Welcome to ITRC's Internet Training

Thank you for joining us.

Today's presentation is focused on the ITRC technical and regulatory guidance document entitled:

"*In Situ* Chemical Oxidation of Contaminated Soil and Groundwater"

Sponsored by ITRC and EPA-TIO

1

Presentation Overview:

Remediation of groundwater contamination using ISCO (in situ chemical oxidation) involves injecting oxidants directly into the source zone and downgradient plume. The oxidant chemicals that are commonly used include permanganate (sodium and potassium), hydrogen peroxide, and ozone. The oxidant chemicals react with the contaminant, producing innocuous substances such as carbon dioxide ($C0_2$), water (H_20), and inorganic chloride. However, the full spectrum of reaction intermediates and products is not fully understood at this time for all contaminants. Examples of potential contaminants that are amenable to treatment by ISCO include BTEX (benzene, toluene, ethylbenzene, and xylenes), tetrachloroethylene (PCE), trichloroethylene (TCE), dichloroethylenes, vinyl chloride (VC), MTBE (methyl- tert-butyl-ether), PAH (polyaromatic hydrocarbons) compounds, and many other organic contaminants.

The purpose of this training is to familiarize you with the recently released ITRC In Situ Chemical Oxidation Technical and Regulatory Guidance document. It provides technical and regulatory information to help you understand, evaluate and make informed decisions on ISCO proposals. Included is a description of the various chemical oxidants, regulatory considerations, stakeholder concerns, case studies, and technical references.

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ITRC – Interstate Technology and Regulatory Council (www.itrcweb.org)

EPA-TIO – Environmental Protection Agency – Technology Innovation Office (www.clu-in.org)

ITRC Course Moderator:

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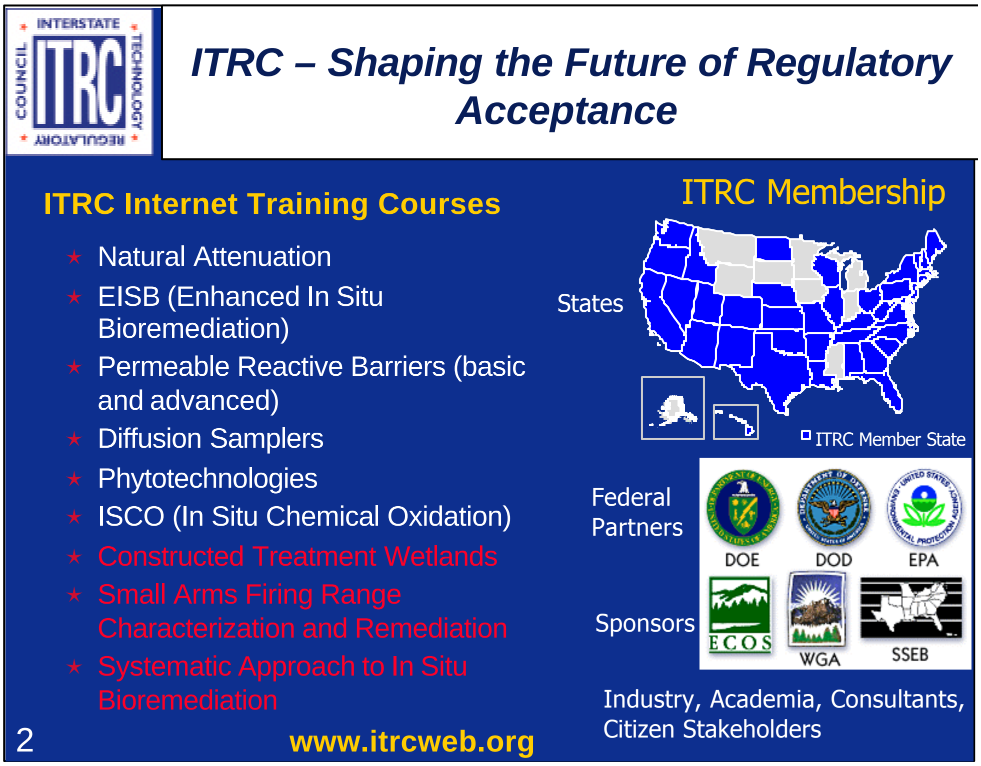

The bulleted items are a list of ITRC Internet Training topics – go to www.itrcweb.org and click on "internet training" for details.

The **Interstate Technology and Regulatory Council (ITRC)** is a state-led coalition of regulators, industry experts, citizen stakeholders, academia, and federal partners that work to achieve regulatory acceptance of environmental technologies. ITRC consists of 40 states (and the District of Columbia) that work to break down barriers and reduce compliance costs, making it easier to use new technologies and helping states maximize resources. ITRC brings together a diverse mix of environmental experts and stakeholders from both the public and private sectors to broaden and deepen technical knowledge and streamline the regulation of environmental technologies. Together, we're building the environmental community's ability to expedite quality decision-making while protecting human health and the environment. With our network approaching 6,000 people from all aspects of the environmental community, ITRC is a unique catalyst for dialogue between regulators and the regulated community.

ITRC originated in 1995 from a previous initiative by the Western Governors' Association (WGA). In January 1999, it affiliated with the Environmental Research Institute of the States, ERIS is a 501(c)3 nonprofit educational subsidiary of the Environmental Council of States (ECOS). ITRC receives regional support from WGA and the Southern States Energy Board (SSEB) and financial support from the U.S. Department of Energy, the U.S. Department of Defense, and the U.S. Environmental Protection Agency.

To access a list of ITRC State Point of Contacts (POCs) and general ITRC information go to www.itrcweb.org.

ISCO Presentation Overview

- Overview of ISCO
- Oxidants & Safety
- Pilot Studies
- Questions and answers
- Oxidants & Safety (cont.)
- ISCO Design
- Monitoring
- Regulatory Issues
- Questions and answers
- Links to additional resources
- Your feedback

Logistical Reminders

- Phone Audience
  - Keep phone on mute
  - * 6 to mute your phone and again to un-mute
  - Do NOT put call on hold
- Simulcast Audience
  - Use ? at top of each slide to submit questions

No Associated Notes

Today's Presenters

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4

Both were members of the ITRC ISCO team. Other team members are listed in the ISCO document, available for download from the ITRC web site.

Tom Stafford has been working in the fields of environmental remediation, restoration, monitoring, and investigation as an Environmental Scientist for the Remedial Services Division of the Louisiana Department of Environmental Quality for fifteen years. His responsibilities include design of sampling plans, remedial actions, monitoring, oversight of others conducting these activities in the field, inspecting laboratories that are providing data for these activities, and review of work plans for performing these activities submitted by others. Tom leads the ITRC In Situ Chemical Oxidation team.

Wilson S. Clayton, Ph.D., P.E., P.G., is a co-founder and Vice President of Aquifer Solutions, Inc., a small woman-owned business specializing in vadose zone and groundwater hydrology and in-situ remediation. Dr. Clayton was previously employed with Groundwater Technology Inc., and then by acquisition with Fluor Daniel GTI, and IT Corporation. Dr. Clayton held positions including Territory Manager, Treatability Laboratory Director, and National Practice Leader for in-situ chemical oxidation. Dr. Clayton holds a Ph.D. in Geological Engineering from Colorado School of Mines. He has published several technical papers related to in-situ chemical oxidation, dealing with oxidant reaction kinetics, subsurface oxidant transport, and other implementation-related topics.

Key "ISCO" Tech. & Reg. Issues
Most Common Concerns

- UIC (Underground Injection Control) - ISCO doc. p. 12
  - Constituents in the injected fluid exceed a primary or secondary drinking water standard
  - Formation of toxic intermediate products
  - Unknown toxicity of a constituent of the oxidant/catalyst
  - Formation/mobilization of colloids due to breakdown of NOM
  - Migration of contaminants away from the plume or source area
- Effect on Natural Biota
- Health and safety
  - Chemical Mixing and Handling
  - Atmospheric Venting
  - Chemical Transport

5

Each of these concerns will be addressed in our discussion today and are covered in the Guidance Document. There are two problems specific to permanganate that were not discussed in the document: 1. Manganese ore contains chrome. There are are traces of chrome in Na and $KMnO_4$. All of this chrome would be Cr^{6+}. 2. Naturally occurring potassium contains a significant concentration of ^{40}K. Potassium forty is radioactive. Both of these issues can cause problems in some states. In some cases the problems would preclude use of one or both permanganate salts. In others it would increase the suite of chemicals that must be quantified by monitoring.

NOM – natural organic matter

Refer to page 12 of the ITRC ISCO Technical and Regulatory Document for additional information. Document can be downloaded at no-cost at: www.itrcweb.org

Goals of Today's Session

- Introduce the ITRC Document on ISCO
  - "*In Situ* Chemical Oxidation of Contaminated Soil and Groundwater"
- Discuss the Basics of ISCO
  - Oxidation with Permanganate, Hydrogen Peroxide (Fenton's Reagent), and Ozone
- Provide Case Study Examples
- Discuss Potential Regulatory Issues
- Provide Guidance to Address Stakeholder Concerns
- Provide References for Additional Study

No Notes

What is In Situ Chemical Oxidation?

- Definition: A technique whereby an oxidant is introduced into the subsurface to chemically oxidize organic contaminants changing them to harmless substances.
  - Rapidly Emerging Technology
  - Still Subject of Academic Research as Well as Applied Routinely as a Commercialized Process
  - Several Options for Selection of Oxidant Chemicals
  - Requires Good Understanding of Contaminant Characteristics to Ensure Effective Treatment

ISCO is being evaluated as an alternative and applied at an increasing number of sites.

The number of oxidants increases the applicability of the technique.

Taking short cuts during site investigation may lead to inappropriate application and be very costly.

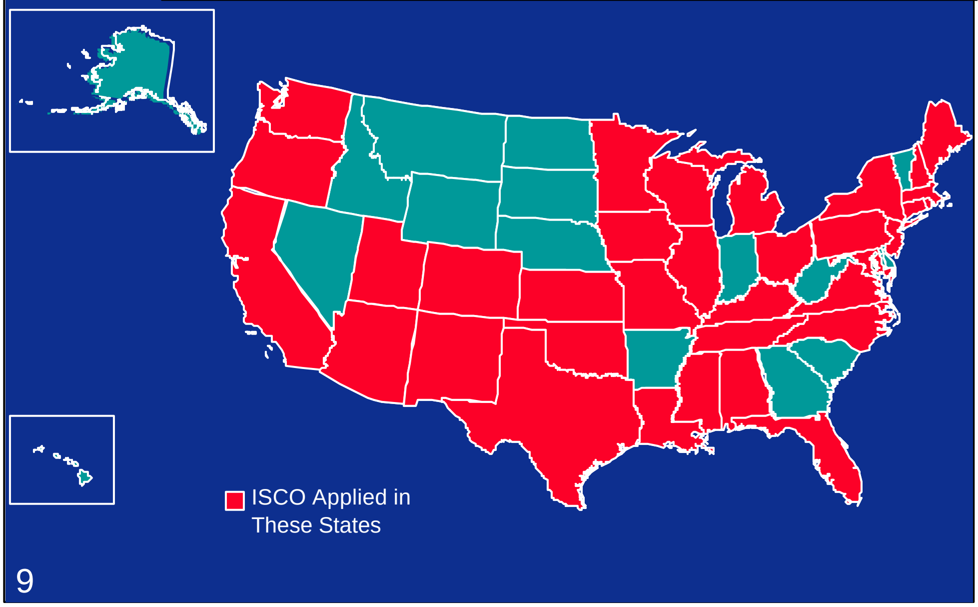
Oxidation Chemistry Is Not New In-Situ Application is New

- **Chemical Oxidation:** 1772 by Antoine Lavoisier
- **Ozone**: Discovered in 1785 by van Marum.
  - Hydrocarbon oxidation in 1855 by Schonbein.
  - Water treatment by ozonation in France in 1907.
- **Hydrogen Peroxide**: Discovered in 1818 by Thenard.
- **Fenton's Reagent**: Discovered in 1876 by Fenton
- **Permanganate:** Alkene oxidation in 1895 by Wagner.

8

As you can see, the concept of chemical oxidation is not new, and in fact has been established for >225 years. The new part is the application of oxidant chemicals to contaminants in situ.

Where has ISCO Been Used?



ISCO has been used in all the states colored red, and likely has been used in others also.

When is ISCO Applicable?

- Organic Contaminants
  - PAHs, Pesticides, Chlorinated Solvents, Petroleum Hydrocarbons, others
- Some Contaminants Require More Aggressive Oxidant Chemicals
- Screening Level Evaluation Needed to Assess Site Feasibility and Appropriate Oxidant Chemicals.

10

ISCO is applicable to a wide variety of chemicals.

However not all oxidants are applicable to all chemicals in all cases.

Bench scale testing is necessary to pair oxidant with the contaminant and geochemistry of the site.

Ozone is also much more applicable to the vadose zone because it is a gas.

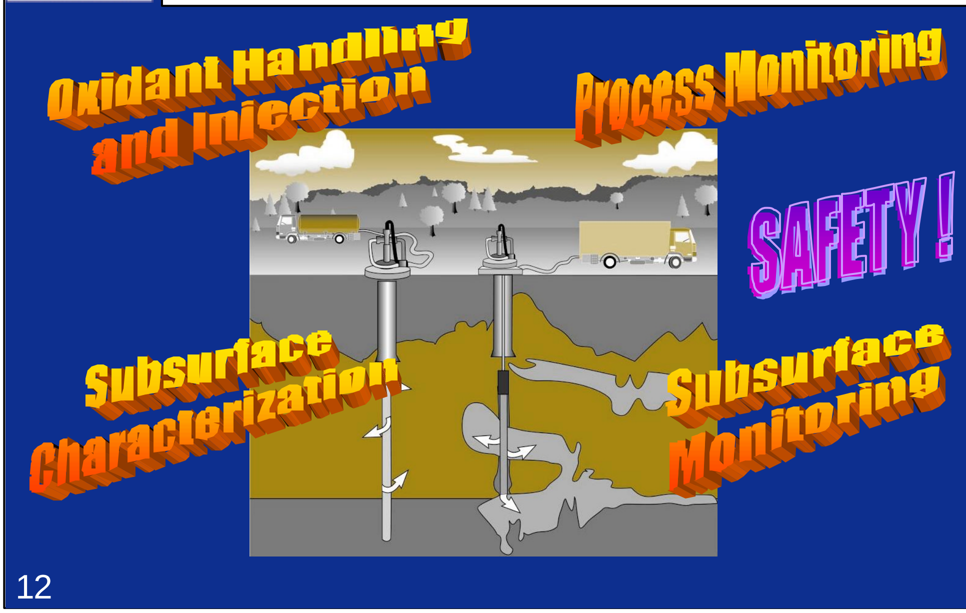
Pilot scale application growing to full application is often the best method

Oxidation Chemistry Primer

- Oxidation involves breaking apart the chemical bonds and removing electrons
- The “Oxidant” is the “Electron Acceptor”, and is Chemically Reduced by the Reaction
- Chemicals with Double Bonds are Most Readily Oxidized
- Strong Oxidants Attack a Wider Range of Bonds

No Notes

Elements of an ISCO Project



12

Safety is always the number 1 concern at an ISCO project.

The Technical Goals of ISCO Can Be Varied

- Source Zone Treatment
  - Non-Aqueous Phase Liquid (NAPL) Treatment
  - Soil Contamination Treatment
  - Mass Reduction vs. Numerical Concentration Goal
- Groundwater Plume Treatment
  - Groundwater Attenuation After Source Zone Oxidation
  - Oxidation of Dissolved Groundwater Plume

Set Your Treatment Goals, Monitoring Parameters and Success Metrics Up-Front !

No Notes

Technical Caveats

- ISCO is Often Not a Sole Solution! – Other Remediation Processes are Often Combined.
- ISCO Performance is Site-Specific.
- Match Monitoring Parameters to Performance Goals.
- Nothing is Effective in All Situations – A Project Failure is Not a Technology Failure.
- “Rules of Thumb” are Meant to Be Broken.

No Notes

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
  - Involves Handling Powerful Oxidants, and Carries Special Safety Requirements

These Lists Assume Appropriate

Technology Selection and Application

No Notes

Importance of Site Goals & Conditions for Success / Failure

- Success Factors
  - Oxidation Reactions
  - Oxidant Dose
  - Oxidant Delivery
- Failure Factors
  - Oxidation Reactions
  - Oxidant Dose
  - Oxidant Delivery

Reaction Chemistry

Heterogeneity

Permeability

Contaminant Mass Distribution

Site Geochemistry

No Notes

Oxidant Selection Criteria – How Do You Pick an Oxidant??

- Target Contaminant Reactivity with Oxidant
- Target Treatment Zone
  - Vadose Zone – Ozone Gas Injection
  - Saturated Zone – Peroxide or Permanganate Liquid
- Size of Treatment Zone
  - Permanganate is More Long-Lived and Can Be Delivered over a Larger Area in the Subsurface
- Cost

No Notes

And the Oxidants Are...

Fenton's Reagent, Ozone, and Permanganate

(Also - Recent Development: Persulfate)

Oxidant	Oxidation Potential (volts)
Hydroxyl Radical (·OH)	-2.87
Ozone (O_3)	-2.07
Hydrogen peroxide (H_2O_2)	-1.77
Permanganate Ion (MnO_4^-)	-1.695

stronger

moderate

Persulfate and Peroxone may be addressed in a future update of the ISCO document.

Oxidation Technology Selection

Oxidant	Pros	Cons
Fenton's Reagent ($OH\bullet$, SOP = -2.87 V)	▪Produces Strong Oxidant, hydroxyl radical ($OH\bullet$). ▪Release of heat and gas enhances volatilization and mixing	▪Requires pH reduction, HCO_3^- Buffering Problematic ▪Peroxide instability ▪Release of heat and gas may mobilize contaminants
Ozone (O_3, SOP = -2.07 V)	▪Strong gaseous oxidant. ▪Can produce free radicals. ▪Gas well suited to vadose zone injection.	▪Requires Continuous Injection Process. ▪Difficult Delivery into Groundwater (Sparging).
Permanganate (MnO_4^-, SOP = -1.7 V)	▪Highly persistent solution can be delivered over large areas in subsurface. ▪Dilute solutions relatively safe to handle	▪Not strong enough oxidizer for some compounds (i.e. TCA, DCA, pesticides, PCBs, others) ▪Impurities in Permanganate significant at very large dose.

Each oxidant has positive and negative aspects to consider. The oxidant must be selected based on the individual site needs.

Safety – All Oxidants

- Chemical Handling Safety
  - Follow All Chemical-Specific Handling and Mixing Precautions.
  - Dilute Oxidants Pose Less Hazard
- Monitor Oxidant Concentrations in Subsurface and at Adjacent Receptors.
- Subsurface Energetic Reactions
  - Mainly an issue with Fenton's / hydrogen peroxide.
  - Monitor Subsurface Reactions and Temp. and Ramp Up Injection Slowly

20

Safety first is the rule with ISCO!

Safety – Specifics

- Fenton's Reagent - Hydrogen Peroxide (H_2O_2)
  - Liquid – very strong oxidizer
  - Hydrogen Peroxide Delivered in Tanker Trucks or Drums
  - Generally Injected with Iron Catalyst
- Ozone (O_3)
  - Gas – very strong oxidizer
  - Ozone Gas Generated on-site Using Electrical Equipment
- Permanganate (K or Na) ($KMnO_4$ or $NaMnO_4$)
  - Liquid Solutions – very strong oxidizers, but less aggressive than peroxide or ozone
  - $KMnO_4$ sold as crystalline solid
  - $NaMnO_4$ sold as 40% liquid solution

21

No Notes

Some Common Questions About ISCO?

- Is the Oxidation Reaction Complete, Are By- Products Present and What Is Their Fate?
- Will I Oxidize/Mobilize Metals?
- Will Oxidation Kill-Off Subsurface Microbes and Halt Natural Attenuation Processes?
- Are There Any Short-term Hazards During Treatment?
- How Much Oxidant Do I Need?
- Is It Expensive?

The Answers to These Questions Are Not Universal. Up-Front Evaluation and Design Work Is Needed to Answer These Questions for a Site.

No Notes

Is the Oxidation Reaction Complete, Are By- Products Present and What Is Their Fate?

- Same Fundamental Question for All Destructive Treatment Mechanisms
  - Bioremediation
  - Natural Attenuation
  - Chemical Reduction Treatment
  - Chemical Oxidation Treatment
- Important Site Specific Factors
  - What Dose of Treatment is Applied?
  - What is Site Geochemistry?
  - How Will Chemical/Biological Processes Interact?

No Notes

Will I Oxidize/Mobilize Metals?

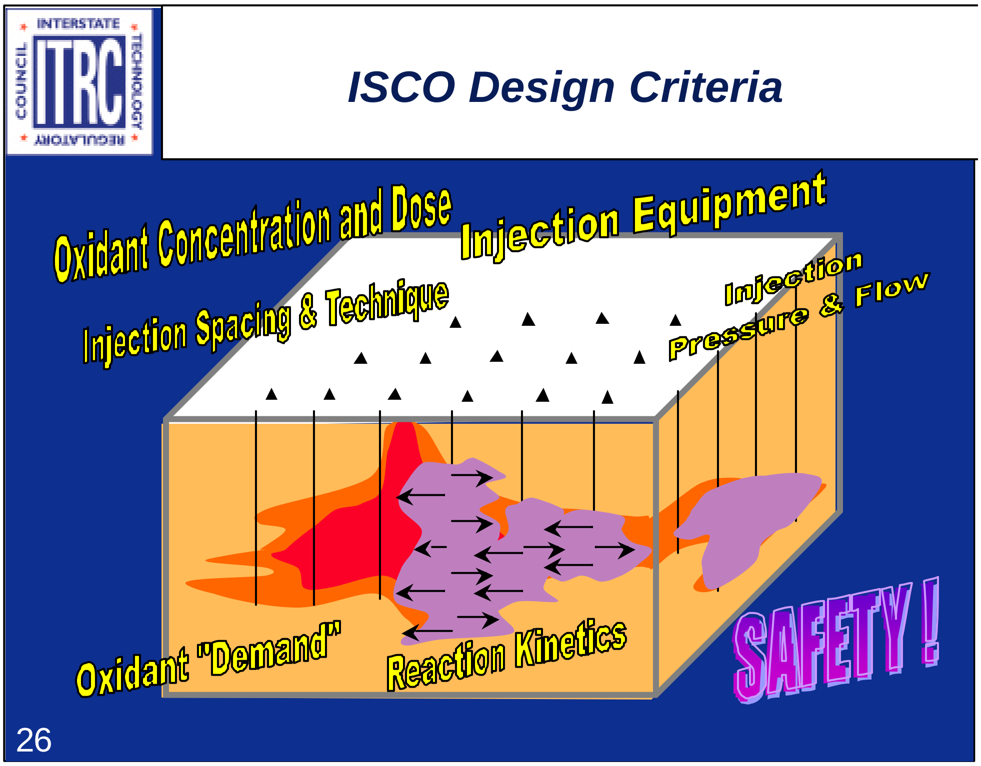
- All Oxidation Technologies Can Potentially Oxidize Redox Sensitive Metals to a More Mobile Valence State
  - Chromium, Uranium, Selenium, Arsenic
- Occurs with Naturally Occurring Metals as Well as Contaminants
- In Most Cases Documented, Metals Naturally Revert Back to the Reduced State After Oxidation Treatment is Complete
- Site-Specific Bench and Field Testing Required

No Notes

Will Oxidation Kill-Off Subsurface Microbes and Halt Natural Attenuation Processes?

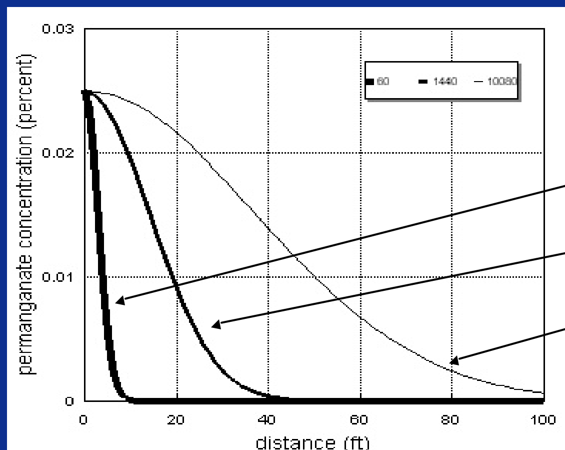
- Subsurface Microbes are Very Robust and Difficult to Eliminate
- Difficult to Deliver Enough Oxidant to Completely Contact All Microbes
- Generally, Microbial Populations Decline Temporarily and then Rebound After Treatment

No Notes



A primary design concern is the proper oxidant concentration and dose. The concentration and dose are determined by the oxidant demand and reaction kinetics. Other variables include the horizontal and vertical spacing of injections, which are largely determined by the site geology.

Oxidant Reaction Kinetics Control Transport



Oxidant Half Lives:

One Hour

One Day

One Week

Analytical Model Based on 1st Order Kinetics
Injection Scenario: 5 gpm of 2.5% permanganate
Into 5 foot layer in Saturated Zone

27

The lateral distance that the oxidant will travel from the point of injection is dependent on the reaction kinetics. The oxidant is consumed by the reaction, and can only travel as far as the reaction kinetics allow

Oxidant Demand – Primary Design Factor

- Soil Matrix (TOC) is Generally Dominant
- Groundwater Constituents Relatively Unimportant
- Matrix Demand May Exceed Contaminant Demand
- Bench Scale Testing Critical

Q: When is Oxidant Demand Too Great?

A: 1. Cost

2. Can't Deliver The Oxidant Volume

3. If Groundwater or Soil Quality Is Impacted by Oxidant

No Notes

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
  - Sophisticated Bench Tests
    - Research Tool
    - For Most Projects, Site Specific Field Pilot Testing is More Valuable than Detailed Column Tests, etc.
- Field Pilot Testing
  - Often Pilot Test Achieves Treatment of a Target Zone
  - Designed to Provide Full-Scale Design Parameters
  - Need Close Monitoring

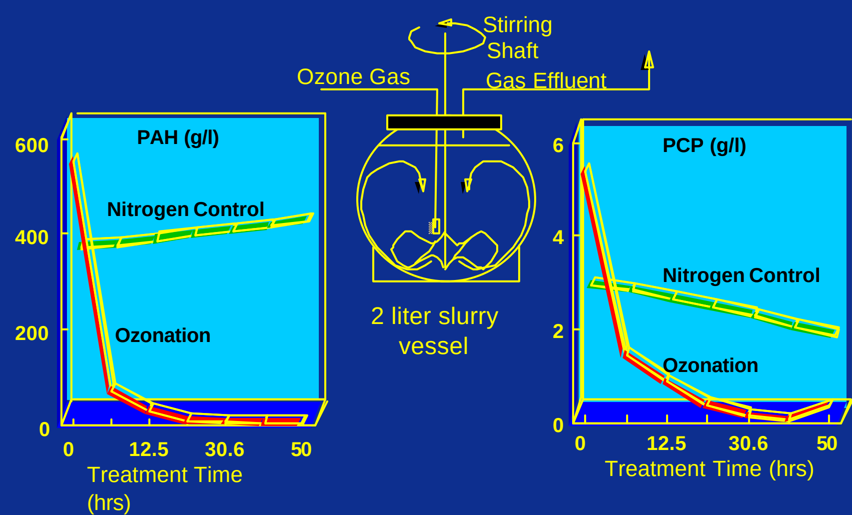
No Notes

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
  - Not Commonly Conducted on ISCO Projects

No Notes

Example Bench Test – Slurry Ozonation of PAHs and PCP



Credit: IT Corporation

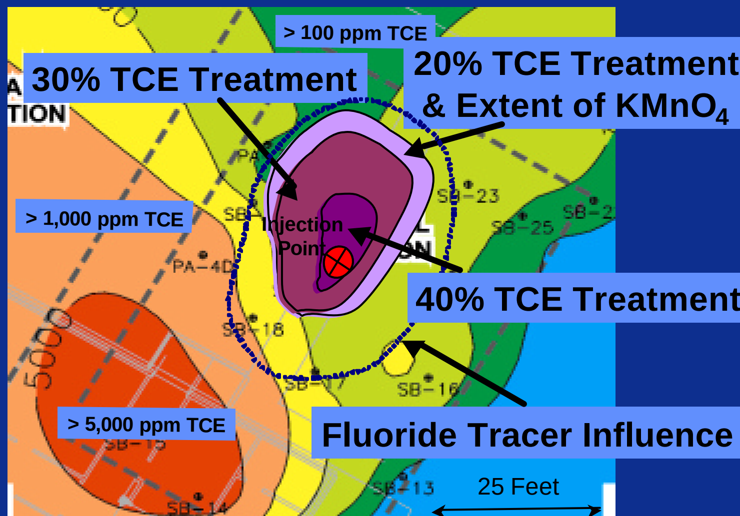
No Notes

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.
- Need to Monitor/Sample Soils to Assess Level of Mass Reduction

Results from a pilot test will often modify the design.

Example Field Pilot Test – Cape Canaveral Demonstration



Credit: IT Corporation

No Notes

Question & Answers

Effective Depth of Application?

Horizontal Well Spacing?

Will it work on free product ?

Cost?

At this time we will consider any questions you may have.

Fenton's Reagent

- Process:
  - Hydrogen Peroxide and Iron Catalyst React to Produce Hydroxyl Radicals (OH•).
- Basic Reaction:
  - $H_2O_2 + Fe^{+2} \rightarrow Fe^{+3} + OH^- + OH•$
  - Hydroxyl Radicals are non-Specific Oxidizing Agents
  - Contaminants converted to H_2O, CO_2, & Halides (Cl^-)

No Notes

Fenton's Reagent Treatment Mechanisms

- Advanced Oxidation Via Hydroxyl Radicals
  - Amended Catalyst
  - Soil Mineral Catalyst
- Direct Oxidation by Hydrogen Peroxide
- Contaminant Boiling and Volatilization
  - Hydrogen Peroxide Decomposition is Exothermic
- Assess the Degree of Treatment by Oxidation Vs. Volatilization Through Subsurface Monitoring
  - Temperature
  - Vapor Concentrations
  - CO2 Production

36

Injection at concentrations greater than 11 percent peroxide can cause the ground water to boil

Each pound of hydrogen peroxide can release 1,200 BTUs of heat energy and up to six cubic feet of oxygen gas

Safety - Hydrogen Peroxide

- Chemical Handling, Transportation, and Storage
  - Hydrogen Peroxide Is Highly Reactive and Must Be Handled by Trained Personnel in Accordance with Appropriate Procedures
- Subsurface Application Hazards
  - Heat
  - Off-Gas
  - Vapor Migration
- Well-Head Pressurization and Blow-Offs are Common to Some Peroxide Applications.
- Peroxide Injection into Free Product Must Be Closely Monitored to Prevent Fire or Explosion.
- Subsurface Peroxide Injection Should Be Closely Monitored, and Reactions Ramped-Up Slowly.

No Notes

Applying Fenton's Reagent

- Mixture of 35% H_2O_2 and Ferrous Sulfate is Typical
  - Lower concentrations may be used to reduce heat and gas generation
- Delivered at Depth Using:
  - Lance Permeation
  - Soil Mixing Techniques
  - Injected Water Amendments

No Notes

Fenton's Design Considerations

- What Hydrogen Peroxide Dose is Required?
  - Based on Contaminant Mass and Oxidation Side-Reactions
- How Much Catalyst is Needed
- What Hydrogen Peroxide Concentration is Appropriate?
  - Higher Concentrations More Aggressive
  - Higher Concentrations Lead to Peroxide Decomposition and Heat and Off-Gas Generation
- How Persistent is the Peroxide in the Surface and How Far Will it Flow From the Injection Point?

No Notes

Fenton's Reagent; Specific Data Needs & Limiting Factors

- Additional Data Needs
  - VOCs
  - LEL
  - CO_2, O_2
  - Fe in Soil & Groundwater
  - Alkalinity of Soil and Groundwater
- Limiting Factors
  - High TOC Levels
  - Low Soil Permeability
  - Highly Alkaline Soils

No Notes

Fenton's Reagent Process Options

- Several Proprietary Process Options are Commercialized
- Variations Between Processes Generally Relate to
  - Hydrogen Peroxide Concentration
  - Iron Catalyst Formulation and Delivery
  - Injection Equipment
  - Injection Pressure and Flow
- Some Fenton's Processes Involve Aggressive, Energetic Treatment, Others Involve More Controlled Treatment

No Notes

Hydrogen Peroxide Injection

Credit: SECOR

Oxidants can be injected via driven lances or wellheads.

Fenton's "Slurry Oxidation" in Open Trench

Oxidant may be applied directly to contaminated soil.

Ozone Oxidation

- Ozone (O_3) is a Gas that is Generated On-Site
- Ozone is a Very Powerful Oxidizer
- Applicable Contaminants
  - Chlorinated Solvents
  - PAHS, Chlorinated Phenols
  - PCBs, Pesticides
- Ozone is Generated From Oxygen, and Degrades to Oxygen
- Since Ozone is a Gas it is most Ideal for Vadose Zone Treatment, Compared to Liquid Oxidants

No Notes

Ozone Safety

- Subsurface Ozone Reactions are Non-Energetic
- Catalyst Beds Can Be Used for Ozone Gas Destruction in SVE off-gas.
- Ozone Generators Produce up to 50,000 ppm 0_3, while the IDLH is 10 ppm and the TLV is 0.1 ppm
- Confined Spaces with Ozone Generators Need Continuous Air Monitoring.
- All Equipment in Contact with Ozone Must Be Stainless Steel or Teflon and Oil-Free.
- Ozone Injection System Leak Testing is Critical.
  - Pressure Testing May Not Find All Leaks.
  - Use Potassium Iodide solution (ozone colorimetric detector) on a paper towel to detect small leaks.

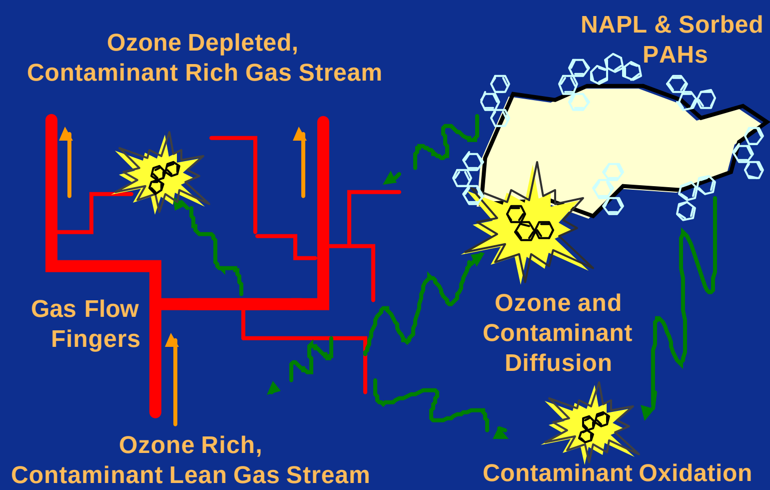
No Notes

Ozone Implementation

- Gas Injection Above Water Table (Vadose Zone)
  - Ozone Gas Applicable to Source Zone Treatment in Vadose Zone
  - Gas Flow Easier to Control than Injection of Liquid Solutions
- Gas Sparging Below Water Table (Saturated Zone)
  - Ozone Sparging More Difficult to Ensure Uniform Delivery Compared to Liquid Solutions
  - Applicable to Source Zone Treatment of “Reactive Barrier” Implementation
- Both Approaches Usually Combined with Soil Vapor Extraction to Control Ozone Off-Gas

No Notes

Ozone Gas Mass Transfer



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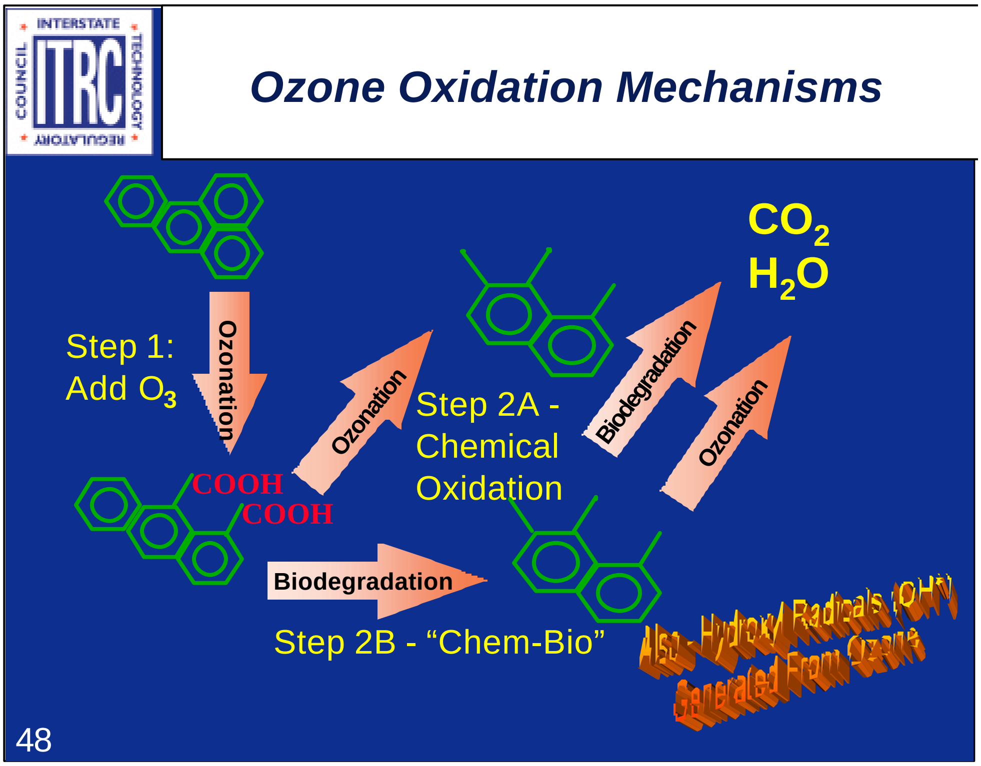

INTERSTATE TECHNOLOGY REGULATORY COUNCIL
ITRC
Ozone Oxidation Mechanisms
Step 1:
Add O_3
Ozonation
COOH
COOH
Ozonation
Step 2A -
Chemical
Oxidation
Biodegradation
Ozonation
CO_2
H_2O
Biodegradation
Step 2B - "Chem-Bio"
Also - Hydroxyl Radicals (OH*)
Generated From Ozone
48

No Notes

Ozone Oxidation Implementation and Logistics

- Ozone Generation systems
  - Continuous Pressure and Flow
  - Continuous Ozone Output
- Injection systems
  - Continuous Injection
  - Multi-Level Wells Help Ozone Distribution
- Proprietary Systems
  - C-Sparge, involves Ozone Sparging and Recirculation Well

No Notes

Ozone Oxidation Design Specifics

- Ozone Treatment is a “Continuous Injection” Process
- Ozone Generators Produce a Fixed # of lbs O_3 per day
- Time For Treatment = lbs O_3 required / lbs O_3 per day
- For example, if 1,000 lbs contaminant are present, and ozone consumption is 7 lbs O_3 per lb contam., then 7,000 lbs O_3 is Required. To Achieve Treatment in 1 Year, Requires ~ 20 lbs O_3 per day.

50

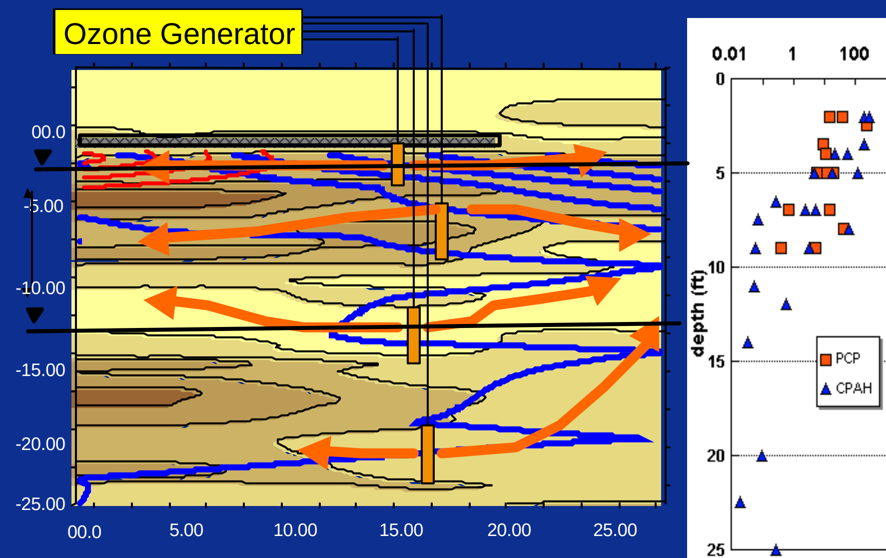
No Notes

Ozone Monitoring Specifics

- Subsurface
  - Contaminants in Soil and Aqueous Phases
  - Ozone Gas Distribution
  - Dissolved Ozone Distribution
  - Vadose Zone Soil Moisture Monitoring
- Work Space Air Monitoring – Safety
  - Time-Weighted Ozone Monitoring in Breathing Space
  - Confined Spaces with Ozone Generators Require Continuous Monitoring

No Notes

Example of Ozone Treatment System



52

Clayton, 2000

Reference: Clayton, 2000, “Injection of Gas-Phase Oxidants: Ozone Gas” in <u>Vadose Zone Science and Technology Solutions V. II</u>, eds. Looney and Falta. Battelle Press.

Ozone Injection Research and Demonstration Plot

53

Manifold system and injection points are visible in the foreground.

Permanganate Oxidation

- Permanganate is the Most Stable But Least Aggressive Oxidant (compared to ozone and peroxide)
- Permanganate is available as either KMnO4 or NaMnO4
- Application Methods Employed To Date:
  - Batch Injection of Liquid Solution
  - Recirculation of Liquid Solution
  - Fracture Emplacement of Liquid Solution
  - Fracture Emplacement of Crystalline Solids

54

Two Forms of Permanganate Commercially Available

Namn04 at 40% (by Wt) Concentration in Solutions

Kmno4 Solid Crystals, With Aqueous Solubility of 4% to 7%, Depending on Chemistry and Temp. Of Mix Water.

Contact Carus Chemical, Perus, Il for Further Information, Including Msds.

KMnO4

Solid Crystals Commonly Mixed to Create Aqueous Solutions.

Process May Involve Manual or Automated Mixing Systems.

Lower Solubility of Kmno4 Limits Possibility for Energetic Reactions.

NaMno4

Liquid Product Facilitates Mixing Compared to Solid Crystals.

Diluted Namno4 Is Safer to Handle Than Full-strength 40% Solution.

40% Namno4 Is a Strong Oxidizing Solution, That Can React Energetically. Never Neutralize Concentrated Namno4 Liquid Solution.

Safety - Permanganate

- Subsurface Reactions Generally Non-Energetic
- Proper Oxidant Handling is Needed.
  - Crystalline Solids Represent Dust Hazard
  - Concentrated NaMnO4 must be diluted before neutralization
- While Permanganate is the Least Aggressive Oxidant – It Can Still React Energetically During Handling
  - Accident Occurred in Piketon Ohio Resulting in Thermal Burns From Explosion of Concentrated NaMno4 During Handling.

55

Safety first with ISCO! Worker safety training is a must.

Permanganate Oxidation

- Applicable Contaminants
  - Chlorinated Ethenes (TCE, DCE, etc)
  - PAHs
  - Other Double-Bonded Organics
- Non-Applicable Contaminants
  - PCBs, Pesticides
  - Chlorinated Ethanes (TCA, DCA, etc.)
- Frequently Asked Questions:
  - What About MnO_2 Precipitation?
  - What About Manganese Residual in Soil or Groundwater?

No Notes

$KMnO_4$ Reactions with Chlorinated Solvents

- *Perchloroethene (PCE)*

  $4KMnO_4 + 3C_2Cl_4 + 4H_2O \rightarrow 6CO_2 + 4MnO_2 + 4K^+ + 12Cl^- + 8H^+$

- *Trichloroethene (TCE)*

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

- *Dichloroethene (DCE)*

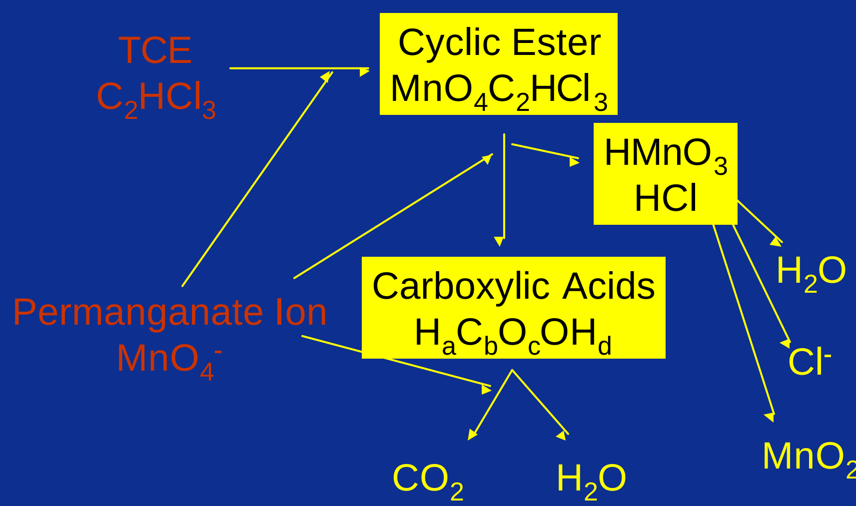
  $8\,KMnO_4 + 3C_2H_2Cl_2 + 2H^+ \rightarrow 6CO_2 + 8MnO_2 + 8K^+ + 6Cl^- + 2H_2O$

- *Vinyl Chloride (VC)*

  $10KMnO_4 + 3C_2H_3Cl \rightarrow 6CO_2 + 10MnO_2 + 10K^+ + 3Cl^- + 7OH^- + H_2O$

This slide shows the reactions of potassium permanganate with common chlorinated solvent contaminants.

TCE-Permanganate Reactants, Intermediates, and Products



Yan and Schwartz, 1998

Intermediate products are produced during the reaction. (Ref. Yan and Schwartz, 1998, in Physical, Chemical, and Thermal Technologies, Battelle Press, Columbus, OH)

Permanganate Oxidation Design Basics

- Selecting K vs. Na
- Determining Oxidant Dose and Concentration
- Mixing systems
- Injection systems
  - Fracture-Based
  - Batch Injection
  - Continuous Injection
  - Using Existing Wells Common

No Notes

$KMnO_4$ Mixing Operations


Credit: IT Corporation

Batches of permanganate are mixed on site prior to injection.

Permanganate Oxidation Design Specifics

- Permanganate Solutions Can Be Readily Mixed from less than 0.5% solution up to 40% ($NaMnO_4$)
- The Ability to Vary the Concentration Allows Flexibility in Designing Dose (Oxidant Mass) vs. Solution Volume (Dictated by Geology)
- Injection of Higher Concentrations Decreases the Chemical Usage "Efficiency"
- Batch Injection Common For Permanganate Because of Its Persistence

No Notes

Permanganate Monitoring Specifics

- Permanganate can Persist in the Subsurface for Several Months – Monitoring Should Extend Over This Full Period to Capture The Treatment Effectiveness
- Soil Core Sampling Needed to Assess Mass Reduction
- Purple Color of Permanganate Solution Allows Qualitative Detection – However visual detection cannot differentiate 100 ppm vs. 100,000 ppm

Permanganate leaves a distinctive purple stain.

Monitoring Issues – All Oxidation Technologies

- Treatment and Process Monitoring
- Closure Monitoring
- Post-Closure Monitoring

No Notes

Treatment Monitoring

- Oxidation is a “Destructive” Technology
  - No Ability to Measure/Track Extracted Contaminant Mass
  - Documentation of Treatment Effectiveness Requires “Before and After” Contaminant Delineation
  - Sampling and Analysis of all Phases (especially soils) Required to Characterize Contaminant Mass Destruction.

No Notes

Subsurface Treatment Monitoring

- Pressure
- Temperature
- ORP, pH, other basic chemistry
- Contaminant Concentrations
  - Vapor
  - Dissolved
  - Sorbed
  - NAPL
- Metals

65

No Notes

Post-Treatment and Closure Monitoring

- Allow Sufficient Time to Evaluate Conditions After the Site Reaches a New, Post-treatment Equilibrium
- All Oxidant Must Be Consumed Before Post-treatment Conditions Are Assessed
- Post-treatment Rebound (Increase) in Dissolved Contaminants Can Be Observed Due to Desorption and NAPL Dissolution

No Notes

ISCO Permitting

- Underground Injection Control (UIC)
  - Usually Oxidation Treatment Viewed as Beneficial to Aquifer Quality
  - Common Concerns
    - Constituents in the injected fluid exceed a primary or secondary drinking water standard
    - Formation of toxic intermediate products
    - Unknown toxicity of a constituent of the oxidant/catalyst
    - Formation/mobilization of colloids due to breakdown of NOM
    - Migration of contaminants away from the plume or source area

67

There are few regulatory concerns specific ISCO. However, the oxidants will oxidize metals making some of them more mobile. Pb, As, U, & Cr are some that may trigger regulatory concern. Ozone and peroxide degrade to oxygen and oxygen and hydrogen respectively. MnO_4 degrades to MnO_2. Manganese dioxide is a brown black crystalline solid that is a regulatory concern due to aesthetic considerations rather than health effects. (It stains anything but glass.)

The injection well requirements that the injected solution stay in the targeted zone, that the injectant does not mobilize secondary contaminants, that it does not further degrade an aquifer, and other technical requirements still apply.

Additional details available in the ITRC ISCO Technical and Regulatory Guidance Document – download at no-cost at: www.itrcweb.org

ISCO Permitting (continued)

- Federal Programs (RCRA & CERCLA)
  - RCRA
  - CERCLA
  - EPCRA
  - Other (TSCA, FIFRA)
- State Programs
  - May Require a Permit, or May be Waived by Statute
  - Refer to Regulatory Examples in Appendix A of ISCO Document

68

Federal programs require that “substantive technical requirements” be complied with, however, “administrative requirements” may be avoided in some circumstances.

The administrative requirements such as; fees, public hearings, and other non-technical requirements are waived. The public hearing process is often part of the remedial process under CERCLA and RCRA.

Stakeholder & Tribal Issues

- Identify Stakeholders
  - Local Officials
  - Indian Tribes
  - Neighborhood Organizations
  - Individual Citizens
- Involve Stakeholders in the Process
  - Problem Identification
  - Site Investigation & Remedy Selection
  - Timely Response to Inquiries

Stakeholder issues with ISCO are primarily the same as with any invasive treatment technique. “Stakeholders” are any person or group that is interested in the site. The best way to address their concerns is to include them at as many steps of the process as possible.

In Closing

- ISCO Technologies are an option for fast remediation
- Oxidants and contaminants degrade to harmless substances
- Limitations like any other technique
- No unique regulatory issues for ISCO
- Safe Handling of chemicals is essential
- ITRC States are in the process of concurring on using the "ITRC ISCO Tech & Reg Guidance" as a tool to evaluate the appropriateness of proposals containing ISCO (States already concurring: AL, IL, KS, LA, ND, NH, NY, OK, OR, SC, TN, VA, VT)

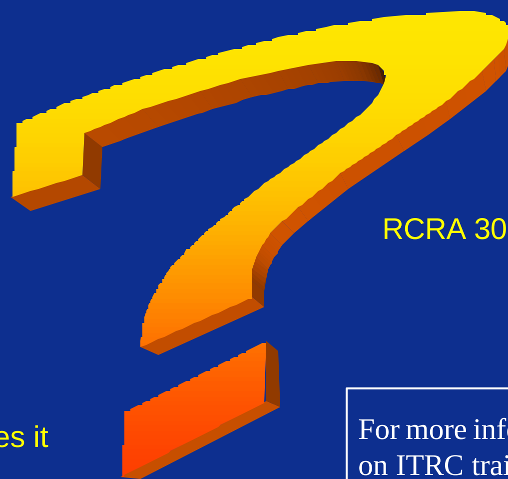
70

What is the ITRC state concurrence process?
State concurrence is the formal review and documented acceptance of the willingness to use/test ITRC Technical and Regulatory Guidance Documents. It does not mean that your state concurs on the technology, but that your state is concurring on the use of the document as a decision-making tool to evaluate the appropriateness of the use of the technology at sites in your state. The Point of Contact (POC) in each ITRC state is responsible for having the appropriate personnel in their state agency review the ITRC Technical and Regulatory Guidance Documents and to provide their state's level of concurrence on each document. The POC will then send a letter to the ITRC State Engagement Coordinator indicating their state's level of concurrence on the specific document. This information is maintained and updated in a concurrence matrix. The intent is to provide concurrence information to document users via the website.

Why is the concurrence process important?
The concurrence process serves as a formal mechanism to gain state commitment to use the ITRC products and services. In addition, concurrence on ITRC Technical and Regulatory Guidance Documents provides predictability for parties wanting to use an innovative technology in an ITRC state.

Question & Answers

Stakeholder Issues?



Is it safe?

RCRA 3020(b)?

Is it proprietary?

How long does it take?

For more information on ITRC training opportunities visit:
www.itrcweb.org

71

You may download a free copy of the ITRC document “Technical and Regulatory Requirements for In Situ Chemical Oxidation” from the web site.

Thank You!

Links to Additional Resources

72

Additional resources for this ITRC internet training event are available at:

http://clu-in.org/conf/itrc/isco/resource.htm

Information on ITRC at: http://www.itrcweb.org

Your feedback is important – please fill out the form at: http://www.clu-in.org/conf/itrc/isco/feedback.cfm

The benefits that ITRC offers to state regulators and technology developers, vendors, and consultants include:

•helping regulators build their knowledge base and raise their confidence about new environmental technologies

•helping regulators save time and money when evaluating environmental technologies

•guiding technology developers in the collection of performance data to satisfy the requirements of multiple states

•helping technology vendors avoid the time and expense of conducting duplicative and costly demonstrations

•providing a reliable network among members of the environmental community to focus on innovative environmental technologies

How you can get involved in ITRC:

•Join a team – with just 10% of your time you can have a positive impact on the regulatory process

•Sponsor ITRC's technical teams and other activities

•Be an official state member by appointing a POC (Point of Contact) to the State Engagement Team

•Use our products and attend our training courses

•Submit proposals for new technical teams and projects

•Be part of our annual conference where you can learn the most up-to-date information about regulatory issues surrounding innovative technologies