WORKSHOP REPORT

In Situ Chemical Oxidation for Remediation of Contaminated Groundwater: Summary Proceedings of an ISCO Technology Practices Workshop

ESTCP Project ER-0623

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Preface

This document contains a summary of the ISCO Technology Practices Workshop, which was held as part of ESTCP Project ER-0623: *"In Situ Chemical Oxidation for Ground Water Remediation – Technology Practices Manual"*. This Workshop was convened at the Colorado School of Mines on March 7-8, 2007. Prior to the Workshop, a notebook of materials was distributed to all participants. During the Workshop, there were presentations, panel discussions, breakout group sessions, and plenary group discussions. In this document an attempt has been made to summarize the information presented and discussed, and to highlight any apparent consensus among the Workshop participants. This summary was assembled based on information and ideas exchanged at the Workshop. This summary is believed to represent a factual account of the Workshop proceedings and as far as possible, controversy and consensus regarding ISCO technology practices have been described. Many details were necessarily omitted however to keep the summary document to a reasonable length. In addition, to maintain some anonymity for the Workshop participants who made candid remarks during the plenary discussions, panel sessions, and breakout sessions, participant comments were not attributed to specific individuals by name.

The summary was prepared and reviewed by members of the ESTCP ER-0623 project team. Further review of the draft proceedings was completed by 12 of the participants at the Workshop and this final proceedings document was prepared based on all of the comments received.

Many individuals contributed significantly to the successful conduct of the Workshop. In addition to the ER-0623 project team members who edited this document, the following members of the project team were diligent in their contributions to Workshop planning and conduct: Ben Petri (CSM), Fritz Krembs (CSM), Kathryn Lowe (CSM), Tom Palaia (CH2M HILL), Abigail Wren (CH2M HILL), Mike Singletary (NFECSD), and Nancy Ruiz (NFESC).

Marvin Unger (HydroGeoLogic), Dick Brown (ERM), and Rick Watts (Washington State University) are acknowledged for the presentations they each made during the opening session at the Workshop. Also acknowledged are the Workshop organizers and participants who served as chairs or panelists for the panel discussions that took place during the Workshop. Panel discussions were led by Mike Singletary (NFECSD), Junko Munakata Marr (CSM), Michelle Crimi (ETSU), Ben Petri (CSM), Tom Simpkin (CH2M HILL), and Tom Palaia (CH2M HILL).

Several persons took notes throughout the Workshop; deserving special recognition in this regard are Fritz Krembs (CSM), Saebom Ko (ETSU), and Abigail Wren (CH2M HILL) who are gratefully acknowledged for their dedication to this critical task.

A special acknowledgement is made for all of the participants who contributed by attending and participating in the Workshop. Without their interest and enthusiasm for sharing information about ISCO technology practices, the Workshop would not have been as successful as it was.

Kathryn Lowe of CSM is acknowledged for her attention to details regarding the Workshop logistics at CSM. The Workshop ran smoothly and for this, everyone is extremely grateful.

Finally, the ISCO Technology Practices Workshop was sponsored by the Environmental Security Technology Certification Program (ESTCP). Dr. Andrea Leeson, Program Manager, and other ESTCP staff are gratefully acknowledged for their assistance and support.

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Acronyms and Abbreviations

ASTM	-	American Society for Testing and Materials
BTEX	-	benzene, toluene, ethyl benzene, xylenes
CHP	-	catalyzed hydrogen peroxide; catalyzed hydrogen peroxide propagations
COC	-	constituent of concern
COD	-	chemical oxygen demand
CSM	-	Colorado School of Mines
1,1-DCA	-	1,1-dichloroethane
DNAPL	-	dense nonaqueous phase liquid
DOD	-	Department of Defense
DOE	-	Department of Energy
ERD	-	enhanced reductive dechlorination
ESTCP	-	Environmental Security Technology Certification Program
ETSU	-	East Tennessee State University
FAQ	-	Frequently Asked Questions
f_{oc}	-	fractional organic carbon content
GW	-	ground water
H_2O_2	-	hydrogen peroxide
IPR	-	in-progress review
ISCO	-	in situ chemical oxidation
K_{ow}	-	octanol-water partition coefficient
$KMnO_4$	-	potassium permanganate
LNAPL	-	light nonaqueous phase liquid
MCL	-	maximum contaminant level
MIP	-	membrane interface probe
MNA	-	monitored natural attenuation
MnO_2	-	manganese dioxide
MTBE	-	methyl tert butyl ether
NAPL	-	nonaqueous phase liquid
NFECSD	-	Naval Facilities Engineering Command Southeast Division
NFECSWD	-	Naval Facilities Engineering Command Southwest Division
NFESC	-	Naval Facilities Engineering Service Center
NOD	-	natural oxidant demand
NOM	-	natural organic matter
O_3	-	ozone
OH•	-	hydroxyl radical
ORP	-	oxidation-reduction potential
PCE	-	perchlorothene or tetrachloroethene
ppb	-	parts per billion
RI	-	remedial investigation
ROD	-	Record of Decision
SCM	-	site conceptual model
SERDP	-	Strategic Environmental Research and Development Program
TCA	-	1,1,1-trichloroethane
TCE	-	trichloroethene
TPH	-	total petroleum hydrocarbons
TPM	-	technology practices manual
USEPA	-	U.S Environmental Protection Agency
WSU	-	Washington State University

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Executive Summary

The Colorado School of Mines (CSM), in collaboration with East Tennessee State University (ETSU), CH2M HILL, and the U.S. Navy, convened a 2-day ISCO Technology Practices Workshop at the CSM in Golden, Colorado on March 7-8, 2007. The purpose of the Workshop was to provide a forum to share insights and perspectives gained regarding the application of ISCO for remediation of contaminated sites. There were 43 invited participants at the Workshop including SERDP/ESTCP program staff, ISCO project team leaders, and key ISCO stakeholders (chemical companies, technology vendors, environmental consultants, researchers, and remedial project managers). The Workshop program was designed to encourage participation and consisted of a series of technical presentations, four panel discussions, a contaminated site scenario exercise, three breakout group meetings, along with several periods of plenary discussions. This proceedings document summarizes the activities and outcomes of the workshop. Highlights of some views and consensus that emerged from the Workshop are given below.

There was general consensus that while ISCO as a remediation technology may be considered for a wide range of situations, site-specific conditions interact with ISCO technology attributes and determine the performance that would be considered reliably achievable. As an illustration of this view, a strong majority of the Workshop participants responding to the scenario assignment indicated that they would personally consider ISCO for all six of the contaminated site scenarios. However, the degree of anticipated ISCO performance, timeframe necessary and estimated costs varied for all of these scenarios. Furthermore, different types of treatment objectives may be more or less achievable depending on site-specific conditions. Thus the success or failure of an ISCO application is enormously dependent not only on site-specific conditions, but also the remediation objectives laid out for a specific site and the resources (e.g., time and money) made available to implement the ISCO system.

There was general consensus that the previously, and still to some degree, widely held view that ISCO was universally applicable and capable of achieving rapid cleanup at most organically contaminated sites (i.e., ISCO as a 'silver bullet') was an unrealistic distortion of ISCO's potential as an often viable but not universally applicable remediation technology. Similarly, in contrast to a view that an ISCO remediation project can be completed with a short-term, single injection event, there was general consensus that multiple injection events are commonly required and should be planned for. Re-characterization between oxidant injection events was noted to be important to properly design the later events when using a multiple injection approach. These can range from a second treatment across the entire target treatment zone, to a more strategic targeting of hot spots remaining within the treatment zone.

There was general consensus among the Workshop attendees that there were two fundamental reasons for ISCO not achieving performance objectives: 1) the oxidant was not adequately distributed throughout the target treatment zone, or 2) that an insufficient amount of oxidant was delivered to target treatment zone. Performance deficiencies based on these were viewed as more likely to occur under the following circumstances: 1) site characterization is inadequate and the contaminant mass is poorly understood; 2) the subsurface is highly heterogeneous; 3) the design neglects the mass of contaminants that are sorbed in the subsurface; 4) the presence of DNAPLs is unknown or not accounted for; 5) the presence of co-contaminants that also consume oxidants; 6) that oxidants migrate out of the target treatment zone; and 7) that the oxidant doesn't persist as long as expected.

Rebound, defined as an increase in the contaminant concentrations that are observed in ground water within a target treatment zone soon after ISCO is completed (i.e., concentrations go down during ISCO but then increase after ISCO potentially reaching concentrations near (or even greater than) the pre-ISCO baseline conditions), is a relatively common occurrence observed at ISCO sites. However, rebound may or may not be a negative condition or reflect an inherent shortcoming of ISCO or a site-specific performance deficiency. There are several reasons rebound may be experienced, most notably: 1) oxidants did not destroy all of the aqueous and sorbed phased contaminants in the target treatment zone and post-ISCO re-equilibration led to increased ground water concentrations (e.g., diffusion of contaminants out of low permeability zones into transmissive zones), 2) incomplete destruction of DNAPLs within the target treatment zone, which dissolve back into the aqueous phase and lead to higher ground water concentrations, and/or 3) oxidation of natural organic matter (NOM) than can affect partitioning of any untreated organic chemicals and lead to higher aqueous phase concentrations. 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. Then the use of ISCO can be viewed as an ongoing, iterative process that will take advantage of contaminant rebound rather than view it as an indication that the technology was inappropriate for a site or was applied improperly.

In selecting ISCO as a viable remedy for a particular site, contaminant properties, site conditions, and performance objectives interact to determine what type of ISCO might be viable and how it might be implemented. There was consensus that there was no universally applicable ISCO technology and that ISCO was not a silver bullet appropriate for all organically contaminated sites. The Workshop attendees identified site attributes that tended to be favorable versus unfavorable for ISCO to be successfully applied (green flags vs. red flags). There was general consensus that ISCO should be viewed as a remediation technology to be iteratively applied until the remediation goal is reached rather than viewed as a technique that can be used in a single event to achieve site closure.

1. Introduction

1.1. Workshop Purpose

The Colorado School of Mines, in collaboration with East Tennessee State University, CH2M HILL, and the U.S. Navy, are completing a project entitled “In Situ Chemical Oxidation (ISCO) for Ground Water Remediation - Technology Practices Manual” that is being funded by the DOD Environmental Security Technology Certification Program (ESTCP) (ER-0623). The overall goal of the project is to produce guidance and decision-support information and tools to help advance the standard-of-practice for site-specific engineering of ISCO so applications at DOD and other sites yield more predictable and cost-effective outcomes (Figures 1.1 and 1.2). To help achieve this goal, a 2-day ISCO Technology Practices Workshop was held at the Colorado School of Mines in Golden, Colorado on March 7-8, 2007. The purpose of the Workshop was to provide a forum to share insights and perspectives gained regarding the application of ISCO for remediation of contaminated sites. Participants at the workshop included SERDP/ESTCP program staff, ISCO project team leaders, and key ISCO stakeholders including chemical companies, technology vendors, environmental consultants, researchers, and remedial project managers. Presentations and discussions were intended to help identify 1) best practices including technology screening/design criteria and promising tools/techniques, 2) key data and tool gaps for decision-making, and 3) primary factors leading to success/failure. The insights gained from the Workshop were envisioned to directly support development of a frequently asked questions (FAQ) guide and a rational ISCO design protocol, both of which are being developed during ESTCP project ER-0623.

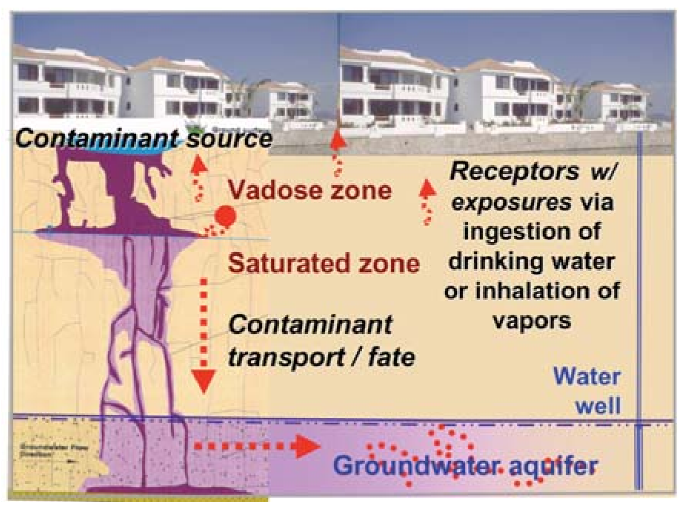

Figure 1.1. Illustration of subsurface contamination of soil and ground water and situations where ISCO may be considered for subsurface clean up and risk reduction.

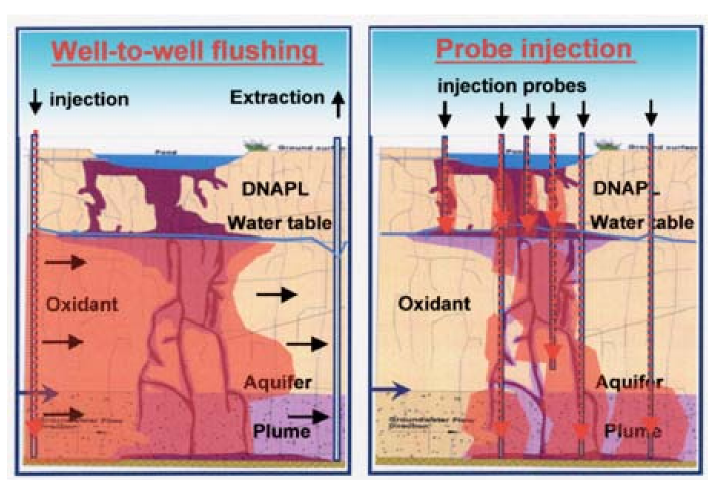

Figure 1.2. Illustration of ISCO and how it might be applied for subsurface remediation using two contrasting delivery approaches.

1.2. Workshop Approach

The Workshop program was developed to consist of a series of presentations, panel discussions and breakout sessions as revealed in the Workshop program given in Table 1.1. Attendance at the Workshop was limited to facilitate informal working interactions and to encourage broad participation during panel and breakout sessions. During Fall 2006, a list of potential participants with varied disciplinary backgrounds, technical and management expertise, and perspectives related to site-specific engineering of ISCO was developed by the ER-0623 project team and shared with the ESTCP Program Office for their concurrence. A list of the 43 persons who participated in the Workshop is presented in Table 1.2.

Prior to the Workshop, background materials were assembled into a notebook by the ER-0623 project team and one was distributed to each of the Workshop participants. The contents of the notebook included the following major items:

1. Workshop Description and Logistics
2. List of SERDP/ESTCP ISCO Projects
3. ER-0623 Project Overview
4. ER-0623 List of Frequently Asked Questions (FAQs) (*draft as of January 2007*)
5. ER-0623 ISCO Decision Diagrams (*draft as of January 2007*)
6. ER-0623 Compilation and Analysis of ISCO Case Study Projects (*draft as of January 2007*)
7. ER-0623 Critical Review of ISCO Literature (*draft as of January 2007*)

As the Workshop was designed to encourage discussion, the Workshop agenda was structured in a way that would foster participation from the group as a whole. On Day 1, the Workshop was convened and during an opening session there were several presentations concerned with the background and status of the DOD ISCO Initiative and the methods and results of several ISCO projects sponsored by SERDP/ESTCP. Following this there were a series of four panel sessions. The panel sessions were focused on ISCO and decision-making during each of the key phases of a typical remediation project:

Panel I: ISCO screening and selection; using ISCO in combined remedies,

Panel II: ISCO feasibility study; oxidant selection and delivery approaches, lab and field tests,

Panel III: ISCO system design and modeling tools, and

Panel IV: ISCO system construction, startup, monitoring.

The panels were constituted prior to the Workshop by inviting some of the confirmed Workshop participants to serve on each of the panels based on each panel topic and their background and area of expertise. During the Workshop, each panel session lasted about 1 hr. During this time there were brief remarks made by the panel chair(s) and each of 3 or 4 other panel members. Then the audience of participants offered their views and posed questions for the panel to respond to or for others in the audience to comment on.

Near the end of the first day, a set of six site scenarios developed by the ER-0623 team was presented to the Workshop participants. A one-page site description along with a one-page questionnaire form was distributed. As a homework assignment, the Workshop participants were asked to respond to a series of questions concerned with the viability of one or more ISCO systems to achieve different remediation goals at each of the six sites. The responses were collected on the morning of Day 2 and tabulated with a brief summary presentation of results made to the participants during Day 2.

Table 1.1. Program for the ISCO Technology Practices Workshop on March 7-8, 2007.

Day/time	Topic/Activity
Wednesday, March 7, 2007	
08:00 a.m.	*Registration and continental breakfast*
08:30 a.m.	Welcome and statement of purpose and approach for the workshop; Introduction of participants ~ Bob Siegrist and Michelle Crimi
09:00 a.m.	ISCO Initiative background and status within SERDP/ESTCP ~ Marvin Unger
09:15 a.m.	Overview and recent project findings concerning site-specific engineering of ISCO ~ Dick Brown, Rick Watts (ER-1288), Bob Siegrist (ER-1290)
10:15 a.m.	Overview of ER-0623: ISCO Technology Practices Manual ~ Bob Siegrist
10:45 a.m.	*Break*
11:00 a.m.	Panel I: ISCO screening and selection; using ISCO in combined remedies Chairs: Mike Singletary and Junko Munakata Marr Panelists: Paul Favara, Michael Pound, Kent Sorenson, Mike Urynowicz
12:00 p.m.	*Lunch provided*
1:00 p.m.	Panel II: ISCO feasibility study; oxidant selection and delivery approaches; lab and field tests Chairs: Michelle Crimi and Ben Petri Panelists: Keith Henn, George Hoag, Scott Huling, Rick Watts
2:00 p.m.	Panel III: ISCO system design and modeling tools Chairs: Tom Simpkin and Tissa Illangasekare Panelists: Dick Brown, Wilson Clayton, Matt Dingens, Dirk Pohlman
3:00 p.m.	*Break*
3:15 p.m.	Panel IV: ISCO system construction, startup, monitoring Chairs: Tom Palaia and Mike Singletary Panelists: Dan Bryant, John Haselow, Bob Luhrs, Bob Norris
4:15 p.m.	Open discussion and recap; set up break out sessions for Day 2, present site scenarios and homework "assignment" ~ Michelle Crimi and Ben Petri
5:00 p.m.	*Adjourn Day 1*
5:30 p.m.	*Reception (5:30 p.m.) and dinner (6:30 p.m.) at the Golden Hotel, Fall River Room*
Thursday, March 8, 2007	
08:00 a.m.	*Continental breakfast, turn in "assignment" re: site scenarios*
08:30 a.m.	Group discussion – Site scenarios and ISCO screening based on "assignment" questions Moderators: Michelle Crimi and Ben Petri
10:00 a.m.	*Break*
10:15 a.m.	Break out session ~ Workshop participants meet in 3 groups to discuss: 1. ISCO delivery and treatability; 2: ISCO design and modeling; and 3: ISCO construction, operation, monitoring
12:00 p.m.	*Lunch provided*
1:00 p.m.	Break out sessions continued
3:00 p.m.	Report out on the scenario responses and from the breakout sessions (15 min. each) ~ Session chairs or volunteers
4:00 p.m.	Open discussion and synthesis – areas of clear agreements and disagreements Moderator: Michelle Crimi
4:45 p.m.	Concluding remarks ~ Bob Siegrist and Michelle Crimi
5:00 p.m.	*Adjourn Workshop*

Table 1.2. List of participants at the ISCO Technology Practices Workshop.

Attendee	Affiliation	Location
Atkinson, Jon	HQ Air Force Center for Environmental Excellence	Brooks City - Base, TX
Block, Philip	FMC Corporation	Philadelphia, PA
Borchert, Susanne	CH2M HILL, Inc.	Freeport, IL
Borden, Robert	North Carolina State University	Raleigh, NC
Brown, Dick	Environmental Resource Management	Ewing, NJ
Bryant, Dan	Geo-Cleanse International, Inc.	Kenilworth, NJ
Clayton, Wilson	Aquifer Solutions, Inc.	Evergreen, CO
Cooper, Eliot	Vironex	Golden, CO
Crimi, Michelle	East Tennessee State University	Johnson City, TN
Dingens, Matthew	Global Marketing Manager, Carus Corporation	Peru, IL
Favara, Paul	CH2M HILL, Inc.	Gainesville, FL
Ficklen, Don	HQ Air Force Center for Environmental Excellence	Brooks City - Base, TX
Haselow, John	Redox Tech, LLC	Cary, NC
Haskins, Stan	In-Situ Oxidative Technologies, Inc.	Arvada, CO
Heiderscheidt, Jeff	Air Force Institute of Technology	Wright-Patterson AFB, OH
Henn, Keith	Tetra Tech NUS, Inc.	Pittsburg, PA
Hoag, George	VeruTEK Technologies, Inc.	Glastonbury, CT
Huling, Scott	U.S. EPA	Ada, OK
Illangasekare, Tissa	Colorado School of Mines	Golden, CO
Kelley, Bob	Regenesis	Plainfield, IL
Kerfoot, William	Kerfoot Technologies, Inc.	Mashpee, MA
Ko, Saebom	East Tennessee State Univ.	Johnson City, TN
Krembs, Fritz	Colorado School of Mines	Golden, CO
Lowe, Kathryn	Colorado School of Mines	Golden, CO
Luhrs, Robert	Remedial Programs, Raytheon Company	Waltham, MA
McGuire, Travis	Env. Sci., Groundwater Services, Inc.	Houston, TX
Munakata Marr, Junko	Colorado School of Mines	Golden, CO
Norris, Bob	Brown and Caldwell	Longmont, CO
Osgerby, Ian	U.S. Army Corps of Engineers	Concord, MA
Palaia, Tom	CH2M HILL, Inc.	Englewood, CO

Table 1.2 (cont.). List of participants at the ISCO Technology Practices Workshop.

Attendee	Affiliation	Location
Petri, Ben	Colorado School of Mines	Golden, CO
Pohlman, Dirk	Shaw Env. & Infrastructure, Inc.	Knoxville, TN
Pound, Michael	Naval Facilities Engineering Command Southwest Div.	San Diego, CA
Ruiz, Nancy	Naval Facilities Engineering Service Center	Port Hueneme, CA
Siegrist, Bob	Colorado School of Mines	Golden, CO
Simpkin, Tom	CH2M HILL, Inc.	Englewood, CO
Singletary, Mike	Naval Facilities Engineering Command Southern Div.	North Charleston, SC
Sorenson, Kent	CDM	Denver, CO
Unger, Marvin	SERDP/ESTCP Support Office (HydroGeoLogic)	Phoenix, AZ
Urynowicz, Mike	University of Wyoming	Laramie, WY
Watts, Rick	Washington State University	Pullman, WA
Wren, Abigail	CH2M HILL, Inc.	Englewood, CO
Young Cha, Ki	North Carolina State University	Raleigh, NC

During most of Day 2, a breakout session occurred with three breakout groups working concurrently. These three groups were focused on the following topics:

Breakout Group 1: ISCO delivery and treatability,
Breakout Group 2: ISCO design and modeling, and
Breakout Group 3: ISCO construction, operation, monitoring.

Workshop participants were assigned to one of the three breakout groups. The assignments were made to achieve some balance in background, perspective, and expertise appropriate for the topical area of each of the sessions.

During the latter portion of the afternoon of Day 2, informal presentations were made to the Workshop participants including (1) the preliminary results of the site scenario homework assignment and (2) a synopsis of the discussions held in each breakout sessions. The Workshop ended with a brief open discussion period before adjourning.

1.3. Workshop Outcome

This Workshop has helped define the frequently asked questions and other technical issues that remedial project managers (RPMs) and others encounter when considering the selection, design, and implementation of ISCO for a particular site. It has also helped identify the inherent limitations of ISCO for certain types of sites and performance goals as well as identify sites and goals that are particularly well suited to one or more ISCO approaches. Moreover, it provided some insight into best practices that will help ensure that success is achieved while performance deficiencies and failures are avoided.

This document presents a summary of the Workshop including a list of attendees, the final agenda, highlights of presentations, panel discussions, site scenario assignment, and breakout session reports.

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2. Summary of Workshop Proceedings

2.1. Introduction

This section presents a summary of the Workshop discussions that occurred during the opening session presentations, the four panel sessions, three breakout group meetings, the site scenario assignment, and the plenary group discussions. Consistent with the chronological order of events over the 2-day period of the Workshop, the order of information presented is divided into the following major sections:

2.2. Opening Session and Presentations,
2.3. Panel Sessions I to IV,
2.4. Site Scenarios and Homework Assignment,
2.5. Breakout Sessions 1 to 3,
2.6. Plenary Discussions, and
2.7. Closing Remarks and Adjournment.

The summary presented in this section was assembled from detailed notes taken by members of the ER-0623 project team throughout the various activities and events that took place at the Workshop. These notes included candid remarks made during the plenary discussions, panel sessions and breakout session, and the site scenario exercise, all of which enabled development of a clearer picture of the technology practices being utilized for ISCO.

2.2. Opening Session and Presentations

2.2.1 Welcome and Introductions

At the opening of the Workshop, Dr. Bob Siegrist (CSM) made a short presentation and outlined the purpose and scope of the Workshop (Appendix A.1). The goal of the ISCO Technology Practices Workshop was to provide a forum for discussion among a cross-section of stakeholders involved in ISCO remediation, and to facilitate discussion in such a way that it would result in the sharing of information in a constructive way. The discussion was intended to determine how best to evaluate and use ISCO in a certain situation, not to promote one way of doing things. The Workshop was convened to further the ongoing ESTCP project ER-0623 titled "In Situ Chemical Oxidation for Remediation of Ground Water: Technology Practices Manual" which will be introduced in more detail below. The Workshop, and project as a whole, focused on the use of ISCO to remediate ground water. This includes sites with or without non-aqueous phase liquids (NAPLs) and source zone and dissolved plume remediation. The Workshop was intended to engage different stakeholders to exchange ideas on site-specific ISCO design, to identify inherent limitations and best practices.

Following the brief opening remarks by Dr. Siegrist, each of the 43 participants at the Workshop introduced themselves and provided a brief statement of their background, expertise, and interest in ISCO.

2.2.2. Background and Status of the DOD ISCO Initiative

Dr. Marvin Unger of HydroGeoLogic, who was representing the SERDP/ESTCP Program Office at the Workshop, gave a short presentation on the background and status of the SERDP/ESTCP ISCO Initiative (Appendix A.2). He stated that the goal of this ISCO Initiative is to produce a product that is greater than the sum of its parts. To do so, SERDP/ESTCP solicits feedback from the USEPA, DOE, and DOD to develop Statement of Needs that are used to select future ISCO projects, and also encourages the interaction of project teams who are engaged in research in similar areas. SERDP/ESTCP evaluates chlorinated solvent remediation technologies in two general categories: well established and developing. Developing technologies that show promise are researched to encourage their development and proper use at DOD/DOE sites. In 2002, the Chlorinated Solvent Workshop identified ISCO as a promising technology, and this technology is currently considered to be in the demonstration and validation phase by SERDP/ESTCP.

Dr. Unger went on to explain that the SERDP/ESTCP ISCO Initiative began with three projects: ER-1288, "Improved Understanding of Fenton-like Reactions for In Situ Remediation of Contaminated Ground Water Including Treatment of Sorbed Contaminants and Destruction of DNAPLs", Dr. Richard Watts; ER-1289, "Improved Understanding of In Situ Chemical Oxidation (ISCO)", Dr. Eric Hood; and ER-1290, "Reaction and Transport Processes Controlling In Situ Chemical Oxidation of DNAPLs", Dr. Robert Siegrist. These three projects were reviewed and guided in part by a Technical Advisory Committee (TAC) comprised of Drs. Dick Brown, Bob Norris, Ian Osgerby, and Mr. Mike Marley.

The ISCO Initiative provides support to practitioners by addressing the following areas: the need for standard operating procedures and guidance documents; the remediation of emerging contaminants; and group response to ASTM during its development of a proposed ASTM natural oxidant demand (NOD) test procedure. The ISCO Initiative has transitioned from the original three projects described above to over 10 currently funded projects being conducted at both the laboratory and field scales.

The overall goal of the ISCO Initiative is technology transfer to those who are at the "front lines" in environmental remediation within the DOD/DOE complex. This vital technology transfer can include cost and performance reports, frequently asked question (FAQ) guides, and guidance documents. The current ESTCP project (ER-0623), of which this workshop is a part, will wrap all of the above together and produce comprehensive guidance and decision support. SERDP/ESTCP wants to be the organization that environmental professionals go to when they want to learn about ISCO, and the Technology Practices Manual produced by this project (ER-0623) will be the vehicle through which they do that.

2.2.3. Overview of ISCO

"Site-Specific ISCO Engineering: Who Needs It?" Dr. Dick Brown of ERM made a presentation that was focused on why it is not acceptable to simply dump oxidants into the ground, and then add more if the first treatment doesn't work (Appendix A.3). Dr. Brown presented an example to illustrate why site-specific engineering is needed to properly implement ISCO. He went on to state that, fundamentally, the success of ISCO depends on having enough of the *correct* oxidant in contact with the contaminants of concern (COCs) for a long enough period of time. Enough oxidant does not simply include enough to degrade the COCs, but must also account for NOD, reduced metals, and oxidant decomposition. These three factors are all oxidant type and site-specific. Distribution occurs at four scales, ranging from smallest to largest: the DNAPL scale, the lithological scale (to account for heterogeneities), the plume scale, and the site scale. All of these must be addressed in ISCO design.

The macro scale distribution of contaminants can take on one of two modes, depending on the rates of oxidant decomposition/consumption and travel time through the treatment area. Circulation approaches, such as well injections, galleries, trenches, and gravity feed systems, are used when the half-life of the oxidant is greater than the required travel time. Emplacement approaches, such as soil mixing, pressure injection, direct push injection, hydraulic/pneumatic fracturing, and air sparging, are used when the oxidant's half-life is less than the required travel time. The question remains as to the optimum method to enhance distribution of oxidant in the subsurface at different scales.

Two alternative analogies to compare to ISCO are a race to the finish or a demolition derby. As practitioners, we want to make sure that our design is a sure win, and to do so we must apply the correct oxidant through the proper delivery methods. In other words, the oxidant dosage, delivery, and activation are all key to the success of an ISCO remediation.

Dr. Brown stated that we've learned a great deal from the three initial projects completed as part of the ISCO Initiative. Dr. Rick Watts' project (ER-1288) showed that there are more reactive species involved in catalyzed hydrogen peroxide (CHP) reactions than the hydroxyl radical alone (OH•), and that what is really happening is considerably different than the reactions that HJH Fenton described over 100 years ago. Dr. Bob Siegrist's project (ER-1290) demonstrated that the transport and kinetics of oxidation using potassium permanganate ($KMnO_4$) are not nearly so simple as many people think, and that lots of engineering is required to properly account for these issues. Dr. Eric Hood's project (ER-1289) developed a permanganate chemical oxidant demand (COD) test and a two-hour site-screening tool to be used to evaluate oxidant demand.

Following the presentation, there were several comments and questions from the audience. One Workshop participant noted that the description of a COD test to estimate NOD will be released in a journal article and a final SERDP report within the next year. Another commented that field scale preconditioning is also a valuable tool that can be used to remove NOD, and we must also be cautious not to assume that the laboratory bench scale in which samples are completely mixed is completely applicable at the field scale. Another participant noted that his company has used the injection of air during site pre-conditioning to oxidize reduced iron. Another commented that as an example of previous underperformance / under design of ISCO remediation, a 1999 ESTCP report titled "Technology Status Review: In Situ Oxidation" evaluated approximately 50 field sites at which ISCO was applied, and saw significant rebound at many of them. These results were likely caused by an inadequately low oxidant dosage or use of the wrong delivery approach.

2.2.4. Overview of Two Recently Completed DOD ISCO Projects

"Improved Understanding of Fenton-like Reactions for In Situ Remediation of Contaminated Ground Water Including Treatment of Sorbed Contaminants and Destruction of DNAPLs." Dr. Rick Watts of Washington State University (WSU) made a presentation highlighting the goal, methods and findings of his project focused on ISCO using Fenton's chemistry (ER-1288). The overall goal of this project was to better understand catalyzed hydrogen peroxide ISCO reaction chemistry. As a result of this project, the terminology "Fenton's Chemistry/Reaction" has been changed to Catalyzed Hydrogen Peroxide Propagation Reactions (CHP). This change reflects the fact that there are more reactive species and pathways than the generation of hydroxyl radicals by reacting hydrogen peroxide (H_2O_2) with an iron catalyst in strict Fenton's chemistry.

To accomplish the project's goals, six tasks were performed as described below. Tasks 1 and 2 determined the rate of hydrogen peroxide decomposition in the subsurface, and the dependence of the rate upon subsurface mineralogy. Hydrogen peroxide decomposed fastest in the presence of manganese oxides, and relatively slower in the presence of iron oxides. However, given that iron oxides are generally more abundant in the subsurface, both these oxide species have an important impact on hydrogen peroxide decomposition. The presence of manganese oxides controls which radicals form, especially the super oxide anion, which is a weak nucleophile reductant and relatively more stable radical, which can last up to seconds. There was a low correlation between the rate of hydrogen peroxide decomposition and the both the soil surface area and NOD.

Task 3 evaluated the degradation pathways of several contaminants, included carbon tetrachloride and tetrachloroethene (PCE). The former does not react with hydroxyl radicals, but does degrade in CHP reactions due to its reactivity with superoxide anions. This reaction mechanism highlights the importance of superoxide in the degradation of contaminants. It was also found that the presence of excess, free hydrogen peroxide in solution increases the reactivity of superoxide radicals by acting as an aprotic solvent.

Tasks 4 and 5 examined the reactions between CHP and sorbed and DNAPL phase contaminants. Mass transfer from these two phases was increased as reactions with aqueous phase COCs maintained a negligible concentration in the aqueous phase, increasing the concentration gradient. The superoxide radical was found to have natural surfactant capabilities, and DNAPL was destroyed faster than could be accounted for due to increased concentration gradients alone. Specifically carbon tetrachloride and PCE were destroyed faster in the presence of superoxide radials.

Task 6 focused on the enhanced delivery of hydrogen peroxide. The destruction chemistry of CHP with many contaminants is known, yet delivery of the CHP to the contaminants in the subsurface remains an issue with respect to successful ISCO applications using CHP. To achieve more successful in situ treatment through providing better contact with COCs and increasing the transport of CHP, there is a need to understand how soil minerals can initiate free radical reactions and what stabilizers can slow down the initiation reactions with hydrogen peroxide. Without the presence of an initiator, hydrogen peroxide will slowly degrade over a period of months or years depending on the subsurface mineralogy. Naturally occurring mineral iron increases the decomposition rate, and soluble iron increases it relatively more. When considering stabilizers, the project team examined citrate, phytate and malonate. All three of these compounds slowed down the reaction of CHP in a slurry with minerals (goethite, and two natural soils from Maine and California) yet did not compromise radical formation.

Column studies were performed in Task 6 using 1-m long columns filled with manganese and iron coated silica sand. The experimental design consisted of water flow, a pulse injection of CHP, followed by water flow. Without a stabilizer, hydrogen peroxide traveled approximately 10 cm into the column. The addition of phytate allowed the hydrogen peroxide to travel through the entire column. The results of this study are currently in press for journal publication. These results will be applied at the field scale soon under an ongoing SERDP project. Both the stabilizer and hydrogen peroxide can be added together.

Following the presentation by Dr. Watts, there were several comments and questions from the audience. One participant commented that at a site in Jacksonville, FL with a high natural iron content, an initial injection of Fenton's reagent did not achieve the desired result. However, in a second application using sodium citrate at a concentration of 500 ppm and a 5% hydrogen peroxide solution, much better contaminant destruction was achieved. However, another participant remarked that in another similar application into a formation with a lower natural iron content the results achieved were not as good as at the Jacksonville site. A different participant commented that some compounds, such as MTBE, will secondarily release peroxides during degradation, and this may be an important reaction mechanism to consider. Yet another participant questioned whether the difference in the observed results mentioned above might have been due to a differing fraction of organic carbon (f_{oc}) between the two sites. In response, the participant who commented that the sodium citrate was beneficial at the Jacksonville site acknowledged that citrate did not work as well as a stabilizer at another site that had a high f_{oc}. These remarks led another participant to comment that these observations raise the question of how does one make the decision to use citrate, and at what concentration.

"Reaction and Transport Processes Controlling In Situ Chemical Oxidation of DNAPLs." Dr. Bob Siegrist of CSM made a presentation highlighting the goal, methods and results of project ER-1290 (Appendix A.5). He noted that this recently completed SERDP project examined the mass transfer rates from TCE and tetrachloroethylene (PCE) dense nonaqueous phase liquids (DNAPL) in various experimental situations, the effect of porous media of varying characteristics, the potential to couple ISCO with bioremediation, surfactant/cosolvent flushing and partitioning interwell tracer tests (PITTs), and the influence of DNAPL architecture on degradation rates during ISCO. The overall theme behind this work was to examine the engineering issues at the macro and micro scales rather than focus on the contaminant degradation chemistry.

The experimental systems were designed to evaluate the injection of ISCO reagents through an injection well, where there are relatively higher oxidant concentrations and transport velocities closer to the well and relatively lower concentrations and velocities farther from the well. The oxidants used in experiments were CHP and permanganate. Both advective and diffusive transport mechanisms were considered. The COCs used were TCE and PCE. Coupling with bioremediation, surfactants/cosolvents, and PITTs were considered. The project included a literature review, batch studies, column studies, and 2D tanks of varying sizes. The full copy of the project report is available at the SERDP website.

The project found that oxidation of DNAPL in an aqueous system can be reliably and predictably achieved. ISCO can be used to enhance the rate of mass transfer from the DNAPL phase to the aqueous phase. The relative rates of reaction between oxidant and COCs and the DNAPL dissolution rates are important factors. Both the oxidant delivery velocity and concentration are also important factors in the results achieved. Specifically, high delivery velocity at a lower oxidant concentration results in the faster dissolution of DNAPL relative to lower velocity / higher concentration systems. If the rate of dissolution is greater than the rate of oxidation, the reaction occurs in a "reaction cloud" that extends down gradient of the DNAPL source zone. Conversely, if the rate of dissolution is less than the rate of reaction, the reaction occurs at the DNAPL interface, which can result in deposition of solid reaction byproducts in this area which in turn slow further mass transfer from the DNAPL to the aqueous phase. The former "reaction cloud" scenario is more likely to occur during delivery at higher velocities and lower oxidant concentrations. Regarding DNAPL architecture, pools are more problematic and the results of ISCO treatment more variable than ganglia and residual phase DNAPL. The project results also showed that ISCO can enhance the overall rate of biological degradation that occurs following ISCO treatment.

The experiments carried out in this project showed that near 100% reductions in source area concentrations are not necessary to reduce plume strength. The change in plume strength is a function of source zone architecture, biological mechanisms and other factors. The project also identified existing knowledge gaps relating to ISCO implementation, including the use of developing oxidants and quantitative means to evaluate when and how ISCO should be coupled with other technologies.

Following the presentation there were several questions and comments from the audience. In response to a comment by one participant concerned with rebound, Siegrist responded that rebound was considered but not as a primary focus. Changes in the subsurface, for example changes in f_{oc}, as a result of ISCO may alter the partitioning behavior of contaminants, further confounding the evaluation of whether or not rebound has occurred at a site following ISCO remediation. Research is ongoing through another SERDP project to evaluate and quantify the changes in f_{oc} , which result from ISCO treatment, and the overall impact of these changes on partitioning behavior (e.g., ER-1490). In response to a question by another participant, Siegrist noted that the use of tank studies to evaluate process performance for DNAPL source zone depletion was not a specific goal of this SERDP project. Process performance was evaluated as part of the SERDP/ESTCP source zone initiative (e.g., ER-1294). In responding to a comment by a different participant regarding the definition of DNAPL, Siegrist noted that DNAPL is an organic chemical present in its own liquid phase that is denser than water; it will not ever have a more precise definition than that in terms of concentrations that can be measured in the subsurface, such as a given percent in solution relative to the aqueous solubility or a certain soil concentration. Along these same lines, Marvin Unger stated that during a study that involved extensive sampling at 25 sites, even though there was good evidence based on contaminant concentration data that DNAPL was present in the subsurface, of the 25 sites, the investigators were only able to find DNAPL at four of them.

2.2.5. Overview of ESTCP Project ER-0623

Dr. Bob Siegrist gave a short presentation highlighting the purpose, scope, and approach for ESTCP project ER-0623 (Appendix A.6). He stated that the ultimate goal of the project of which this workshop is a part is to produce a Technology Practices Manual (TPM) for the use of ISCO to remediate ground water. The project is being performed by the Colorado School of Mines, Eastern Tennessee State University, CH2M HILL, and the U.S. Navy. The purpose of the TPM is to improve the standard of practice and to achieve more predictable results when using ISCO to remediate ground water. This project began in the summer of 2006 and will be completed in early 2009.

This project will produce an engineering guidance document and tools to be used by practitioners, remedial project managers (RPMs) and site owners to evaluate whether ISCO is an appropriate remedial technology at their site, and if so, how best to implement it. The technical approach used to create this document will involve the following tasks: 1) design a logical and science-based protocol to be used to evaluate and design an ISCO remediation based upon site specific information; 2) test the protocol against existing DOD case studies in which ISCO was used to remediate ground water; 3) refine the protocol based on testing results, and 4) disseminate the TPM, along with a stand alone FAQ guide.

The Workshop is a part of Task 1, along with a comprehensive literature review, creation of a draft ISCO Integrated Protocol (IIP), and collection and examination of case studies. The IIP will have multiple tiers, the first tier being the overall process, the second tier being a series of decision diagrams that pertain to each specific step of the overall process, and the third tier being the specific details of what testing and decision processes are involved at each step of the second tier decision diagrams.

The design and population of a database of ISCO case studies was initiated in the summer of 2006 and provides insights into past and present technology practices being employed for ISCO. While the data collection effort is ongoing, over 150 case studies have been identified as of January 2007, though the level of detail varies greatly among these case studies. Some preliminary results of the analysis of technology practices as revealed through this database are: 1) of the case studies identified so far, more have included permanganate and CHP compared to ozone (O_3) and sodium persulfate ($Na_2S_2O_8$), 2) ISCO is being used primarily for chloroethenes, 3) risk-based and percent reduction goals appear to be more likely to be met than MCL-based goals, 4) a positive correlation between use of bench and pilot scale testing and achieving the desired goal has not yet been clearly identified, and 5) ISCO has been coupled with several technologies, including bioremediation, pump and treat, excavation, and surfactant flushing

In closing, Dr. Siegrist stressed the importance of the Workshop stating that it was the ER-0623 project team's desire to avoid creating the TPM in a vacuum. The Workshop was viewed as an opportunity for a cross section of environmental professionals to share their views with the goal of advancing ISCO as a remediation technology.

At the close of the above opening presentations, several comments were made by the Workshop participants. One participant posed the question of how much money should be spent on investigation prior to ISCO remediation. Another noted that in light of the increasing use of fixed-price contracting, we are often forced to cut back on the amount of investigation we can perform within the amount of money we've budgeted for the project. For this reason, we often go into a project not having enough information. One participant went on to share an experience. He stated that a telling example regarding characterization is a site at which over 1000 borings had been executed and ISCO was used to remediate a smaller portion of the site. Based on the extensive sampling data, total mass calculations were completed using three different techniques. Based on the results of the ISCO implementation, it was concluded that the contaminant mass was underestimated using all three of the techniques. Related to this, a participant added that "when we collect data" is as important as "if we collect data and how much we collect"; it is important to collect the data at the RFI stage.

2.3. Panel Sessions

During Day 1 of the Workshop, there were four panel sessions, each approximately 1-hr long. Prior to the start of the Workshop, panel co-chairs were assigned and some of the confirmed Workshop participants were invited to serve on a panel. The chairs for each panel worked with their respective panel participants to develop a plan for identifying and addressing key questions in the topical area to be covered by their panel. As a result, the four panels operated somewhat differently in how they addressed the panel topics, including the focus of the panel, the remarks made by panel members, and the nature and extent of interactions with the Workshop participants in the audience. The topics addressed by each panel and the members of each panel are given below. Highlights of the panel discussions, including remarks made by panel members and Workshop participants, are summarized in Table 2.1.

Panel I: ISCO Screening and Selection

Co-chairs: Junko Munakata Marr (CSM) and Mike Singletary (NFECSD)

Members: Paul Favara (CH2M HILL), Michael Pound (NFECSWD), Kent Sorenson (CDM), and Mike Urynowicz (Univ. Wyoming)

This panel was charged with addressing three of the frequently asked questions that the ER-0623 team had identified prior to the workshop: 1) What are critical parameters for screening and design? 2) What are site-specific ISCO limitations, and 3) Feasibility study and conceptual designs for combined (Coupled) ISCO remedies?

Panel II: ISCO Feasibility Study; Oxidant Selection and Delivery Approaches; Laboratory and Field Testing

Co-chairs: Michelle Crimi (ETSU) and Ben Petri (CSM)

Members: Keith Henn (Tetra Tech NUS), George Hoag (VeruTek), Scott Huling (USEPA), and Rick Watts (WSU)

Dr. Crimi opened this session by explaining that Panel II was focused on the decision-making concerned with the selection and delivery of oxidants and ISCO treatability studies, respectively. The panel members were charged with several questions regarding these issues, and asked to consider and explain the process through which they would answer these questions: 1) What is the process and the criteria for selection of an oxidant and activation method? 2) How do you determine the optimum oxidant delivery technique at a site? 3) What criteria are used to determine when pilot scale testing is needed?

Panel III: ISCO System Design and Modeling Tools

Co-chairs: Tom Simpkin (CH2M HILL) and Tissa Illangasekare (CSM)

Members: Dick Brown (ERM), Wilson Clayton (Aquifer Solutions), Matt Dingens (Carus Corporation), and Dirk Pohlman (Shaw)

Dr. Simpkin began by explaining that this panel was charged with addressing the critical components of ISCO design, including: oxidant volume and mass; well spacing; injection flow rate and duration; number of injection events, and well design and location. Members of Panel III addressed a series of questions, sharing their views on the topic. Workshop participants in the audience were also encouraged to share their views.

Panel IV: ISCO Implementation and Performance Monitoring

Co-chairs: Tom Palaia (CH2M HILL) and Mike Singletary (NFECSD)

Members: Dan Bryant (Geo-Cleanse), John Haselow (Redox Tech), Bob Luhrs (Raytheon), and Bob Norris (Brown and Caldwell)

Panel IV was focused on implementation and monitoring and the session began by each of the panelists providing some remarks concerning their views on this topic. Then the participants in the Workshop were encouraged to share their views.

Table 2.1. Highlights of the remarks made during the four panel discussions.

Panel	Summary of general consensus expressed during the Workshop panels
I: ISCO Screening and Selection	* Selection of ISCO depends on a good site conceptual model – this is particularly important for pay-for-performance or performance-based contracts. * Confidence in the location of COCs and the fate and transport of oxidants in the subsurface, as estimated based on characterization data, is of particular importance for ISCO. * A critical parameter for ISCO is an understanding of the natural oxidant demand (NOD) and the oxidant persistence over time during transport in the subsurface. * Methods to measure and interpret representative data regarding oxidant NOD and persistence for a given site have been have been highly varied; new methods are under development. * Reducing conditions (e.g., low ORP) are important to consider in ISCO design and its viability relative to other treatment technologies (e.g., ERD); reducing conditions alone do not rule out ISCO from consideration at a site. * Oxidant dissipation (e.g., by NOD) is generally more of a factor that may adversely impact ISCO implementation than just reducing conditions. * Use of ISCO does not have sustained adverse impacts on aerobic and anaerobic biological mechanisms; after ISCO there are increases in biomass and subsequent biodiversity that are equivalent to baseline levels.
II: ISCO Feasibility Study; Oxidant Selection and Delivery Approaches; Laboratory and Field Testing	* The first step in the oxidant selection process is to consider what oxidants are able to degrade the contaminants present at the site; the literature and personal experience can provide information regarding the amenability of certain oxidants. Treatability studies are also a valuable tool to confirm the results reported in the literature or to examine contaminants for which the literature does not provide guidance. * The presence of relatively more insoluble organics (e.g., high K_{ow}) and presence of NAPL can limit the choice of oxidants and/or hinder performance. * The geology of the site may constrain what delivery approaches are viable, which may in turn limit the oxidants that may be used at a site. * Subsurface permeability is a constraint, but not one that cannot be overcome. Low permeability is more of an issue for faster acting oxidants. With the use of soil mixing technologies, there is almost no permeability limit below which ISCO cannot be applied. * Bench scale testing has the advantages that it can demonstrate the ability of an oxidant to degrade the site's COCs, it can estimate the NOD, reaction byproducts, metals mobilization, and it can help refine the design parameters which can be used in estimating full scale remediation costs and the overall feasibility of the ISCO remediation. Disadvantages to conducting bench-scale testing include the costs associated with the tests and the difficulty of extrapolating the results to the field scale. * Advantages to pilot scale testing beyond those associated with bench scale testing include the ability to: 1) monitor distribution and transport of oxidants, 2) evaluate contaminant rebound, 3) aid refinement of system design and performance monitoring plans, and 4) permit trial and error modifications to the system design. Drawbacks of pilot testing include the time and cost associated with it. * ISCO design should include the consideration of coupling with other technologies (e.g., bioremediation) up front, and during bench scale testing rather than just at the end of the process. * It can be difficult to convince clients to pay for a treatability study. * Regulatory restrictions can impact the design of ISCO systems; e.g., restrict the maximum concentration of oxidants that may be injected at a site.

Table 2.1 (cont.). Highlights of the remarks made during the four panel discussions.

Panel	Summary of general consensus expressed during the Workshop panels
III: ISCO System Design and Modeling Tools	* Critical components of ISCO design, include: oxidant volume and mass, well or probe spacing, injection flow rate and duration, number of injection events, and well or probe design and location. * There are many uncertainties in the subsurface that impact ISCO design, including heterogeneity, contaminant architecture, and mass transfer. * The ability to distribute the oxidant into the subsurface is a key determinant of the total mass needed. It is difficult to achieve complete contact in the treatment area. A lot more oxidant is necessary when mixing injection methods (e.g., oxidant recirculation methods) are used. * Safety factors must estimate the percentage of the subsurface that will be contacted during the injection process. It is also important not to overdose the subsurface, which can create potential problems as well (e.g., metals accumulation and oxidant persisting too long). * A consideration when designing the volume and concentration of an ISCO system is that volume impacts time, which in turn impacts the cost of the remediation. For this reason, design cannot be based upon injecting as much volume as possible, but injecting too little volume is a common reason for failure of ISCO designs. * The number of pore volumes is not a precise design parameter, but is a useful tool that can be used to perform a retrospective analysis as a check of the remediation design. * Pulsed injections can increase the efficiency of the oxidation process, requiring a smaller number of pore volumes to be injected; Use of multiple injection events (redosing) also renders the pore volume concept not as relevant. * Redosing must be designed based on data collected between oxidant injection events. * Air or water injection can be used in some situations to increase oxidant distribution, and help overcome the density effect of oxidant solutions.
IV: ISCO Implementation and Performance Monitoring	* Pilot testing may be a key aspect of ISCO full scale system design. * Direct push technologies when used during application allow for much greater ability to modify the program during injection if the performance monitoring shows that the oxidants aren't being delivered to the entire target zone. * Performance monitoring must include those parameters that are necessary during any remediation, and also certain ISCO-specific parameters (e.g., oxidant concentrations, products of oxidation reactions). * Chemicals can be used to quench the oxidation reaction during sampling organics in the presence of oxidants; instead of quenching, extractants (e.g., hexane) can be used to remove organics from samples that contain oxidants. * The MIP is a great tool for subsurface investigation and for performance monitoring as well. Electrical conductivity profiling is also valuable when used to determine subsurface permanganate or persulfate distribution. The use of geoprobe for collection of soil cores can also give good real time results at a relatively low cost. * Rebound is a relatively common occurrence after ISCO and may be caused by several processes: (1) oxidation of organic carbon to which organics were previously sorbed, (2) the continuing dissolution of DNAPL, which was not entirely oxidized during ISCO, and (3) incomplete oxidation of the entire target treatment zone, such as back-diffusion from low permeability strata. * Another aspect of rebound that is generally overlooked is the benefit that it provides to the SCM; the occurrence of rebound in localized areas provides evidence of where there is untreated NAPL and this information can be used to guide the next injection event.

2.4. Breakout Session

During most of Day 2, there was a breakout session during which each of three breakout groups were focused on different aspects of ISCO site-specific engineering. The focus of each breakout group and the Workshop participants that were involved in each are presented below. During the breakout session, the group discussions were guided in part by working versions of the ISCO decision diagrams developed under ESTCP Project ER-0623. These three breakout groups met concurrently in different rooms and notes were taken to document the discussions held. At the end of the day, the Co-chairs for each of the breakout groups reported back on their discussions during a plenary session with all of the Workshop participants present. Highlights of the breakout group discussions are presented in Table 2.2.

Breakout Group1: ISCO Delivery and Treatability

Co-chairs: Michelle Crimi (ETSU) and Junko Munakata Marr (CSM)

Members: Michelle Crimi (ETSU), Ben Petri (CSM), Junko Munakata Marr (CSM), Jon Atkinson (AFCEE), Phil Block (FMC), Paul Favara (CH2M HILL), Don Ficklen (AFCEE), Keith Henn (TetraTech NUS), George Hoag (VeruTEK), Scott Huling (USEPA), Ian Osgerby (USA COE), Kent Sorenson (CDM), Marvin Unger (SERDP/ESTCP), Rick Watts (WSU), Abigail Wren (CH2M HILL)

Breakout Group 2: ISCO Design and Modeling

Co-chairs Tom Simpkin (CH2M HILL) and Tissa Illangasekare (CSM)

Members: Susanne Borchert (CH2M HILL), Bob Borden (NSCU), Dick Brown (ERM), Wilson Clayton (Aquifer Solutions), Matt Dingens (Carus), John Haselow (Redox Tech), Jeff Heiderscheidt (AFIT), Fritz Krembs (CSM), Dirk Pohlman (Shaw), Michael Pound (NFECSWD), Mike Urynowicz (Univ. Wyoming), Ki Young Cha (NCSU), Kathryn Lowe (CSM) and Bob Siegrist (CSM)

Breakout Group 3: ISCO Construction, Startup, Monitoring

Co-chairs Tom Palaia (CH2M HILL) and Mike Singletary (NFECSD)

Members: Dan Bryant (Geo-Cleanse), Eliot Cooper (Vironex), Stan Haskins (ISOTEC), Bob Kelley (Regenesis), Bill Kerfoot (Kerfoot Tech.), Saebom Ko (ETSU), Bob Luhrs (Raytheon), Travis McGuire (Groundwater Services), Bob Norris (Brown and (Caldwell), Nancy Ruiz (NFESC)

2.5. Site Scenario Assignment

At the end of Day 1, six site scenarios were presented as representative contaminated sites, and in some cases very challenging ones, where ISCO might be considered for remediation. These contaminated site scenarios spanned a wide range of hydrogeologic, geochemical and contaminant conditions. A summary of the SCM including the subsurface conditions and contaminant conditions is presented in Table 2.3. A summary of the methods and results of this site scenario exercise are provided in this section, while further details are presented in Appendix B (e.g., in Figures B.1 to B.6, detailed site characterization data are provided for each of the six scenarios).

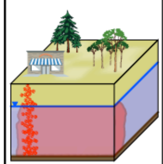
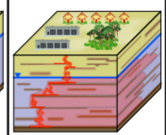
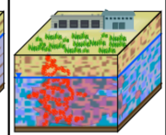
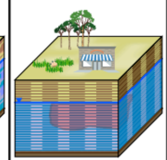
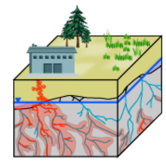
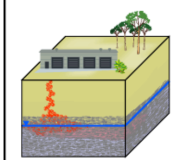
With the characterization data provided, the Workshop participants were given a homework assignment to be completed between the end of Day 1 and beginning of Day 2. This homework assignment included a series of questions for each scenario that encompassed the assessed viability of ISCO at the site, preferred application approaches, and potential for success in achieving different remediation goals given different remediation timeframes and cost constraints (see Figure B.7, Table B.2). Survey forms allowed respondents to give a response with respect to the ability of ISCO to achieve different remediation goals (see Table B.2). The response forms were kept anonymous but respondents were asked several questions to aid in qualifying their professional backgrounds and experience.

Table 2.2. Summary of the discussions and key points made in the three breakout groups as reported back to the Workshop participants by the group co-chairs during the plenary session on Day 2.[1]

Group	Highlights of discussions and points made in each of the three breakout groups
1: ISCO Delivery and Treatability	* Consensus was reached regarding the approach to ISCO screening at a given site. The decision diagram in the final TPM will be updated to reflect this discussion. * It is important to consider coupling early on in the process rather than only if ISCO alone is deemed not to be appropriate at a site. * There is a need to have an "escape route" through which to reject the use of ISCO at more stages of the decision process than were given in the version of the decision diagrams circulated at the workshop. * There was considerable discussion on coupling of ISCO with other technologies. The breakout group tried to call out case studies that show the utility of coupling. * The overall goal of treatability studies is to reduce the uncertainty of the results that ISCO can achieve at a site. * Instead of using a prescribed decision framework at a prescribed point in the process, it was considered to be more useful to have steps throughout the process in which laboratory tools/testing are used to reduce the uncertainty at that point as needed. * In rare cases treatability studies have not been used. The omission of treatability studies may be acceptable in certain situations. However, this should be the exception rather than the standard of practice. * There was discussion of tying the treatabilty study approach into the full scale implementation approach. This may be conceptually desirable and could provide insight into up-scaling effects as well.
2: ISCO Design and Modeling	* A repeat loop should be added to the design and modeling decision diagrams because of the frequent need for repeated injection events at a site. * The Observational Approach is a useful tool to adapt to ISCO remediation. This approach allows for the continual modification and refinement of the SCM and remediation technology application and avoids being constrained to a single design. * A new spreadsheet-based model will be developed for ISCO design. While such a model may not be perfect, it will be inherently useful because it will be an improvement upon what is currently available and in use.
3: ISCO Construction, Startup, Monitoring	* The decision diagrams as presented to the group were okay but generally too complicated * The final decision diagrams need to be interactive with respect how users employ them. * The distinction between process monitoring and performance monitoring must be made clear, as these are two different facets of the fieldwork with different functions. * The use of performance-based specifications (e.g., reduction in contaminant levels) (versus those that specify means and materials) for contracting requires a well-defined SCM. * There is a need to include vendor input into preliminary and final design. * Rebound of contaminant concentrations is a likely occurrence. Because of this fact, an optimization process is required to be implemented between each subsequent delivery event. Because of the many potential causes of rebound, the breakout group did not agree on any quantitative metric to define whether or not rebound had occurred at a site. However, the time after which contaminant concentrations rebound is an important factor to note as it may indicate why the concentrations rebounded (e.g. desorption vs inflow from upgradient). * Regarding process optimization, there are four options: 1) additional ISCO injection events, 2) refinement of SCM and ISCO practices, 3) stop ISCO and proceed to MNA, or 4) ???

[1] Draft ISCO decision diagrams were prepared under ER-0623 and included in the Workshop notebook.

Table 2.3. Summary details concerning site characteristics at each of six site scenarios.[1]

Scenario parameter	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	Scenario 6
Site conceptual model						
Hydrogeology						
Morphology	Unconsolidated homogeneous	Unconsolidated heterogenous	Unconsolidated heterogeneous	Unconsolidated homogeneous	Fractured igneous rock	Fractured sedimentary rock
Permeability	Permeable	Permeable	Impermeable	Impermeable	Low matrix porosity	High matrix porosity
Velocity (m/day)	1.5	0.1	0.01	0.01	0.01	0.2
Geochemistry						
foc	0.0095	0.003	0.005	0.03	0.0005	0.005
pH	6.5	7.0	7.5	6.5	6.0	8.0
Eh (mV)	150	100	-150	-100	-200	-100
Contaminant conditions						
Primary COCs (phase)	Chloroethene (DNAPL)	Chloroethene (DNAPL)	Chloroethane (DNAPL)	Chloroethene (aqueous)	Chloroethene (DNAPL)	BTEX and MTBE (LNAPL)
Approximate age of spill	2 years	15 years	20 years	15 years	20 years	5 years
Source zone area (m^2)	400	8000	1000	n/a	2000	150
Plume area (m^2)	20000	80000	3000	500	13000	7000
Depth of COCs (m bgs)	7	50	15	6	30	12

All Workshop attendees were presented with the opportunity to fill out surveys; all members of the ESTCP ER-0623 project team (the Workshop hosts) recused themselves from answering the survey. Workshop participants were asked to complete the homework assignment and turn it in at the beginning of Day 2 so that the results could be tabulated and shared with all in attendance. At the beginning of Day 2, the completed site scenario questionnaire forms were turned in by the Workshop participants. Then there was a period of open discussion among the Workshop participants regarding the applicability of an ISCO technology to each of the six contaminated sites. To facilitate this discussion, a question posed to the Workshop participants was: *For each of the six site scenarios that were circulated, would you consider ISCO as a remediation technology at the screening stage?* Following a period of open discussion, a second question was posed to the Workshop participants: *Given the information provided for each scenario, what additional information is needed?* Tables 2.4 and 2.5 contain a summary of the views expressed by the Workshop participants during this plenary discussion regarding each of these questions for the six site scenarios, respectively.

Following the Workshop, a more detailed analysis was completed by CSM to interpret the responses provided on scenario questionnaires submitted by a total of 21 Workshop participants, which represented 75% of the participants exclusive of the ER-0623 project team members present. Analysis of the responses provided one method to reveal the current standard of practice for ISCO. The detailed results of this analysis are presented in Appendix B while a summary of the findings is given below.

- A majority of the professionals queried during this survey indicated that ISCO should at least be considered for each of the six challenging scenarios presented to them, which spanned a range of hydrologic, geologic and contaminant conditions. This implies a large amount of optimism regarding the applicability of ISCO to challenging conditions, provided treatment objectives and ISCO designs are carefully matched to site conditions.
- Based on the specific scenarios developed for this survey, scenarios 1 and 4 were likely to achieve the highest degree of performance as well as meet monetary and timeframe constraints, while scenarios 2 and 5 were likely to achieve the lowest degrees of performance and unlikely to meet goals within monetary or timeframe constraints. Scenarios 3 and 6 were intermediate in terms of performance expectations.

Table 2.4. Views expressed by Workshop participants during open discussion about the selection of ISCO as a viable remediation technology during screening options for each site scenario. [1]

Scenario	Views expressed by Workshop participants during open discussion during the morning of Day 2
Scenario 1 – PCE in homogenous sand (DNAPLs)	Yes, though reductive dechlorination would also be considered.
Scenario 2 – TCE in layered sand with silt (DNAPLs)	Lack of consensus, with more saying no they would not consider ISCO than saying yes they would. Some claimed that the source area was too big to make ISCO a feasible technology, while others said that coupling should be considered at this site. The feasibility of ISCO for this site would depend on the goals of the remediation, with MCLs not being a feasible goal.
Scenario 3 – 1,1,1-TCA and 1,1-DCA in heterogeneous sand and silt (DNAPLs)	Some commented that 1,1-DCA is difficult to oxidize, though others countered that they'd had successful applications of persulfate to oxidize this contaminant at a field site. This site was considered borderline by some, while others suggested soil mixing as a coupled approach. 1,4-dioxane could also become a regulatory driver in this situation. The use of ISCO at this site was also tied to the goals that would be required by the owner. A pilot test would be helpful to analyze the response of ISCO in the subsurface.
Scenario 4 – PCE in clay	Many said that they would not use ISCO due to a lack of risk at this site, citing both the immobility of the contaminant in the clay media and also the presence of the naturally dechlorinating mineral siderite. Given the shallow depth of contamination excavation is also a viable option in this scenario. Based on the shallow depth and clay soil conditions, a mixing technology would likely be required for the use of ISCO.
Scenario 5 – TCE DNAPL in fractured granite	There was an approximately equal mixture of yes and no answers as to whether or not ISCO would be rejected at the screening stage. Those that said that ISCO should be considered cited a lack of better options and the ability of certain oxidants to diffuse into the rock matrix as well as oxidize contamination in the fractures. Those that argued against the use of ISCO at this site mentioned the possible mobilization of DNAPL due to the introduction of oxidants, the irregular fracture pattern, and the possibility the DNAPL is present within dead-end fractures as red flags for the use of ISCO. Additional comments included the possibility of requesting a Technical Impracticability waiver, though no one in the workshop had ever worked on a site that received this waiver. Others stated that an appropriate goal for this site would be to control the source zone of the contamination and protect receptors rather than meet MCLs or treat the entire plume. This site is also a good one to make the case for contaminant flux reduction as a goal of the remediation.
Scenario 6 - BTEX and MTBE in fractured shale (LNAPL)	It was generally agreed that ISCO was an acceptable solution at this site, though the pH of 8 and the contaminants present precluded the use of certain oxidants and activation agents.

[1]Views expressed by Workshop participants during a plenary discussion on the morning of Day 2. Note that most all of the Workshop participants were engaged in the open discussion reflected by the views summarized in Table 2.4, but some may not have turned in fully completed questionnaires that were analyzed following the Workshop (Appendix B).

Table 2.5. Views expressed by Workshop participants during open discussion about the additional information needed to consider ISCO as a viable remediation technology during screening options for each site scenario.[1]

Scenario	Views expressed by Workshop participants concerning the need for additional data to properly consider ISCO during screening
For all sites	* NOD / oxidant persistence. * NAPL saturation. * Geologic cross sections with dissolved and sorbed COC levels. * Boring logs. * Good RI data, including contaminant delineation, soil stratigraphy. * Location of potential receptors. * Changes in contaminant concentrations over time. * Stakeholder goals and time constraints. * Future land use. * Regulatory context (e.g. adversary vs cooperative). * Visit to site to determine access restrictions. * Timing and data quality (ISCO specific).
Scenario 1 – PCE in homogenous sand (DNAPLs)	* Microbial molecular data.
Scenario 2 – TCE in layered sand with silt (DNAPLs)	* Better delineation of vertical extents and definition of contamination. * Soil gas survey due to likely presence of multiple source zones. * Further information on pooled DNAPL. * MIP measurements or subsampled soil cores. * Knowledge of well construction to assess the likelihood of installation through confining layers and NAPL transport through these conduits. * Presence and concentrations of other co-contaminants.
Scenario 3 – 1,1,1-TCA and 1,1-DCA in heterogeneous sand and silt (DNAPLs)	* Presence and concentration of 1,4-dioxane, if any. * MIPs sampling due to heterogeneity. * How source removal excavation was backfilled. * Soil gas survey to identify other source zones, if any. * TPH sampling. * Chemical Oxygen Demand (COD) testing.
Scenario 4 – PCE in clay	* None other than those listed under "For all sites".
Scenario 5 – TCE DNAPL in fractured granite	* Bedrock geophysics. * Pump testing in multiple wells to evaluate fracture flow pathways. * Vertical profile testing. * Timeframe of remediation as ISCO may be too slow to meet needs.
Scenario 6 - BTEX and MTBE in fractured shale (LNAPL)	* Pump testing - Fracture connectivity testing and/or tracer testing? Many said these two were unnecessary because the plume acts as a tracer. * General geochemistry including major ions. * The reactivity between the shale bedrock and potential oxidants. * Soil gas survey. * GW flow measurements.

[1] Summary of views shared by Workshop participants during a plenary discussion that occurred at the beginning of Day 2 of the ISCO Technology Practices Workshop.

- Hydrology is a critical factor that interacts with the likelihood of performance meeting project monetary and timeframe constraints.
    - Hydraulic conductivity, heterogeneity and media type (consolidated vs. unconsolidated) are major parameters that often pose challenges to ISCO performance.
    - In unconsolidated media, higher hydraulic conductivity and lower heterogeneity improve treatability overall.
    - Consolidated media are challenging but possible to treat. Treatment effectiveness is likely enhanced when lower contaminant masses are present, the fractured rock has lower matrix porosity and more regular, well-understood fracture patterns.
- ISCO performance inherently relates to remediation goals. Some remediation goals are likely to require higher degrees of performance than others, and the degree of achievability varies with site-specific conditions.
    - Respondents agreed that the highest degree of performance (e.g., x% concentration reduction) will likely be achieved when ISCO is coupled with monitored natural attenuation (MNA) for a period of time after ISCO application.
    - Mass flux reduction goals were also largely agreed to be achievable with a high degree of confidence.
    - Risk-based clean up goals were the next most achievable goal type.
    - MCLs either at site property lines or site wide were the least achievable type of goal.
- The survey respondent's perspectives on ISCO applicability were found to vary depending on the respondents professional background and experience
    - Consultants were less optimistic than academic, research or vendor backgrounds when anticipating ISCO remediation performance.
    - Consultants were less optimistic than vendors but more optimistic than academic or research backgrounds with respect to meeting monetary or timeframe constraints.
    - There appeared to be interactions between the experience of a respondent and their responses to questions concerned with specific scenarios; that is, responses appeared to be influenced by experience with a particular scenario type.
- The applicability of specific oxidants varies with respect to both hydrology and contaminant specific conditions. Some oxidants were more variable than others in terms of responses from one scenario to the next, but there were no universally applicable oxidants.
- Well and probe injection are by far the most popular delivery methods. Probe injection was more popular than well injection in unconsolidated media. Use of other delivery technologies was driven strongly by site-specific conditions.
- Multiple injections events are a standard feature of ISCO applications.

The findings of the site scenario exercise revealed that while ISCO as a remediation technology might be considered for a wide range of situations, site-specific conditions interact with the performance that can be reasonably expected to be achieved. A strong majority of the Workshop participants responding to the scenario assignment indicated that they would personally consider ISCO for all six of the contaminated site scenarios. However, the degree of anticipated ISCO performance, timeframe necessary and costs varied for all of these scenarios. Furthermore, different types of treatment objectives may be more or less achievable depending on site-specific conditions. Thus the success or failure of an

ISCO application is enormously dependent not only on site-specific conditions, but also the remediation objectives laid out for a specific site and the resources (e.g., time and money) made available to implement the ISCO system.

2.6. Plenary Discussions

Apart from the opening session on Day 1 of the Workshop, there were two periods when all of the participants were engaged in discussions about ISCO technology practices. The first occurred at the beginning of Day 2. As just described in Section 2.5, the Workshop participants turned in their site scenario assignment and there was a period of open discussion about the six scenarios and the perceived viability of ISCO as a successful remediation technology for each. This was followed by a period when the Workshop participants shared their views regarding the general process of technology screening and selection of ISCO as a viable remediation technology at a specific site.

This discussion began with a general query about what information was needed to determine viability of ISCO - that is, what data should be collected up front when evaluating ISCO as a remediation technology? Workshop participants offered general and detailed input on this topic. After discussing the information needs for screening ISCO, the general query was made to the Workshop participants: *"What do you do with the above data? What are red flags and green flags for ISCO?"* In this case a red flag may not rule out ISCO, but would raise concerns about its use at a site, and would possibly require further testing or investigation. The Workshop participants identified "flags" for ISCO at a given site as presented in Table 2.6.

A second period of plenary discussion occurred at the end of Day 2 of the Workshop. During this period, the three breakout groups reported on their respective deliberations as summarized in Table 2.2. During the balance of this plenary discussion, there was open discussion about various issues and concerns. One participant commented that all ground water treatment technologies leave the site in a better condition than it was prior to treatment. However, they may affect the ground water quality, and this fact needs to be addressed in the FAQs. Dr. Siegrist responded that this problem might be more perceived than real. There have been some documented instances of nickel mobilization during the use of CHP, manganese from permanganate, chloromethane generated during persulfate injections, acetone concentration increases when remediating PAHs, and other breakdown products. The production and stability of breakdown products can be evaluated during laboratory scale testing, though this is rarely done within the current standard of practice. Other potential concerns are exceedences of secondary ground water standards, such as sulfate or total dissolved solids.

A question posed to the participants was: "How should the system be designed to minimize these side effects?" One participant commented that there is an ongoing SERDP project being performed at ETSU that is examining the link between monitoring of ground water chemistry and ISCO results. In rare situations, such as extremely low NOD sites, ISCO must be carefully designed to avoid overdosing the subsurface and creating new problems such as manganese exceedences. However, quenching agents can be used to halt the oxidation process in these situations. Also, the presence of nearby receptors may require the use of shorter-lived oxidants.

A Workshop participant noted that during the preparation of the TPM the ER-0623 project team will need to stay abreast of evolving technologies, including sensing and monitoring technologies, so that the TPM will not be out of date as soon as it is released. It was also noted that electronic books can be more easily updated to include new information as it becomes available. Dr. Siegrist responded that the preceding point is a valid one. However, the ER-0623 project team hopes that the thought process within the TPM and its components (e.g., decision diagrams) will be able to withstand the test of time and new ISCO technologies.

Table 2.6. Screening of ISCO at a particular site – flags for go and no-go decisions.[1]

Go vs. No-Go decision	Views expressed by Workshop participants during open discussion during the morning of Day 2
Green Flags	* Time-driven remediation need, e.g. risk to nearby receptor or property transfer. * High hydraulic conductivity site. * Maximum concentrations at site are low (e.g., about 200 ppb and too low for bio). * Small footprint of contamination. * Shallow contamination. * Site features and geology allow for easy injection of reagents. * Well-defined source zone. * Low percent reduction of contaminant concentrations is needed.
Green or Orange Flag Considerations	* Prevailing regulatory climate may present barriers to use of ISCO. * Access is not a major problem. * ISCO fit to SCM. * Presence of bedrock.
Orange/Red Flags *(Considerations and potential problems but not definite no's)*	* High mass of NAPL and/or high COC concentrations. * Site is ideal for biological attenuation. * Presence of high levels of reducing agents (e.g. petroleum spill or injected oil from previous biological enhancement). * High heterogeneity. * Where there are silts. * Contaminants may not be readily amenable to oxidation. * High NOD. * Presence of downgradient receptors that may be impacted by oxidant, though this is more of a concern with permanganate than with other oxidants. * Presence of USTs or other sensitive subsurface site features [Many said that USTs are something that can be designed around]. * Presence of an ongoing release or uncontrolled source. * Regulatory bias against ISCO. * Very high ground water velocity, though this is more of an issue with oxidants that require a relatively longer contact time [This was a fairly contentious issue. Some argued that they only needed one day of oxidant contact and that there wasn't an upper bound on the gw velocity. Some suggested >20 ft/day as an upper limit, but others thought that upper limit was too high].
Red Flags	*`Contaminants not amenable to oxidation. This depends to a great degree on the oxidants being considered. However, there seemed to be general agreement that PCBs, perchlorate and certain energetics were not readily amenable to oxidation by any of the oxidants currently in use. * High NAPL mass, especially when site concentrations must be reduced to MCLs * Presence of redox-sensitive metals that could be mobilized (e.g., chromium) and yield a clear risk to local receptors. * Alternative technology is clearly preferable. * High levels of nitrate. * Above and/or below grade obstructions that prevent the delivery of oxidants to the contaminated area. * Hydraulic conductivity of less than 10^{-6} cm/sec is too low for ISCO to be used without a simultaneous mixing technology. * Costs and performance goals dictate that ISCO cannot be used effectively.

[1] Summary of views shared by Workshop participants during a plenary discussion that occurred at the beginning of Day 2 of the ISCO Technology Practices Workshop.

Dr. Siegrist posed a question to audience: "Is there a wariness/fear/anxiety that the release of the TPM will constrain ISCO practices?" Responses from the Workshop participants included the following.

- There are certain issues that are applicable to all oxidants, while other issues are only specific to a certain oxidant. The TPM must be aware of these distinctions and make them clear to the users.
- Considering the variability in the current standard of practice, the release of the TPM can only improve the situation. For example, using a screening level model for final design is better than using no model at all.
- There is a potential worry that the TPM may constrain regulators or consultants if it does not allow creative site-specific engineering and consideration of new ISCO technologies or approaches.
- A practices manual also becomes a buyer's manual, so the TPM must be applicable to site owners as well.
- There were long lists of items that were identified at this workshop as data needs during an ISCO evaluation and design. The TPM should segregate these lists into those parameters that are vital vs. nice to have. The project team should place the parameters list in the proper context in an effort to avoid a situation in which a regulator requires monitoring of all of the parameters identified here for every quarter in every ISCO remediation.
- It is also important to consider ISCO when used as a removal action as opposed to just as a ROD-driven remediation.
- Failure analysis should be conducted to determine what went wrong, how it happened, and how to prevent it. Failure analysis is inherent to the Observational Approach.

2.7. Workshop Adjournment

Bob Siegrist concluded the wrap-up discussion by stating that the process of producing the TPM has already begun. The proceedings from this Workshop will be an important resource in support of this effort. The Workshop was adjourned at the end of Day 2.

3. Appendix

A. Slide Presentations Made by Opening Speakers

Appendix A contains a reproduction of the slides presented during the opening session of the Workshop. The presentations included in Appendix A are listed in Table A.1.

Table A.1. Topics and speakers for the opening session presentations.

Slide section	Topic	Presenter(s)
A.1	In Situ Chemical Oxidation for Ground Water Remediation. ESTCP ISCO Technology Practices Workshop	Bob Siegrist and Michelle Crimi
A.2	ISCO Initiative background and status within SERDP/ESTCP	Marvin Unger
A.3	Site Specific ISCO Engineering. Who Needs It???	Dick Brown
A.4	Advances in CHP ISCO through SERDP Project ER-1288	Rick Watts
A.5	Reaction and Transport Processes Controlling In Situ Chemical Oxidation of DNAPLs. Highlights of SERDP Project ER-1290	Bob Siegrist
A.6	In Situ Chemical Oxidation for Ground Water Remediation – Technology Practices Manual. ER-0623 Project Overview based on Winter IPR Feb ‘07	Bob Siegrist and Michelle Crimi

A.1. In Situ Chemical Oxidation for Ground Water Remediation - ESTCP ISCO Technology Practices Workshop. Presentation by Bob Siegrist and Michelle Crimi.

In Situ Chemical Oxidation for Groundwater Remediation

ESTCP ISCO Technology Practices Workshop

March 7-8, 2007

at the Colorado School of Mines
Golden, Colorado

1

- Welcome to the Colorado School of Mines
  - Public university, 130+ years old, 4,000 students
  - Environmental Science and Engineering Division
    - Remediation related research for SERDP/ESTCP *et al.*

"An exemplary public research university focused on science and engineering related to earth, energy, materials, and environment"

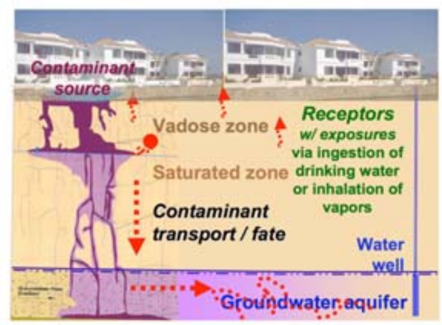
2

- Workshop purpose and approach
  - A task within a new ESTCP project, ER-0623:
    "*In Situ Chemical Oxidation of Groundwater - Technology Practices Manual*"
  - Engage key stakeholders
    - Chemical companies, technology vendors, engineering consultants, researchers, and remedial project managers
  - Share and constructively discuss ISCO and technology practices for site-specific engineering
  - Workshop agenda has presentations, panel discussions, scenario assignment, and breakout sessions…

3

- The focus…contamination of soil and groundwater by organic chemicals ~ site-specific application of ISCO

Major challenges occur at sites with dense nonaqueous phase liquids (DNAPLs) such as PCE and TCE solvents



4

- Workshop outcome
  - This workshop should:
    - Help define the frequently asked questions and other technical issues that remedial project managers (RPMs) and others encounter when considering the selection, design, and implementation of ISCO for a particular site
    - Help identify the inherent limitations of ISCO for certain types of sites and performance goals
    - Help identify sites and goals that are particularly well suited to one or more ISCO approaches
    - Provide insight into best practices that will help ensure that success is achieved while performance deficiencies and failures are avoided

5

- A summary of the workshop including attendees, final agenda, highlights of presentations, panel discussions, and breakout session reports, will be prepared
  - A draft summary will be distributed for review and comment
  - A final summary will be prepared and distributed to the ESTCP Program Office and all workshop participants

6

A.1. In Situ Chemical Oxidation for Ground Water Remediation - ESTCP ISCO Technology Practices Workshop. Presentation by Bob Siegrist and Michelle Crimi (*continued*).

Table 1.1. Program for the ISCO Technology Practices Workshop on March 7-8, 2007. *(Updated 03-06-07*

Day/time	Topic/Activity
	Wednesday, March 7, 2007
08:00 a.m.	*Registration and continental breakfast*
08:30 a.m.	Welcome and statement of purpose and approach for the workshop; Introduction of participants – Bob Siegrist and Michelle Crimi
09:00 a.m.	ISCO initiative background and status within SERDP/ESTCP – Marvin Unger
09:15 a.m.	Overview and recent project findings concerning site-specific engineering of ISCO – Dick Brown, Rick Watts (ER-1288), Bob Siegrist (ER-1290)
10:15 a.m.	Overview of ER-0623: ISCO Technology Practices Manual – Bob Siegrist
10:45 a.m.	*Break*
11:00 a.m.	Panel I: ISCO screening and selection; using ISCO in combined remedies Chairs: Mike Singletary and Junko Munakata Marr Panelists: Paul Favara, Michael Pound, Kent Sorenson, Mike Urynowicz
12:00 p.m.	*Lunch provided*
1:00 p.m.	Panel II: ISCO feasibility study; oxidant selection and delivery approaches; lab and field tests Chairs: Michelle Crimi and Ben Petri Panelists: Keith Henn, George Hoag, Scott Haling, Rick Watts
2:00 p.m.	Panel III: ISCO system design and modeling tools Chairs: Tom Simpkin and Tissa Illangasekare Panelists: Dick Brown, Wilson Clayton, Matt Dingens, Dirk Pohlman
3:00 p.m.	*Break*
3:15 p.m.	Panel IV: ISCO system construction, startup, monitoring Chairs: Tom Palaia and Mike Singletary Panelists: Dan Bryant, John Haselow, Bob Luhrs, Bob Norris
4:15 p.m.	Open discussion and recap; set up break out sessions for Day 2 – Michelle Crimi
5:00 p.m.	*Adjourn day 1*
5:30 p.m.	*Reception (5:30 p.m.) and dinner (6:30 p.m.) at the Golden Hotel, Fall River Room*

7

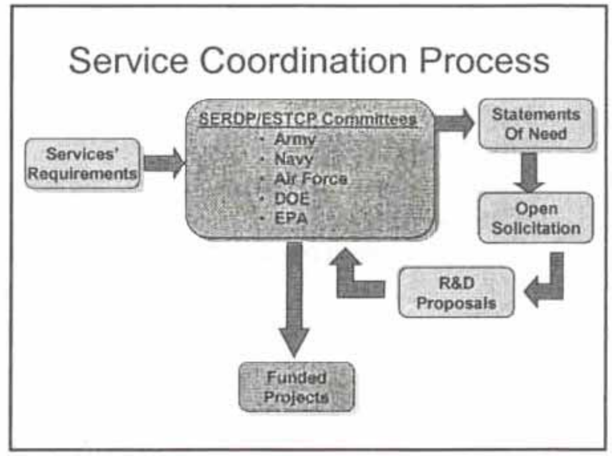
	Thursday, March 8, 2007
08:00 a.m.	*Continental breakfast, turn in "assignment" re: site scenarios*
08:30 a.m.	Group discussion – Site scenarios and ISCO screening based on "assignment" questions Moderators: Michelle Crimi and Ben Petri
10:00 a.m.	*Break*
10:15 a.m.	Break out sessions – Workshop participants meet in 3 groups to discuss: 1. ISCO delivery and treatability; 2: ISCO design and modeling; and 3: ISCO construction, operation, monitoring
12:00 p.m.	*Lunch provided*
1:00 p.m.	Break out sessions continued
3:00 p.m.	Report out on the scenario responses and from the breakout sessions (15 min. each) – Session chairs or volunteers
4:00 p.m.	Open discussion and synthesis – areas of clear agreements and disagreements Moderator: Michelle Crimi
4:45 p.m.	Concluding remarks – Bob Siegrist and Michelle Crimi
5:00 p.m.	*Adjourn workshop*

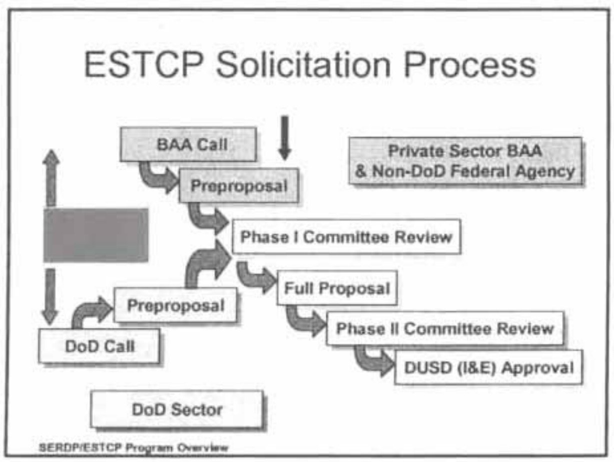
8

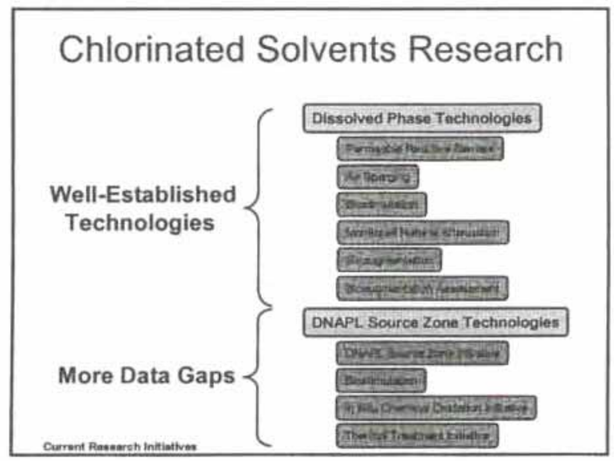
- **Workbook and handout materials**
- **Introduction of participants**
  - **Name, affiliation, role and experience with ISCO**
- **Logistics**
  - **Cell phones**
  - **Restrooms**
  - **Book store, coffee cart, snack bar,…**
- **Questions?**

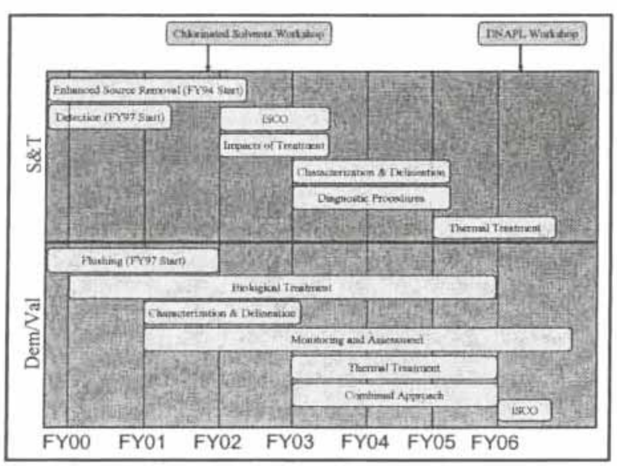
9

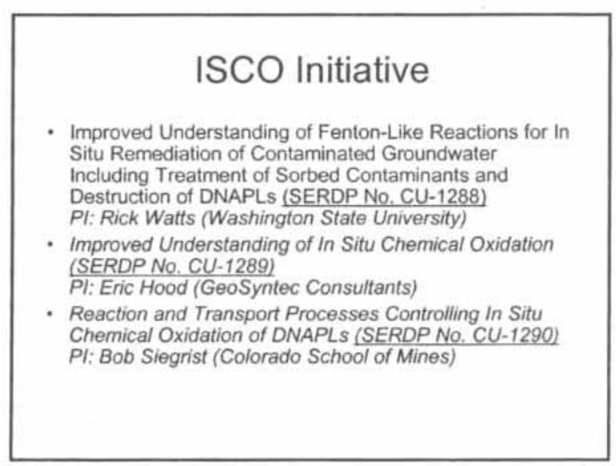
A.2. ISCO Initiative background and status within SERDP/ESTCP. Presentation by Marvin Unger.



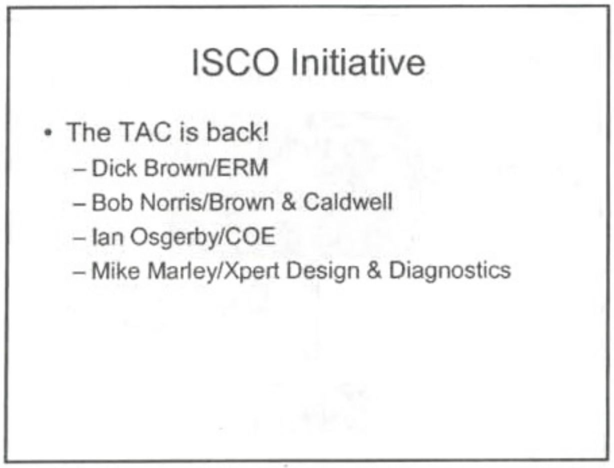


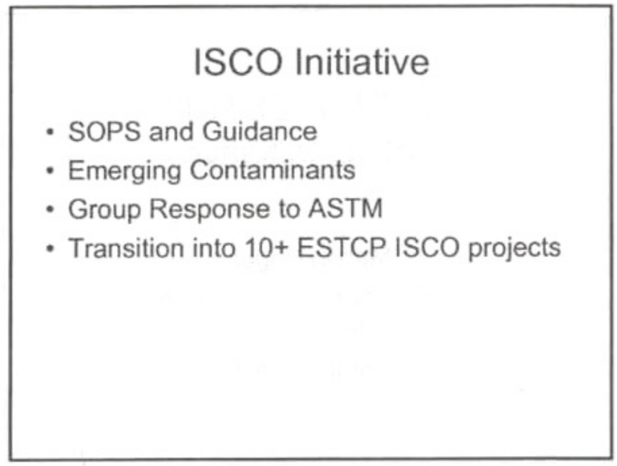


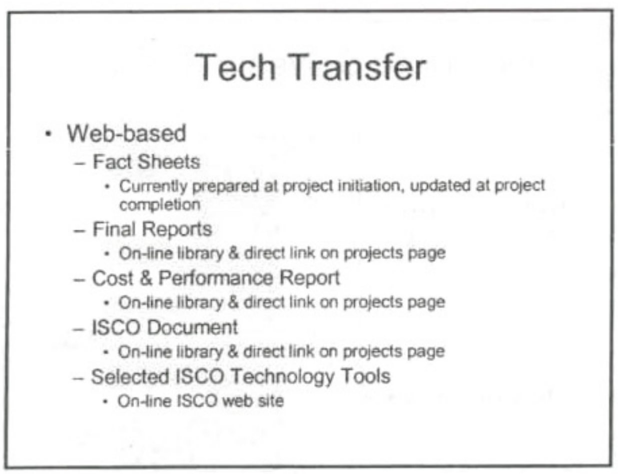




A.2. ISCO Initiative background and status within SERDP/ESTCP. Presentation by Marvin Unger (*continued*).







A.3. Site Specific ISCO Engineering. Who Needs It??? Presentation by Dick Brown.

Site Specific ISCO Engineering
Who Needs It???

Richard A. Brown
ERM
Ewing, NJ

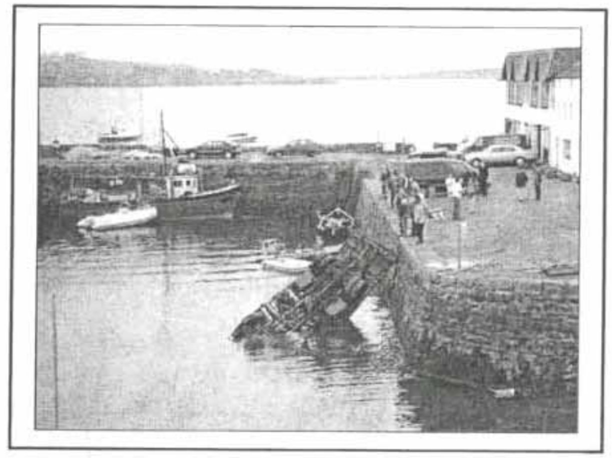
Oxidants

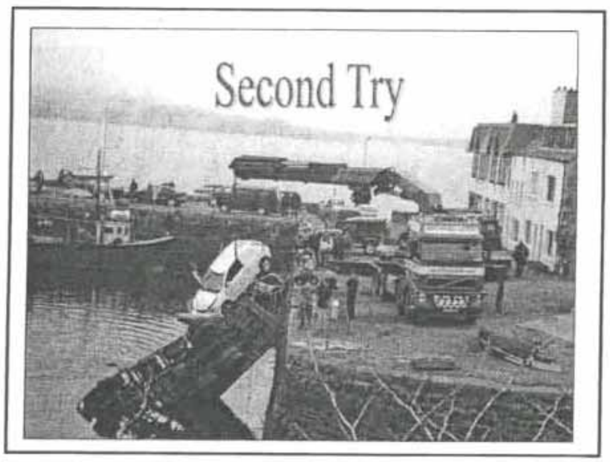
Why not just dump them in the ground? They'll work!

Who needs engineering?

A Cautionary Tale

A.3. Site Specific ISCO Engineering. Who Needs It??? Presentation by Dick Brown (*continued*).





A.3. Site Specific ISCO Engineering. Who Needs It??? Presentation by Dick Brown (*continued*).

Site Specific ISCO Engineering
Who Needs It???

When does ISCO Work?

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

Success is *enough oxidant* (→ Dosage) *in contact* (→ Distribution)
with the contaminant for a
long enough period of time (→ Kinetics Persistence)
to *react effectively* (→ Contaminant Destruction)

Oxidant Dosage

$[\text{Oxidant}]_{\text{Required}}$ =

$[\text{Stoichiometric Demand}]_{\text{Contaminant}}$

+ [Soil Oxidant Demand]

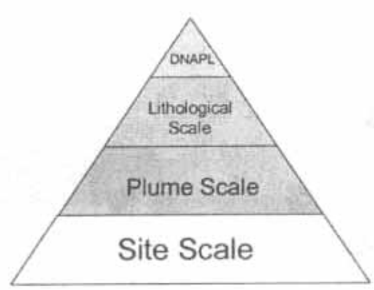
$[\text{Metals}]_{\text{Red}}$

$[\text{Organic Carbon}]_{\text{Oxidizable}}$

+ $[\text{Decomposition}]_{\text{Oxidant}}$

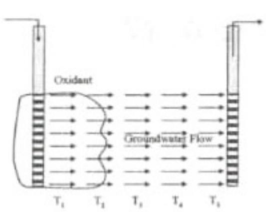
These factors are oxidant and site specific

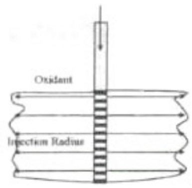
Distribution Scales



Macro Distribution Methods

- Circulation
  - $T_{1/2}$ > Travel Time
- Emplacement
  - $T_{1/2}$ < Travel Time





Types of Circulation Methods

- Injection Only
  - Galleries
  - Wells
    - Vertical
    - Horizontal
  - Trenches
  - Gravity Feed
- Injection & Recovery
  - Galleries & Wells
  - Trenches
  - Conventional Wells
    - Vertical
    - Horizontal
  - Recirculation Wells

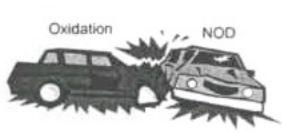
Types of Emplacement Methods

- Soil Mixing
  - Augers
  - MITU (Trencher)
  - Back-hoe, Excavator
- Pressure injection in Wells
- Geoprobe Injection
  - Pressure pulse
- Pneumatic Fracturing
  - Channel creation
  - Direct injection
- Hydraulic fracturing
  - Channel creation
  - Direct injection
- Air Sparging Wells (Ozone)

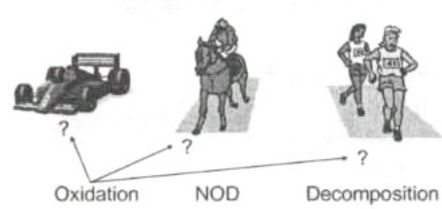
Can we enhance distribution on the meso or micro scale?

Kinetics Versus Persistence

A Race to the Finish? or A Demolition Derby?



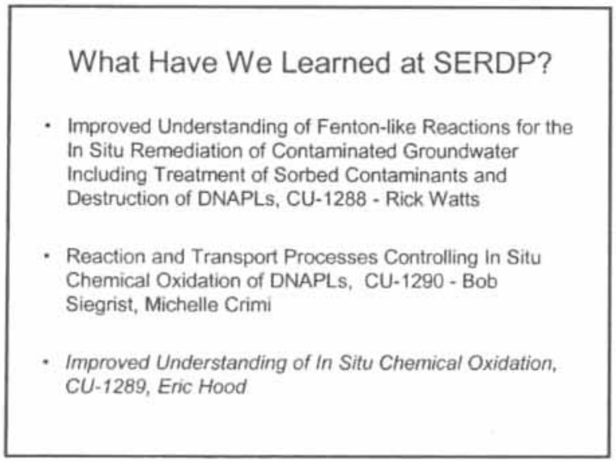
Kinetics Versus Persistence

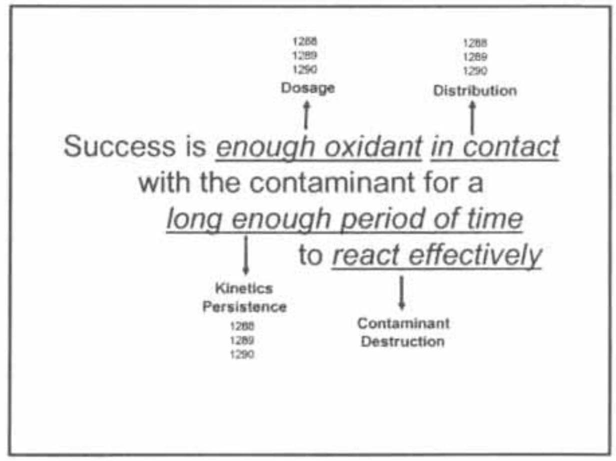


Make it a sure win

- Choose the right oxidant
- Apply it properly
  - Dosage
  - Delivery
  - ??

A.3. Site Specific ISCO Engineering. Who Needs It??? Presentation by Dick Brown (*continued*).





A.4. Advances in CHP ISCO through SERDP Project ER-1288. Presentation by Rick Watts.

Advances in CHP ISCO through SERDP Project ER-1288

Richard J. Watts and Amy L. Teel

Department of Civil & Environmental Engineering
Washington State University

Catalyzed H_2O_2 Propagation Reactions (CHP)

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH\bullet + OH^-$$

$$OH\bullet + H_2O_2 \rightarrow O_2\bullet^- \; H_2O + H^+$$

$$HO_2\bullet + Fe^{2+} \rightarrow HO_2^- + Fe^{3+}$$

ER-1288 Objectives

- Overall objective:
  - To provide increased understanding of modified Fenton's reagent for the remediation of contaminated groundwater with emphasis on the importance of different reactive oxygen species.
- Specific objectives:
  - Tasks 1 & 2: Hydrogen peroxide decomposition mediated by soluble iron and subsurface minerals
  - Task 3: Contaminant degradation pathways
  - Task 4: Destruction of DNAPLs
  - Task 5: Enhanced contaminant desorption
  - Task 6: Process conditions that promote effective reagent delivery

Summary of Task 1 & 2 Results: Rates of H_2O_2 Decomposition by Naturally-Occurring Minerals

- Manganese oxides: highest rate of H_2O_2 decomposition (half-life in minutes)
- Iron oxides: moderate rate of H_2O_2 decomposition (half-life in hours)
- Trace minerals: lowest rate of H_2O_2 decomposition (half-life in days to weeks)

Summary of Task 1 & 2 Results: Rates of H_2O_2 Decomposition by Subsurface Solids

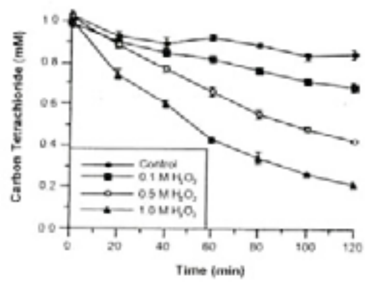
- Low correlation with surface area and soil organic carbon content
- pH 7: Highest correlation with crystalline iron and manganese oxides
- pH 3: Highest correlation with amorphous iron and manganese oxides

Summary of Task 1 & 2 Results: Generation of Reactive Oxygen Species through Catalysis by Metals and Metal Oxides

- Manganese oxides: Superoxide only
- Soluble manganese: Hydroxyl radical only
- Iron oxides: Both hydroxyl radical and superoxide

A.4. Advances in CHP ISCO through SERDP Project ER-1288. Presentation by Rick Watts (*continued*).

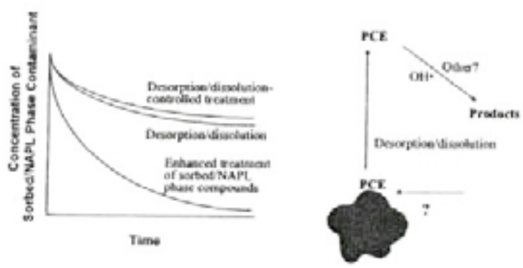
Task 3 Results: Mechanism of Carbon Tetrachloride Destruction in CHP Systems



Summary of Task 3 Results

- Superoxide, although generally unreactive in water, has increased reactivity with carbon tetrachloride when hydrogen peroxide concentrations are sufficiently high to provide a solvent effect.
- Carbon tetrachloride is transformed in CHP systems to phosgene, which is then rapidly converted to carbonate and chloride.

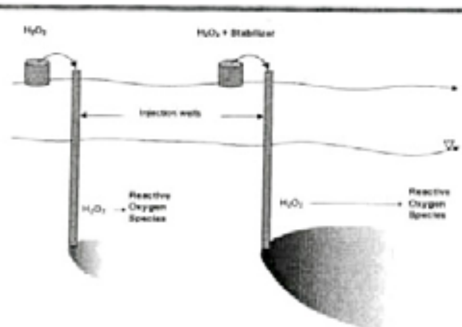
Task 4 & 5: Rapid Destruction of DNAPLs and Sorbed Compounds



Results of Task 4 & 5: Rapid Destruction of DNAPLs and Sorbed Compounds

- Six DNAPLs (carbon tetrachloride, chloroform, TCE, PCE, 1,1,1-TCA, and 1,2-DCA) were destroyed by CHP under laboratory conditions.
- Some DNAPLs, such as PCE and carbon tetrachloride, were destroyed at rates faster than dissolution.
- Degradation products formed during the destruction of a PCE DNAPL included both reduced and oxidized species.
- Superoxide is the reactive oxygen species responsible for the rapid destruction of DNAPLs and sorbed compounds.
  - DNAPL destruction more rapid than rates of dissolution
  - Dodecane treatment more rapid than its rate of gas-purge dissolution

Task 6: Enhanced Delivery of H_2O_2



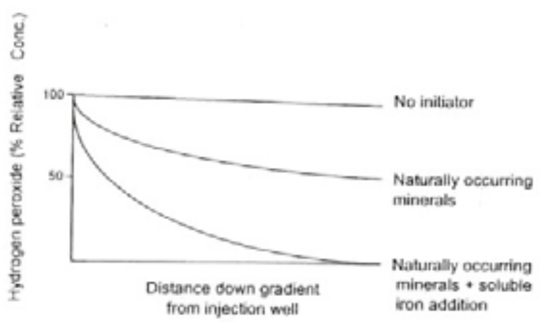
CHP Initiators and Catalysts

H_2O_2 + Initiator → Reactive Oxygen Species

- Iron (II)
- Iron (III): Superoxide-driven reaction
- Iron chelates
- Iron oxide minerals
  - Goethite
  - Hematite
  - Ferrihydrite
- Manganese oxide minerals

A.4. Advances in CHP ISCO through SERDP Project ER-1288. Presentation by Rick Watts (*continued*).

Effect of Iron Addition on Hydrogen Peroxide Decomposition Rate

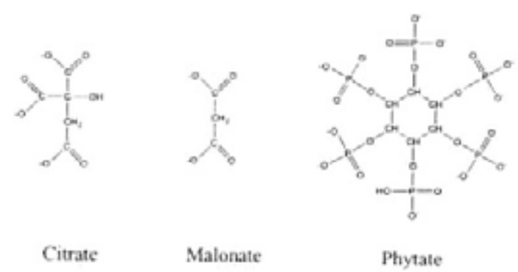


"Ineffective" Iron-Chelates

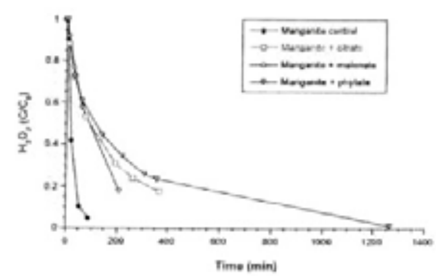
(Sun, Y., and J.J. Pignatello. 1992. *J. Agric. Food Chem.* 40:322-327)

- DTPA (Diethylenetriamine pentaacetic acid)
- Citrate
- Gallate
- Malate
- Malonate
- Oxalacetate
- Oxalate
- Pyruvate
- Phytate
- Succinate

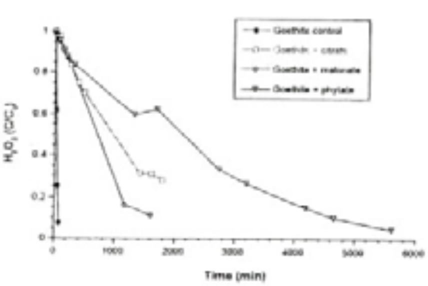
Most Effective Stabilizers



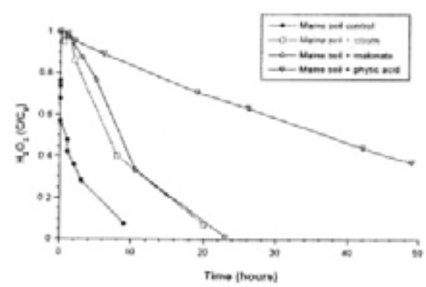
H_2O_2 Stabilization of Manganite



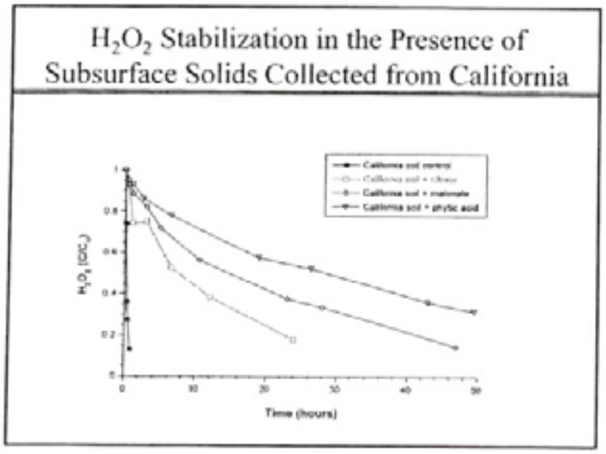
H_2O_2 Stabilization of Goethite

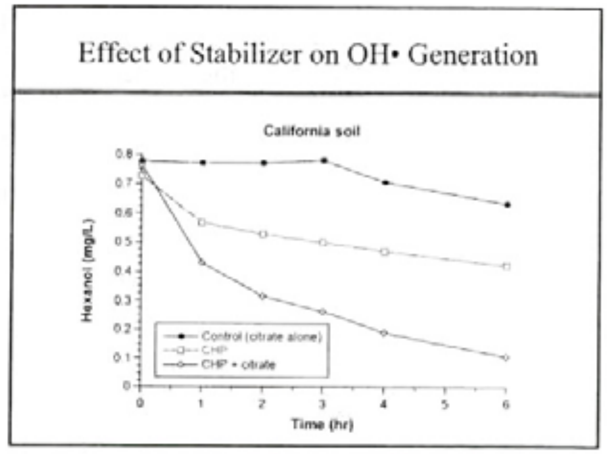


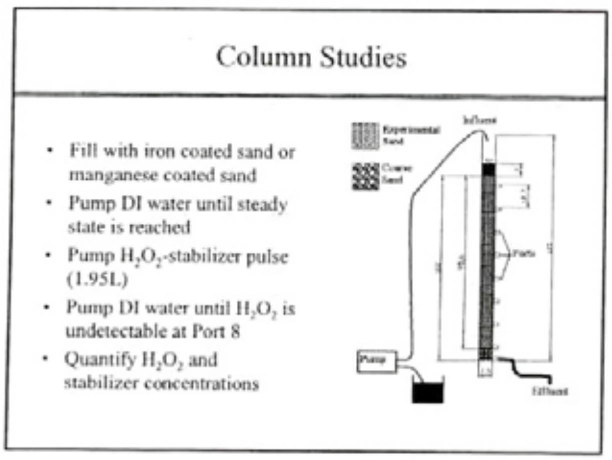
H_2O_2 Stabilization in the Presence of Subsurface Solids Collected from Maine

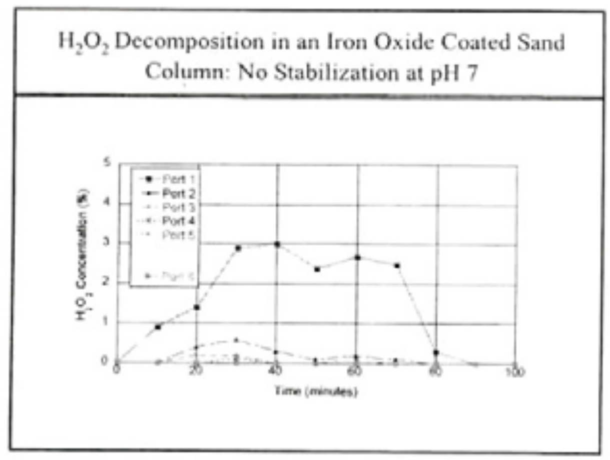


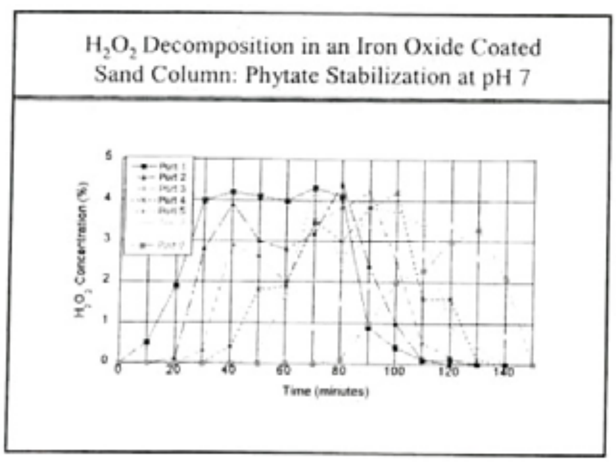
A.4. Advances in CHP ISCO through SERDP Project ER-1288. Presentation by Rick Watts (*continued*).

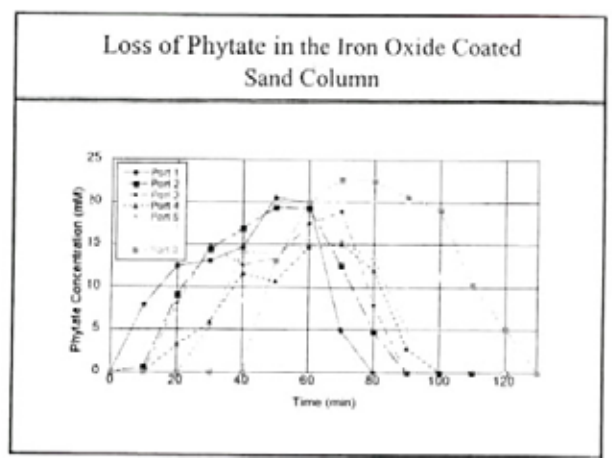






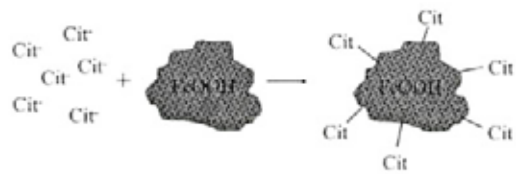






A.4. Advances in CHP ISCO through SERDP Project ER-1288. Presentation by Rick Watts (*continued*).

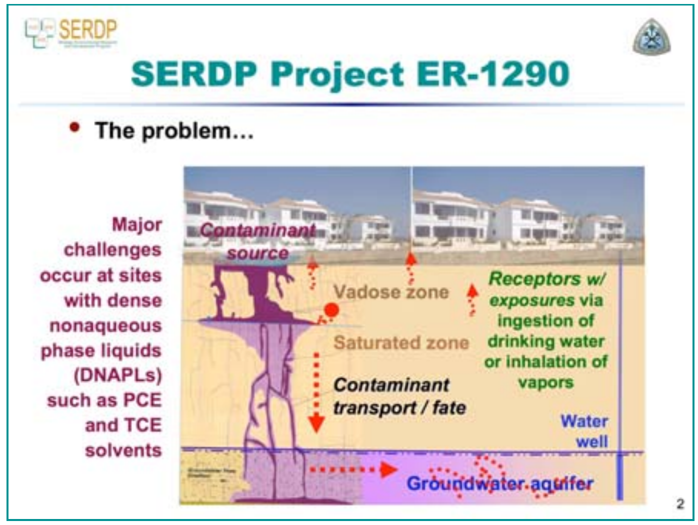
Possible Stabilization Mechanism: Binding to Mineral Surfaces

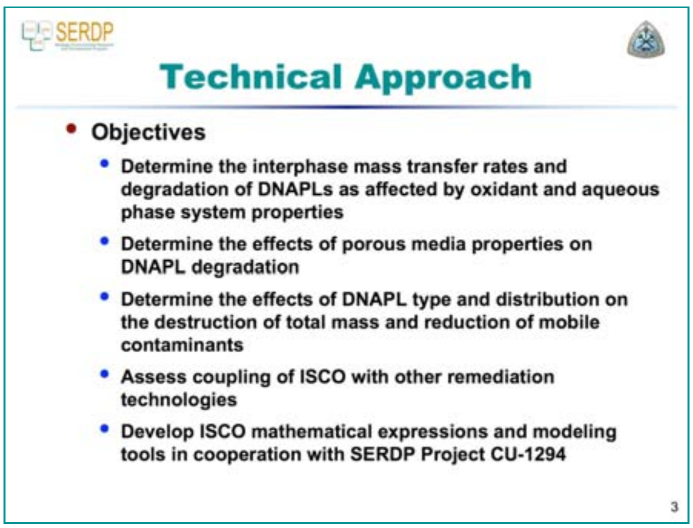


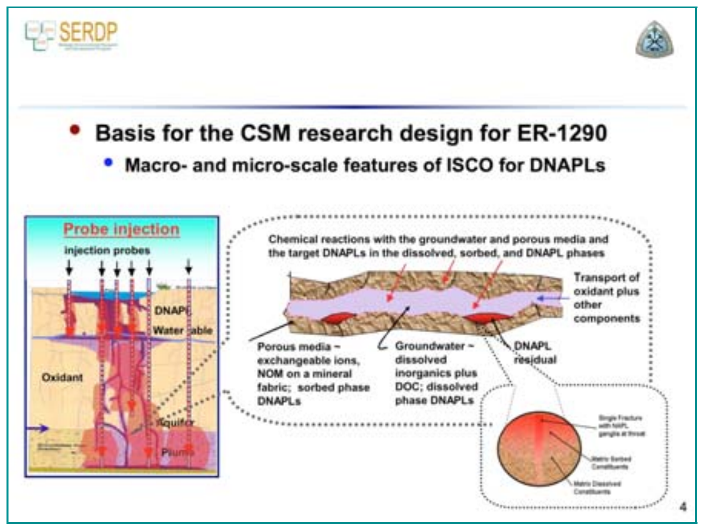
ER-1288: Summary and Conclusions

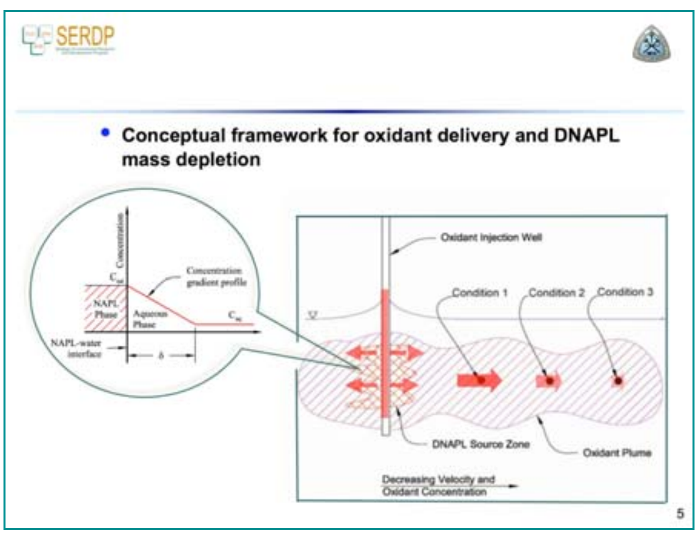
- Iron and manganese oxide minerals in the subsurface control CHP chemistry.
  - Hydrogen peroxide decomposition
  - Generation of reactive oxygen species
- CHP reactions can destroy sorbed and DNAPL contaminants more rapidly than corresponding rates of mass transfer into the aqueous phase.
- Superoxide has a significant role in the effectiveness of CHP ISCO.
- The most effective application and delivery of CHP is the use of native minerals as catalysts with stabilization by citrate, phytate, or malonate.

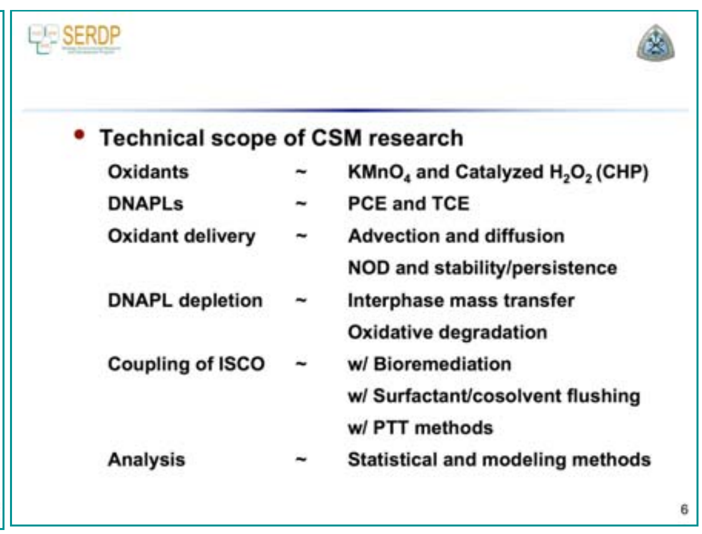
A.5. Reaction and Transport Processes Controlling In Situ Chemical Oxidation of DNAPLs. Highlights of SERDP Project ER-1290. Presentation by Bob Siegrist.











A.5. Reaction and Transport Processes Controlling In Situ Chemical Oxidation of DNAPLs. Highlights of SERDP Project ER-1290. Presentation by Bob Siegrist (*continued*).

SERDP

- Technical methods
  - Literature review and analysis
  - Laboratory experiments using:
    - Batch-reactors (VRs, MVRs, ZHRs) and microcosms
    - 1-D cells, 1-D FTRs, 1-D columns, 2-D cells, 2-D tanks
  - Mathematical modeling
    - CORT3D

Note: most experiments were designed to study ISCO processes and were not carried out to achieve high %DNAPL destruction

7

SERDP

Highlights of Findings

- The following slides contain several generalized findings of SERDP Project ER-1290 that relate to site-specific engineering of ISCO
- Further information is contained in the final report, student theses, and other project publications
  - Siegrist, R.L., M.L. Crimi, J. Munakata-Marr, T. Illangasekare, K. Lowe, S. Van Cuyk, P. Dugan, J. Heiderscheidt, S. Jackson, B. Petri, J. Sahl, S. Seitz (2006). *Reaction and Transport Processes Controlling In Situ Chemical Oxidation of DNAPLs.* Final report to SERDP for project CU-1290, November 1, 2006. 233 pg.

8

SERDP

- Oxidation of DNAPLs in an aqueous system can be reliably and predictably achieved
  - Chemical oxidation, using $KMnO_4$, H_2O_2, can rapidly and completely destroy the common DNAPL contaminants, PCE and TCE, when they are:
    - Dissolved in aqueous, well-mixed systems
    - Present as DNAPLs immersed in aqueous systems
  - The oxidants studied, $KMnO_4$, H_2O_2, have relatively predictable behaviors:
    - Reaction pathways and products
    - Rates of reaction
    - Sensitivities to matrix conditions

9

SERDP

- Depletion / destruction of DNAPL phase organics (at the interface scale) can be enhanced by ISCO
  - The degree of enhancement depends on DNAPL type and the relative rates of DNAPL dissolution and aqueous phase reactions
    - Even in the absence of porous media, DNAPL depletion and destruction depends on DNAPL properties
      - TCE was degraded more rapidly than PCE
    - Oxidant concentration and velocity of oxidant delivery can interact strongly in determining DNAPL depletion rates and extents
    - In general, a higher delivery velocity at a lower concentration leads to more rapid and extensive depletion

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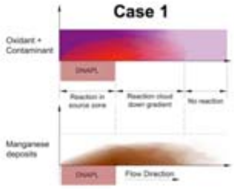
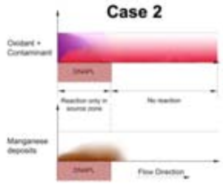
SERDP

- Oxidation vs. dissolution during DNAPL mass depletion
  - Case 1: rate of dissolution > rate of reaction, resulting in a "reaction cloud" - reaction cloud could yield faster cleanup and reaction byproducts are dispersed
  - Case 2: rate of oxidation > rate of dissolution - reaction occurs closer to the interface and reaction byproducts deposit at and near the DNAPLs

Case 1



Case 2



11

SERDP

- Depletion and destruction of DNAPLs that are present within a subsurface setting also depends on the contaminant mass, entrapment architecture, and system hydraulics
  - For DNAPLs present as residual ganglia, oxidant flushing with $KMnO_4$ can achieve depletion and destruction
  - However, when pooled DNAPL was present, oxidation effectiveness was more variable
  - Mass depletion was enhanced by aqueous phase contaminant oxidation, as well as possibly other impacts, based on lab studies and modeling results

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A.5. Reaction and Transport Processes Controlling In Situ Chemical Oxidation of DNAPLs. Highlights of SERDP Project ER-1290. Presentation by Bob Siegrist (*continued*).

SERDP

- **Unproductive oxidant loss occurs in the subsurface and can hinder DNAPL depletion and destruction**
  - Natural oxidant demand ($KMnO_4$) and oxidant decomposition (H_2O_2) increased with:
    - Increasing complexity of porous media (e.g., higher reduced mineral content, NOM, or clay/silt particle fractions)
    - Increasing oxidant concentration and contact time
  - Oxidants with slower reaction rates can be delivered and transported further in the subsurface
    - e.g., $KMnO_4$ can be distributed further than H_2O_2
  - High density probe injection or short-radius well-to-well flushing methods should generally be most effective

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SERDP

- **ISCO can alter subsurface conditions yielding beneficial or negative impacts, depending on ISCO methods used and site conditions**
  - Examples include:
    - Water chemistry (e.g., pH depression, increased DOC,…)
    - Porous media surface properties
    - Porous media permeability
    - Microbiology
  - However, changes can normally be anticipated and these should be accounted for during ISCO design and operation

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- **ISCO can be combined synergistically with other remediation approaches and technologies**
  - The prime example is ISCO and bioremediation
    - ISCO can enhance anaerobic reductive dechlorination of contaminants such as TCE and PCE and this coupling can represent a viable remediation strategy
  - Other potential combinations include:
    - ISCO with surfactant flushing
    - ISCO with thermal treatment

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SERDP

- **Effects of ISCO DNAPL mass depletion on associated ground water PCE and TCE levels**
  - Mass depletion of DNAPLs can lead to reduced levels of PCE and TCE in a ground water plume
  - Near 100% mass depletion may not be needed to achieve substantial declines in mobile PCE and TCE
    - Relationship is dependent on the extent and character of the mass depletion achieved during active ISCO
    - Also depends on enhancements to relevant processes such as natural attenuation within and near the source

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SERDP

- **Some gaps and potential areas for further R&D…**
  - Methods for enhanced delivery and predictably achieving increased oxidant stability and targeted reactivity
  - New and novel oxidants and oxidant systems
  - More quantitative understanding to enable effective coupling of ISCO with other remediation technologies
    - We know coupling is viable, but when and how to transition is less clear
  - Mathematical expressions, models, and decision support tools are still limited
    - Site-specific engineering remains uncertain and variable

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SERDP

Acknowledgments

- **CSM SERDP ER-1290 Project Team**
  - Co-P.I.'s: M. Crimi, J. Munakata Marr, T. Illangasekare
  - Students/staff: B. Petri, P. Dugan, J. Heiderscheidt, J. Sahl, S. Seitz,…
- **SERDP/ESTCP Program Staff**
- **ISCO Expert Panel**
- **SERDP Project ER-1294 *et al.***

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A.6. In Situ Chemical Oxidation for Ground Water Remediation – Technology Practices Manual. ER-0623 (Project Overview based on Winter IPR Feb '07). Presentation by Bob Siegrist and Michelle Crimi.

In Situ Chemical Oxidation for Groundwater Remediation – Technology Practices Manual

ESTCP Project No.: ER-0623

Project overview based on the Winter IPR Feb '07

Robert L. Siegrist, Ph.D., P.E.
Professor and Division Director
Colorado School of Mines
Golden, Colorado USA

Michelle Crimi, Ph.D.
Assistant Professor
East Tennessee State University
Johnson City, Tennessee USA

ESTCP ISCO Technology Practices Workshop

March 7-8, 2007 at the Colorado School of Mines
Golden, Colorado

1

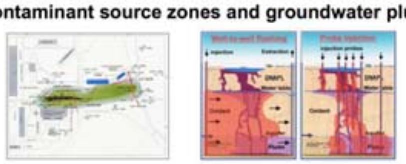
Project Participants

Principal Investigators:	Robert L. Siegrist, Ph.D., P.E. (CSM) Michelle Crimi, Ph.D. (ETSU)
Co-Principal Investigators:	Tissa Illangasekare, Ph.D., P.E. (CSM) Junko Munakata Marr, Ph.D. (CSM) Thomas A. Palaia, P.E. (CH2M Hill) Thomas J. Simpkin, Ph.D. (CH2M Hill)
Key Team Members:	Fritz Krembs (CSM) Kathryn Lowe, M.S. (CSM) Ben Petri, M.S. (CSM) Michael A. Singletary, P.E. (NAVFAC) Abigail Wren, M.S. (CH2M Hill)
ESTCP Project Liaison:	Nancy Ruiz, Ph.D. (NFESC)

2

Technical Objectives

- Project focus and overall goal of ER-0623
  - The focus is on in situ chemical oxidation (ISCO) to clean up contaminant source zones and groundwater plumes



  - The goal is to enable more predictable, cost-effective application at DOD sites by providing knowledge and know-how within an ISCO Technology Practices Manual (TPM)
  - Project was initiated in mid-2006 and will be completed during early 2009

3

- To produce an ISCO TPM, this 3-year project will:
  - Focus on site-specific engineering of ISCO
    - Build on existing technical and regulatory guidance
  - Evaluate and integrate the current knowledge and know-how base for ISCO
    - Literature sources and case study reports
    - Findings and new tools developed in recent and currently funded SERDP/ESTCP projects and from other sources
  - Develop and test an ISCO design protocol
    - Existing historic case studies – test predictive capabilities
    - Sites with an ISCO application in progress – test ease of use, functionality, comprehensiveness
  - Provide specific procedural information, tools, and design details for practitioners and site managers

4

Technical Approach

Task 1. Develop a design protocol for site-specific engineering of an ISCO field application

Task 2. Test the ISCO design protocol, including decision tools, against DOD case studies

Task 3. Select DOD sites for field application of the ISCO design protocol

Task 4. Apply the ISCO design protocol to DOD field sites

Task 5. Refine the ISCO design protocol and tools based on evaluation results

Task 6. Prepare an ISCO Technology Practices Manual and Frequently Asked Questions Guide

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Technical Progress

- During 2006, project activities have focused on
  - Project start up including staffing and subcontracting
  - Task 1: Develop an ISCO design protocol
    - Subtask 1A. Coordinate and conduct a workshop at CSM
    - Subtask 1B. Conduct a critical literature review and integration of ISCO work
    - Subtask 1C. Develop/document design protocol for site-specific ISCO engineering
    - Subtask 1D. Perform broad-scale analysis of DOD sites which have reached at least the feasibility study stage
  - Progress has been made in several other tasks as well

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A.6. In Situ Chemical Oxidation for Ground Water Remediation – Technology Practices Manual. ER-0623 (Project Overview based on Winter IPR Feb '07). Presentation by Bob Siegrist and Michelle Crimi (*continued*).

- **Task 1: Develop an ISCO design protocol**
  - Subtask 1A. Coordinate and conduct a workshop at CSM
    - Technology practices workshop - March 7-8, 2007
    - Diverse participants: technology vendors, chemical companies, environmental consultants, researchers, and remedial project managers
    - Presentations, panel discussions, break-out sessions
    - Identify best practices, promising tools/techniques, key data gaps, and primary factors leading to success/failure

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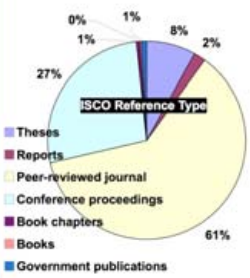
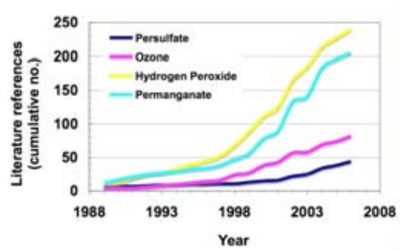
- Subtask 1B. Conduct a critical literature review and integration of ISCO work
  - Review has been focused on the common ISCO oxidants
    - Catalyzed hydrogen peroxide, sodium and potassium permanganate, ozone, and sodium persulfate
  - Over 600 references have been identified so far by searching sources including:
    - Online abstract services (e.g., sciencedirect.com)
    - Webpages (e.g., ACS)
    - Conference proceedings (e.g., Battelle Press)
    - Journal publications (e.g., ES&T, GWMR)
  - Literature has been classified, and review and tabulation of methods and key findings is in progress

8

- Some initial observations
  - Trends in ISCO publications





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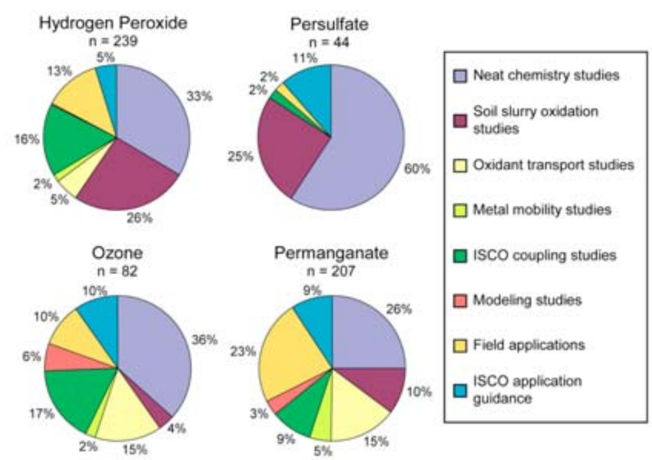

- Preliminary observations based on a review of the ISCO literature examined so far
  - H_2O_2 and $KMnO_4$ most commonly studied
  - Large % of H_2O_2 studies deal with reaction chemistry
  - Persulfate studies are almost exclusively reaction chemistry
  - Relative low number of transport studies for H_2O_2 compared to the total number of H_2O_2 studies
  - Transport of MnO_4^- has been well studied in comparison to H_2O_2
  - Majority of metals mobility studies focused on permanganate
  - Biocoupling and MNA most extensively investigated technologies for coupling with ISCO
  - Examples of ISCO field applications extensively reported

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- Subtask 1C. Develop/document design protocol for site-specific ISCO engineering
  - Initial ISCO design protocol is based on the information being gained during Subtasks 1A and 1B
  - Design protocol is being developed through a collaborative effort by CSM, ETSU, CH2M Hill, and the Navy
    - Initial development has occurred through multiple, day-long work sessions held with the team during Fall 2006
    - Initial framework is built on a set of tiered decision diagrams to help guide site-specific engineering of ISCO
    - Linked narrative and metrics for decision making with supporting tools

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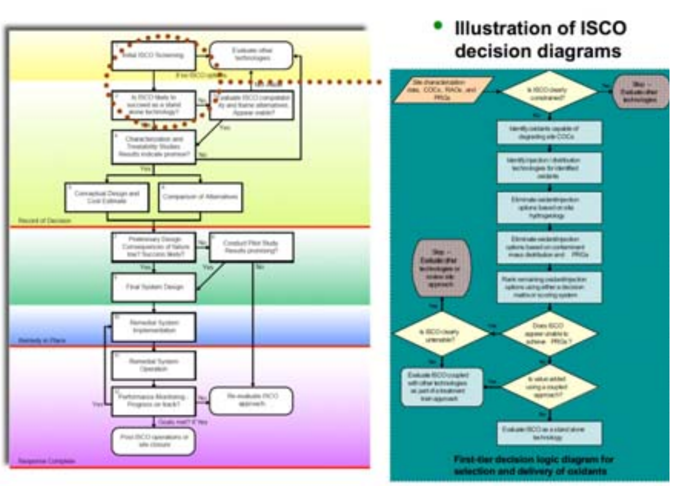
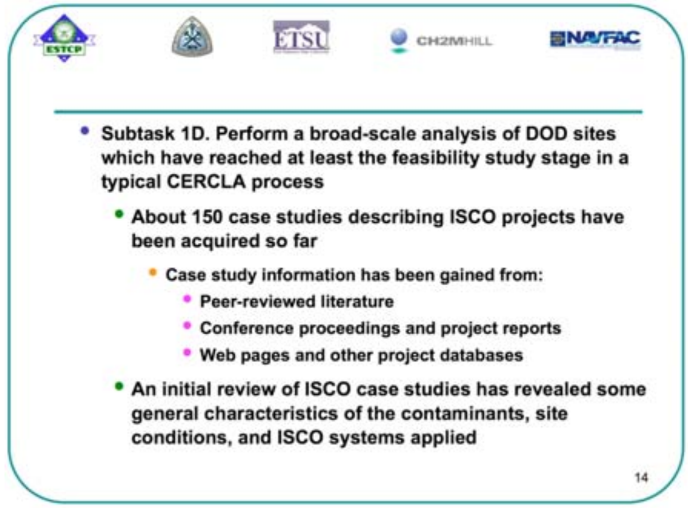
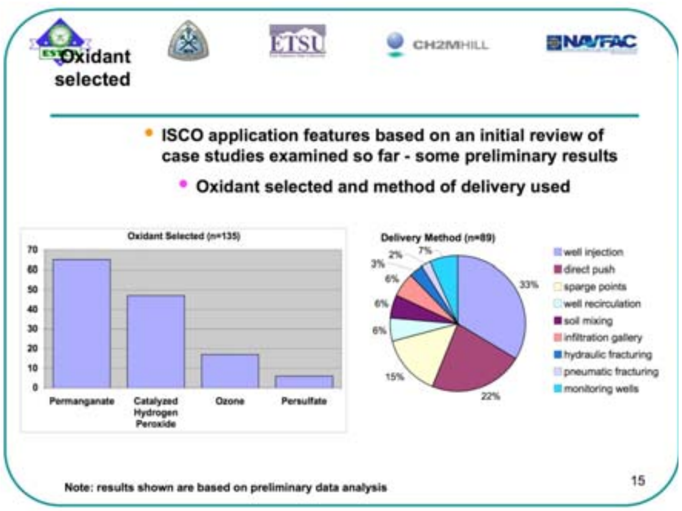
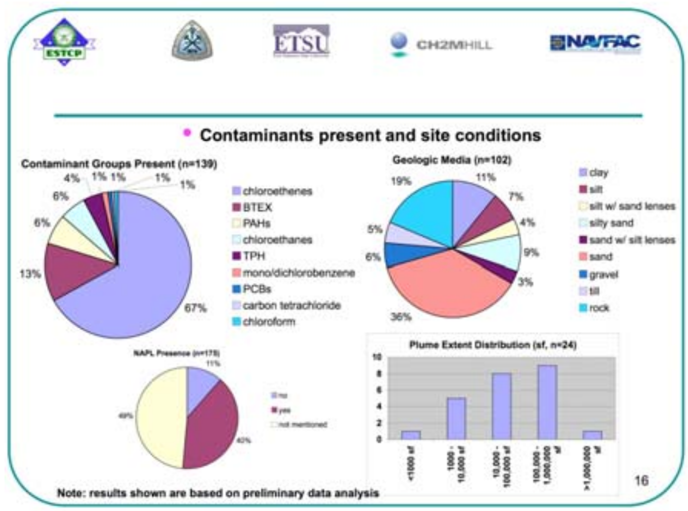
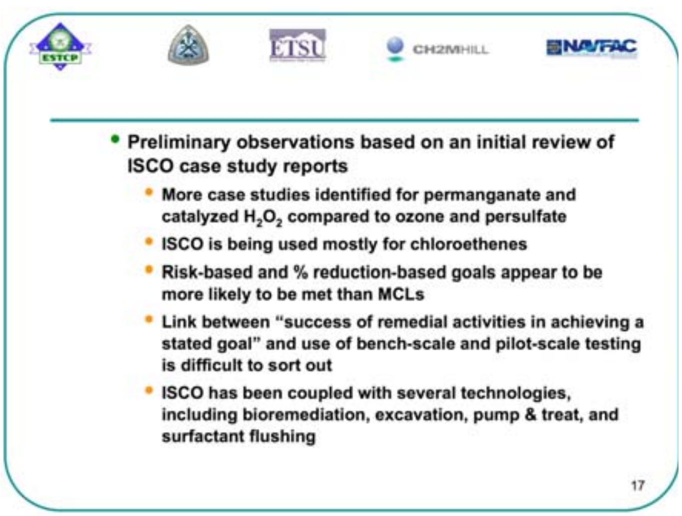
A.6. In Situ Chemical Oxidation for Ground Water Remediation – Technology Practices Manual. ER-0623 (Project Overview based on Winter IPR Feb '07). Presentation by Bob Siegrist and Michelle Crimi (*continued*).

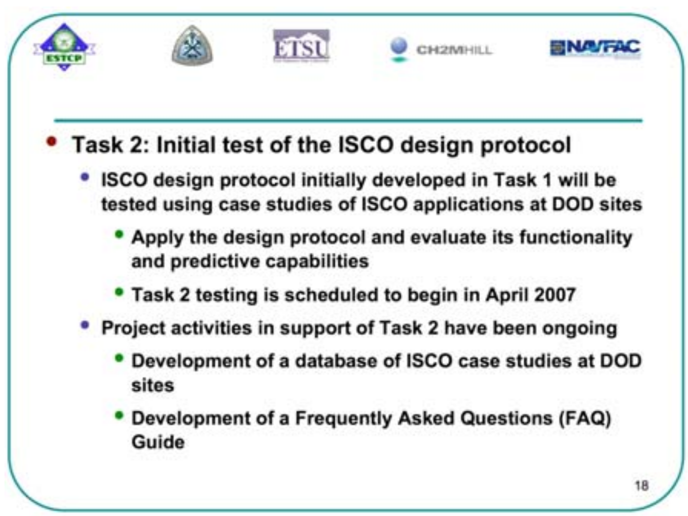












A.6. In Situ Chemical Oxidation for Ground Water Remediation – Technology Practices Manual. ER-0623 (Project Overview based on Winter IPR Feb ’07). Presentation by Bob Siegrist and Michelle Crimi (*continued*).

- Database of project information for ISCO sites both completed and in progress
  - Database will enable focused evaluation of ISCO projects
    - Types of contaminants, geologic settings, remediation goals, impacts of site characterization, etc.
    - Summary statistics and customized searches
  - This new database is being facilitated by leveraging with complementary database efforts
  - Status
    - Database design document has been completed
    - Database preparation is ongoing

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- Example of summary statistics that will be generated from the new ISCO database

Summary Statistics
Groundwater PCE concentration greater than 0, predominan t geologic material of sand, contaminated volumes between 5000 and 15000 cubic feet

n=29

% Mass Reduction	*Cost (US $)*	*Contaminant Rebound (y/n)*	*Deli very Method*
			0.33 Lance Injection (n=11)
88 mean	1200 mean	0.63 mean	0.67 Well Injection (n=10)
70 min	700 min	0 min	0.00 Well Recirculation (n=6)
98 max	5000 max	1 max	0.00 Deep Soil Mixing (n=1)
29 n	28 n	24 n	0.00 Hydrauli c Fracturing (n=1)

Note: This table presents hypothetical summary statistics and is intended for illustration purposes only.

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- List of Frequently Asked Questions (FAQs) with responses
  - Resource for site managers to enable informed decision-making for site-specific consideration and engineering of ISCO
  - Preliminary list of FAQ’s has been developed covering:
    - Screening
    - Characterization
    - Oxidant selection and delivery
    - Coupling
    - Treatability studies
    - Design, construction, and implementation
    - Operation and performance monitoring

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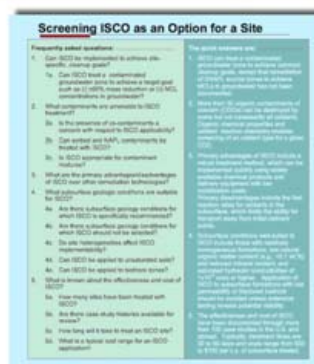
- Optional formats for a FAQ Guide have been considered
  - Example page is shown here



22

- Tasks being continued and initiated in 2007
  - Tasks 1 and 2: Protocol development and initial testing will continue
  - Tasks 3 and 4: Site selection and field testing of an ISCO design protocol will be initiated in 2007
    - Task 3 will identify sites for testing a design protocol for ISCO
      - Strategically select sites to fill identified data gaps and incorporate a range of site attributes
        - e.g., field conditions, infrastructure, collaborations
      - Potential sites were identified early in the project and these and others are under consideration
        - Focused efforts were initiated in January 2007
    - Task 4 will involve field application and evaluation of the ISCO design protocol at one or more DOD sites
      - Efforts are scheduled to begin in July 2007

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The Workshop

- This ISCO Technology Practices Workshop is very important
  - The insights gained from the workshop will directly support development of a rational ISCO design protocol and frequently asked questions (FAQ) guide, both of which are being developed during ESTCP project ER-0623
- We appreciate your participation and look forward to the interactions during the workshop
- Opportunities also exist for input as ESTCP project ER-0623 continues
- Questions…?

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B. Site Scenarios and Views about ISCO Design and Performance

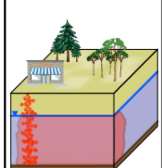
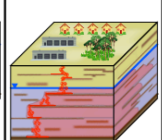
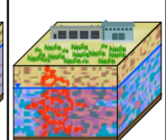
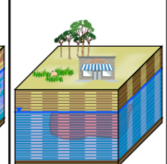
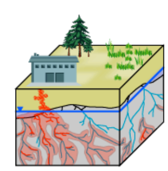
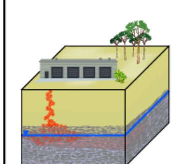
B.1. Description of Contaminated Sites and Survey of ISCO Applicability

At the end of Day 1, six contaminated sites were presented to the Workshop participants as representative, and in some cases challenging, site scenarios where ISCO might be considered for remediation. These contaminated site scenarios spanned a wide range of hydrogeologic, geochemical and contaminant conditions and were developed in part based on the information acquired through the analysis of case studies. A summary of the SCM including the subsurface conditions and contaminant conditions is presented in Table B.1. In Figures B.1 to B.6, further details are provided for each of the six scenarios.

With the characterization data provided for each site scenario, the Workshop participants were given a homework assignment to be completed between the end of Day 1 and beginning of Day 2. This homework assignment included a series of questions for each scenario that encompassed the assessed viability of ISCO at the site, preferred application approaches, and potential for success in achieving different remediation goals given different remediation timeframes and cost constraints (Figure B.7). Survey forms allowed respondents to give a response with respect to the ability of ISCO to achieve different remediation goals as presented in Table B.2. The response forms were kept anonymous but respondents were asked several questions to aid in qualifying their professional backgrounds and experience.

All Workshop attendees were presented with the opportunity to fill out questionnaires; all members of the ESTCP ER-0623 project team (the Workshop hosts) recused themselves from answering the survey. Workshop participants were asked to complete the homework assignment and turn it in at the beginning of Day 2 so that the results could be tabulated and shared with all in attendance.

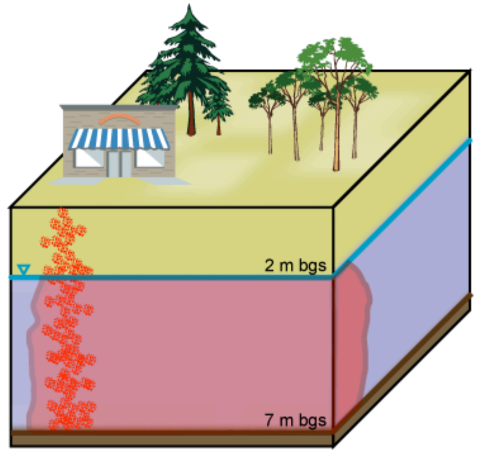
Table B.1. Summary details concerning site characteristics for each of the six site scenarios.[1]

Scenario parameter	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	Scenario 6
Site conceptual model						
Hydrogeology						
Morphology	Unconsolidated homogeneous	Unconsolidated heterogenous	Unconsolidated heterogeneous	Unconsolidated homogeneous	Fractured igneous rock	Fractured sedimentary rock
Permeability	Permeable	Permeable	Impermeable	Impermeable	Low matrix porosity	High matrix porosity
Velocity (m/day)	1.5	0.1	0.01	0.01	0.01	0.2
Geochemistry						
foc	0.0095	0.003	0.005	0.03	0.0005	0.005
pH	6.5	7.0	7.5	6.5	6.0	8.0
Eh (mV)	150	100	-150	-100	-200	-100
Contaminant conditions						
Primary COCs (phase)	Chloroethene (DNAPL)	Chloroethene (DNAPL)	Chloroethane (DNAPL)	Chloroethene (aqueous)	Chloroethene (DNAPL)	BTEX and MTBE (LNAPL)
Approximate age of spill	2 years	15 years	20 years	15 years	20 years	5 years
Source zone area (m^2)	400	8000	1000	n/a	2000	150
Plume area (m^2)	20000	80000	3000	500	13000	7000
Depth of COCs (m bgs)	7	50	15	6	30	12

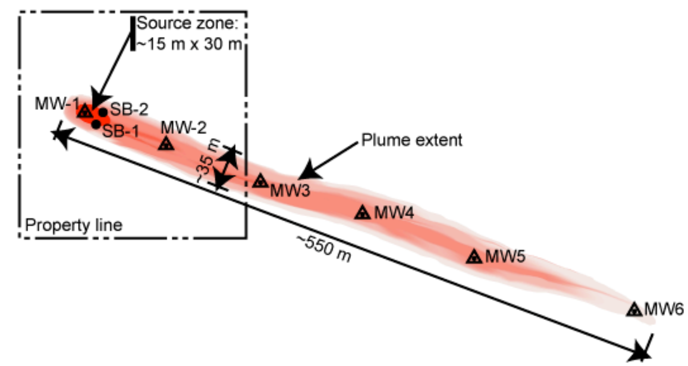
[1] Refer to Figures B.1 to B.6 for detailed site information.

Scenario One

Scenario one consists of a former dry-cleaning operation in Florida where a leaking PCE storage tank has resulted in a spill into a homogenous permeable sandy soil. The spill was discovered 2 years ago. Groundwater at the site is encountered at 2 m bgs and an impermeable aquitard is encountered at 7 m bgs. Soil cores taken on the property have indicated the presence of DNAPL phase PCE as residual saturation in a source zone that is approximately 15 m x 30 m, and extends the full depth of the aquifer. However, no evidence of pooled DNAPL has been found, and no contamination is suspected below the aquitard. Groundwater velocity is very high at this site with an average pore velocity of 1.5 m/day moving in a southeasterly direction. A plume approximately 1/2 km long has migrated off-site and is threatening nearby drinking water supply wells. In the down-gradient plume areas, low concentrations of TCE and cis-1,2-DCE have been discovered, indicating that natural reductive dechlorination may be occurring. However, no vinyl chloride has been detected. The property line intersects the plume about 130 m from the site of the spill. A site conceptual model and site plan are presented at right, and limited characterization data below.



Site conceptual model: (not to scale)



Site plan

Scale: 1:4000

Major site parameters

Hydrogeology	
Geologic setting	Unconsolidated porous media
Media type	Silica sand
Morphology	Homogeneous
Hydraulic conductivity (cm/s)	10^{-3}
Hydrology	Saturated unconfined aquifer
Depth to groundwater surface	2 m bgs
Depth to impermeable layer (bottom of aquifer)	7 m bgs
Velocity	1.5 m/day
Geochemistry	
Organic carbon content (foc)	0.0095
Alkalinity	60 mg/L as $CaCO_3$
pH	6.5
Eh	0.15 V
Temperature	25 C
Dissolved iron	0.2 µg/L
Dominant iron mineralogy	Geothite
Contaminant hydrology	
Contaminant	PCE residual DNAPL, dissolved Phase TCE and 1,2-cis-DCE
Source zone size	400 m^2
Plume size	20000 m^2
Maximum depth of contamination	7 m bgs

Site characterization data

Groundwater sampling analytical data

Sample Location		MW-1	MW-2	MW-3	MW-4	MW-5	MW-6	SB-1	SB-1	SB-2	SB-2
Sample Depth	(m bgs)	4 - 7	2 - 7	2 - 7	2 - 7	2 - 7	2 - 7	2 - 3	6 - 7	2 - 3	6 - 7
PCE concentration	(µg/L)	260,000	100,000	26,000	10,000	1,800	10	310,000	290,000	148,000	160,000
TCE concentration	(µg/L)	250	500	1,100	2,000	900	5	170	300	280	400
cis-DCE concen.	(µg/L)	100	260	900	1,900	2,800	50	90	180	75	50

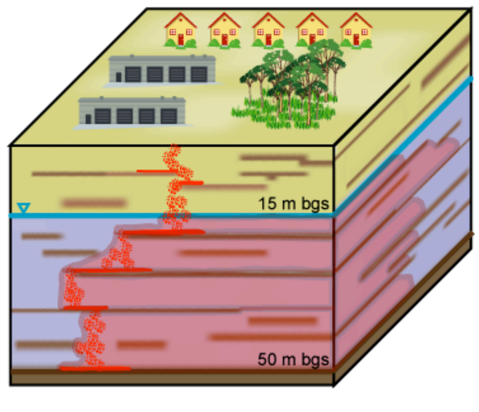
Soil sampling analytical data

Sample Location		MW-1	MW-1	MW-2	SB-1	SB-1	SB-2	SB-2
Sample Soil Description		Sand	Sand	Sand	Sand	Sand	Sand	Sand
Sample Depth	[m bgs]	2.5	6.5	6.5	2.5	6.5	2.5	6.5
PCE concentration	[mg/kg]	23,000	31,000	500	29,000	26,500	27,000	19,000
TCE concentration	[mg/kg]	ND	ND	2	2	6	4	5
cis-DCE concen.	[mg/kg]	1	ND	1	3	ND	1	6

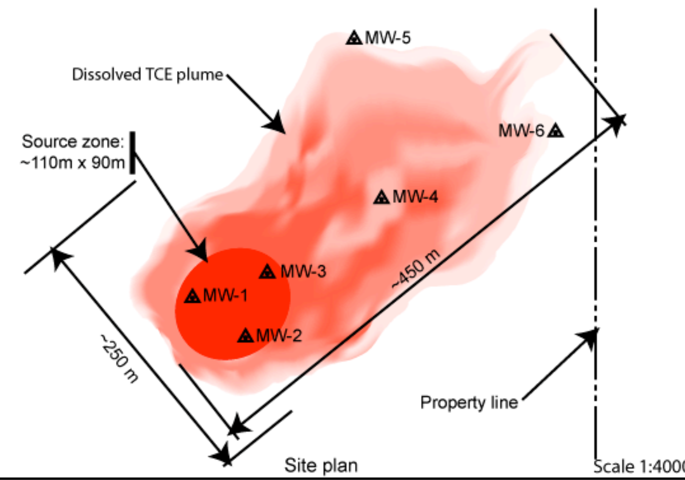
Figure B.1. Site characterization data for contaminated site scenario 1.

Scenario Two

Scenario two consists of an active military facility in Missouri where a large volume of TCE was released into the subsurface environment, along with minor amounts of chlorobenzene. Releases discontinued 20 years ago. A large volume of DNAPL phase TCE is known to persist within a source zone at the site. The geologic setting of the site is fine sandy soil with thin clay-silt lenses interbedded. Soil cores taken during characterization of the site determined DNAPL was present at both residual saturation as well as in pools up to 3 cm thick on top of the clay-silt lenses. Contamination extends to 50 m bgs, where a thick clay aquitard prevents further downward DNAPL migration. A contaminated groundwater plume extends down-gradient approximately 1/2 km, but does not extend beyond the facility boundaries. The average pore velocity of the site is 10 cm/day in a northeasterly direction, but varies seasonally. The interaction of seasonal velocity variation combined with low permeability clay-silt lenses has resulted in a complex three-dimensional plume shape. A large mass of TCE is suspected to have sorbed into these lenses. Low concentrations of chlorobenzene have only been observed within the source area. A site plan, site conceptual model and limited characterization are given below.



Site conceptual model (not to scale)



Site plan

Major site parameters

Hydrogeology	
Geologic setting	Unconsolidated porous media
Media type	Silt with sand stringers
Morphology	Layered heterogeneous
Hydraulic conductivity (cm/s)	10^{-4} in fine sand 10^{-6} in clay-silt stringers
Hydrology	Saturated unconfined aquifer
Depth to groundwater surface	15 m bgs
Depth to aquitard	50 m bgs
Average pore velocity	0.1 m/day
Geochemistry	
Organic carbon content (foc)	0.015 in silt, 0.003 in uncontaminated sand
Alkalinity	80 mg/L as $CaCO_3$
pH	7.0
Eh	0.10 V
Temperature	15 C
Dissolved Iron	0.2 µg/L
Dominant iron mineralogy	Geothite
Contaminant hydrology	
Contaminant	Residual and pool DNAPL TCE low levels of chlorobenzene
Source zone size	8000 m^2
Plume size	80000 m^2
Maximum depth of contamination	50 m bgs

Site characterization data

Groundwater sampling analytical data

Sample location		MW-1	MW-1	MW-1	MW-2	MW-2	MW-3	MW-4	MW-5	MW-6
Sample depth	(m bgs)	15 - 18	30 - 33	47 - 50	15 - 18	47 - 50	15 - 18	15 - 18	15 - 18	15 - 18
TCE concentration	(µg/L)	950,000	250,000	890,000	660,000	780,000	780,000	7,000	100	85
Chlorobenzene	(µg/L)	180	100	180	260	50	900	ND	ND	ND

Soil sampling analytical data

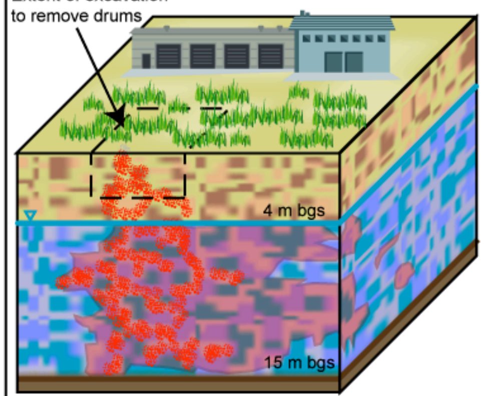
Sample location		MW-1	MW-1	MW-2	MW-2	MW-2	MW-3	MW-3
Sample soil description		Sand	Silt	Silt	Sand	Silt	Sand	Silt
Sample depth	[m bgs]	20	40	20	40	50	20	40
TCE concentration	[mg/kg]	90,000	31,000	45,000	60,000	34,500	32,000	19,000
Chlorobenzene	[mg/kg]	900	550	800	ND	1200	100	1400

Figure B.2. Site characterization data for contaminated site scenario 2.

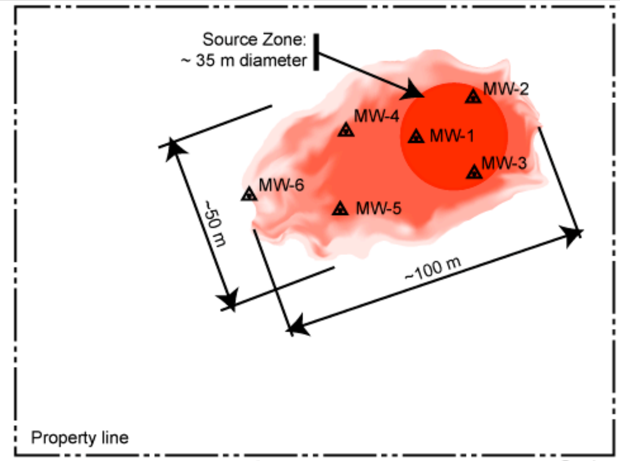
Scenario Three

Scenario three consists of a former industrial facility which included a metal degreasing operation using 1,1,1-TCA . Drums containing waste solvent were buried onsite, but were removed 20 years ago. Site characterization revealed that 1,1,1-TCA was present below the former burial site in residual DNAPL form. Since discovery 20 years ago, hydraulic containment has been used to keep the associated groundwater plume from migrating offsite. Recent redevelopment of surrounding areas has renewed interest in remediating the contaminant source zone, attaining site closure and developing the property.

Site geology consists of glacial outwash composed of sands, silts and clays in a random heterogeneous distribution. Residual DNAPL extends to the full depth of the aquifer, which is bounded by a bedrock aquitard at 15 m bgs. Contamination of the bedrock is not suspected. Groundwater average linear velocity at the site is approximately 1 cm/day in a westerly direction, but varies within the heterogeneous formation. Low levels of 1,1-DCA, 1,1-DCE, and vinyl chloride in the distal plume areas indicate a low rate of biodegradation is occurring, but is insufficient to contain the plume without pump and treat.



Site conceptual model (not to scale)



Site plan

Scale: 1:1500

Major site parameters

Hydrogeology	
Geologic setting	Unconsolidated porous media
Media type	Glacial outwash
Morphology	Randomly distributed sands, silts and clays
Hydraulic conductivity (cm/s)	10^{-5}
Hydrology	Saturated unconfined aquifer
Depth to groundwater surface	4 m bgs
Depth to aquitard	15 m bgs
Average pore velocity	0.01 m/day
Geochemistry	
Organic carbon content (foc)	0.005
Alkalinity	100 mg/L as $CaCO_3$
pH	7.5
Eh	-0.15 V
Temperature	10 C
Dissolved Iron	250 µg/L
Dominant iron mineralogy	Goethite
Contaminant hydrology	
Contaminant	1,1,1-TCA residual DNAPL dissolved phase 1,1-DCA, 1,1-DCE and VC.
Source zone size	1000 m^2
Plume size	3000 m^2
Maximum depth of contamination	15 m bgs

Site characterization data

Groundwater sampling analytical data

Sample location		MW-1	MW-1	MW-2	MW-2	MW-2	MW-3	MW-3	MW-4	MW-5	MW-6
Sample depth	(m bgs)	4 - 7	10 - 13	4 - 7	10 - 13	12 - 15	4 - 7	12 - 15	4 - 9	4 - 9	4 - 9
TCA concentration	(µg/L)	990,000	120,000	265,000	710,000	180,000	91,000	310,000	32,000	27,000	190
DCA concentration	(µg/L)	7,200	500	1,100	2,000	900	5	170	300	280	10
1,1-DCE conc.	(µg/L)	9,500	300	5,500	11,000	7,000	270	5,600	700	580	55
VC conc.	(µg/L)	5,900	260	900	1,900	3,100	50	80	180	75	4

Soil sampling analytical data

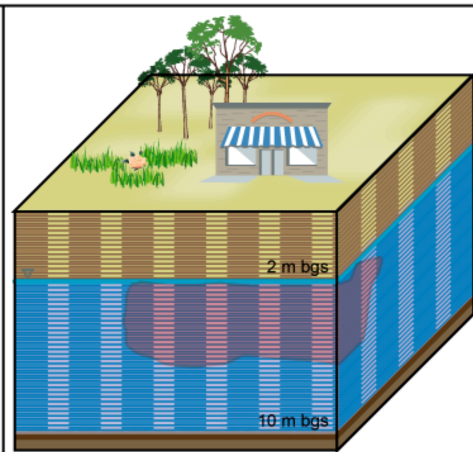
Sample location		MW-1	MW-1	MW-2	MW-2	MW-2	MW-3	MW-3
Sample soil description		Silt	Sand	Sand	Silt	Sand	Sand	Clay
Sample depth	(m bgs)	4.5	10	5	10	14	5	12
TCA concentration	(mg/kg)	18,900	900	3,000	29,000	34,500	1,100	20,000
DCA concentration	(mg/kg)	110	3	2	150	6	3	90
1,1-DCE conc.	(mg/kg)	600	50	65	740	ND	2	ND
VC conc.	(mg/kg)	1	ND	1	3	ND	2	ND

Figure B.3. Site characterization data for contaminated site scenario 3.

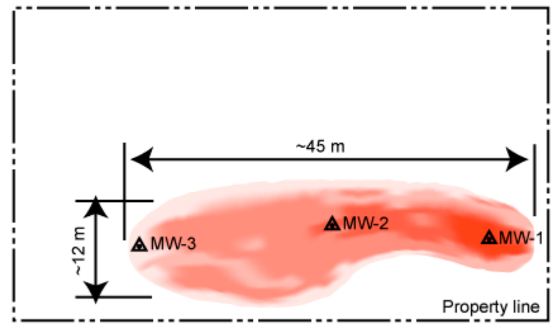
Scenario Four

Scenario four consists of a recently discovered PCE vapor and groundwater plume underlying a dry-cleaning operation in New York. During a phase II investigation, it was discovered that free phase PCE leaked from a pipe and ponded under a building foundation. The duration of the spill is unknown, but the dry-cleaner occupied the building for 15 years. A subsequent characterization study determined that the free phase PCE was unable to penetrate the site's low permeability clay. However, a vapor and groundwater plume developed underneath the PCE pool. The building and pool have since been removed.

Site hydrogeology consists of homogeneous clay with groundwater encountered at 2 m bgs, and bedrock at 10 m bgs. Groundwater average pore velocity is approximately 0.5 cm/day in a westerly direction. Characterization data indicate that the groundwater plume only extends to 6 m bgs, and has not migrated offsite. However, the plume does threaten the southern property line. Remediation is required to address this threat, as well as facilitate a possible property transfer. Results from a characterization study are presented below.



Site conceptual model (not to scale)



Site Plan

Scale: 1:500

Major site parameters

Hydrogeology	
Geologic setting	Unconsolidated porous media
Media type	Clay
Morphology	Homogeneous
Hydraulic conductivity (cm/s)	10^{-7}
Hydrology	Saturated unconfined aquifer
Depth to groundwater surface	2 m bgs
Depth to aquitard	10 m bgs
Average pore velocity	0.01 m/day
Geochemistry	
Organic carbon content (foc)	0.03
Alkalinity	80 mg/L as $CaCO_3$
pH	6.5
Eh	-0.10 V
Temperature	10 C
Dissolved Iron	35 mg/L
Dominant iron mineralogy	Siderite / Goethite
Contaminant hydrology	
Contaminant	PCE in dissolved and sorbed phases
Source zone size	None
Plume size	500 m^2
Maximum depth of contamination	6 m bgs

Site characterization data

Groundwater sampling analytical data

Sample location		MW-1	MW-1	MW-2	MW-3
Sample depth	(m bgs)	2 - 5	7 - 10	2 - 5	2 - 5
PCE concentration	(μg/L)	450	1.5	95	7.0
TCE concentration	(μg/L)	11	ND	2	ND

Soil sampling analytical data

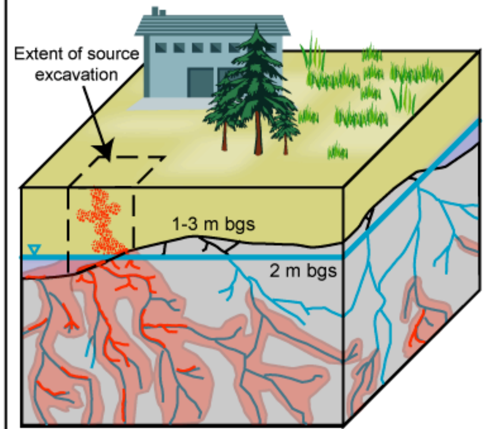
Sample location		MW-1	MW-1	MW-1	MW-2	MW-2	MW-3
Sample soil description		Clay	Clay	Clay	Clay	Clay	Clay
Sample depth	(m bgs)	2	2.5	3	2	3	2
PCE concentration	(mg/kg)	4.1	2.5	0.5	0.9	ND	ND
TCE concentration	(mg/kg)	ND	ND	ND	ND	ND	ND

Figure B.4. Site characterization data for contaminated site scenario 4.

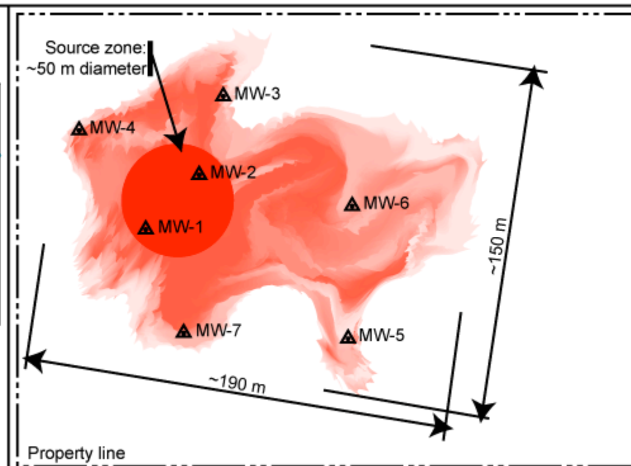
Scenario Five

Scenario five is an active industrial facility that used TCE as a solvent in a degreasing operation. An tank farm was used to store TCE, and a leak was discovered in one of the tanks in 1989. A RCRA facility investigation at the time revealed a large mass of TCE DNAPL had been released into the subsurface beneath the tank farm. The tank was removed and a groundwater pump and treat system installed to contain the contaminant plume. The contaminant source zone was removed to bedrock. Due to tailing of contaminant recovery with the pump and treat system, source zone treatment is being investigated as a possible way to speed site closure.

Site hydrogeology consists of a fractured granite monolith overlain by 1-3 m of permeable sand. The fracture pattern is irregular and DNAPL is known to have permeated into the fractures The average depth of the phreatic surface is 2 m bgs, and the contaminated groundwater plume is primarily within the fractured rock monolith. Rock cores have shown that TCE has diffused into the rock matrix where DNAPL or contaminated groundwater was present. Groundwater velocity and direction varies with the fracture patterns and apertures, but is on generally easterly at about 1 cm/day.



Site conceptual model (not to scale)



Site plan

Scale: 1:2000

Major site parameters

Hydrogeology	
Geologic setting	Consolidated bedrock
Media type	Fractured granite overlain by sandy soil
Morphology	Irregular fracture pattern
Hydraulic conductivity (cm/s)	10^{-4} in fractures, sand
Hydrology	Saturated unconfined aquifer
Depth to groundwater surface	2 m bgs
Depth to aquitard	n/a
Average pore velocity	0.01 m/day
Geochemistry	
Organic carbon content (foc)	0.0005
Alkalinity	40 mg/L as $CaCO_3$
pH	6.0
Eh	-0.20 V
Temperature	15 C
Dissolved Iron	2.5 ug/L
Dominant iron mineralogy	Pyrite
Contaminant hydrology	
Contaminant	TCE DNAPL
Source zone size	2000 m^2
Plume size	13000 m^2 highly heterogeneous
Maximum depth of contamination	30 m bgs

Site characterization data

Groundwater sampling analytical results

Sample location		MW-1	MW-1	MW-1	MW-1	MW-2	MW-2	MW-2	MW-3	MW-3
Sample depth	(m bgs)	3 - 6	13 - 16	23 - 26	33 - 36	3 - 6	13 - 16	23 - 26	3 - 6	13 - 16
TCE concentration	(µg/L)	45,000	27,000	39,000	4	66,000	7,800	35,000	18	1,500
Sample location		MW-3	MW-4	MW-4	MW-5	MW-5	MW-6	MW-6	MW-7	MW-7
Sample depth	(m bgs)	23 - 26	13 - 16	23 - 26	13 - 16	23 - 26	13 - 16	23 - 26	13 - 16	23 - 26
TCE concentration	(µg/L)	650	180	56	6	89	55	50	360	85

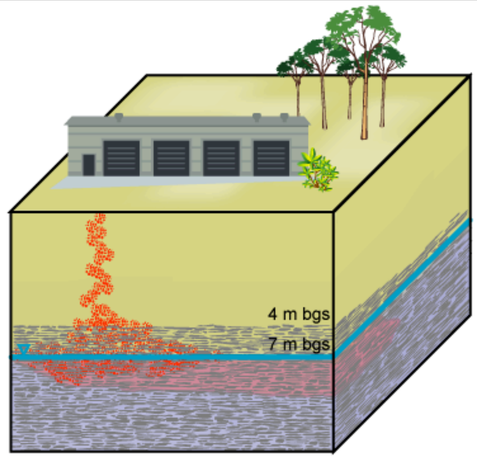
No data on concentrations in rock matrix available

Figure B.5. Site characterization data for contaminated site scenario 5.

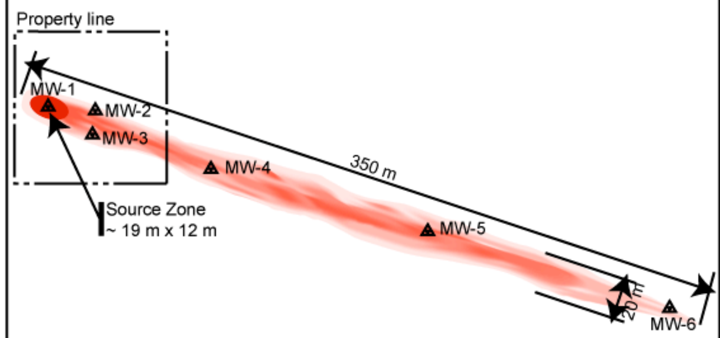
Scenario Six

Scenario six entails a former gas station property in which a phase II ESA turned up evidence of contamination under USTs that contained gasoline and diesel fuel. The gas station operated the property from 1953 to 1995, but the age of the leak is unknown. Site characterization detected LNAPL in residual form in the vadose zone and in a smear zone along the phreatic surface. No significant LNAPL pools were found.

Site hydrogeology consists of a shale aquifer overlain by a permeable sand. The shale is encountered at a depth of 4 m, bgs, and the phreatic surface is entirely within the shale at a depth of 7 m. The shale is highly fractured along it bedding planes, which are horizontal, and the aquifer is anisotropic. The phreatic surface elevation is known to vary about 4 m on a yearly basis. Groundwater average pore velocity is 20 cm/day in a southeasterly direction. Despite annual variations in the groundwater table, the flow direction in this aquifer is relatively stable. A BTEX and MTBE plume has been found to migrate off-site approximately 1/3 km, and is threatening water supply wells at neighboring properties. The maximum depth of the plume is 12 m bgs. Remediation is required to address the groundwater plume, but source zone reduction is also being considered.



Site conceptual model (not to scale)



Site plan

Scale: 1:2000

Major site parameters

Hydrogeology	
Geologic setting	Consolidated bedrock
Media type	Fractured Shale overlain by sandy soil
Morphology	Highly fractured along bedding planes
Hydraulic conductivity (cm/s)	Anisotropic, 10^{-4} along bedding planes, 10^{-6} perpendicular to planes
Hydrology	Saturated unconfined aquifer
Depth to groundwater surface	7 m bgs
Depth to aquitard	n/a
Average pore velocity	0.2 m/day
Geochemistry	
Organic carbon content (foc)	0.005
Alkalinity	200 mg/L as $CaCO_3$
pH	8.0
Eh	-0.10 V
Temperature	10 C
Dissolved Iron	1 ug/L
Dominant iron mineralogy	Goethite
Contaminant hydrology	
Contaminant	Gasoline and diesel LNAPL smear zone, Aqueous BTEX and MTBE plume
Source zone size	150 m^2
Plume size	7000 m^2
Maximum depth of contamination	12 m bgs

Site characterization data

Groundwater sampling analytical data

Sample location		MW-1	MW-1	MW-1	MW-2	MW-2	MW-3	MW-3	MW-4	MW-4	MW-5	MW-5	MW-6	MW-6
Sample depth	(m bgs)	4 - 5	7 - 8	10 - 11	4 - 6	10 - 12	4 - 6	10 - 12	4 - 6	10 - 12	4 - 6	10 - 12	4 - 6	10 - 12
Benzene conc.	(µg/L)	9,400	8,900	4	5,000	260	4,750	310	480	375	30	50	5	4
MTBE conc.	(µg/L)	200	250	18	270	60	900	80	1,200	1,100	1,400	500	60	100

No data from sampling of rock matrix available

Figure B.6. Site characterization data for contaminated site scenario 6.

	Question	Scenario number:					
1.	Given this scenario, would you consider using ISCO as a remediation technology? (circle)	yes	no				
2.	Which oxidant(s) would you consider potentially viable for this site? (circle all that apply)	H_2O_2	MnO_4^-	O_3	$S_2O_8^{2-}$		
3.	What distribution methods would you consider potentially viable at this site? (circle all that apply)	Well injection	Probe injection	Well recirculation	Sparging	Fracturing	Other: ______
4.	What delevery strategy(s) would you consider?	Single injection round	Multiple injection rounds	Continuous injection	Coupled approach		
5.	Which category of conditions present the most challenge for this scenario? (circle one)	Hydrogeological	Geochemical	Contaminant conditions			
	For the category selected above, identify the condition causes the most challenge for this scenario. (circle one, if desired choice is not listed, please specify in the comments section)	Media type Heterogeneity Hydraulic conductivity Depth of treatment area	Organic carbon content System pH System Eh Alkalinity	Contaminant type Contaminant mass/conc. Contaminant distribution Size of contaminated area			
6.	How many of the remediation goals below appear achievable using ISCO at for this scenario?	Circle the answer that best describes how you feel about the likelihood for successfully meeting the goal. For goals G1-G5, specify the highest reduction you think is achievable.					
G1	Risk reduction (GW exposure pathways only) Highest achievable risk reduction	yes 50% 90% 99% 99.9%	no (<50%)	Too difficult to tell: reason: ______			
G2	Contaminant mass reduction Highest achievable mass reduction	yes 50% 90% 99% 99.9%	no (<50%)	Too difficult to tell: reason: ______			
G3	Mass flux reduction Highest achievable mass flux reduction	yes 50% 90% 99% 99.9%	no (<50%)	Too difficult to tell: reason: ______			
G4	Site wide concentration reduction Highest achievable concentration reduction	yes 50% 90% 99% 99.9%	no (<50%)	Too difficult to tell: reason: ______			
G5	Concentration reduction followed by 10 years MNA Highest achievable concentration reduction w/MNA	yes 50% 90% 99% 99.9%	no (<50%)	Too difficult to tell: reason: ______			
G6	MCLs at a property line (see site plans)	yes	no	Too difficult to tell: reason: ______			
G7	MCLs site wide	yes	no	Too difficult to tell: reason: ______			
7.	Consider the additional constraints below	Could the remediation goals below be achievable considering constraints C1-C6? (please circle yes / no for each goal-contstraint pair)					
	Remediation goal ======================>	90% risk reduction	90% mass reduction	90% flux reduction	90% conc. reduction	MCLs at property line	MCLs site wide
C1	Remediation for property sale within 5 years	Y N	Y N	Y N	Y N	Y N	Y N
C2	Remediation for property sale within 1 year	Y N	Y N	Y N	Y N	Y N	Y N
C3	Remediation for property sale within 4 months	Y N	Y N	Y N	Y N	Y N	Y N
C4	Remediation budget not to exceed $1,000,000	Y N	Y N	Y N	Y N	Y N	Y N
C5	Remediation budget not to exceed $500,000	Y N	Y N	Y N	Y N	Y N	Y N
C6	Remediation budget not to exceed $100,000	Y N	Y N	Y N	Y N	Y N	Y N
8.	Do you have personal experience working with sites similar to this?	Yes	No				
9.	What is the basis for your choices? (circle one)	Information from colleagues	Existing literature or guidance	Personal judgment	Personal experience		
10.	What is your background?	Remedial project manager / Site owner	Consultant	Academic / research	Technology vendor		
11.	Comments? (continue on extra leaves if necessary)						

Figure B.7. Site scenario questionnaire completed by Workshop participants.

Table B.2. Definition of remediation goals and constraints for the scenario survey.

Goal or constraint	Definitions	
Remediation goal type	G1: Risk reduction	
	G2: Mass reduction	
	G3: Mass flux reduction	
	G4: Concentration reduction	
	G5: Concentration reduction following 10 years MNA	
	G6: MCLs at a property line	
	G7: MCLs site wide	
Remediation constraints	Constraint type	Specific goal for each constraint
	C1: Remediation for property sale in 5 years	90% risk reduction
	C2: Remediation for property sale in 1 year	90% mass reduction
	C3: Remediation for property sale in 4 months	90% flux reduction
	C4: Remediation budget not to exceed $1,000,000	90% concentration reduction
	C5: Remediation budget not to exceed $500,000	MCLs at a property line
	C6: Remediation budget not to exceed $100,000	MCLs site wide

B.2. Initial Plenary Discussion about ISCO Applicability to Each of the Six Site Scenarios

At the beginning of Day 2, the completed questionnaire forms were turned in by the Workshop participants. Prior to any analysis of the responses on the questionnaire forms, there was a period of open discussion among the Workshop participants regarding the applicability of an ISCO technology to each of the six contaminated sites. A question posed to the Workshop participants was: *For each of the six site scenarios that were circulated, would you consider ISCO as a remediation technology at the screening stage?* Following this open discussion, a second question was posed to the Workshop participants: *Given the information provided for each scenario, what additional information is needed?* The collective views expressed during open discussion period are highlighted previously in Section 2.5 (Tables 2.3 and 2.4).

B.3. Analysis of Survey Responses for ISCO Applicability to the Six Site Scenarios

Following the Workshop, more detailed analysis was completed by CSM (Ben Petri) to interpret the surveys completed by a total of 21 Workshop participants and to identify any trends in the responses to the questions posed regarding each of the six site scenarios. This section summarizes an analysis completed while additional details may appear in a forthcoming publication.

B.3.1. Respondent Views on the Use of ISCO as a Technology for Each Scenario

A number of scenario specific trends were noted within the analysis and these are outlined below.

B.3.1.1. Views on Use of ISCO. Scenario specific trends yield information about the applicability of ISCO to site-specific conditions.

- The majority (>50%) of all respondents indicated that they would consider ISCO as a remediation technology for all six scenarios. The proportion of respondents answering affirmatively for considering ISCO was lowest for scenario 4 (homogeneous-impermeable), followed by scenarios 3, 5, and 6 (heterogeneous-impermeable, fractured rock with low matrix porosity, fractured rock with high matrix porosity, respectively). For scenario 1 (homogeneous-permeable), consensus was achieved that ISCO should be considered.

- Respondents indicated that scenarios 1 & 4 could be expected to have the highest performance, followed by scenarios 3 & 6. Scenarios 2 and 5 were predicted to have the lowest overall performance.
    - Due to the variation in hydrology, geochemistry and contaminant conditions from one scenario to the next, pinpointing the principal causes of this effect can be difficult. However, both scenarios 1 & 4 were homogeneous, with the differences being permeable with a high contaminant mass density (DNAPL) and impermeable with a low contaminant mass density. Thus the low contaminant mass density of scenario 4 may have been able to offset the challenges to ISCO posed by the low permeability of this system. Furthermore, while scenario 4 had the most "no to ISCO" responses, those who did respond positively to evaluating ISCO at this site were very optimistic in their responses that this site could be treated.
    - Scenarios 2 and 5 (heterogeneous permeable and fractured rock low matrix porosity) were singled out as being the least positive of the scenarios in terms of performance, This was most likely due to the large nature of these sites, as well as the high contaminant mass densities, which have both been commonly indicated to be disadvantageous to ISCO. The heterogeneous nature of the sources and plumes also likely contributed.
    - Scenarios 3 and 6 (heterogeneous-impermeable and fractured rock with high matrix porosity) were intermediate in terms of optimism of responses. This is possibly due to the smaller size of these sites' source zones (and plume in scenario 3), which probably makes them more treatable. The random heterogeneity in the impermeable media and the matrix porosity in the fractured rock may also improve oxidant distribution ability to some degree within the otherwise impermeable or consolidated media. However, this is probably offset in survey responses by the different contaminants in these systems as mentioned previously which are susceptible to degradation by only certain oxidants, and the high contaminant mass densities in both systems, which may have generated more negative responses.
- Scenario 4 (homogeneous impermeable) was considered the most treatable within monetary or timeframe project constraints, while scenarios 2 and 5 were the least treatable within monetary or timeframe constraints.
    - The apparent amenability of scenario 4 to be treated within project monetary or timeframe constraints is most likely due to the small areal extent of the contamination, as well as the low contaminant mass densities (only dissolved and sorbed phases are present), despite the low permeability of this system. Mean response for remediation costs and timeframes at this site ranged from $400,000 - $500,000 and 9-12 months for various non-MCL based remediation goals.
    - Scenarios 2 and 5 were widely agreed to be the least treatable in within the given constraints. The lack of treatability within timeframe constraints may apparently be due to the large mass as well as the nature of contaminant architecture present at these sites, while the inability to met budgetary constraints is likely due to the large aerial size, mass of contaminant and long operating time anticipated for these sites. The mean response in terms of remediation costs and timeframes at both these sites were anticipated to exceed $1,000,000 and 5 years regardless of the remediation goal pursued. Concentration reduction after ISCO application followed by 10 years of MNA was indicated to be the goal most likely to be attained for these sites, followed by mass flux reduction based goals.

- Scenarios 1 & 6 were more treatable within monetary constraints (C4 and C5) than timeframe constraints (C1 and C2). While the mean response values fell into a range hovering around the C2 and C5 constraints, the spread in values was wider and less certain for timeframes than costs. Scenario 1 mean responses varied from $475,000-$650,000 and 11-19 months, while scenario 6 mean responses varied from $425,000-$500,000 and 12-39 months with the value depending on the specific goal pursued (see Table B.5).

- Some degree of "no to ISCO" responses for some of these scenarios may be more due to oxidant specific preferences of some of the respondents, and the reactivity of those oxidants with site COCs. For example, scenario 3 contained chloroethanes, and site 6 contained BTEX and MTBE, both of which have limited reactivity with permanganate. Thus consultants or vendors familiar only with permanganate may have been more likely to say no to considering ISCO in these scenarios.

<u>B.3.1.2. Ability of ISCO to Achieve Remediation Goals.</u> Valuable information about the ability of ISCO to achieve certain remediation goals was noted based on the survey. Although each survey answer was a specific response to one scenario or the other, many of the trends herein were found to be applicable across the various scenarios, and thus indicate a main effect between ISCO's ability to attain certain remediation goals.

- For goals G1-G5, where performance can be quantitatively assessed (<50, 50, 90, 99, or 99.9 % reduction) the following trends were noted:
  - Goal G5, Concentration reduction following ISCO and 10 years MNA was consistently indicated as likely to achieve the highest degree of performance (i.e. highest overall reduction)
  - Goal G3, mass flux reduction, was indicated as the second most achievable goal. However, this type of goal is not widely accepted by the regulatory community and some respondents indicated that they had little experience with this type of goal.
  - Goal G1, risk reduction was the third most likely to succeed. Although risk reduction was not specifically defined in the survey handouts, risk based objectives typically involve reducing concentrations based on a risk exceedence map determined by a risk assessment, and the degree of concentration reductions required are typically much lower than meeting MCLs, yielding a more attainable concentration reduction goal.
  - Goal G2, contaminant mass reduction, was selected as the second least likely goal to be attained of the goals quantitatively assessing performance.
  - Goal G4, contaminant concentration reduction, was selected as the lowest performing goal overall of the quantitatively assessed goals.

- For goals G6 and G7, where performance is linked to a simple benchmark of meeting MCLs at certain points, the following trends were noted:
  - Goal G6, meeting MCLs at a site property line, was considered much more achievable than goal G7, meeting MCLs across an entire site. However, some bias may be present in the goal G6 responses, as according to site plans for scenarios 2, 3, 4, and 5, property lines were already at MCLs prior to remediation. Many respondents remarked that goal G6 should always be achievable at these sites regardless of remediation costs or timeframes, as any remediation technology application should not allow the spread of contamination beyond property lines. These respondents always marked yes as their response. However, if these scenarios had already exceeded MCLs at property lines, respondent answers would likely be different. Scenarios 1 and 6 which did have plumes

crossing property lines were both indicated as needing more than 60 months to achieve the remediation goal. Scenario 1 was indicated as needing >$1,000,000 to achieve MCLs at the property line, while scenario 6 was predicted to achieve this goal for $500,000 based on mean responses.

  - Scenario 4 was indicated as the most likely to achieve goal G7, MCLs across the entire site. This is likely due to the low contaminant mass density (only aqueous and sorbed phase contamination) in this system.
  - Survey responses for all scenarios consistently indicated that achieving MCLs site wide (G7) was the least likely goal to be achieved. For all scenarios, the mean cost and timeframe to achieve MCLs site wide was outside of the bounded constraints, and thus for all scenarios the predicted timeframe and costs exceeded $1,000,000 and 5 years.

B.3.1.3. Respondent Views on ISCO Based on Professional Position and Background. A number of interesting trends and interactions were noted with regard to the professional positions held by the respondents. Not enough RPMs or site owners participated in the exercise to give meaningful results, and thus, these were omitted from this discussion. A description of major trends with regard to background is given for the remaining professional background populations (consultants, technology vendors, and academic or research backgrounds).

- Remediation consultants
  - Were more likely to say no to considering ISCO
  - Were more likely to consider multiple injection rounds or continuous oxidant injection as oxidant injection strategies
  - Were more likely to consider coupling ISCO with other remediation approaches
  - Were more likely to consider well injection as a delivery approach
  - Were less likely to identify contaminant conditions as a site's biggest challenge.
  - Predicted lower remedial performance than vendors and academics
  - Gave a less optimistic response than vendors toward meeting project monetary or timeframe constraints, but were more optimistic than academics.
  - Were mostly negative about meeting MCLs site wide but somewhat more optimistic about meeting MCLs at property lines.
- Technology vendors
  - Were more likely to say yes to considering ISCO
  - Were more likely to consider a single injection round or continuous injection for delivery strategy
  - Were less likely to consider coupling with other remediation technologies
  - Were less likely to consider well injection for delivery approach
  - Were less likely to identify contaminant conditions as a site's principal challenge
  - Predicted higher remediation performance than academics or consultants
  - Were most positive in responses toward meeting project monetary or timeframe constraints
  - Had a wider spread in terms of answers with regard to individual scenarios than consultants or academics.
  - Vendors were mostly negative about meeting MCLs either at property lines or site wide.
- Academics and researchers
  - Were more likely to say yes to considering ISCO
  - Were more likely to consider a single injection round delivery strategy but less likely to consider a continuous injection delivery strategy
  - Were less likely to consider coupling with other remediation technologies

    - Were more likely than vendors or consultants to identify contaminant conditions as a site's principal challenge
    - Predicted lower performance than vendors, but higher performance than consultants
    - Were least optimistic and gave less variable responses in terms of meeting remediation goals within monetary or timeframe constraints

Several trends were noted with respect to whether or not the respondent indicated they had experience with scenarios similar to the ones presented.

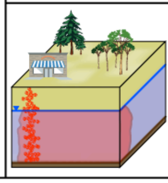
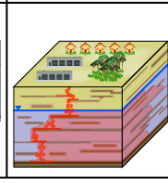
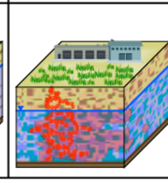
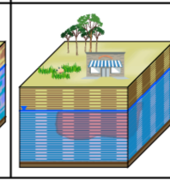
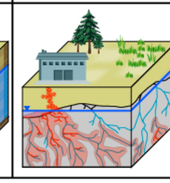
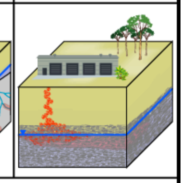
- An interaction between the scenario and the respondent's experience was noted.
    - For scenarios 1 & 4, (homogeneous permeable, homogeneous impermeable) respondents who indicated they had experience with similar sites were likely to predict higher performance than those who did not.
    - For scenario 6 (fractured rock with high matrix porosity), survey respondents indicated about the same level of anticipated performance regardless of whether they had experience with similar sites.
    - For scenarios 2, 3, and 5, (heterogeneous permeable, heterogeneous impermeable, fractured rock with low matrix porosity), respondents with experience at similar sites predicted lower performance than those who did not have experience
- Similar trends were noted with respect to the ability to treat these scenarios within any project monetary or timeframe constraints
    - Those with experience were more optimistic about treating scenarios 1 & 4 within constraints than those without experience.
    - For scenarios 3 & 6, the ability to meet constraints was roughly independent of respondent's experience.
    - For scenarios 2 & 5, those with experience were less optimistic about meeting project constraints than those without experience.
- With respect to constraints, those without experience gave more variable responses than those with experience.

B.3.2. Respondent Views on Specific ISCO Design Details

A number of interesting trends were also noted with respect to the respondents' replies about ISCO design. The data in Table B.3 indicate the preference of the surveyed ISCO professionals for various oxidants, distribution technologies, distribution strategies and nature of the principal challenges to ISCO for each scenario.

B.3.2.1. Choice of Oxidant for Each Site. The oxidant-specific preferences of the respondents varied by scenario. It should first be noted that many of the survey participants were either consultants or vendors that have strong oxidant specific preferences, often towards only 1 or 2 oxidants, depending on which oxidants they've used most in the field or services they provide. Due to the nature of workshop attendance, some oxidants are better represented than others simply due to the nature of who was present at the workshop. Because of this, the responses regarding specific oxidants in Table B.3 should not be interpreted as preferences from among all possible oxidants as votes are made for the best oxidant for a given scenario. However, the responses do provide information about the applicability of each oxidant type to the various scenarios, especially when comparing the changes in response for a particular oxidant from one scenario to the next.

Table B.3. Summary of Workshop participant responses to questions concerned with site-specific design details for ISCO applied at each site.

Site conceptual model	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	Scenario 6
						
Percentage of respondants indicating that ISCO should be considered for the scenario						
Percent positive responses	100%	90%	78%	61%	78%	78%
Percentage of respondents considering each oxidant type for the scenario						
Hydrogen peroxide	60%	58%	71%	20%	25%	93%
Permanganate	85%	58%	12%	87%	94%	20%
Ozone	20%	11%	12%	40%	13%	33%
Persulfate	55%	68%	76%	73%	50%	67%
Percent of respondents considering each distribution technology for the scenario						
Well Injection	80%	79%	47%	13%	75%	100%
Probe Injection	90%	53%	88%	53%	19%	33%
Recirculation	25%	37%	18%	20%	31%	13%
Sparging	35%	16%	12%	13%	6%	13%
Fracturing	0%	26%	18%	53%	19%	27%
Other	15%	0%	6%	40%	6%	7%
Percent of respondents considering each distribution strategy for the scenario						
Single injection round	11%	6%	0%	14%	7%	7%
Multiple injection rounds	74%	89%	86%	79%	93%	79%
Continuous injection	21%	33%	21%	29%	36%	29%
Coupled approach	37%	56%	36%	36%	29%	29%
Circumstances identified as the scenarios largest challenge						
Hydrologic conditions	16%	53%	83%	93%	92%	77%
Geochemistry conditions	11%	0%	0%	7%	0%	0%
Contaminant conditions	63%	58%	33%	0%	8%	23%

Persulfate was considered the most consistently of any of the oxidants for all six of the scenarios. The range of values was 50%-76% of respondents indicating that persulfate should be considered. The lowest responses for persulfate were under scenario 5, the fractured igneous rock system and scenario 1, the homogeneous permeable system. The lower ranking in the fractured rock system may be due in part to the smaller experience base with this oxidant, and performance of this oxidant in this type of system may be more unknown. The fact that responses appeared lower for persulfate application to scenario 1 (homogeneous-permeable) was likely an artifact, as this scenario was universally agreed to be the most treatable by all the respondents. There was general consensus that ISCO be considered, and because of this, all respondents selected oxidants. Since no respondents omitted responses for this scenario, the number of respondents with strong oxidant specific preferences was also highest for this scenario; the effect was that they likely "diluted" each other's responses causing the percentage to drop not just for persulfate, but probably all of the other oxidants as well.

For permanganate, a wide range of responses were found (12%-94%) (Table B.3). The largest positive responses occurred for scenarios 1 (homogeneous, permeable), 4 (homogeneous, impermeable) and 5 (fractured rock, low matrix porosity). Scenario 1, as already discussed, was decided to be the most treatable of all of the scenarios, and thus this finding is not surprising. For scenario 4, the fact that 87% of respondents indicated this oxidant should be considered is probably due to the long oxidant persistence of permanganate once natural oxidant demand is exhausted. This long persistence also has the effect of promoting diffusive transport of this oxidant, which can be a major delivery mechanism in low permeability media, such as the clay present in scenario 4. The very high number of respondents (94%) indicating permanganate should be considered for scenario 5 is also interesting. This may be due in part to the ability of permanganate to achieve density driven delivery, which might be helpful in a fractured rock matrix such as this. Also the long oxidant persistence of permanganate, which can continue treatment of contaminants long after injection occurred, may be advantageous in such a system as contaminants slowly back diffuse out of dead end fractures. Plugging of fractures with MnO_2 solids might also have an entombing effect on DNAPLs trapped within fractures. In contrast, responses indicating that permanganate should be considered for scenario 2 (heterogeneous-permeable) were at a more intermediate value than for the other scenarios. This might indicate more of a reluctance to consider permanganate for this scenario, and may be due in part to the large aerial extent of contamination and large mass of contaminant present in this system (e.g. DNAPL pools). Field applications of permanganate into systems with high contaminant mass densities have sometimes encountered permeability reductions challenging effective oxidant delivery, which in turn can lead to ineffective oxidant contact with the contaminant. The reason for this reduction in responses cannot be confirmed, but this inefficiency due to high contaminant densities may play a role. Scenarios 3 and 6 had the fewest respondents indicating that permanganate should be considered. This response is not surprising as permanganate is generally understood to either weakly reactive or un-reactive with the contaminants in these scenarios.

Hydrogen peroxide, like permanganate, was viewed as viable for several of the scenarios (20%-93%) (Table B.3). Responses were most positive for scenario 6 (fractured rock with high matrix porosity), followed by scenarios 1 (homogeneous-permeable), 2 (heterogeneous-permeable), and 3 (heterogeneous-impermeable). The fact that 93% of respondents indicated that hydrogen peroxide should be considered for scenario 6 clearly implies that a large number of respondents believe this oxidant to be capable of achieving treatment in this situation. This may be due in part to the amenability of the COCs to treatment with this oxidant coupled with the ability to deliver the oxidant within this environment. While Scenario 6 involves a site with consolidated bedrock, it is a shale fractured in a highly regular pattern with a reasonable primary permeability to it, which would assist in delivery of hydrogen peroxide. For scenarios 1, 2, and 3, large numbers of respondents indicated that hydrogen peroxide should be considered. Particularly for scenario 1, and possibly scenario 2, these percent responses being lower than that of scenario 6 may again be due to the “dilution” effect described earlier. Again, scenario 1 was largely agreed to be the most treatable. The scenario 2 response is a little lower, especially considering the other oxidant responses are also mostly lower, potentially indicating that the high contaminant mass in this system may pose a challenge to hydrogen peroxide treatment. Scenario 3 (heterogeneous-impermeable) generated a high number of respondents indicating that hydrogen peroxide should be considered, albeit somewhat lower than scenario 6. This is particularly in contrast with scenario 4 (homogeneous-impermeable), where a very low number of respondents indicated that hydrogen peroxide should be considered. This may be due in part to the heterogeneity in this system possibly improving the ability of hydrogen peroxide to achieve contact in this media. Hydrogen peroxide is a short lived oxidant and thus does not achieve diffusive transport in low permeability media. However, when heterogeneities are present, they may improve delivery by providing higher permeability zones where oxidant is easily transported through, causing a higher degree of oxidant contact. In scenario 4, which is homogeneous and impermeable, this is not possible as there are no zones of high permeability present. The number of respondents indicating that they would consider hydrogen peroxide for scenario 5 (fractured igneous rock) was also very low. This may in part be due to the off-gassing that often occurs with hydrogen peroxide injection, as well as due to the short lived nature of the oxidant which would not leave a sufficient residual to treat back diffusion of contaminant out of dead end fractures. Off-gassing can cause a severe permeability reduction should it occur within the tight fractures within this system, causing operational problems.

The last oxidant, ozone, generally had the fewest responses for all of the scenarios. This is probably because the workshop had fewer attendees present that are experienced in using ozone as opposed to the other oxidants. Responses for ozone varied from 11%-40%, indicating a fairly consistent level of support for it, despite its prevalence amongst the respondents being lower than for the other oxidants. The scenarios that had the highest responses were scenarios 1 (homogeneous, permeable), 4 (homogeneous, impermeable), and 6 (fractured rock, high matrix porosity). Again, scenario 1 was widely agreed to be the most treatable, and thus there is no surprise that ozone received a high degree of responses for this scenario. The high degree of response for scenario 4 however is somewhat surprising. The lower contaminant density in this system would certainly make it more amenable to ozone treatment, but the low permeability of the media would make sparging a considerable challenge. Scenario 4 also received a large number of responses indicating fracturing should be considered. The high degree of response for scenario 6 may in part be due to the nature of the contaminant being treated, as well as the more permeable nature of the site. The system is fractured along horizontal bedding planes which to some degree improve sparging gas delivery by achieving more lateral spread of the treatment zone. Furthermore, fuel hydrocarbons such as BTEX and MTBE may have a larger base of experience with ozone, as many LNAPL sites that have been treated with SVE or air sparging may have also investigated ozone as the infrastructure requirements of these remediation technologies are very similar. Scenarios 2, 3, and 5 received lower responses for ozone consideration, probably due in part to the high contaminant mass densities and large sizes of source zones, which may pose a challenge to ozone treatment.

B.3.2.2. Choice of Oxidant Delivery Technology for Each Site. A number of conclusions can also be drawn from data about respondents' selection of various distribution technologies to be considered for each of the scenarios (Table B.3). Like oxidants, some respondents may have strong preferences toward one injection technology versus another. However, because many of the oxidants can be delivered using multiple delivery technologies, this effect is probably weaker with respect to delivery technologies as opposed oxidant types.

Well injection was the single most commonly considered delivery technology. This is probably due in part to the relative ease of implementation and adaptability of this specific oxidant delivery technique. For scenario 6 (fractured rock, high matrix porosity), there was consensus that well injection should be considered among respondents that stated that ISCO should be considered for this scenario. The only scenarios where many respondents indicated that they would not consider well injection were scenario 4 (homogeneous, impermeable) and to a lesser extent scenario 3 (heterogeneous impermeable). This is not surprising as impermeability is a major challenge to well injection. The moderately higher favorable response for the heterogeneous system is probably due to the fact that heterogeneities in this otherwise low permeability media may actually improve injectability distribution, as opposed to challenging delivery as heterogeneity often does in more permeable systems.

Probe injection was the most commonly considered distribution technology in the scenarios involving only unconsolidated media, and was second only to well injection in terms of the most commonly considered delivery method overall. The preference for probe injection over well injection in these systems is probably due in part to ability to specifically target oxidant delivery to heterogeneous areas or areas of high contaminant mass density. Probe injection in the lower permeability media (scenarios 3 and 4) could also likely achieve better distribution in tight media due to high injection pressures, although responses for scenario 4 were lower possibly due to homogeneity of this impermeable system which might challenge delivery more. Probe injection was largely rejected for the consolidated media systems due to the technical infeasibility of the technique in these systems.

The other injection technologies categories (recirculation, sparging, fracturing and "other") were selected with much less frequency than well or probe injection. However, they were selected for specific scenarios. For instance, fracturing and "other" had very high responses for scenario 4, due to its low permeability. Most of the "other" responses for this scenario, when described, frequently specified some sort of mixing approach. Sparging results roughly paralleled ozone results, as this technique is highly specific to ozone. Recirculation was selected most frequently for scenarios 2 and 5. This is not particularly surprising as these scenarios were consistently indicated to be the most challenging, probably due to their large aerial extent, mass and the nature of their contaminant architectures. Recirculation poses challenges due infrastructure and regulatory constraints, but does provide advantages when large areas or contaminant masses need to be treated, and thus the high degree of response for these scenarios is understandable.

B.3.2.3. Choice of Oxidant Delivery Strategy for Each Site. Several important trends were also noted with respect respondents' answers regarding consideration of various distribution strategies. Again, like the oxidant specific preferences of some of the respondents, certain biases towards to delivery strategies may exist (Table B.3). However, delivery strategies are even less oxidant specific than delivery technologies and thus this is not anticipated to have a major effect on responses. Multiple injection rounds were by far the most favored for all of the scenarios and a single injection rounds were the least selected. This agrees with anecdotal field observations that multiple injection rounds were needed or used much more frequently than a single injection round. Given that all 6 scenarios presented here were designed to present some challenge to ISCO via either lithology or contaminant mass densities, the unpopularity of single injection rounds is not surprising. However, single injection rounds might still be appropriate under some circumstances not represented amongst the scenarios here, such as small sites with straightforward lithology or low contaminant mass densities. The number of respondents indicating continuous injection did not change markedly from one scenario to another. The percentages are slightly higher for scenarios 2 and 5, possibly mirroring the recirculation effect seen with respect to delivery technologies. The number of respondents indicating that coupling with other technologies should be considered also did not differ markedly from one scenario to the next, with the sole exception of scenario 2 (heterogeneous-permeable). Scenario 2 was a very large site, with a large mass density of contaminants (DNAPL pools and residuals). Over 50% of respondents indicated that coupling should be considered for this site, and is understandable as pre or post ISCO treatment steps would probably be necessary to markedly decrease contaminant concentrations in such a system.

B.3.3. Respondent Views on Principal Challenges to ISCO Performance

As part of the survey, respondents were asked to identify the principle source of challenges to ISCO performance for each scenario (Table B.3). Respondents had the option to choose between three different categories, which were hydrologic, geochemical or contaminant conditions. Then for the principal challenge selected, they could select more specific parameters under each of these categories based on which specific parameter they thought challenged ISCO the most. The responses to the questions regarding the principle challenge for ISCO were also found to be scenario specific. Hydrologic conditions were selected as the principle challenge most frequently, and dominated responses to scenarios 3, 4, 5, and 6. This is not surprising as these scenarios encompassed impermeable or consolidated media systems, often with varying degrees of heterogeneity that hinder effective characterization, design and implementation of ISCO, as well as other remediation technologies. Contaminant conditions yielded higher responses for scenarios 1 and 2. These systems were both permeable reducing the degree of challenge posed by hydrology and also contained high contaminant mass densities (i.e., DNAPL levels). Geochemistry was consistently found by the respondents to be the least of the challenges for all six scenarios.

When respondents were allowed to pick specific parameters that they found to be particularly challenging, the trends tended to verify much of the discussion given above for the nature of the challenges. They also mirrored the effect where scenarios 1 and 2 were dominated by challenges due to contaminant conditions and scenarios 3, 4, 5, and 6 were dominated by hydrology issues. For hydrology conditions, heterogeneity, hydraulic conductivity and media type were all cited often as major sources of challenge with these scenarios. Heterogeneity dominated responses from scenarios 2 and 3, hydraulic conductivity dominated responses from scenario 4, and media type (fractured rock) dominated scenarios 5 and 6. Depth of treatment zone was seldom identified as a problem, but did generate some responses for the deepest site which was scenario 2. In contrast with contaminant conditions, contaminant distribution was selected the most frequently as the principle challenge to ISCO. It was particularly dominant in scenarios 2, 4, 5, and 6, all of which would present some challenge in gaining access to the contaminated areas with suitable oxidant delivery. The contaminant mass was the second most often cited parameter, again helping to confirm some of the previously discussed effects. For challenges posed by geochemistry conditions, based on the limited number of replies, it is difficult to say which were most important with confidence. However, system Eh as a major challenge was the most often selected, followed by pH, possibly indicating challenges that may be encountered when optimizing oxidant delivery or reaction chemistry.

B.4. Summary of Findings and Implications

A number of potentially important conclusions can be drawn from the data collected from this ISCO survey effort. These help reveal the current standard of practice for ISCO, and provide insight into the ability of ISCO to achieve certain goal types and the need for guidance to assist future ISCO applications in achieved the highest degree of performance possible. Major findings from this effort have been provided earlier in Section 2.5 but they are repeated here to aid the reader.

- A majority of the professionals queried during this survey indicated that ISCO should at least be considered for each of the six scenarios presented to them, which spanned a range of hydrologic, geologic and contaminant conditions, some of which were very challenging. This implies broad applicability of ISCO, provided treatment objectives and ISCO designs are carefully matched to site conditions.
- Based on the specific scenarios developed for this survey, scenarios 1 and 4 were deemed likely to achieve the highest degree of performance as well as meet monetary and timeframe constraints, while scenarios 2 and 5 were likely to achieve the lowest degrees of performance and unlikely to meet goals within monetary or timeframe constraints. Scenarios 3 and 6 were intermediate in terms of performance expectations.
- Hydrology is a critical factor that influences the likelihood of achieving a desired ISCO performance within project monetary and timeframe constraints.
    - Hydraulic conductivity, heterogeneity and media type (consolidated vs. unconsolidated) are the major parameters that often pose challenges to ISCO performance.
    - In unconsolidated media, higher hydraulic conductivity and lower heterogeneity improve treatability overall. However, for specific oxidants, heterogeneities in low permeability systems may actually improve treatability somewhat.
    - Consolidated media are challenging but possible to treat. Treatability probably improves when lower contaminant masses are present, the fractured rock has lower matrix porosity and more regular, well understood fracture patterns.
- ISCO performance inherently relates to remediation goals. Some remediation goals are likely to require higher degrees of performance than others, and the degree of achievability varies with site-specific conditions.
    - Respondents agreed that highest degree of performance (e.g., x% concentration reduction) will likely be achieved when ISCO is coupled with monitored natural attenuation (MNA) for a period of time after ISCO application.
    - Mass flux reduction goals were also largely agreed to be achievable with a high degree of confidence.
    - Risk-based clean up goals were the next most achievable goal type.
    - MCLs either at site property lines or site wide were the least achievable type of goal.

- The survey respondents' perspectives on ISCO applicability were found to vary depending on the respondents professional background and experience
    - Consultants were less optimistic than academic, research or vendor backgrounds when anticipating ISCO remediation performance.
    - Consultants were less optimistic than vendors but more optimistic than academic or research backgrounds with respect to meeting monetary or timeframe constraints.
    - The experience of a respondent appeared to influence their responses to questions concerned with specific scenarios.
- The applicability of specific oxidants varies with respect to both hydrology and contaminant specific conditions. Some oxidants were more variable than others in terms of responses from one scenario to the next, but there were no universally applicable oxidants.
- Well and probe injection are by far the most popular delivery methods. Probe injection was more popular than well injection in unconsolidated media. Use of other delivery technologies was driven strongly by site-specific conditions.
- Multiple injections events are a standard feature of ISCO applications.

The findings of the site scenario assignment revealed that while ISCO as a remediation technology might be considered for a wide range of situations, site-specific conditions interact with the performance that can be reasonably achieved. A majority of the Workshop participants responding to the scenario assignment indicated that they would personally consider ISCO for all six of the contaminated site scenarios. However, the degree of anticipated ISCO performance, timeframe necessary and costs varied for all of these scenarios. Furthermore, different types of treatment objectives may be more or less achievable depending on site-specific conditions. Thus the success or failure of an ISCO application is dependent not only on site-specific conditions, but also the remediation objectives laid out for a specific site and the resources (e.g., time and money) made available to implement the ISCO system.