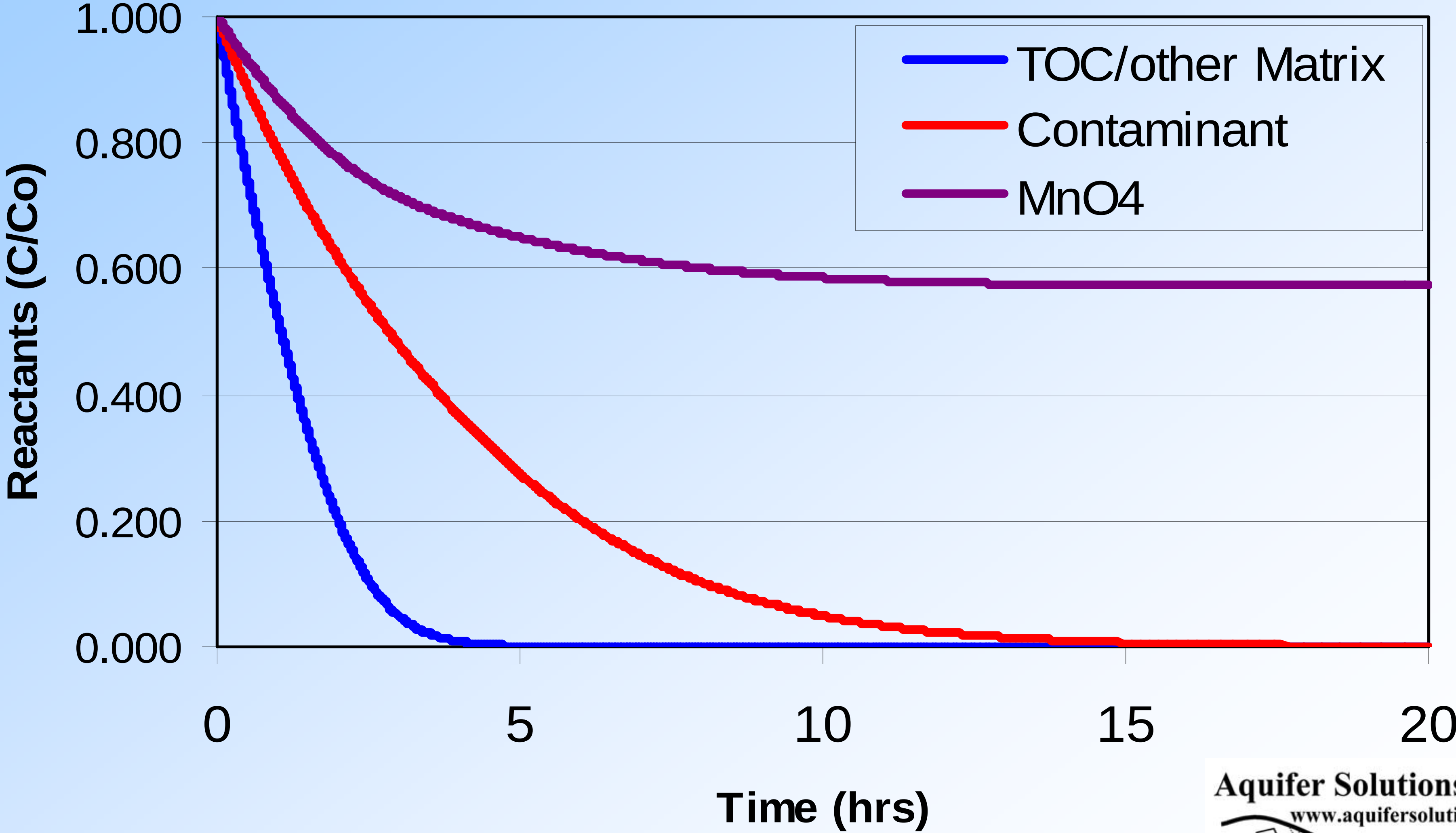
# Permanganate Reaction Kinetics Second Order - Multiple Species

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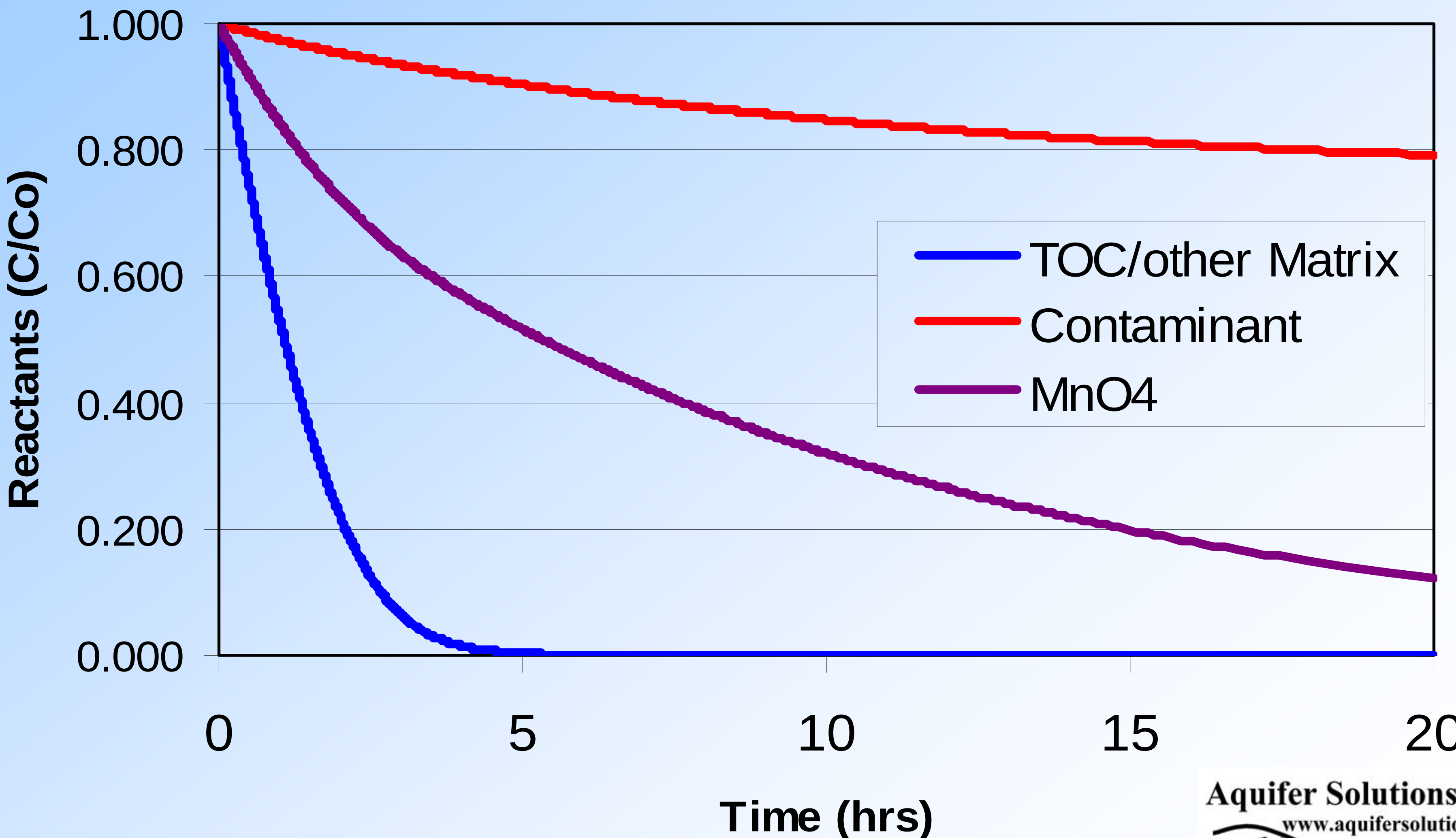
# Permanganate Kinetics at High Contaminant Concentrations

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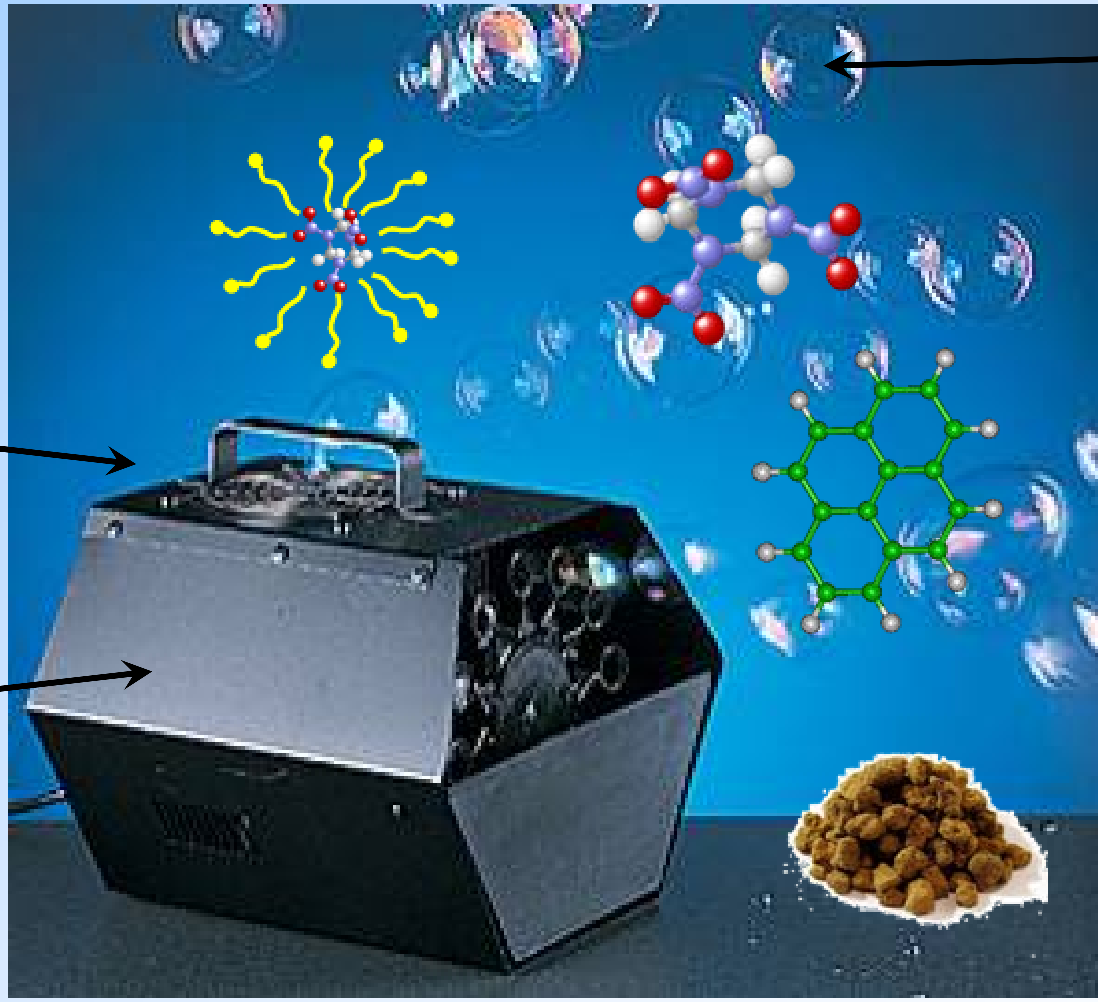
# Advanced Oxidation is Like… The Bubble Machine!

**Activator**
- $Fe^{2+}$
- hydroxide ($OH^-$)
- heat
- soil minerals

**Supply of Oxidant**
- ozone
- peroxide
- persulfate



**Radical Species Propagated**
- hydroxyl radical
- sulfate radical
- hydroperoxide
- superoxide

**Oxidizable Species**
- Contaminants
- Soil Minerals
- Soil Organic Carbon
- Surfactants

Radical Scavengers Compete with Contaminants

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# Catalyzed Hydrogen Peroxide Summary

- Advanced Oxidation Process
  - Hydrogen Peroxide Reactions Produce Highly Reactive radical species
  - Radicals are the active oxidants

<u>Characteristics</u>

- Fairly Fast Reaction Chemistry
- Peroxide Stabilizers Can Slow Down Process
- Wide Range of Radicals Produced
- Radical Production Subject to Optimal Process Chemistry

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# Catalyzed Hydrogen Peroxide Reactions

- Classic Fenton's Reaction (pH 2.5/3.5; 300 ppm peroxide)
  - $H_2O_2 + Fe^{2+}$ (acid) $\rightarrow$ $OH^{\bullet} + OH^{-} + Fe^{3+}$

**Examples of Radical Propagation Reactions**

- $OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$
- $H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+}$
- $HO_2^{\bullet} \rightarrow O_2^{\bullet -} + H^{+}$

Examples of Diverse Reactions

$OH^{\bullet}$ = hydroxyl radical (oxidant)

$HO_2^{\bullet}$ = hydroperoxide radical (reductant)

$O_2^{\bullet -}$ = superoxide radical (oxidant and reductant)

Source: ITRC ISCO-2, 2005

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# Persulfate Summary

- Advanced Oxidation Process
  - Persulfate Reactions Produce Highly Reactive radical species
  - Radicals are the active oxidants
  - Unactivated Persulfate is Stable and Persistent
- Many Different possible Activation Methods
  - iron
  - base
  - heat
  - ozone
  - hydrogen peroxide
  - solid peroxygens (yield hydrogen peroxide)

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# Persulfate Chemistry

**The Simplified Paradigm for Persulfate Activation:**

- **Catalyzed Persulfate**:

$$Me^{n+} + S_2O_8^{\,2-} \rightarrow SO_4^{-\bullet} + Me^{(n+1)+} + SO_4^{2-}$$

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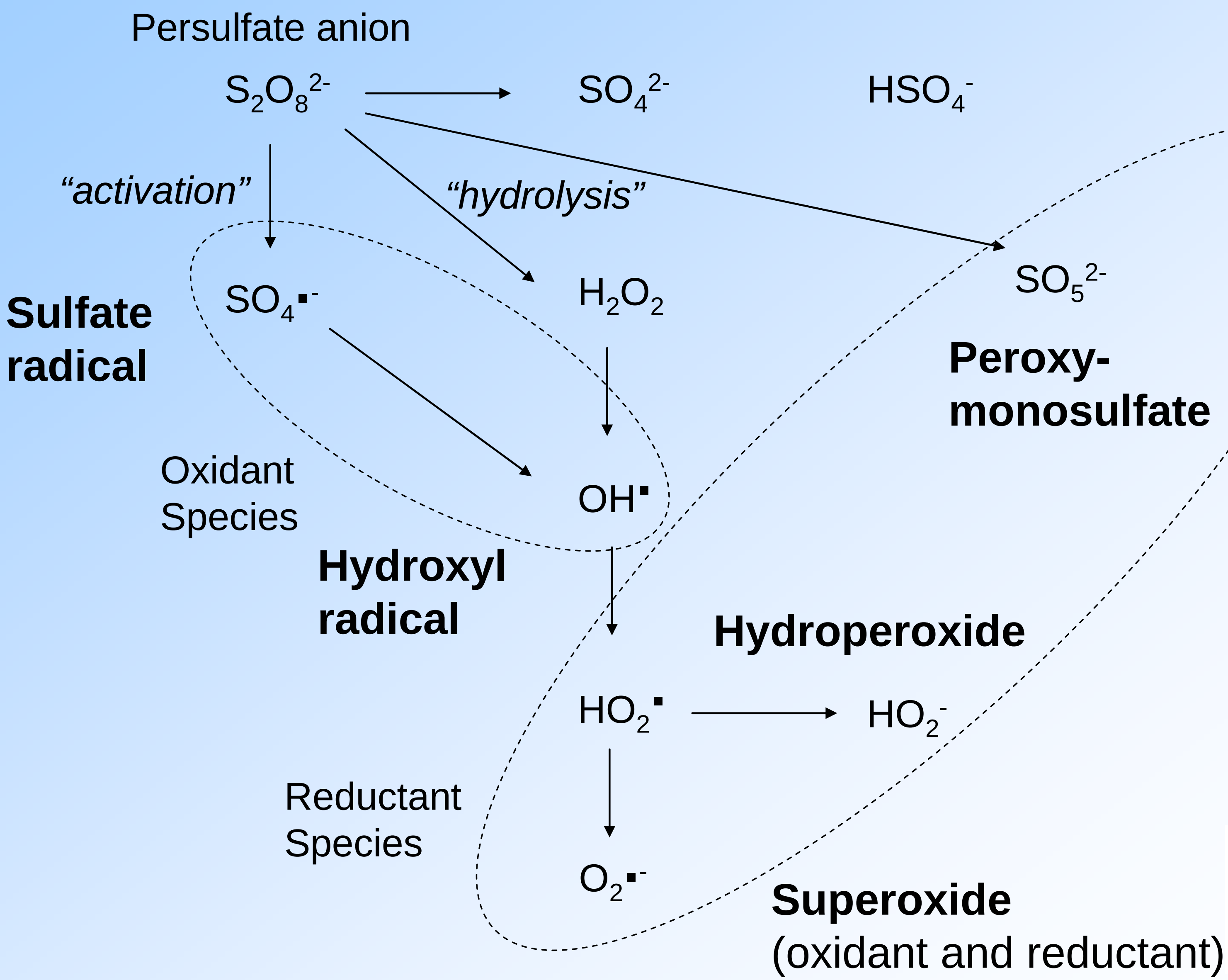
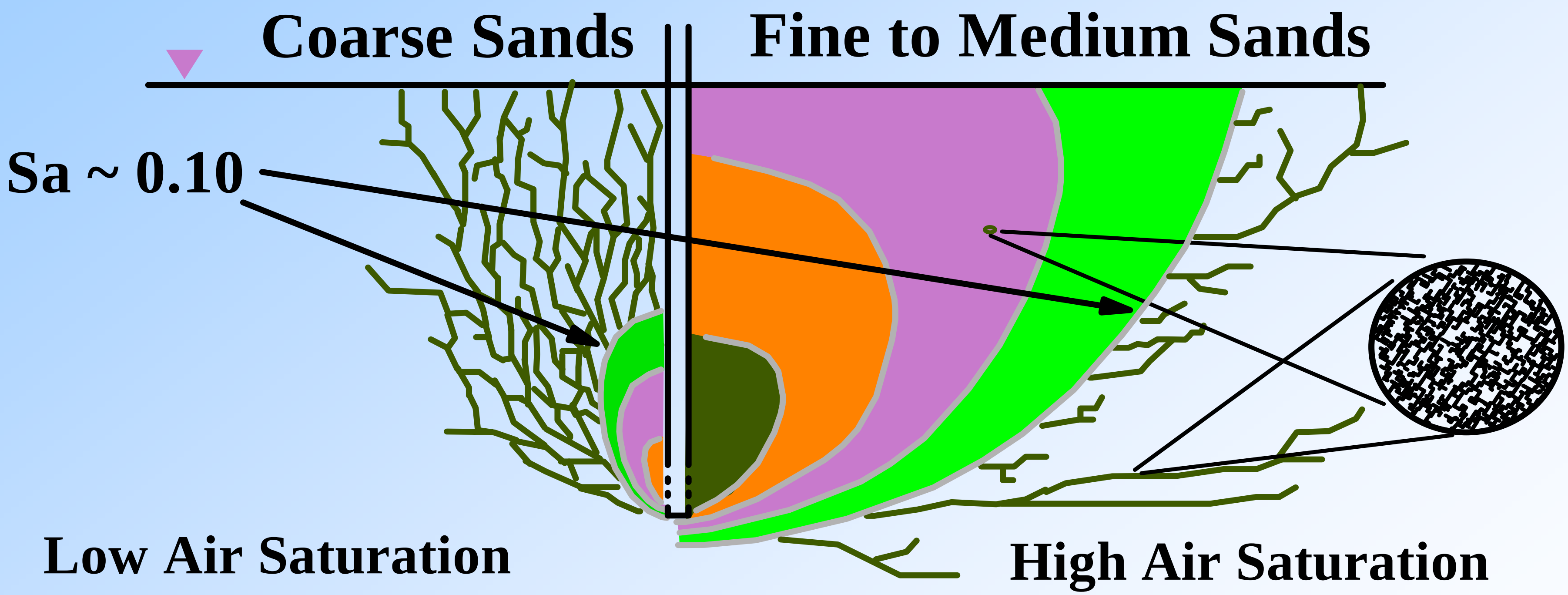
# Emerging Understanding of Persulfate Radical Propagation



# Ozone Summary

- Ozone ($O_3$) is a gas
- Can be Direct Oxidation or Advanced oxidation
  - often activated by naturally occurring minerals
- Ozone Sparging or Vadose Zone
- Continuous Process, not Batch

# Gas (Ozone) Sparging Physics




**Low Air Saturation**
**Air Channeling**
**Continuum Flow in Core**
**Vertical Flow Dominant**

**High Air Saturation**
**Continuum Flow**
**Stratigraphic Channeling**
**Larger Flow Radius**

# Ozone Chemistry

- Chain Initiation Reactions:
  - $O_3 + OH^- \rightarrow O_2^{\bullet -} + HO_2^{\cdot}$
- Chain Propagation Reactions:
  - $HO_2^{\bullet} \leftrightarrow O_2^{\bullet -} + H^+$
  - $HO_2^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + HO_2^{-}$
  - $O_3 + HO_2^{-} \rightarrow OH^{\bullet} + O_2^{\bullet -} + O_2$

$OH^{\bullet}$ = hydroxyl radical (oxidant)
$HO_2^{\bullet}$ = hydroperoxide radical (reductant)
$O_2^{\bullet -}$ = superoxide radical (oxidant and reductant)

**Source: ITRC ISCO-2, 2005**

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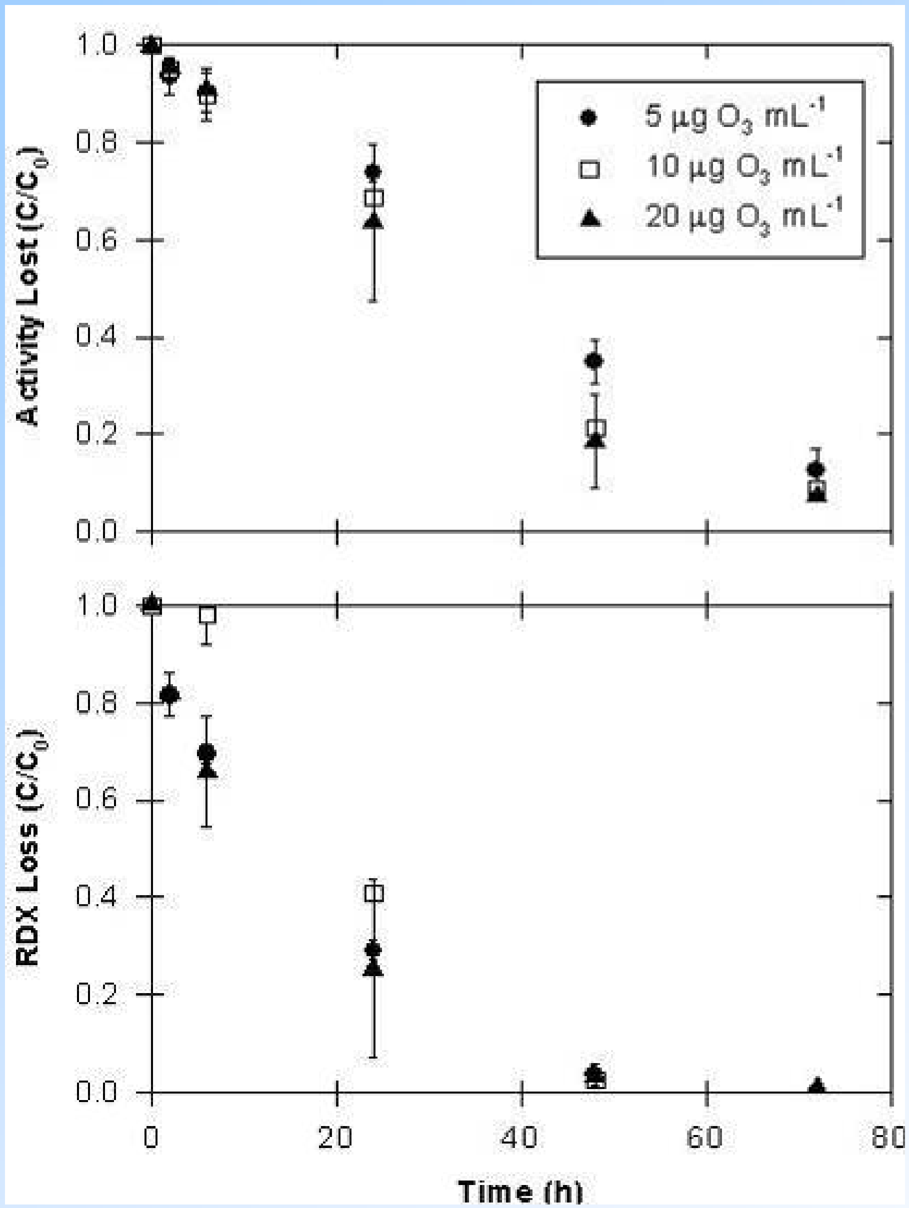
# Bench Test Results
# Ozone-RDX Soil Columns




**Bench Testing Data Courtesy of:**

**Dr. Steve Comfort**

School of Natural Resources

University of Nebraska

- Radio-labeled RDX used to assess mineralization to $CO_2$.
- 100% RDX Destruction in 3 days.
- ~90% RDX Mineralization in 3 days.
- Ozonation improved aerobic biodegradation of RDX

*Adam, et al., J. Env. Eng. Vol. 132, No. 12, December 2006, pp. 1580-1588.*

University of Nebraska Lincoln

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# DESIGN

- Design Issues Involve:
  - Oxidant Chemical Selection
  - Oxidant Dose Determination
  - Injection Volume and Concentration
  - Number of Application Events Required
  - Subsurface Oxidant Delivery and Transport
- Engineering
- Application/Execution

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# Ultimately, the goal of the amendment delivery designer is to…

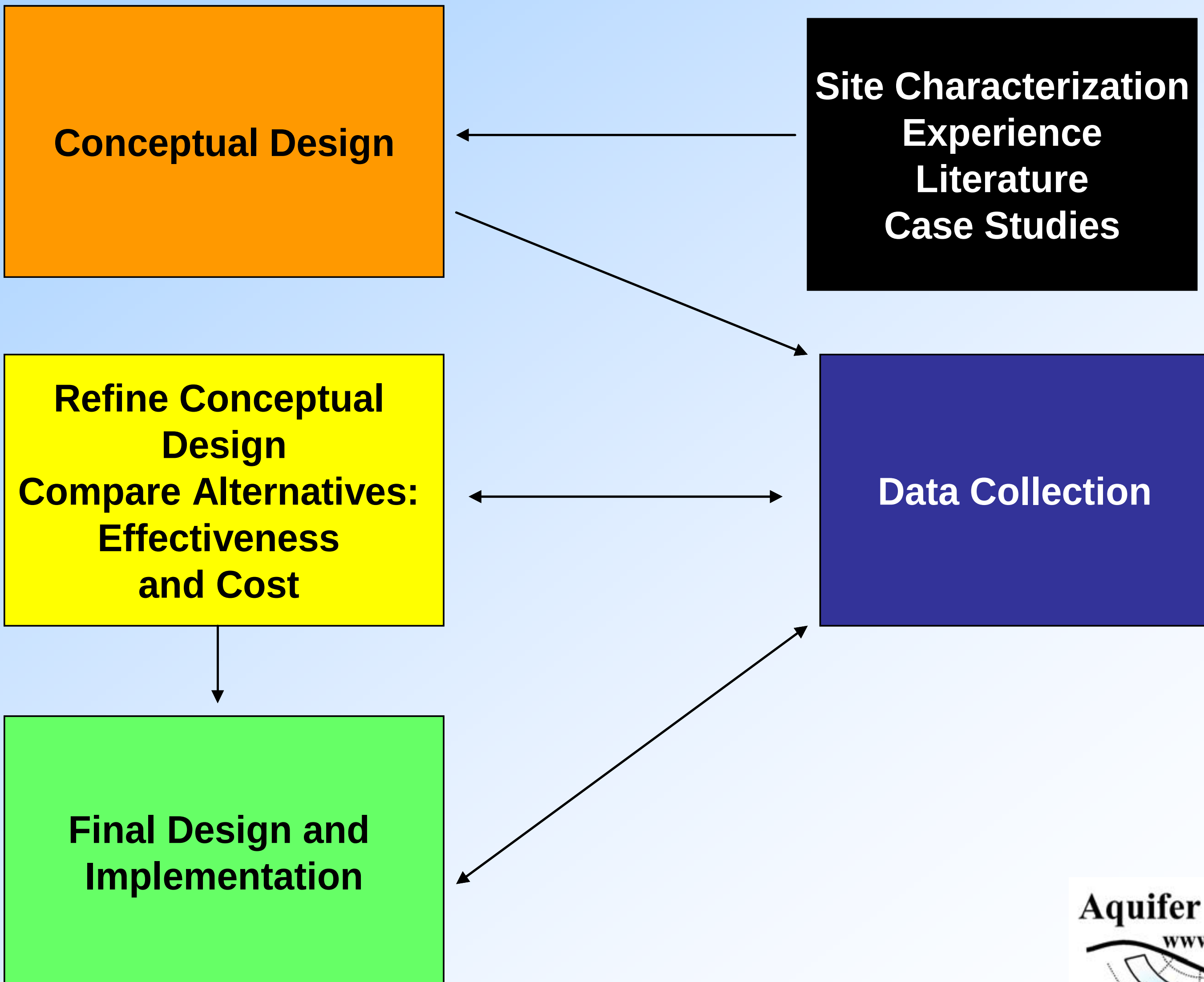
*Integrate a range of chemical, physical, and geological variables to develop a strategy which will deliver an adequate amendment concentration in contact with the contaminants for an adequate duration to achieve the treatment goals.*

# Factors for Success / Failure

- Success Factors
  - Oxidation Reactions
  - Oxidant Dose
  - Oxidant Delivery
  - Project Execution

- Failure Factors
  - Oxidation Reactions
  - Oxidant Dose
  - Oxidant Delivery
  - Project Execution

# Iterative Design Process

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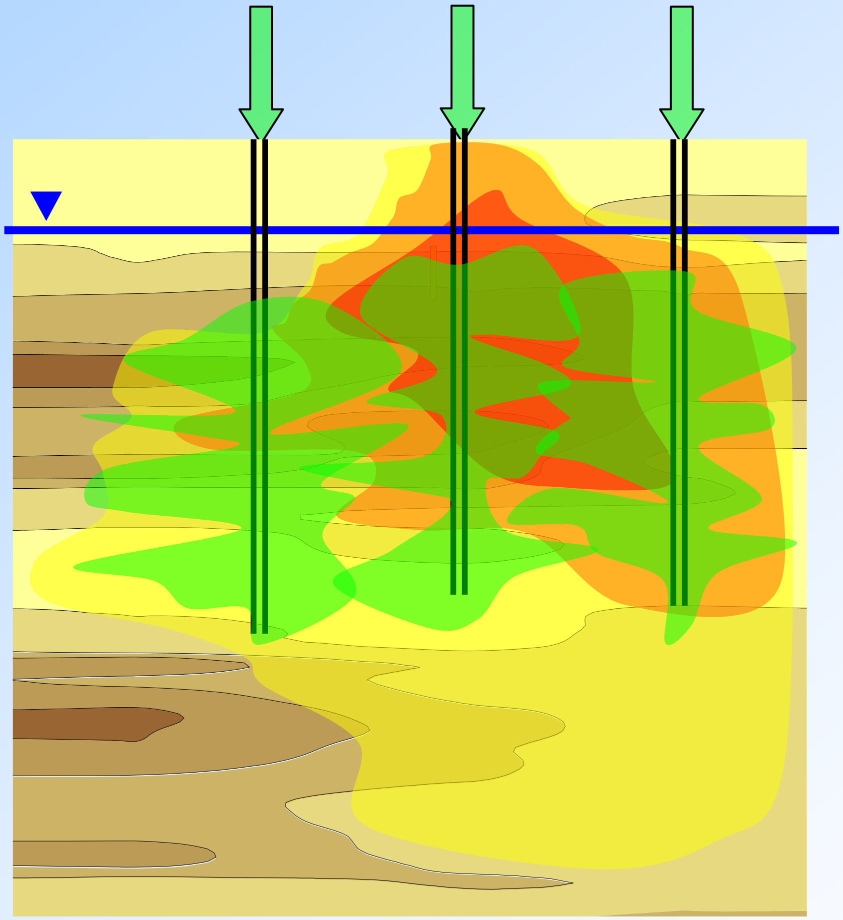
# Design Variables vs. Process Variables

*Design Variables*

<u>Injection Geometry:</u>
Inject Only
Recirculation
Pull/Push
Screen Intervals
Well Spacing
Drill/Inject Tooling

<u>Amendment:</u>
Concentration
Volume
Injection Rate
Injection Duration



*Process Variables*

Heterogeneity
Advection-Dispersion
Mass Transfer
Diffusion Limitations
Reaction Limitations
Reaction Order

<u>Dependence On:</u>
Concentration
Temperature
Time
Geologic Media

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# Oxidant Dose Design Approaches

| **Approach** | **When is it Appropriate** | **Limitations/Challenges** |
|---|---|---|
| Contaminant Stoichiometry | Never, Except as Minimum Estimate | Ignores Side-Reactions<br>Assumes One-Step Reaction |
| Soil Oxidant Demand | Permanganate and Low Contaminant Concentrations | Ultimate Demand Approach is Simplified |
| Soil and Contaminant Demand | Permanganate and High Contaminant Concentrations | Ultimate Demand Approach is Simplified |
| Reaction Rate and Kinetics | When You Have the Data. | Estimating the Reaction Rates |
| Empirical Measurements (Bench or Field) | When You Have the Data. | Requires Representative and Valid Testing |

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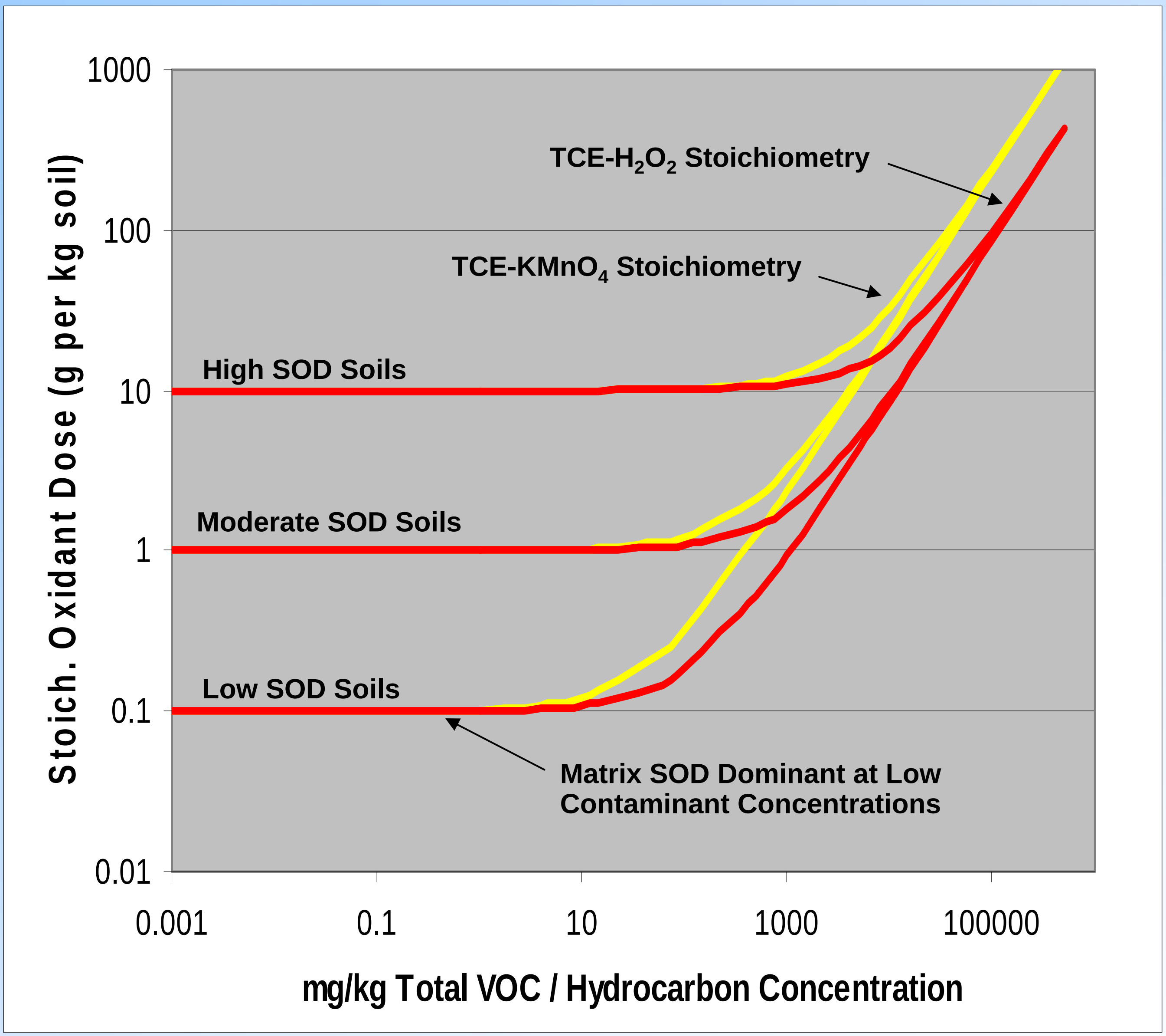
# Simplified Oxidant Stoichiometry and Dose




- Accounts for Soil and Contaminant Demand
- Assumes Uniform Oxidant Distribution
- Does Not Account for Oxidant Concentration-Dependant Reactions of Transport Effects

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# When Reaction Kinetics Drive Dose Determination

- Advanced Oxidation
  - The Bubble Maker only Works Until it Runs out of Soap
- Reactive Transport-Limited Delivery Scenarios
  - Oxidant Concentrations Vary in Space and Time
  - “Average” Dose is Not Limiting
  - Concentration/Persistence at a Point in Space is Limiting

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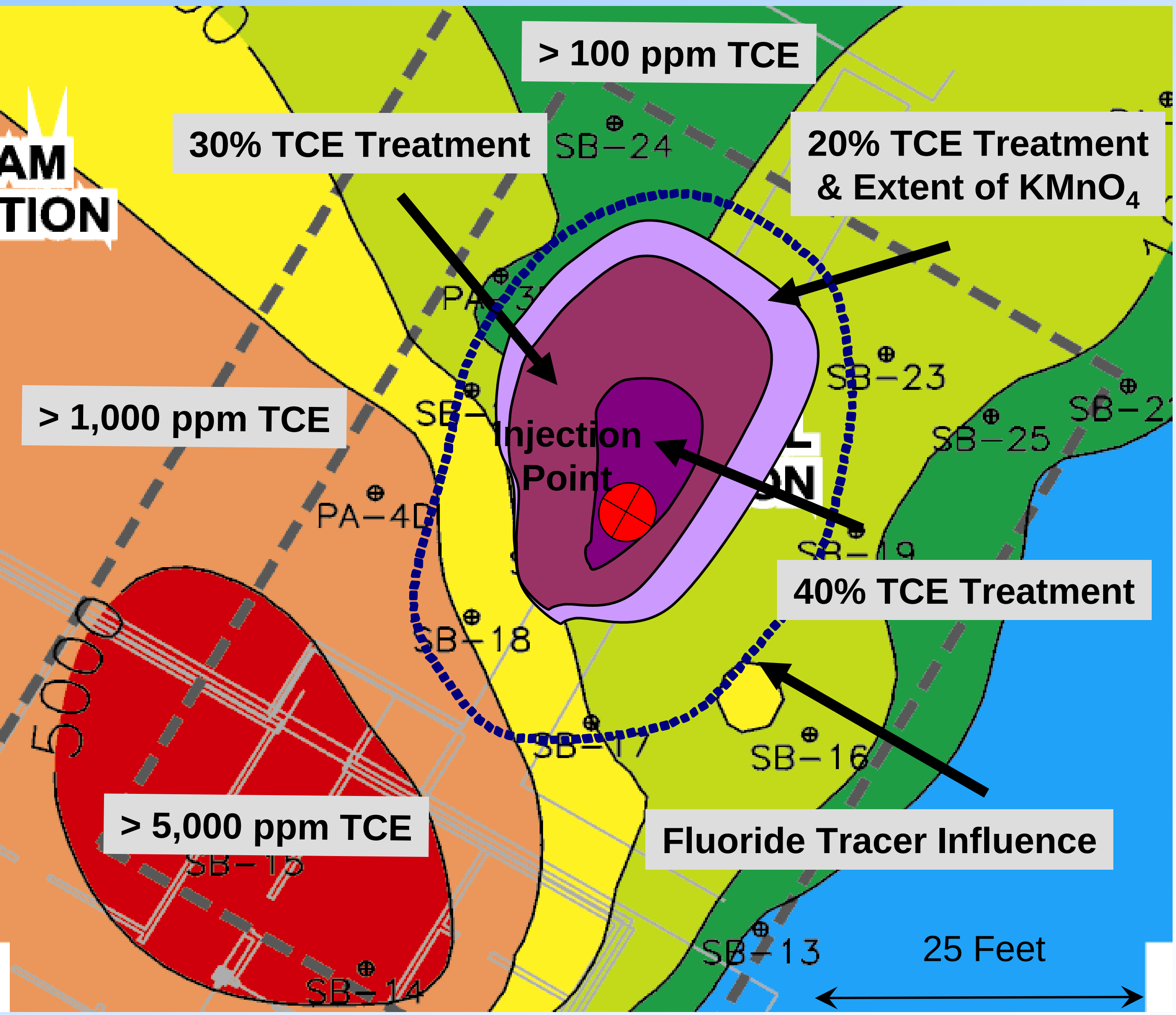
# Reaction-Limited Oxidant Transport/Delivery




- Uniform Delivery of the Dose is Impacted by Heterogeneity, etc.
- Reactive Transport
- Oxidant is Consumed Rapidly in Presence of DNAPL

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# Subsurface Processes Controlling Amendment Delivery

- Advection and Dispersion
- Interphase Mass Transfer
  - COPCs, native species, and Amendment
- Reaction-Limited Transport
  - COPCs, native species, and Amendment
- Density-Driven Transport

# Important Factors in Amendment Transport

- Chemical/Physical Properties of the Amendment Solution,
- Concentration-Dependent Amendment Reactions
  - Second-Order
  - Pseudo First-Order
  - Decomposition
- Amendment-Induced Changes in Sorption and other Geochemical Behaviors,
- Geologic Heterogeneity and Low Permeability Media

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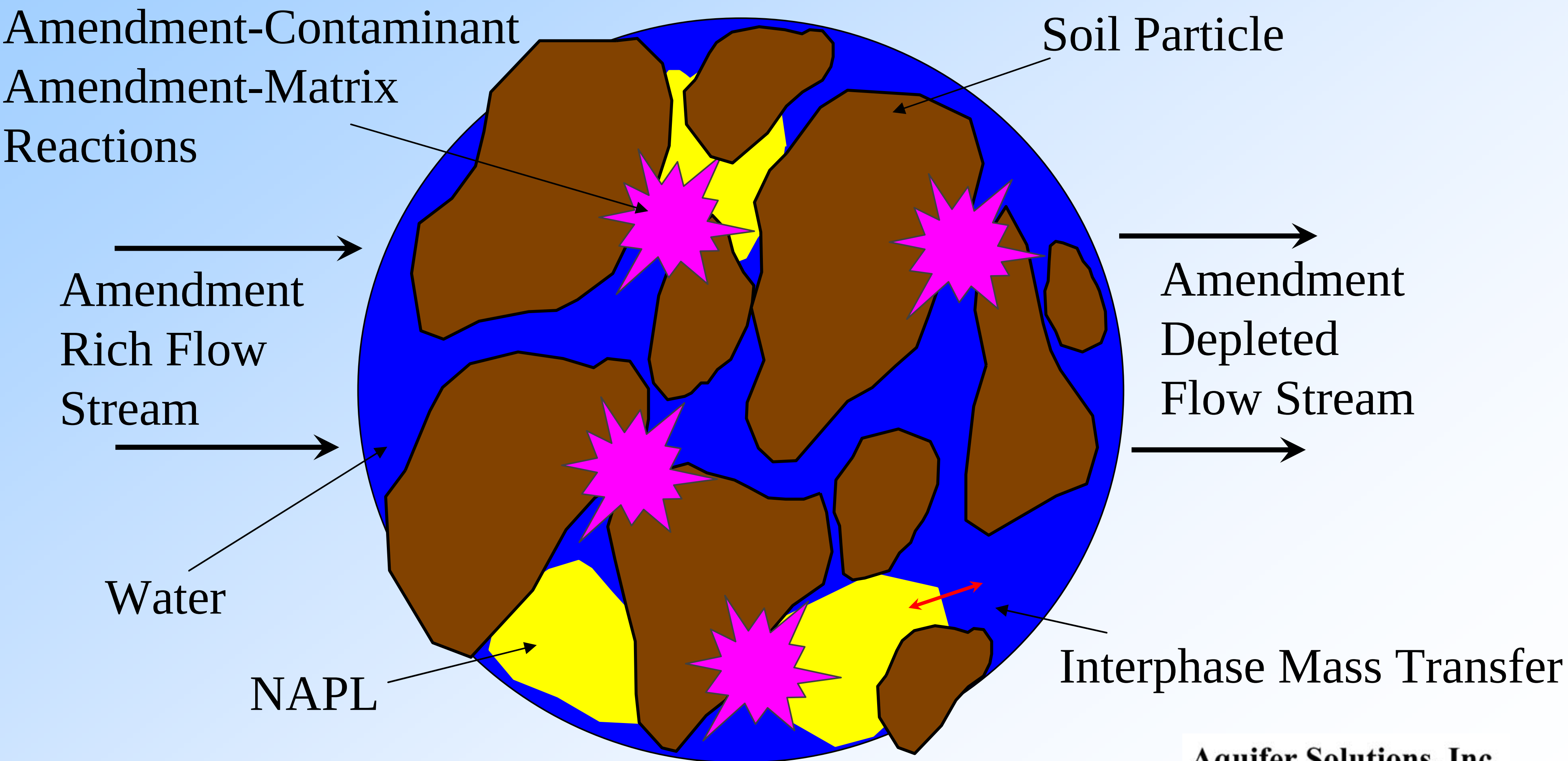
# Pore Scale View of Amendment Reactive Transport

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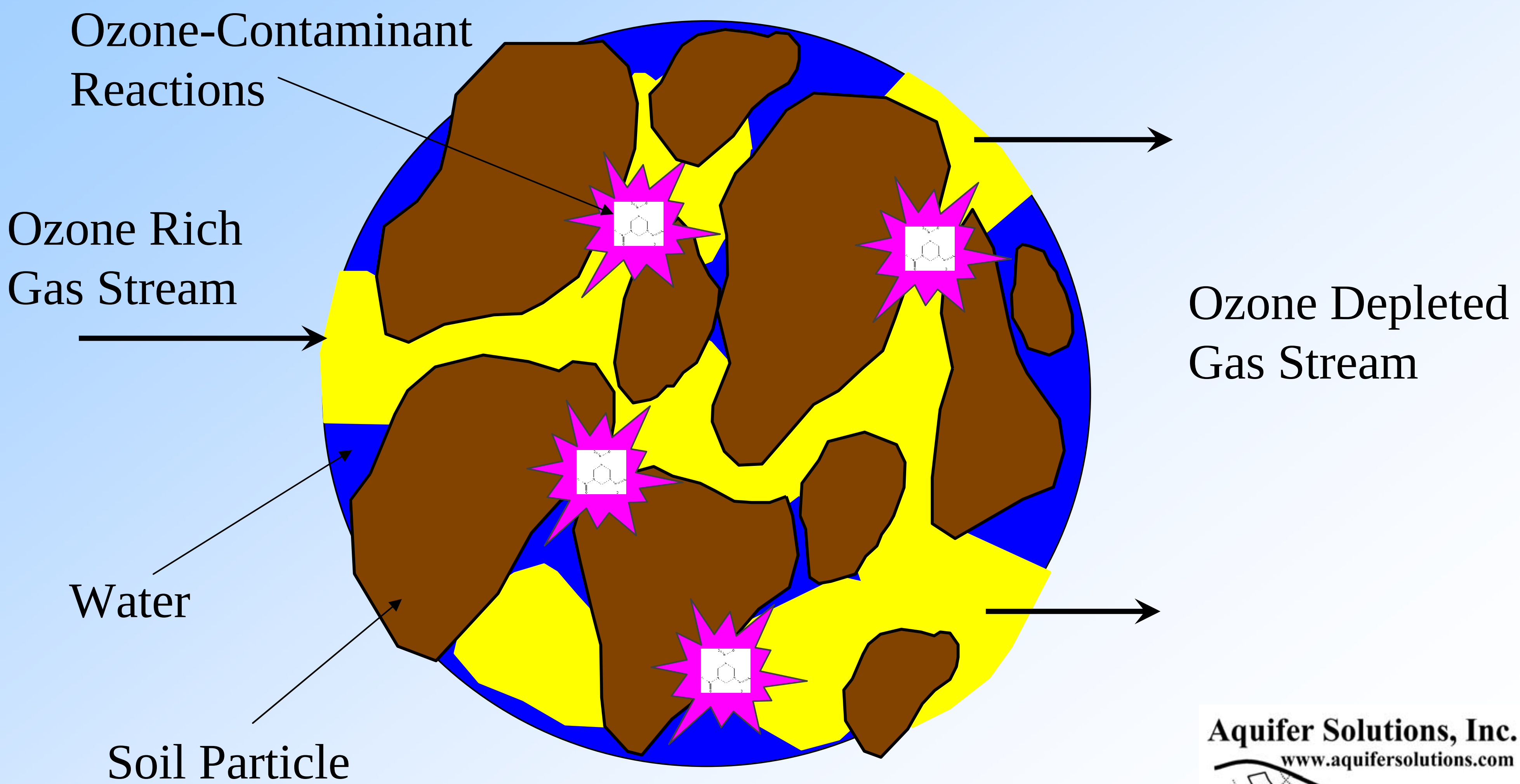
# Ozone Gas
# Mass Transfer and Transport

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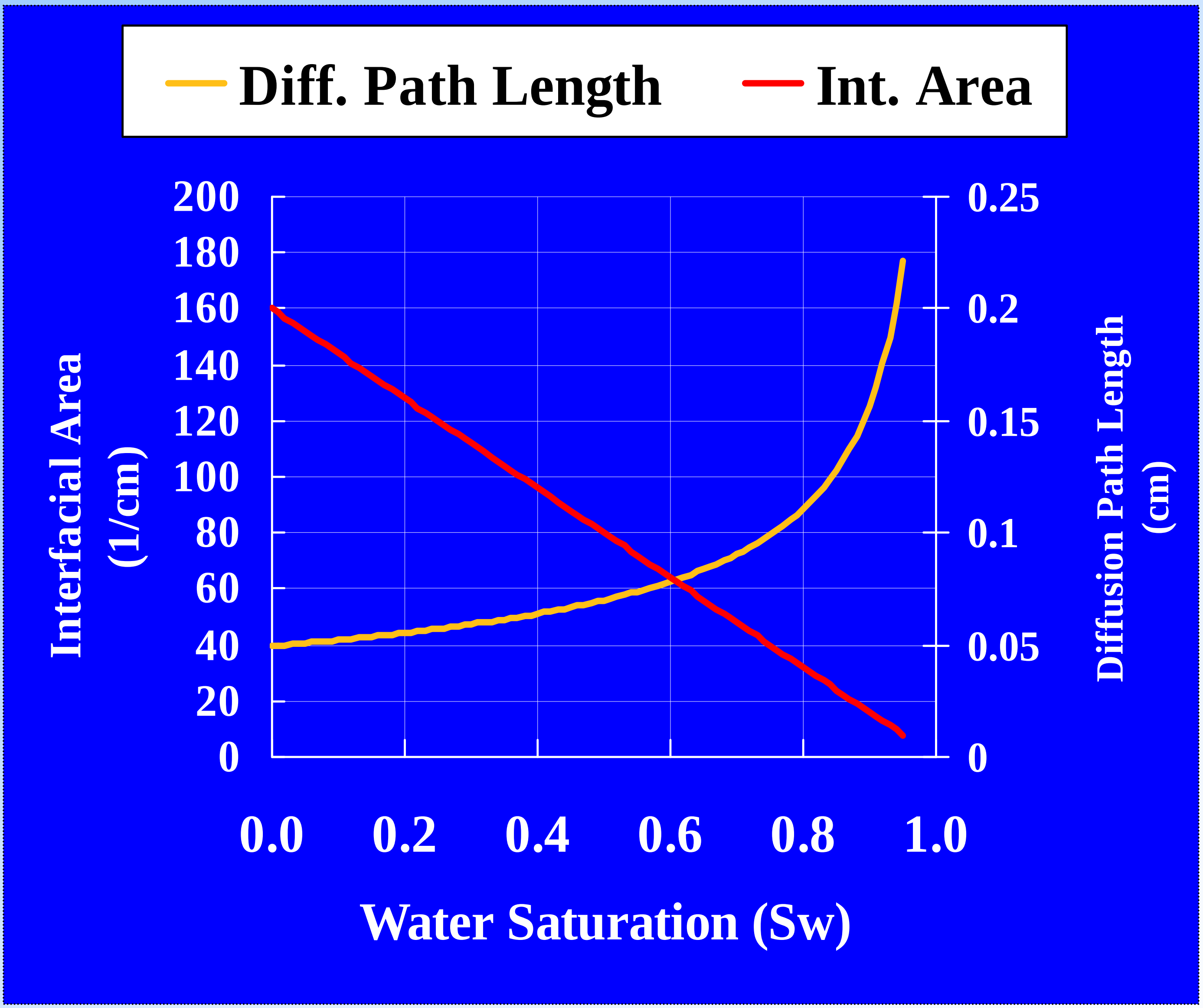
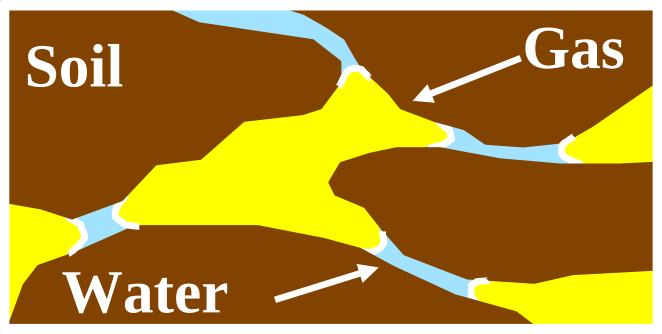
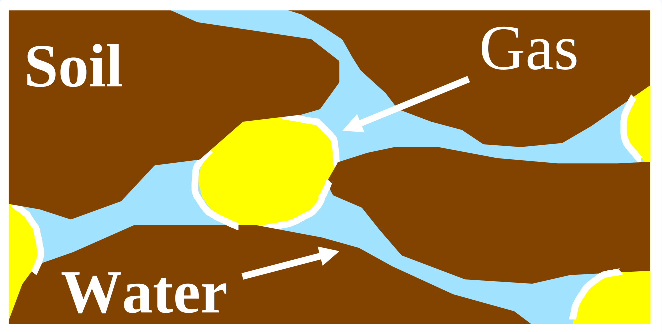
# Ozone Mass Transfer Parameters vs. Fluid Saturation




Water Saturation ~ 0.2




Water Saturation ~ 0.8

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# Amendment Reactive Transport

1-D Advective-Dispersion-Reaction Equation:

$$\frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} - kC$$

Transport = f(Advection + Dispersion – Reaction)

(for simplicity - ignores Interphase Mass Transfer)

Amendment Reaction Rate Controls Transport:

Fast Reaction = transport limited

Slow Reaction = not transport limited

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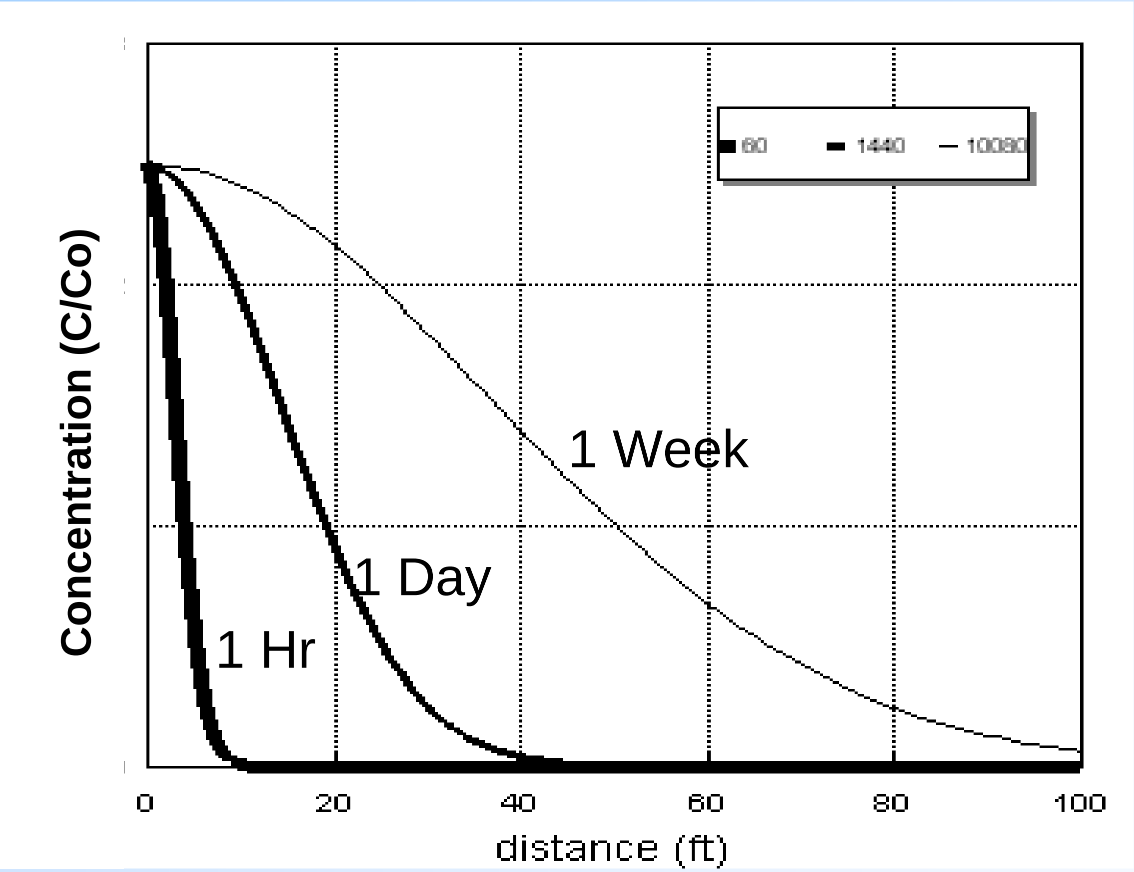
# Illustration of Importance of Amendment Reaction Rate

Scenario: 5 gpm flow, 5 foot layer




Analytical Solution
for Radial Flow Geometry
and First-Order Reaction
(Clayton, W. S. 1998 "Ozone and Contaminant Transport During In-Situ Ozonation“, Battelle Monterey Proceedings)

Steady State Solution
Concentration = f(distance)

Curves Depict Amendment Half-Lives

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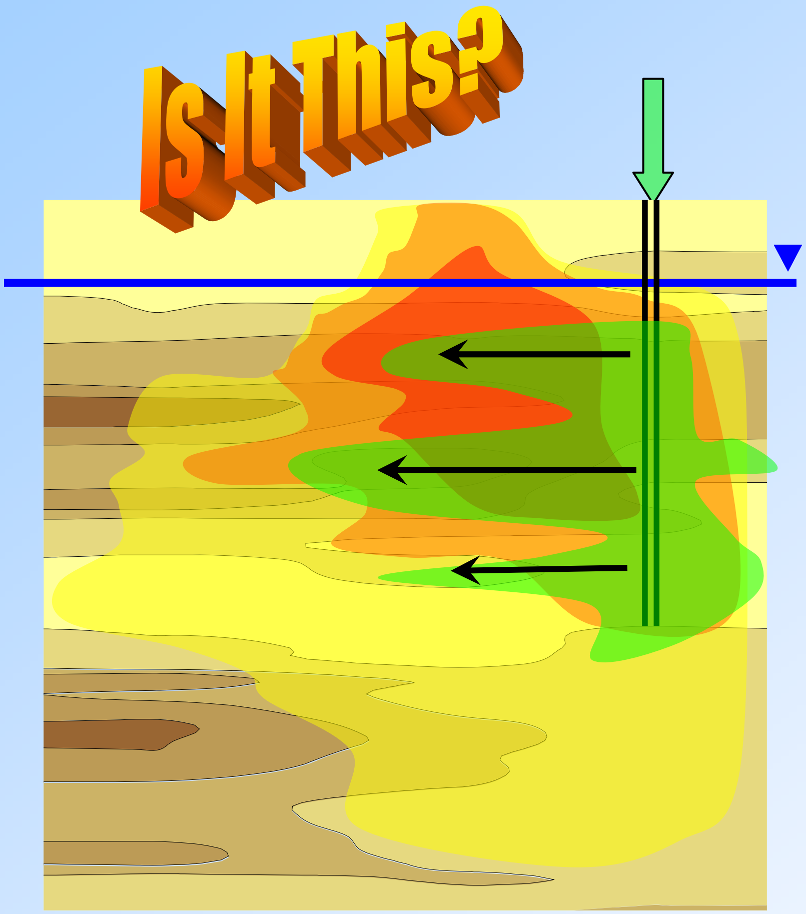
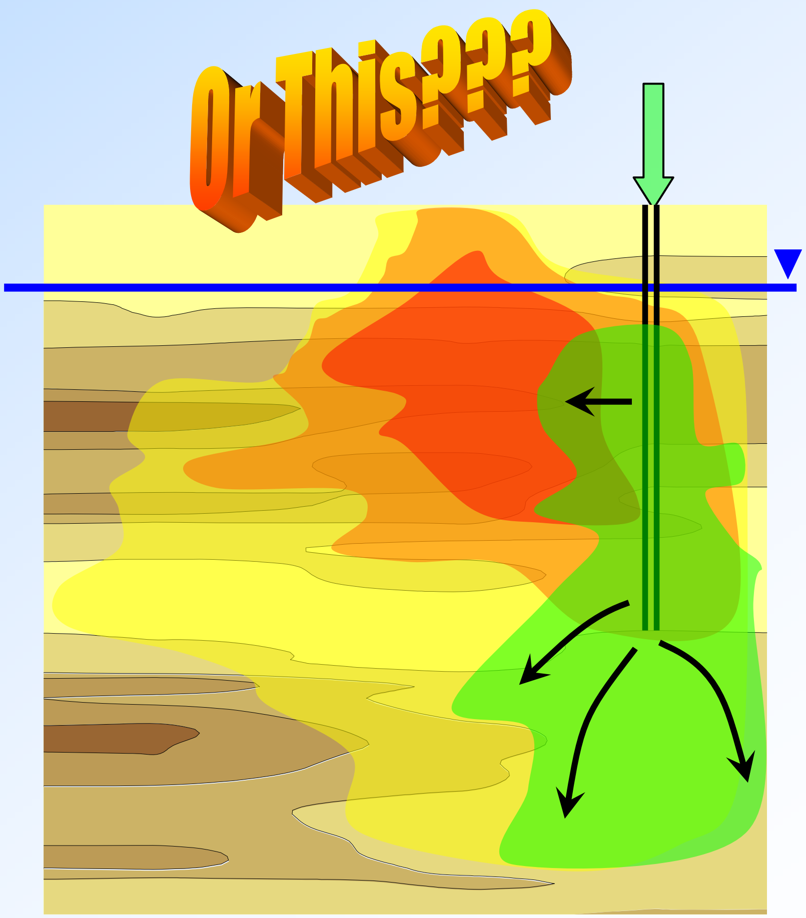
# The Question of Density-Driven Flow

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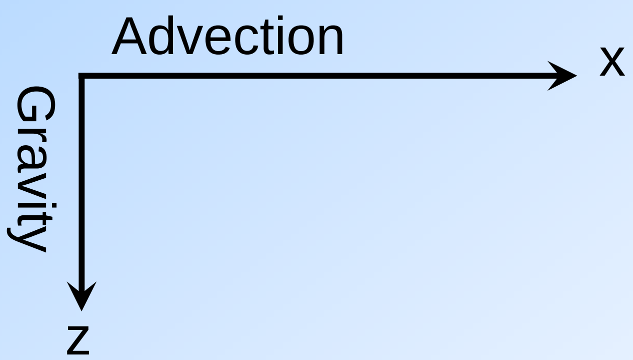
# Density-Driven Flow Dimensional Analysis

Ratio of gravitational to viscous forces:

$$Co = \frac{Rayleigh\ number}{Peclet\ number} = \frac{k \cdot g \cdot \Delta\rho}{\mu \cdot v}$$

(From: Holzbecher and Yusa, Numerical Experiments on Free and Forced Convection in Porous Media, *Int. J. Heat Mass Transfer*, 1995)

<u>In Our Case:</u>




Which is Bigger? When?
Are Both Significant?
How does it change over time?

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# Density-Driven Flow Dimensional Analysis

Simplify in Context of Field Hydrogeologic Parameters:

$$Co = \frac{k \cdot g \cdot \Delta\rho}{\mu \cdot v} = \frac{K \cdot \Delta\rho}{\rho_{am} \cdot v} = \frac{\Delta\rho}{\rho_{am} \cdot i}$$

Where, $k = \frac{K \cdot \mu}{\rho_{am} \cdot g}$ and, $K = \frac{v}{i}$

(assumes hydraulic gradient is only in x-dir)

Add Consideration of Anisotropy:

$$Co = \frac{\Delta\rho \cdot K_z}{\rho_{am} \cdot i \cdot K_h}$$

$$Co = \frac{\Delta\rho \cdot \frac{K_z}{K_h}}{\rho_{am} \cdot i}$$

$k$ = intrinsic permeability
$K$ = hydraulic conductivity
$\rho_{am}$ = amendment solution density
$\Delta\rho$ = amendment density minus groundwater density
$\mu$ = fluid viscosity
$g$ = acceleration of gravity
$v$ = darcy velocity
$i$ = dH/dx

# Results of Dimensional Analysis
## (for the case of remediation amendments)

| Approx. Amend. Concentration mg/L | wt % | Density (mg/L) | Horizontal Hydraulic Gradient @ Kz/Kh = 1.0: 0.001 | 0.005 | 0.01 | 0.05 | 0.1 | 0.5 |
|---|---|---|---|---|---|---|---|---|
| 500 | 0.05 | 1.0005 | 0.5 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1,000 | 0.1 | 1.001 | 1.0 | 0.2 | 0.1 | 0.0 | 0.0 | 0.0 |
| 2,000 | 0.2 | 1.003 | 3.0 | 0.6 | 0.3 | 0.1 | 0.0 | 0.0 |
| 5,000 | 0.5 | 1.005 | 5.0 | 1.0 | 0.5 | 0.1 | 0.0 | 0.0 |
| 10,000 | 1 | 1.01 | 9.9 | 2.0 | 1.0 | 0.2 | 0.1 | 0.0 |
| 50,000 | 5 | 1.03 | 29.1 | 5.8 | 2.9 | 0.6 | 0.3 | 0.1 |
| 100,000 | 10 | 1.05 | 47.6 | 9.5 | 4.8 | 1.0 | 0.5 | 0.1 |
| 400,000 | 40 | 1.27 | 212.6 | 42.5 | 21.3 | 4.3 | 2.1 | 0.4 |

green = density-driven flow minor relative to advection
yellow = density driven flow may be significant
red = may result in density-driven miscible fingering

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# Results of Dimensional Analysis
## (for the case of remediation amendments)

| Approx. Amend. Concentration | | | Horizontal Hydraulic Gradient @ Kz/Kh = 0.1 | | | | | |
|---|---|---|---|---|---|---|---|---|
| mg/L | wt % | Density (mg/L) | 0.001 | 0.005 | 0.01 | 0.05 | 0.1 | 0.5 |
| 500 | 0.05 | 1.0005 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1,000 | 0.1 | 1.001 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2,000 | 0.2 | 1.003 | 0.3 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 |
| 5,000 | 0.5 | 1.005 | 0.5 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 |
| 10,000 | 1 | 1.01 | 1.0 | 0.2 | 0.1 | 0.0 | 0.0 | 0.0 |
| 50,000 | 5 | 1.03 | 2.9 | 0.6 | 0.3 | 0.1 | 0.0 | 0.0 |
| 100,000 | 10 | 1.05 | 4.8 | 1.0 | 0.5 | 0.1 | 0.0 | 0.0 |
| 400,000 | 40 | 1.27 | 21.3 | 4.3 | 2.1 | 0.4 | 0.2 | 0.0 |

green = density-driven flow minor relative to advection

yellow = density driven flow may be significant

red = may result in density-driven miscible fingering

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| Approx. Amend. Concentration mg/L | wt % | Density (mg/L) | Horizontal Hydraulic Gradient @ Kz/Kh = 0.01: 0.001 | 0.005 | 0.01 | 0.05 | 0.1 | 0.5 |
|---|---|---|---|---|---|---|---|---|
| 500 | 0.05 | 1.0005 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1,000 | 0.1 | 1.001 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2,000 | 0.2 | 1.003 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 5,000 | 0.5 | 1.005 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 10,000 | 1 | 1.01 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 50,000 | 5 | 1.03 | 0.3 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 |
| 100,000 | 10 | 1.05 | 0.5 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 |
| 400,000 | 40 | 1.27 | 2.1 | 0.4 | 0.2 | 0.0 | 0.0 | 0.0 |

green = density-driven flow minor relative to advection
yellow = density driven flow may be significant
red = may result in density-driven miscible fingering

# Conclusions – Density-Driven Flow

Preliminary Analysis Shows…

- Increasing Significance For:
  - High Amendment Concentrations
  - Small Hydraulic Gradients
  - Isotropic and/or Homogeneous Media
- Likely Minimal Effects below 10,000 mg/l Amendment Concentration and/or at Moderate Hydraulic Gradient
- An Emerging Area in Need of Additional Research and Design-Tools

# Design Basis – Bench and Field Testing

- Bench Testing
  - Proof of Concept for New Applications
  - Measurement of Oxidant Consumption in Soil
  - Measurement of Treatment Under "Ideal" Conditions
  - Analytical Testing to Determine Field Monitoring Requirements (i.e. metals)
- Field Pilot Testing
  - Often Pilot Test Achieves Treatment of a Target Zone
  - Designed to Provide Full-Scale Design Parameters Not Readily Measured in Lab (i.e. transport, well spacing, etc)
  - Need Close Transient Monitoring

# Bench Testing

- Groundwater-Only Systems
  - Don't Account for Soil Interactions
  - Can provide very preliminary information
- Soil – Groundwater Slurry Systems
  - Allows Measurement of Soil Interactions
  - Provides Soil Matrix Demand
  - Allows Measurement of Metals Solubility and Attenuation
- Flow Through Column Tests
  - Useful for Kinetic-Transport Studies & Research
  - Less Commonly Conducted than Slurry Tests

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# Field Pilot Testing

- Site the Pilot Test in a Representative Area
- Conduct Sufficient Background and Pre-Test Monitoring to Assess changes in Site Conditions
- Allow Sufficient Duration for All Oxidation Reactions to Go to Completion
- Some Common Observations:
  - Increase of Dissolved Contaminants at Early Time.
  - Rapid Decrease in Dissolved Levels at Later Time.
  - Post-Treatment Rebound in dissolved levels.
- Groundwater-Only Sampling Will Not Assess Mass Reduction
- Soil Sampling is Imperfect, but Valuable
- Mass Flux Measurements Emerging as Important Tool

# Sodium Permanganate Recirculation Emplacement

Permanganate Breakthrough Curve →

# Batch Permanganate Mixing

# Constant Head Injection $KMnO_4$

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# Direct-Push Permanganate Injection

**Geoprobe™ Rig**

**Cone Penetrometer Rig**

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# Variety of Ozone Equipment Systems


**Ozone Mass Production Ranges:**

**50 grams per day**

**26 lbs per day**

C-SPARGER®


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# Persulfate Field Mixing/Recirculation

# Lessons Learned From Published ISCO Case Studies: A Quantitative Literature Review

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# Objective

**Perform a basic assessment of the current industry practice related to oxidant dose and delivery volume for in situ oxidation.**

i.e.,

***How Much Oxidant Are We Injecting?***

***How Much Volume Are We Injecting?***

***and How Does This Compare to "Good Practice"?***

# Methods

- **Quantitative Analysis of a Very Large Population (*n*>120) of Published ISCO Case Studies**
- ***Calculations were limited to "bulk" calculations* of the amount of oxidant injected in terms of *Oxidant Dose* and *Pore Volumes Injected*, as defined below:**

  - **Oxidant Dose =**
    **Total Oxidant Dose Delivered to Site (g per kg soil (g/kg))**
  - **Pore Volumes (PV) Injected =**
    **Solution Volume Injected / Pore Volume of Target Zone**

.

Bonus Material:

Focused Dose Evaluation of A Few Case Studies with Successful DNAPL Source Zone Treatment

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# Case Study Sources

- **EPA CLU-IN Technology Descriptions, Chemical Oxidation Site Profiles. http: //www.clu-in.org/products/chemox/**
- **Miscellaneous Vendor Web Sites**
- **EPA Tech-Trends Newsletters**
- **State Coalition of Dry Cleaners Web Site http://www.drycleancoalition.org/state.cfm**
- **Interstate Technology and Regulatory Council (ITRC) Technical Regulatory Guidance Document for In Situ Chemical Oxidation. http://www.itrcweb.org/ISCO-1.pdf**
- **(and a few more)**

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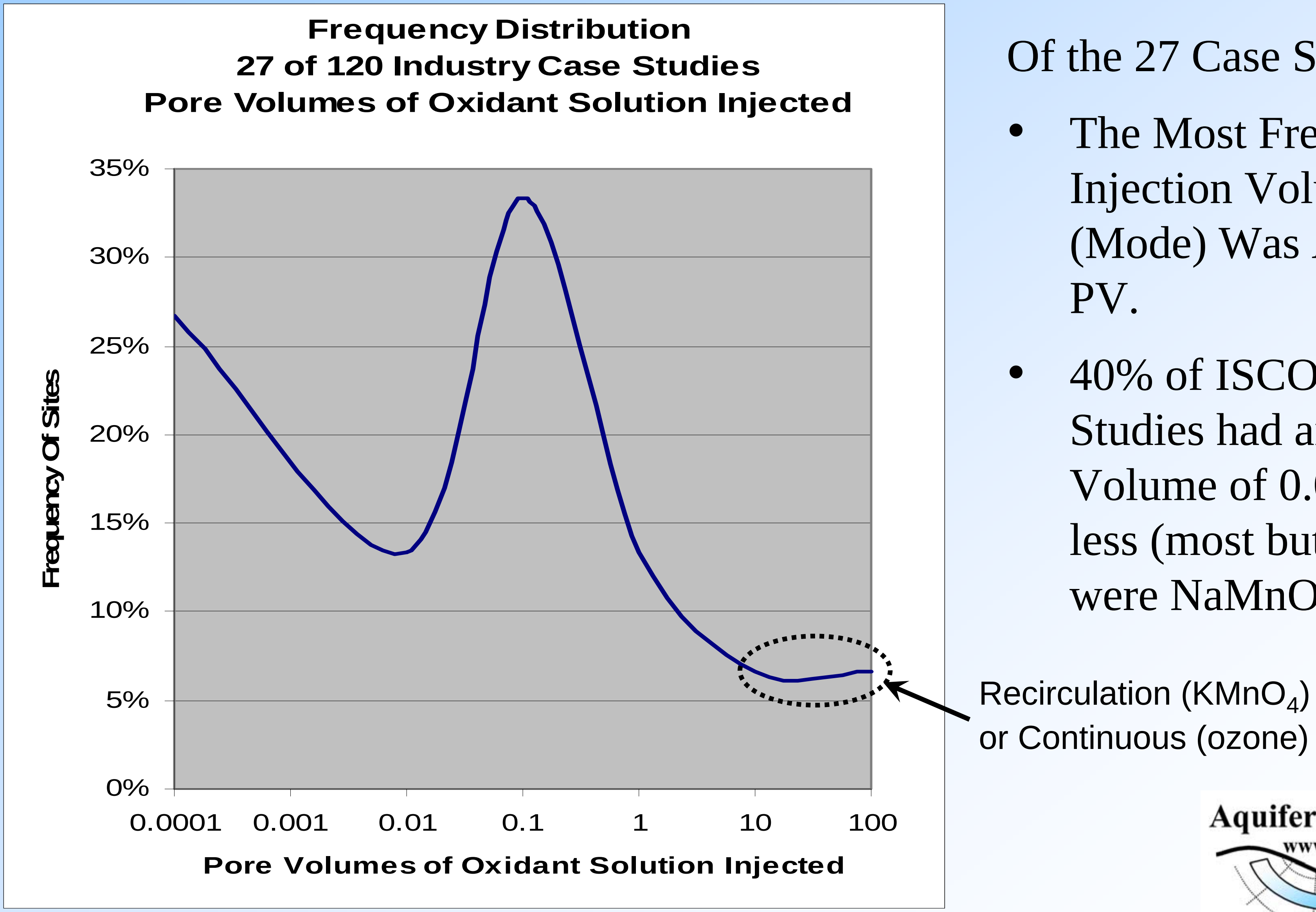
# Sacrificial Losses To the "Broad Brush"

- **Influence of Geologic Setting**
- **Differences Between Oxidants**
- **Injection Characteristics (i.e. flow rate, pressure, etc.)**
- **No Fractured Bedrock Cases Considered (too complex w.r.t. PV and oxidant dose)**

# General Observations of the 120 Case Studies

- Most ISCO Case Studies are Lean on Details.
- Of 120 case studies reviewed:
  - 27 allowed calculation of PV and Dose, and
  - 5 stated the overall Dose applied.
- We Analyze Only the 27 Case Studies Herein
  - The 93 less documented case studies likely involved smaller PV and Dose.
  - No statistical correlation of PV or Dose to contaminant treatment effectiveness was attempted.

# Injection Volume




Of the 27 Case Studies:

- The Most Frequent Injection Volume (Mode) Was About 0.1 PV.
- 40% of ISCO Case Studies had an Injection Volume of 0.01 PV or less (most but not all were $NaMnO_4$)

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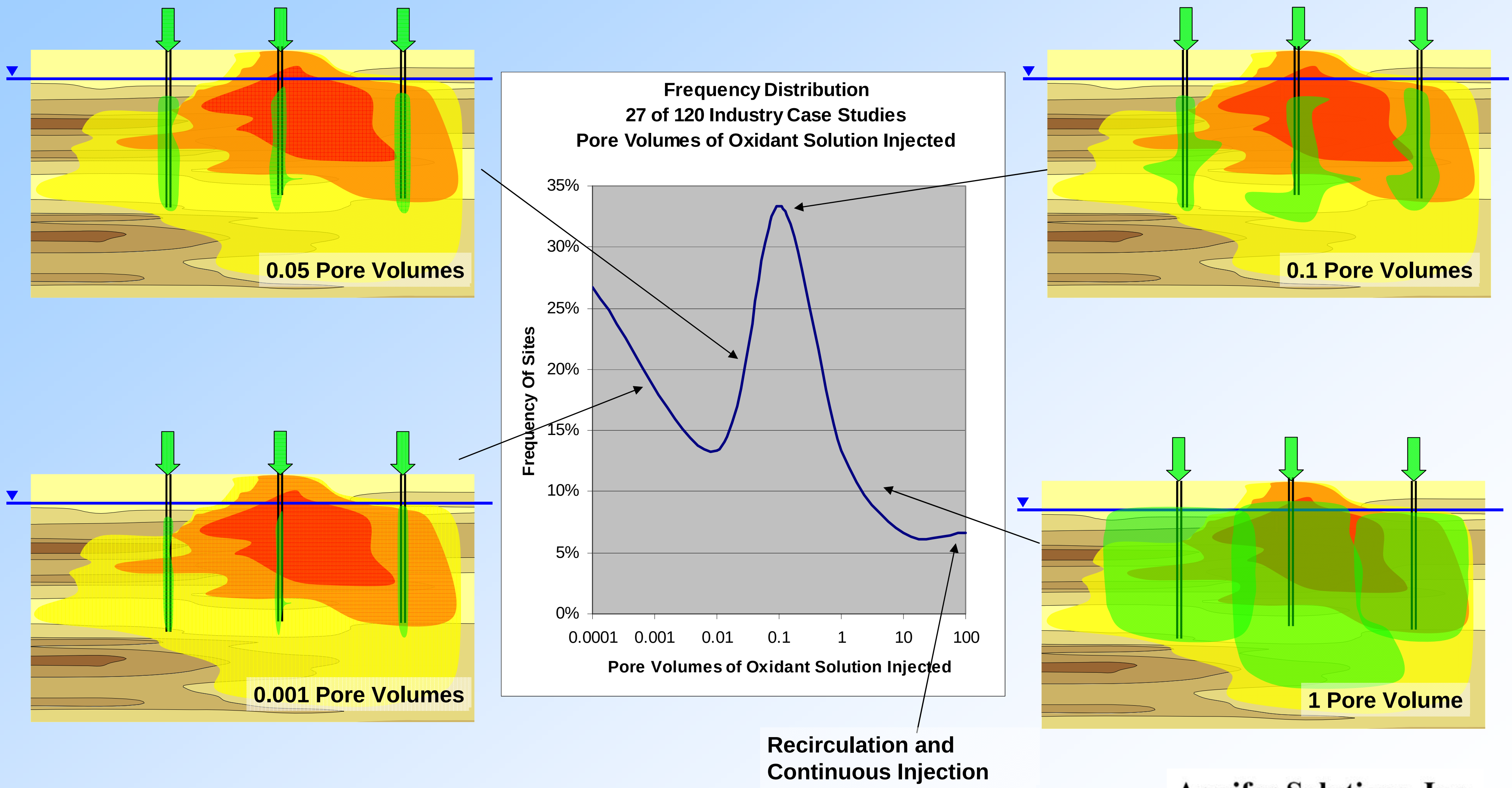
# Injection Volume

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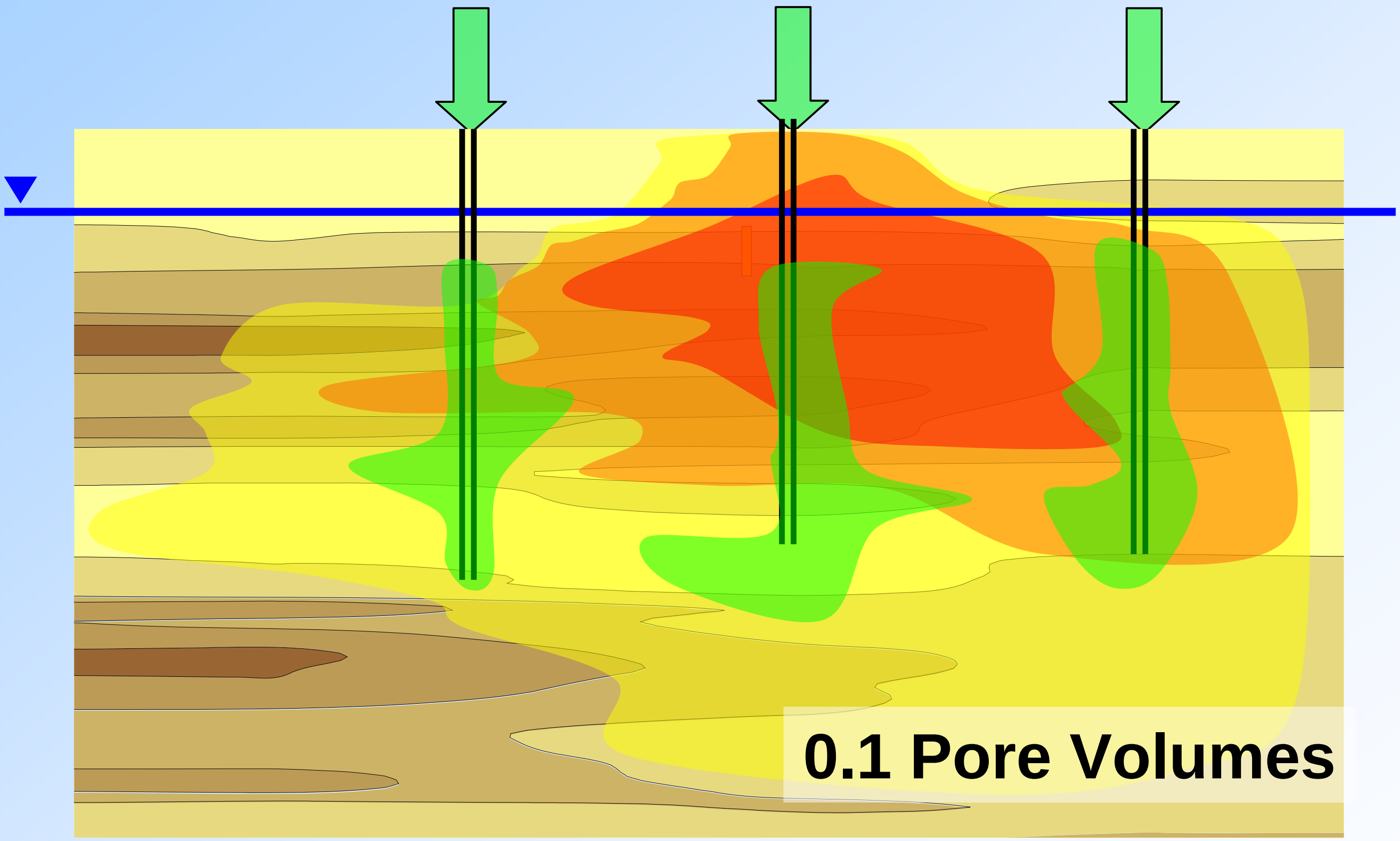
# Alternate Injection Geometries Fixed at 0.1 Pore Volumes

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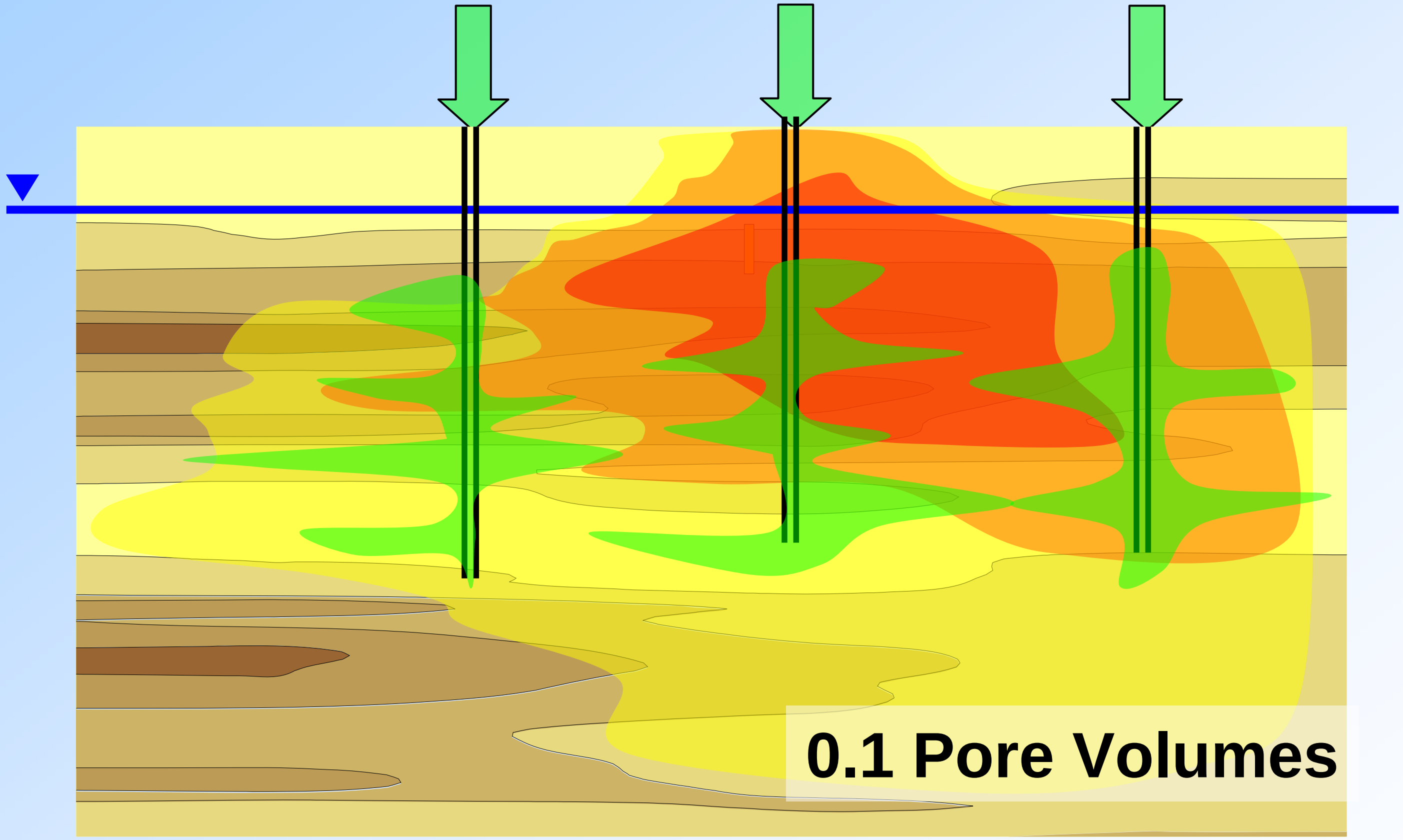
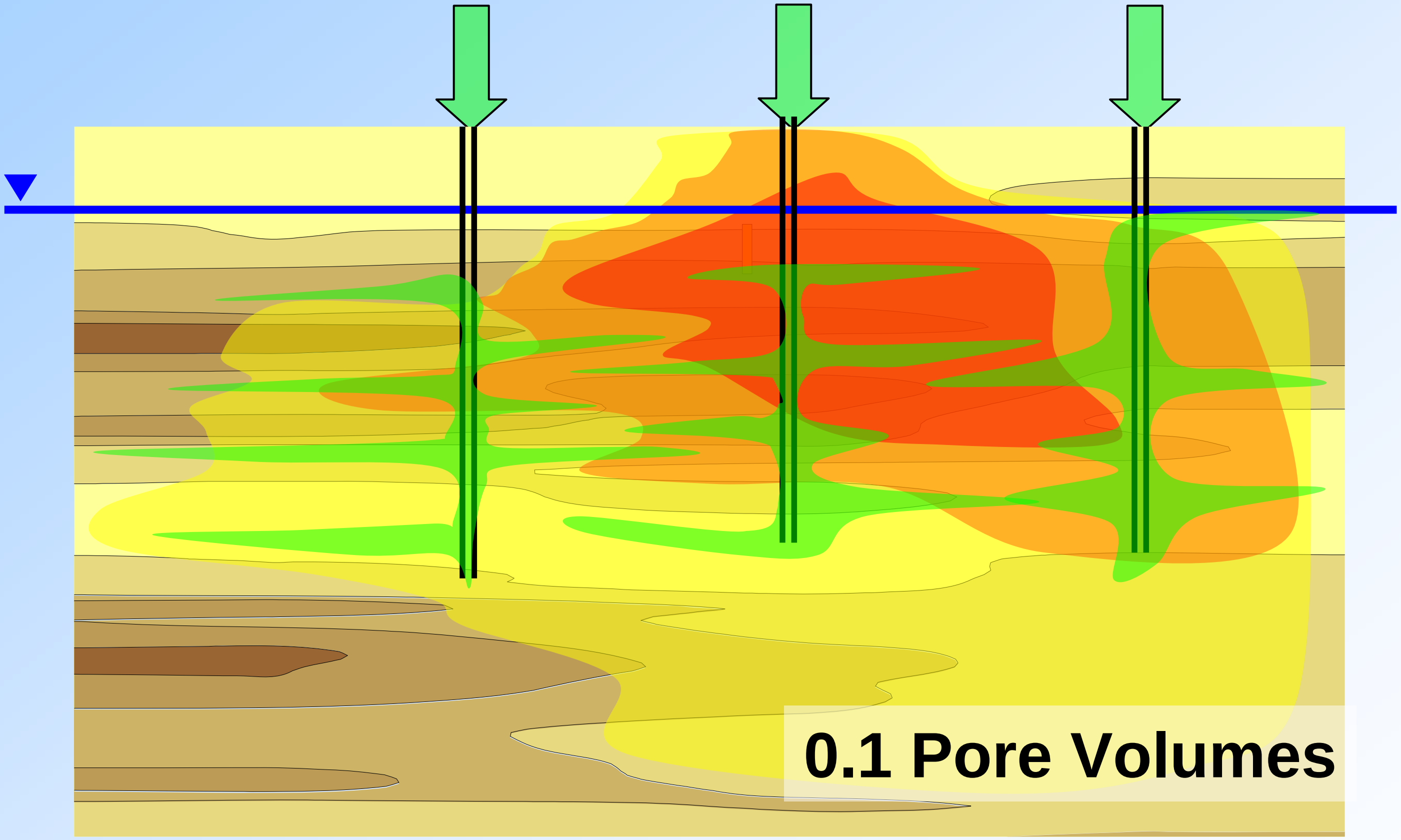
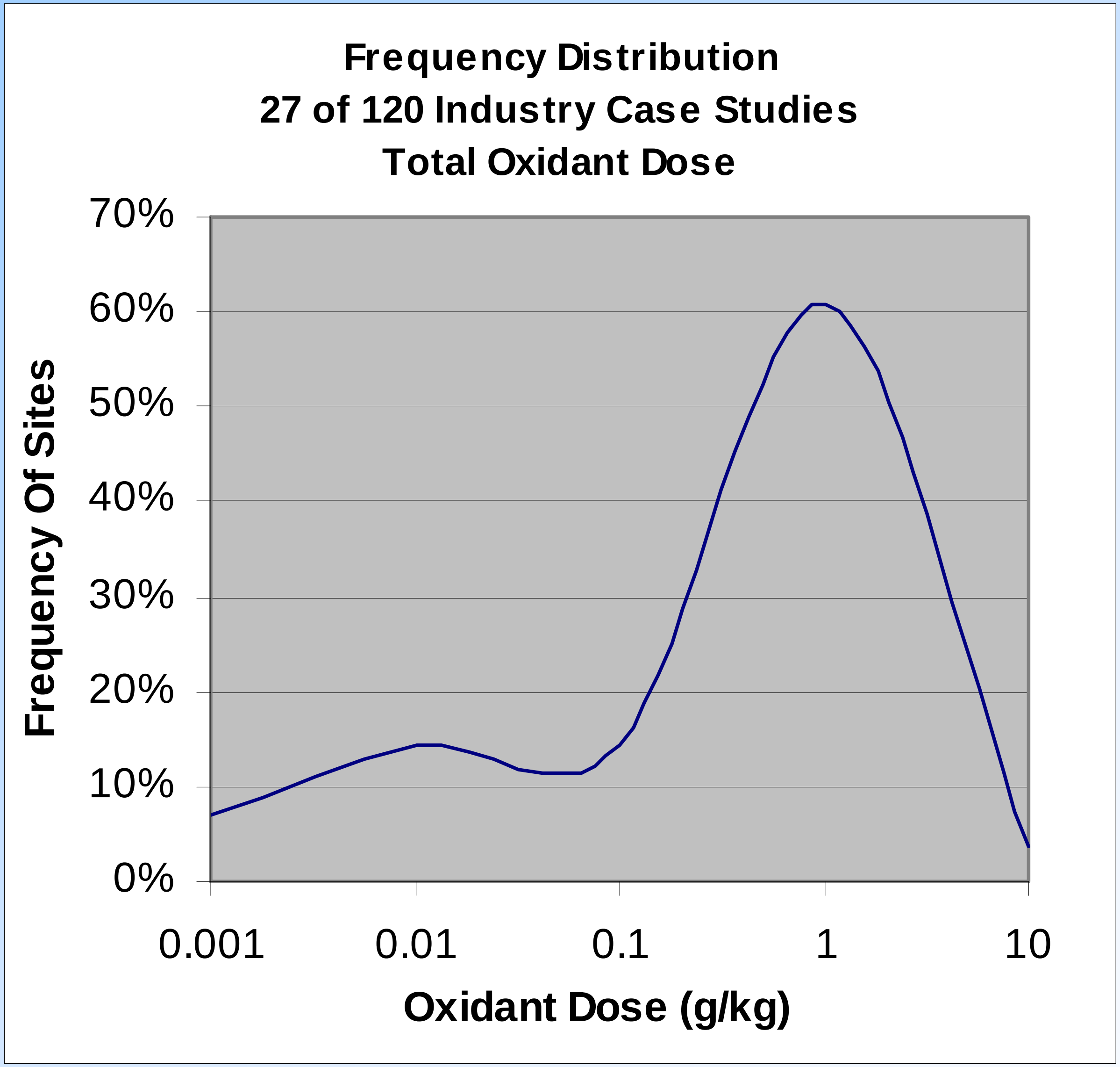


# Alternate Injection Geometries Fixed at 0.1 Pore Volumes



# Oxidant Dose




The Most Frequent Oxidant Dose Was About

1 g. oxidant per kg. soil.

Somewhat Normal Distribution with Tail at Low Dose

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# Example of ISCO Case Study Regulator Comments

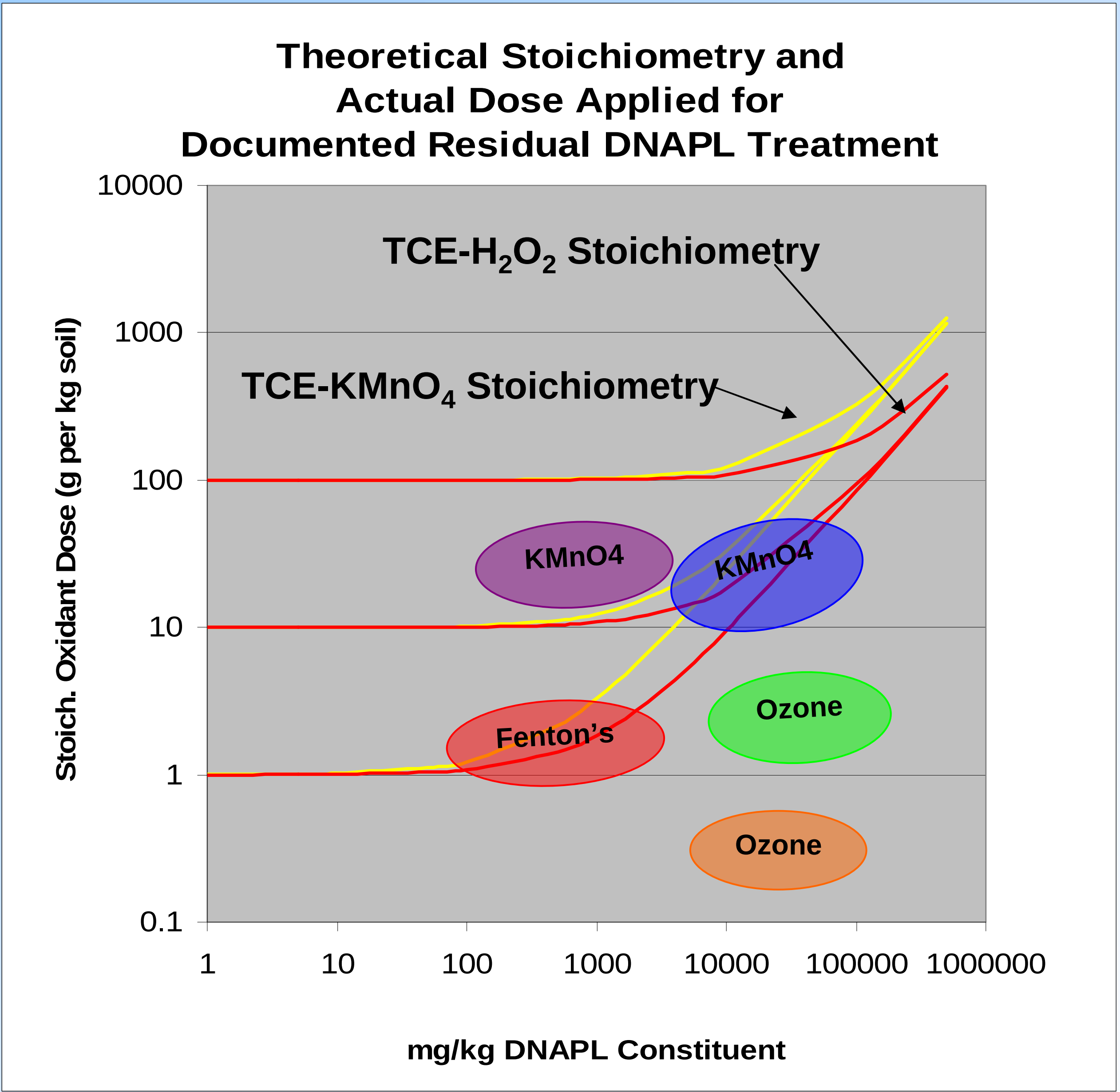
- *"Residual DNAPL in the soil appears to inhibit the success of the injected solutions."*
- *"The source has not been removed and continues as a source for groundwater contamination."*
- *"Insufficient quantities of [ISCO product trade name] may limit the success of the treatment."*

Actual $KMnO_4$ Injection Conditions:

Injected Volume = 0.00012 PV

Dose = 0.002 g/kg

# Focus on ISCO Treatment of DNAPL Source Zones




5 case studies:

Well documented treatment of residual DNAPL source zones.

Observations:

1) Must Meet Stoichiometric Dose for DNAPL Source Treatment

2) Ozone may be an exception (aerobic biodegradation of oxidation products in parallel to oxidation?)

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# What Have We Learned From Published ISCO Case Studies?

- Most ISCO Case Studies are Lean on Details.
- Successful Residual DNAPL Treatment Observed at Doses > 1 g/kg
- Many ISCO Case Studies reflect under-designed Dose and Volume
- Maybe *The Industry* is doing better on Dose than Volume

# Potential ISCO Health and Safety Issues

- Process residuals
- Chemical storage
- Preferential pathways During Injection
- Exposure to process chemicals
- Thermodynamics - waste neutralization
- Gas evolution
- Fugitive emissions
- Oxygen-enrichment

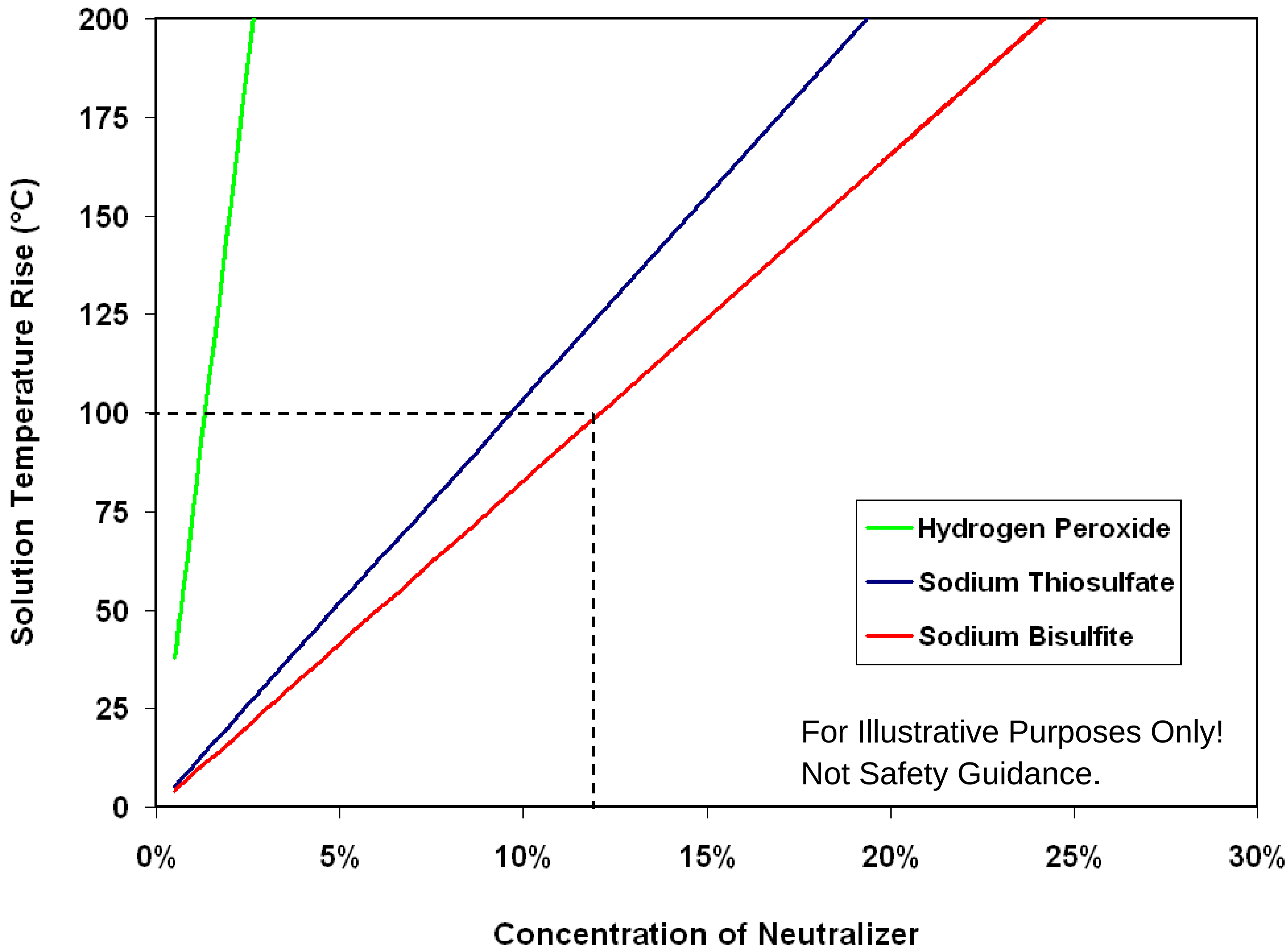
# Thermodynamics

- Oxidants have stored chemical energy
- Concentration and volume
  - Control amount of heat released
  - Rate is controlled by oxidant – reductant chemistry
- *In-situ* vs. *Ex-situ*
- Rate of reaction is important
  - Slower is better w.r.t safety
- Understanding Thermodynamics Can Prevent Accidents!

# Case Study – Process Residuals Waste Neutralization

- Summer, 2000 – DOE Portsmouth Plant
- Concentrated sodium permanganate and sodium thiosulfate
- Combined in an open 5-gallon bucket
- Violent exothermic reaction - steam
  - Rapid release of stored energy
- Extended hospitalization
- Over 30 causal factors

# Thermodynamics of Permanganate Neutralization




**Permanganate Neutralizer Selection and Concentration Dilution are Important!**

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# Case Study – Fugitive Emissions

- Summer, 1999 – Southern California
- 50% $H_2O_2$ and phosphoric Acid
  - 385 pounds into three wells
- Effervescing “a large vapor cloud”.
- Street closing and fines
- Lessons learned
  - Injection concentration was high
  - Reaction increased with time
  - Real-time temperature measurement

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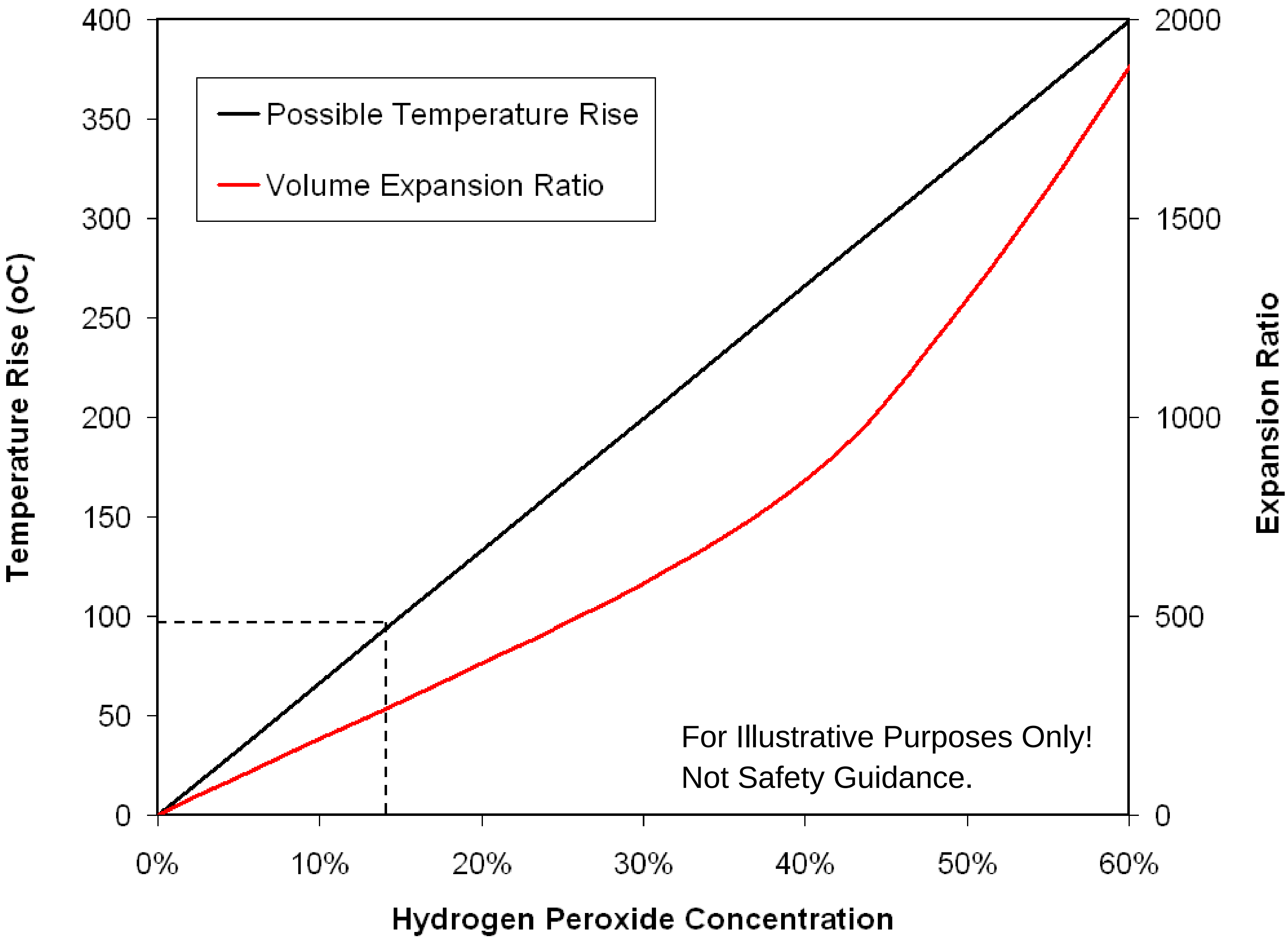
# Gas Evolution During Peroxide Decomposition




**Peroxide Off-Gas and Heat Production More Severe at Higher concentrations!**

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# Safety Conclusions and Recommendations

- Start your Health and Safety Plan early
- Integrate experienced personnel to project
- The process only begins with the MSDS
- Manage the Concentrations of Materials On-Site
- Manage Storage of Incompatible Materials
- The development of standard practices is needed to learn from past lessons

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Photo 1. Reaction occurring during pressure injection.

Quote From Published Case Study (Site in North Texas):

*"In most (applications) heat never exceeds the boiling point of water because of the large amounts of water present... This is generally assured in applications such as the one done at this site..."*

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