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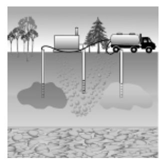
Welcome – Thanks for joining us.
ITRC's Internet-based Training Program

What's New with In Situ Chemical Oxidation



ITRC Technical and Regulatory Guidance:
In Situ Chemical Oxidation of Contaminated Soil and Groundwater *Second Edition*

This training is co-sponsored by the EPA Office of Superfund Remediation and Technology Innovation

Presentation Overview:

In the United States, an estimated 200,000+ remediation sites potentially threaten groundwater resources. When conventional treatment methods (e.g., pump and treat technology) are costly and inefficient, emerging in situ groundwater and subsurface soil treatment technologies may provide effective, lower-cost alternatives. The remediation of groundwater contamination using in situ chemical oxidation (ISCO) involves injecting oxidants and potentially co-amendments directly into the source zone and downgradient plume. The oxidant chemicals react with the contaminants, producing substances such as carbon dioxide, water, and in the case of chlorinated compounds, inorganic chloride. This course provides information to help understand, evaluate, and make informed decisions on ISCO proposals. The primary oxidants addressed in this training are hydrogen peroxide, potassium and sodium permanganate, sodium persulfate, and ozone.

This training presents updated guidance and technology advancement information for in situ chemical oxidation. Topics include a regulatory discussion related to ISCO implementation; details on the chemistry behind ISCO technology; considerations for system design and application, including health and safety; and performance evaluation information. The course is based on the ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater, 2nd Edition (ISCO-2, 2005), with sections on technology overview and applicability, remedial investigations, safety concerns, regulatory concerns, injection design, monitoring, stakeholder concerns, and case studies.

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

Training Co-Sponsored by: EPA Office of Superfund Remediation and Technology Innovation (www.clu-in.org)

ITRC Course Moderator: Mary Yelken (myelken@earthlink.net)

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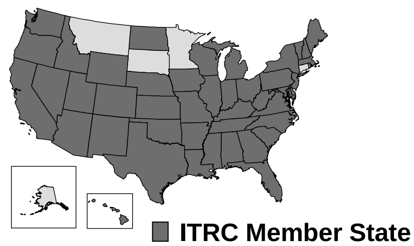
ITRC (www.itrcweb.org) – Shaping the Future of Regulatory Acceptance

- Network
  - State regulators
  - Federal government
  - Industry
  - Consultants
  - Academia
  - Community stakeholders
- Documents
  - Technical and regulatory guidance documents
  - Technology overviews
  - Case studies
- Training
  - Internet-based
  - Classroom

Host Organization ECOS

ITRC State Members



Federal Partners

DOE DOD EPA

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 and innovative approaches. ITRC consists of 45 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 advance the regulatory acceptance 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 7,500 people from all aspects of the environmental community, ITRC is a unique catalyst for dialogue between regulators and the regulated community.

For a state to be a member of ITRC their environmental agency must designate a State Point of Contact. To find out who your State POC is check out the "contacts" section at www.itrcweb.org. Also, click on "membership" to learn how you can become a member of an ITRC Technical Team.

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ITRC Course Topics Planned for 2006

Popular courses from 2005

- Alternative Landfill Covers
- Constructed Treatment Wetlands
- Environmental Management at Operational Outdoor Small Arms Ranges
- DNAPL Performance Assessment
- Mitigation Wetlands
- Perchlorate Overview
- Permeable Reactive Barriers: Lessons Learn and New Direction
- Radiation Risk Assessment
- Radiation Site Cleanup
- Remediation Process Optimization
- Site Investigation and Remediation for Munitions Response Projects
- Triad Approach
- What's New With In Situ Chemical Oxidation

New in 2006

- Characterization, Design, Construction and Monitoring of Bioreactor Landfills
- Direct-Push Wells for Long-term Monitoring
- Ending Post Closure Care at Landfills
- Planning and Promoting of Ecological Re-use of Remediated Sites
- Rads Real-time Data Collection
- Remediation Process Optimization Advanced Training
- More in development…….

Training dates/details at www.itrcweb.org
Training archives at http://cluin.org/live/archive.cfm

More details and schedules are available from www.itrcweb.org under "Internet-based Training."

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What's New with In Situ Chemical Oxidation

Logistical Reminders

- Phone line audience
  - ✓ Keep phone on mute
  - ✓ *6 to mute, *7 to un-mute to ask question during designated periods
  - ✓ Do NOT put call on hold
- Simulcast audience
  - ✓ Use ? at the top of each slide to submit questions
- Course time = 2¼ hours

Presentation Overview

- Introduction and regulatory issues
- ISCO technology
- Questions and answers
- Design considerations
- Application considerations
- Process monitoring
- Regulatory evaluation
- Links to additional resources
- Your feedback
- Questions and answers

No associated notes.

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Meet the ITRC Instructors

Jeff Lockwood
Florida DEP
Tallahassee, FL
(850) 245-7504
jeff.lockwood@dep.state.fl.us

Ian Osgerby
USACE--New England District
Concord, MA
(978) 318-8631
ian.t.osgerby@usace.army.mil

Doug Carvel
MEC^{X}, LLC
Bellaire, TX
(713) 585-7003
doug.carvel@mecx.net

Jeff Lockwood is an engineer in the Bureau of Waste Cleanup at the Florida Department of Environmental Protection where he is responsible for managing cleanups of contaminated military sites. He has over 10 years experience in waste cleanup technology from a regulatory perspective. Previously he was engaged in the design of wastewater treatment systems, air pollution control testing, and chemical process simulation. Mr. Lockwood holds a B.S. in chemical engineering from the University of South Florida and is a registered Professional Engineer in the State of Florida.

Dr. Ian Osgerby is the senior chemical engineer and innovative technology advocate for the New England District of the US Army Corps of Engineers, based in Concord, MA. He has presented papers in many symposia and conferences on subjects as diverse as thermal desorption, bioattenuation, chemical oxidation, electric resistive heating, groundwater treatment including perchlorate treatment technologies. He represents the government on domestic and international committees on remediation and chemical oxidation in particular, including SERDP/ESTCP, ITRC, and EPA TIO. He was responsible for the assembly and production of the EPA TIO web based ISCO collection of vendor case studies and continues to encourage development of the state of the art in ISCO through personal involvement with vendor applications of chemical oxidants.

Douglas Carvel is a Civil/Environmental/Structural engineer with over 28 years of experience in project engineering design and construction, and engineering project planning and cost estimating, project management, environmental regulatory analysis, environmental audits, and hazardous waste site investigations. Remediation and closure experience includes the design, implementation, and closure using a wide range of remedial options and closure programs including innovative ISCO technology applications for petroleum products and chlorinated solvents in soil and groundwater including NAPL. As the President and Principal of MECX LLC, Mr. Carvel's responsibilities include technical and administrative oversight of all operations, which includes hiring and development of the technical and administrative staffs, providing review of contracts, invoices, and deliverables, ensuring the profitability of the regional offices, developing new offices, and marketing throughout the US, Canada, Far East and Europe. Mr. Carvel also serves as primary client contract for several key Regional and National clients for whom he performs project management and technical tasks.

Frank Camera, M.P.H., has worked over 23 years in the environmental field and has been with the New Jersey Department of Environmental Protection for over 19 years, previously as a lab certification officer as well as safety and health consultant. Since 1989, Mr. Camera has been a technical coordinator, mainly responsible for overseeing investigations/remediations of the most complex industrial sites (100+) within the Site Remediation Program. Special project have included interior decontamination/residential conversions, asbestos and air-sampling requirements, field-screening methods/Triad, innovative/alternate technologies, and methanol preservation (VOC soil samples). Since 1996, Mr. Camera has been involved with ITRC. He is currently the team leader of the ISCO team. Previously, he has been the New Jersey state point of contact and a member of the DNAPL and SCAPs teams. Mr. Camera has a M.P.H. in Environmental Health from UMDNJ/RW Johnson Medical School/Rutgers University and a BS in biology from St. Josephs University.

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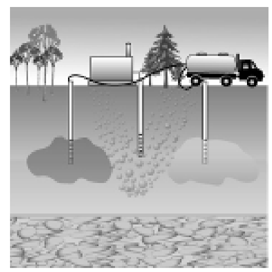
What you will learn…

- What regulators are looking for in ISCO applications
- Understand how ISCO works so you can select the right oxidant
- Importance of a thorough design to ensure successful implementation
- Importance of health and safety
- What, where, and why to monitor
- Regulatory evaluation goals



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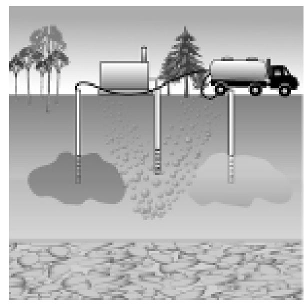
Section I: What is ISCO and Regulatory Issues

- Defining in situ chemical oxidation
- General applicability
- Regulatory review



No associated notes.

8

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 and site characteristics to ensure effective treatment

From ISCO-1 Internet-based training

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.

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Advantages and Disadvantages of ISCO

- Advantages
  - Fast treatment (weeks to months)
  - Temporary facilities
  - Treatment to low levels
  - Effective on some hard-to-treat compounds
- Disadvantages
  - Requires earlier spending commitment
  - Involves handling powerful oxidants, and carries special safety requirements

From ISCO-1 Internet-based training

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General Applicability of ISCO

- ISCO has been successfully used in every state

★Cases studies in the ISCO-2 document

- Addresses organic contaminants
  - Including hydrocarbons, pesticides, and PCBs
- Addresses contaminant phases
  - High soil/groundwater concentration
    - Standard application
  - Low soil/groundwater concentration
    - Possible, but may not be cost-effective
  - Mobile NAPL (free product)
    - Applicable, but requires more knowledge/control
  - Residual NAPL (sorbed)
    - Applicable, but requires a high oxidant dose

See ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater, 2nd Edition (ISCO-2, 2005):

Table 1-5. General applicability of ISCO

Table 1-6. Oxidant effectiveness for contaminants of concern

Table 8-1. Case studies included in Appendix D

ISCO guidance document is available on www.itrcweb.org under “Guidance Documents” and “In Situ Chemical Oxidation.”

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Regulatory Approval

- How it used to be
  - Inconsistent, bureaucratic permitting
  - Resource Conservation and Recovery Act (RCRA) often caused delays
  - Fear of liability on the part of contractors, stakeholders, etc.
- Today
  - Underground Injection Control (UIC) program
    - To protect drinking water
  - Resource Conservation and Recovery Act (RCRA)
  - Comprehensive Environmental Response, Compensation and Liability Act (CERCLA)
  - Emergency Planning and Community Right to Know Act (EPCRA)

See ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater, 2nd Edition (ISCO-2, 2005):

Section 4. Regulatory Barriers

ISCO guidance document is available on www.itrcweb.org under “Guidance Documents” and “In Situ Chemical Oxidation.”

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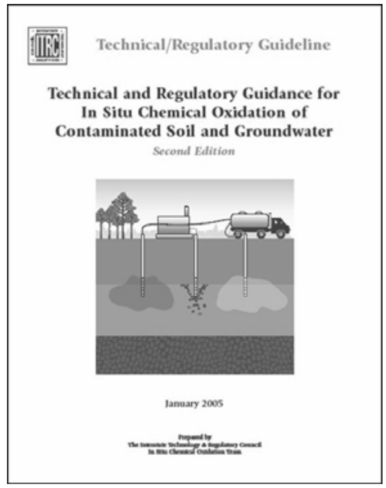
State Regulatory Requirements

- States that require an Underground Injection Control (UIC) permit/registration include
  - AL, CT, DE, FL, GA, KS, LA, MD, MO, NE, NV, NH, NJ, NM, NC, OK, OR, RI, SC, WV, WY
- All other states require other approvals
  - See Table 4-1: Regulatory permitting requirements for oxidant injection by state



ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition (ISCO-2, 2005) available at www.itrcweb.org

ISCO guidance document is available on www.itrcweb.org under “Guidance Documents” and “In Situ Chemical Oxidation.”

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Regulatory Review of ISCO Proposals

- Remediated to applicable groundwater remediation standard
- Ensure that the injection
  - Will not cause the plume to migrate
  - Will not create adverse vapor impacts
  - Is of sufficient volume to get the job done, and if not, that additional round(s) of injection will be necessary
- Additional injectant-specific requirements would apply, depending on contaminant and injectant

In New Jersey and in many states, groundwater contamination must be remediated to the applicable groundwater remediation standard. The applicable groundwater remediation standard will be typically determined by the aquifer classification.

For information on additional injectant-specific requirements, see ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater, 2nd Edition (ISCO-2, 2005):

Section 6.1 Process and Performance Monitoring

Section 6.1.1 Permanganate

Section 6.1.2 Sodium Persulfate

Section 6.1.3 Hydrogen Peroxide

Section 6.1.4 Ozone

ISCO guidance document is available on www.itrcweb.org under “Guidance Documents” and “In Situ Chemical Oxidation.”

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Regulatory Review of ISCO Proposals: Effectiveness of Remedial Actions

Generic evaluation criteria regarding the effectiveness of active soil and groundwater remedial actions

- Groundwater elevation contour maps
- Graphs of contaminant concentrations over time
- Summary of the volume of soil/groundwater treated
- Summary of contaminant concentrations above/below applicable remediation standards

No associated notes.

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Regulatory Review of ISCO Proposals: Performance-based Evaluation

- If contamination continuously decreases, even after the injectant is used up
  - Natural attenuation mode
  - Post-treatment monitoring for at least 8 quarters
- If concentrations rebound soon after the injectant is used up, it does not necessarily mean the technology has failed – need to continue monitoring to determine if:
  - Concentrations continue to rebound
  - Concentrations stabilize
  - Concentrations decrease

Sorbed and non-aqueous phase mass converts to dissolved during treatment and until site reaches post treatment final equilibrium

Possible “rebound” causes

Dissolution of sorbed or non-aqueous phase

Inadequate site characterization

Change in groundwater flow direction

Decrease in total mass may not be reflected in short-term dissolved concentrations

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Section II: ISCO Technology

- Importance of ISCO chemistry
- Terminology
- Reaction sequences/products/byproducts
- Oxidant selection/contaminants
- Do’s/don’ts
- Combination technologies

No associated notes.

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ISCO Terminology

- Conceptual Site Model – ITRC Triad Document
- Dose
- Concentration
- Injection volume
- Radius of influence
- Rebound
- Mass (distribution - sorbed, NAPL, dissolved)
- DNAPL/LNAPL - phase definition
- Oxidant demand (natural oxidant demand (NOD) / soil oxidant demand (SOD))

See also, "Technical and Regulatory Guidance for the Triad Approach: A New Paradigm for Environmental Project Management" (SCM-1, December 2003) available from www.itrcweb.org under "Guidance Documents" then "Sampling, Characterization, and Monitoring."

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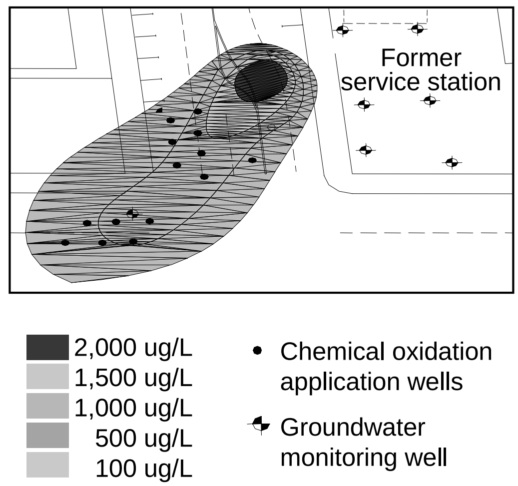
Performance Expectations: Source Area vs. Plume

- ISCO reduces contaminant mass through the oxidation process
- Mass reduction = reduction in risk
- Source versus plume
- Usually combined with something else (e.g., monitored natural attenuation)



No associated notes.

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In Situ Oxidants with More Than Ten Years of History

- Permanganate
  - Potassium permanganate ($KMnO_4$)
    - Crystalline solid
  - Sodium permanganate ($NaMnO_4$)
    - Concentrated liquid
- Ozone
  - O_3 (gas)
- Peroxide (Fenton's Reagent)
  - H_2O_2 and ferrous iron react to produce radicals
  - More accurately catalyzed peroxide propagation

No associated notes.

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Emerging Oxidants

Persulfate

- Sodium persulfate - most commonly used
- Potassium persulfate - very low solubility
- Persulfate anions ($S_2O_8^{2-}$) dissociate in water
- Oxidative strength greatly increased with addition of heat or a ferrous salt (Iron II)
  - Attributed to production of sulfate free radical ($SO_4^{-\bullet}$)

Other oxidants – solid peroxides

- Magnesium peroxide (MgO_2)
- Calcium peroxide (CaO_2)
- Sodium percarbonate ($Na_2CO_3 \bullet 3H_2O_2$)

No associated notes.

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Considerations for ISCO Treatment

	Peroxide	Ozone	Permanganate	Persulfate
Vadose zone treatment	**Successful (need adequate soil moisture)**			
Potential detrimental effects	Gas evolution, heat, **By-products, resolubilization of metals**	Gas evolution, **By-products, resolubilization of metals**	**By-products, resolubilization of metals**	**By-products, resolubilization of metals**
pH/alkalinity	**Effective over a wide pH range**, but carbonate alkalinity must be taken into consideration		**Effective over a wide pH range**	**Effective over a wide pH range**, but carbonate alkalinity must be taken into consideration
Persistence	**Easily degraded in contact with soil/groundwater unless inhibitors are used**	**Easily degraded in contact with soil/ groundwater**	**The oxidant is very stable**	
Oxidant demand	**Soil oxidant demand varies with soil type and oxidant and contaminant oxidant demand is based on total mass and mass distribution (sorbed, dissolved and free phase)**			
Soil permeability and heterogeneity	**Low-permeable soils and subsurface heterogeneity offer a challenge for the distribution of injected or extracted fluids**			

See Table 1–7 in ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition (ISCO-2, 2005) available from www.itrcweb.org under "Guidance Documents" then "In Situ Chemical Oxidation."

Permanganate Chemistry

- pH < 3.3
  - $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (1)
- 3.5 < pH < 12
  - $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2(s) + 4OH^-$ (2)
- pH > 12
  - $MnO_4^- + e^- \rightarrow MnO_4^{2-}$ (3)
- Under acidic conditions
  - $3MnO_2 + 2MnO_4^- + 4H^+ \rightarrow 5MnO_2(s) + 2H_2O$ (4)
  - $MnO_2(s) + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$ (5)

No associated notes.

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Practicality of Radical Chemistry

Generation of radicals is a function of the following

- pH
- Chemistry
- Concentration
- Temperature

No associated notes.

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Practicality of Radical Chemistry

Important points to consider about radical generation

- Activation is necessary
- A range of radicals are generated subsequent to initiation
- Radicals are aggressive and short lived
- Competition exists between propagation of radicals and radical termination
- Oxidant demand is a result of the competition between propagation and termination reactions
- It is difficult to calculate a stochiometric amount of radicals

No associated notes.

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Peroxide (Fenton's) Chemistry

- Fenton's Reaction (pH 2.5/3.5; 300 ppm peroxide)
  - $H_2O_2 + Fe^{2+}$ (acid) $\rightarrow OH^{\bullet} + OH^{-} + Fe^{3+}$ (1)
  - **Organic Contaminant $\rightarrow$ Alcohols, Acids, CO_2, H_2O**

Chain Initiation Reactions (>1 % peroxide)

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

No associated notes.

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Catalyzed Peroxide Propagation

- Chain Propagation Reactions (excess peroxide):
  - $HO_2^{\bullet} + Fe^{2+} \rightarrow HO_2^{-} + Fe^{3+}$ (4)
  - $OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$ (5)
  - $HO_2^{\bullet} \rightarrow O_2^{\bullet -} + H^{+}$ (6)
  - $OH^{\bullet} + R \rightarrow R^{\bullet} + OH^{-}$ (7)
  - $R^{\bullet} + H_2O_2 \rightarrow ROH + OH^{\bullet}$ (8)
- Chain Termination Reactions (excess iron):
  - $HO_2^{\bullet} + Fe^{2+} \rightarrow O_2 + H^{+} + Fe^{3+}$ (9)
  - $O_2^{\bullet -} + Fe^{3+} \rightarrow Fe^{2+} + O_2$ (10)
  - Fe^{3+} + n $OH^{-} \rightarrow$ Am. iron oxides (precipitate) (11)

No associated notes.

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Ozone Chemistry

- Chain Initiation Reactions:
  - $O_3 + OH^- \rightarrow O_2^{\bullet -} + HO_2^{\cdot}$ (1)
- Chain Propagation Reactions:
  - $HO_2^{\bullet} \leftrightarrow O_2^{\bullet -} + H^+$ (2)
  - $HO_2^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + HO_2^-$ (3)
  - $O_3 + HO_2^- \rightarrow OH^{\bullet} + O_2^{\bullet -} + O_2$ (4)

No associated notes.

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Persulfate Chemistry

- Chain Initiation Reactions (Me is a metal ion; R is an organic compound):
  - $S_2O_8^{2-} \rightarrow 2\ SO_4^{-\bullet}$ (1)
  - $S_2O_8^{2-} + RH \rightarrow SO_4^{-\bullet} + R^{\bullet} + HSO_4^{-}$ (2)

  Catalyzed Persulfate:

  - $Me^{n+} + S_2O_8^{2-} \rightarrow SO_4^{-\bullet} + Me^{(n+1)+} + SO_4^{2-}$ (3)

No associated notes.

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Persulfate Chemistry

- Chain Propagation Reactions:
  - $Me^{(n+1)+} + RH \rightarrow R^{\bullet} + Me^{n+} + H^{+}$ (4)
  - $SO_4^{-\bullet} + RH \rightarrow R^{\bullet} + HSO_4^{-}$ (5)
  - $SO_4^{-\bullet} + H_2O \rightarrow OH^{\bullet} + HSO_4^{-}$ (6)
  - $OH^{\bullet} + RH \rightarrow R^{\bullet} + H_2O$ (7)
  - $R^{\bullet} + S_2O_8^{2+} + H^{+} \rightarrow SO_4^{-\bullet} + HSO_4^{-} + R$ (8)
- Chain Termination Reactions (excess metal/catalyst):
  - $SO_4^{-\bullet} + Me^{n+} \rightarrow Me^{(n+1)+} + SO_4^{2-}$ (9)
  - $OH^{\bullet} + Me^{n+} \rightarrow Me^{(n+1)+} + OH^{-}$ (10)
  - $R^{\bullet} + Me^{(n+1)+} \rightarrow Me^{n+} + R$ (11)
  - $2R^{\bullet} \rightarrow$ Chain termination (12)

No associated notes.

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Geochemical Considerations

- Manganese dioxide precipitation
- Naturally occurring iron
- Metals mobilization
- Carbonate and other scavenger reactions
- Background redox conditions

No associated notes.

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Oxidant Effectiveness

Oxidant	Amenable contaminants of concern	Reluctant contaminants of concern	Recalcitrant contaminants of concern
Peroxide/Fe	TCA, PCE, TCE, DCE, VC, BTEX, chlorobenzene, phenols, 1,4-dioxane, MTBE, *tert*-butyl alcohol (TBA), high explosives	DCA, CH_2Cl_2, PAHs, carbon tetrachloride, PCBs	$CHCl_3$, pesticides
Ozone	PCE, TCE, DCE, VC, BTEX, chlorobenzene, phenols, MTBE, TBA, high explosives	DCA, CH_2Cl_2, PAHs	TCA, carbon tetrachloride, $CHCl_3$, PCBs, pesticides
Ozone/ Peroxide	TCA, PCE, TCE, DCE, VC, BTEX, chlorobenzene, phenols, 1,4-dioxane, MTBE, TBA, high explosives	DCA, CH_2Cl_2, PAHs, carbon tetrachloride, PCBs	$CHCl_3$, pesticides
Permanganate (K/Na)	PCE, TCE, DCE, VC, TEX, PAHs, phenols, high explosives	Pesticides	Benzene, TCA, carbon tetrachloride, $CHCl_3$, PCBs
Activated Sodium Persulfate	PCE, TCE, DCE, VC, BTEX, chlorobenzene, phenols, 1,4-dioxane, MTBE, TBA	PAHs, explosives, pesticides	PCBs

See ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition (ISCO-2, 2005) available from www.itrcweb.org under “Guidance Documents” then “In Situ Chemical Oxidation.”

Table 1-6. Oxidant effectiveness for contaminants of concern

Appendix B: Acronyms

Appendix C: Glossary

Acronyms used on slide:

BTEX benzene, toluene, ethylbenzene, xylene

CH_2Cl_2 dichloromethane

$CHCl_3$ trichloromethane (chloroform)

DCA dichloroethane

DCE dichloroethene

MTBE methyl *tert*-butyl ether

PAHs polycyclic aromatic hydrocarbons

PCBs polychlorinated biphenyls

PCE perchloroethene or tetrachloroethene

TBA *tert*-butyl alcohol

TCA trichloroethane

TCE trichloroethene

VC vinyl chloride

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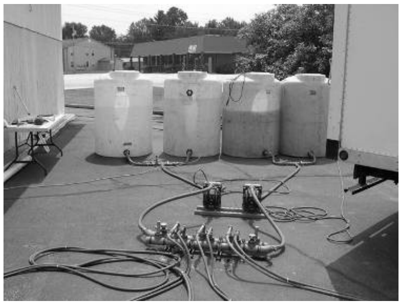
Questions and Answers



No associated notes.

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Section III: Design Considerations

- Combination technologies
- Site characterization/model development
- Oxidant demand
- Bench/pilot tests
- Modeling
- Dosage
- Costs

In this section we will look at some of the information we need before applying ISCO.

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Combination System Strategies - ISCO with ISCO

- Multiple ISCO technologies are sometimes used in concurrent or sequential fashion to take advantages of the unique properties of each
- Sequential example
  - Permanganate following persulfate or peroxide
- Concurrent example
  - Persulfate with hydrogen peroxide
    - Peroxide reduces soil oxidant demand (SOD)
    - Multi-radical attack
    - Peroxide desorbs and dissolves mass/persulfate is persistent

No associated notes.

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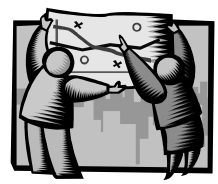
Combination System Strategies: ISCO with Mass Transfer Technologies

- Mass transfer technologies limited in their effectiveness because they must rely on the natural slow and inefficient desorption of the contaminants of concern from the soil
- ISCO enhances mass transfer from soil to groundwater by breaking down natural organic matter (NOM) (and sorption sites) and increasing temperature (peroxide co-addition)



No associated notes.

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Combination System Strategies: Bio with ISCO

- Usually microorganisms are inactive / dormant before remediation due to toxic concentrations
- ISCO reduces toxicity and supplies essential chemicals (e.g., O_2 for aerobic microbes)
- Rebound in microbial populations increases biodegradation of organic contaminants/ byproducts
- ***It is very difficult to render a site biologically inactive***. Even those with anaerobic bacteria

No associated notes.

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Conceptual Site Model Development

First and most important step in remediation project includes

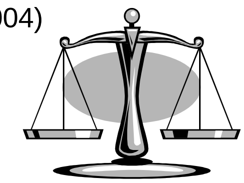
- Characterization of nature and mass of contaminants present
  - Sorbed
  - Dissolved
  - Free product phases
- Subsurface geology, site topography, aquifer geochemistry
- Identification of major migration pathways for contaminants of concern (COC)
  - Surface and subsurface structures
  - Underground utilities
- Direction / gradient / velocity of groundwater flow
- Surface water features / uses, and potential receptors in the area

No associated notes.

38

Value of Data Quantity vs. Certified Analytical Data

- ISCO requires contaminant delineation, precise concentration data quality not as critical as for closure confirmation
- References – available at www.itrcweb.org under “Guidance Documents”
  - ITRC Technical and Regulatory Guidance for the Triad Approach: A New Paradigm for Environmental Project Management (SCM-1, December 2003)
  - ITRC Strategies for Monitoring the Performance of DNAPL Source Zone Remedies (DNAPLs-5, August 2004)



ITRC Guidance Documents are available at www.itrcweb.org under “Guidance Documents.”

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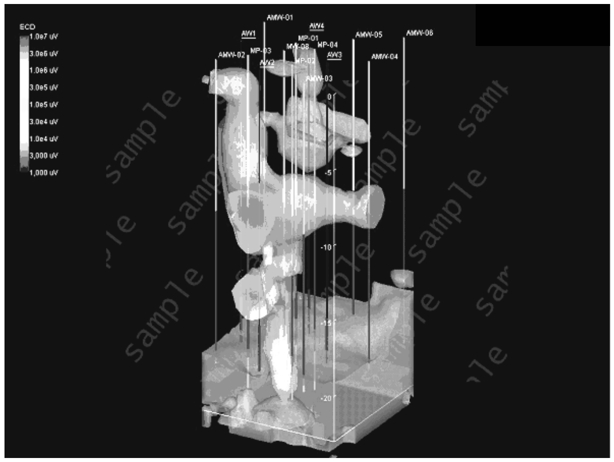
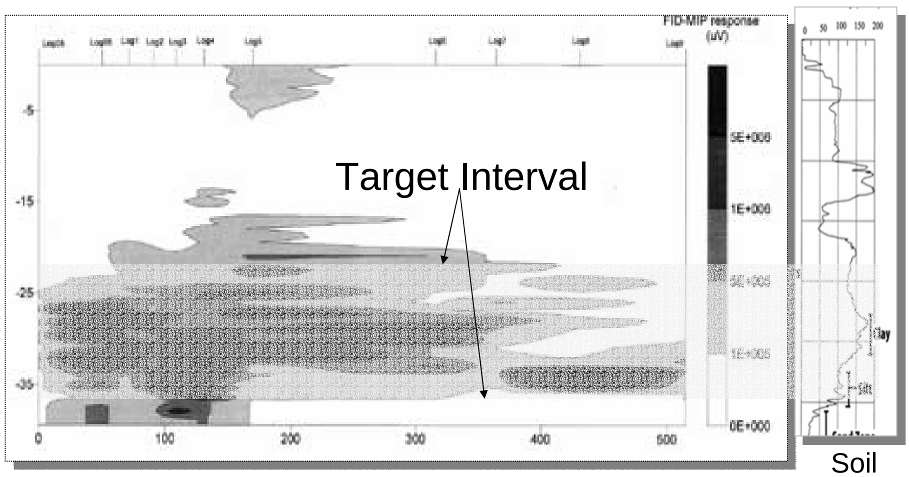
Conceptual Site Model Example of 3-D Delineation



No associated notes.

40

Conceptual Site Model
Target Interval Identification



Contaminant Mass

Soil Conductivity

No associated notes.

41

Oxidant Demand Nomenclature

- Natural oxidant demand (NOD)
- Soil oxidant demand (SOD)
- Total oxidant demand (TOD)
- Natural organic matter (NOM)
- Standard laboratory measurements of oxidizable matter in groundwater include
  - Chemical oxygen demand (**COD**)
  - Total organic carbon (**TOC**)
  - Total inorganic carbon (**TIC**)

No associated notes.

42

Comparison of Treatability and Pilot Tests

	Bench Tests	Field Tests (Pilot)
Goals	Proof of concept	Design/engineering step; not proof of concept
Limitations	Do not determine return on investment	Not just a small scale demonstration of ISCO; dispersion/costs/rebound
Advantages	Determine oxidant of choice	Determine if field test confirms applicability
Alternatives	Applicability of combined ISCO	Verify if field application confirms ISCO approach

No associated notes.

43

Treatability Tests for Evaluation of Design Parameters

- Treatability tests are usually performed on water and soil samples from the specific site with the following objectives
  - To determine the reactivity of the soils
  - To select the optimum oxidation mix/dose strength for the site
  - To observe any adverse reactions that could affect the field application
  - Estimate the post-oxidative potential of bacteria to enhance remediation (source zone residuals, plume)
- Results may be scaled up (non-linearly) for the pilot scale study
- Limited by lack of heterogeneity in sample and small volume of sample compared to field site

No associated notes.

44

Pilot Tests for Design Considerations

Pilot tests are performed on a small part of the field site to determine

- Radius of influence, rate of application, and bulk mass transport effectiveness
- Subsurface temperature and pressure can be maintained in a safe and efficient manner
- Field oxidant volume estimates (dosing important)
- Cost estimates
- Sustained exfiltration rates can be achieved
- Effectiveness of injection design

No associated notes.

45

ISCO Modeling

- **Not plume modeling**, but modeling of ISCO process
- Promising but not yet used routinely
- Strategic Environmental Research and Development Program (SERDP) ongoing research on ISCO + Aquifer modeling
- **Benefits, limitations, data needed**

No associated notes.

46

Dosage Considerations

- Natural Organic Matter (NOM) and Reduced Inorganic Matter (RIM) **contribute heavily to the oxidant demand**
- High dose strengths increase bacterial stress
- Nutrients and electron acceptors/donors important to bacterial recovery if post ISCO remediation desirable

- **Non-Radical Chemistry: Permanganate Dosing**:
- Sodium permanganate: Up to 20% - batch / recirculation
- Potassium permanganate: Up to 4% - batch / recirculation

No associated notes.

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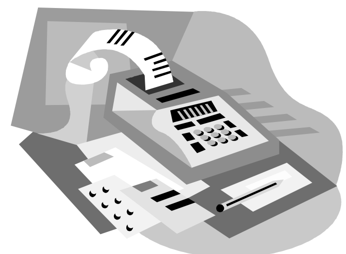
Dosage Considerations
Radical Chemistry

- **Peroxide** Generally 4% to 20%
  - Options: Low pH / iron addition
    Neutral pH / chelants / iron < 15%
    High pH
  - Excess peroxide and iron effects the reaction chemistry negatively
- **Ozone** < 10% in oxygen; < 1% in air
- **Persulfate** < 10%; buffer acidity with sodium carbonate (Na_2CO_3)
  - Excess catalyst and chelant effects reaction chemistry negatively; very corrosive

No associated notes.

Overview of Cost Considerations

- Site characterization
- Design parameter evaluation
- Application well installation
- Application of reagents
- Post treatment monitoring
- Subsequent polishing treatment if necessary



No associated notes.

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Section IV: Application Considerations

- Health and safety
  - All oxidants
  - Site Information
  - Oxidant-specific
- Delivery systems
  - Design
  - Application

No associated notes.

50

Health and Safety – All Oxidants

- Present inhalation and dermal contact hazard
- Present extreme contact risk, especially to eyes It is imperative to wear proper personal protective equipment (PPE) and maintain eyewash and shower
- Storage - protection from environment and material compatibility
- Site-specific Health and Safety Plans in accordance with 29 CFR 1910.120 guidance
- Always consult material safety datasheet (MSDS) prior to handling of material (MSDS websites listed in notes)

Information on 29 CFR 1910.120 guidance is available at http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=9765.

ISCO-related Material Safety Datasheets (MSDSs) available at:

Hydrogen Peroxide 35% and 50%

http://www.fmcchemicals.com/Industrial/V2/MSDS/0,1881,1087,00.html#

Sodium Persulfate

http://www.fmcchemicals.com/Industrial/V2/MSDS/0,1881,134,00.html#

Sodium and Potassium Permanganate
http://www.caruschem.com/pdf/MunicipalPermanganateApplications/Carusol_20.pdf and http://www.caruschem.com/pdf/new_files/CAIROX_MSDS.pdf

Ozone

http://www.bocgases.ca/newsite_eng/gases/pdfengli/G443.pdf

51

Organized Workplace

No associated notes.

52

Proper Personal Protective Equipment (PPE)

No associated notes.

53

Health and Safety – All Oxidants (continued)

- Know the site well
  - Traffic
  - Short circuiting, underground utilities, fractures
  - Runoff to sewers and surface water bodies
  - Site accessibility – flooding, muddy roads, and load limited bridges
  - Undermining of structures
  - Weather impacts

No associated notes.

54

Protection of Chemicals

No associated notes.

55

Health and Safety – All Oxidants (continued) Before and After

No associated notes.

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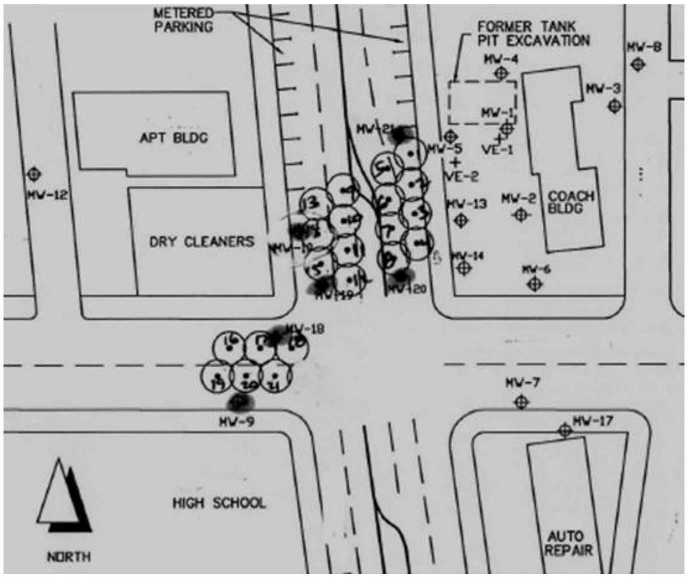
High Traffic Areas



No associated notes.

57

Night Operations

No associated notes.

58

Manage Site Access

No associated notes.

Underground Utilities and Vegetation

No associated notes.

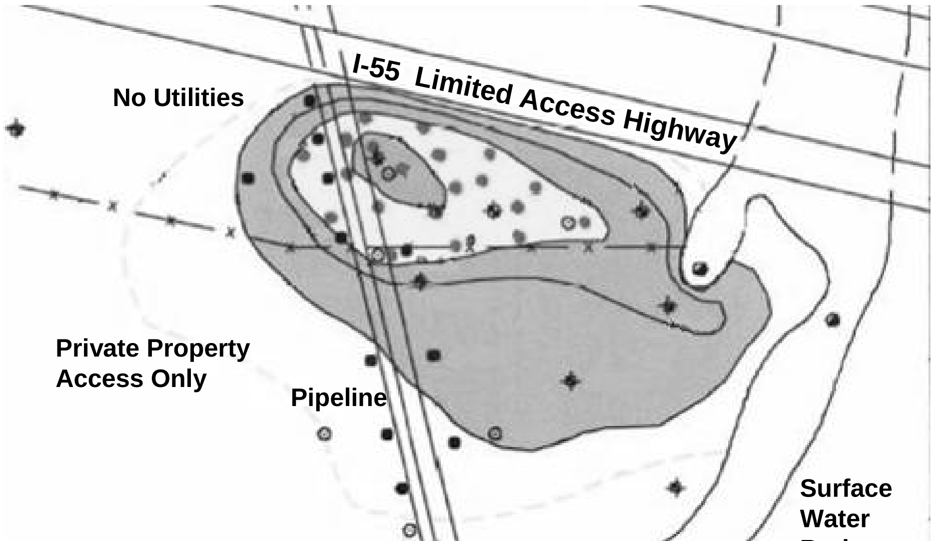
60

Weather and Equipment

No associated notes.

61

Prepare for All Issues



Flood Prone Area with Dirt Roads

No associated notes.

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Material Safety Data Sheet (MSDS) Table of Contents

1 - Chemical Product Name(s)
2 - Hazardous Contents
3 - Hazards Identification
4 - First Aid Measures
5 - Fire Fighting Measures
6 - Health and Safety
7 - Accidental Release Measures
8 - Handling and Storage
9 - Physical and Chemical Properties
10 - Stability and Reactivity
11 - Toxicological Issues
12 - Ecological
13 - Disposal
14 - Transportation
15 - Regulatory Issues
16 - Other

No associated notes.

63

Health and Safety - Ozone

- High concentration ozone (>2 ppm) presents inhalation and eye hazards
- Ignition sources should be kept away from ozone generation equipment and area should be well ventilated
- Ensure material compatibility when using ozone

Ozone Material Safety Datasheets (MSDSs) available at:

http://www.bocgases.ca/newsite_eng/gases/pdfengli/G443.pdf

64

Health and Safety - Peroxide (Fenton's)

- Peroxide or combined catalyzed peroxide presents inhalation and dermal contact hazard
- Peroxide presents an extreme contact risk, especially to eyes
- Strong reactions produce high heat and abundant gas, weakening hoses and raising pressures
- Peroxide is shipped with an inhibitor - delays reactions
- When comes in contact with various metals, reactions become uncontrollable
- Peroxide can expand 300 times its original volume
- It's very important not to recycle peroxide

Hydrogen Peroxide 35% and 50% Material Safety Datasheets (MSDSs) available at: http://www.fmcchemicals.com/Industrial/V2/MSDS/0,1881,1087,00.html#

65

Health and Safety - Permanganate

- Potassium permanganate ($KMnO_4$) [solid] presents inhalation hazard
- Sodium permanganate ($NaMnO_4$) [liquid] and potassium permanganate ($KMnO_4$) present extreme contact risk, especially to eyes. It is imperative to wear proper personal protective equipment (PPE) and maintain eyewash and shower
- Avoid contact with oxidizable material as reactions are extremely hot - fire hazard

Sodium and Potassium Permanganate Material Safety Datasheets (MSDSs) available at:

http://www.caruschem.com/pdf/MunicipalPermanganateApplications/Carusol_20.pdf and http://www.caruschem.com/pdf/new_files/CAIROX_MSDS.pdf

66

Health and Safety - Persulfate

- Persulfate particulate presents inhalation hazard
- Persulfate presents extreme contact risk, especially to eyes. It is imperative to wear proper personal protective equipment (PPE) and maintain eyewash and shower
- Avoid contact with oxidizable material as reactions are extremely hot - fire hazard
- Persulfate is not compatible with carbon steel pipes, risers, valves, impellers, etc.

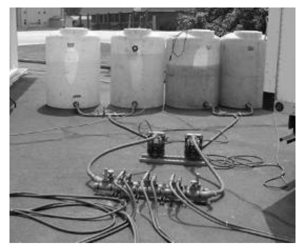
Sodium Persulfate Material Safety Datasheets (MSDSs) available at:

http://www.fmcchemicals.com/Industrial/V2/MSDS/0,1881,134,00.html#

67

Health and Safety - Other Practical Issues

- Disconnection of pressurized lines is the single most common mistake made by inexperienced operators. Tips to avoid this problem:
  - Work only with experienced operators
  - Treat pressurized lines with the same respect as high voltage wires
  - Use gauges and check valves
- Always follow Material Safety Data Sheet (MSDS) and National Fire Prevention Association guidelines
- Health and Safety Plan (HASP)



No associated notes.

68

Design of Delivery Systems

- Sufficient number of wells to provide adequate overlap of "effective zones"
  - Can use trenches
- Usually multiple application events
- Oxidant transport can be reaction limited
  - Effective radius of treatment will be substantially smaller than hydraulic/pneumatic radius of influence
  - Higher oxidation reaction rates lead to smaller treatment radii
- Caution should be used when designing injection / monitoring wells
  - Stainless steel injection points may be needed

No associated notes.

69

Conditions that Require Special Consideration

- Low permeable soils
- Deep aquifers
- LNAPL/DNAPL
- Confined formations
- Swamps or high organic soils
- Old landfills and dumps
- River embankments
- Under buildings

No associated notes.

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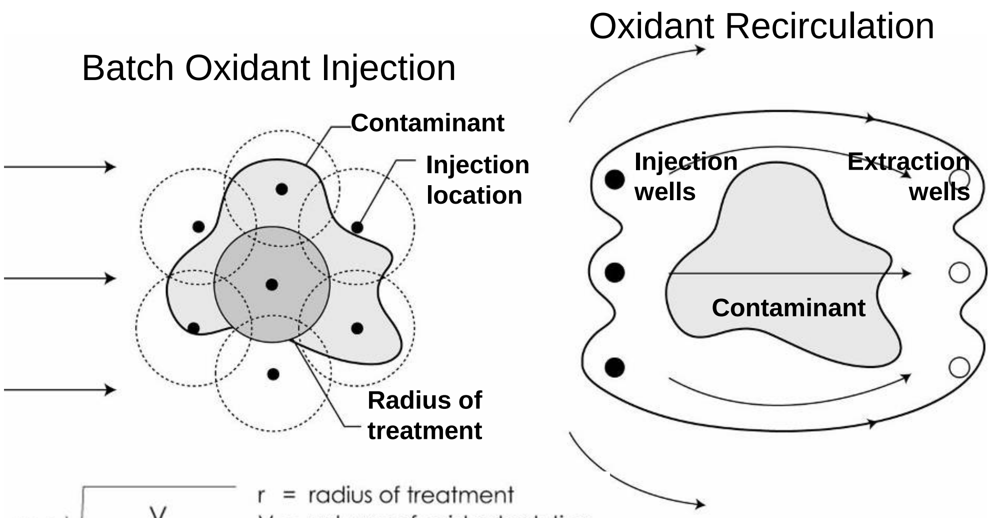
Delivery Systems
Batch vs. Recirculation



$$r = \sqrt{\frac{V}{\theta \pi t}}$$

r = radius of treatment
V = volume of oxidant solution
θ = porosity
t = thickness of treatment zone

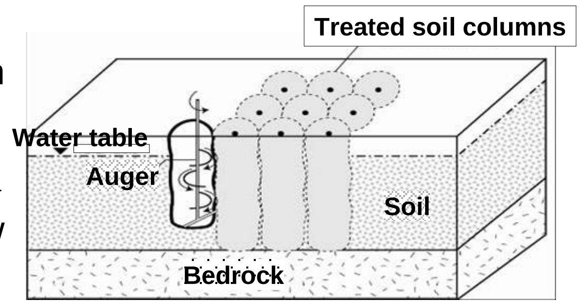
No associated notes.

71

Delivery Systems Application

Conventional delivery configurations

- ▶ Direct injection
- ▶ Horizontal injection
- ▶ Pulsing
- ▶ Soil mixing
- ▶ Density-driven flow
- ▶ Lance permeation



No associated notes.

72

Delivery Systems Application

Innovations to increase effectiveness

- Recirculation
- Pneumatic fracturing
- Hydraulic fracturing
- Ozone sparging
- Unsaturated zone delivery

No associated notes.

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Section V: Process Monitoring

- Oxidant-specific monitoring parameters
  - Injection concentrations
  - Volumes
  - Flow rates
  - Return on investment
- Injection well
  - Temperature
  - Pressure
- Important component of the health and safety program

No associated notes.

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Oxidant Specific Monitoring Parameters

- Permanganate
  - Monitor well - color, oxidation / reduction potential (ORP), conductivity, chloride, manganese dioxide
- Persulfate
  - pH, dissolved oxygen (DO), ORP, conductivity, and/or persulfate in monitor wells
- Ozone
  - Continuous monitoring of ozone gas, carbon dioxide (CO_2), volatile organic compounds (VOCs), and oxygen (O_2)
- Peroxide (Fenton's)
  - Injection well - pH, temperature, pressure
  - Monitor well - pH, temperature, color, ORP, DO, conductivity, and VOCs

See section 6 from ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition (ISCO-2, 2005) available from www.itrcweb.org under "Guidance Documents" then "In Situ Chemical Oxidation."

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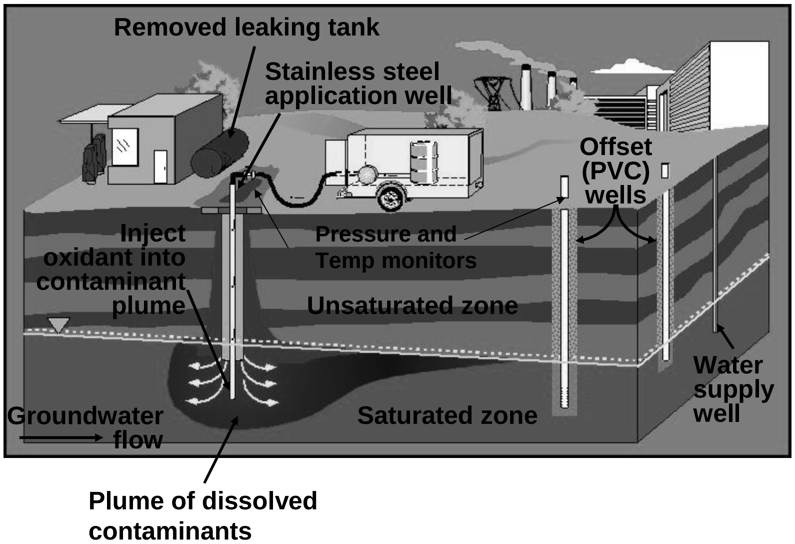
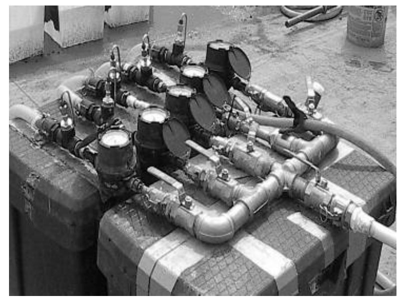
Monitoring Locations



No associated notes.

Pressure and Flow Monitoring

Temperature and Pressure Gauges



Flow Metering

No associated notes.

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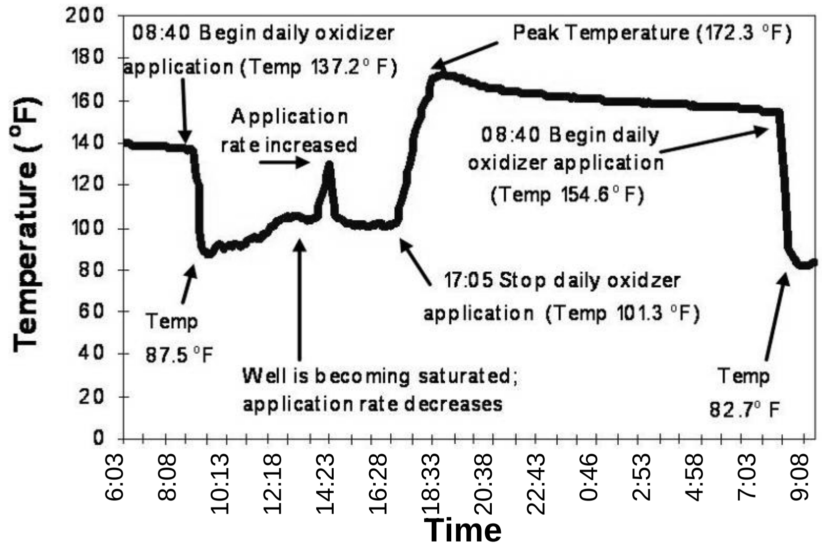
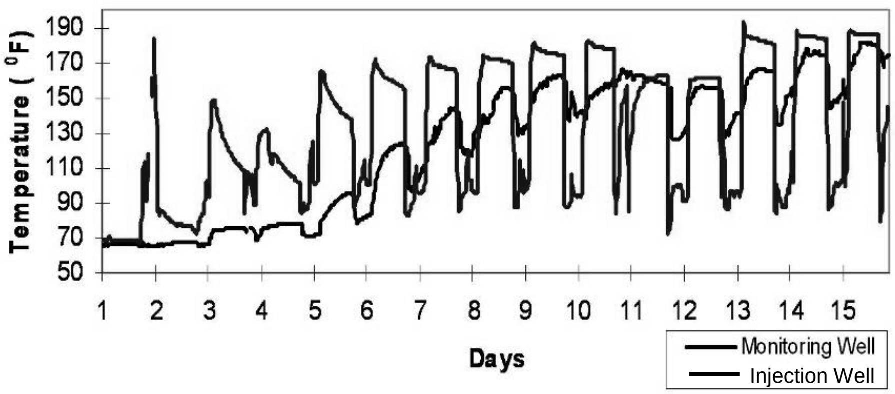
Daily Temperatures



No associated notes.

Temperature Trends

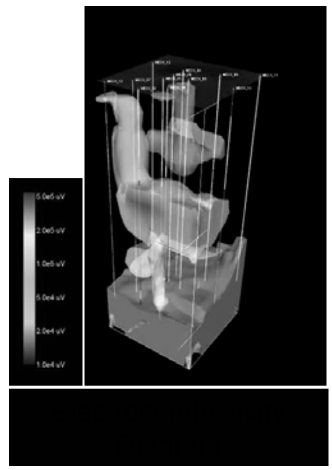
Daily Peroxide Injections



No associated notes.

Section VI: Regulatory Evaluation

- Performance monitoring
- Performance expectations
- Total mass evaluation
- Regulatory perspective

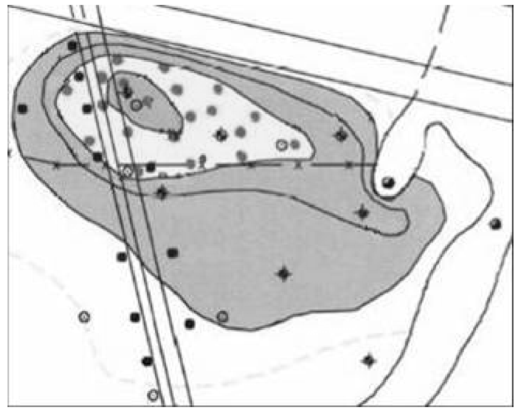


No associated notes.

80

Performance Monitoring

- Establish baseline conditions and sampling locations before treatment
- Determine contaminant mass / concentration reduction
- Monitor contaminant release and/or mobilization
- Includes post-treatment and possibly closure monitoring



● **Application Wells**
● **Monitor Wells**

No associated notes.

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Performance Expectations

Risk, Mass, and Toxicity Reductions

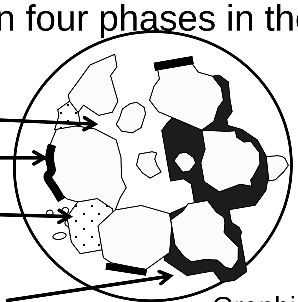
- ISCO reduces contaminant mass through the oxidation process
- Mass reduction = reduction in risk
- Rapid reduction of source area concentrations to acceptable levels for biological polishing and plume control

No associated notes.

82

Total Mass Evaluation
Nature of Contamination

- Contamination mass exists in four phases in the contaminated zone
  - Soil gas
  - Sorbed
  - Dissolved
  - Non-aqueous phase liquid (NAPL) or phase-separated



Graphic source: Suthersan, 1996

- Geochemistry, partitioning coefficient (K_{ow}) determines the relationship between phases in the saturated zone
- Majority of mass (normally >80%) is sorbed and phase-separated

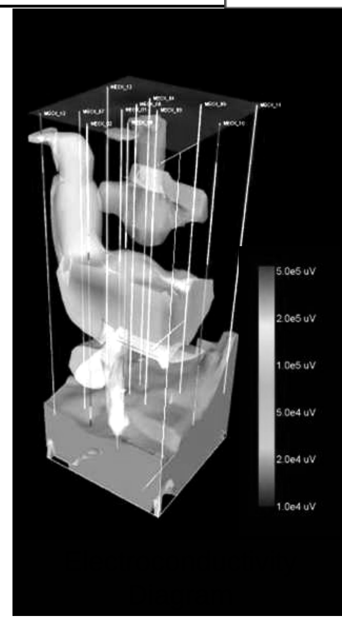
The partitioning coefficient (Kow) is a measure of the equilibrium concentration of a compound (contaminant) that describes the potential for the compound to partition into soil organic matter. The contaminant with the highest partitioning coefficient will partition into soil organic matter first.

Suthersan, S.S., Remediation Engineering: Design Concepts. CRC Press, Inc., Boca Raton, Fla.

83

Total Mass Evaluation
Importance of Mass Calculations

- Evaluate pre- and post- total contaminant mass
- Sorbed and non-aqueous phase mass converts to dissolved during treatment and until site reaches post treatment final equilibrium
- Possible “rebound” causes
  - Dissolution of sorbed or non-aqueous phase
  - Inadequate site characterization
  - Change in groundwater flow direction
- Decrease in total mass may not be reflected in short-term dissolved concentrations



Evaluation of pre- and post- total contaminant mass is recommended

Mass is converted from sorbed and non-aqueous phase to dissolved during treatment and until site reaches post treatment final equilibrium

“Rebound” in dissolved concentrations can be caused by dissolution of sorbed or non-aqueous phase, inadequate site characterization, change in groundwater flow direction, etc

A decrease in total mass may not be reflected in short-term dissolved concentrations

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Regulatory Perspective Summary

Life of a regulator

- Too many cases/many deadlines
- Needs to make sound technical decisions in a timely manner

The ISCO-2 document

- Allows a regulator to feel much more confident in reviewing an ISCO proposal
- Provides a list of contacts

Contacts in the form of ISCO team members as well as case study participants represent an invaluable resource.

For contact information, see ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater, 2nd Edition (ISCO-2, 2005):

Appendix D. Case Studies – includes contact information for case study participants

Appendix E. ITRC ISCO Team Contacts

ISCO guidance document is available on www.itrcweb.org under “Guidance Documents” and “In Situ Chemical Oxidation.”

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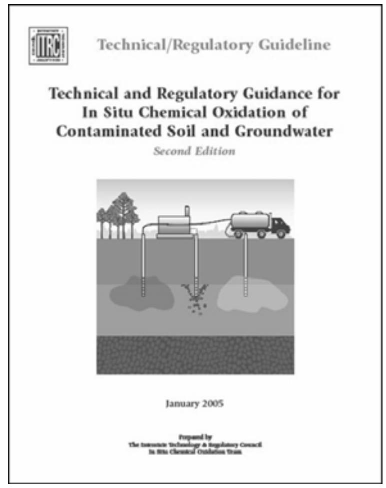
Topics Included in ISCO-2 Document

- Regulatory permits
- Health and safety issues
- Oxidant application
- Conceptual site model
- System strategies
- Dosage considerations
- Performance monitoring
- Cost considerations
- Emerging ISCO technologies
- Acronyms, glossary, case studies
- ITRC ISCO team contacts



The ISCO-2 document provides a detailed ready reference for anyone that is involved with an ISCO proposal/project. ISCO guidance document is available on www.itrcweb.org under “Guidance Documents” and “In Situ Chemical Oxidation.”

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Thank you for participating

- **Links to additional resources**
- **2nd question and answer session**

Links to additional resources:

http://www.clu-in.org/conf/itrc/advisco/resource.cfm

Your feedback is important – please fill out the form at:

http://www.clu-in.org/conf/itrc/advisco

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 with ITRC:

Join an ITRC Team – with just 10% of your time you can have a positive impact on the regulatory process and acceptance of innovative technologies and approaches

Sponsor ITRC's technical team and other activities

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

Use ITRC products and attend training courses

Submit proposals for new technical teams and projects