Developing the ISCO Technology Practices Manual: The SERDP/ESTCP ISCO Initiative

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ISCO Short Course

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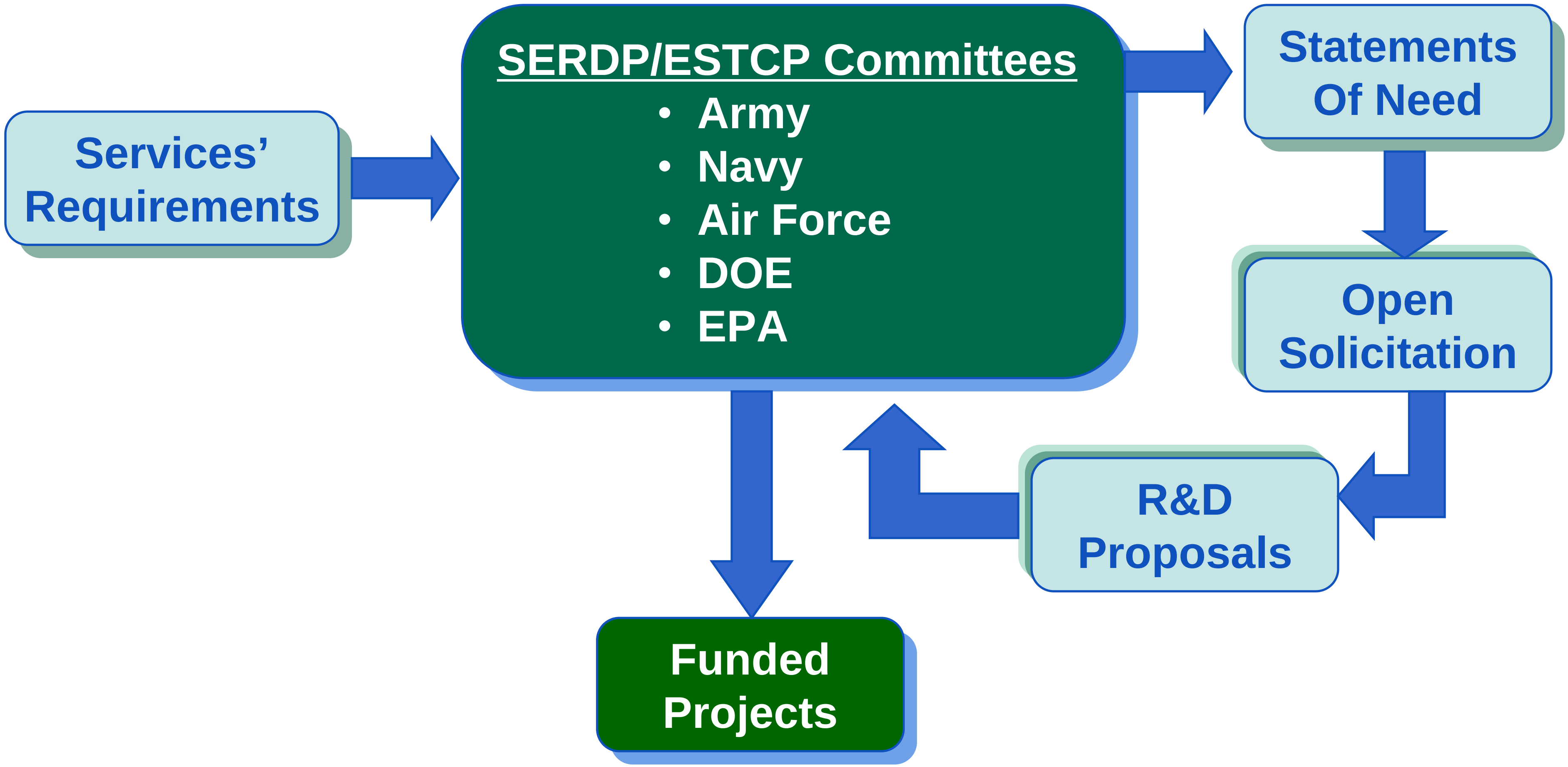
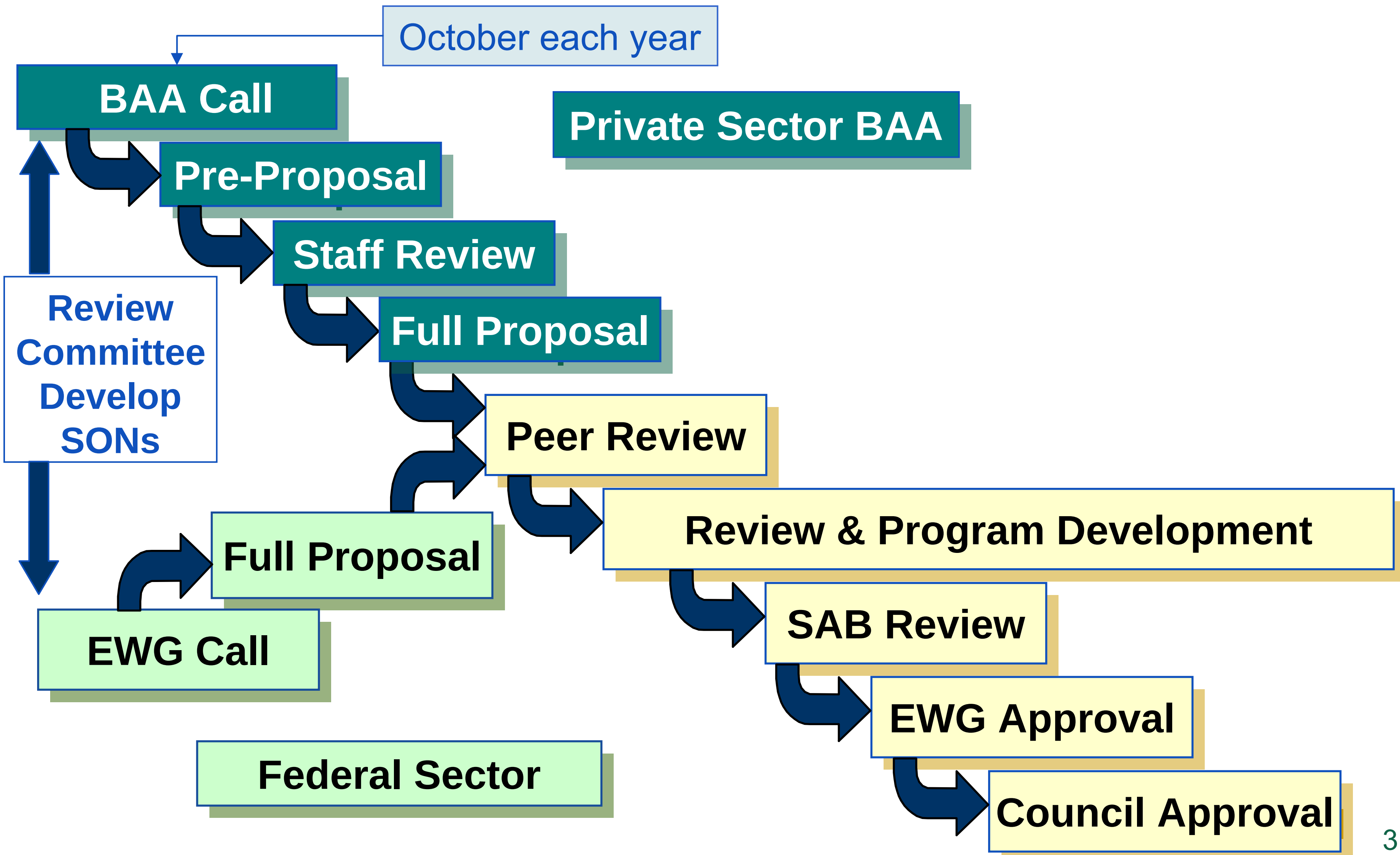
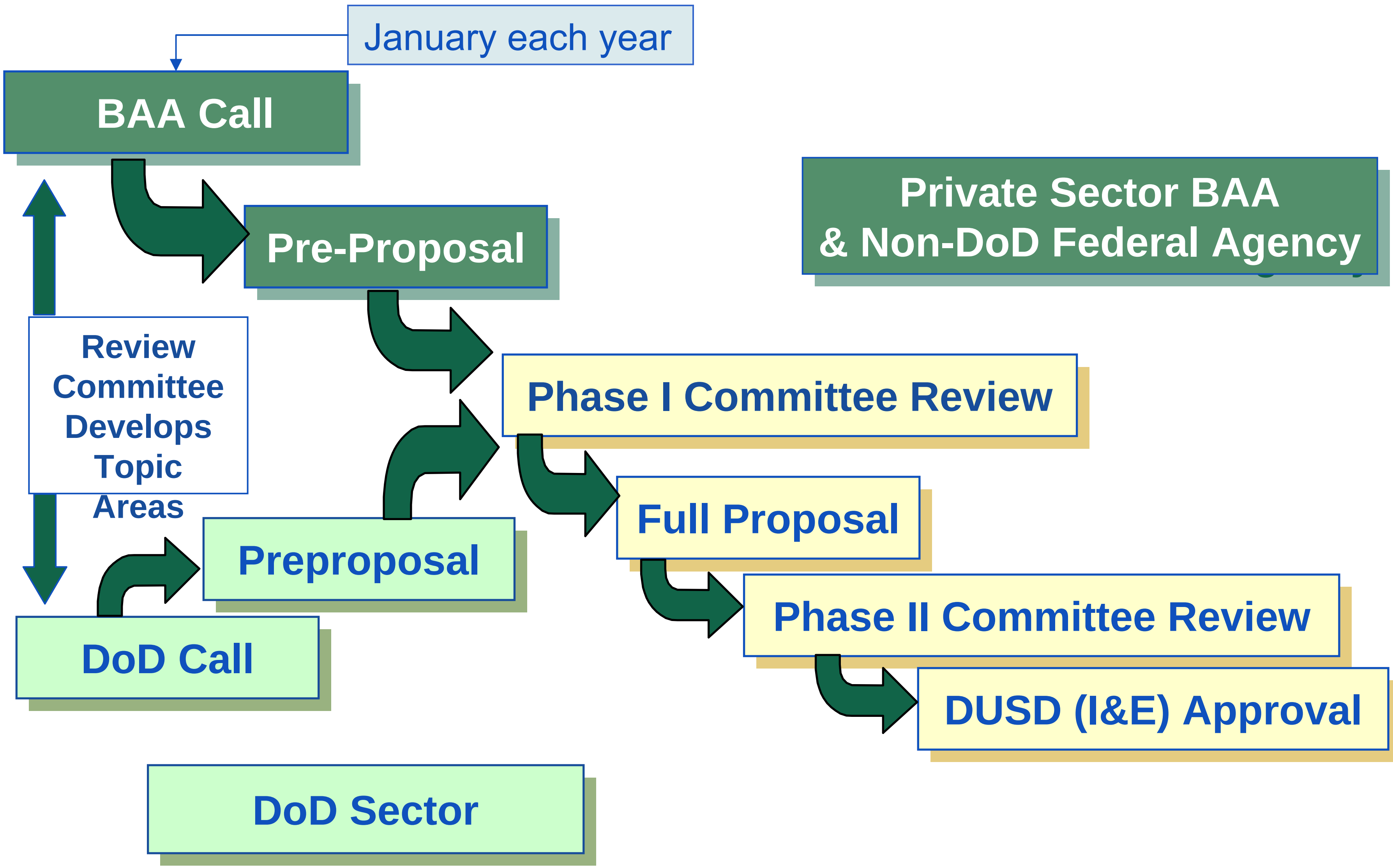
Service Coordination Process



SERDP Solicitation Process



ESTCP Solicitation Process



Chlorinated Solvents Research Initiatives

Well-Established Technologies

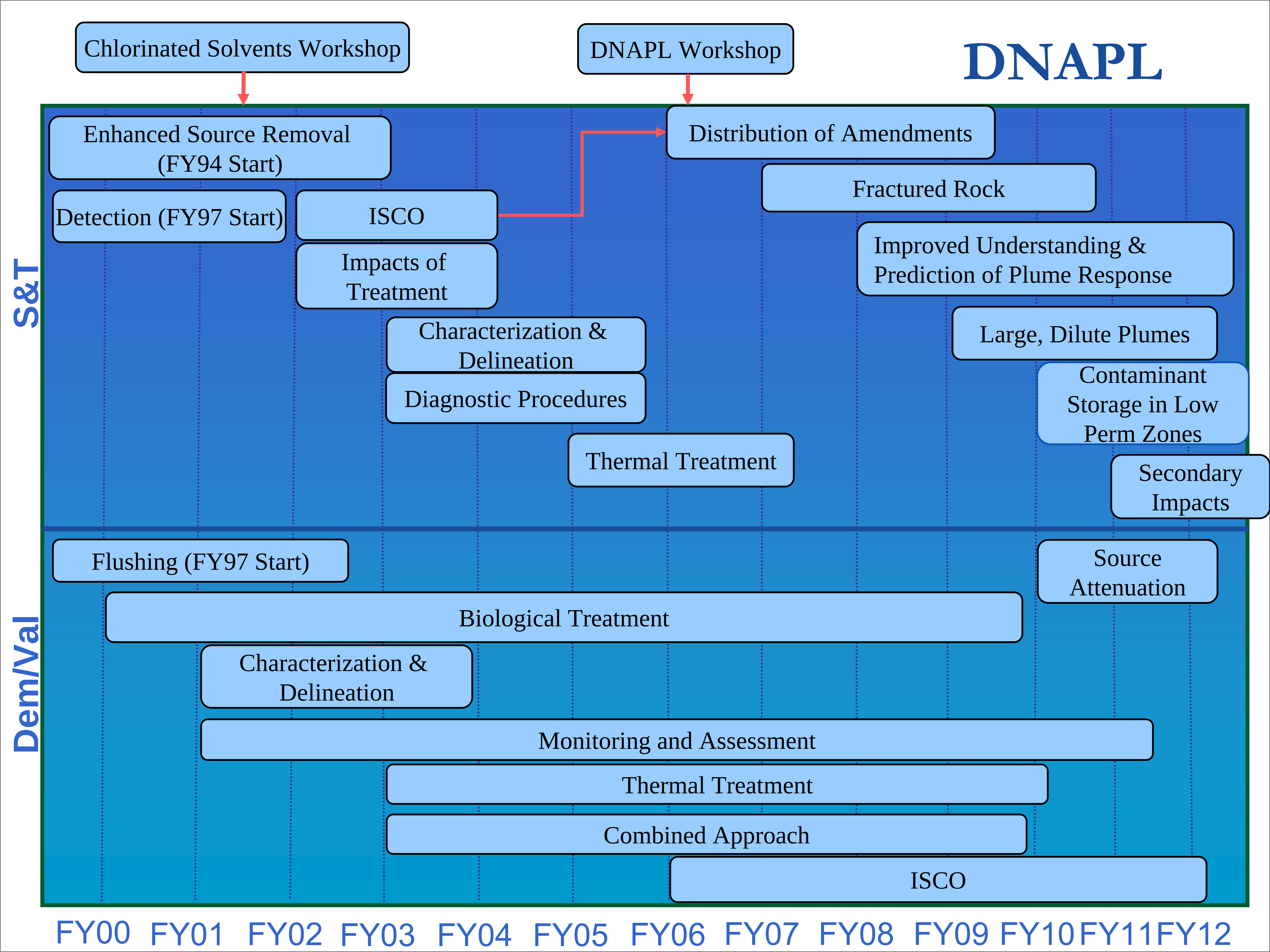
Dissolved Phase Technologies

- Permeable Reactive Barriers
- Air Sparging
- Biostimulation
- Monitored Natural Attenuation
- Bioaugmentation
- Bioaugmentation Assessment

More Data Gaps

DNAPL Source Zone Technologies

- DNAPL Source Zone Initiative
- Biostimulation
- In Situ Chemical Oxidation Initiative
- Thermal Treatment Initiative


DNAPL
Chlorinated Solvents Workshop
DNAPL Workshop
S&T
Enhanced Source Removal (FY94 Start)
Detection (FY97 Start)
ISCO
Impacts of Treatment
Characterization & Delineation
Diagnostic Procedures
Thermal Treatment
Distribution of Amendments
Fractured Rock
Improved Understanding & Prediction of Plume Response
Large, Dilute Plumes
Contaminant Storage in Low Perm Zones
Secondary Impacts
Dem/Val
Flushing (FY97 Start)
Source Attenuation
Biological Treatment
Characterization & Delineation
Monitoring and Assessment
Thermal Treatment
Combined Approach
ISCO
FY00 FY01 FY02 FY03 FY04 FY05 FY06 FY07 FY08 FY09 FY10 FY11 FY12

ISCO Initiative

- SERDP and ESTCP have funded ~20 projects over the past 12 years focused on ISCO remediation and monitoring.

SERDP/ESTCP Investment	
SERDP	5.2M
ESTCP	4.5M
Total	**9.7M**

ISCO Initiative

- A Technical Advisory Committee (TAC) was created with experts in the field to advise the projects
  - TAC Members
    - Richard Brown/ERM
    - Michael Marley/Xpert Design & Diagnostics
    - Robert Norris/Brown & Caldwell
    - Ian Osgerby/USACE

ISCO Initiative

- Transition into ESTCP ISCO projects
- Emerging Contaminants
- SOPS and Guidance

Basic Research Projects

- Improved Understanding of Fenton-Like Reactions for the In Situ Remediation of Contaminated Groundwater Including Treatment of Sorbed Contaminants and Destruction of DNAPLs (SERDP ER-1288)

  PI: Richard Watts (Washington State University)
- Improved Understanding of In Situ Chemical Oxidation (SERDP ER-1289)

  PI: Eric Hood (Geosyntec)
- Reaction and Transport Processes Controlling In Situ Chemical Oxidation of DNAPLs (SERDP ER-1290)

  PI: Robert Siegrist (Colorado School of Mines)
- Control of Manganese Dioxide Particles Resulting from In Situ Chemical Oxidation Using Permanganate (SERDP ER-1484)

  PI: Michelle Crimi (East Tennessee State University)
- Multi-Scale Experiments to Evaluate Mobility Control Methods for Enhancing the Sweep Efficiency of Injected Subsurface Remediation Amendments (SERDP ER-1486)

  PI: John McCray (Colorado School of Mines)
- Enhanced Reactant-Contaminant Contact through the Use of Persulfate In Situ Chemical Oxidation (SERDP ER-1489)

  PI: Richard Watts (Washington State University)
- Impacts on Groundwater Quality following the Application of ISCO: Understanding the Cause of and Designing Mitigation for Metals Mobilization (SERDP ER-2132)

  PI: Kevin Gardner (University of New Hampshire)

Demonstration & Validation Projects

- In Situ Chemical Oxidation for Groundwater Remediation - Technology Practices Manual (ESTCP ER-200623)

  PI: Robert Siegrist (Colorado School of Mines)
- Biological Oxidation of DCE through Manganese Addition (ESTCP ER-200625)

  PI: Robert Borden (Solutions - IES)
- Development of a Design Tool for Planning Aqueous Amendment Injection Systems (ESTCP ER-200626)

  PI: Robert Borden (North Carolina State University)
- Field Demonstration, Optimization, and Rigorous Validation of Peroxygen-Based ISCO for the Remediation of Contaminated Groundwater (ESTCP ER-200632)

  PI: Richard Watts (Washington State University)
- Cooperative Technology Demonstration: Polymer-Enhanced Subsurface Delivery and Distribution of Permanganate (ESTCP ER-200912)

  PI: Michelle Crimi (Clarkson University)

Tech Transfer

- Fact Sheets
  - Currently prepared at project initiation, updated at project completion
- Final Reports
  - Direct link on projects page
- Cost & Performance Reports
  - Direct link on projects page
- ER-200623: ISCO Technology Practices Manual
  - Decision-Making Guides
  - Design-Based Spreadsheet Tools
  - Comprehensive ISCO Data Base
  - Frequently Asked Questions Guide
- ISCO Monograph

Website

www.serdp-estcp.org

Short Course Agenda

Time	Topic	Presenter
1:45-2:00 PM	Introduction and Overview	Marvin Unger
2:00-2:30 PM	ISCO Principles and Practices	Robert Siegrist
2:30-2:50 PM	Overview of ISCO e-TPM: Protocol Component Flow Diagrams and Key Tools	Thomas Simpkin
2:50-3:10 PM	Break	
3:10-3:40 PM	ISCO Screening: Scenarios, Oxidant Selection, & Outcomes vs. Expectations	Michelle Crimi
3:40-4:00 PM	ISCO Conceptual Design: Scenarios, Oxidant Selection, & Outcomes vs. Expectations	Thomas Simpkin
4:00-4:20 PM	CDISCO: Detail and Demonstration of Design Tool	Robert Borden
4:20-4:40 PM	Breakout Exercise: Scenario Selection and Design	Michelle Crimi
4:40-4:55 PM	Discussion of Breakout Scenario	Michelle Crimi
4:55-5:00 PM	Closing Remarks and Future Directions	Robert Siegrist
5:00 PM	Adjourn	

In Situ Chemical Oxidation:
2. Overview of Principles and Practices

Bob Siegrist
Robert L. Siegrist, Ph.D., P.E., BCEE
Professor, Environmental Science and Engineering
Colorado School of Mines
Golden, Colorado USA

SERDP DOD ▪ EPA ▪ DOE | ESTCP

Presentation Overview

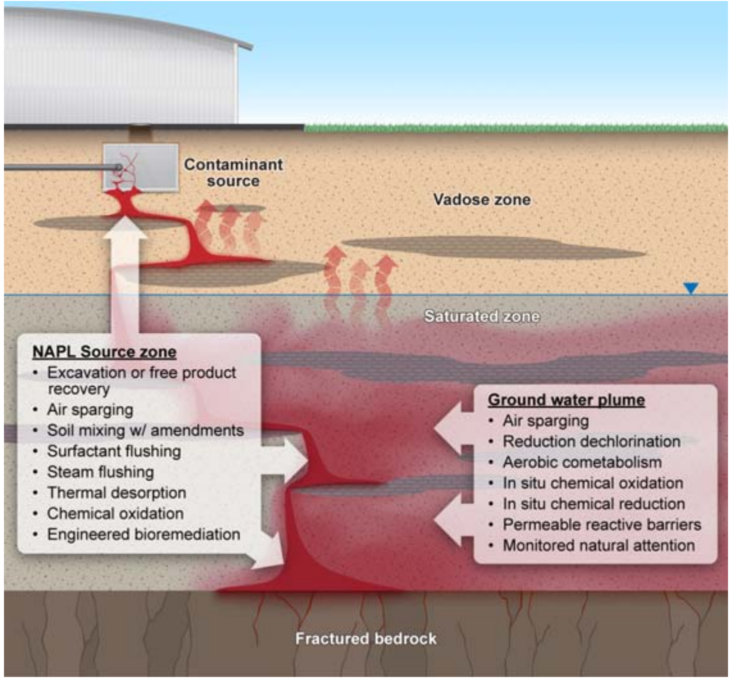
1. Principles of ISCO as a remediation technology
2. Practices employed during field applications
3. Supporting a standard of practice for ISCO

Acknowledgments

- ✓ SERDP/ESTCP
  - ✧ The ISCO initiative and sponsored projects
- ✓ Colleagues and collaborators
- ✓ Team members involved in ESTCP Project ER-0623 and Contributors to a new ISCO reference text

1. Principles: ISCO for Site Remediation

- ISCO involves the delivery of chemical oxidants into the subsurface to transform COCs and reduce their mass, mobility, and/or toxicity
  - ♦ Treatment of a wide variety of contaminants of concern (COCs)
    - Solvents
    - Fuels
    - Pesticides
    - Explosives
    - Other organics
  - ♦ In a range of media
    - Soil, sludges, sediments
    - Groundwater
      - Source zones
      - Plumes



Source: Siegrist *et al.* 2011.

Chemical oxidants for ISCO

- Various chemical oxidants can be used for ISCO
  - Oxidants are usually injected into the subsurface as a liquid or gas

Oxidant[1]	Oxidant Chemical	Commercial Form	Activator	Reactive Species
Permanganate*	$KMnO_4$ or $NaMnO_4$	Powder, liquid	None	MnO_4^-
Hydrogen peroxide*	H_2O_2	Liquid	None, Fe(II), Fe(III)	$OH\bullet$, $O_2\bullet^-$, $HO_2\bullet$, HO_2^-
Ozone*	O_3 (in air)	Gas	None	O_3, $OH\bullet$
Persulfate*	$Na_2S_2O_8$	Powder	None, Fe(II), Fe(III), heat, H_2O_2, high pH	SO_4^{2-}, $SO_4\bullet^-$
Peroxone	H_2O_2 plus O_3 (in air)	Liquid, gas	O_3	O_3, $OH\bullet$
Percarbonate	$Na_2CO_3 \cdot 1.5H_2O_2$	Powder	Fe(II)	$OH\bullet$
Calcium peroxide	CaO_2	Powder	None	H_2O_2, HO_2^-

[1]Those oxidants with an " * " have been most commonly used for in situ applications

  - A particular oxidant and set of conditions can yield one or more reactive species

Reactive Species	Formula	Electrode Potential (Eh), volts (V)
Hydroxyl radical	$OH\bullet$	+2.8 V
Sulfate radical	$SO_4\bullet^-$	+2.6 V
Ozone	O_3	+2.1 V
Persulfate anion	SO_4^{2-}	+2.1 V
Hydrogen peroxide	H_2O_2	+1.77 V
Permanganate anion	MnO_4^-	+1.7 V
Perhydroxyl radical	$HO_2\bullet$	+1.7 V
Oxygen	O_2	+1.23 V
Hydroperoxide anion	HO_2^-	-0.88 V
Superoxide radical	$O_2\bullet^-$	-2.4 V

Source: Siegrist *et al.* 2011.

Achieving ISCO in the subsurface

- A scientific basis underpins the potential capability of ISCO to completely destroy organic COCs in the subsurface…

  …..but its realization depends on:

  - Susceptibility of the target organics to oxidative destruction
  - If there are sorbed and nonaqueous phase liquids (NAPLs), the rate and extent of mass transfer into the aqueous phase
  - Ability to deliver and transport the oxidant in a target treatment zone (TTZ)
  - Effects of ambient subsurface conditions on ISCO reactions
  - ISCO effects on subsurface permeability and biogeochemistry

Oxidation of organic COCs

- Oxidation of organics in an aqueous phase to CO_2, water, salts and oxides, with possible intermediates
  - Highly simplified oxidation stoichiometries for TCE:

Catalyzed H_2O_2 (CHP) $C_2HCl_3 + 3H_2O_2 + \mathit{Fe} \rightarrow 2CO_2 + 2H_2O + 3H^+ + 3Cl^- + \mathit{Fe}$

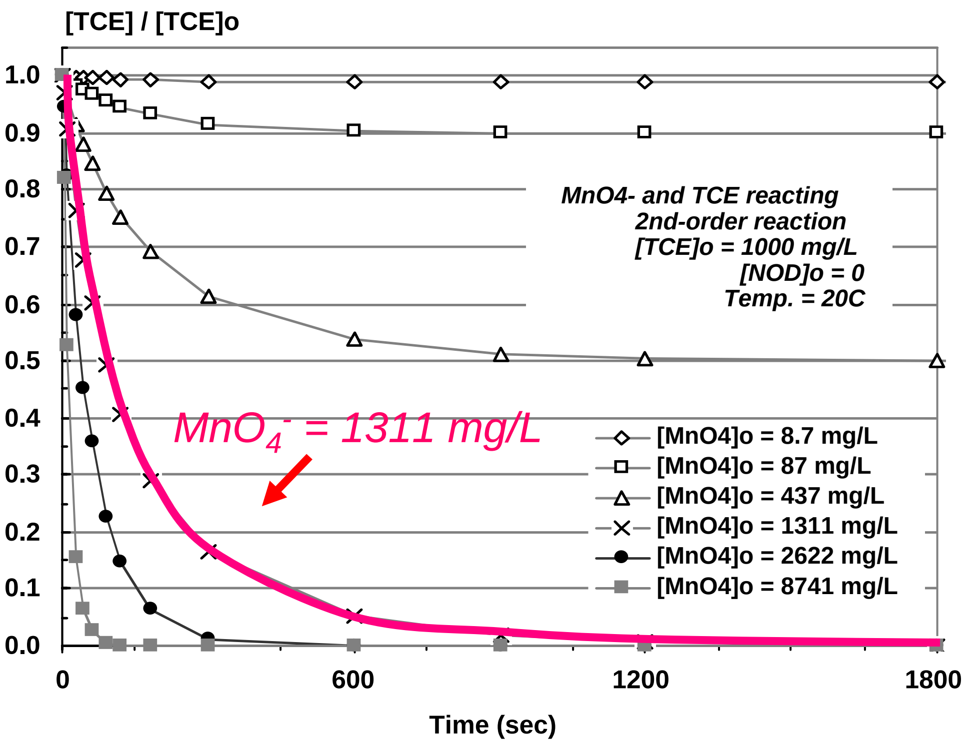
Ozone $C_2HCl_3 + O_3 + H_2O \rightarrow 2CO_2 + 3H^+ + 3Cl^-$

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

  - Reactions involve free-radicals and/or redox electron transfers
  - Kinetics are 2^{nd}-order, very fast, and temperature dependent

- Mass of oxidant delivered must satisfy the stoichiometric requirements of the target organics plus nonproductive oxidant depletion in the subsurface

- Illustration of MnO_4^- destruction of TCE in water
  - Well-mixed reaction vessel with TCE initial = 1,000 mg/L
    - The system contains no other substances that react with MnO_4^-
  - Concentrations of MnO_4^- varied from 8.7 to 8,741 mg/L



$$\frac{d[TCE]}{dt} = -k_2 [TCE]^1 [MnO_4^-]^1$$

k_2 = 0.89 L mol^{-1} s^{-1}

E_a = 78 kJ mol^{-1}

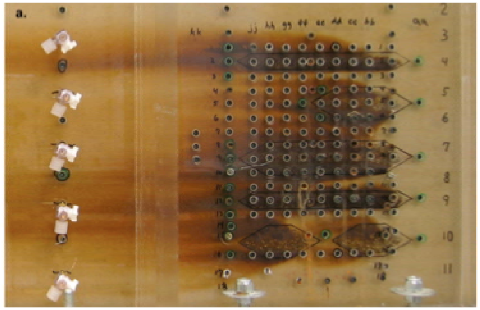
k_2 = 0.89 at 20C

0.30 at 10C

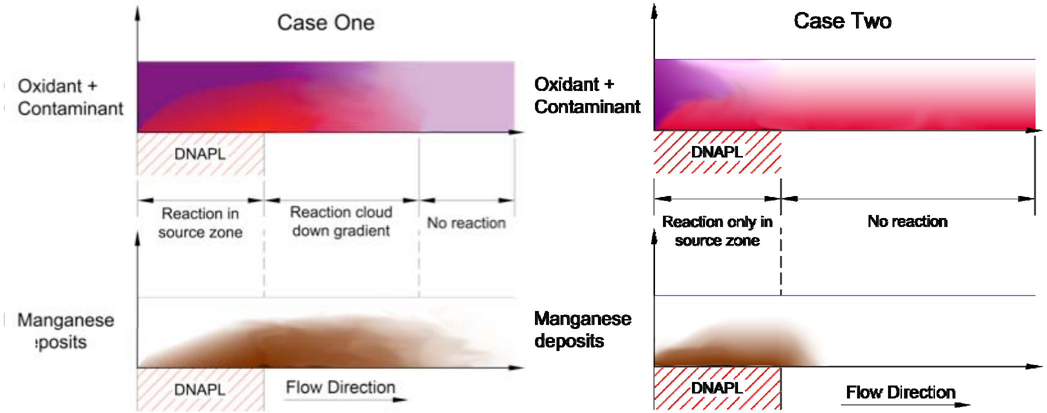
Source: Siegrist *et al.* 2001.

- NAPLs can be degraded via enhanced mass transfer
  - ♦ Enhanced NAPL degradation depends on no adverse effects on interphase mass transfer from the NAPL into the water phase
  - ♦ The oxidant type and conditions can affect mass transfer
    - Notably, with MnO_4^- there is potential for films, rinds, or crusts due to MnO_2 deposition
    - Potential for chemo-stabilization (?)

a) MnO_2 film formation on a TCE droplet in water.



b) MnO_2 film and pore filling near PCE source zones in a sand tank.

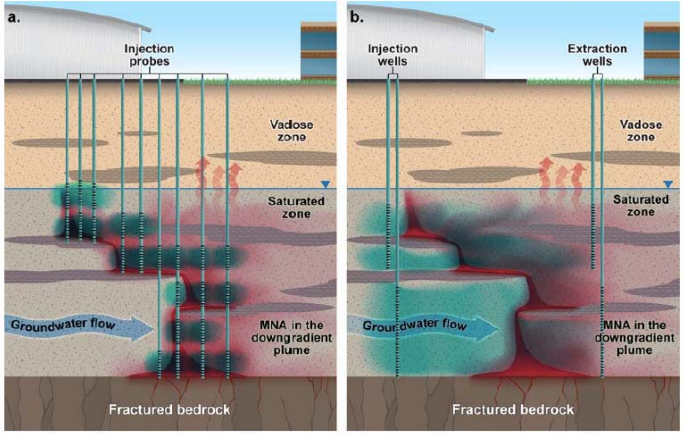


C) Conceptual model of MnO_2 deposition under high flow, low conc. (Case 1) vs. low flow, high conc. (Case 2).

Sources: a) Urynowicz and Siegrist 2005; b) Heiderscheidt *et al.* 2008; c) Petri *et al.* 2008.

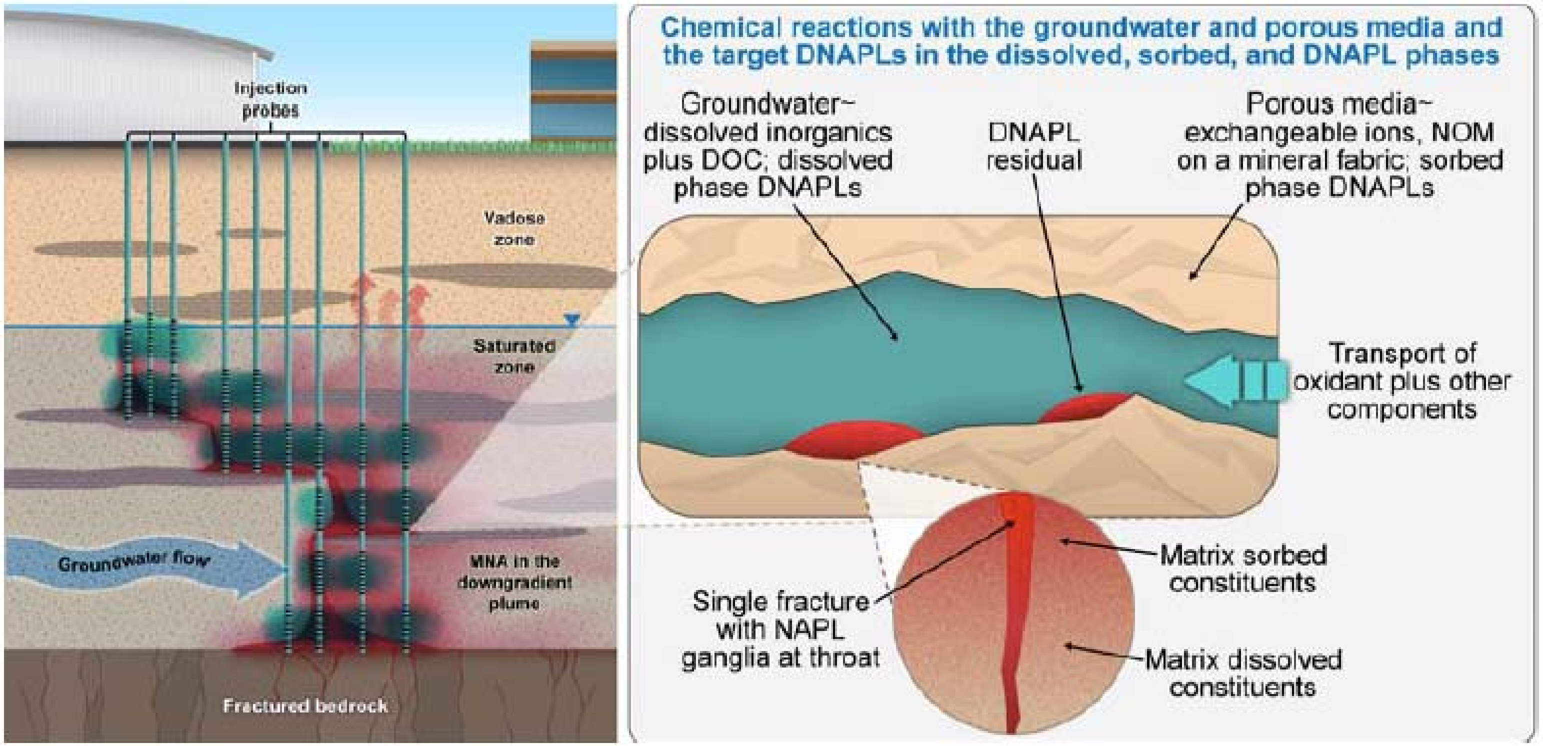
Oxidant delivery and subsurface transport

- Application of ISCO to remediate a target treatment zone (TTZ) requires delivery of an oxidant - and in some cases amendments - into and throughout the TTZ
  - ♦ Optional delivery methods for ISCO include:
    - Direct-push probes, drilled wells, specialized injectors, fracturing, soil mixing
    - Recirculation schemes, permeable barriers
    - Multiple delivery events, multiple modes of delivery
  - ♦ Viability of a given delivery method depends on the oxidant used and site-specific conditions



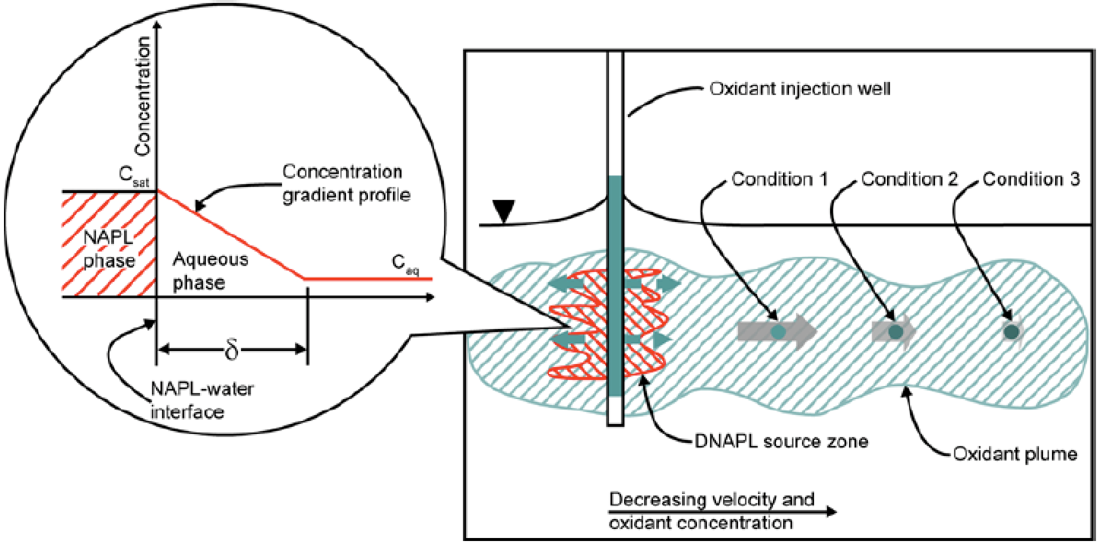
Source: Siegrist *et al.* 2011.

- During oxidant transport in the subsurface, macro- and micro-scale features within a TTZ can control ISCO processes and effectiveness



Source: Siegrist *et al.* 2011.

- Oxidant distribution within a TTZ are dependent on oxidant delivery design (e.g., method and rate of injection) and subsurface conditions (e.g., permeability, heterogeneity)
  - ♦ Subsurface transport normally relies on advection but fast reactions can limit transport distances; diffusion is often very limited
  - ♦ Subsurface flow regimes can control reaction rates and extents:



Source: Petri *et al.* 2008.

Oxidant injection out of a well yields a forced gradient such that:

Condition 1 has a high flow velocity and high oxidant concentration;

Condition 2 has a lower velocity and moderate oxidant concentration;

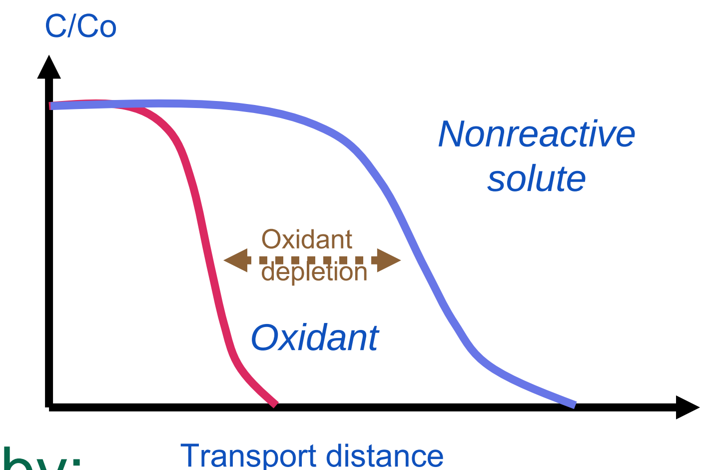
Condition 3 has near-ambient groundwater velocity and near-zero oxidant level.

Nonproductive oxidant depletion

- Oxidant transport throughout a TTZ can be greatly affected by nonproductive oxidant depletion in the subsurface, including:
  - Natural oxidant demand (NOD)

    e.g., for permanganate
  - Decomposition and quenching

    e.g., for CHP, ozone, persulfate



- Nonproductive depletion can occur by:
  - Reactions with reduced substances (e.g., NOM, S^-, Fe^{+2}, CO_3^{-2})
  - Interactions with mineral surfaces
- Nonproductive oxidant depletion can exert major effects on ISCO remediation effectiveness and project costs

Other subsurface interactions

- Various interactions can potentially occur during ISCO
  - Altered behavior of COCs and co-Contaminants
    - Organic COCs (…films, displacement)
    - Metal co-COCs (…redox metals)
  - Permeability loss in injectors and within porous media
    - Particles (…permeability loss at interfaces)
    - Gas evolved (…at NAPL interfaces)
  - Biogeochemical changes
    - Chemical impurities (…MnO_4^- type/dose, sorption)
    - pH (negl. in most systems, high at NAPL interfaces)
    - Ion behavior (…CEC)
    - Natural organic matter (…release of DOC, residual NOM)
    - Microbiology (…short-term perturbations)
    - Toxicity (…intermediates/byproducts)

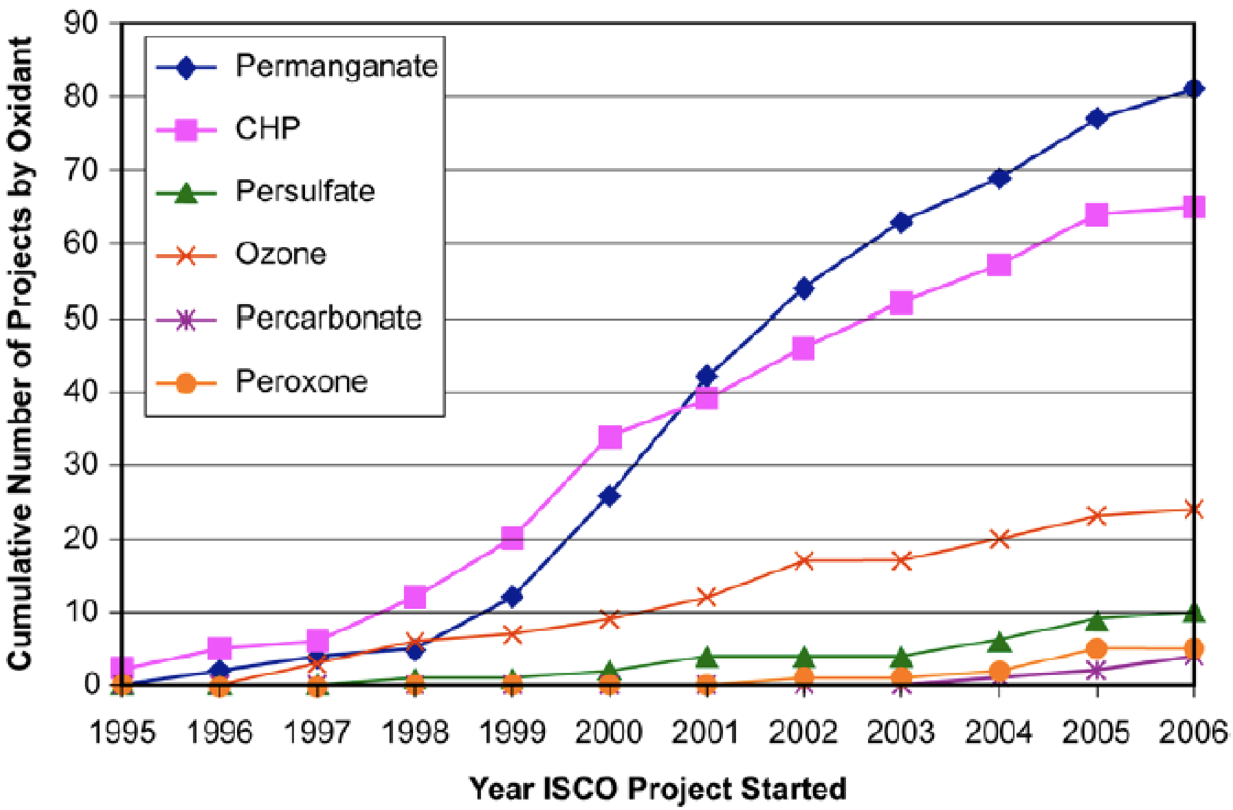
- Interactions can depend on the oxidant used
  - ♦ Examples of interactions for three common oxidants

Interaction	CHP	Permanganate	Ozone
Subsurface effects on the oxidation of target COCs			
Reduced substances	<---------- Can cause high nonproductive depletion --------->		
Optimal pH	Acidic pH	pH 3 to 12	Acidic pH
Effect of TDS	<----------- Little to no effect likely ------------------------>		
Effect of CO_3^{2-}	Scavenger	None	Scavenger
Effect of temp.	<--------------- Affects rate of reaction ----------------------->		
Potential for ISCO to alter ambient conditions			
pH	<----------- Can drop, depending on NAPLs, buffering ------->		
Temperature	Minor to high	None to minor	Minor to high
Metal mobility	<----------- redox metals, local and short-term effects --------->		
Permeability	Gas & particles	Particles & MnO_2	Gas & particles
Microbiology	<------------------ Short-term perturbations ------------------------>		

2. Practices: ISCO Field Applications

- Growing number of ISCO projects
  - ♦ The number of field applications of ISCO in the U.S. and abroad has grown rapidly during the past 10 to 15 yr

Cumulative number of ISCO projects based on a review of 242 projects involving ISCO field applications from 1995 to 2006 (Database named DISCO)



Source: Krembs 2008.

- ISCO can be considered as a viable option - why?
  - Many sites have contaminants that ISCO can treat
    - Examples: dry cleaners, machining and metal working, vehicle repair, chemical factories, testing labs, etc.
  - At these sites, ISCO can be relatively easy to use
    - Engineers are ‘comfortable’ with chemical oxidation based on training and experience (e.g., with waste treatment)
    - ISCO can be used with available materials and equipment
    - ISCO does not require large or highly specialized equipment
    - ISCO does not have unusual power supply or other utility needs
    - ISCO can be done relatively quickly (days to a few weeks) and if needed, multiple injection events can be employed
    - ISCO is conducive to an “observational approach”

a. $NaMnO_4$...injection wells...TCE

b. $KMnO_4$...injection wells...TCE

c. H_2O_2...direct-push probes...CB

d. $KMnO_4$ delivery and feed manifold...injection wells...TCE

e. $KMnO_4$...feed manifold on truck shown in d)

f. $NaMnO_4$ feed manifold... well-to-well recirculation...TCE

g. O_3...sparging wells ...former MGP site

h. O_3 feed and controls at g)

i. O_3 sparging wellhead at g)

j. $Na_2S_2O_8$...direct-push probes ...pesticides

k. $NaMnO_4$...multi-level injection wells...VOCs

Source:
Siegrist *et al.* 2011.

Features of ISCO applications

- Remediation objectives for ISCO
  - ♦ Established within the context of the overall remediation goals and cleanup levels established for a particular site
  - ♦ The objectives for ISCO generally fall into one of the following:
    - Reduce the contaminant concentration or mass in the ISCO-treated zone by some fraction (e.g., >90%)
    - Achieve a specified post-ISCO contaminant concentration in an ISCO-treated zone (e.g., <1 mg/kg in subsurface solids or <100 µg/L in groundwater)
    - Achieve a specified concentration in a groundwater plume at compliance points down gradient of an ISCO-treated source zone
  - ♦ In some cases, these objectives might be met by combining ISCO with another remedial technology or approach

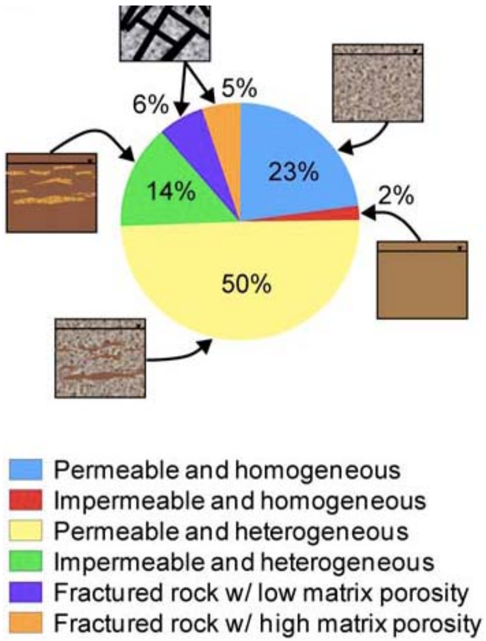
- Most commonly, ISCO has been used to treat source zones where COCs are chloroethenes (e.g., PCE, TCE)

COCs Present	% of 223 Sites
Chloroethenes	70.4%
BTEX	17.5%
TPH, GRO, DRO	11.2%
Chloroethanes	8.1%
MTBE	6.7%
PAHs	6.7%
Chlorobenzenes	4.9%
Methylene chloride	2.7%
Other COCs (8)	<2%

Source: Krembs 2008; DISCO in Siegrist *et al.* 2010.

- ISCO is commonly used for permeable subsurface conditions; homogeneous and heterogeneous

No. = 149



Permeable K>10^-5 cm/s = 0.028 ft/d
Homogeneous K_{max}/K_{min} < 1000

- Delivery by injection wells and direct push probes is common

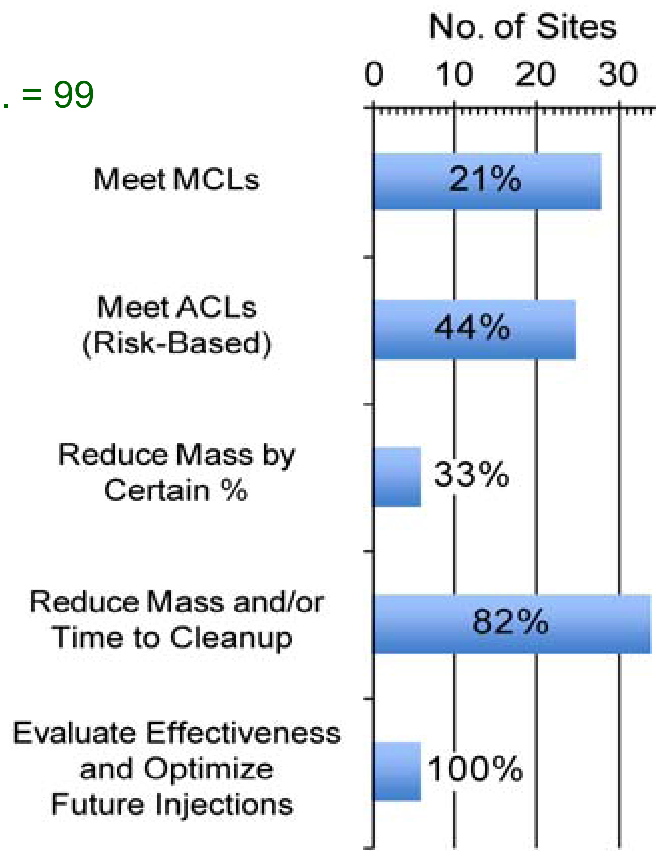
Delivery Method	% of 181 Sites
Injection wells	40%
Direct push probes	23%
Sparge points	14%
Infiltration	10%
Injectors	7%
Recirculation	7%
Fracturing	6%
Mechanical mixing	2%
Horizontal wells	1%

Source: Krembs 2008; DISCO in Siegrist *et al.* 2010.

- ISCO project performance based on field applications

Goals set and % achieving them

No. = 99



Project costs

- Krembs (2008) reported the median total cost for 55 ISCO projects to be $220,000; the median unit cost was $94 per cubic yard (cy) treated based on 33 projects with unit cost data
- McDade *et al.* (2005) reported median and unit costs of $230,000 and $125/cy, respectively, for 13 ISCO projects
- Cost of an ISCO project can vary by an order of magnitude or more depending on various site-specific factors

Source: Krembs 2008; Siegrist *et al.* 2011.

- Impacts of DNAPL being present?
  - At sites with DNAPLs, ISCO often includes a higher no. of pore volumes and higher no. of delivery events
    - Higher total costs
  - DNAPL sites are more likely to be treated by ISCO with other remedies, especially post-ISCO remedies
  - Performance achieved at DNAPL sites?
    - Less likely to meet MCLs but no less likely to meet ACLs
      - ACLs have been met
      - 99.7% maximum reductions in CVOCs have been achieved
    - Achieving MCLs remains elusive
    - ISCO pilot testing can help improve results

Perspectives on ISCO practices

- Views and consensus developed at a CSM workshop
  - ♦ Two reasons for ISCO not achieving performance objectives:
    - The oxidant was not distributed throughout the TTZ
    - An insufficient amount of oxidant was delivered to TTZ
  - ♦ Performance deficiencies are more likely to occur when:
    - Site characterization is inadequate and the contaminant mass is poorly understood
    - The subsurface is highly heterogeneous
    - The design neglects the mass of COCs sorbed in the subsurface
    - The presence of DNAPLs is unknown or not accounted for
    - The presence of co-contaminants that also consume oxidants
    - That oxidants migrate out of the target treatment zone
    - That the oxidant doesn't persist as long as expected

Source: Siegrist *et al.* 2008; also in Siegrist *et al.* 2010.

- “Rebound” in COC concentrations in groundwater is a relatively common occurrence
  - It may or may not be a negative condition or reflect an inherent shortcoming of ISCO or a site-specific performance deficiency
  - The rebound observed at an ISCO treated site can be beneficial

    …. if it is used in an observational approach to refine the site conceptual model and refocus subsequent treatment
  - The use of ISCO can be viewed as an ongoing, iterative process

    …. it can take advantage of contaminant rebound

    …. rather than view it as an indication that the technology was inappropriate for a site or was applied improperly

Points to Consider for ISCO Applications

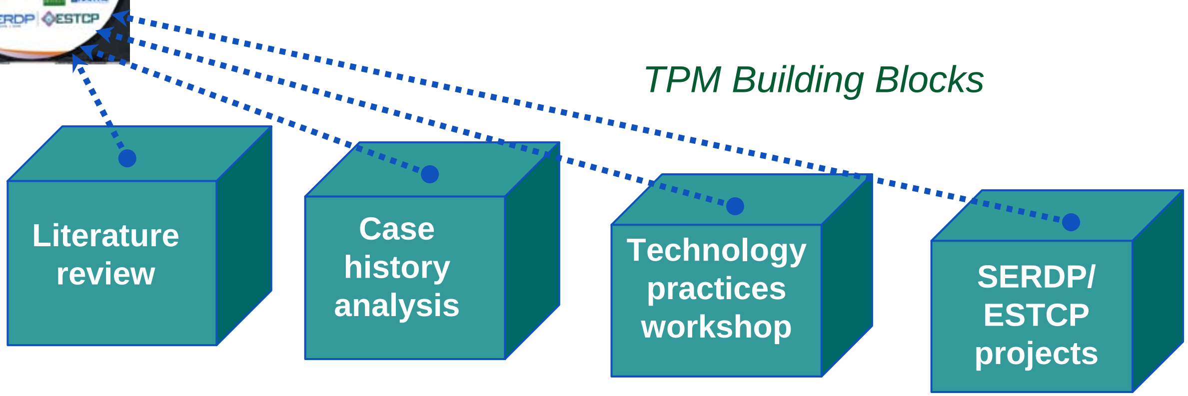
- To enable success & avoid problems, keep in mind:
  - ISCO has great potential for successful use at some, but not all sites
  - ISCO can successfully achieve treatment goals
  - Effective in situ delivery within a TTZ is essential
  - ISCO will normally require two or more active delivery events
  - One or more oxidants can destroy most, if not all, of the common organic COCs
  - ISCO can be, and often must be, synergized with other remedies
  - So-called “rebound” will often occur, more so at some sites than others
  - ISCO can temporarily perturb subsurface conditions
  - Oxidant transport by diffusion is often negligible
  - The cost of ISCO varies widely

Source: Siegrist *et al.* 2010; Siegrist *et al.* 2011.

- And…
  - Environment, health and safety (EHS), as well as waste management and disposal, must be carefully accounted for during ISCO planning and implementation
  - ISCO involves use of potentially hazardous chemicals under adverse working conditions in the field
    - Accidents have happened during ISCO projects
    - Proper EHS is critical to safe and effective use of ISCO

3. Supporting an ISCO Standard of Practice

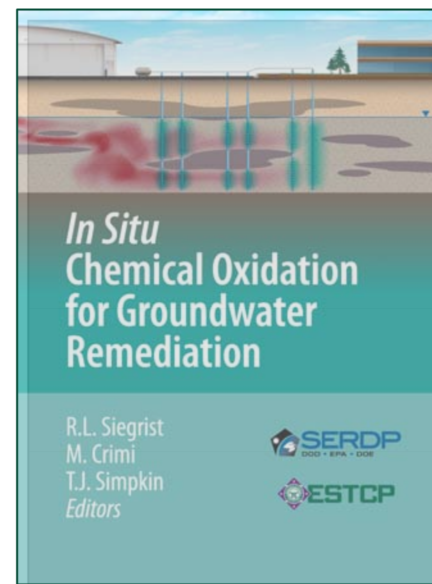
- ESTCP project ER-0623: 'Technology Practices Manual'
  - ♦ Design protocol with decision diagrams, links to explanatory text, and design tools; Case history analysis and database; Technology practices assessment; Frequently asked questions guide



- Preparation of an ISCO reference text
  - ♦ Edited volume with 24 contributing authors

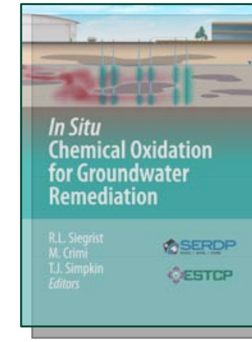
Approx. 700-pg. text published within the SERDP/ESTCP Remediation Technology Monograph Series

by Springer Science+Business Media (www.springer.com)
1st Edition., 2011, Hardcover; ISBN: 978-1-4419-7825-7



- Contents of the ER-0623 ISCO TPM
  - Frequently Asked Questions Guide concerning ISCO
  - E-Protocol for Site Specific Engineering and Application
    - Introduction and User’s Guide
    - ISCO Screening
    - Conceptual Design
    - Detailed Design and Planning
    - Implementation and Performance Monitoring
    - References
  - Supplementary Information and Tools
    - Annotated Review of the ISCO Literature
    - Critical Review of Field Applications and Experiences
    - DISCO – Database of Field Applications and Experiences
    - ISCO Technology Practices Workshop – Summary Proceedings
    - CORT3D Numerical Model for Permanganate ISCO

- Contents of the ISCO reference text
  1. In Situ Chemical Oxidation: Technology Description and Status
  2. Fundamentals of ISCO Using Hydrogen Peroxide
  3. Fundamentals of ISCO Using Permanganate
  4. Fundamentals of ISCO Using Persulfate
  5. Fundamentals of ISCO Using Ozone
  6. Principles of ISCO Transport and Modeling
  7. Principles of Combining ISCO with Other Remedial Approaches
  8. Evaluation of ISCO Field Applications and Performance Results
  9. Systematic Approach to Engineering of an ISCO System
  10. Site Characterization and ISCO Treatment Goals
  11. Oxidant Delivery Approaches and Contingency Planning
  12. ISCO System Performance Monitoring
  13. ISCO Project Costs and Sustainability Considerations
  14. ISCO Status and Future Directions



References cited in the slides

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- Siegrist RL, M Crimi, TJ Simpkin (eds). 2011. In Situ Chemical Oxidation for Groundwater Remediation. Springer Science+Business Media, LLC, New York, New York. A volume in SERDP/ESTCP Remediation Technology Monograph Series, C.H. Ward (Series ed). http://www.springer.com/environment/environmental+management/book/978-1-4419-7825-7. ~700 p.
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In Situ Chemical Oxidation: 3. Overview of e-Technical Practices Manual

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CH2M HILL, Denver, CO

SERDP
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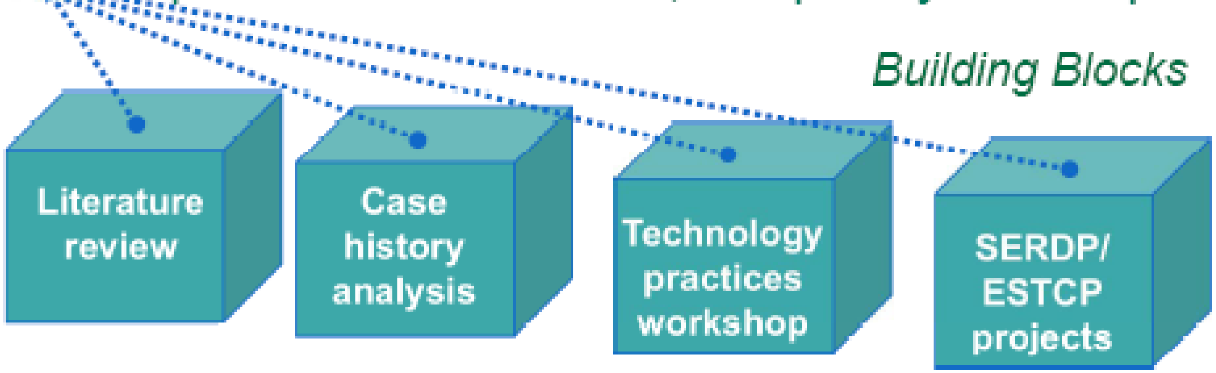
ESTCP

Developing an ISCO Standard of Practice

- ESTCP project to develop an interactive CD (ER-0623)

  - Design protocol with decision diagrams, links to explanatory text, and design tools; Case history analysis and database; Technology practices assessment; Frequently asked questions guide



- Preparation of an ISCO reference text
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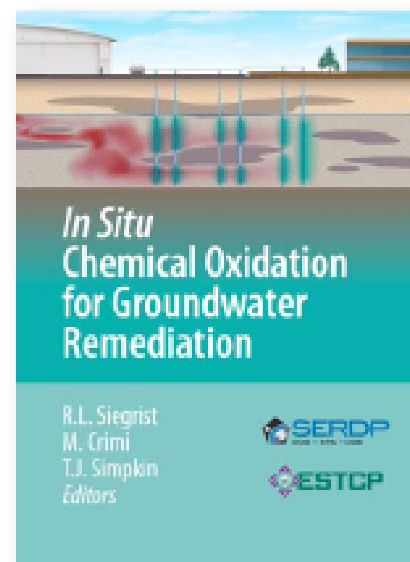
  - 700-page text published by Springer



Overview of e-TPM – Opening of "readme"

In Situ Chemical Oxidation for Groundwater Remediation

Site Specific Engineering and Technology Application

ESTCP project ER-0623

CD Purpose

This CD contains materials and tools concerning in situ chemical oxidation (ISCO) and represents the culmination of DoD's ESTCP Project ER-0623, *"In Situ Chemical Oxidation for Remediation of Groundwater – Technology Practices Manual"*. This project was completed during 2006 to 2009 as a collaborative effort between a team of academics, environmental consultants, and agency personnel associated with the Colorado School of Mines, CH2MHILL, Clarkson University, and the Navy. The enclosed CD is the first public release version of a CD (PRv1) that contains the site-specific engineering and technology application materials and tools developed through ER-0623.

What is on the CD

Name	Size	Type
Files Currently on the CD		
1-ISCO CD Intro and User Info		File Folder
2-ISCO FAQ Guide		
3-ISCO E-Protocol for Site Specific Eng & App		
4-ISCO Case History & Analysis Database		File Folder
5-ISCO Supplemental Info & Tools		File Folder
ER0623_CD_Readme_First_PRv1.pdf	145 KB	Adobe Acrobat Dc

Intro and background material

2 – ISCO FAQ Guide - Frequently Asked Questions

Contents

Example FAQ

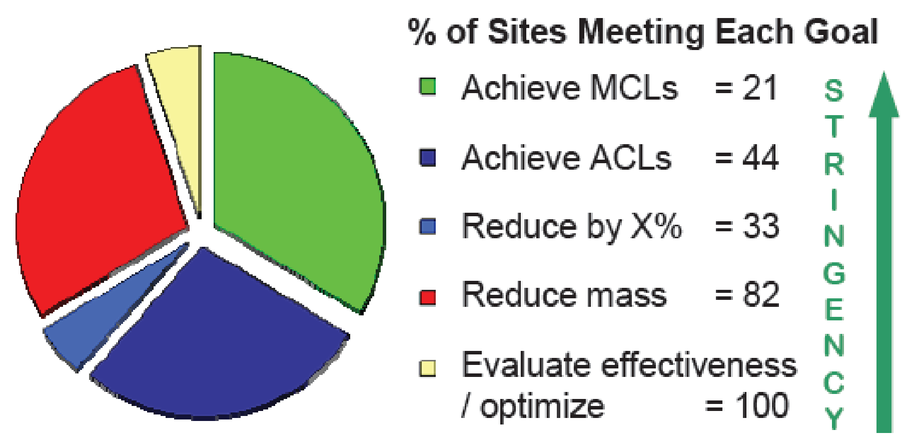
2. What treatment goals can ISCO achieve?

A properly designed ISCO system that achieves effective contact (i.e., mixing) of the right oxidant with the COCs can remediate contaminated groundwater to common treatment goals (e.g., 99.9% reduction in concentration). However, as of this writing, remediation of DNAPL source zones by ISCO alone to USEPA MCLs in groundwater (e.g., TCE = 5 ppb) has not been documented. Therefore, for DNAPL source zones where cleanup goals are stringent, ISCO is typically implemented in a treatment train approach where ISCO is combined with pre-ISCO treatments such as DNAPL extraction techniques and/or post-ISCO treatments such as enhanced reductive dechlorination or monitored natural attenuation.

ISCO treatment goals:

The pie chart shows how frequently specific goals have been set for sites included in a review of ISCO case histories as part of this project (ER-0623). MCLs (most stringent) are the goal most frequently set for sites. However, as shown by the % listed, MCLs have been achieved with a lower frequency than other less stringent goals.

Site distribution by goal set:



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5-ISCO Supplemental Info & Tools		File Folder
ER0623_CD_Readme_First_PRv1.pdf	145 KB	Adobe Acrobat Dc

Files Currently on the CD

DISCO_Glossary.pdf	59 KB	Adobe Acrobat Doc..
DISCO_v2.pdf	1,299 KB	Adobe Acrobat Doc..
Krembs2008_Thesis.pdf	2,434 KB	Adobe Acrobat Doc..

Introduction to DISCO

The Database for ISCO (DISCO) is an interactive database whose purpose is to share data from past ISCO projects as well as to provide some commentary to highlight key results. To query DISCO, users must provide inputs on the two main components that impact ISCO design and performance: Contaminants of Concern (COCs) being treated, including the presence of NAPL; and the subsurface geologic media in the treatment zone. This query format is primarily intended for users (e.g. RPMs, consultants, project owners) who are considering ISCO as a remediation technology at a particular site, and know what contaminants and geologic media must be treated. Those users who are interested in a more global view of ISCO that is independent of COC or geologic conditions may use the "select all" buttons on the query pages.

The contents of DISCO are based upon a collection of case studies compiled by the ER-0623 project team as a component of the ISCO Technology Practices Manual (TPM) project. The methods used are documented in Krembs

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Example of DISCO

Query Part 1: Geology

Click on the category that best describes the geology of the target treatment zone

for unconsolidated media

- homogeneous & permeable
- homogeneous & impermeable
- heterogeneous & permeable
- heterogeneous & impermeable

Permeable defined as average saturated hydraulic conductivity (K) > 10^{-5} cm/s
Homogeneous defined as K_{max} / K_{min} < 1000 as based on assessments of distinct strata (e.g. clay stringer vs. coarse sand is heterogeneous)

for fractured rock

- high matrix porosity
- low matrix porosity

High Matrix Porosity most sedimentary rocks
Low Matrix Porosity most igneous and metamorphic rocks

- select all six

open DISCO Glossary | return to introduc

Example of DISCO

Query Part 2: Contaminants of Concern (COCs)

Click on the COC / NAPL conditions to be treated

(pick one button, and run again if multiple groups are present)

chloroethenes (PCE, TCE, cis-DCE etc.)	w/ DNAPL	w/out DNAPL
BTEX (Benzene, Ethylbenzene etc.)	w/ LNAPL	w/out LNAPL
chloroethanes (1,1,1-TCA, 1,1-DCA etc.)	w/ DNAPL	w/out DNAPL
TPH (e.g. DRO, RRO)	w/ LNAPL	w/out LNAPL
MTBE	w/ LNAPL	w/out LNAPL
chlorobenzenes (dichlorobenzene isomers etc.)	w/ DNAPL	w/out DNAPL
PAHs (pyrene, anthracene etc.)	w/ NAPL	w/out NAPL
methylene chloride	w/ DNAPL	w/out DNAPL
select all	w/ NAPL	w/out NAPL

open DISCO Glossary | return to Query Par

Example of DISCO

Design Conditions

(for query of heterogeneous, permeable geology & chloroethene COCs without DNAPL)

Design Parameters: Permanganate

	Q1	Med.	Q3	n
injected oxidant concentration (g/L)	9.4	24	62	11
# of pore volumes delivered	0.050	0.090	0.16	9
oxidant dose (g oxidant / kg media)	0.089	0.25	0.29	8
design ROI (ft)	15	25	33	7
# of delivery events	1	1	2	11
mean duration of delivery events (days)	2	7	9	7

on other coupled technologies are available in the TPM Part III and Krembs (2008). MNA was only entered as a coupling technology when project documents specifically stated it would be used. n refers to the sample size (number of sites that match the query and had data for that parameter). na is not applicable.

Delivery Method

	# Sites
injection wells	7
direct push	5
sparge points	2
infiltration gallery / trench	2
recirculation	1
fracturing	3
soil mixing	0
horizontal wells	1

Oxidant Selected

	# Sites
permanganate	14
CHP	7
ozone	3
persulfate	0
peroxone	1
percarbonate	0

23 of the 242 DISCO case studies match this query

(Continued on following page)

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ER0623_CD_Readme_First_PRv1.pdf	145 KB	Adobe Acrobat Dc

Files Currently on the CD

S1 ISCO Literature Review Summary.pdf	268 KB	Adobe /
S2 Annotated ISCO Bibliography.xls	442 KB	Microso
S3 ER0623_ISCO_Workshop_Pro.pdf	6,719 KB	Adobe /
S4 CORT3D Manual.pdf	12,119 KB	Adobe /
S5 CORT3D_Setup.exe	65,358 KB	Applicat

What is on the CD

Name

Files Currently on the CD

- 1-ISCO CD Intro and User Info
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- 4-ISCO Case History & Analysis Database
- 5-ISCO Supplemental Info & Tools
- ER0623_CD_Readme_First_PRv1.pdf

Contents of 3-ISCO E-Protocol for Site Specific Eng & App:

- A1 ISCO Site Characterization Needs.pdf
- A2 Relevance to COCs Geology Goals.pdf
- A3 CSM Certainty Evaluation Tool.xls
- A4 Pre-ISCO Coupling Processes.pdf
- A5 ISCO Screening Tool.xls
- A6 ISCO Screening Tool Users Manual.pdf
- A7 Additional Screenning Considerations.pdf
- A8 ISCO Screening Tool Lookup Tables.xls
- A9 ISCO Coupling Tables.pdf
- A10 Oxidant Specific Design Considerations.pdf
- A11 CDISCO Design Tool April 2010.xls
- A12 CDISCO Description and Input Parameter Sensitivity.pdf
- A13 Conceptual Design Ranking Tool.xls
- A14 Contingency Planning Tool.xls
- A15 Contingency Planning Example.pdf
- A16 Lab Bench Test - Oxidant Persistence.pdf
- A17 Lab Bench Test - Cont Treatability Byproducts.pdf
- A18 Field-Scale Pilot Testing Guidance.pdf
- A19 Additional Modeling Guidance.pdf
- A20 FS Cost Estimate Guidelines.pdf
- A21 FS Cost Estimate Example.pdf
- A22 Basis of Design Report Outline Example.pdf
- A23 Example Operation Decision Logic.pdf
- A24 Example Design Specs and Drawings.pdf
- A25 QAPP Elements.pdf
- A26 PMP Elements.pdf
- A27 Infrastructure Const and Delivery Effectiveness.pdf
- ReadMe First_Protocol_Master_Index_PRv1.pdf

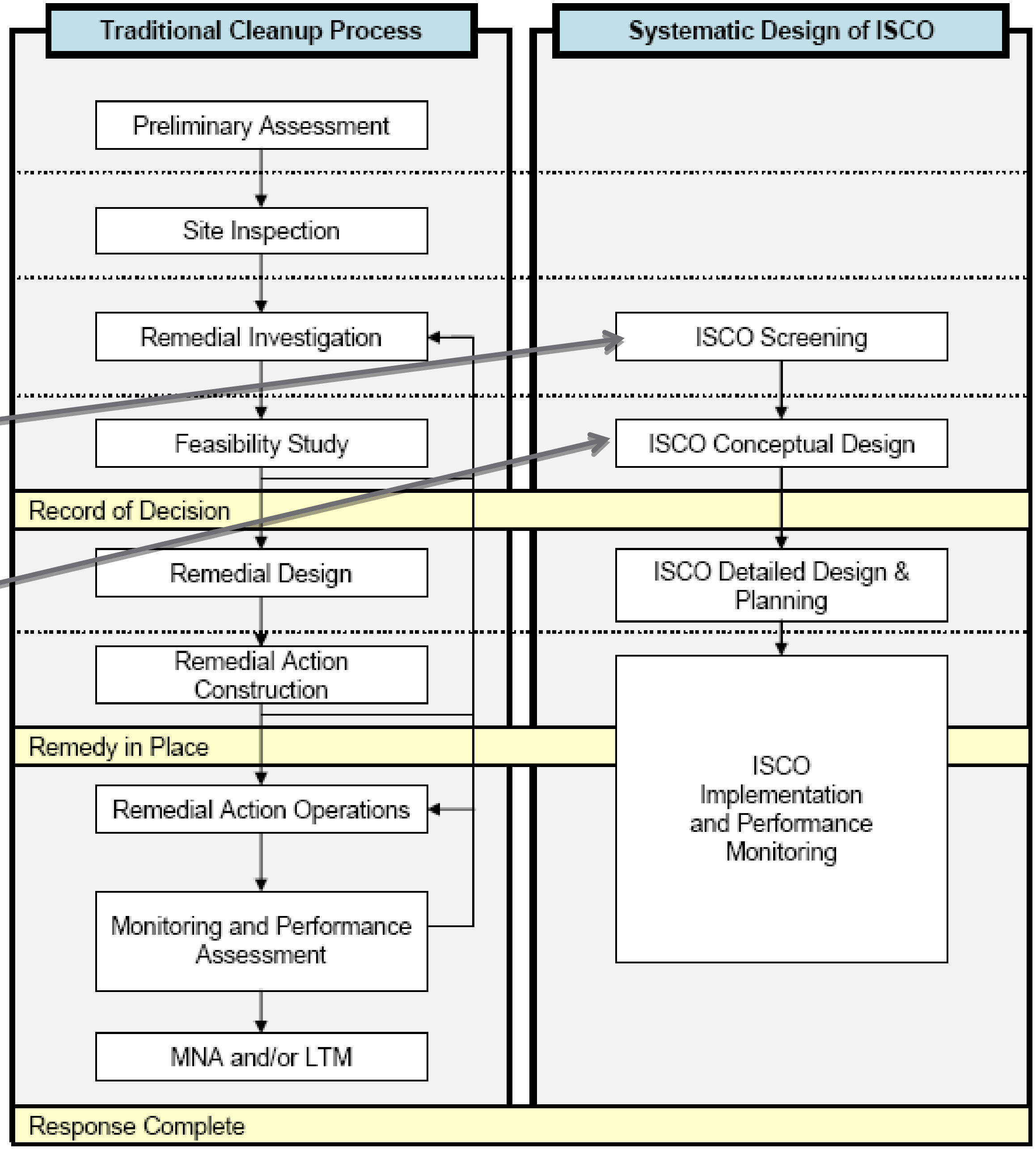
3- ISCO e-Protocol for Site-Specific Engineering and Application

- What is the ISCO Protocol?
  - Decision support tool to assist making informed decisions about implementation of ISCO
  - Goal is to improve the ISCO state of the pracitce
- What does it consist of?
  - Flow diagrams illustrating typical procedures
  - Text to guide the user throught eprocess
  - “Tools” for key processes and decision points
    - Science-based text, look-up tables, spreadsheets calculations, etc.

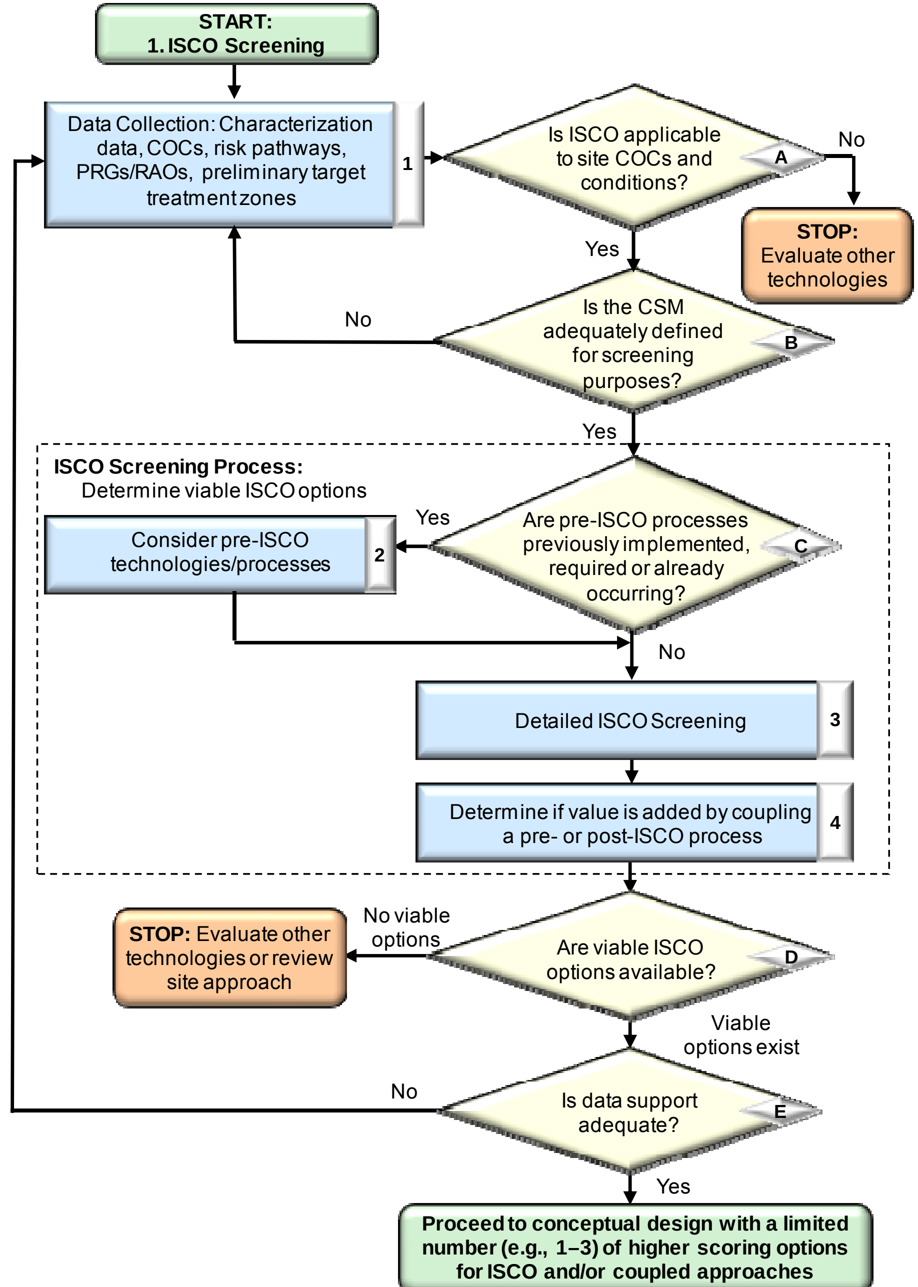
Overall ISCO Protocol Flow

Covered by Dr. Crimi

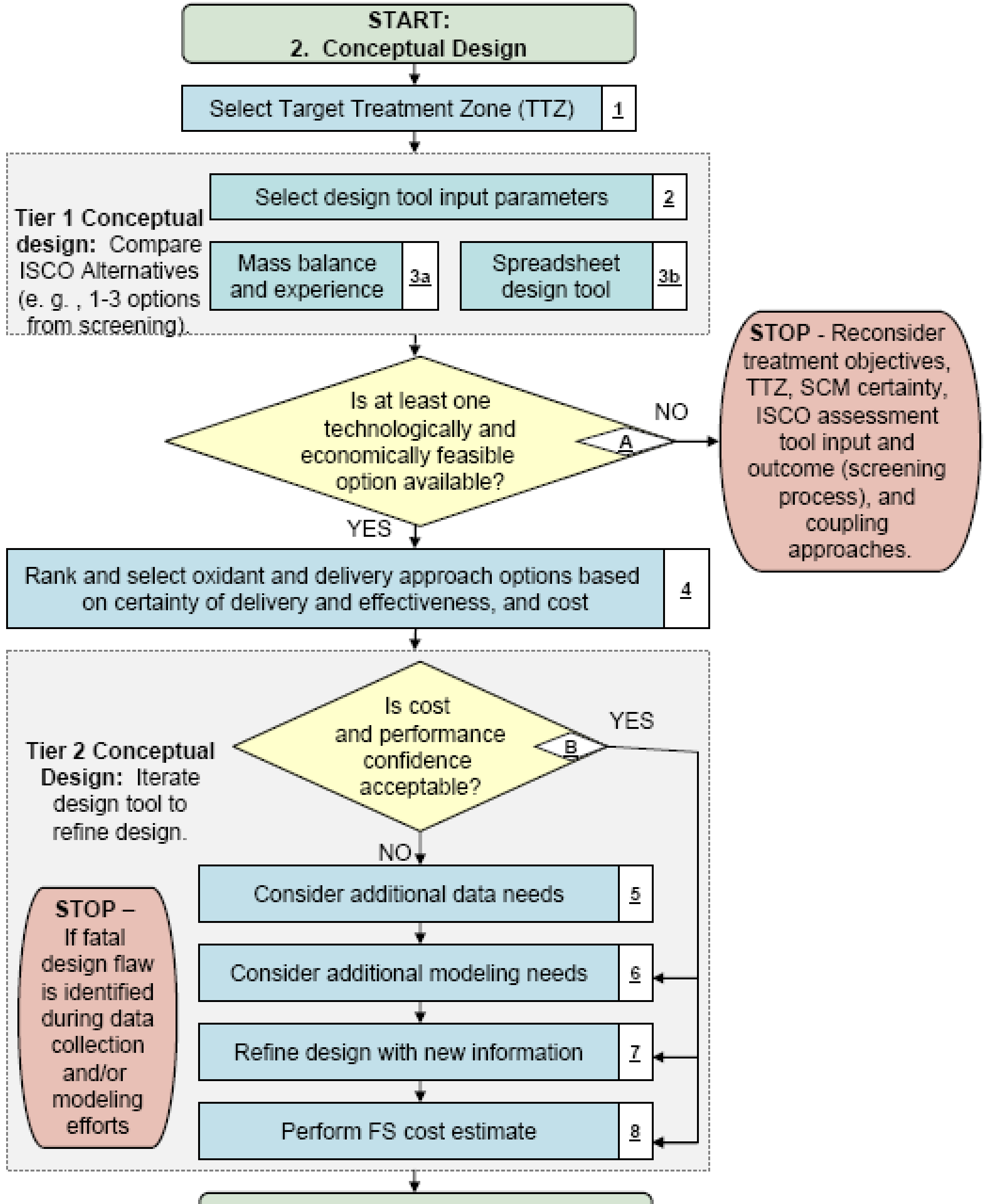
Covered by Dr. Simpkin and Dr. Borden



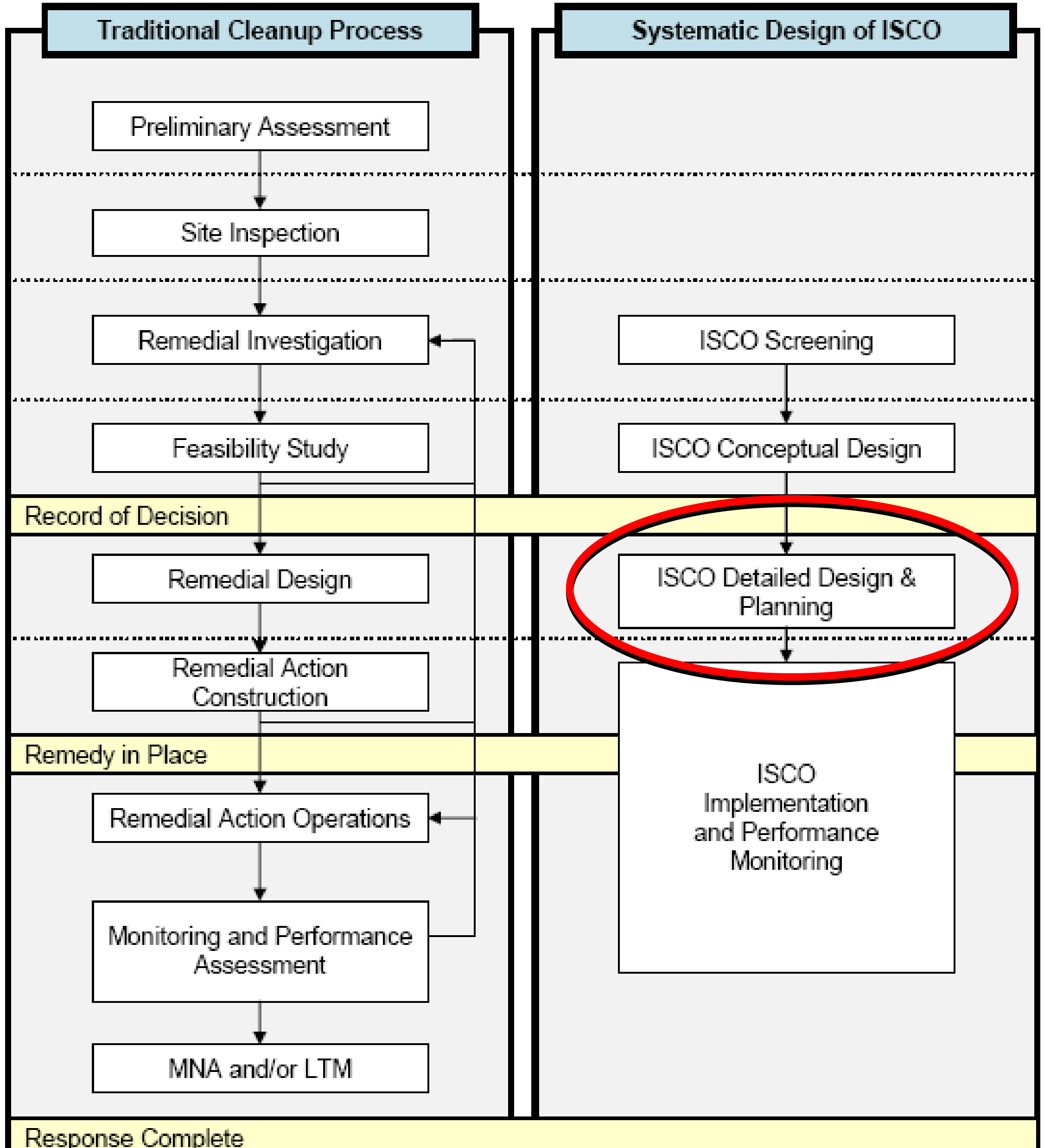
ISCO Screening Process



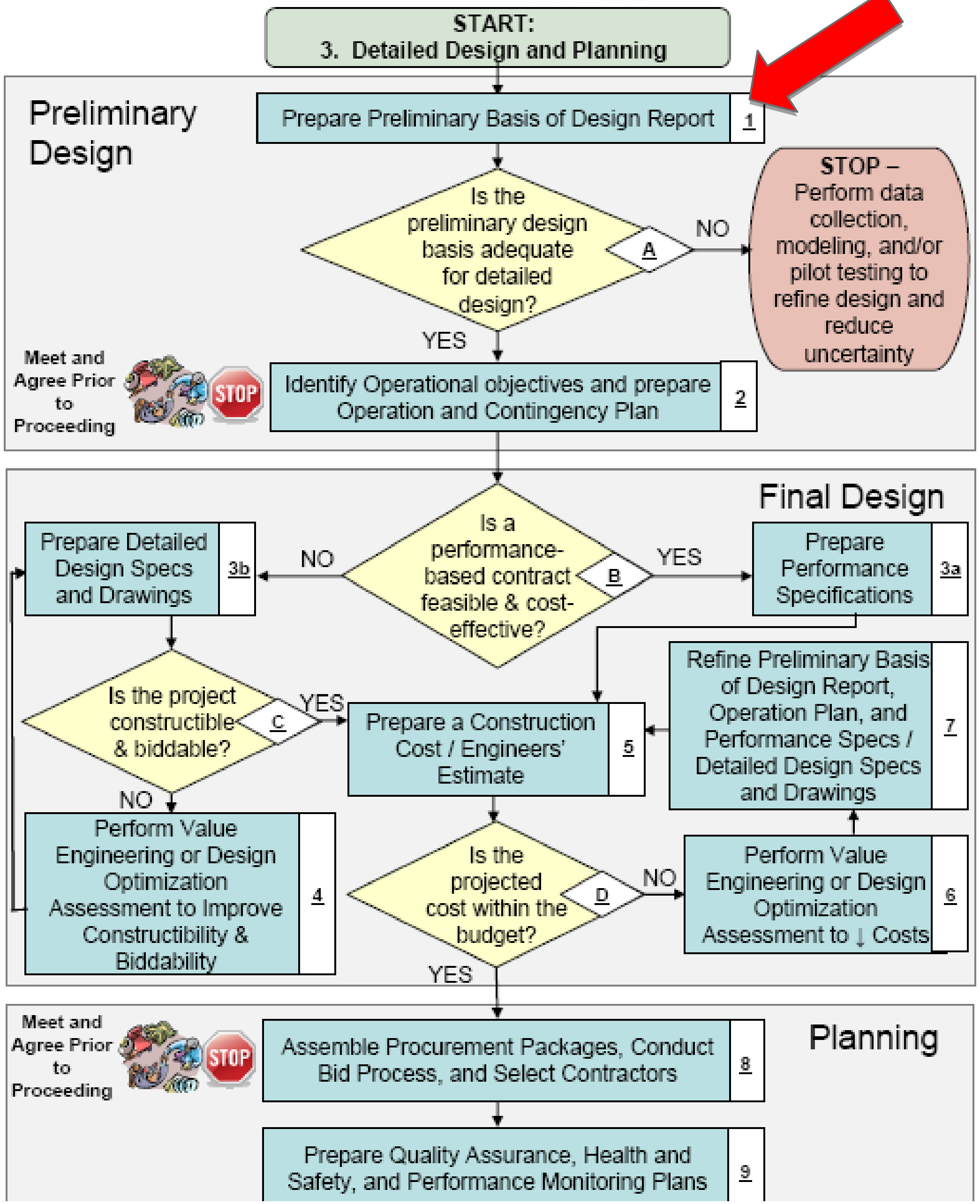
ISCO Conceptual Design Flow Diagram



Overall ISCO Protocol Flow



ISCO Detailed Design and Planning



e.g. Prepare Preliminary BOD Report

DD.2 PRELIMINARY DESIGN PHASE

DD.2.1 DETAILED DESIGN AND PLANNING PROCESS 1: Prepare Preliminary Basis of Design Report

Using the results from the previous ISCO Protocol components, a Preliminary Basis of Design Report is prepared as the initial step in the ISCO Detailed Design and Planning process. The purpose of the Preliminary Basis of Design Report is to formally establish and describe the design parameters in text format, which can then be used for the Final Design phase. The Final Design typically prescribes the design in construction contract terms (specifications and drawings). The Preliminary Basis of Design Report is typically reviewed and approved by all project stakeholders to ensure consensus on critical design parameters is built prior to proceeding with the Final Design of ISCO implementation.

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, and user

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ion; target

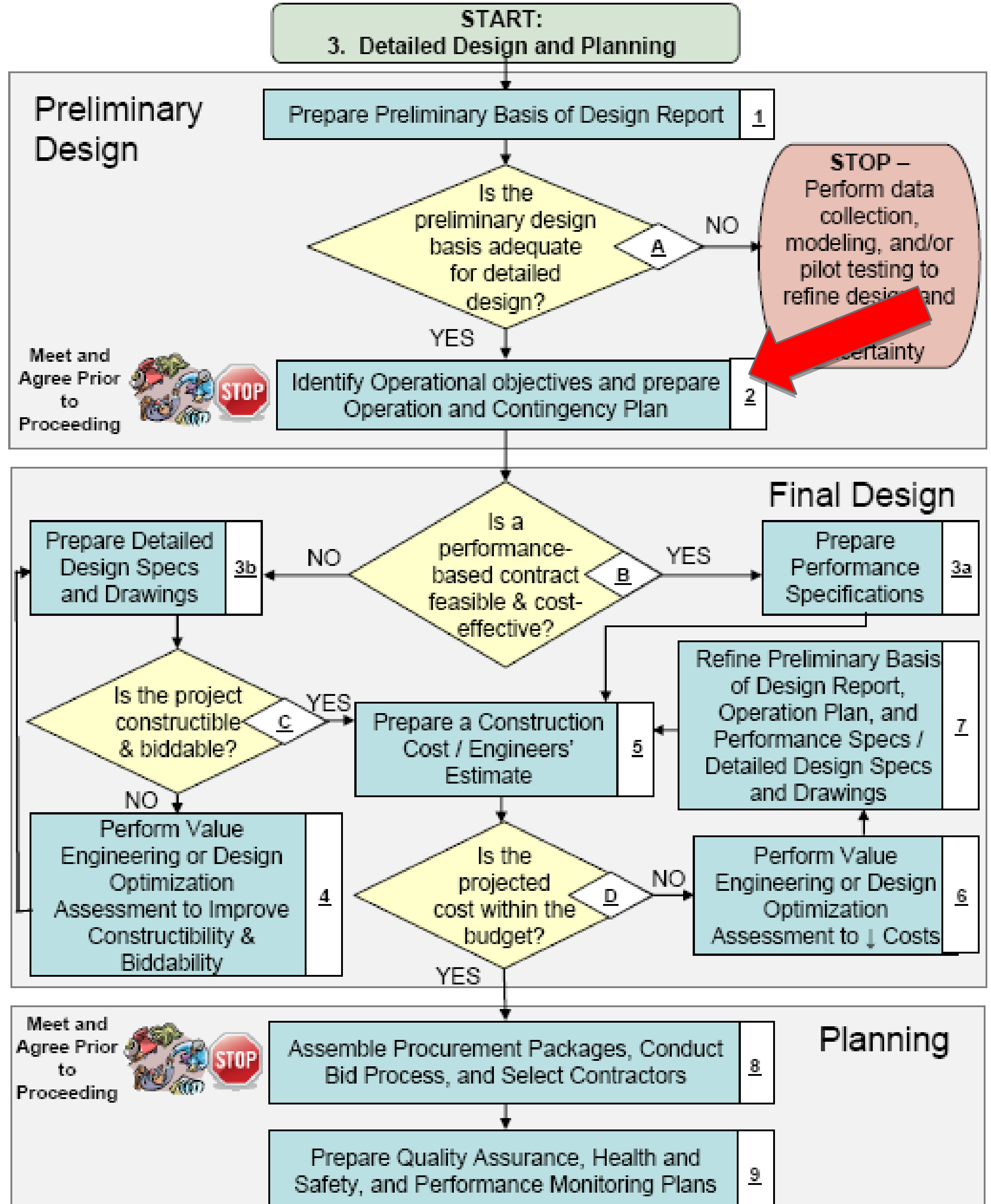
monitoring

ATTACHMENT 22: Basis of Design Report Outline Example

The following is an example of a Basis of Design Report outline for In Situ Chemical Oxidation by Permanganate Direct Injection. It should be noted that certain components of the Preliminary Basis of Design Report specified below may be omitted if a performance-based contracting approach will be adopted (see Detailed Design and Planning Decision B). Examples of omitted design components include the oxidant volume/dosage, injection infrastructure, and injection well design.

1. Project Introduction
   - 1.1 Site Background and Remediation Status
   - 1.2 Summary of Previous ISCO Test Results
   - 1.3 Remediation Drivers
2. Brief Summary of Conceptual Site Model
   - (Reference other documents for details)
   - 2.1 Source Description
   - 2.2 Lithology
   - 2.3 Hydrogeology
   - 2.4 Geochemical Setting
   - 2.5 Contaminant Geometry
     - 2.5.1 Nature and Phases
     - 2.5.2 Extent and Location
3. ISCO Treatment Goals and Milestones

ISCO Detailed Design and Planning



e.g. Contingency Planning Tool

ATTACHMENT 14: Contingency Planning Tool

Site Remediation Contingency Evaluation Form

Site Name:

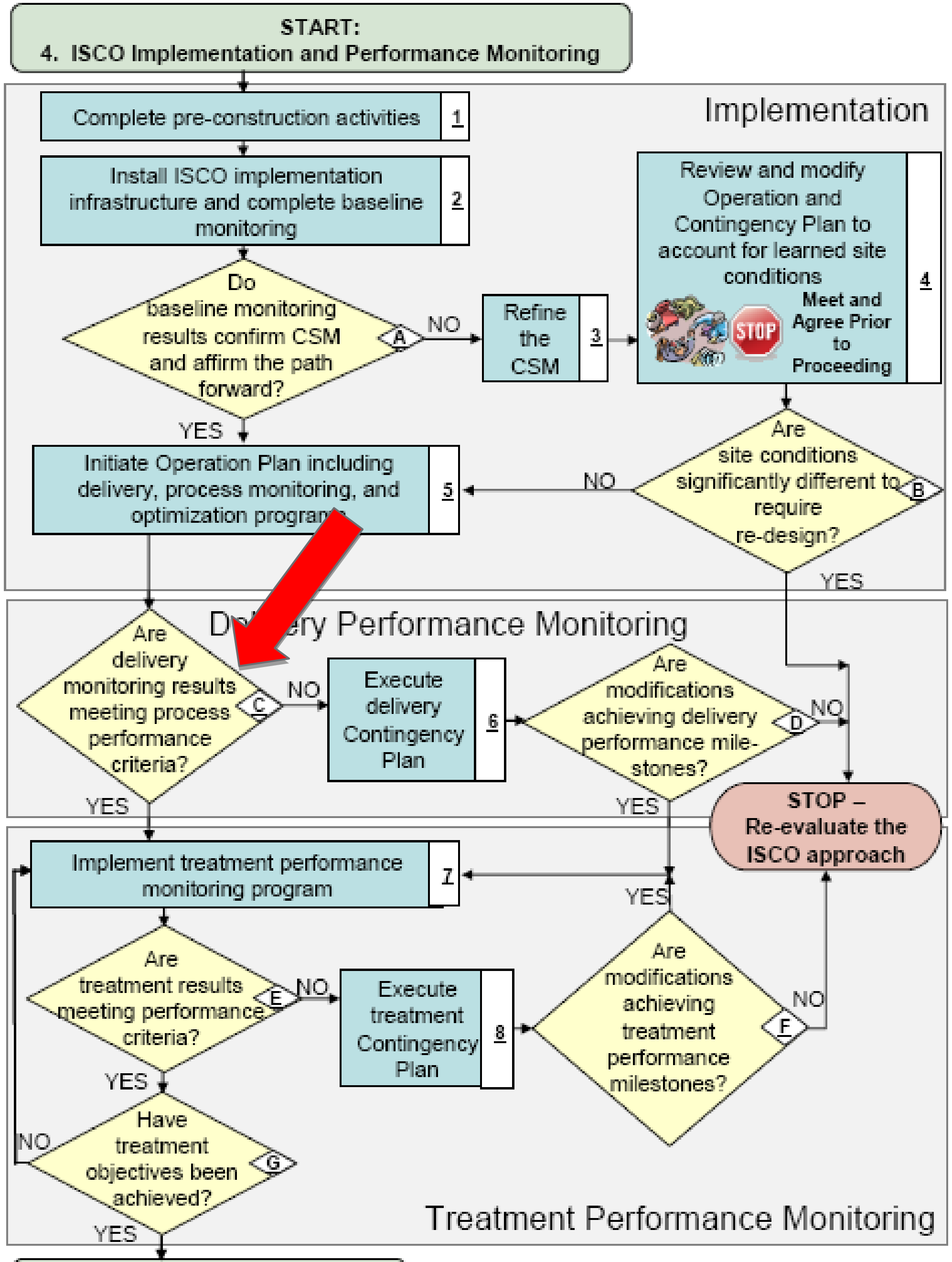
Project Name:

#	Uncertainty/Contingency Category [1]	Contingency Statement: Condition	Contingency Statement: Consequence	Status	Probability (%)	Impact ($)	Exposure ($)	Schedule Impact	Mitig
Unique ID		Capture the "likely cause" of the contingency. Be detailed enough so that you can start forming mitigation plans.	Capture the result of the contingency, should it happen. If the consequences cannot be mitigated, you will have to deal with them in a contingency plan.	Active, retired, no concern	Estimate of the probability the contingency will occur.	Estimate of the amount of impact or severity of the contingency.	Probability x impact in $. Sort by this column to prioritize biggest $ impacts.	Estimate of the amount of time delay/extension that could be caused by the contingency	Document plan probability or to impact ahead o require a more written up sepa
High Priority									
Moderate Priority									

Notes:

1. Consider Uncertainty/Contingency Categories of Performance, Schedule, PM Experience, Client, Scope, Resources, Budget, Technology, Endorsement, and Contract.

ISCO Implementation and Performance Monitoring



e.g. Delivery Performance Monitoring

IM.3 DELIVERY PERFORMANCE MONITORING PHASE

The following sections describe the process and decision steps for the delivery performance monitoring phase of the ISCO Implementation and Performance Monitoring Flow Diagram. These process and decision steps are independent of those conducted for the treatment performance monitoring (i.e., contaminant treatment efficiency) phase and are intended to ensure that the oxidant is delivered into the TTZ as designed.

IM.3.1 IMPLEMENTATION AND PERFORMANCE MONITORING DECISION C: Are Delivery Monitoring Results Meeting Performance Criteria?

Oxidant delivery monitoring should be conducted in accordance with the Performance Monitoring Plan (A26. Elements of a Performance Monitoring Plan). Oxidant monitoring results should be evaluated to determine if the specific oxidant delivery objectives (i.e., operational metrics) and milestones established in the ISCO Detailed Design and Planning Process 2 are being met. Each ISCO design will have its own

e.g. Delivery Performance Monitoring

ATTACHMENT 26:
Elements of a Performance Monitoring Program

An adequately designe
data that are consister
the three primary stag
and treatment perform

- Clearly define
- Baseline moni
- Delivery perfo
- Treatment per
- Number and lo
- Frequency of
- Field and labo

Table A26-2. Delivery Performance Monitoring Parameters.

Parameter	MnO_4^-	CHP	$S_2O_8^{-2}$	Ozone	Example Monitoring Frequency*
Oxidant	FS, V	FK	FK	FI, FK	baseline and end of injection
Color	V				daily during injection
pH		FI, FK	FI, FK	FI, FK	daily during injection (or real-time monitoring with datalogger)
ORP	FI	FI	FI	FI	daily during injection (or real-time monitoring with datalogger)
Temperature		FI		FI	daily during injection (or real-time monitoring with datalogger)
Alkalinity		L, FK			daily during injection
Vadose Zone Offgas (CO_2, O_2, VOC, ozone)		FI		FI	daily during injection
Dissolved oxygen		FI		FI	daily during injection (or real-time monitoring with datalogger)
Specific conductance	DPT, FI		DPT, FI		daily during injection (or real-time monitoring with datalogger), or once the day after injection
Sodium			L, FK		daily during injection
Sulfate			L, FK		daily during injection
Iron		L, FK	L, FK		daily during injection
Injection pressure	FI	FI	FI	FI	constant
Injection flow rate	FI	FI	FI	FI	constant

In Situ Chemical Oxidation: 4. Screening Applicability of ISCO for Site-Specific Conditions

Michelle Crimi

Assistant Professor

Institute for a Sustainable Environment

Clarkson University, Potsdam, NY

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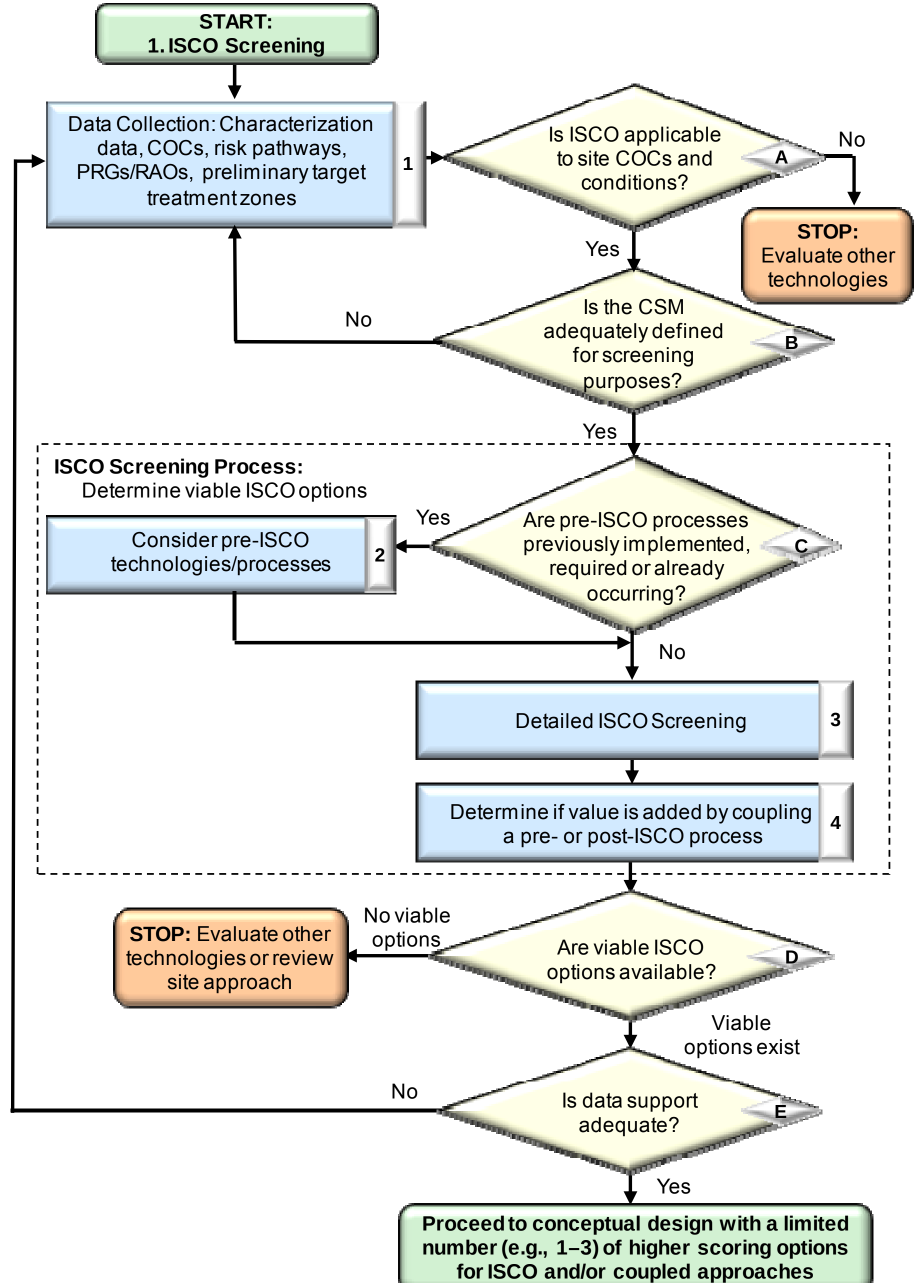
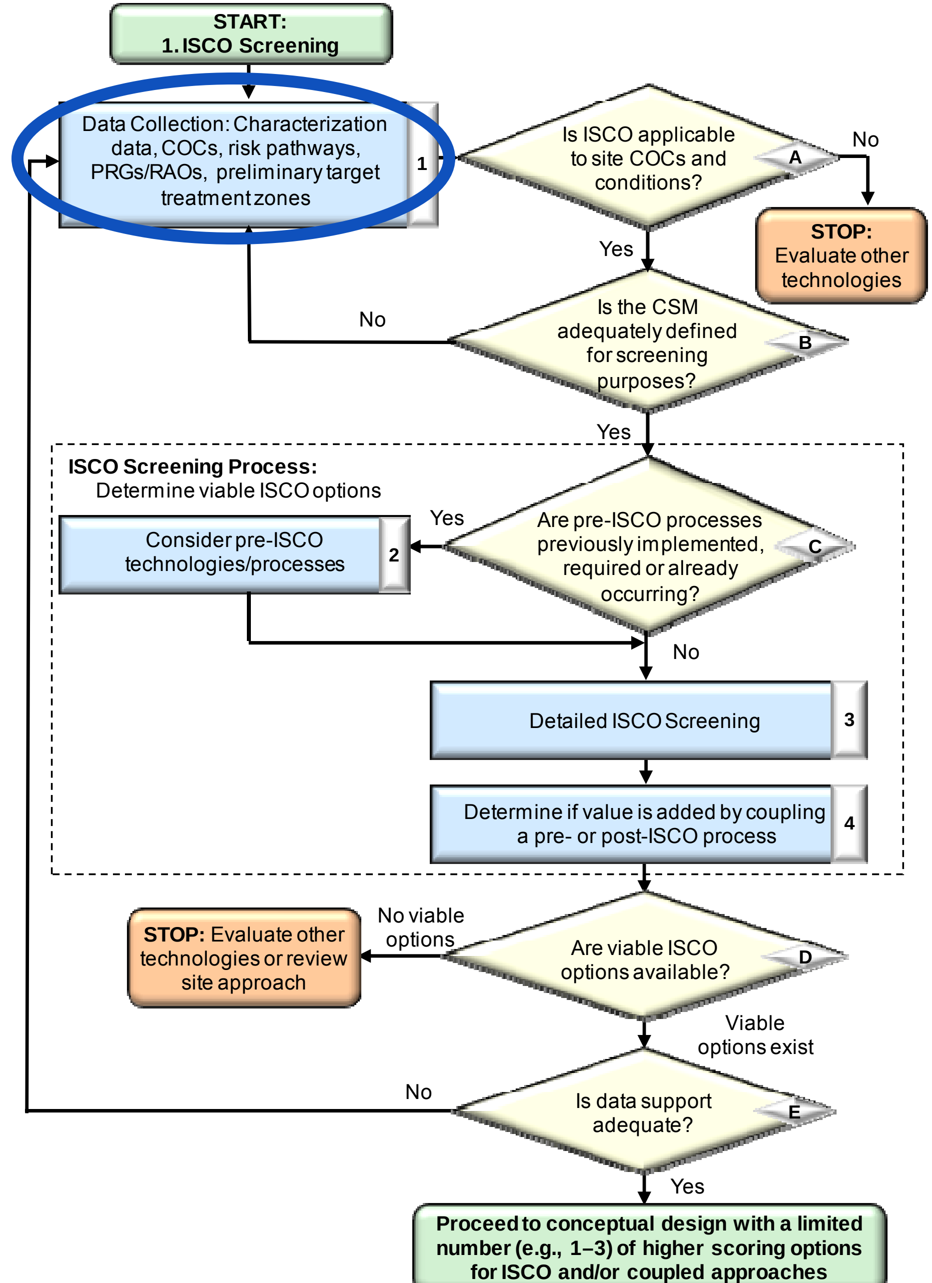
ISCO Screening Process

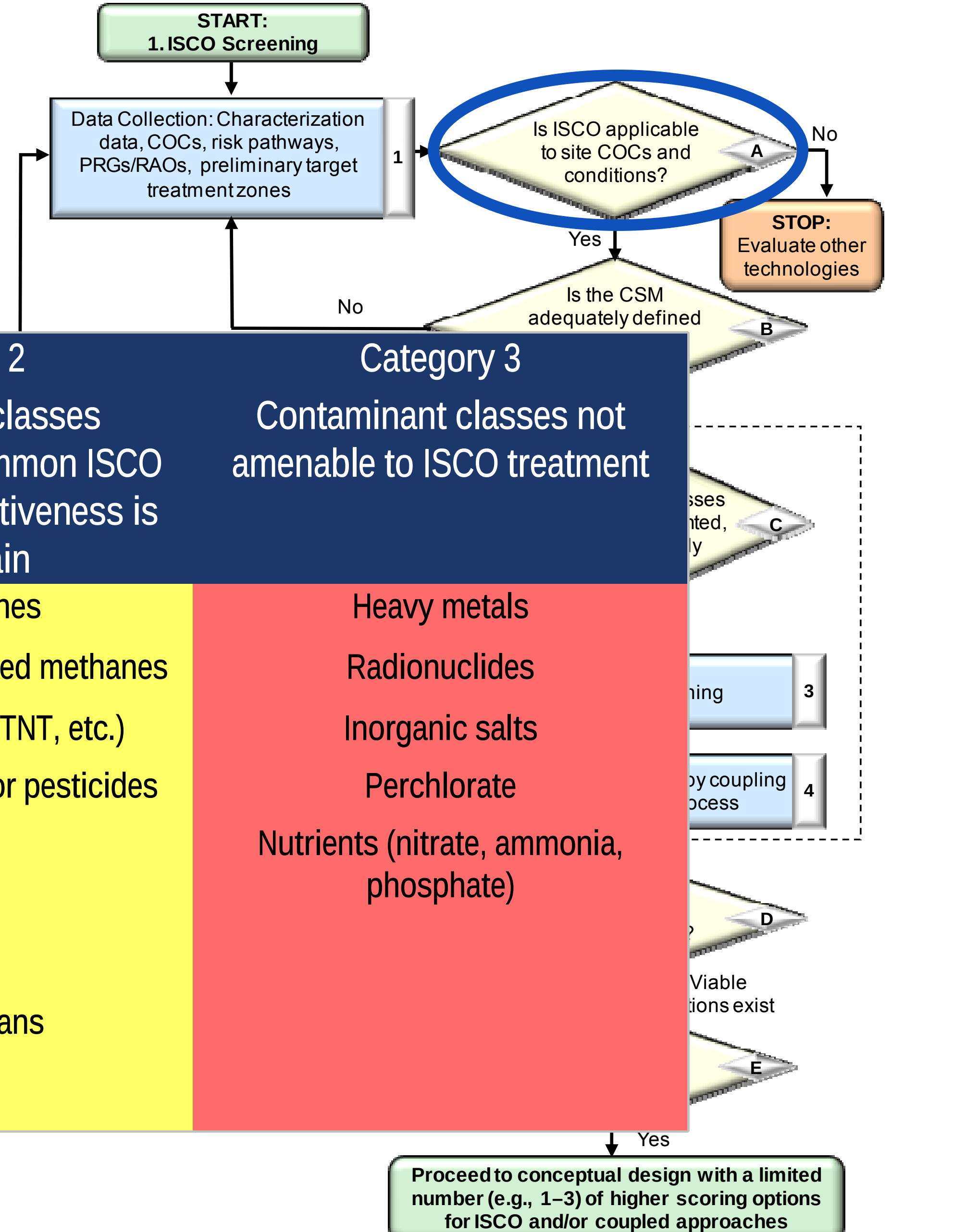


Data Collection

- Conceptual Site Model (CSM)
  - Contaminant
  - Hydrogeology
  - Geochemistry
  - Goals and objectives
  - Site plan
- ISCO-specific
  - Collect soil and groundwater to store if ISCO is even a remote possibility
    - For oxidant demand/persistence and treatability evaluations



Basic Screening

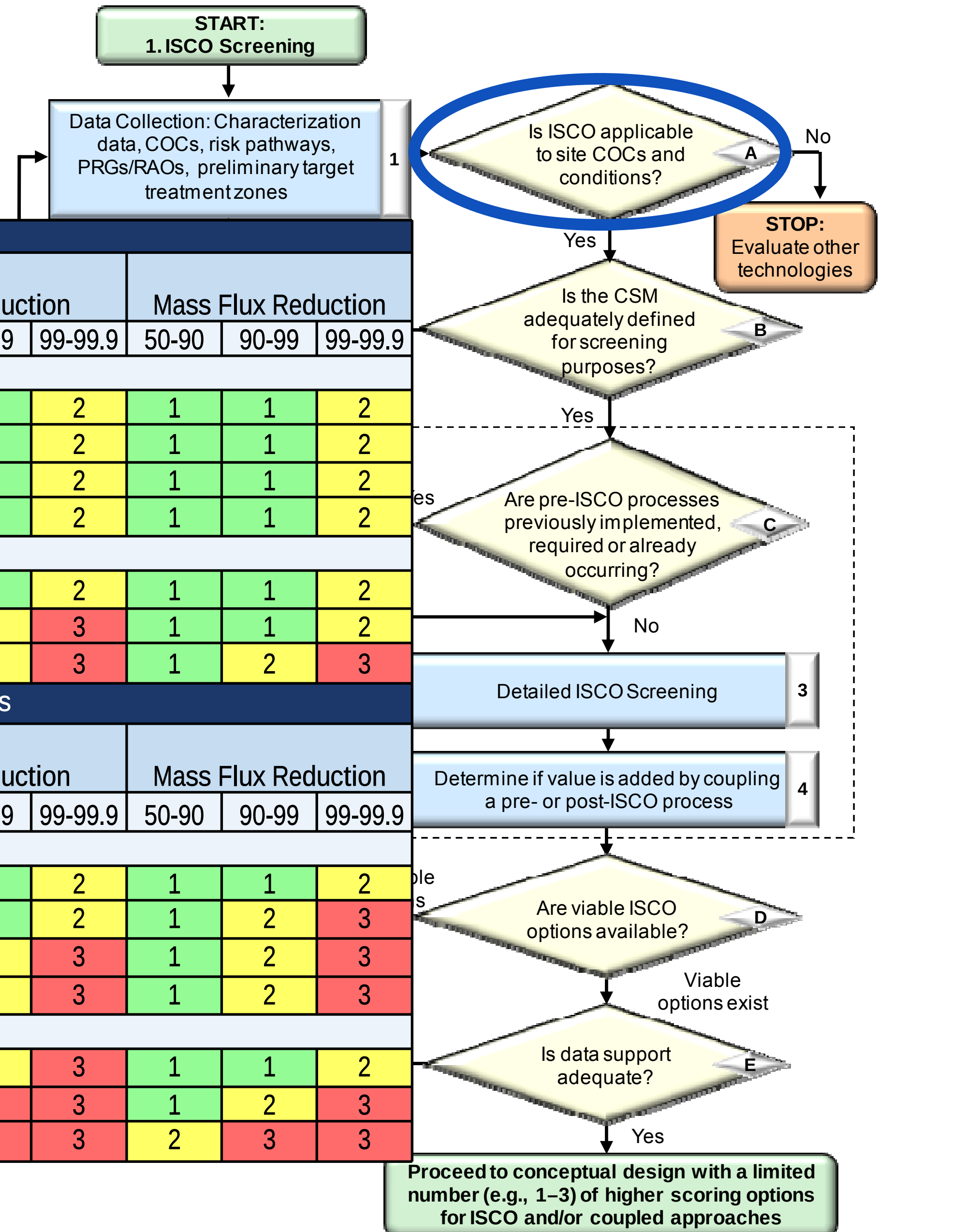


Category 1 Contaminant classes highly amenable to effective degradation by commonly used ISCO oxidants	Category 2 Contaminant classes degradable by common ISCO oxidants but effectiveness is less certain	Category 3 Contaminant classes not amenable to ISCO treatment
Chloroethenes	Chloroethanes	Heavy metals
BTEX	Chlorinated/brominated methanes	Radionuclides
TPH	Explosives (RDX, TNT, etc.)	Inorganic salts
PAHs	Organic herbicides or pesticides	Perchlorate
Chlorobenzenes	NDMA	Nutrients (nitrate, ammonia, phosphate)
Phenols (e.g., chlorophenols)	Ketones	
Fuel oxygenates (MTBE, TAME)	PCBs	
Alcohols	Dioxins/Furans	
1,4-dioxane		

Basic Screening

Low Contaminant Concentration/Mass									
Type of ISCO Treatment Goal:	Concentration Reduction			Mass Reduction			Mass Flux Reduction		
Removal magnitude (%)	50-90	90-99	99-99.9	50-90	90-99	99-99.9	50-90	90-99	99-99.9
Unconsolidated media									
Homogeneous permeable	1	1	2	1	1	2	1	1	2
Heterogeneous permeable	1	2	2	1	1	2	1	1	2
Homogeneous low permeability	1	2	2	1	1	2	1	1	2
Heterogeneous low permeability	1	2	2	1	1	2	1	1	2
Consolidated media (fractured)									
Sedimentary	1	2	2	1	1	2	1	1	2
Igneous/metamorphic	1	2	3	1	2	3	1	1	2
Karst	1	2	3	2	2	3	1	2	3

High Contaminant Concentration/Mass									
Type of ISCO Treatment Goal:	Concentration Reduction			Mass Reduction			Mass Flux Reduction		
Removal magnitude (%)	50-90	90-99	99-99.9	50-90	90-99	99-99.9	50-90	90-99	99-99.9
Unconsolidated media									
Homogeneous permeable	1	1	2	1	1	2	1	1	2
Heterogeneous permeable	1	2	3	1	1	2	1	2	3
Homogeneous low permeability	1	2	3	1	2	3	1	2	3
Heterogeneous low permeability	1	2	3	1	2	3	1	2	3
Consolidated media (fractured)									
Sedimentary	1	2	3	1	2	3	1	1	2
Igneous/metamorphic	2	2	3	2	3	3	1	2	3
Karst	2	3	3	3	3	3	2	3	3



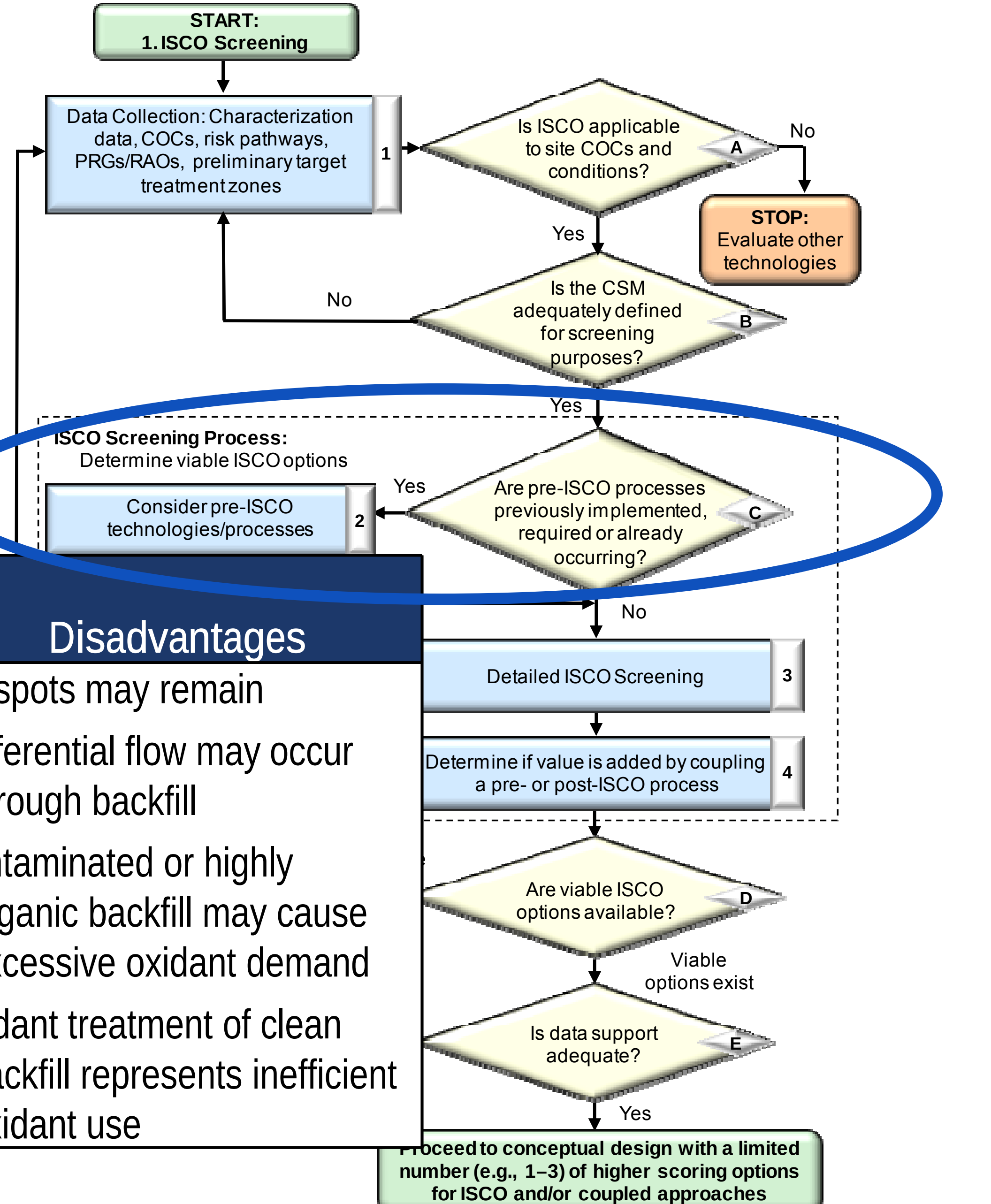
Basic Screening

Low Contaminant Concentration/Mass									
Type of ISCO Treatment Goal:	Concentration Reduction			Mass Reduction			Mass Flux Reduction		
Removal magnitude (%)	50-90	90-99	99-99.9	50-90	90-99	99-99.9	50-90	90-99	99-99.9
Unconsolidated media									
Homogeneous permeable	1	1	2	1	1	2	1	1	2
Heterogeneous permeable	1	2	2	1	1	2	1	1	2
Homogeneous low permeability	1	2	2	1	1	2	1	1	2
Heterogeneous low permeability	1	2	2	1	1	2	1	1	2
Consolidated media (fractured)									
Sedimentary	1	2	2	1	1	2	1	1	2
Igneous/metamorphic	1	2	3	1	2	3	1	1	2
Karst	1	2	3	2	2	3	1	2	3

High Contaminant Concentration/Mass									
Type of ISCO Treatment Goal:	Concentration Reduction			Mass Reduction			Mass Flux Reduction		
Removal magnitude (%)	50-90	90-99	99-99.9	50-90	90-99	99-99.9	50-90	90-99	99-99.9
Unconsolidated media									
Homogeneous permeable	1	1	2	1	1	2	1	1	2
Heterogeneous permeable	1	2	3	1	1	2	1	2	3
Homogeneous low permeability	1	2	3	1	2	3	1	2	3
Heterogeneous low permeability	1	2	3	1	2	3	1	2	3
Consolidated media (fractured)									
Sedimentary	1	2	3	1	2	3	1	1	2
Igneous/metamorphic	2	2	3	2	3	3	1	2	3
Karst	2	3	3	3	3	3	2	3	3

High Contaminant Concentration/Mass									
Type of ISCO Treatment Goal:	Concentration Reduction			Mass Reduction			Mass Flux Reduction		
Removal magnitude (%)	50-90	90-99	99-99.9	50-90	90-99	99-99.9	50-90	90-99	99-99.9
Unconsolidated media									
Homogeneous permeable	1	1	2	1	1	2	1	1	2
Heterogeneous permeable	1	2	3	1	1	2	1	2	3
Homogeneous low permeability	1	2	3	1	2	3	1	2	3
Heterogeneous low permeability	1	2	3	1	2	3	1	2	3

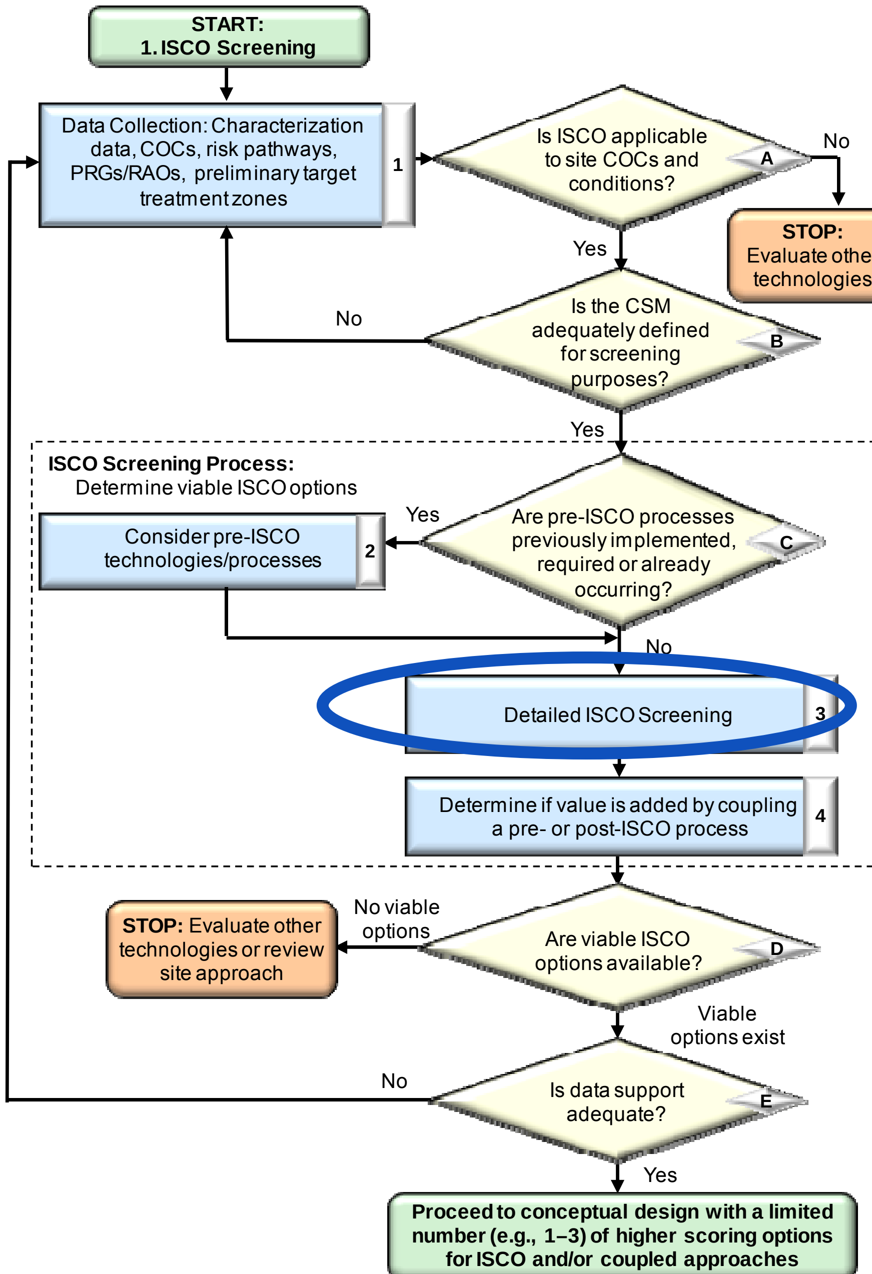
Detailed Screening



Pre-ISCO Technology	Advantages	Disadvantages
Excavation	Rapid implementation Easy to apply oxidant at the infiltrative surface Soil mixing approaches may be more easily implemented	Hotspots may remain Preferential flow may occur through backfill Contaminated or highly organic backfill may cause excessive oxidant demand Oxidant treatment of clean backfill represents inefficient oxidant use

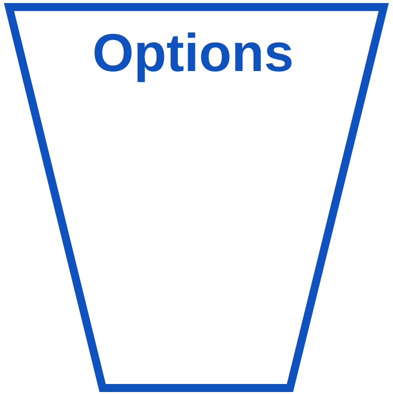
Detailed Screening

- Screening tool for site-specific conditions



Detailed Screening

- Site factors
  - Basic geology
  - Contaminants and co-contaminants
  - Geochemistry (e.g., pH, alkalinity, chloride, organic carbon content)
  - Aquifer hydrology parameters (e.g., permeability and heterogeneity)
- Lookup categories
  - Appropriate oxidant and activation approaches for contaminant(s)
  - Appropriate oxidant and activation approaches for geochemistry
  - Appropriate delivery approach for viable oxidants
  - Appropriate delivery approach for geology

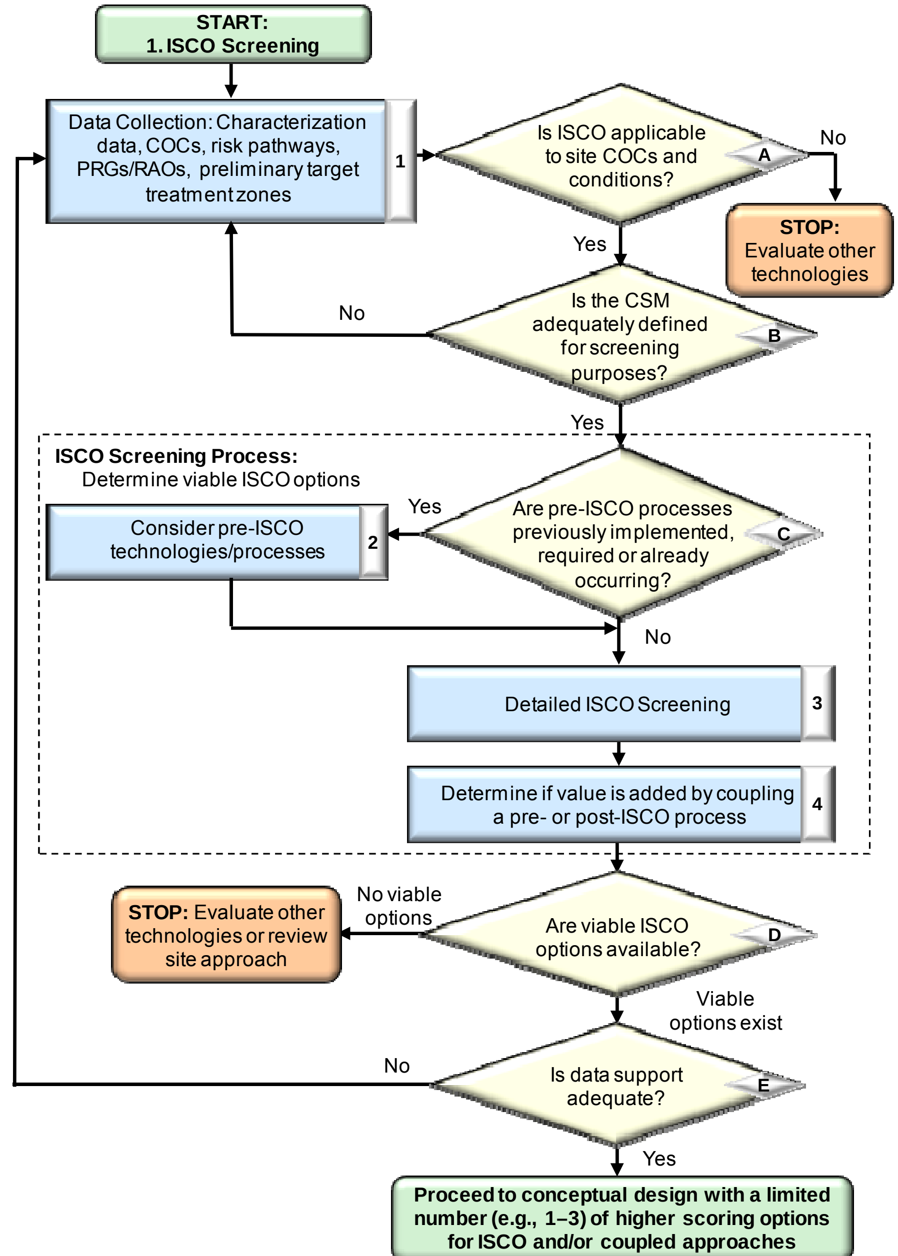


Detailed Screening

- Output
  - Narrower range of viable options for the site based on site-specific factors
  - These are the options that can be carried to the Conceptual Design phase
- NOTE
  - There is room for practitioner experience and expertise in the process!
  - Other key considerations in selecting the oxidant and delivery approach
    - Issues of implementability
      - Are there operations/activities or structures that cannot be disrupted?
      - Are there subsurface utilities that must be considered?

Summary

- Data Collection
- Basic Screening
- Pre-ISCO Processes
- Detailed Screening
- Coupling ISCO
- Select Top Options

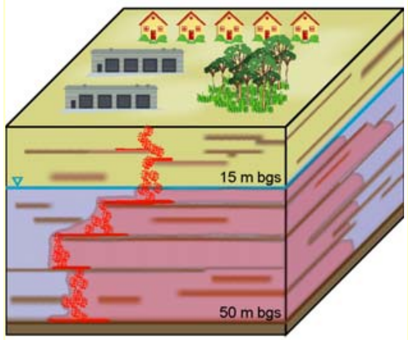


Examples

- Example #1 (see details in handout)

Key Features of the Site

- Active military facility
- Large volume of TCE was released to subsurface until ~20 yrs ago
- DNAPL confirmed – residual and pools
- Chlorobenzene co-contamination at low concentrations
- Contamination to about 50 m below ground surface (bgs)
- Fine sandy soil with thin clay-silt lenses interbedded
- Plume approximately ½ km long downgradient
- Treatment goal = **MASS REDUCTION**



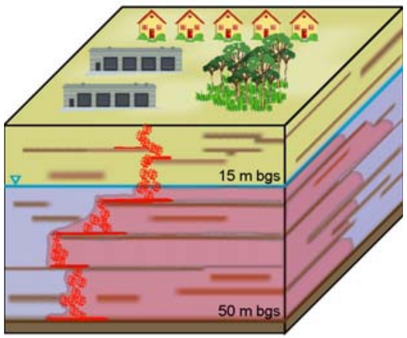
- Is ISCO viable?
- What if the treatment goal = 99.9% concentration reduction?

Examples

- Example #2 (see details in handout)

<u>Key Features of the Site</u>

- Industrial facility, inactive
- Chlorobenzene, NAPL suspected
- Contamination to about 50 m below ground surface (bgs); Majority between 15 – 25 feet
- Glacial till; permeable and heterogeneous
- Treatment goal = **MASS REDUCTION**



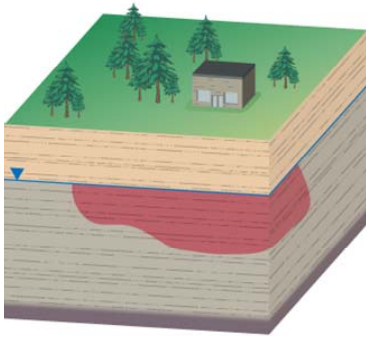
- What oxidants are feasible?
- What delivery approaches are feasible?

Examples

- Example #3 (see details in handout)

Key Features of the Site

- Dry cleaner in New York State
- Tetrachloroethylene (PCE) DNAPL
- PCE has penetrated homogeneous, low permeability clay
- Groundwater at 2 m bgs and bedrock at 10 m bgs; plume extends to 6 m bgs
- Groundwater pore velocity is 0.5 cm/day
- Treatment goal = **MASS REDUCTION**

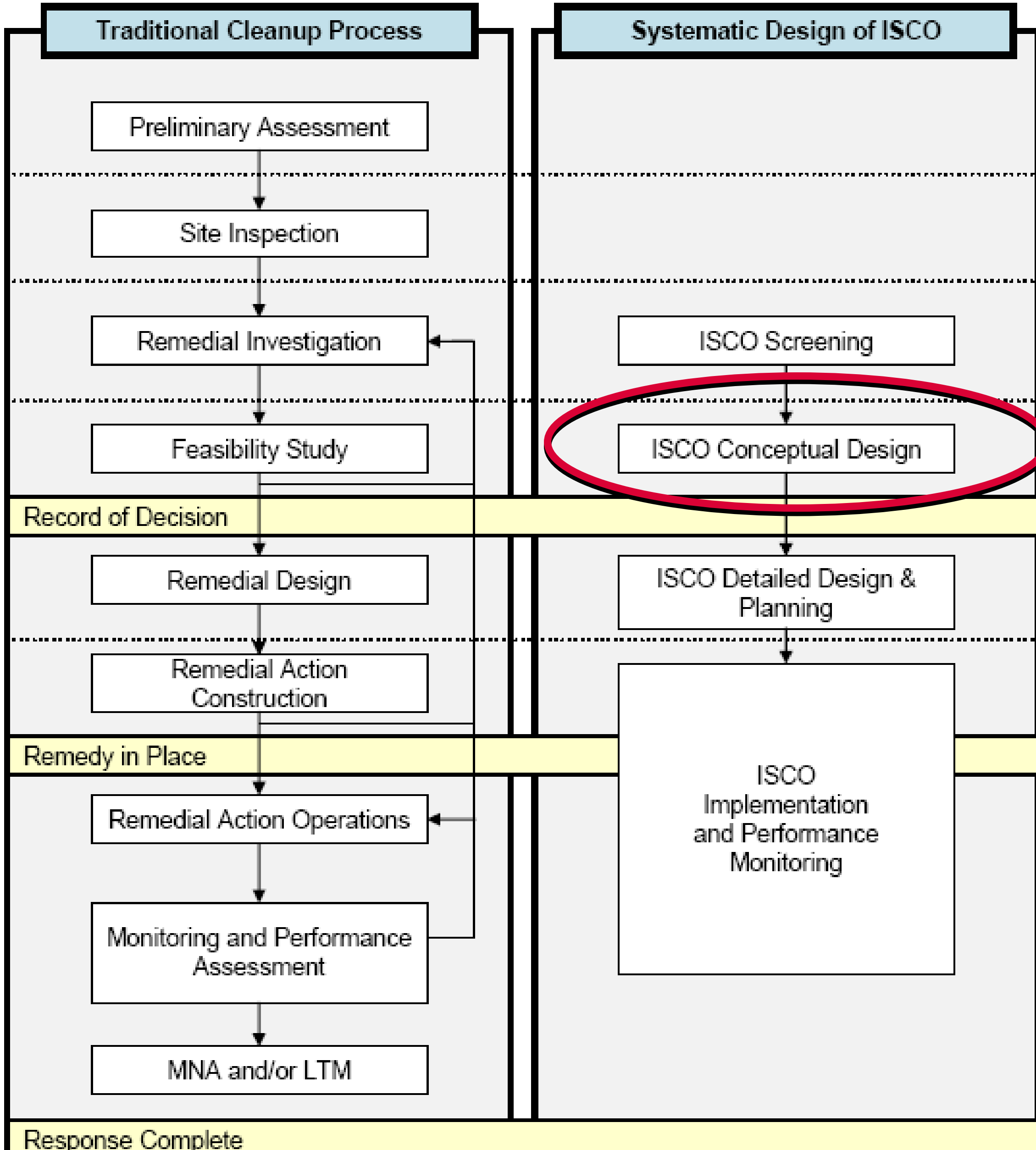


- What oxidants are feasible?
- What delivery approaches are feasible?

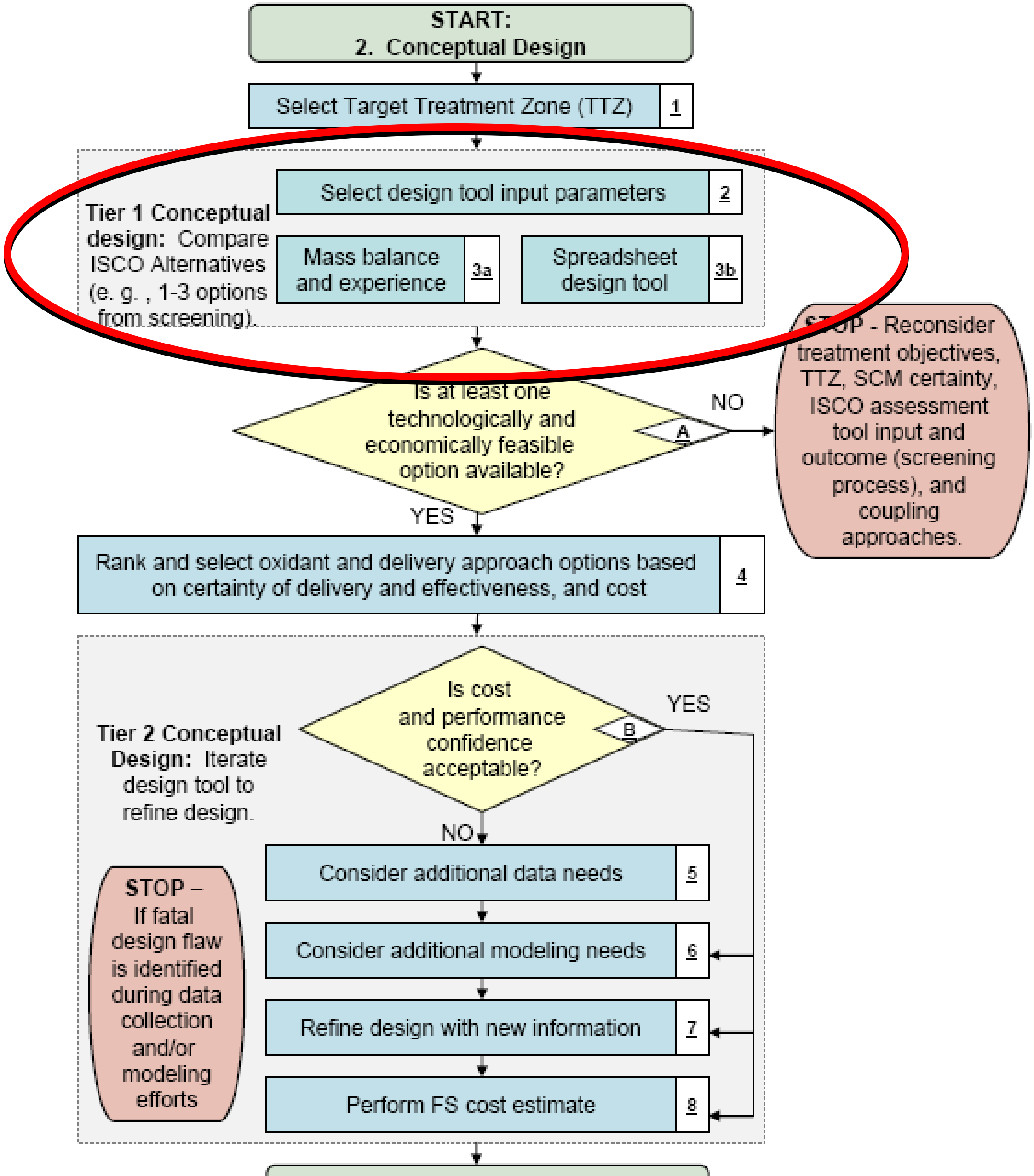
In Situ Chemical Oxidation: 5. Conceptual Design

Tom Simpkin, Ph.D., P.E.
Remediation Practice Director
CH2M HILL, Denver, CO

Overall ISCO Protocol Flow



ISCO Conceptual Design Flow Diagram



Tiered Approach to Conceptual Design

- Tier 1 Conceptual Design Objectives
  - Provide a preliminary evaluation of the cost and applicability of ISCO
  - Compare the options for ISCO developed in the screening process
  - Provide information on the uncertainty, decide on the need to collected additional information to reduce the uncertainty
- Tier 2 Conceptual Design Objectives
  - Refine the design, possibly with new data,
  - Provide information to feed into a Feasibility Study (compare against other alternatives)
  - Provide a foundation for a refined design if ISCO is selected

Conceptual Design Questions

- Spacing between wells and/or spacing between rows
- Mass of chemical needed
- Concentration of chemical to inject
- Flow rate and total volume to inject (thus time)
- Number of injections

Possible Conceptual Design Approaches

- Mass balance and experience
  - Mass balance on oxidant demand (based on NOD tests)
  - Experience for well spacing, oxidant concentration, and oxidant flow
- Spreadsheet ISCO design tool (discussed next)
- Numeric models
- Combinations of the above, along with the Observational Method

Use the "Observational Method" to Design/Implement

- Plan on multiple injections. It's not failure
- Develop contingency plan and decision flow diagrams as part of the design process
- Do not need complete and perfect characterization, but need adequate monitoring during implementation.
- Review and adjust the design based on initial injection/findings

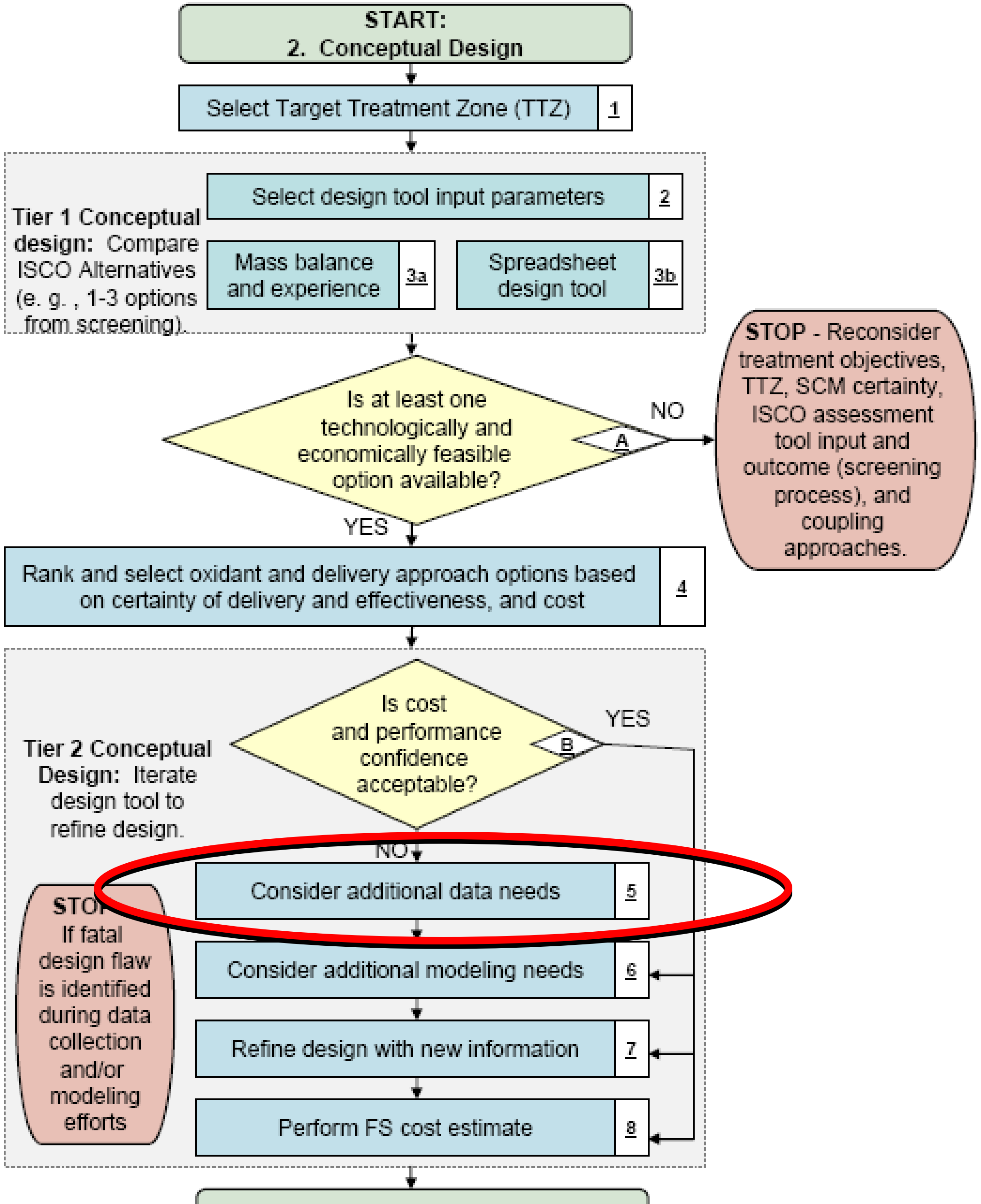
Mass Balance/Experience Approach

- Take advantage of DISCO, with appropriate judgment and consideration on improving over historic performance

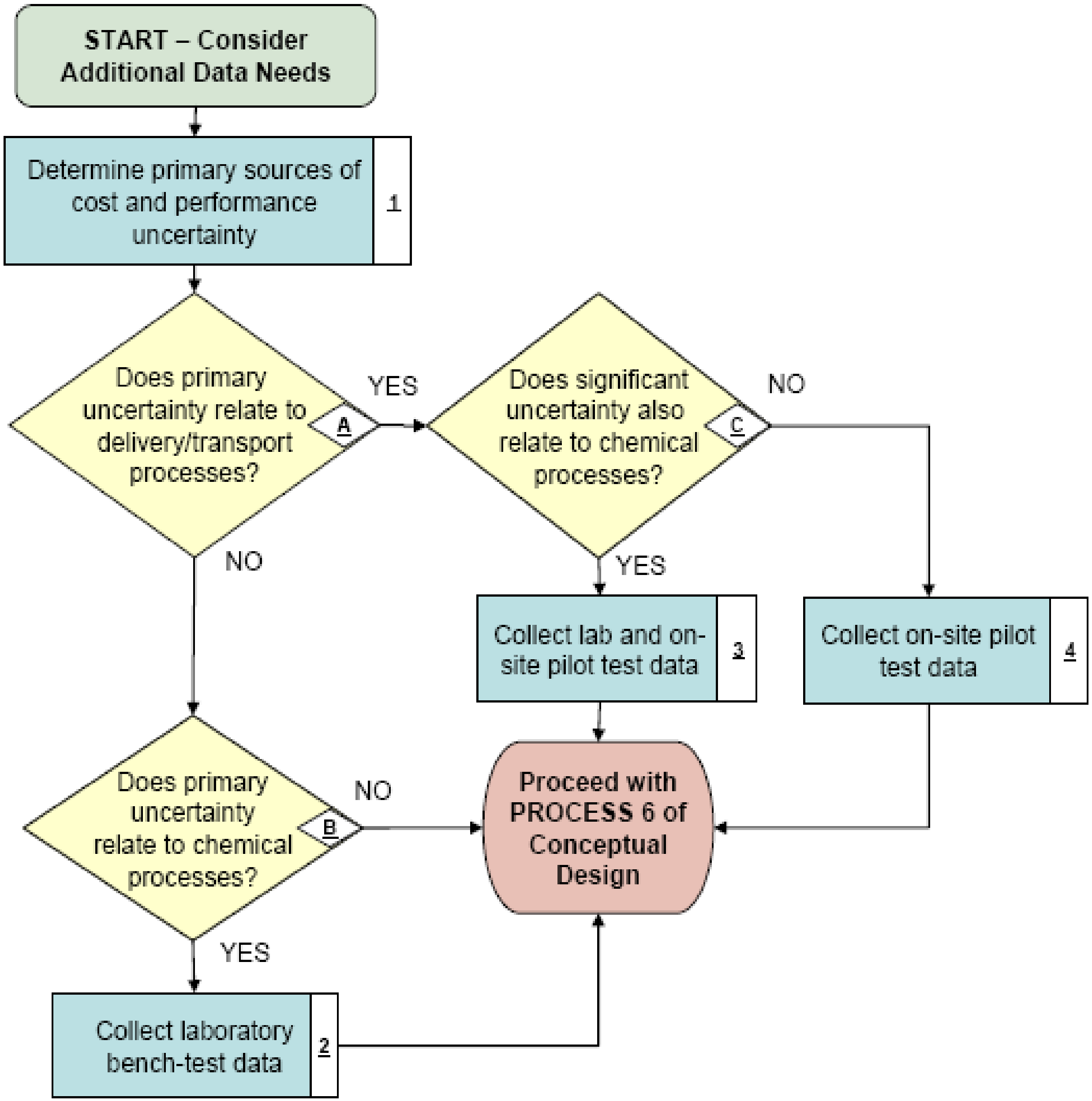
Table CD-1. Median Values for ISCO Design Parameters by Common Oxidant.

	Permanganate	CHP	Persulfate	Ozone
Median design ROI (ft)	15 (33)	15 (35)	12.5 (6)	25 (6)
Median observed ROI (ft)	25 (13)	15 (8)	20 (3)	40 (3)
Median oxidant dose (g oxidant / kg media)	0.41 (37)	1.2 (21)	3.4 (7)	0.041 (5)
Median number of pore volumes delivered	0.16 (34)	0.086 (27)	0.82 (7)	no data
Median number of delivery events	2 (70)	2 (63)	1 (11)	1 (16)
Median duration of delivery events (days)	4 (49)	6.5 (48)	4.5 (8)	280 (16)

ISCO Conceptual Design Flow Diagram



Additional Data Needs Decision



ATTACHMENT 17: Laboratory Bench Testing for Contaminant Treatability and Byproducts

INTRODUCTION

While ISCO Screening assists with identifying viable oxidants and appropriate oxidant activation approaches, the ultimate effectiveness is site-specific. It may be necessary to compare or optimize these approaches using site media to improve design and treatment effectiveness certainty. The data collected using these tests may be used to further compare ISCO options where certainty in oxidant distribution, treatment effectiveness, and cost differences between options are unclear, even after Tier 1 Conceptual

CONTAMINANT TREATABILITY AND BYPRODUCTS TEST PROCEDURE 1: Optimize Oxidation Chemistry

The goal of this procedure is to determine the most efficient and effective approach for ISCO with respect to: (1) the ranges of oxidant activation approaches; (2) the ratio of oxidant to contaminant; and (3) the ratio of activator(s) to oxidant. NOTE: These evaluations are deemed critical for CHP and persulfate oxidants, and the A16. Laboratory Bench Testing for Oxidant Persistence can be conducted concurrent with this procedure (i.e., it is not necessary to conduct both procedures separately).

Based on the results of ISCO Screening, there may be more than one oxidant and more than one activation approach (as appropriate per oxidant) viable for general site conditions. The ISCO Spreadsheet Design Tool was the first step to evaluating appropriate oxidant concentrations as per preliminary conceptual design possibilities given site contaminant and hydrogeological conditions. In support of the Tier I Conceptual Design process, kinetic parameters critical to oxidant distribution are assumed and contaminant destruction rates based on the literature are applied. The values are used in the design tool to assess the most promising injection configuration(s) and oxidant delivery

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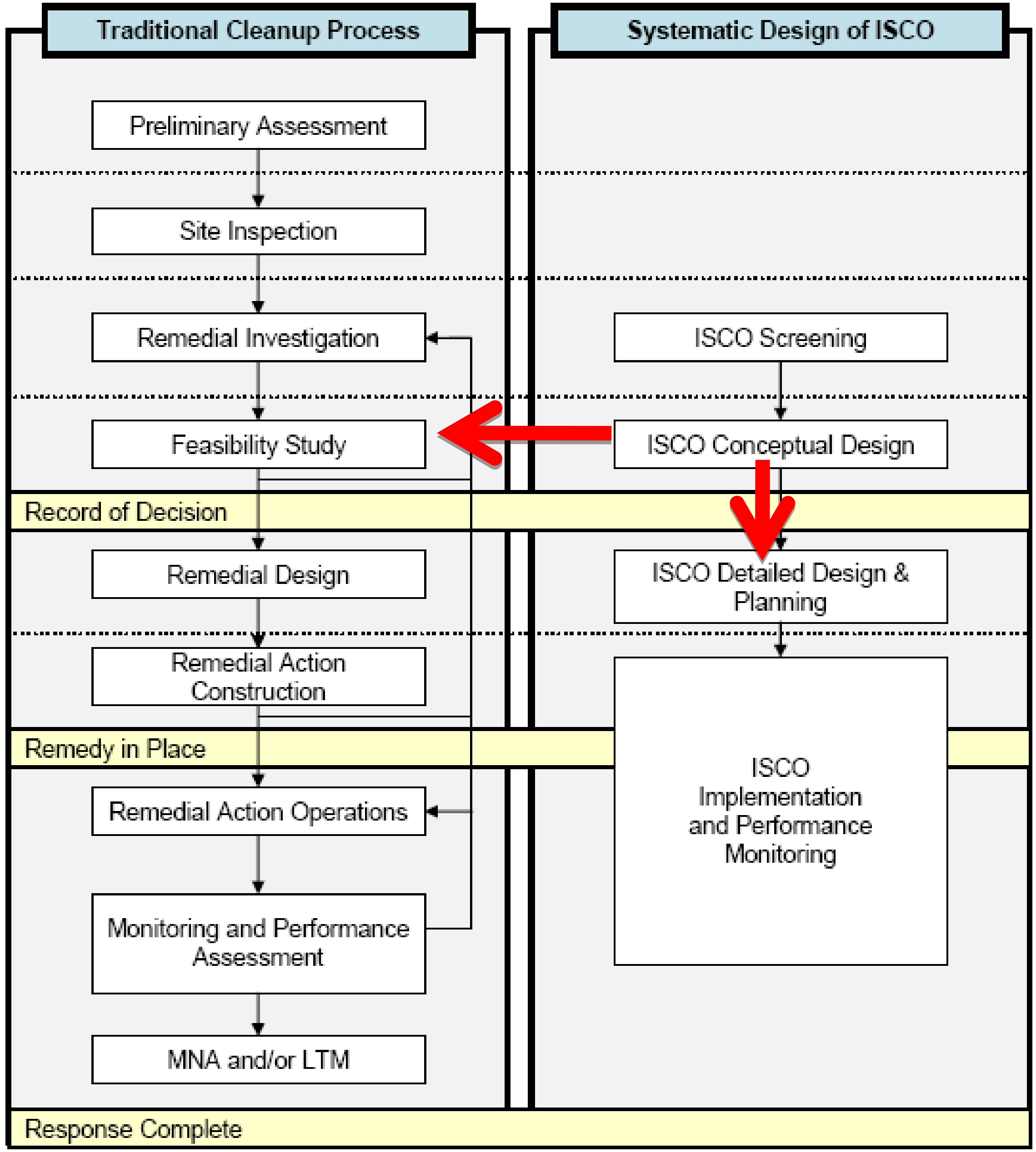
Overall ISCO Protocol Flow



In Situ Chemical Oxidation: 6. CDISCO – Conceptual Design of Permanganate Injection Systems

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SERDP DOD · EPA · DOE | ESTCP

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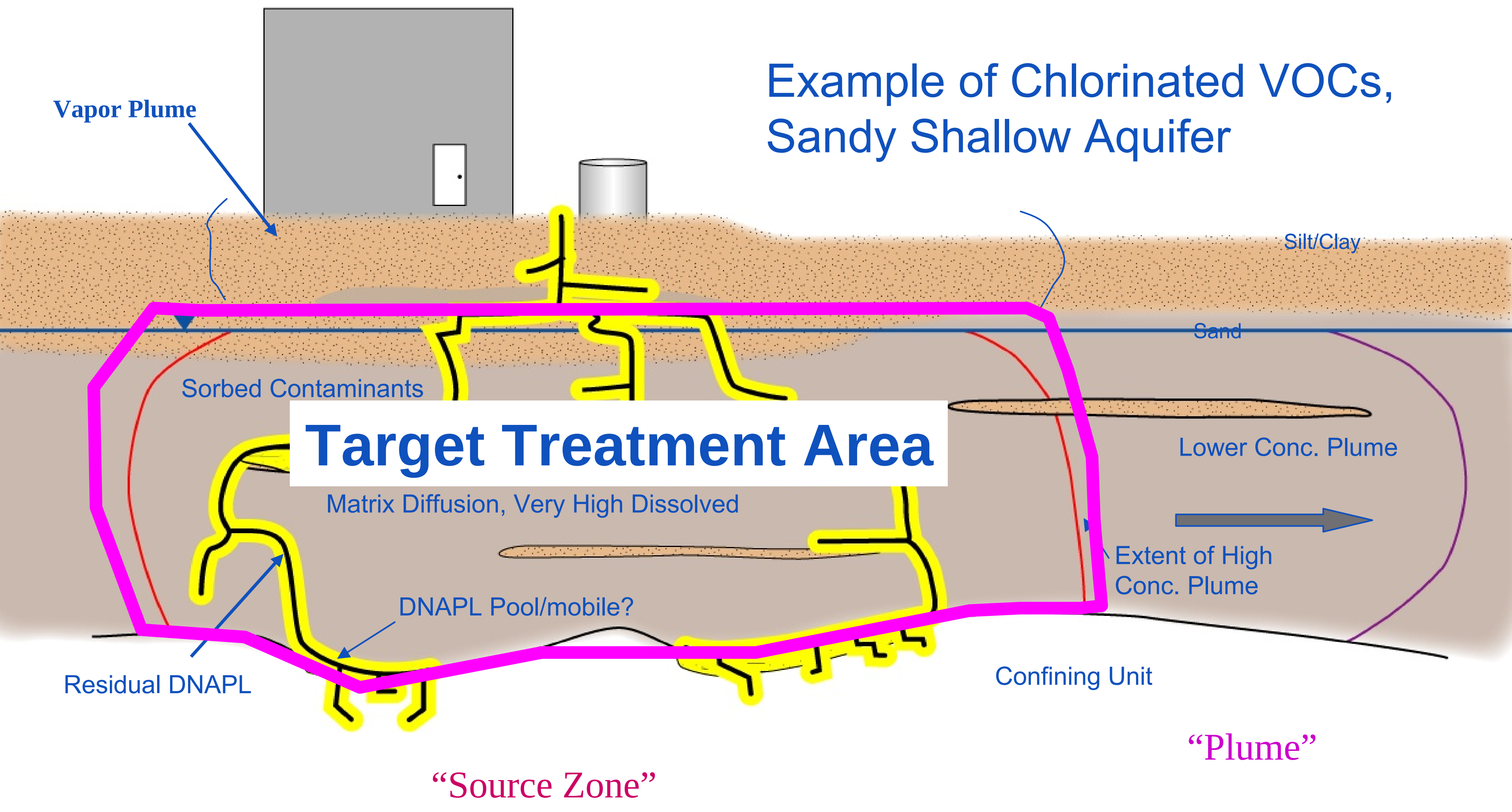
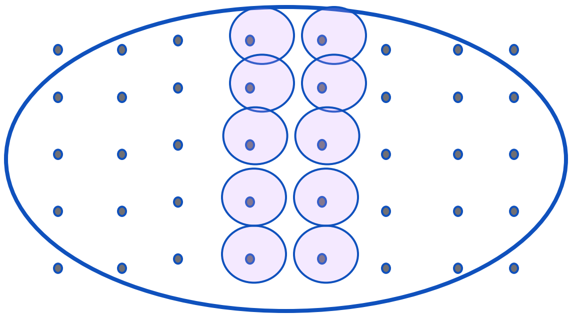
  - Ki Young Cha and Bob Borden
  - Tom Simpkin
  - M. Tony Lieberman
- ER-0623 Team
- Financial and technical support from ESTCP
- NCSU is not sponsoring or endorsing this presentation

Example Conceptual Site Model

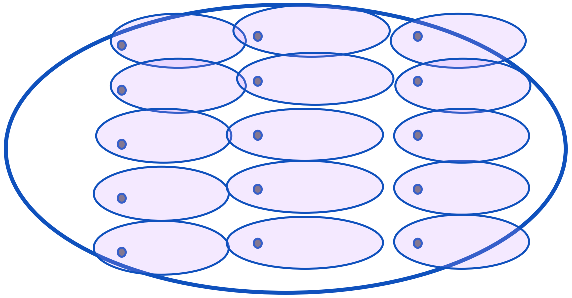


Delivery Approaches

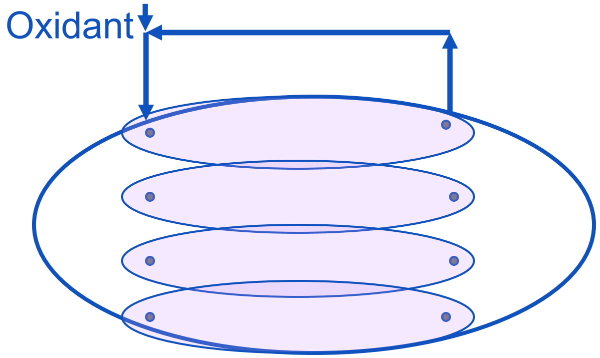
- Grids
  - Injection points or wells



- Inject and Drift
  - Limited by GW velocity



- Recirculation Systems
  - Good when drilling costs are high
  - More complicated design
  - More O&M



What is the Secret to making ISCO Work?

"Success is achieved by
having enough oxidant in contact with the contaminant
for a long enough period of time to react effectively"

ISCO Technology Practices Workshop
Colorado School of Mines, March 2007

- CDISCO Performance Criteria
  - Reagent distributed throughout target zone
  - MnO_4 concentration > ______ mg/L after _____ days
    - Target MnO_4 Concentration ~ 200 to 1000 mg/L
    - Target contact time ~ 4 to 30 days

Conceptual Design Questions

- Well spacing?
- Mass of permanganate injected?
- Permanganate injection concentration?
- Injection flow rate and total fluid volume?
- Number of injections?

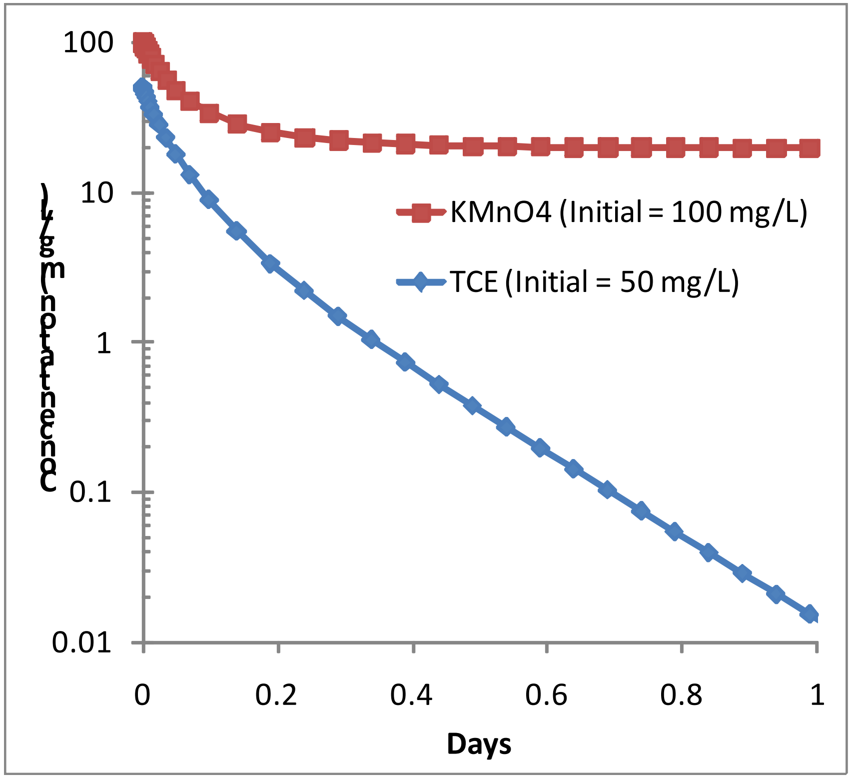
- All controlled by permanganate transport and consumption in aquifer

Factors Controlling Permanganate Distribution

- Physical transport in aquifer
- Consumption during reaction with contaminant
- Consumption by reaction with Natural Oxidant Demand (NOD)
  - Natural organic matter
  - Reduced minerals (Fe[II] and sulfides)

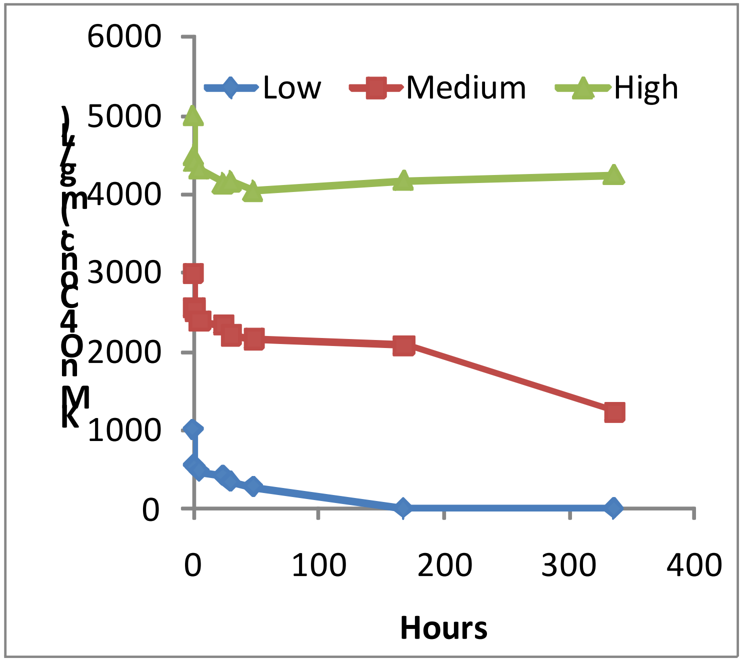
PCE and TCE Degradation Kinetics

- Well defined kinetics
  - Rate = K_2 [TCE] [MnO_4]
  - PCE $K_2 = 0.03 - 0.04\ M^{-1}s^{-1}$
  - TCE $K_2 = 0.5 - 0.8\ M^{-1}s^{-1}$
- Reaction kinetics are rapid relative to GW flow
  - Small excess of $KMnO_4$ results in 'complete' destruction in 24 hr
- CDISCO
  - Assumes MnO_4 loss is instantaneous
  - Does not directly simulate contaminant loss



Permanganate Consumption by NOD

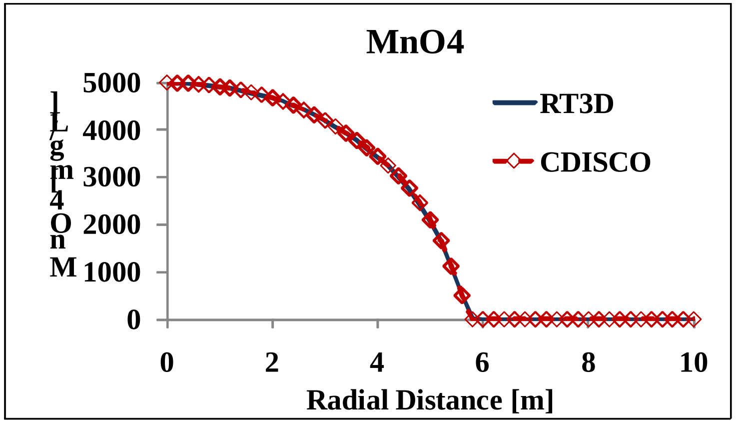
- Typical NOD Test
  - Add sediment to bottle with varying $KMnO_4$ concentrations
  - Monitor $KMnO_4$ conc. with time
- Common results
  - Oxidant consumption increases with
    - Oxidant concentration (mg per liter water)
    - Oxidant dose (mg / g sediment)
  - Rapid initial decline and then slower decline (days to months)
    - Highly reactive NOD is consumed first
    - Less reactive NOD is consumed later

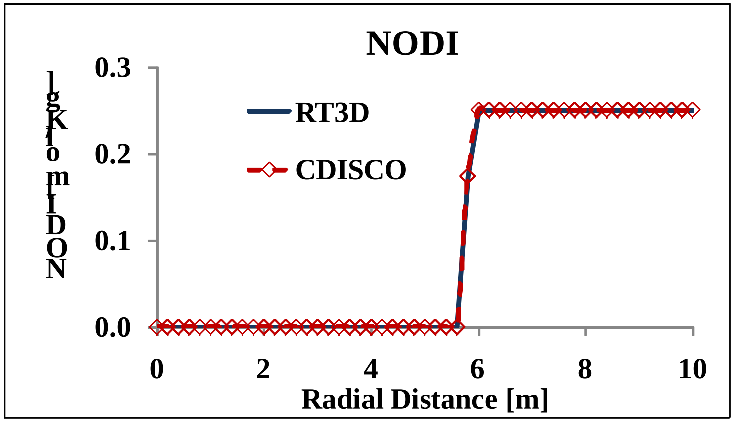


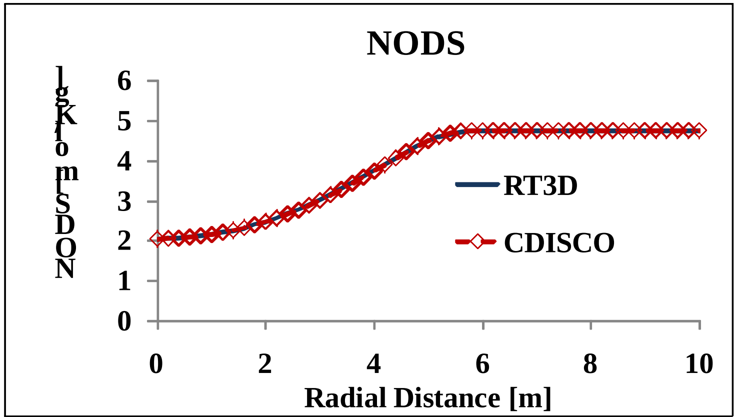
- CDISCO assumes
  - NOD composed of two components – instantaneous NOD and slow NOD
  - Rate of slow NOD consumption = K_2 [NOD_S] [MnO_4]

Permanganate Transport Model

- CDISCO –
  Conceptual Design of ISCO
  - MS Excel based Numerical Model
  - Developed jointly by ER-0623 and ER-0625
- Mechanics
  - MnO_4 transport and consumption
  - Based on series of CSTRs
  - NOD kinetics identical to RT3D
  - Includes cost estimating tool to aid in comparing alternatives
- Model Validation
  - Results ‘identical’ to full RT3D for homogeneous aquifers







Designing an Injection System with CDISCO

1. Enable Macros
2. Enter site data
3. Enter Design Criteria
   a. Target MnO_4 concentration (typical ~ 200 – 1000 mg/L)
   b. Target contact time (typical ~ 4 – 30 days)
   c. Overlap Factor (OF)
4. Click ‘calculate’ (run MnO_4 transport model)
5. Enter cost data
6. Review cost summary
7. Revise design and repeat model run

Site Data

1. Model run parameters
   a. simulation duration
   b. time step
2. Hydrogeologic characteristics
   a. Permeability
   b. Porosity
   c. effective thickness
3. NOD parameters
   a. Total NOD
   b. Fraction instantaneous
   c. Slow NOD rate coefficient
4. Oxidant and contaminant info
5. Injection info
   a. Injection well diameter and design flow per well
   b. Hours per day of injection and days of injection
6. Design criteria
   a. Target oxidant concentration and contact time
   b. Radius of influence overlap factor (OF)

Hydrogeologic Characteristics		
Top of Injection Interval	30	ft bgs
Bottom of Injection Interval	40.00	ft bgs
Aquifer Thickness	10	ft
Thickness of Mobile Zone (Z)	10.0000	ft
Porosity	0.20	L/L
Longitudinal Dispersivity	2.0000	ft
Hydraulic Conductivity (k)	50.00	ft/day
Depth to Water Table	15	ft
Soil and NOD Characteristics		
Bulk Density	1.60	Kg/L
NOD	1	g/Kg
Fraction Instantaneous	0.20	
Second Order Slow NOD Consumption Rate (Ks)	0.1000	L / mmol - d
Oxidants Information		
Name of Oxidant	Permanganate (MnO_4^-)	
Molecular Weight of Oxidant	118.94	g/mol
Initial Oxidant Concentration	0.00	mg/L

Cost Data

1. Categories
   a. Prime contractor (mobe, hourly labor, expenses)
   b. Subcontractor (mobe, hourly labor, expenses)
   c. Reagent, materials and equipment rental
2. Activities
   a. Fixed costs (design, permitting, etc.)
   b. Injection well or probe installation
   c. Reagent injection

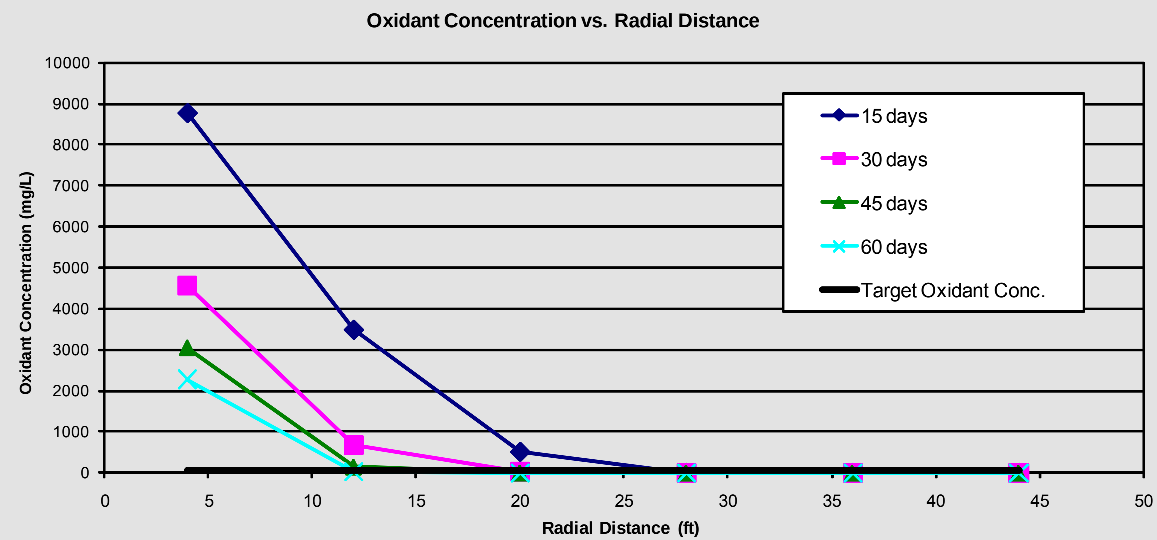
NOTE:

Costs are NOT all inclusive. Only use to compare similar layouts.

1	***Well and Injection Information***		
a	Top of Injection Interval	30	ft
b	Bottom of Injection Interval	40	ft
c	Injection rate to be used in Design	15,000	gpd/well
d	Number of wells injected simultaneously, or number of wells injected per day	5	
2	***Well Drilling Fixed Costs***		
a	Prime contractor mobilization	2000	$
b	Subcontractor mobilization	2000	$
h	**Total well drilling fixed cost**	**4,000**	**$**
3	***Prime Contractor Information and Daily Well Drilling Costs***		
a	Prime contractor personnel on-site each day of well installation	1	person(s)
b	Average labor rate of prime contractor personnel	100	$/hr
c	Hours billed per person per day	10	hr/person/day
d	Per Diem (e.g., meals, travel, vehicle rental, lodging)	200	$/person/day
e	Additional costs (consumables, H&S, and monitoring equipment)	150	$/day
f			$/day
g	**Total daily well drilling cost for prime contractor**	**1,350**	**$/day**

Transport Model Output

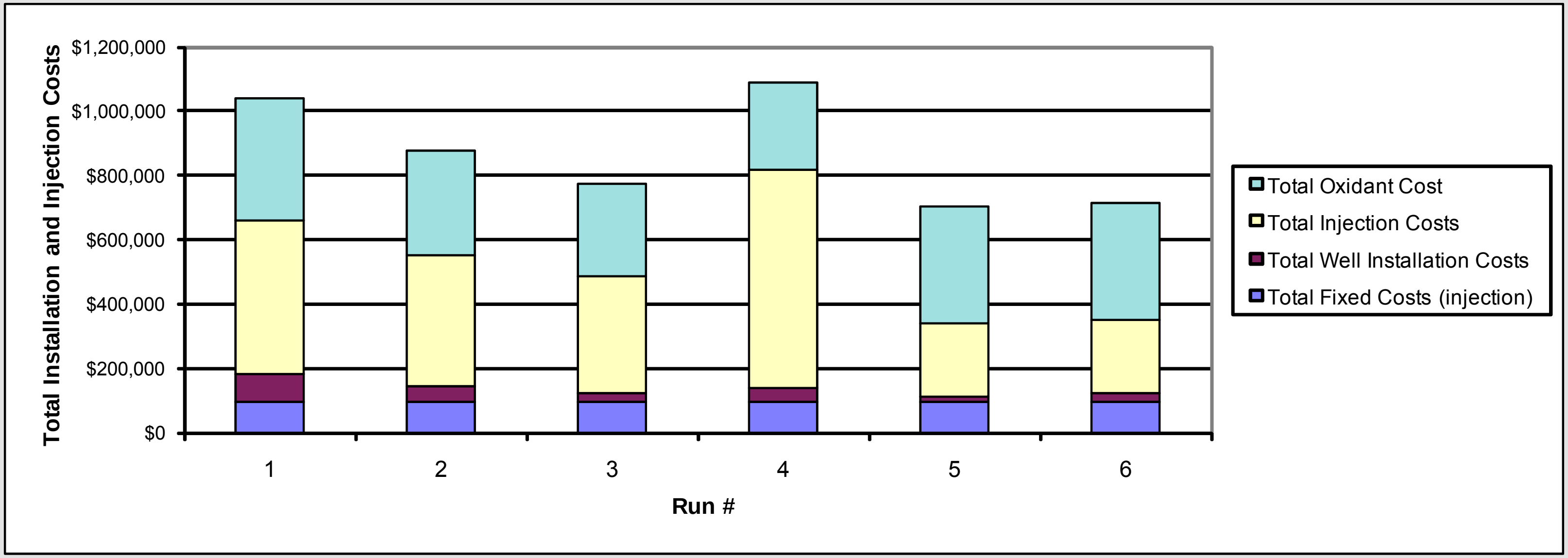
- Typical Output
  - Generates graphs of MnO_4 conc. vs distance for different injection conditions
- Determines effective Radius of Influence (ROI) based on
  - Minimum MnO_4 Conc.
  - Contact Time
- Determines injection well spacing based on
  - ROI
  - Overlap factor



Selected	Run Number	Injection Duration	Aquifer Thickness	Thickness of Mobile Zone	NOD Fraction Instantaneous	NOD (g/kg)	Slow NOD Rate	Injection Oxidant Conc (mg/L)	Injection Rate gal/Day	ROI	Minimum Oxidant Conc to Calc ROI	Target Number of Days to Calc ROI
✓	1	3	20	10	0.1	5	0.001	10,000	3,000	10.41	50	30
✓	2	5	20	10	0.1	5	0.001	10,000	3,000	14.46	50	30
✓	3	10	20	10	0.1	5	0.001	10,000	3,000	21.25	50	30
✓	4	10	20	10	0.1	5	0.001	5,000	3,000	15.56	50	30
✓	5	10	20	10	0.1	5	0.001	20,000	3,000	27.23	50	30
✓	6	5	20	10	0.1	5	0.001	20,000	3,000	19.64	50	30

Comparison of Alternatives

Run	1	2	3	4	5	6
Total Fixed Costs (injection)	$94,800	$94,800	$94,800	$94,800	$94,800	$94,800
Total Well Installation Costs	$85,667	$47,700	$25,367	$41,000	$18,667	$29,833
Total Injection Costs	$478,800	$410,400	$364,800	$684,000	$228,000	$228,000
Total Oxidant Cost	$378,547	$324,469	$288,417	$270,391	$360,521	$360,521
Total Installation and Injection Costs	$1,037,814	$877,369	$773,384	$1,090,191	$701,988	$713,155
Number of probes or wells required	35	18	8	15	5	10
NOD (g/kg)	5	5	5	5	5	5
Injection Oxidant Concentration	10000	10000	10000	5000	20000	20000
Injection Oxidant Mass (lbs)	26288	22533	20029	18777	25036	25036
Injection Duration (days)	3	5	10	10	10	5
Volume Injected per Day (gal/d)	3000	3000	3000	3000	3000	3000
Thickness of Mobile/Target Thickness	0.5	0.5	0.5	0.5	0.5	0.5

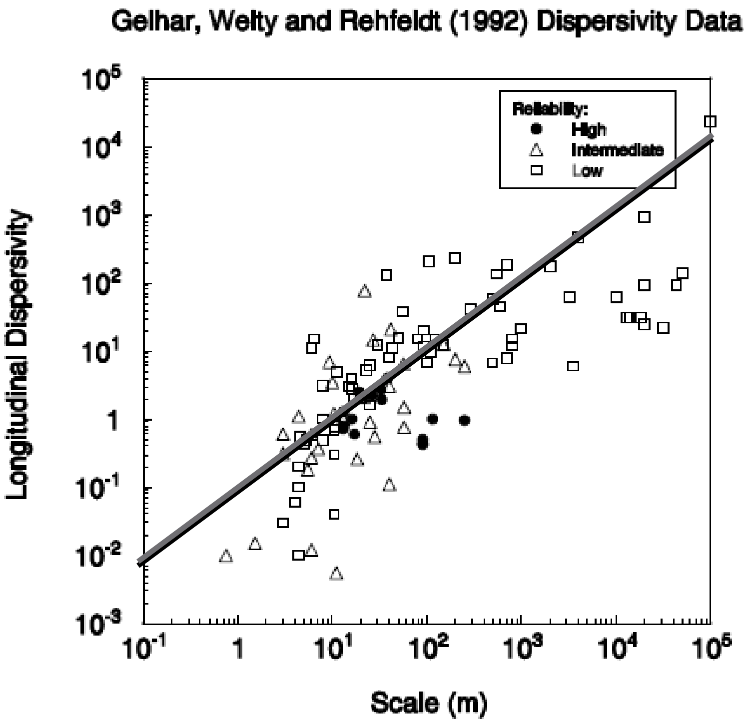


Input Parameters

- Longitudinal Dispersivity
- NOD Kinetic Parameters
- Overlap Factor

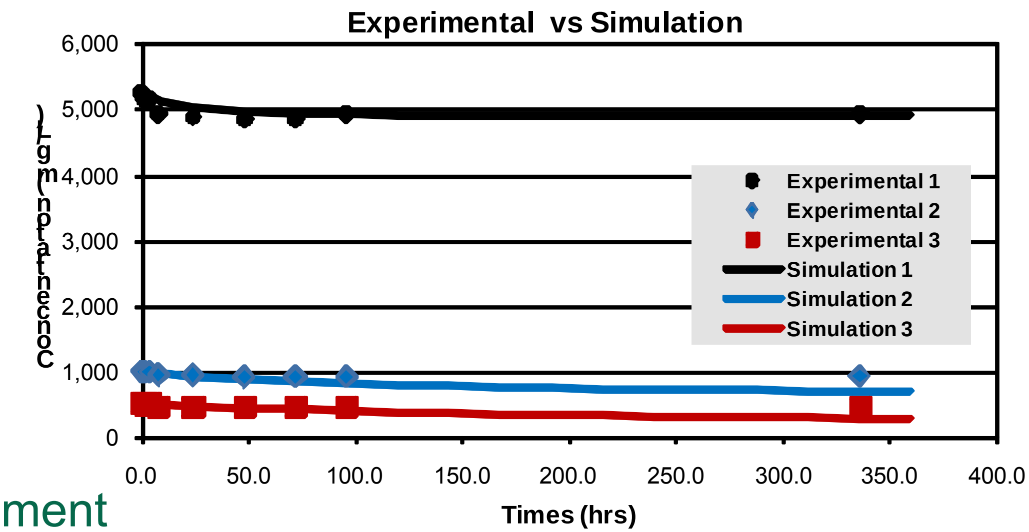
Longitudinal Dispersivity (α_L)

- Commonly observed to increase with transport distance
- Graph at right shows field data with line where
  α_L = 10% of distance
- Common assumption
  α_L = 0.1 * model length



- CDISCO
  - Reactor length = 2 * α_L
  - Small α_L → larger # or reactors → long run times
  - For α_L = 10% of model length, model will have 5 reactors

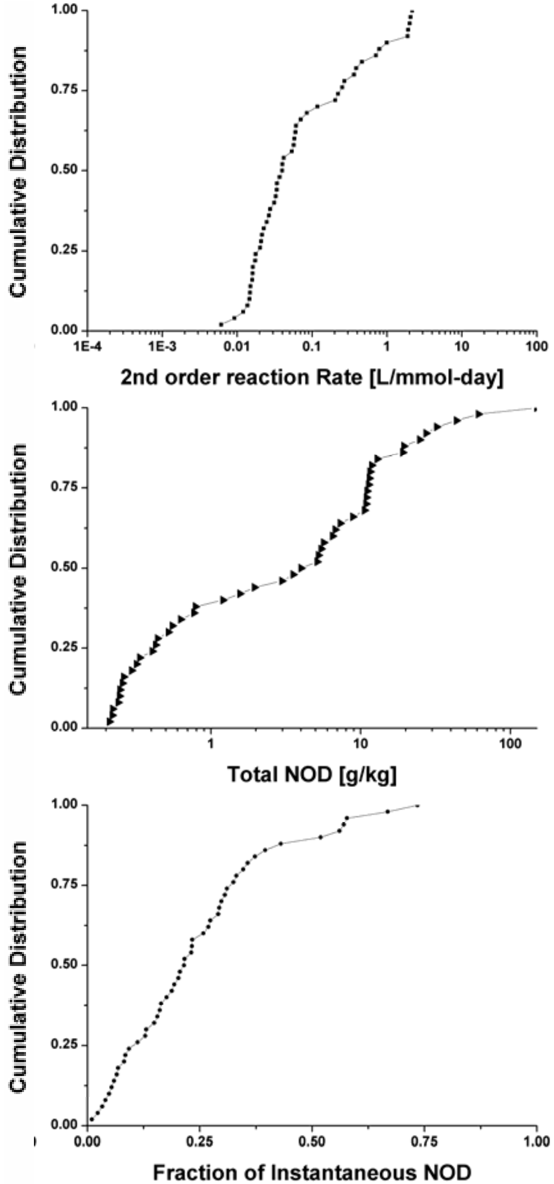
NOD Kinetics



- Tool available to estimate kinetic parameters from NOD test data
- Enter
  - Amount of water and sediment
  - Permanganate conc. vs time
- Click ‘calculate coefficients’
  - Solver tool searches for best fit parameters
- Output is
  - Total NOD
  - Fraction instantaneous NOD
  - 2^{nd} Order Slow NOD reaction rate

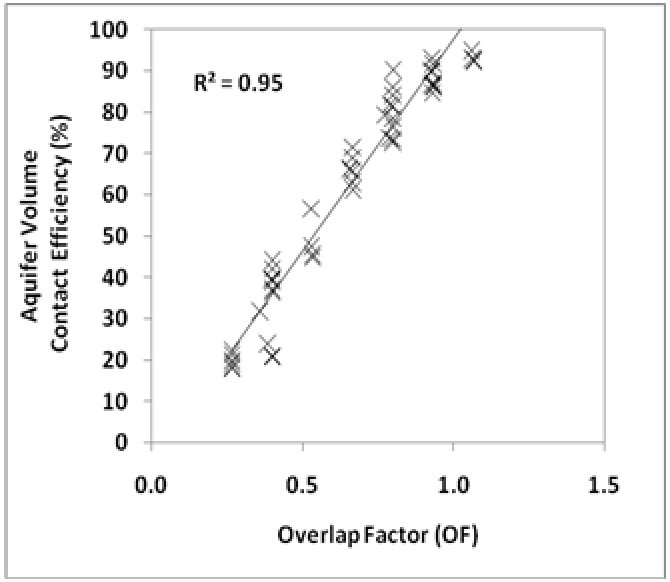
NOD Kinetics

- When NOD lab data not available, can use 'literature values'
- Applied parameter estimation tool to NOD data from 50 samples
- Results are cumulative frequency distributions for
  - 2^{nd} order reaction rate for slow NOD
  - Total NOD (this is NOT 48 hr NOD)
  - Fraction instantaneous NOD
- NOTE: At many of the sites, NOD is too high for ISCO with permanganate to be practical!



Overlap Factor (OF)

- Overlap Factor (OF)
  - Well Spacing = 2*ROI / OF
  - ROI = radius of influence
- CDISCO calculates ROI
  - Minimum MnO_4 concentration after __ days
- User must pick OF
  - Currently, no guidance on correct OF
  - Increasing OF increases cost
- Comparison of RT3D and CDISCO
  - Obtain E_V and E_M from 3D heterogeneous simulations
  - Obtain ROI from CDISCO
- Conclusion
  - OF between 0.8 and 1.2 generates good results
  - Note: Must stage injections to get high OF
  - CDISCO assumes each well is injected individually



In Situ Chemical Oxidation: 7. ISCO Screening and Conceptual Design Breakout Exercise

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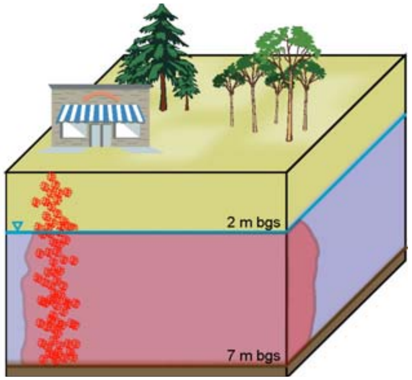
SERDP
DOD ▪ EPA ▪ DOE
ESTCP

- Example #4 (see details in handout)

Key Features of the Site

- Dry cleaner in Florida
- Tetrachloroethylene (PCE) DNAPL not suspected
  - Maximum concentration of 1 mg/L in groundwater
  - Maximum concentration of 49 mg/kg in porous media
- PCE has leaked into homogeneous, permeable sand
- Contamination to confining layer at 20 ft bgs
- Homogeneous, permeable sand
- Treatment goal = **MASS REDUCTION**



- Example #4 (see details in handout)
  - ♦ Determine an appropriate design for permanganate application using direct push or injection wells.
  - ♦ Determine the “best” oxidant concentration (between 1,000 and 10,000 mg/L) to achieve 100 mg/L at the delivery radius of influence for 10 days (to allow for some desorption / dissolution).
  - ♦ How many injection wells or points are needed?
  - ♦ What is the associated cost (roughly)?
  - ♦ What is the added cost for a 2nd injection? A third?