

In Situ Chemical Oxidation for Groundwater Remediation

R. L. Siegrist
M. Crimi
T. J. Simpkin
Editors



In Situ
**Chemical Oxidation
for Groundwater
Remediation**

SERDP and ESTCP Remediation Technology Monograph Series

Series Editor: C. Herb Ward, Rice University

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Edited by

Robert L. Siegrist

Colorado School of Mines, Golden, Colorado

Michelle Crimi

Clarkson University, Potsdam, New York

Thomas J. Simpkin

CH2M HILL, Englewood, Colorado

Authors

Robert C. Borden	Friedrich J. Krembs	Brant A. Smith
Richard A. Brown	Richard W. Lewis	Kent S. Sorenson, Jr.
Wilson S. Clayton	Michael C. Marley	Amy L. Teel
Michelle Crimi	Junko Munakata-Marr	Neil R. Thomson
James B. Cummings	Tom Palaia	Aikaterini Tsitonaki
Jeffrey L. Heiderscheidt	Benjamin G. Petri	Michael A. Urynowicz
Scott G. Huling	Robert L. Siegrist	Marvin Unger
Tissa H. Illangasekare	Thomas J. Simpkin	Richard J. Watts

Editors

Robert L. Siegrist, Ph.D., P.E., BCEE
Colorado School of Mines
Environmental Science and Engineering Division
Coolbaugh Hall
1012 14th Street
Golden, Colorado 80401 USA
siegrist@mines.edu

Michelle Crimi, Ph.D.
Clarkson University
Institute for a Sustainable Environment
8 Clarkson Avenue
Potsdam, New York 13699 USA
mcrimi@clarkson.edu

Thomas J. Simpkin, Ph.D., P.E.
CH2M HILL
9192 S. Jamaica Street
Englewood, Colorado 80112 USA
Tom.Simpkin@ch2m.com

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SERDP/ESTCP Remediation Technology Monograph Series

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SERDP and ESTCP have joined to facilitate the development of a series of monographs on remediation technology written by leading experts in each subject area. This volume provides a review of the state-of-the-art on *in situ* chemical oxidation for groundwater remediation. Additional volumes planned for publication in the near future include:

- Delivery and Mixing in the Subsurface: Processes and Design Principles for *In Situ* Remediation
- Bioaugmentation for Groundwater Remediation
- Chlorinated Solvent Source Zone Remediation
- Processes, Assessment and Remediation of Contaminated Sediments
- Remediation of Munition Constituents in Soil and Groundwater



U.S. Department of Defense Strategic
Environmental Research &
Development Program (SERDP)
901 North Stuart Street, Suite 303
Arlington, VA 22203



U.S. Department of Defense
Environmental Security Technology
Certification Program (ESTCP)
901 North Stuart Street, Suite 303
Arlington, VA 22203

Preface

In the late 1970s and early 1980s, our nation began to grapple with the legacy of past disposal practices for toxic chemicals. With the passage in 1980 of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), commonly known as Superfund, it became the law of the land to remediate these sites. The U.S. Department of Defense (DoD), the nation's largest industrial organization, also recognized that it too had a legacy of contaminated sites. Historic operations at Army, Navy, Air Force, and Marine Corps facilities, ranges, manufacturing sites, shipyards, and depots had resulted in widespread contamination of soil, groundwater, and sediment. While Superfund began in 1980 to focus on remediation of heavily contaminated sites largely abandoned or neglected by the private sector, the DoD had already initiated its Installation Restoration Program in the mid-1970s. In 1984, the DoD began the Defense Environmental Restoration Program (DERP) for contaminated site assessment and remediation. Two years later, the U.S. Congress codified the DERP and directed the Secretary of Defense to carry out a concurrent program of research, development, and demonstration of innovative remediation technologies.

As chronicled in the 1994 National Research Council report, "Ranking Hazardous-Waste Sites for Remedial Action," our early estimates on the cost and suitability of existing technologies for cleaning up contaminated sites were wildly optimistic. Original estimates, in 1980, projected an average Superfund cleanup cost of a mere \$3.6 million per site and assumed only around 400 sites would require remediation. The DoD's early estimates of the cost to clean up its contaminated sites were also optimistic. In 1985, the DoD estimated the cleanup of its contaminated sites would cost from \$5 billion to \$10 billion, assuming 400 to 800 potential sites. A decade later, after an investment of over \$12 billion on environmental restoration, the cost-to-complete estimates had grown to over \$20 billion and the number of sites had increased to over 20,000. By 2007, after spending over \$20 billion in the previous decade, the estimated cost to address the DoD's known liability for traditional cleanup (not including the munitions response program for unexploded ordnance) was still over \$13 billion. Why did we underestimate the costs of cleaning up contaminated sites? All of these estimates were made with the tacit assumption that existing, off-the-shelf remedial technology was adequate to accomplish the task, that we had the scientific and engineering knowledge and tools to remediate these sites, and that we knew the full scope of chemicals of concern.

However, it was soon and painfully realized that the technology needed to address the more recalcitrant environmental contamination problems, such as fuels and chlorinated solvents in groundwater and dense nonaqueous phase liquids (DNAPLs) in the subsurface, was seriously lacking. In 1994, in the "Alternatives for Ground Water Cleanup" document, the National Research Council clearly showed that as a nation we had been conducting a failed 15-year experiment to clean up our nation's groundwater and that the default technology, pump-and-treat, was often ineffective at remediating contaminated aquifers. The answer for the DoD was clear. The DoD needed better technologies to clean up its contaminated sites and better technologies could only arise through a better scientific and engineering understanding of the subsurface and the associated chemical, physical, and biological processes. Two DoD organizations were given responsibility for initiating new research, development, and demonstrations to obtain the technologies needed for cost-effective remediation of facilities across the DoD: the Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP).

SERDP was established by the Defense Authorization Act of 1991 as a partnership of the DoD, the U.S. Department of Energy, and the U.S. Environmental Protection Agency; its mission is “to address environmental matters of concern to the Department of Defense and the Department of Energy through support of basic and applied research and development of technologies that can enhance the capabilities of the departments to meet their environmental obligations.” SERDP was created with a vision of bringing the capabilities and assets of the nation to bear on the environmental challenges faced by the DoD. As such, SERDP is the DoD’s environmental research and development program. To address the highest-priority issues confronting the Army, Navy, Air Force, and Marine Corps, SERDP focuses on cross-service requirements and pursues high-risk and high-payoff solutions to the DoD’s most intractable environmental problems. SERDP’s charter permits investment across the broad spectrum of research and development, from basic research through applied research and exploratory development. SERDP invests with a philosophy that all research, whether basic or applied, when focused on the critical technical issues, can impact environmental operations in the near term.

A DoD partner organization, ESTCP, was established in 1995 as the DoD’s environmental technology demonstration and validation program. ESTCP’s goal is to identify, demonstrate, and transfer technologies that address the DoD’s highest priority environmental requirements. The program promotes innovative, cost-effective environmental technologies through demonstrations at DoD facilities and sites. These technologies provide a large return on investment through improved efficiency, reduced liability, and direct cost savings. The current cost and impact on DoD operations of environmental compliance is significant. Innovative technologies are reducing both the cost of environmental remediation and compliance and the impact of DoD operations on the environment, while enhancing military readiness. ESTCP’s strategy is to select laboratory-proven technologies with potential broad DoD application and use DoD facilities as testing beds. By supporting rigorous test and evaluation of innovative environmental technologies, ESTCP provides validated cost and performance information. Through these efforts, new technologies gain end-user and regulatory acceptance.

In the 15 to 19 years since SERDP and ESTCP were formed, much progress has been made in the development of innovative and more cost-effective environmental remediation technology. Recalcitrant environmental contamination problems for which little or no effective technology had been available are now tractable. However, we understand that newly developed technologies will not be broadly used in government or industry unless the consulting engineering community has the knowledge and experience needed to design, cost, market, and apply them.

To help accomplish the needed technology transfer, SERDP and ESTCP have facilitated the development of a series of monographs on remediation technology written by leading experts in each subject area. Each volume will be designed to provide the background in process design and engineering needed by professionals who have advanced training and 5 or more years of experience. The first volume in this series, *In Situ Bioremediation of Perchlorate in Groundwater*, met a critical need for state-of-the-technology guidance on perchlorate remediation. The second volume, *In Situ Remediation of Chlorinated Solvent Plumes*, addresses the diverse physical, chemical, and biological technologies currently in use to treat what has become one of the most recalcitrant contamination problems in the developed world. This volume, *In Situ Chemical Oxidation for Groundwater Remediation*, describes the principles and practices of this emerging technology. Other volumes will follow, including additional volumes that will be written as new remediation technologies are developed and proven to be effective.

This volume provides comprehensive up-to-date descriptions of the principles and practices of *in situ* chemical oxidation (ISCO) for groundwater remediation based on a decade of intensive research, development, and demonstrations, and lessons learned from commercial field

applications. The foundation for this volume was ESTCP Project ER-0623, “*In Situ Chemical Oxidation for Remediation of Groundwater – Technology Practices Manual*”.¹

The intended audience for this volume includes remediation professionals, decision makers, and practicing engineers and scientists who will select, design, and operate ISCO remedial systems, as well as researchers seeking to improve the current state-of-the-art. Topics addressed in this volume include:

- Groundwater contamination, site remediation, and current ISCO technology practices (Chapter 1).
- Fundamentals of chemical oxidation, the use of peroxide, permanganate, persulfate, and ozone oxidants, their reactions with contaminants of concern, and their interactions with naturally occurring subsurface materials (Chapters 2–5).
- Transport and fate of oxidants during use in ISCO and available mathematical models to support ISCO applications (Chapter 6).
- Combination of ISCO with other remedial technologies, including *in situ* bioremediation and monitored natural attenuation (Chapter 7).
- Evaluation of ISCO field applications, performance achieved, and lessons learned (Chapter 8).
- Design and implementation of ISCO, including technology screening, conceptual design, detailed design and planning, and implementation and performance monitoring (examples of procedures, processes, and tools are provided) (Chapter 9).
- Site characterization for development of conceptual site models, treatment goals, and end points for ISCO applications (Chapter 10).
- Oxidant delivery, contingency planning (Chapter 11), and ISCO system performance monitoring (Chapter 12).
- ISCO technology costs and sustainability (Chapter 13).
- Critical gaps in knowledge and research needs to improve ISCO theory, technology development and applications (Chapter 14).

Each chapter in this volume has been thoroughly reviewed for technical content by one or more experts in the subject area covered. The editors and chapter authors have produced a state-of-the-art volume that we hope will prove to be a useful reference for those making decisions on remediation of contaminated groundwater and for those involved in research and development of advanced technology for the *in situ* remediation of groundwater.

SERDP and ESTCP are committed to the development of new and innovative technologies to reduce the cost of remediation of soil, groundwater, and sediment contamination as a result of past operational and industrial practices. We are also firmly committed to the widest dissemination of these technologies to ensure that our investments continue to yield savings for not only the DoD, but also the nation. In facilitating this monograph series, we hope to provide the broader remediation community with the most current knowledge and tools available in order to encourage full and effective use of these technologies.

Jeffrey A. Marqusee, PhD Executive Director, SERDP and ESTCP
Andrea Leeson, PhD Environmental Restoration Program Manager, SERDP and ESTCP

¹ Reports, protocols, and tools developed from SERDP and ESTCP sponsored ISCO projects are available at <http://serdp-estcp.org/>.

About the Editors

Robert L. Siegrist

Dr. Robert L. Siegrist is Professor and former Director of Environmental Science and Engineering at the Colorado School of Mines. He earned his BS (High Honors) and MS in Civil Engineering and his PhD in Environmental Engineering at the University of Wisconsin. Before joining the School of Mines in 1995, Dr. Siegrist held academic and research positions with the University of Wisconsin, Norwegian Institute for Georesources and Pollution Research, and Oak Ridge National Laboratory.

Dr. Siegrist is an internationally recognized expert in *in situ* remediation of contaminated soil and groundwater. He has published 300 technical papers and was lead author of the first reference text concerned with *in situ* chemical oxidation (ISCO): *Principles and Practices of In Situ Chemical Oxidation Using Permanganate* (2001). Dr. Siegrist has given invited lectures at more than 100 workshops and conferences worldwide including the United States, Australia, Norway, Denmark, Spain, Greece, Romania, Nepal, Thailand, and Vietnam. Dr. Siegrist has served as a science and engineering advisor to the U.S. Environmental Protection Agency (USEPA), the Department of Energy (DOE), the Department of Defense (DoD), the National Research Council, and the Government Accountability Office, and he served as a Fellow with the North Atlantic Treaty Organization (NATO) Committee for Challenges to Modern Society.

Dr. Siegrist has received significant recognition for his expertise and research, including a Certificate of Appreciation from NATO for his service as a NATO Fellow from 1986 to 2002, designation as a Board Certified Environmental Engineer by the American Academy of Environmental Engineers, and his award as Principal Investigator for the Strategic Environmental Research and Development Program (SERDP) Outstanding Project of the Year for 2005.

Michelle Crimi

Dr. Michelle Crimi is Assistant Professor in the Institute for a Sustainable Environment at Clarkson University. Her research is focused on *in situ* remediation of contaminated soil and groundwater, chemical oxidation and degradation of organic compounds, impacts of *in situ* remediation on aquifer quality, and human health risk assessment. Dr. Crimi has published extensively in these areas and has delivered invited presentations at numerous workshops and conferences in the United States and abroad. Dr. Crimi is coauthor of the first reference text on ISCO: *Principles and Practices of In Situ Chemical Oxidation Using Permanganate* (2001).

Dr. Crimi received her BS degree in Industrial Hygiene and Environmental Toxicology from Clarkson University, an MS in Environmental Health from Colorado State University, and a PhD in Environmental Science and Engineering from the Colorado School of Mines.

Thomas J. Simpkin

Dr. Thomas J. Simpkin is global Remediation Practice Director for CH2M HILL in Englewood, Colorado. In this role, he coordinates technology transfer across the firm and the development of best practices for site characterization and remediation. He also leads his firm's efforts in the development of new tools and technologies for improved delivery of site characterization and remediation projects.

Dr. Simpkin earned BS and MS degrees in Civil Engineering and his PhD in Environmental Engineering at the University of Wisconsin. He has 24 years of experience in the areas of site investigation, feasibility studies, remediation planning, remediation design, remediation construction, and remediation operation. He has experience in a large number of remediation technologies, including ISCO, soil mixing, and bioremediation.

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About the Authors

Robert C. Borden

Dr. Borden is a Professor of Civil, Construction, and Environmental Engineering at North Carolina State University and Principal Engineer at Solutions-IES, Inc. His research and consulting work is focused on the natural and enhanced remediation of hazardous materials in the subsurface. He has been a faculty member at North Carolina State University since 1986, teaching and conducting research in surface water hydrology, groundwater hydrology, subsurface contaminant transport, and *in situ* remediation. His research includes laboratory studies, fieldwork and mathematical model development. Recently, much of his research has focused on remediation of chlorinated solvents, perchlorate, chromium and acid mine drainage using emulsified oils. At Solutions-IES, Dr. Borden supports many of the firm's projects including traditional remediation approaches, *in situ* bioremediation, *in situ* chemical oxidation (ISCO), monitored natural attenuation (MNA), and expert witness testimony. Dr. Borden received his BS and ME degrees in Civil and Environmental Engineering from the University of Virginia and a PhD in Environmental Engineering from Rice University.

Richard A. Brown

Dr. Brown joined ERM in 1999 as the Director of Technology Development. His responsibilities at ERM include development and implementation of remediation technologies such as bioremediation, *in situ* chemical oxidation and reduction, ozonation, and *in situ* metals fixation. He also is responsible for evaluating and commercializing new technologies for soil and groundwater treatment. Dr. Brown has worked on new technologies for the investigation and treatment of complex, contaminated sites including wood treating, coal gasification, mining, and Superfund. He currently holds 20 U.S. patents and has two additional patent applications on the *in situ* ozonation of recalcitrant organics and two on the use of sodium persulfate for ISCO. Dr. Brown has authored over 100 technical papers and is an expert in hydrogen peroxide and persulfate applications for soil and groundwater treatment. Dr. Brown received his BA degree in Chemistry from Harvard and MS and PhD degrees from Cornell University in Inorganic and Analytical Chemistry and Organometallic Chemistry, respectively.

Wilson S. Clayton

Dr. Clayton is a co-founder and Senior Vice President of Aquifer Solutions, Inc. Dr. Clayton previously served as a corporate-level technology director at Groundwater Technology, Fluor Daniel GTI, and IT Corporation, where he managed research, development, and commercialization of *in situ* oxidation technology. Dr. Clayton has over 23 years of *in situ* remediation experience spanning the full spectrum of technologies, including biological and chemical technologies, as well as more traditional technologies such as air sparging, soil venting, and pump-and-treat. While being broadly involved in all aspects of remediation implementation, Dr. Clayton's special area of technical expertise is in the application of subsurface reactive transport for *in situ* remediation. Dr. Clayton earned his PhD at Colorado School of Mines in Geological Engineering with a minor in Environmental Engineering and his BS and MS degrees in Geology from Clemson University and the University of Connecticut, respectively.

James B. Cummings

Mr. Cummings is an analyst in the Technology Assessment Branch, Office of Site Remediation and Technology Innovation, at U.S. Environmental Protection Agency (USEPA)

Headquarters. He has 20 years of experience in development, evaluation, and deployment of innovative hazardous waste site characterization and remediation technologies. Areas of expertise include *in situ* thermal treatment, ISCO, and combined remedies to achieve cost effective site closure. He provides technical support to USEPA and state remedial project managers, has co-managed large-scale technology demonstrations under the Superfund Innovative Technology Evaluation program, and has conducted technology seminars domestically and internationally. Mr. Cummings received a BS degree in Engineering from the U.S. Air Force Academy and a Juris Doctorate (JD) from George Washington University.

Jeffrey L. Heiderscheidt

Dr. Heiderscheidt is an Assistant Professor of Civil and Environmental Engineering at the U.S. Air Force Academy where he teaches undergraduate environmental engineering courses and conducts research on enhanced source zone remediation and modeling. Dr. Heiderscheidt has over 17 years of civil and environmental engineering experience in the U.S. Air Force. He taught environmental engineering and management courses at the Air Force Institute of Technology (AFIT) prior to coming to the Air Force Academy. He has published 14 book chapters, technical reports, technical articles in refereed journals, and papers in conference proceedings. Dr. Heiderscheidt received his BS degree in Mechanical Engineering from South Dakota State University, his MS in Environmental Engineering from the AFIT, and his PhD in Environmental Science and Engineering from the Colorado School of Mines.

Scott G. Huling

Dr. Huling is a licensed Professional Engineer (PE) and has been an Environmental Engineer with the USEPA Robert S. Kerr Environmental Research Center in Ada, Oklahoma since 1987. Dr. Huling's research is focused on oxidation treatment systems involving a wide array of environmental contaminants. His laboratory- and field-scale research involves fundamental mechanisms and field-scale applications used in the optimization and in the effective and economic deployment of chemical oxidation technologies at pilot- and field-scale. Dr. Huling received his BS degree in Environmental Science from the University of Texas at San Antonio, MS in Environmental Engineering from the University of Texas at Austin, and PhD in Environmental Engineering from the University of Arizona in Tucson.

Tissa H. Illangasekare

Dr. Illangasekare is a Professor and holds the AMAX Chair of Environmental Science and Engineering at the Colorado School of Mines. He also is the Director of the University/Industry/National Laboratory Collaborative Center for Experimental Study of Subsurface Environmental Processes (<http://cesep.mines.edu>). Dr. Illangasekare has 30 years of experience with numerical modeling of saturated and unsaturated flow in soils, surface-subsurface interaction, arid zone hydrology, integrated modeling of hydrologic systems, flow in snow and arctic hydrology, subsurface chemical transport and multiphase flow, environmental impacts of energy development, and physical model testing. He has extensive experience in hydrologic model development and laboratory and field validations of models. He has published numerous book chapters and more than 230 technical articles in refereed journals and proceedings. He is the Managing Editor for hydrology for *Earth Science Review*, past co-editor of *Vadose Zone Journal*, and currently editor of *Water Resources Research*. He is a Fellow of the American Geophysical Union, the American Society of Civil Engineers, and the American Association for the Advancement of Science. Dr. Illangasekare received a BS degree in Civil Engineering from the University of Ceylon (Sri Lanka), an ME from the Asian Institute of Technology, and a PhD in Civil Engineering from Colorado State University.

Friedrich J. Krembs

Mr. Krembs is an Associate Engineer with Aquifer Solutions, Inc. in Evergreen, Colorado. He has experience in environmental site characterization, and design and implementation of multiple remediation technologies, though his primary focus recently has been on ISCO. Mr. Krembs received his BS degree in Geology and Economics from Haverford College and an MS in Environmental Science and Engineering from the Colorado School of Mines. He is a registered Professional Geologist and Engineer Intern.

Richard Lewis

Mr. Lewis is a Certified Professional Geologist and has been a Partner of Environmental Resources Management for the past 8 years in Mansfield, Massachusetts. In this position he provides technical support on assessment and subsurface remediation projects worldwide. Mr. Lewis has worked in the environmental industry for more than 32 years, conducting projects in 47 states, and in more than 20 countries worldwide. Mr. Lewis specializes in hydrogeologic evaluations of hazardous waste releases and has extensive experience investigating, delineating, modeling, and remediating organic and inorganic contaminants. Mr. Lewis specializes in ISCO, dense nonaqueous phase liquid (DNAPL) and light nonaqueous phase liquid (LNAPL) recovery, groundwater extraction and treatment, *in situ* bioremediation, *in situ* thermal treatment, metals fixation, *ex situ* soil treatment and soil vapor control systems. He received his BS degree in Biology and Geology from the State University of New York at Brockport and an MS degree in Geology from the State University of New York at Fredonia.

Michael C. Marley

Mr. Marley is President and co-founder of XDD, LLC in Stratham, New Hampshire, and has over 29 years of experience in environmental and civil engineering. Mr. Marley's expertise focuses on strategies for site closure, including the development and application of innovative remediation technologies for contaminated soils and groundwater. He has been at the forefront of developing design and application protocols for soil vapor extraction, air sparging, and most recently *in situ* chemical oxidation and reduction technologies. As XDD's primary technical expert Mr. Marley directs all applied research and development efforts and serves as the firm's quality assurance officer. Mr. Marley lectures widely on the design and application of vapor extraction, bioventing, sparging/biosparging, chemical oxidation, and innovative remediation technologies for volatile and semivolatiles organic compounds (VOCs and SVOCs) and inorganic compounds. He has been responsible for the modeling support, review, or design of several hundred pilot- and full-scale remediation systems. More recently, Mr. Marley was the principal author of the Electric Power Research Institute (EPRI)-funded study on field applicability of persulfate for chemical oxidation of Manufactured Gas Plant residuals. In addition, Mr. Marley has served as a peer reviewer for the Strategic Environmental Research and Development Program (SERDP)/Environmental Security Technology Certification Program (ESTCP) research on *in situ* technologies. Mr. Marley earned his BS degree in Civil Engineering from Queens University in Belfast, Northern Ireland, performed doctoral research and received his MS in Civil and Environmental Engineering from the University of Connecticut and is a Licensed Environmental Professional (LEP) in the state of Connecticut.

Junko Munakata-Marr

Dr. Munakata-Marr is an Associate Professor in the Environmental Science and Engineering Division at the Colorado School of Mines. Her research and teaching interests are focused on microorganisms in engineered environmental systems, including biological wastewater treatment, microbial source tracking, and methanogenesis from unconventional sources. She

has nearly 20 years of experience in bioremediation. Dr. Munakata-Marr received her BS degree in Chemical Engineering from the California Institute of Technology and her MS and PhD degrees in Civil Engineering from Stanford University.

Tom Palaia

Mr. Palaia is a Principal Technologist with CH2M HILL in Englewood, Colorado. Currently, he is a CH2M HILL corporate global technology leader in Remedial Process Optimization and NAPL Site Management. During his 17 years with CH2M HILL, Mr. Palaia has specialized in remediation strategy and planning, pre-design investigation, design, construction, and optimization of site remediation systems. Mr. Palaia currently serves as project manager, senior technology contact, technical quality reviewer, or project team member on more than 20 remediation projects on a range of contamination issues including dye manufacturing residues, chlorinated solvents, and petroleum products. Mr. Palaia earned his BS degree in Civil Engineering from Lafayette College and his MS in Environmental Engineering from the University of Massachusetts, Amherst.

Benjamin G. Petri

Mr. Petri is a former Research Associate and is presently a doctoral student at the Colorado School of Mines. His research interests include furthering the science of subsurface contaminant transport and improving the practice of *in situ* remediation methods. A particular focus has been on developing guidance for the application of ISCO and evaluating the impact of *in situ* remediation on subsurface contaminant transport. His PhD thesis research is focused on improving understanding of vapor intrusion risks through experimental and mathematical evaluation of the transport of volatile contaminants in the subsurface. Mr. Petri earned his BS degree in Environmental Engineering and an MS in Environmental Science and Engineering from the Colorado School of Mines.

Brant A. Smith

Dr. Smith is a Senior Engineer and Director of XDD's treatability laboratory in Stratham, New Hampshire. His PhD research focused on the destruction of DNAPL using ISCO technologies. Dr. Smith has over 9 years experience working on site remediation and remedial technologies. He is a registered PE in the State of Washington. Dr. Smith's interest includes the research, design, and application of various ISCO technologies, including activated persulfate, permanganate, and catalyzed hydrogen peroxide. The results of his research have been published in *Environmental Science and Technology*, *Journal of Contaminant Hydrology*, *Environmental Toxicology and Chemistry*, and the *Journal of Environmental Engineering*. Dr. Smith earned a BS degree in both Civil and Environmental Engineering and Economics from Worcester Polytechnic Institute. Dr. Smith also holds an MS and PhD in Civil Engineering from the Washington State University.

Kent S. Sorenson, Jr.

Dr. Sorenson is a Senior Environmental Engineer, Vice President, and Assistant Chief Technical Officer at CDM in Denver, Colorado. Dr. Sorenson specializes in applying innovative technologies for remediation of chlorinated solvents in groundwater, holding six U.S. patents related to remediation. His work focuses on *in situ* remediation of contaminants, including aspects of microbiology, hydrogeology, and geochemistry. He is also actively involved in pursuing innovative methods for drilling and injection of amendments in the subsurface. Dr. Sorenson has coauthored at least 38 scientific publications and over 100 presentations at various national and international conferences and symposia. His role in technology development

and application has resulted in awards from Frost & Sullivan, the American Academy of Environmental Engineers, and the National Ground Water Association. He also has been an affiliate faculty member at Idaho State University and the University of Idaho. Dr. Sorenson received a BSE degree in Mechanical Engineering from Tulane University, an MS degree in Civil and Environmental Engineering from the Massachusetts Institute of Technology, and a PhD in Civil Engineering from the University of Idaho.

Amy L. Teel

Dr. Teel is a Research Scientist at Washington State University in Pullman, Washington. She has worked for 13 years in the field of environmental engineering, with a focus on laboratory investigations of reaction mechanisms in ISCO processes such as catalyzed hydrogen peroxide propagations (modified Fenton's reagent) and persulfate. She has published 30 papers related to remediation and ISCO processes, and served as co-principal investigator on several SERDP/ESTCP projects. Dr. Teel received a BS degree in Cell Biology from the University of Washington and a PhD in Cell and Molecular Biology from the University of Minnesota.

Neil R. Thomson

Dr. Thomson is a Professor of Civil and Environmental Engineering, and a member of the Environmental Modeling and Analysis Group and The Water Institute at the University of Waterloo, Ontario, Canada. Dr. Thomson is a featured lecturer in short courses in North America, the United Kingdom, and Mexico. Dr. Thomson has over 20 years of research experience in the use of field investigations, laboratory experiments, and numerical models to explore subsurface contaminant fate and remediation issues. His research interests are focused on the environmental fate of contaminants in subsurface systems including immiscible liquids, vapors and pathogens, the development and application of simulation tools, and the development and assessment of soil and groundwater remediation technologies. At the University of Waterloo he teaches undergraduate and graduate courses in areas such as environmental chemistry, organic contaminants, contaminant transport, and remediation technology design. He provides expert technical assistance on topics that include conceptual groundwater model development; groundwater flow and fate analysis; and remedial alternative selection and system design. Dr. Thomson received his PhD in Environmental Engineering from the University of Waterloo.

Aikaterini Tsitonaki

Dr. Tsitonaki is an Environmental Engineer with Orbicon A/S, in Roskilde, Denmark, where she is part of a multidisciplinary team providing consulting and engineering services on soil and groundwater remediation for government and private clients. Dr. Tsitonaki has completed 4 years of research on ISCO with persulfate and how it affects biodegradation processes. She has authored several scientific publications on this subject, including a review paper on ISCO with persulfate. Dr. Tsitonaki received her diploma in Environmental Engineering from the Technical University of Crete and her MS and PhD degrees in Environmental Engineering from the Technical University of Denmark.

Michael A. Urynowicz

Dr. Urynowicz is a Licensed PE and an Associate Professor of Environmental Engineering in the Department of Civil and Architectural Engineering at the University of Wyoming. Prior to joining the faculty at the University of Wyoming, he was the Founder and Principal Engineer at Envirox LLC, an environmental company specializing in the remediation of complex sites. During his career, Dr. Urynowicz has been involved in a wide range of research related to ISCO

and the remediation of contaminated sites. He also has published numerous technical papers and reports and has given invited lectures across the United States and abroad. He received his BS degree in Chemical Engineering from Michigan State University, his MS in Civil and Environmental Engineering from the University of Wisconsin, and his PhD in Environmental Science and Engineering from the Colorado School of Mines.

Marvin Unger

Dr. Unger is a Principal Scientist with HydroGeoLogic, Inc. with more than 25 years experience in environmental consultation. He specializes in contaminant fate and behavior, state and federal regulations, waste management, strategic planning, and corrective action. Dr. Unger has been working with the SERDP and ESTCP programs for more than 15 years, providing technical support in the areas of environmental restoration, munitions management, technology transfer, and sustainability, wherein he oversees an initiative on ISCO. He has also managed various private sector Resource Conservation and Recovery Act and Superfund projects involving litigation support as well as investigation and remediation projects at petroleum refining, utility, and private sector sites. Dr. Unger received his BS degree in Chemistry from Sul Ross State University, MS degree in Environmental Health Science from Hunter College, and PhD from the University of Arizona in Soil and Water Science.

Richard J. Watts

Dr. Watts is a Professor of Environmental Engineering at Washington State University in Pullman, Washington. He is a licensed Professional Civil Engineer in the state of California. Dr. Watts has 20 years of research experience related to oxidation and reduction processes in environmental systems, has published over 80 refereed papers and a textbook (*Hazardous Wastes: Sources, Pathways, Receptors*, John Wiley & Sons) on these topics, and served as a consultant to numerous companies in the remediation industry. He has served as principal investigator on several SERDP/ESTCP projects. He received his BS degree in Environmental Toxicology from the University of California, Davis, and his PhD in Civil and Environmental Engineering from Utah State University.

External Reviewers

Philip Block

FMC Corporation
1735 Market Street
Philadelphia, PA 19103
USA
Email: philip_block@fmc.com

Dan Bryant

Geo-Cleanse International, Inc.
400 State Route 34
Matawan, NJ 07747
USA
Email: dbryant@geocleanse.com

Doug Carvel

MEC_x
3203 Audley Street
Houston, TX 77098
USA
Email: doug.carvel@mecx.net

Prabhaker Clement

Auburn University
212 Harbert Engineering Center
Auburn, AL 36849
USA
Email: clement@auburn.edu

Eliot Cooper

Vironex, Inc.
13050 W. 43rd Drive, Suite 200
Golden, CO 80403
USA
Email: ecooper@vironex.com

Matthew Dings

Carus Remediation Technologies
315 5th Street
Peru, IL 61354
USA
Email: matt.dings@caruscorporation.com

Linda Fiedler

U.S. Environmental Protection Agency
1200 Pennsylvania Ave., NW
Washington, DC 20460
USA
Email: fiedler.linda@epa.gov

John Haselow

Redox Tech, LLC
200 Quade Drive
Cary, NC 27513
USA
Email: jhaselow@redox-tech.com

Stan Haskins

In-Situ Oxidative Technologies, Inc. (ISOTEC)
6452 Fig St., Suite C
Arvada, CO 80004
USA
Email: shaskins@insituoxidation.com

Keith Henn

Tetra Tech, Inc.
661 Andersen Drive
Pittsburgh, PA 15220
USA
Email: keith.henn@tetrattech.com

George E. Hoag

VeruTEK Technologies, Inc.
65 West Dudley Town Road
Bloomfield, CT 06002
USA
Email: georgehoag@earthlink.net

Michael C. Kavanaugh

Geosyntec Consultants
475 14th St, Suite 400
Oakland, CA 94612
USA
Email: mkavanaugh@geosyntec.com

William B. Kerfoot

Kerfoot Technologies, Inc.
766-B Falmouth Road
Mashpee, MA 02649
USA
Email: WBKerfoot@kerfoottech.com

Larry Kinsman

ORIN Remediation Technologies
McFarland, WI 53558
USA
Email: lkinsman@orinrt.com

William Linn

Florida Department of Environmental Protection
2600 Blair Stone Road
Tallahassee, FL 32399
USA
Email: William.Linn@dep.state.fl.us

Brian Looney

Environmental Sciences and Biotechnology,
Savannah River Technology Center
Building 773-42A
Aiken, SC 29808
USA
Email: Brian02.looney@srnl.doe.gov

Robert Luhrs

Raytheon Company
235 Wyman Street
Waltham, MA 02451
USA
Email: Robert_C_Luhrs@raytheon.com

Susan J. Masten

Michigan State University
A136 Engineering Research Complex
East Lansing, MI 48824
USA
Email: masten@egr.msu.edu

Robert D. Norris

Brown & Caldwell
532 Rider Ridge Drive
Longmont, CO 80501
USA
Email: bnorris@brwnncald.com

Ian T. Osgerby

U.S. Army Corps of Engineers
696 Virginia Road
Concord, MA 01742
USA
Email: ian.t.osgerby@usace.army.mil

Dirk C. Pohlmann

Shaw Environmental & Infrastructure Group
304 Directors Drive
Knoxville, TN 37923
USA
Email: Dirk.Pohlmann@shawgrp.com

Franklin Schwartz

The Ohio State University
125 South Oval Mall
Columbus, OH 43210
USA
Email: frank@geology.ohio-state.edu

Hans F. Stroo

HydroGeoLogic, Inc.
300 Skycrest Drive
Ashland, OR 97520
USA
Email: hstroo@hgl.com

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CHAPTER 1

***IN SITU* CHEMICAL OXIDATION: TECHNOLOGY DESCRIPTION AND STATUS**

Robert L. Siegrist,¹ Michelle Crimi² and Richard A. Brown³

¹Colorado School of Mines, Golden, CO 80401, USA; ²Clarkson University, Potsdam, NY 13699, USA; ³Environmental Resources Management, Ewing, NJ 08618, USA

Scope

Overview of *in situ* chemical oxidation (ISCO) as a remediation technology, including history of development and use, field applications, performance expectations, and costs.

Key Concepts

- ISCO has had a long history of development and use. While research and development still continue, ISCO is a relatively mature technology for the remediation of contaminated groundwater, including source zones and plumes.
- ISCO has primarily been applied for treatment of chlorinated organic solvents and petroleum hydrocarbons to achieve remediation objectives ranging from reducing contaminant mass in a source zone to achieving maximum contaminant levels in a plume. To achieve the more stringent remediation objectives, ISCO is almost always combined with another technology (e.g., bioremediation) or approach (e.g., monitored natural attenuation).
- The effectiveness of ISCO varies and is highly dependent on proper site characterization and design of the oxidant delivery system to achieve oxidative destruction of contaminants of concern in a target treatment zone.
- Typically ISCO applications require a targeted second or third oxidant delivery event since rebound in groundwater contaminant levels following cessation of active ISCO is a common occurrence.
- The median cost of an ISCO project appears to be on the order of \$100 per cubic yard treated. However, costs can vary widely depending on contaminant characteristics, site conditions, and the oxidant used.
- When considering ISCO at a contaminated site, there are a number of frequently asked questions (Table 1.6) and key points to keep in mind to help support successful application (Table 1.7).

1.1 CONTAMINATED SITES AND *IN SITU* REMEDIATION

1.1.1 Introduction

Subsurface contamination by chemicals that pose concerns for human health or environmental quality has been recognized as a widespread problem at industrial and military sites in the United States and abroad. Awareness of the significance of this contamination occurred in the 1970s when adverse health effects were observed at major sites across the United States

(e.g., Times Beach, Love Canal, Valley of the Drums). During the past three decades, substantial progress has been made to identify, investigate, and remediate those sites where unacceptable levels of contamination are present. However, for the foreseeable future, contaminated sites, including thousands of known sites, newly discovered legacy sites, and new sites where recent spills and releases have occurred, will remain an ongoing challenge. Over the next decades, major efforts and funds will be spent cleaning up contaminated sites in the United States in an attempt to protect public health and preserve environmental quality (Figure 1.1).

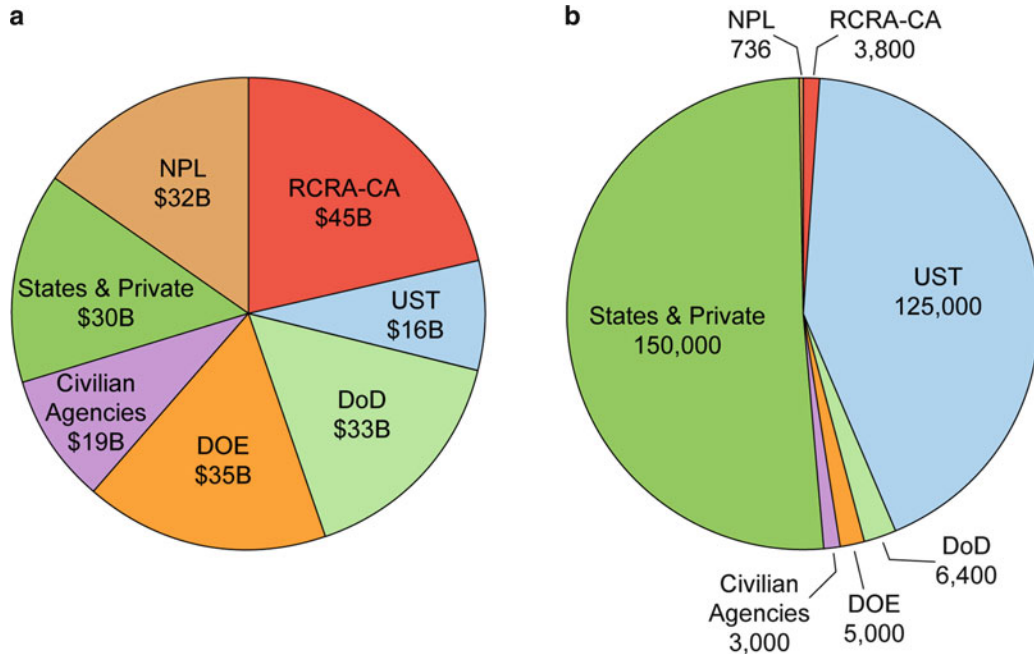


Figure 1.1 Estimated (a) costs for remediation of contaminated sites and (b) total number of sites requiring remediation under current regulations and practices in the USA (during 2004–2033) (USEPA, 2004). Estimates for cleanup costs (total = \$209 billion) and number of sites (total = 294,000) are based on reasonable assumptions regarding the average cleanup cost per site and the number of new site discoveries. Note: NPL - National Priorities List or Superfund, RCRA-CA - Resource Conservation and Recovery Act Corrective Action Program, UST - underground storage tanks, DoD - Department of Defense, DOE - Department of Energy, Civilian Agencies – non-DoD and non-DOE federal agencies; State and Private – state mandatory, voluntary, and brown-field sites, and private sites.

1.1.2 Characteristics of Contaminated Sites

Within the United States, contaminated sites are present at a wide range of facilities and operations spanning simple to complex activities over small to large areas. These sites include gasoline stations, drycleaners, manufacturing plants, energy generation facilities, mining operations, disposal facilities, and nuclear and military installations. Soil and groundwater continue to be the most prevalent contaminated media. The most frequent contaminants of concern (COCs) are volatile organic compounds (VOCs), which are present at a majority of sites. At many sites, semivolatile organic compounds (SVOCs) and metals are also prevalent. The Agency for Toxic Substances and Disease Registry (ATSDR) has identified 275 hazardous substances most commonly found at facilities on the U.S. NPL (ATSDR, 2009). Table 1.1 provides a list of 20 chemicals (or chemical groups), along with their prevalence and priority as COCs at NPL sites in the United States. Some of these same substances are also pervasive at thousands of non-NPL sites.

Table 1.1. Prevalence of Chemicals at NPL Sites and Priority as Contaminants of Concern

Contaminant of concern	Priority as a COC at U.S. hazardous waste sites (ATSDR ranking) ^a	Prevalence at U.S. NPL sites ^b		U.S. drinking water standards (µg/L) ^c
		Number of NPL sites with COC present	Sites with COC present as a % of total NPL sites	
Arsenic	1	1,149	68%	10
Lead	2	1,272	76%	15
Mercury	3	714	49%	2
Vinyl chloride	4	616	37%	2
Polychlorinated biphenyls	5	500	31%	0.5
Benzene	6	1,000	59%	5
Cadmium	7	1,014	61%	5
Polycyclic aromatic hydrocarbons	8	600	42%	–
Benzo(a)pyrene	9	–	–	0.2
Chloroform	11	717	50%	100
Trichloroethene	16	852	60%	5
Chromium	18	1,127	68%	100
Tetrachloroethene	33	771	54%	5
Pentachlorophenol	45	313	20%	1
Carbon tetrachloride	47	425	26%	5
Xylenes (total)	58	840	51%	10,000
Toluene	71	959	60%	1,000
Methylene chloride	80	882	56%	5
1,1,1-Trichloroethane	97	823	50%	200
Ethylbenzene	99	829	49%	700

Note: “–” data not available.

^aATSDR (2009).

^bPrevalence of COCs at NPL sites identified by the U.S. Environmental Protection Agency (USEPA). See ATSDR Toxicological Profiles at <http://www.atsdr.cdc.gov/toxprofiles/index.asp> (accessed June 23, 2010).

^cUSEPA Maximum Contaminant Levels (MCLs); <http://www.epa.gov/ogwdw/contaminants/index.html> (accessed June 23, 2010).

Organic chemicals continue to be the primary COCs in soil and groundwater at contaminated sites in the United States and in other industrialized nations (USEPA, 1997, 2004; Siegrist et al., 2001; Kavanaugh et al., 2003; GAO, 2005). In 2004, there were an estimated 35,000 sites with petroleum contamination from USTs (USEPA, 2004). At most UST sites, the primary COCs are VOCs (e.g., benzene, toluene, ethylbenzene, xylenes). Excluding the UST sites, Kavanaugh et al. (2003) estimated there were 30,000–50,000 sites in the United States with groundwater contamination, of which about 80% were contaminated with organic chemicals. Kavanaugh et al. (2003) also estimated that about 60% of the sites with organic chemicals in groundwater likely have dense nonaqueous phase liquids (DNAPLs) present. Common DNAPLs include trichloroethene (TCE), perchloroethene (PCE; also termed perchloroethylene or tetrachloroethylene), chloroform, and carbon tetrachloride. DNAPLs present a long-term problem due to their chemical properties, including low solubility and high density, and their recalcitrance (stability) in the environment. The chemical properties and

stability can contribute to high contaminant concentrations in groundwater over extensive time frames (Kavanaugh et al., 2003). Similarly, light nonaqueous phase liquids (LNAPLs) in the subsurface (e.g., gasoline and fuel products at UST sites) are also sources of long-term groundwater contamination.

While there are many exposure scenarios that present serious current or future health risks at NPL sites and many other contaminated sites, baseline risk is commonly governed primarily by ingestion exposures to COCs that migrate into groundwater used for drinking water or inhalation exposures to VOCs that enter buildings through vapor intrusion (Figure 1.2). As a result, the main driving force for remediation of groundwater likely will continue to be protecting human health from these exposures. In addition, mitigating ecological impacts will become increasingly important.

Despite general agreement concerning the value of reducing risk through remediation, there are challenges and topics of disagreement concerning the maximum level of contamination that can be left behind safely. There are also conflicting views about how to respond to sites where cleanup to protective levels is not now or likely to be in the future, practical or even possible.

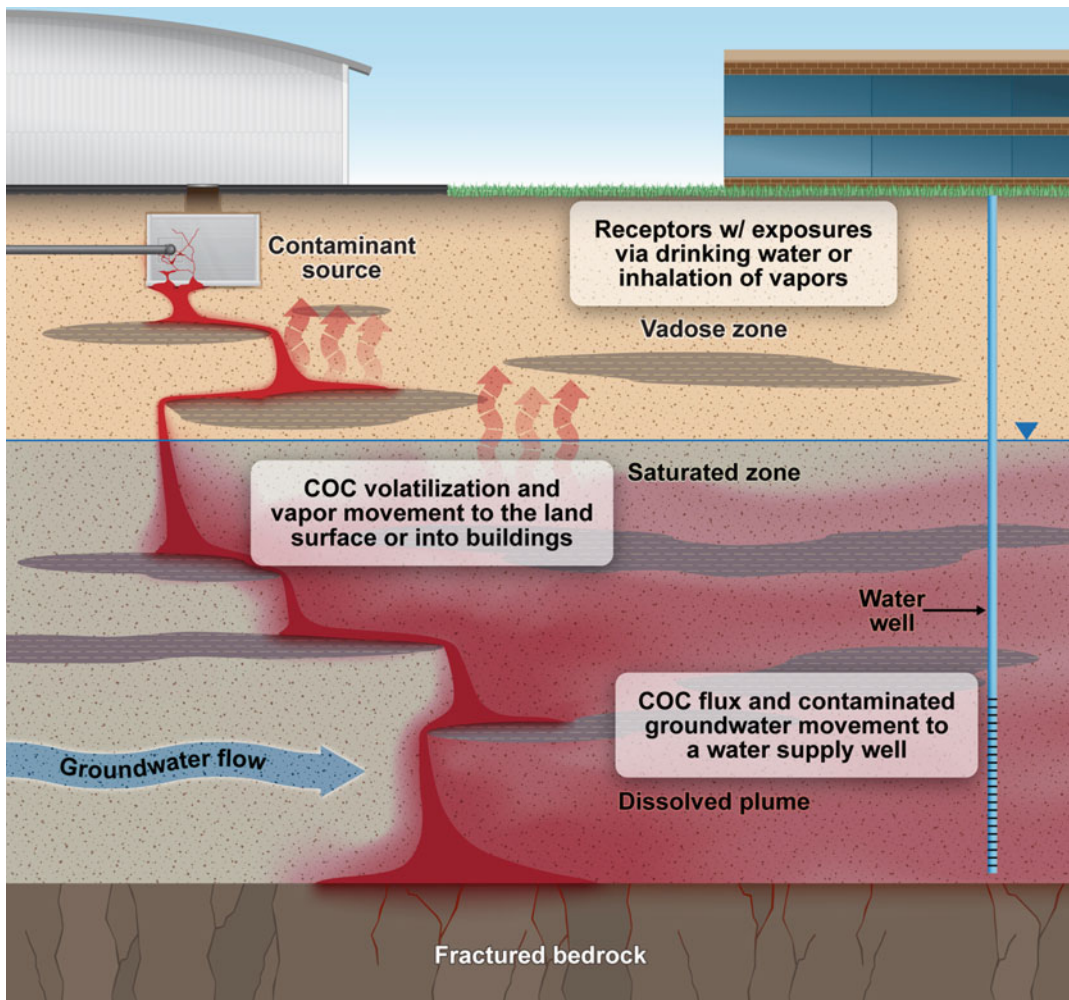


Figure 1.2. Illustration of an organic chemical release (shown in red) leading to long-term contamination of groundwater and potential risks to human health.

1.1.3 Site Remediation Approaches

Initially, the most common approach to the cleanup of groundwater contaminated by organic chemicals involved using pumping wells to extract contaminated groundwater, followed by treatment of the extracted groundwater aboveground (i.e., pump-and-treat). Over time, it became apparent that this approach had severe performance limitations and high costs (Mackay and Cherry, 1989; NRC, 1994; USEPA, 1999). Based on the cleanup costs for 15,000–25,000 U.S. sites with DNAPL contamination, Kavanaugh et al. (2003) estimated that the median cost to operate a groundwater pump-and-treat system is roughly \$180,000 per year, with a range of \$30,000–\$4,000,000. The combined annual costs for all U.S. sites using pump-and-treat are \$2.7–\$4.5 billion a year. Assuming a 30-year life and a 5–10% interest rate, life cycle costs of “cleanup” of DNAPL sites could range from \$50 to \$100 billion (Kavanaugh et al., 2003). A widely held view that has emerged is that cleanup of contaminated groundwater using pump-and-treat alone is virtually impossible, though pump-and-treat can be used as a hydraulic containment technology. As a result, interest in, and development of, alternative *in situ* technologies and approaches has grown appreciably (NRC, 1994, 2005; Kavanaugh et al., 2003; GAO, 2005).

Over the years, research and development efforts have been directed at advancing the scientific and technological understanding of the fate and transport of organic contaminants. These efforts have led to development of *in situ* technologies based on both engineered and natural attenuation processes (NRC, 1994, 1997, 2005). The major *in situ* technologies for groundwater remediation are listed in Table 1.2, along with their advantages and limitations (Stroo, 2010). *In situ* technologies are based on a number of different technical principles and can be applied for contaminated groundwater zones and, to varying extents, for treatment of near surface soil and vadose zones. Examples of technologies that exploit mass transfer and recovery methods include soil vapor extraction, air sparging, or surfactant/cosolvent flushing. Examples of those that use in place destruction include bioremediation or chemical oxidation/reduction. The viability of *in situ* technologies has been enhanced by developments in delivery methods and enabling technologies, such as soil mixing, hydraulic fracturing, and soil heating.

Table 1.2. Advantages and Limitations of the Major *In Situ* Groundwater Remediation Technologies (Stroo, 2010)

Technology	Advantages	Limitations
Enhanced reductive dechlorination (ERD)	<ul style="list-style-type: none"> • Moderate cost • Complete destruction possible • Flexible – numerous site adaptations possible • Effective for several co-contaminants • Compatible with other technologies 	<ul style="list-style-type: none"> • Possible accumulation of toxic intermediates • Possible harmful volatile emissions • Sensitive to geochemistry and hydrogeology • Possible degradation of water quality • Relatively slow treatment
Aerobic cometabolism	<ul style="list-style-type: none"> • Complete destruction possible • Few byproducts of concern 	<ul style="list-style-type: none"> • Cometabolites often of environmental concern • Difficult process to control under field conditions • Sensitive to geochemistry and hydrogeology • Intermediates toxic to degrader organisms • Very limited field-scale experience

(continued)

Table 1.2. (continued)

Technology	Advantages	Limitations
Phytoremediation	<ul style="list-style-type: none"> • Low cost • High public acceptability • Little impact on water quality parameters • May include contaminant destruction 	<ul style="list-style-type: none"> • Depth and climate restrictions • Relatively slow process • Subject to seasonal fluctuations • May require large land area for treatment/capture • Volatile emissions possible
Monitored natural attenuation (MNA)	<ul style="list-style-type: none"> • Low cost • Non-intrusive • Compatible with other technologies 	<ul style="list-style-type: none"> • Very slow removal rates • Sustainability difficult to predict • Long-term monitoring can be costly • Extensive evaluation needed • Possible accumulation of toxic metabolites • Rarely acceptable without source treatment
<i>In situ</i> chemical oxidation	<ul style="list-style-type: none"> • Moderate cost (for high-concentration areas) • Rapid treatment • Complete destruction possible • Compatible with bioremediation 	<ul style="list-style-type: none"> • High cost for dilute plumes • Short oxidant lifetimes • Health and safety threats • Not effective for low permeability zones • Rebound commonly observed • Oxidants may be consumed by other materials
<i>In situ</i> chemical reduction	<ul style="list-style-type: none"> • Moderate cost (for zero-valent iron barriers) • Compatible with other technologies, such as ERD • Lifetimes appear to be cost effective at many sites • Can degrade many co-contaminants 	<ul style="list-style-type: none"> • Passivation can be rapid at some sites • Potential short circuiting or flow-around • Slow downgradient clean front migration
Electrochemical reduction	<ul style="list-style-type: none"> • Moderate cost • Low power requirements • Flexible operation (reversals between electrodes) • Can potentially degrade most co-contaminants 	<ul style="list-style-type: none"> • Relatively immature technology • Depth limitations • May not be feasible at sites with high total dissolved solids
<i>In situ</i> air sparging	<ul style="list-style-type: none"> • Low to moderate cost (depends on vapor treatment) • Relatively easy to design and install 	<ul style="list-style-type: none"> • Not effective for low permeability zones • Poor performance in heterogeneous or stratified aquifers • Not feasible for deep or thick aquifers • Not effective if DNAPL present

The strategy for remediating sites has also evolved. Early strategies based on pump-and-treat focused on containment. However, as discussed above, pump-and-treat did little to address the high residual mass of contaminants in nonaqueous phase liquid (NAPL) source zones. Currently, remediation of sites with source zones is increasingly viewed as best accomplished by combining remedies simultaneously or sequentially for different zones of contamination (NRC, 2005). For example, treatment of a DNAPL source zone with an aggressive technology like thermally enhanced extraction or *in situ* chemical oxidation (ISCO) might

enable remediation of the associated groundwater plume using engineered bioremediation and permeable reactive barriers (Figure 1.3).

ISCO is one of several technologies that have emerged with the potential for cost effective remediation of contaminated soil and groundwater. ISCO involves the subsurface delivery of a chemical oxidant to destroy organic COCs and thereby reduce potential risks to public health and environmental quality. The current chemical oxidants in relatively widespread use for ISCO are hydrogen peroxide (H_2O_2), potassium and sodium permanganate ($KMnO_4$, $NaMnO_4$), sodium persulfate ($Na_2S_2O_8$), and ozone (O_3).

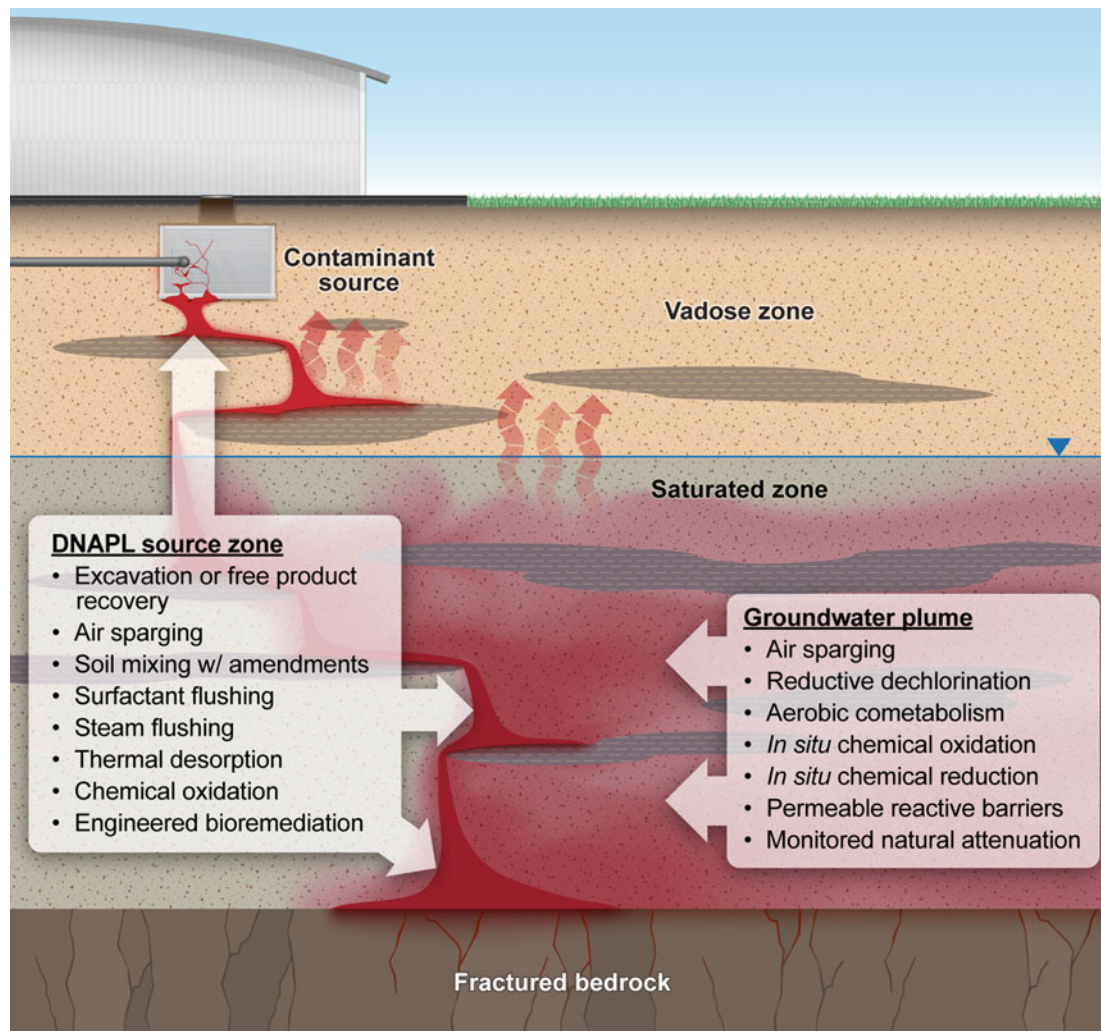


Figure 1.3. Illustration of *in situ* technologies that might be viable for a combined remedy for a site with a DNAPL source zone and associated groundwater plume. (Note: DNAPL contamination is shown in red)

1.1.4 Organization of This Volume on ISCO

This chapter presents an overview of ISCO, its evolution and current status, a summary of current costs and performance information, and the key points for practitioners and managers to consider when using this technology. Details regarding the principles and

practices of ISCO for groundwater remediation are presented in the subsequent chapters of this volume, as highlighted in Table 1.3. While the focus of this volume is on use of ISCO for groundwater remediation, many of the principles and practices presented are applicable to the use of chemical oxidation for remediation of contaminated soils and other media.

Table 1.3. Chapters in this Volume and Coverage in Each

No.	Focus	Coverage
1	<i>In situ</i> chemical oxidation: technology description and status	ISCO attributes, evolution, field experiences, performance expectations and costs, and key points for use
2	Fundamentals of ISCO using hydrogen peroxide	Hydrogen peroxide properties, reaction chemistry, oxidant interactions in the subsurface, and treatability of different contaminants
3	Fundamentals of ISCO using permanganate	Permanganate properties, reaction chemistry, oxidant interactions in the subsurface, and treatability of different contaminants
4	Fundamentals of ISCO using persulfate	Persulfate properties, reaction chemistry, oxidant interactions in the subsurface, and treatability of different contaminants
5	Fundamentals of ISCO using ozone	Ozone properties, reaction chemistry, oxidant interactions in the subsurface, and treatability of different contaminants
6	Principles of ISCO transport and modeling	Fate and transport processes affecting oxidant delivery and distribution in the subsurface, and analytical and numerical modeling approaches
7	Principles of combining ISCO with other <i>in situ</i> remedial approaches	Options for combining ISCO simultaneously or sequentially with remedial actions and considerations to ensure beneficial coupling
8	Evaluation of ISCO field applications and performance results	Case studies of ISCO for different COCs and site conditions, the cleanup goals set, performance achieved, and project costs
9	Systematic approach to engineering of an ISCO system	Step-by-step guidance on ISCO screening, conceptual design, detailed design, implementation, and performance monitoring
10	Site characterization and ISCO treatment goals	Site characterization for a conceptual site model to properly screen ISCO and develop a conceptual design to achieve ISCO treatment goals
11	Oxidant delivery approaches and contingency planning	Methods of aboveground handling and subsurface delivery of different oxidants, and contingency planning
12	ISCO system performance monitoring	Monitoring required for process control and performance assurance
13	ISCO project costs and sustainability considerations	Framework for estimating costs for ISCO projects and issues related to sustainability
14	ISCO status and future directions	Summary of the current status of ISCO and research needs to enhance current and future applications

1.2 ISCO AS A REMEDIATION TECHNOLOGY

A wide range of organic chemicals are susceptible to oxidative degradation through chemical reactions with oxidants, such as catalyzed hydrogen peroxide (also known as CHP or modified Fenton's reagent), potassium and sodium permanganate, sodium persulfate, and

ozone (Table 1.4). There are also a few new oxidants or combination of oxidants, such as peroxone, percarbonate, and calcium peroxide. There is less information on these oxidants and they have been implemented less frequently so they are not discussed extensively in this volume.

Table 1.4. Characteristics of Chemical Oxidants Used for Destruction of Organic Contaminants (adapted from Huling and Pivetz, 2006)

Oxidant ^a	Oxidant chemical	Commercial form	Activator	Reactive species
Permanganate*	KMnO ₄ or NaMnO ₄	Powder, liquid	None	MnO ₄ ⁻
Hydrogen peroxide*	H ₂ O ₂	Liquid	None, Fe(II), Fe(III)	OH [•] , O ₂ ^{•-} , HO ₂ [•] , HO ₂ ⁻
Ozone*	O ₃ (in air)	Gas	None	O ₃ , OH [•]
Persulfate*	Na ₂ S ₂ O ₈	Powder	None, Fe(II), Fe(III), heat, H ₂ O ₂ , high pH	S ₂ O ₈ ²⁻ , SO ₄ ^{•-}
Peroxone	H ₂ O ₂ plus O ₃ (in air)	Liquid, gas	O ₃	O ₃ , OH [•]
Percarbonate	Na ₂ CO ₃ ·1.5H ₂ O ₂	Powder	Fe(II)	OH [•]
Calcium peroxide	CaO ₂	Powder	None	H ₂ O ₂ , HO ₂ ⁻

^aThose oxidants with an "*" have been most commonly used for ISCO applications (see Section 1.3).

Under the right conditions, oxidants yield reactive species (Table 1.5) that can transform and often mineralize many COCs including chlorinated hydrocarbons (e.g., TCE, PCE), fuels (e.g., benzene, toluene, methyl *tert*-butyl ether), phenols (e.g., pentachlorophenol), polycyclic aromatic hydrocarbons (e.g., naphthalene, phenanthrene), polychlorinated biphenyls, explosives (e.g., trinitrotoluene), and pesticides (e.g., lindane). Through laboratory experimentation, reaction stoichiometries, pathways, and kinetics have been established for many common COCs. Degradation reactions tend to involve electron transfer or free radical processes, involve simple to complex pathways with various intermediates, and follow second-order kinetics. The need for activation to generate free radicals and the sensitivity to matrix conditions, such as temperature, pH, and salinity, vary with the different oxidants and specific contaminants.

Table 1.5. Reactive Species Associated with Oxidant Chemicals (Huling and Pivetz, 2006)

Reactive species	Formula	Standard reduction potential (V)
Hydroxyl radical	OH [•]	+2.8
Sulfate radical	SO ₄ ^{•-}	+2.6
Ozone	O ₃	+2.1
Persulfate anion	S ₂ O ₈ ²⁻	+2.1
Hydrogen peroxide	H ₂ O ₂	+1.77
Permanganate anion	MnO ₄ ⁻	+1.7
Perhydroxyl radical	HO ₂ [•]	+1.7
Oxygen	O ₂	+1.23
Hydroperoxide anion	HO ₂ ⁻	-0.88
Superoxide radical	O ₂ ^{•-}	-2.4

The ISCO systems that can be (and have been) applied in the field vary significantly in their features based on the nature and extent of contamination, the site conditions present, and the remediation goals and objectives (Siegrist et al., 2001; ITRC, 2005; Huling and Pivetz, 2006; Krembs, 2008). Remediation objectives for ISCO are established within the context of the overall remediation goals and cleanup levels established for a particular site. The objectives generally fall into one of the following three categories:

- Reduce the contaminant concentration or mass in the ISCO-treated zone by some fraction (e.g., >90%).
- Achieve a specified post-ISCO contaminant concentration in an ISCO-treated zone (e.g., ≤ 1 mg/kg in subsurface solids or ≤ 100 $\mu\text{g/L}$ in groundwater).
- Achieve a specified concentration in a groundwater plume at compliance points down-gradient from an ISCO-treated source zone.

In some cases, these objectives might be met by combining ISCO with another remedial technology or approach, as described in Chapter 7.

Oxidant can be delivered into the subsurface at varied concentrations and mass loading rates in liquid, gas, or solid phases through different subsurface delivery methods. Oxidant delivery has most commonly been accomplished through permeation by vertical direct-push injection probes or flushing by vertical groundwater wells (Figure 1.4). Other delivery methods have also been employed using horizontal wells, infiltration galleries, soil mixing, and hydraulic or pneumatic fracturing.

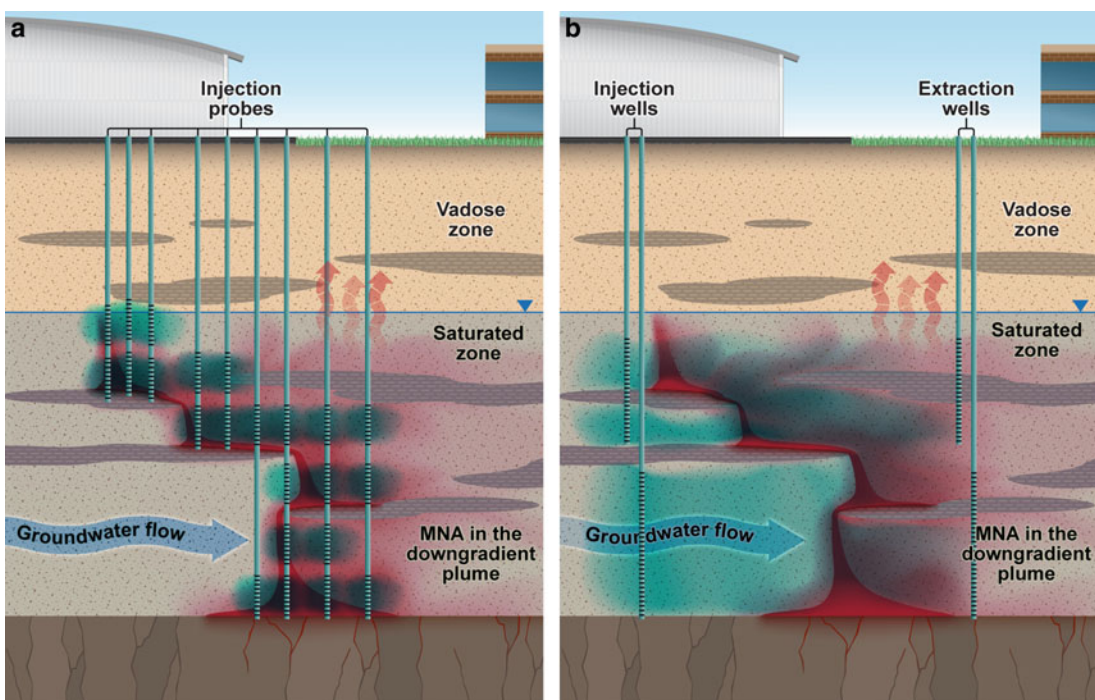


Figure 1.4. *In situ* chemical oxidation using (a) direct-push injection probes or (b) well-to-well flushing to deliver oxidants (shown in blue) into a target treatment zone of groundwater contaminated by DNAPL compounds (shown in red).

Research completed by Siegrist et al. (2006, 2008a), along with that of other investigators funded under the DoD ISCO initiative (<http://www.serdp-estcp.org/ISCO.cfm>), has demonstrated that the successful use of ISCO for remediation of contaminated groundwater fundamentally depends on the reaction chemistry of the oxidant used and its ability to degrade the COCs at a site. Success also depends on effective delivery of oxidants into the subsurface, which is determined by the oxidant reactive transport under the hydrogeologic and geochemical conditions present at a site. Oxidant reaction chemistry (both with the COCs and with natural organic matter and minerals) and subsurface transport affect ISCO application, COC destruction, and cost effectiveness.

The application of ISCO can be affected by, and also effect changes in, the pre-ISCO subsurface conditions (e.g., groundwater flow direction and velocity, oxidant concentrations, Eh, pH, temperature, dissolved organic carbon). These effects should be considered and accounted for during ISCO system design and implementation (e.g., Figures 1.5 and 1.6).

1.3 EVOLUTION OF ISCO

1.3.1 Research and Development Activities

ISCO has evolved out of a long history of using chemical oxidation to destroy organic contaminants in water within the municipal and industrial water and waste treatment industry. The first step in the evolution of ISCO involved research and development (R&D) to adapt use of chemical oxidants like hydrogen peroxide and ozone to treat organic COCs in groundwater that was pumped to the surface and containerized in tank-based reactors (i.e., *ex situ* treatment) (Barbeni et al., 1987; Glaze and Kang, 1988; Bowers et al., 1989; Watts and Smith, 1991; Venkatadri and Peters, 1993). While a concept underlying *in situ* chemical oxidation was patented in 1986 (Brown and Norris, 1986), the first commercial *in situ* application of hydrogen peroxide occurred in 1984 to treat groundwater contaminated with formaldehyde (Brown et al., 1986).

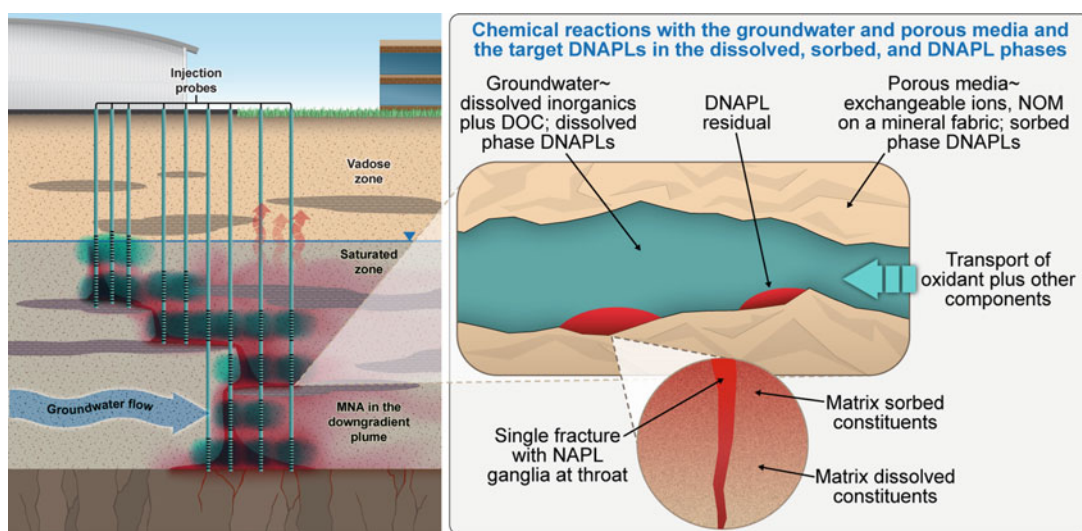


Figure 1.5. Macro- and micro-scale features of contaminated groundwater zones where organic contaminants of concern may exist in the aqueous, sorbed, and nonaqueous phases (adapted from Siegrist et al., 2006). Note: DOC - dissolved organic carbon, NOM - natural organic matter.

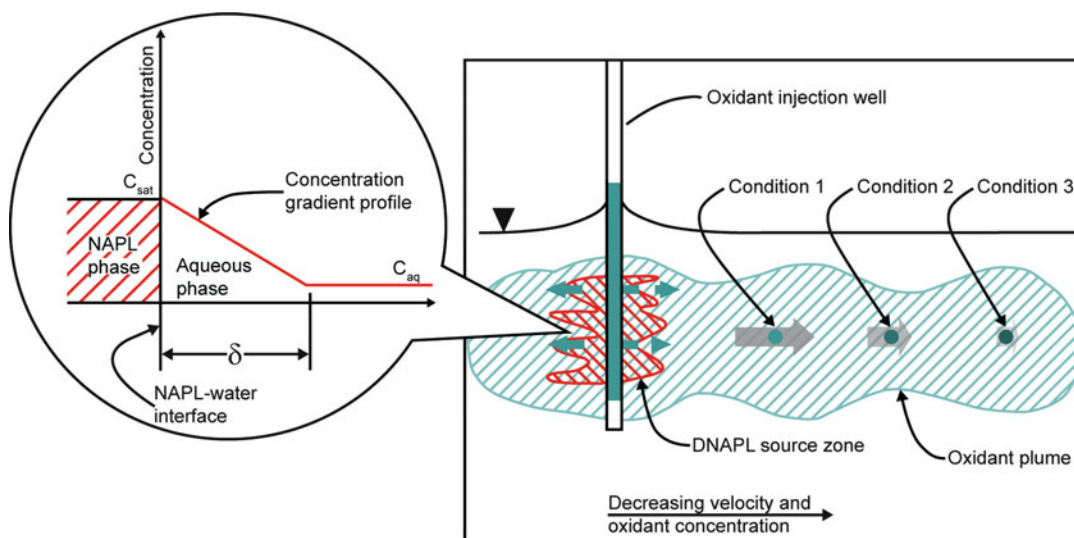


Figure 1.6. ISCO delivery methods can affect groundwater velocity, oxidant concentrations, and NAPL depletion within a target treatment zone (Siegrist et al., 2006; Petri et al., 2008a). Oxidant injection out of a well yields a forced gradient such that Condition 1 has a high flow velocity and high oxidant concentration; Condition 2 has a lower velocity and moderate oxidant concentration; and Condition 3 has near-ambient groundwater velocity and near-zero oxidant level.

Starting in 1990, researchers began to explore hydrogen peroxide and modified Fenton's reagent oxidation as applied in soil and groundwater environments (Watts et al., 1990, 1991, 1997; Watts and Smith, 1991; Tyre et al., 1991; Ravikumar and Gurol, 1994; Gates and Siegrist, 1993, 1995). Research was also initiated with alternative oxidants such as ozone (Bellamy et al., 1991; Nelson and Brown, 1994; Marvin et al., 1998) and potassium permanganate (Vella et al., 1990; Vella and Veronda, 1994; Gates et al., 1995; Schnarr et al., 1998; West et al., 1997; Siegrist et al., 1998a, b, 1999; Yan and Schwartz, 1998, 1999; Tratnyek et al., 1998; Urynowicz and Siegrist, 2000). The development of ISCO continues to expand as evidenced by more recent research with newer oxidants like sodium persulfate and sodium carbonate peroxide (percarbonate) (e.g., Brown et al., 2001; Block et al., 2004; Crimi and Taylor, 2007).

In a parallel development, alternative methods of delivering oxidants into the subsurface were explored. ISCO was deployed by a range of methods including permeation through vertical probes (e.g., Jerome et al., 1997; Siegrist et al., 1998c; Moes et al., 2000), flushing by vertical and horizontal groundwater wells (e.g., Schnarr et al., 1998; West et al., 1997, 1998; Lowe et al., 2002), and reactive zone emplacement by either soil mixing (e.g., Gates and Siegrist, 1993) or pneumatic and hydraulic fracturing (e.g., Murdoch et al., 1997a, b; Siegrist et al., 1999).

In the late 1990s and early 2000s, case study reports became available (e.g., USEPA, 1998; ESTCP, 1999), followed by the publication of the first reference book (Siegrist et al., 2001) and the first technical and regulatory reference manual (ITRC, 2001). These documents provided valuable insight into principles and practices, field experiences, and regulatory requirements. However, they did not provide the state-of-the-science knowledge and engineering know-how needed for a standard of practice to ensure effective, timely, and cost effective site-specific application of ISCO alone or in combination with other remedial options. As a result, the implementation of ISCO was plagued by uncertain and variable design and application practices. This caused ISCO performance to be unpredictable for some site conditions and remediation applications.

To advance the science and engineering of ISCO and resolve questions regarding ISCO design and performance capabilities, ISCO research and development efforts escalated during the early 2000s. This research has been catalyzed in large part by the promising potential of ISCO and growing interest in its use, notably at DoD sites across the country. Around 2002, a major ISCO research initiative was launched within DoD's Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) (<http://www.serdp.org/Research/ISCO.cfm>).

A portfolio of ISCO projects and activities, both within the DoD ISCO initiative and through other sponsored research programs, has increased the understanding of ISCO. Advancements have included improved fundamental understanding of the following:

- COC oxidation chemistry and treatment (e.g., Gates-Anderson et al., 2001; Jung et al., 2004; Qiu et al., 2004; Smith et al., 2004; Watts et al., 2005a).
- Oxidant interactions with subsurface media (e.g., Siegrist et al., 2002; Crimi and Siegrist, 2003, 2004a, b; Anipsitakis and Dionysiou, 2004; Shin et al., 2004; Jung et al., 2005; Monahan et al., 2005; Mumford et al., 2005; Bissey et al., 2006; Jones, 2007; Teel et al., 2007; Sun and Yan, 2007; Sirguy et al., 2008; Urynowicz et al., 2008; Woods, 2008).
- Oxidative destruction of DNAPLs (e.g., Crimi and Siegrist, 2005; Heiderscheidt, 2005; Kim and Gurol, 2005; Urynowicz and Siegrist, 2005; Watts et al., 2005b; Siegrist et al., 2006; Smith et al., 2006; Heiderscheidt et al., 2008a; Petri et al., 2008a).
- Examination of newer oxidants (e.g., Liang et al., 2004a, b; Crimi and Taylor, 2007; Waldemer et al., 2007; Liang and Lee, 2008).
- Oxidant transport processes and deliverability (e.g., Choi et al., 2002; Lowe et al., 2002; Struse et al., 2002; Lee et al., 2003; Tunnicliffe and Thomson, 2004; Heiderscheidt, 2005; Ross et al., 2005; Zhang et al., 2005; Petri, 2006; Heiderscheidt et al., 2008a; Petri et al., 2008a).
- Combining ISCO with other remedies (e.g., Sahl, 2005; Dugan, 2006; Sahl and Munakata-Marr, 2006; Sahl et al., 2007).
- Treatability test methods (e.g., Haselow et al., 2003; Mumford et al., 2004; ASTM, 2007).
- Formulation of mathematical models and decision support tools (e.g., Kim and Choi, 2002; Heiderscheidt, 2005; Heiderscheidt et al., 2008b).

The escalation in interest and R&D activities in ISCO during the early 2000s led to a dramatic increase in the published literature concerning the fundamental and applied understanding regarding chemical oxidants and their application for *in situ* remediation. In 2008, a critical review of the published literature relevant to ISCO science and technology was completed by Petri et al. (2008b) as a component of a DoD ESTCP project (Siegrist et al., 2010). Petri et al. identified nearly 600 ISCO-relevant publications encompassing four oxidants: permanganate, persulfate, hydrogen peroxide, and ozone. The publications were initially characterized and classified to provide insight into the evolution and current state of ISCO science (Figures 1.7 and 1.8). Then, a detailed review and analysis was made to elucidate key findings regarding ISCO and the implications for site-specific engineering and performance.

The Petri et al. (2008b) review of the published literature concerning ISCO revealed the dramatic increase in published information beginning in the late 1990s (Figure 1.7). It also revealed marked differences in the scope of work carried out and the breadth and depth of understanding for each of the four oxidants and their application *in situ* (Figure 1.8). For example, the published literature concerning ISCO using hydrogen peroxide or permanganate oxidants markedly exceeds the literature base available for ozone and persulfate (Figure 1.8). The published information on

ISCO using hydrogen peroxide is primarily focused on reaction chemistry with relatively less information concerning oxidant transport and modeling. In contrast, the published information on ISCO using permanganate spans reaction chemistry as well as transport and modeling (Figure 1.8).

The review by Petri et al. (2008b) also included several findings that apply to all four oxidants and ISCO in general. For example, regardless of oxidant type, ISCO is challenged by hydrogeologic conditions, as are many non-ISCO remediation technologies. Also, ISCO can enhance or interfere with the use of other remediation technologies. The impacts of ISCO on biological processes and bioremediation were the most extensively investigated, yielding the following conclusions:

- ISCO does *not* sterilize the subsurface.
- Bioprocesses are often disrupted, but activity rebounds with time.
- Some ISCO effects may be beneficial to bioprocesses.

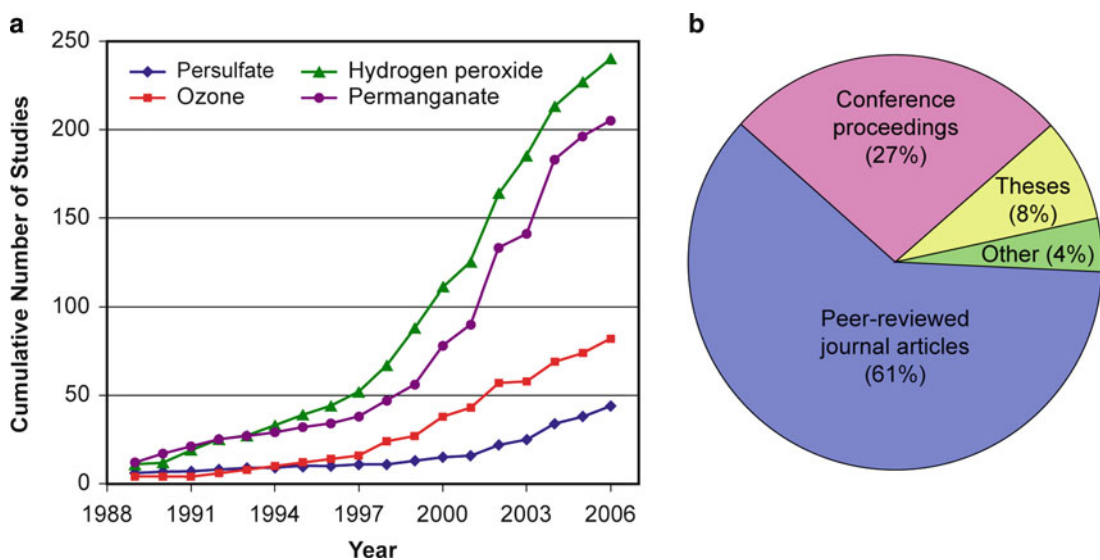


Figure 1.7. Evolution of the (a) published literature base concerning ISCO and (b) the types of publications within a database of about 600 articles, theses and reports (Petri et al., 2008b).

Further detailed information concerning the fundamental understanding that has evolved out of the R&D completed concerning the use of hydrogen peroxide, permanganate, persulfate, and ozone for ISCO is provided in Chapters 2–5, respectively. Each of these chapters describes the respective oxidant properties, reaction chemistry, interactions in the subsurface, and treatability of different COCs. Information regarding the reactive transport of oxidants in a groundwater environment, including mathematical modeling approaches, is given in Chapter 6. The potential to combine ISCO with bioremediation, MNA and other technologies and approaches is described in Chapter 7.

1.3.2 Field Applications

The number of field applications of ISCO in the United States and abroad has grown rapidly during the past decade. Around 2000, the applications of ISCO using hydrogen peroxide (or modified Fenton's reagent), ozone, and permanganate were highlighted in several published reports and texts (ESTCP, 1999; USEPA, 1998; Yin and Allen, 1999; Siegrist et al., 2001). More recently, Krembs (2008) completed a review of prior case history studies and carried out a critical review of 242 projects involving ISCO field applications to examine the site-specific design and

performance of ISCO projects. Based on the projects reviewed by Krembs (2008), the number of applications of ISCO has grown rapidly since the late 1990s (Figure 1.9).

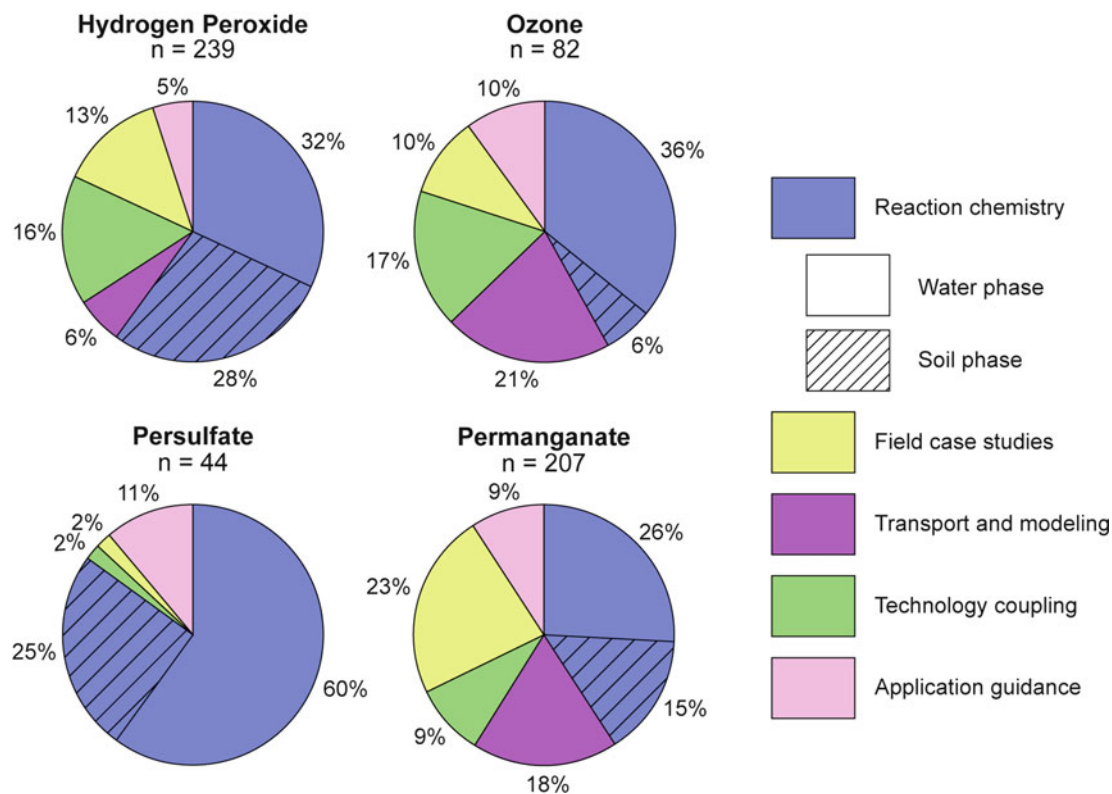


Figure 1.8. Classification of ISCO literature in Figure 1.7 based on the scope of the work (Petri et al., 2008b).

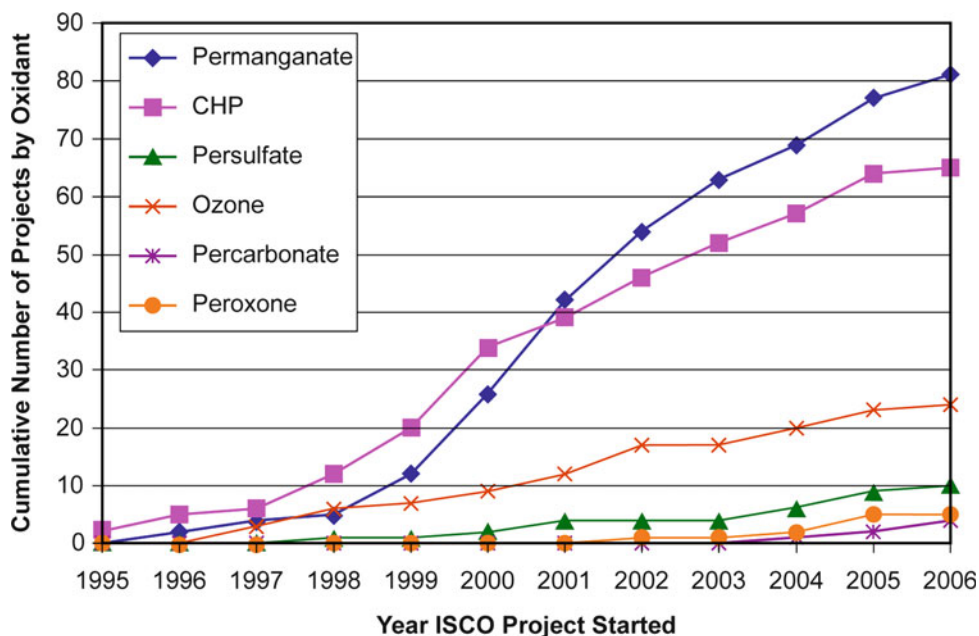


Figure 1.9. Cumulative number of ISCO projects from 1995 to 2006 (Krembs, 2008).

Based on the review by Krembs (2008), ISCO has been applied to sites with different geologic conditions (Figure 1.10a) and used to achieve different remediation goals and objectives (Figure 1.10b). Figure 1.11 shows several photographs illustrating the conditions and infrastructure present at sites where ISCO has been deployed. Further details concerning ISCO field applications and experiences are presented in Chapter 8.

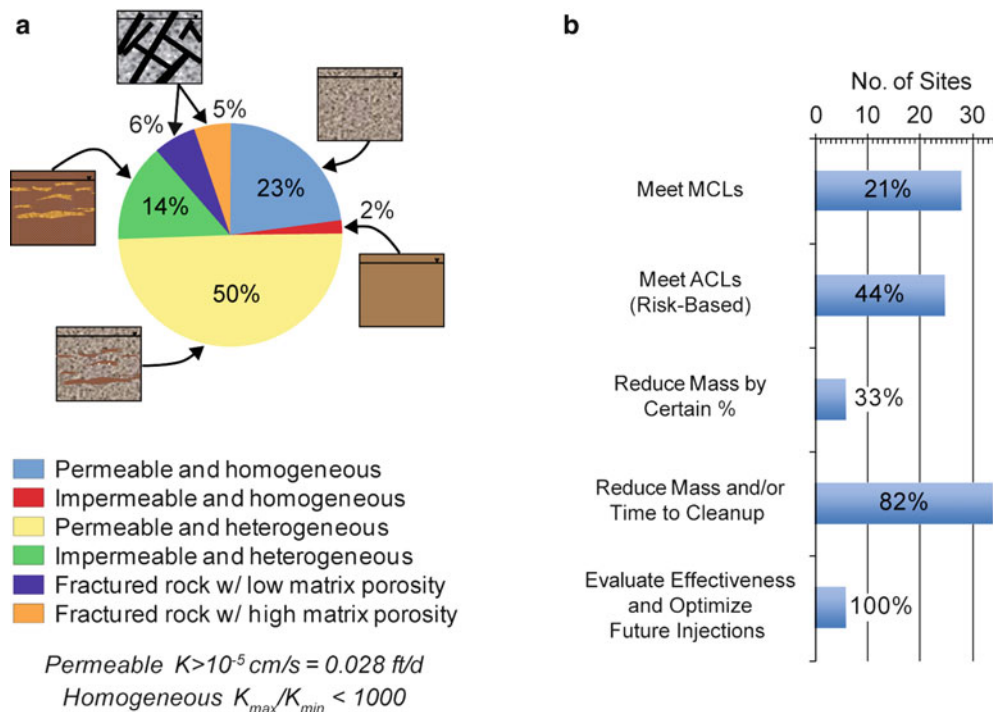
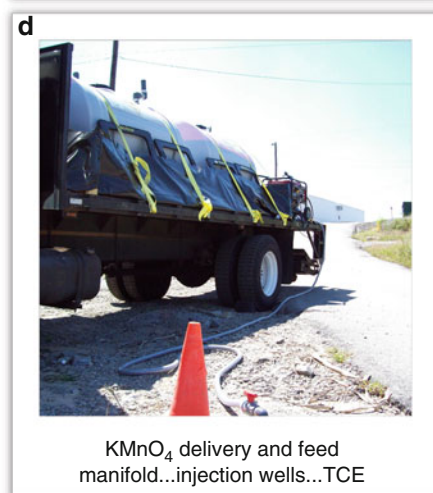
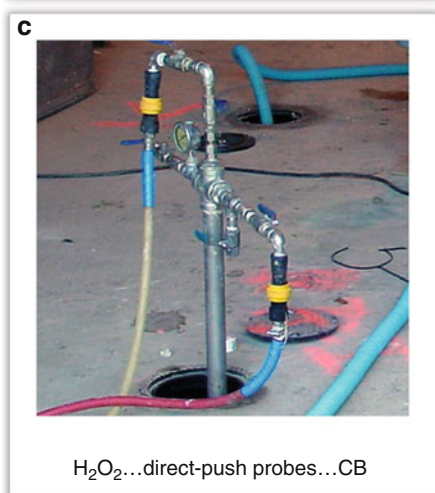
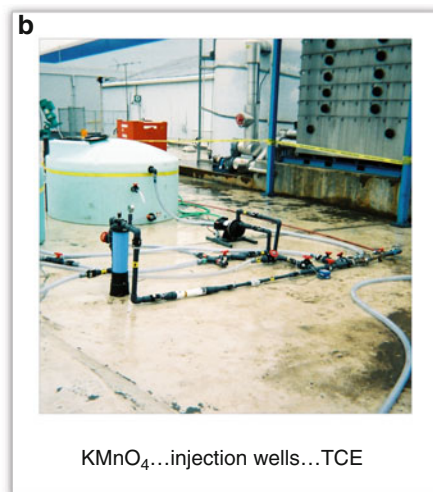
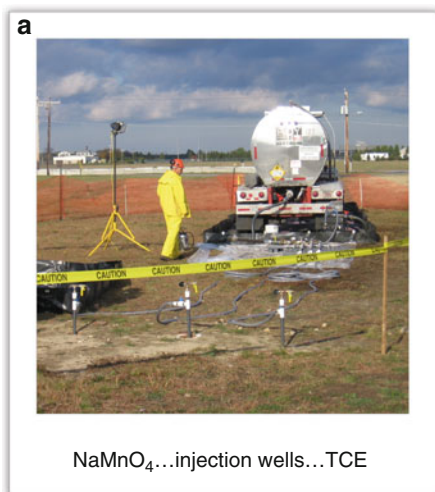


Figure 1.10. Relative number of ISCO applications (a) to sites with different geologic conditions ($n = 149$) and (b) for full-scale projects with different remediation objectives ($n = 99$) (Krembs, 2008). In (b) the length of the bar corresponds to the number of sites with the goal specified and the % label indicates the percentage of those sites meeting the goal set. Note: ACL - alternative (risk-based) cleanup levels, cm/s - centimeters per second, ft/d - feet per day, K - saturated hydraulic conductivity.

1.4 SYSTEM SELECTION, DESIGN, AND IMPLEMENTATION

ISCO system selection, design, and implementation practices should rely on a clear understanding of ISCO and its applicability to a given set of contaminant and site conditions to achieve site-specific remediation objectives. A number of key issues may be relevant and need to be addressed during the selection, design, and implementation of ISCO regardless of the oxidant and delivery system being employed. These issues are listed below:

- Amenability of the target COCs to oxidative degradation.
- Effectiveness of the oxidant for NAPL destruction.
- Optimal oxidant loading (dose concentration and delivery) for a given target treatment zone in a given subsurface setting.
- Nonproductive oxidant consumption due to natural oxidant demand (NOD) exerted by natural organic matter, reduced inorganic species, and some mineral phases in the subsurface.



(continued)

Figure 1.11. Photographs illustrating some of the conditions and infrastructure at sites where ISCO has been deployed for groundwater remediation. Image captions give oxidant used, delivery method, and target contaminants. Note: CB - chlorobenzene, MGP - manufactured gas plant.

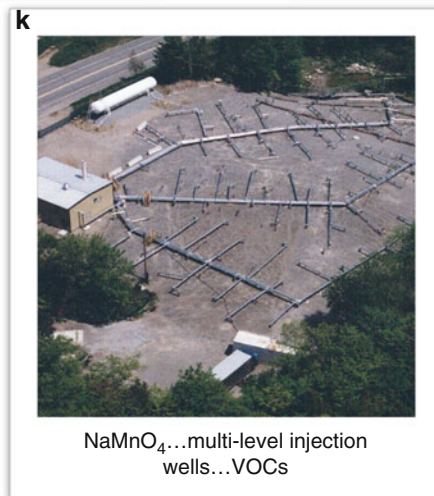
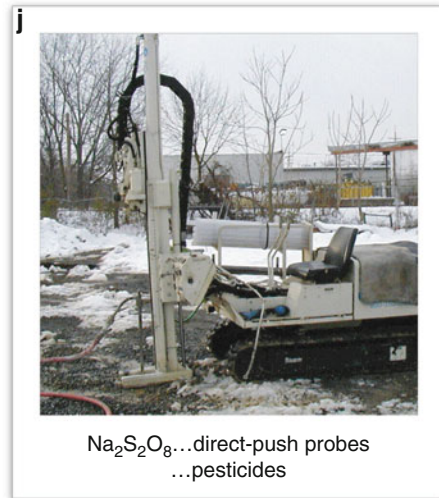


Figure 1.11. (Continued)

- Nonproductive oxidant consumption by autodecomposition reactions and free radical scavenging reactions.
- Potential adverse effects (e.g., mobilizing metals such as chromium, forming toxic byproducts, reducing formation permeability, generating off-gases and heat).
- Potential to combine ISCO with other remediation technologies and approaches.

Matching the oxidant and delivery system to the COCs and site conditions is important for achieving site-specific remediation objectives. Moreover, the objectives need to be realistic and achievable, for ISCO as a stand-alone technology or as part of a combined remedy, based on the resources allocated for the ISCO project.

The selection, design, and implementation of a remedial action are generally accomplished within a phased project approach, as depicted in Figure 1.12 (GAO, 2005) and described for ISCO in Chapter 9. During the feasibility study for a given site, consideration of ISCO as a viable remedial option is often based on the general benefits that ISCO can offer. These include rapid and extensive reactions with various COCs, applicability to many subsurface environments, ability to tailor ISCO to a site, and rapid implementation that can support property transfers and site redevelopment projects. Potential limitations for ISCO are also considered during decision-making, including the resistance of some COCs to complete chemical oxidation, the level of NOD exerted by the subsurface, the stability of the oxidant in the subsurface, constraints on effective oxidant distribution, possible fugitive gas emissions, the potential for contaminant rebound, and the effects of chemical addition on water quality.

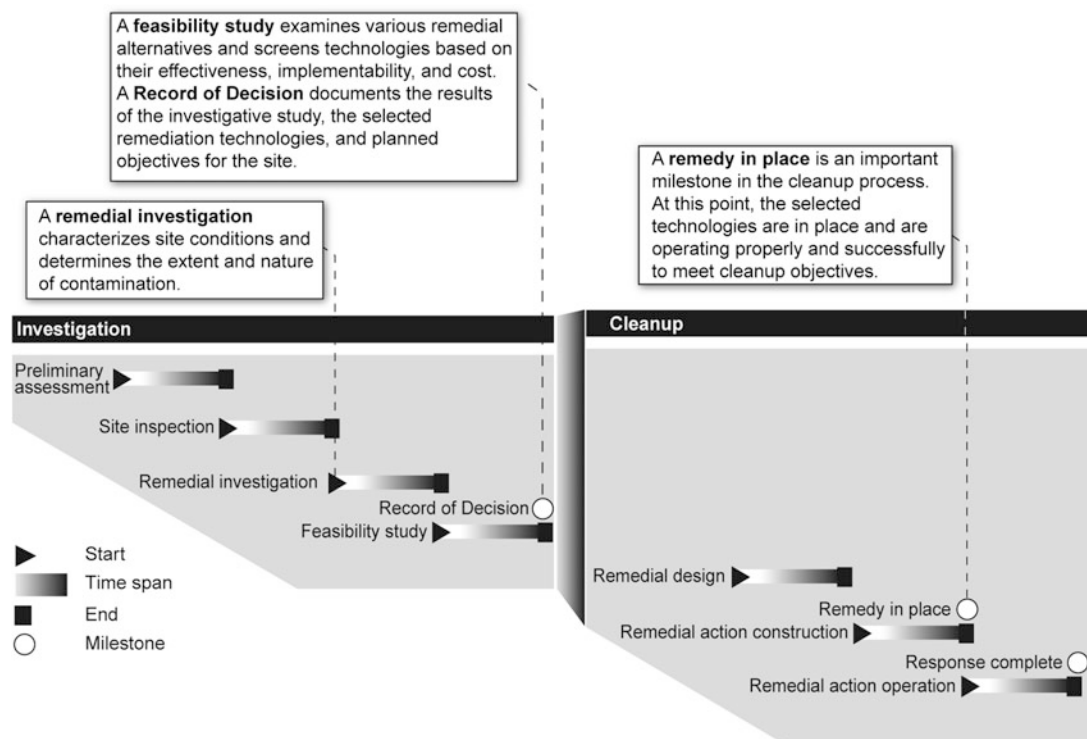


Figure 1.12. Selected phases and milestones in DoD’s environmental cleanup process (GAO, 2005).

If ISCO is selected as a viable alternative for a particular site and a site-specific design must be accomplished, many choices and decisions have to be made. For example, choices must be made between oxidant type (e.g., hydrogen peroxide, persulfate, permanganate, ozone), delivery method (e.g., direct push probes, injection wells, air sparging wells), process control and performance monitoring, and so forth. As described in Chapter 9, these choices should be carefully made to improve the chances that the ISCO system will yield a sufficient concentration of a suitable oxidant in contact with the target COCs under amenable conditions over a sufficient period of time for the COCs to be destroyed.

As discussed earlier, the ISCO systems that can be (and have been) applied in the field are highly varied in their features. Different oxidants and additives (such as stabilizers or activators) have been used. Concentrations and injection flow rates can vary widely, and a variety of subsurface delivery methods can be employed. In addition, overall site remediation goals and regulatory constraints may influence the remediation objectives established for the ISCO technology. To improve the confidence level in the choices and decisions made, treatability studies and field-scale pilot tests are frequently necessary. If ISCO is selected for a site, remedial design and system construction must be accomplished. Lastly, ISCO operation and performance monitoring ensues. Eventually site closure should be achieved through ISCO alone or in conjunction with another remediation technology or approach.

Given the properties of chemical oxidants, the use of ISCO requires diligent attention to safety and waste management issues. ISCO involves the use of hazardous chemicals under field conditions and as such, worker and environmental safety must be carefully considered and effectively managed. Potential worker safety risks include those typically associated with standard construction operations and work at a contaminated site, as well as risks specific to ISCO, which are primarily associated with the aboveground handling of the oxidants. The nature and seriousness of the risks will depend on the oxidant form and concentrations used and the methods employed for general handling and subsurface delivery. Once oxidants are delivered into the subsurface, worker risk should be low because the ground surface is normally not disturbed by well-designed *in situ* delivery methods. Environmental risk includes daylighting of oxidants into streams or water bodies where there can be concern over water quality degradation and adverse effects on aquatic life. This risk can be managed through adequate engineering controls to prevent oxidant or contaminant movement away from the site to a sensitive environmental receptor.

Waste management issues are related to type and volume of ISCO-generated waste. Possibly the most difficult wastes to manage are the containers, materials, and personal protective equipment that have oxidant residual in them. Flushing such materials with water can reduce the residual oxidant concentration and mass to acceptable levels. A reducing agent (e.g., sodium thiosulfate) can also be used to neutralize oxidants such as permanganate, however this will generate manganese (IV) oxide (MnO_2) solids that need to be dewatered and disposed of appropriately. Care must be taken to avoid disposing of combustible materials that have contacted oxidants in bulk waste containers because fires are possible in such situations. Additional generated wastes expected during ISCO are drill cuttings produced during installation of oxidant delivery access points and other monitoring locations. Driven casing techniques are available to minimize this waste when it is a concern.

1.5 PROJECT PERFORMANCE AND COSTS

The effectiveness of ISCO varies: at some sites, ISCO has been applied and the destruction of the target COCs has occurred such that cleanup goals have been met in a cost-effective and timely manner, whereas at other sites, ISCO applications have had uncertain or poor *in situ*

treatment performance. Poor performance has often been attributed to poor uniformity of oxidant delivery caused by low permeability zones and formation heterogeneity, excessive oxidant consumption by natural subsurface materials, or presence of large masses of DNAPLs (Siegrist et al., 2001, 2006, 2008a). In some applications, there have been concerns over secondary effects, such as mobilization of metals, loss of well screen and formation permeability, and gas evolution and fugitive emissions, as well as health and safety practices (Siegrist et al., 2001; Crimi and Siegrist, 2003; Krembs, 2008).

Of the 242 ISCO projects examined by Krembs (2008) (the results of the study are included in Chapter 8), PCE or TCE were the targeted COCs at 70% of the sites, the subsurface conditions were characterized as permeable at 75% of the sites, and oxidants were delivered using permanent or temporary injection wells at 70% of the sites. Krembs (2008) also examined the reported performance and cost of ISCO projects. The percentage of full-scale ISCO projects that attempted to meet a specific goal and reported that they had met it were as follows:

- 21% of 28 Projects attempting to achieve MCLs met this goal.
- 44% of 25 Projects attempting to achieve ACLs met this goal.
- 33% of Six projects attempting to reduce the COC mass by a certain percentage met this goal.
- 82% of 34 Projects attempting to reduce the COC mass and/or time to cleanup met this goal.
- 100% of Six projects attempting to evaluate effectiveness and optimize future injections met this goal.

Krembs (2008) reported the median total cost for 55 ISCO projects to be \$220,000; the median unit cost was \$94 per cubic yard (cy) treated based on 33 projects with unit cost data. McDade et al. (2005) reported median and unit costs of \$230,000 and \$125/cy, respectively, for 13 ISCO projects. It is important to recognize that the cost of an ISCO project can vary by an order of magnitude or more depending on various factors. For example, sites with fuel hydrocarbons and permeable subsurface conditions typically cost less than those with DNAPLs or complex subsurface conditions. High unit costs can also result where ISCO has been used to treat relatively smaller source zones.

To gain an understanding of the current status of technology practices and the performance associated with ISCO, an ESTCP workshop was convened at the Colorado School of Mines in 2007 (Siegrist et al., 2008b). More than 40 experts attended, representing chemical companies, technology vendors, environmental consultants, academics, and remedial project managers. The workshop included a series of presentations, panel sessions, and breakout sessions, along with an exercise where six site scenarios were used to obtain views regarding ISCO design and performance. The following views expressed and consensus developed at the workshop provide insights into ISCO applications and performance expectations:

- ISCO may be considered for a wide range of situations, but site-specific conditions interacting with ISCO technology attributes determine the performance that could be considered reliably achievable.
 - As an illustration of this view, a strong majority of the workshop participants indicated that they would consider ISCO for a range of contaminated site scenarios. However, the degree of anticipated ISCO performance, the timeframe necessary, and the costs varied between different scenarios.
- The success or failure of an ISCO application is strongly dependent not only on the site-specific conditions but also on the remediation objectives and the resources (e.g., time and money) made available to implement the ISCO system.

- Multiple injection events are commonly required and should be anticipated.
- Where ISCO has not achieved treatment goals, the two fundamental reasons are:
 - Oxidant was not distributed throughout the target treatment zone (TTZ).
 - An insufficient amount of oxidant was delivered to the TTZ.
- Performance deficiencies based on these two reasons were viewed as *more likely* to occur under the following circumstances:
 - Site characterization is inadequate and the contaminant mass is poorly understood.
 - The subsurface is highly heterogeneous.
 - The design neglects the mass of contaminants that are sorbed.
 - Presence of DNAPLs is unknown or not accounted for.
 - Co-contaminants are present that also consume oxidants.
 - Oxidants migrate out of the target treatment zone.
 - The oxidant does not persist as long as expected.
- Rebound, where post-ISCO concentrations of target COCs in groundwater within a TTZ return to levels near or even above those present prior to ISCO, is a relatively common occurrence that may or may not be a negative condition or reflect an inherent shortcoming of ISCO or a site-specific performance deficiency.
 - The rebound observed at an ISCO treated site can be beneficial if it is used in an observational approach to refine the conceptual site model and refocus subsequent treatment.
 - 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.

1.6 SUMMARY

Groundwater contamination by organic chemicals is a widespread problem throughout the United States and industrialized world. At sites with contaminant source zones remaining in the subsurface (e.g., NAPLs), groundwater contamination can persist for decades, requiring large expenditures of public and private funds to mitigate public health and environmental risks. ISCO has proven to be a useful remediation technology for the most prevalent organic contaminants in groundwater. Its advantages include its applicability to several of the most prevalent organic COCs, its adaptability to a wide range of subsurface conditions, its potential to treat a site rapidly, and its ability to be combined with other *in situ* technologies and remediation approaches. Its limitations include the resistance of some COCs to complete chemical oxidation, the NOD exerted by the subsurface, the short longevity of many oxidants in the subsurface, constraints on effective oxidant distribution, potential for COC rebound, and detrimental side effects, such as fugitive gas emissions or mobilization of some metals.

The evolution of a successful remediation technology typically involves a series of stages, from the initial idea generation through research and development, demonstration and testing, increasing field applications by practitioners, and eventual establishment of widely accepted standards of practice. The evolution of ISCO has followed this path. During the 1990s, fundamental and applied laboratory research elucidated many aspects

of the chemical oxidation reactions for common organic chemicals in aqueous systems. Laboratory research also explored the transport processes affecting oxidant delivery and dispersal in soil or groundwater systems. Pilot-scale and full-scale applications demonstrated *in situ* treatment of low levels of solvents and petrochemicals and, to a lesser degree, NAPLs. Results of this work were disseminated in journal articles and technical reports. In the late 1990s and early 2000s, case study reports became available (e.g., USEPA, 1998; ESTCP, 1999) and the first reference book (Siegrist et al., 2001) and reference manual (ITRC, 2001) were published. Subsequently, research and development efforts were catalyzed by a major initiative within SERDP and ESTCP. Fundamental understanding of ISCO evolved, and the number of publications in the open literature grew exponentially. Simultaneously, the number and diversity of field applications expanded substantially. A standard of practice for ISCO began to emerge and be documented and disseminated for widespread use by new and experienced practitioners and regulators (e.g., ITRC, 2005; Huling and Pivetz, 2006; Siegrist et al., 2008b, 2010).

The site-specific selection, design, and implementation of ISCO require consideration of a variety of questions (Table 1.6) and careful attention to key points to enable success and avoid problems (Table 1.7). The chapters that follow provide details regarding the principles and

Table 1.6. Frequently Asked Questions on ISCO Selection, Design, and Implementation (Crimi et al., 2008)

Remediation process category	Frequently asked question	
ISCO at a glance	1.	What is ISCO and how does it work?
	2.	What treatment goals can ISCO achieve?
	3.	What are potential positive and negative attributes of ISCO?
	4.	Is ISCO an established remedy with a clear standard of practice?
ISCO screening	5.	What ISCO options are available?
	6.	What are key characterization needs for ISCO?
	7.	Where does ISCO work best?
	8.	What conditions are challenging for ISCO?
	9.	Can ISCO be used in combination with other remedies?
ISCO conceptual design	10.	How are ISCO systems designed?
	11.	How many injection points are used?
	12.	How many injection events are needed?
	13.	How much oxidant solution should be delivered?
	14.	Why perform lab treatability tests?
	15.	Why perform field pilot tests?
	16.	What are the advantages and disadvantages of lab and field testing?
	17.	What does an ISCO project cost?
ISCO detailed design and planning	18.	Are there regulatory requirements that can hinder the application of ISCO?
	19.	Are there special safety precautions with ISCO?
	20.	How is ISCO optimized during implementation?
	21.	What are appropriate milestones, metrics, and endpoints for ISCO?

(continued)

Table 1.6. (continued)

Remediation process category	Frequently asked question	
ISCO implementation and performance monitoring	22.	What should be monitored for an ISCO project?
	23.	What is rebound? Is it a problem?
	24.	How successful has ISCO been at achieving site closure?
	25.	Where can I find more information on the principles and practices of ISCO?

Table 1.7. Key Points to Consider Which Can Enable Success with ISCO and Help Avoid Problems (Siegrist et al., 2010)

Key points to keep in mind for <i>in situ</i> chemical oxidation
<p>1. ISCO has great potential for successful use at some, but not all sites. ISCO is very applicable to sites with relatively small TTZs where there are permeable subsurface conditions and low to moderate mass levels of COCs. ISCO can successfully achieve common treatment goals at these types of sites.</p>
<p>2. ISCO can successfully achieve treatment goals. Aggressive treatment goals can be met with proper ISCO design in smaller TTZs where effective oxidant delivery can be achieved in permeable subsurface conditions. USEPA MCLs have been achieved at such sites, but only when DNAPLs are absent. Treatment goals need to be realistically set and based upon site-specific conditions and challenging circumstances. The likelihood of achieving a goal is inversely proportional to how stringent the goal is (e.g., ACLs vs. MCLs) and the complexity of the challenges posed by the site conditions (e.g., permeable and homogeneous sites without DNAPL vs. less permeable and heterogeneous sites with DNAPLs). Achieving MCLs in a TTZ is possible for certain sites, but achievement should be expected <20% of the time, even where conditions might appear favorable.</p>
<p>3. Effective <i>in situ</i> delivery is essential. <i>In situ</i> delivery methods must be matched to the oxidant and site conditions to achieve ISCO treatment goals. Several delivery methods can be used, but not all methods are viable with all oxidants or site conditions. Due to oxidant reactions with naturally occurring reducing agents (e.g., natural organic matter, reduced minerals), the radius of influence (ROI) of oxidant from an injection location has typically been less than about 15–20 ft. Oxidant distribution over longer distances by forced advection or passive drift is not likely in most settings. Within the ROI, it is virtually impossible to achieve 100% uniformity and truly complete distribution of oxidant or oxidizing reaction conditions.</p>
<p>4. ISCO will normally require two or more active delivery events. To achieve effective distribution of oxidant throughout a TTZ, and the essential contact of oxidant and target COCs, normally two or more active delivery events will be required in all of, or just portions of, the TTZ.</p>
<p>5. One or more oxidants can destroy most, if not all, of the common organic COCs. Reaction rates and the extent of destruction are not limiting, if a compatible oxidant is used for the target COCs and if they are brought into contact with each other for a long enough time to achieve treatment. There are six or more types of chemical oxidants and even more varieties of oxidant solutions (e.g., oxidant plus activator[s]). Their reaction chemistries are different and of varying complexity with respect to reactive species and need for activation, reactivity with different COCs, stoichiometry, and kinetics. Success or failure of ISCO with one oxidant cannot necessarily be extrapolated to all oxidants.</p>
<p>6. ISCO can be, and often must be, synergized with other remedies. ISCO is very compatible with other remedies and combined remedies can be designed for synergistic outcomes. A prime example of a combined remedy involves ISCO followed by ERD or MNA. However, ISCO may not be viable as a follow-up treatment within a TTZ where organic remedial amendments have previously been delivered (e.g., organic substrates for biostimulation or surfactants for enhanced recovery) due to the reaction of oxidants with those amendments.</p>

(continued)

Table 1.7. (continued)

Key points to keep in mind for <i>in situ</i> chemical oxidation	
7.	So-called “rebound” will often occur, more so at some sites than others. Rebound is defined as an increase in the concentrations of COCs in groundwater observed in monitoring wells located in the TTZ after active ISCO operations have ended. This phenomenon is common and independent of oxidant type, but the frequency and magnitude of occurrence depends on ISCO system design and site conditions. Rebound is typically unwanted, but it can be useful to help refine the conceptual site model and to optimize the design of follow-up treatments.
8.	ISCO can temporarily perturb subsurface conditions. ISCO can change conditions within a TTZ (e.g., depress pH, mobilize certain redox-sensitive metals, decrease the activity of certain microbes), but effects are normally not long lasting or of consequence to performance in most settings. Biogeochemical conditions within an ISCO TTZ can recover to pre-treatment conditions shortly after the oxidant is depleted. The time needed for this re-equilibration depends on site conditions and ISCO operations.
9.	Oxidant transport by diffusion is often negligible. Oxidants with slower reaction rates and the ability to penetrate lower permeability media (LPM) (e.g., permanganate or persulfate) theoretically should help mitigate back diffusion from LPM. However, the rate of oxidant diffusion into these LPM zones is typically extremely slow compared to the rate of reaction and thus the penetration distance is very limited (e.g., millimeter or centimeter scale).
10.	The cost of ISCO varies widely. The median cost of ISCO projects as determined from a review of cost data for 33 sites is \$94/cy of TTZ, but the range can vary by almost three orders of magnitude depending on various factors. For example, sites with fuel hydrocarbons and permeable subsurface conditions typically cost less while those with DNAPLs or complex subsurface conditions typically cost more. High unit costs can also result where ISCO has been used to treat relatively smaller TTZ. Appropriate screening, design, and in some cases lab treatability testing and field pilot-scale testing, can generally help improve cost effective application of ISCO.

practices of ISCO, providing a sound basis for site-specific engineering to achieve successful remediation of contaminated groundwater.

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CHAPTER 2

FUNDAMENTALS OF ISCO USING HYDROGEN PEROXIDE

Benjamin G. Petri,¹ Richard J. Watts,² Amy L. Teel,² Scott G. Huling³,
and Richard A. Brown⁴

¹Colorado School of Mines, Golden, CO 80401, USA; ²Washington State University, Pullman, WA 99164, USA; ³U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Center, Ada, OK 74820, USA; ⁴Environmental Resources Management, Ewing, NJ 08618, USA

Scope

Chemistry and use of hydrogen peroxide for *in situ* chemical oxidation (ISCO) of subsurface contaminants, including free radical and other reaction mechanisms, catalysts, and reactive transport.

Key Concepts

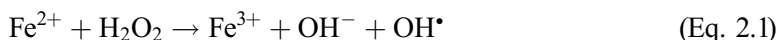
- Hydrogen peroxide reaction chemistry is complex, but potentially capable of degrading a wide range of organic contaminants depending on conditions.
- Ferrous [Fe(II)] and ferric [Fe(III)] iron, iron and manganese soil minerals, and other metals in solution may catalyze hydrogen peroxide to form free radicals. These catalysts may be naturally present in the matrix, or added during ISCO to augment the reaction.
- pH has a strong effect on hydrogen peroxide chemistry and effectiveness. pH impacts catalyst solubility and reactivity towards hydrogen peroxide, as well as the radicals formed and the degradation of target contaminants. Some hydrogen peroxide applications include the injection of amendments (acids or alkalis) to modify pH to an optimal range.
- Radicals known to play significant roles in hydrogen peroxide chemistry include the hydroxyl radical (OH[•]), superoxide radical (O₂^{•-}), and perhydroxyl radical (HO₂[•]).
- Different radicals dominate the reaction under different chemistry conditions, and are controlled by parameters such as concentration of the oxidant, catalyst, organic or inorganic solutes, and pH. This can affect performance as some contaminants may only degrade under specific chemistry conditions.
- Carbonate, bicarbonate, chloride, other inorganic ions, and hydrogen peroxide itself are reactive with radicals and may affect reaction efficiency and effectiveness.
- The lifetime of hydrogen peroxide in the subsurface is short, generally hours to days.
- The reactive transport of hydrogen peroxide in the subsurface is limited, primarily because of its fast reaction rate.

2.1 INTRODUCTION

Hydrogen peroxide is a strong oxidant that long has been used in industrial applications and in water treatment processes. When catalyzed in water, hydrogen peroxide may generate a wide variety of free radicals and other reactive species that are capable of transforming or decomposing organic chemicals. Hydrogen peroxide is often applied in combination with a catalyst or activator, and the term catalyzed hydrogen peroxide (CHP) has been used to refer to hydrogen peroxide systems. Reactive species formed in CHP systems can include both oxidants and reductants.

In environmental applications, CHP has proven to be particularly useful in the degradation and detoxification of organic contaminants. While the utility of this oxidant was appreciated long ago by industry, detailed scientific understanding of the reactive species formed and of the reaction mechanisms involved lagged behind its use in industry. In the early 1990's, the expansion of the use of hydrogen peroxide for environmental applications in soil necessitated the use of catalysts and chemistry approaches that deviated from the traditional applications of "Fenton's reagent" in industry. Early publications by Watts et al. (1990, 1991a, b), Pignatello (1992), Watts (1992), Pignatello and Baehr (1994), and others began to explore the roles of soil mineralogy and different chemical amendments on hydrogen peroxide effectiveness. This subsequent research determined that the reaction chemistry of hydrogen peroxide is quite complex. Despite these advances in understanding, knowledge gaps persist and the chemistry and application of this oxidant are still fields of active research.

Fenton (1894) discovered that soluble Fe(II) salts could act as a catalyst with dilute hydrogen peroxide (several mg/L) under mildly acidic conditions to initiate a very powerful oxidation process. This combination of soluble Fe(II) salts and hydrogen peroxide at pH 3–5 produces hydroxyl radicals according to the following reaction (Equation 2.1), which is commonly referred to as "Fenton's reagent" or "Fenton's process".



The significance of Fenton's discovery has evolved over time. It was first applied in industry for wastewater treatment (Schumb et al., 1955). With the growth of the environmental industry, iron-catalyzed hydrogen peroxide was adapted to site remediation and has been used for approximately 25 years as an oxidant for treatment of contaminated soil and groundwater.

The original concept behind early applications of hydrogen peroxide *in situ* chemical oxidation (ISCO) was to apply the "Fenton's process" within the subsurface. However, applications of this oxidant *in situ* result in a dramatically more complex chemistry than simply generating hydroxyl radicals (OH^\bullet) as presented by Equation 2.1. Many other catalysts and radicals that are not present in the original "Fenton's" process have been found to play major roles in contaminant degradation reactions when hydrogen peroxide is applied *in situ*. To acknowledge the complexity of the chemistry that occurs with ISCO, the process of using hydrogen peroxide for ISCO has been termed "catalyzed hydrogen peroxide propagations" (Watts and Teel, 2005) or simply "catalyzed hydrogen peroxide" (CHP). It should be noted that other terms such as "modified Fenton's reagent" or "Fenton-like" reactions have been used to refer to ISCO application with CHP. However, these terms have been used to describe several different modifications to Fenton's original chemistry, so the term has multiple meanings. To avoid confusion, CHP will be used to describe hydrogen peroxide reactions within a porous media.

This chapter provides a summary of present knowledge on CHP and its implications for ISCO. Much of this information was gained from a critical review of the literature on hydrogen peroxide and its use in subsurface environments. This literature search and review included over 239 published studies that have relevance to hydrogen peroxide based ISCO. These studies

include peer reviewed journal articles, conference proceedings, theses and dissertations from academic research, government publications, and unpublished reports.

2.2 CHEMISTRY PRINCIPLES

To understand the use of CHP in ISCO applications and the reasoning behind proper implementation of this technology, it is important to understand the basics of reaction chemistry. Hydrogen peroxide reaction chemistry is complex, but it can be broken into several major concepts and reaction mechanisms, including free radical chain reactions involving initiation, propagation and termination steps; radical scavenging; oxidation of organic contaminants; and competing and nonproductive reactions. Because hydrogen peroxide is a very reactive oxidant and it is rapidly consumed in the subsurface, attempts have been made to stabilize the oxidant to promote its delivery and transport in the subsurface.

2.2.1 Physical and Chemical Properties

Several fundamental properties of hydrogen peroxide and two of the most commonly used forms of soluble iron catalysts are given in Table 2.1. The catalysts are often supplied as hydrated salts. Properties are given for the most common forms of these chemicals but they may be available at different concentrations or formulations than shown.

Table 2.1. Chemical Properties of Selected CHP Compounds (from Lide, 2006)

Compound	Formula	Molecular weight (g/mol)	Density (g/cm ³)	Physical state	Solubility limit in water
Hydrogen peroxide	H ₂ O ₂	34	1.11 (30% solution)	Liquid	Miscible
Ferrous sulfate heptahydrate	FeSO ₄ ·7H ₂ O	278	1.895	Solid	30 wt. %
Ferric chloride	FeCl ₃	162.2	2.90	Solid	91 wt. %

Note: g/cm³ - grams per cubic centimeter; g/mol - grams per mole; wt. % - weight percentage.

2.2.2 Oxidation Reactions

CHP involves a large number of different reactive species and mechanisms. These reactive species are ultimately responsible for the transformation and degradation of organic contaminants. The following sections describe the free radicals that are formed, their properties, and the role they play in CHP chemistry.

2.2.2.1 Direct Oxidation

Direct oxidation refers to a direct electron-transfer reaction between a reactant and hydrogen peroxide. The direct reaction between hydrogen peroxide and organic substances has typically been thought to be of minor importance, with the exception of some biologic enzymes that serve to decompose the oxidant. While hydrogen peroxide has a high standard reduction potential ($E^\circ = 1.776$ V; Lide, 2006) that would indicate a favorable potential for direct oxidation of many organic compounds, these reactions are thought to be generally too slow to be of significance (Watts and Teel, 2005). This is in part because many common soil

minerals are inherently reactive with hydrogen peroxide and produce free radicals, so it is often difficult to separate direct oxidation mechanisms from free radical mechanisms in porous media systems. Hence, the direct oxidation mechanism typically has been viewed as not playing a major role in the degradation of organic contaminants by CHP.

While hydrogen peroxide is presumed to have little direct reactivity with organic compounds, it does have a high degree of direct reactivity with inorganic compounds; indeed direct oxidation between hydrogen peroxide and inorganic compounds is typically responsible for the initiation of free radical reactions and mechanisms. Also, despite its high reduction potential, hydrogen peroxide is capable of acting as both an oxidizing and reducing agent. For instance, at low pH, hydrogen peroxide readily oxidizes Fe(II) to ferric iron [Fe(III)], but it also reductively dissolves manganese dioxide [Mn(IV)] to dissolved Mn(II) (Neaman et al., 2004). Inorganic compounds that have high degrees of direct reactivity with hydrogen peroxide include dissolved transition metals, inorganic anions, and mineral surfaces. Since these reactions typically produce free radicals, they are discussed more extensively in Sections 2.2.2.2 and 2.2.3.

2.2.2.2 Free Radicals and Other Reactive Intermediates

There are a number of radicals and other reactive intermediates that are either known or suspected to play a role in the degradation of organic contaminants. These radicals are formed as the result of a reaction between hydrogen peroxide and some catalyst (see Section 2.2.3 on catalysis). Often the existence and importance of these radicals in CHP systems is difficult to determine because they are very short lived (half lives of seconds to even microseconds) and conventional direct analytical methods cannot be used to detect and quantify them. Instead, their presence or absence within a system is confirmed using indirect chemical methods often involving considerable complexity. Because of analytical difficulties, considerable uncertainty remains concerning the roles these radicals play in CHP reactions. Table 2.2 provides a summary of some key radicals and reactive intermediates thought to play a major role in CHP systems, while the following section provides more detail on each individual species.

Table 2.2. Reactive Species Known or Suspected of Contributing to CHP Reactions

Species	Species formula	Standard reduction potential (V) ^a	pH where present ^b	Role
Hydrogen peroxide	H ₂ O ₂	1.776	pH < 11.6	Strong oxidant, weak reductant
Hydroxyl radical	OH•	2.59	pH < 11.9	Strong oxidant
Superoxide anion	O ₂ ^{•-}	-0.33	pH > 4.8	Weak reductant
Perhydroxyl radical	HO ₂ •	1.495	pH < 4.8	Strong oxidant
Hydroperoxide anion	HO ₂ ⁻	0.878	pH > 11.6	Weak oxidant, weak reductant
Ferryl ion [Fe(IV)]	FeO ²⁺	Unknown	Unknown	Strong oxidant
Solvated electrons	e ⁻ (aq)	-2.77	pH > 7.85	Strong reductant
Singlet oxygen	¹ O ₂	Not applicable	Unknown	Participates in Diels–Alder and Ene reactions
Atmospheric (triplet) oxygen	O ₂	1.23	Any	Weak oxidant

^aLide (2006).

^bBuxton et al. (1988).

Hydroxyl Radical (OH^\bullet)

The hydroxyl radical traditionally has been viewed as the workhorse of hydrogen peroxide oxidation systems. It is a strong non-specific oxidant that reacts with a wide variety of organic and inorganic compounds. Hydroxyl radicals generally react with organic compounds via three mechanisms: hydrogen abstraction, addition to multiple bonds, and direct electron transfer (Bossmann et al., 1998). The product of a reaction between a hydroxyl radical and an organic compound includes an organic radical, which may react with water or other species and degrade (Sedlak and Andren, 1991b).

Hydroxyl radicals are extremely reactive; concentrations in aqueous systems tend to be very low even in vigorously oxidizing systems because they are consumed nearly instantaneously. Despite the strong standard reduction potential of this radical ($E^\circ = 2.59\text{V}$ at pH 0, 1.64V at pH 14; Bossmann et al., 1998), different organic compounds will react with hydroxyl radicals at differing kinetic rates, depending on their affinity for the oxidant (e.g., Buxton et al., 1988). ISCO systems involve large numbers of compounds, including contaminants and natural organic matter, as well as inorganic minerals and dissolved solutes. Because of competition between all of these constituents for hydroxyl radicals, the extent to which hydroxyl radicals will degrade a particular contaminant often depends on whether the contaminant's rate of reaction with hydroxyl radicals is competitive with that of the other constituents in solution.

Superoxide Anion ($\text{O}_2^{\bullet-}$)

Superoxide anion is a free radical that has been recently implicated as a major reactive species responsible for the degradation of organic contaminants in CHP systems. It is a mild reductant and nucleophile. Recent research has implicated it in playing a key role in the degradation of highly oxidized organic compounds including chloromethanes and chloroethanes. Superoxide anion is the conjugate base of the perhydroxyl radical (HO_2^\bullet) with an acid dissociation constant (pK_a) of 4.8 (Afanas'ev, 1989); thus superoxide will only be available in appreciable concentrations when the pH is above 4.8.

While it long has been known to be generated in aqueous systems, superoxide has traditionally been viewed as a weak or slow-reacting radical. Traditional applications of hydrogen peroxide often have been optimized by using dilute hydrogen peroxide solutions (e.g., several mg/L) to maximize production of hydroxyl radicals and minimize quantities of other reactive species present. However, recent research has shown that when high concentrations of hydrogen peroxide ($\sim 3.5\text{--}35\text{ g/L}$) are present, the reactivity of superoxide is significantly enhanced (Smith et al., 2004). This phenomenon in high-concentration systems appears to be due to a higher rate of superoxide generation and improved solvation of the superoxide anion, which increases its reactivity. Furthermore, Furman et al. (2009) documented that superoxide reactivity is increased in the presence of solids, including metal oxides; therefore, aquifer solids may actually increase superoxide reactivity.

Perhydroxyl Radical (HO_2^\bullet)

Perhydroxyl radical is the protonated form of superoxide anion. With a pK_a of 4.8 (Afanas'ev, 1989), this radical is the dominant form of superoxide present at acidic pH, such as in traditional Fenton's systems conducted at pH 3. However, in neutral to alkaline CHP systems, superoxide anion is the favored form. Perhydroxyl radical is considered a mild oxidant and is important in chain propagation reactions involving hydrogen peroxide (Teel and Watts, 2002).

Hydroperoxide Anion (HO_2^-)

Hydroperoxide anion is the conjugate base of hydrogen peroxide with a pK_a of 11.6 (Lide, 2006). Hydroperoxide anion is a strong nucleophile that may readily attack contaminants that

have electron-deficient functional groups. Once generated in a CHP system, it recombines with protons at diffusion-controlled rates; nonetheless, it also likely reacts with some contaminants at near diffusion-controlled rates, which would allow hydroperoxide anion reactivity with some contaminants, even at low to moderate pH regimes.

Ferryl Ion [$\text{Fe(IV)} \pm \text{FeO}^{2+}$]

Research over the last 20 years has revealed that the ferryl ion might be a principal reactive intermediate in the Fenton's reaction, instead of hydroxyl radicals, at least as the very first reactive intermediate formed by the Fenton's reaction. This theory has generated some controversy in the chemistry community. Researchers have proposed that it is thermodynamically unfavorable to directly produce a hydroxyl radical from the reaction between dissolved Fe(II) and aqueous hydrogen peroxide, as is suggested by Fenton's reaction (Bossmann et al., 1998). This is because in aqueous solutions, Fe(II) is complexed with water [e.g., $\text{Fe(OH)(H}_2\text{O)}_5^+$ instead of free Fe^{2+}], and in order for hydrogen peroxide to react with Fe(II), it must first be incorporated into the complex [e.g., $\text{Fe(OH)(H}_2\text{O}_2)(\text{H}_2\text{O)}_4^+$]. Thermodynamic calculations by Bossmann et al. (1998) based on these complexes indicate that it may be more thermodynamically favorable to produce Fe(IV) than OH^\bullet . Instead, it has been proposed that the ferryl ion, which contains iron in an unusual tetravalent state [Fe(IV)], is formed as an intermediate and is extremely reactive (Rush and Bielski, 1986; Bossmann et al., 1998). This intermediate may then rapidly react to form either hydroxyl radicals or possibly oxidize organic compounds directly. The existence of the ferryl ion was proposed as early as 1932 by Bray and Gorin. Yet, the controversy over the role this intermediate plays in iron-catalyzed hydrogen peroxide reactions is still unresolved. Thus, it is unknown what role, if any, this intermediate may play in the degradation of organic contaminants by CHP. Bossmann et al. (1998) implicated it in the degradation of an aromatic organic compound, which implies that the ferryl ion may play a role in contaminant oxidation in CHP systems. However, its present importance to ISCO systems, if any, is largely unknown.

Solvated Electrons [$\text{e}^- (\text{aq})$]

Solvated electrons are free electrons dissolved in aqueous solution. Solvated electrons are the conjugate base of the solvated hydrogen atom (H^\bullet), with a pKa of 7.85 (Rush and Bielski, 1986 and references within). They are short lived reactive species in water, and have been implicated in dechlorination reactions, such as with polychlorinated biphenyl compounds (PCBs) (Pittman and He, 2002). While their presence in CHP systems has been suspected (Hasan et al., 1999; Watts et al., 2005a), it remains unclear when or how they are formed, and their role has not been extensively investigated.

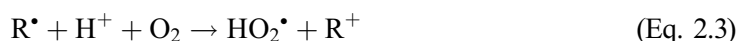
Singlet Oxygen ($^1\text{O}_2$)

Singlet oxygen is a form of molecular oxygen (O_2) that has a higher energy than oxygen in the ground state, which is commonly referred to as triplet oxygen (e.g., atmospheric oxygen). The energy difference between singlet oxygen and triplet (atmospheric) oxygen amounts to 94.2 kJ/mol and is derived from the configuration and spin of electrons in the molecule's 2p orbital (Braun and Oliveros, 1990). This higher energy allows it to react with certain organics. Singlet oxygen is relatively long lived in the gas phase (half life of 72 min), but is very short lived in water (half life of microseconds). The importance of singlet oxygen in CHP systems is largely unknown. Singlet oxygen was identified in a molybdenum-catalyzed hydrogen peroxide system investigated by Tai and Jiang (2005) and was determined to be the species responsible for degradation of chlorophenols in that system. However, this reactive species has not been widely investigated in iron-catalyzed hydrogen peroxide systems, which are of more relevance to ISCO.

However, given the complexity of CHP systems, this does not preclude the possibility that singlet oxygen may play a role, and some have speculated that it may be present in CHP systems.

Atmospheric Oxygen (O₂)

Atmospheric oxygen is the most stable reactive oxygen species produced by the decomposition of hydrogen peroxide. Oxygen gas is often evolved in large quantities, particularly because some minerals, such as manganese oxides, tend to catalyze the decomposition of hydrogen peroxide via Equation 2.2 (Hasan et al., 1999). Direct oxidation of organic contaminants by atmospheric oxygen is slow, often considered too slow to be of significance during the CHP treatment of organic contaminants. However, there is some evidence that molecular oxygen may play a role in CHP reaction pathways. For example, Rodriguez et al. (2003) reported that when CHP was used to degrade nitrobenzene in an aqueous system under a nitrogen only atmosphere, only nitrophenols were produced as reaction byproducts. When the same system was reacted under an oxygen atmosphere, perhydroxyl radicals were produced in addition to nitrophenols, indicating a shift of mechanism. Similarly, a shift of mechanism was observed by Sedlak and Andren (1991b), who noted that when treating chlorobenzene under anoxic conditions (difficult, but possible), polymerization reactions resulted in generation of dichlorobiphenyl (a PCB), while under oxic conditions, yields of this PCB were much reduced. Voelker and Sulzberger (1996) speculated that organic radicals produced by radical attacks on organic compounds, such as fulvic acid, may have reduced oxygen to form perhydroxyl radicals as given by Equation 2.3. Thus, despite its low rate of direct reactivity with organic contaminants, dissolved oxygen may contribute to CHP reaction propagations. In addition, oxygen certainly contributes to aerobic biodegradation, which is a ubiquitous process in the subsurface whenever dissolved oxygen is present.



2.2.2.3 Impact of pH on Radical Intermediates

The rate of radical production and reactivity is often pH-dependent. For example, some radicals are weak acids and bases, which will deprotonate (e.g., superoxide vs. perhydroxyl radical). Deprotonation affects their reaction pathways and mechanisms, as well as their standard reduction potential, which is the thermodynamic property that drives oxidation and reduction reactions. Select half-reactions and their standard reduction potentials are presented in Table 2.3. Note that the reduction potential of a species is generally lower in alkaline systems than in acidic systems.

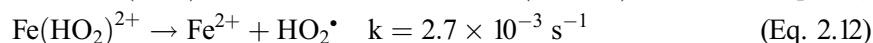
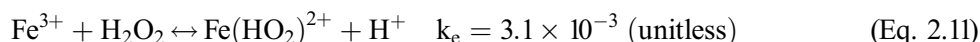
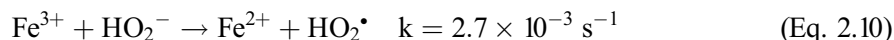
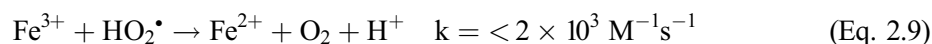
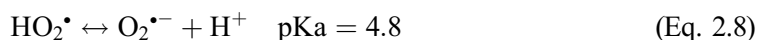
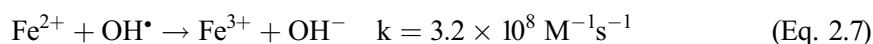
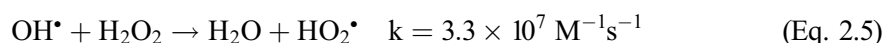
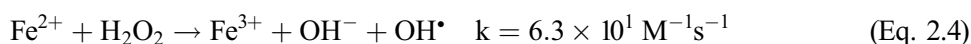
Table 2.3. Reduction Potentials of Select Reaction Species in CHP Systems

Reaction	Standard reduction potential E° (V vs. NHE)	pH range	References
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \leftrightarrow 2\text{H}_2\text{O}$	1.776	Acidic	Lide (2006)
$\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \leftrightarrow 3\text{OH}^-$	0.878	Alkaline	Lide (2006)
$\text{OH}^\bullet + \text{H}^+ + \text{e}^- \leftrightarrow \text{H}_2\text{O}$	2.59	Acidic	Bossmann et al. (1998)
$\text{OH}^\bullet + \text{e}^- \leftrightarrow \text{OH}^-$	1.64	Alkaline	Bossmann et al. (1998)
$\text{HO}_2^\bullet + \text{H}^+ + \text{e}^- \leftrightarrow \text{H}_2\text{O}_2$	1.495	Acidic	Lide (2006)
$\text{O}_2 + \text{e}^- \leftrightarrow \text{O}_2^{\bullet-}$	-0.33	Alkaline	Afanas'ev (1989)

NHE - normal hydrogen electrode.

2.2.3 Catalysis of Hydrogen Peroxide

In 1934, a key paper by Haber and Weiss indicated that radical reactions and chain propagations were a key part of oxidation caused by iron-catalyzed hydrogen peroxide systems. They also observed that the iron in these systems could be cycled back and forth between Fe(II) and Fe(III) forms, thus acting like a catalyst because it is continually regenerated and consumed by the reaction. They further speculated that other dissolved transition metals may catalyze similar reactions with hydrogen peroxide, particularly if they can undergo a single valance change [e.g., Fe(II) to Fe(III) or Cu(I) to Cu(II)]. In chemistry, this has been named the Haber–Weiss mechanism and is thought to be the main mechanism for catalytic decomposition of peroxide by dissolved metals. The original reactions proposed by Haber and Weiss (1934) for iron-catalyzed decomposition of hydrogen peroxide are summarized by Equations 2.4–2.7. De Laat and Gallard (1999) found the reactions shown in Equations 2.8–2.12 to be significant as well.



(k = rate constant, k_e = equilibrium constant, M = molarity, s = seconds; De Laat and Gallard, 1999 and references therein)

A chain reaction is one where multiple reactions occur, and the products of one reaction provide reactants for another. Thus, a series of reactions occur simultaneously until a key reactant is depleted. Chain reactions are common in radical chemistry because when a free radical reacts with a compound, the product of the reaction is often another radical. Free radical chain reactions may be generally categorized as involving three types of reactions: initiation reactions, propagation reactions, and termination reactions. Initiation reactions are reactions in which a free radical is produced by a non-radical reactant such as in Equations 2.4 and 2.10 above. Propagation reactions occur when a radical reacts with another reactant to produce a different radical, such as in Equations 2.5 and 2.6. Termination reaction occurs when a radical reacts with another species and no new radical is produced, such as in Equations 2.7 and 2.9. Termination reactions may be desirable because they may involve the oxidation of a target organic contaminant or regeneration of the Fe(II) catalyst as in Equation 2.9. They also may be undesirable when they involve non-target species or neutralize other radicals. Such non-target species, termed “scavengers,” represent a source of inefficiency in CHP systems.

2.2.3.1 Catalysis with Dissolved Iron

Free radical-producing chain reactions, such as those described above, can be catalyzed by reactions between a number of different dissolved transition metals and hydrogen peroxide. Transition metals other than iron that have shown catalytic activity with hydrogen peroxide

include copper (Haber and Weiss, 1934), molybdenum (Tai and Jiang, 2005), ruthenium (Anipsitakis and Dionysiou, 2004), and manganese (Watts et al., 2005b). However, with the exception of manganese, most of these metals are unlikely to be present in the subsurface at appreciable concentrations, and their expense or toxicity makes them unlikely catalysts for ISCO. Furthermore, while dissolved manganese [Mn(II)] did catalyze radical production in the system studied by Watts et al. (2005b), it took substantial concentrations of Mn(II) (e.g., 11,000 mg/L) to effectively catalyze the reaction, suggesting this metal is a weak catalyst. Indeed, Anipsitakis and Dionysiou (2004) also evaluated Mn(II) as a catalyst but at much lower concentrations and found that there was effectively no reaction. Hence, of the dissolved transition metals, iron is likely to be the most important dissolved metallic species of concern within CHP systems.

Haber and Weiss (1934), Bossmann et al. (1998), De Laat and Gallard (1999), and Smith et al. (2004) identified a series of reactions as being important in iron catalyzed hydrogen peroxide systems. Most of these reactions are presented in Equations 2.4 through 2.12. From this, a simplified reaction scheme is proposed that describes the possible roles of iron and radicals in CHP systems (Figure 2.1). The blue pathways represent reactions involving reactive oxygen species (e.g., the free radicals produced by initiation and propagation reactions) and the red pathways demonstrate the cycling of iron in the system. As can be seen in Figure 2.1, dissolved iron is cycled back and forth between Fe(II) and Fe(III), while hydrogen peroxide and associated species are continually depleted.

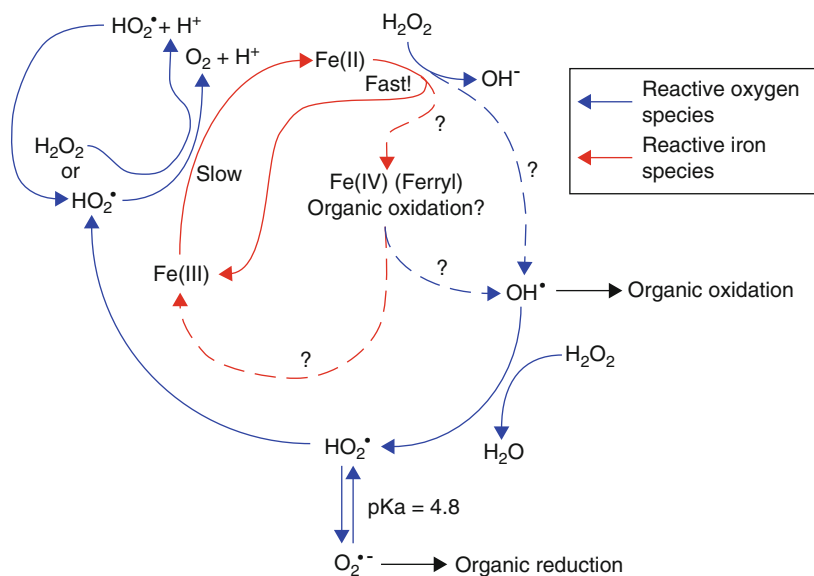


Figure 2.1. Proposed reaction scheme for reactive intermediates formed by hydrogen peroxide when catalyzed by soluble iron species.

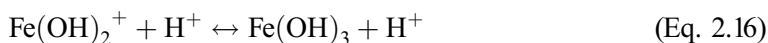
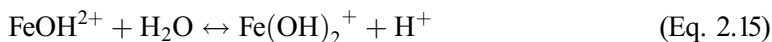
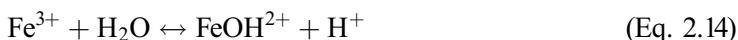
Most of the reactions in Equations 2.4–2.11 obey second-order kinetics, where the generic rate of reaction is expressed by Equation 2.13.

$$\frac{\partial C_{\text{reactant}1}}{\partial t} = -k_2 C_{\text{reactant}1} C_{\text{reactant}2} = -k_{p1} C_{\text{reactant}1} \quad (\text{Eq. 2.13})$$

where $C_{\text{reactant}1}$ is the concentration of the reactant of interest, $C_{\text{reactant}2}$ is the concentration of the other reactant, k_2 is the second-order rate constant for the reaction, and k_{p1} is the pseudo first-order rate constant defined as the product of $C_{\text{reactant}2}$ and k_2 . Hydrogen peroxide concentrations are high in CHP systems because it is often delivered at a concentration of

approximately 1–20 wt.% (10^{-1} – 10^0 M). Because of this elevated concentration of hydrogen peroxide, as well as the relatively fast second-order reaction rate for reaction (Equation 2.4), (fast for a reaction not involving free radicals as a reactant), the pseudo first-order rate constant of this reaction may be expected to be very fast. As a result, Fe(II) may be expected to be depleted from solution via Equation 2.4 at a rapid rate, often within minutes or seconds. Now considering the back reactions of Equations 2.10–2.12 that regenerate Fe(II) from Fe(III), these are observed to be considerably slower than Equation 2.4. Thus, the cycling of iron from Fe(III) back to Fe(II) via Equations 2.10–2.12 will generally be the limiting step in the reaction scheme presented in Figure 2.1, and the bulk of the iron in the system may be assumed to be Fe(III). Because of this, either Fe(II) or Fe(III) catalysts may be used for ISCO applications and may be effective catalysts of the oxidant, but Fe(III) will dominate regardless after several minutes of reaction. The existence and importance of the ferryl ion [Fe(IV)] in hydrogen peroxide systems is still uncertain (see Section 2.2.2.2), but it is included in Figure 2.1 in the way it is currently conceptualized, and dashed lines represent the suspected or proposed pathways.

The reaction scheme shown in Figure 2.1 is oversimplified because it does not include the effect of pH, particularly on iron availability. Like all dissolved metals, iron complexes with water and hydroxide species. As discussed, after several minutes of reaction the bulk of iron is anticipated to be in the Fe(III) form in CHP systems. Ferric hydroxide [Fe(III)(OH)₃] forms a solid precipitate at neutral pH, and dissolved Fe(III) concentrations will be extremely low. However, at acidic pH, Fe(III) is much more soluble and available for reaction. In addition, other Fe(II) and Fe(III) hydroxy-complexes affect the catalytic activity of iron species with hydrogen peroxide. Important complexation reactions are summarized in Equations 2.14–2.18.



Because of the insolubility of Fe(OH)₃ at neutral pH, traditional Fenton's reactions have been conducted at low pH to prevent the precipitation of Fe(III). Furthermore, the potency of strong oxidants is enhanced in the reducing conditions typical of low pH (Watts and Teel, 2005). However, the rates of hydroxyl radical generation by the Fenton's reaction (Equation 2.1) have been shown to increase with increasing pH (Beltrán et al., 1998 and references within). Through years of experience, it generally has been determined that the best breakpoint between the highest level of hydroxyl radical activity while still keeping iron in solution lies around pH 3. Hence, much of the research into iron-catalyzed hydrogen peroxide in aqueous systems has focused on the acidic pH range of 2–4. However, subsurface systems are often well buffered in the neutral pH range (e.g., pH 6–8), and it can be difficult to alter this pH. Thus, neutral pH (ranging from 6 to 8) has also been investigated. The frequency of which various pH ranges have been investigated is illustrated in Figure 2.2.

Some sites have employed pH adjustment in the field by injecting an acid into the subsurface to improve iron availability. However, at some sites, this may be impractical because the buffer capacity of the aquifer may be too large to allow for effective acidification. Heightened concerns over metals concentrations may also preclude the injection of an acid. To overcome such constraints, recent research has focused on how to provide effective catalysis of hydrogen peroxide systems at neutral pH despite the low solubility of Fe(III) in these systems. This has been most commonly achieved by either relying on natural iron and manganese mineral

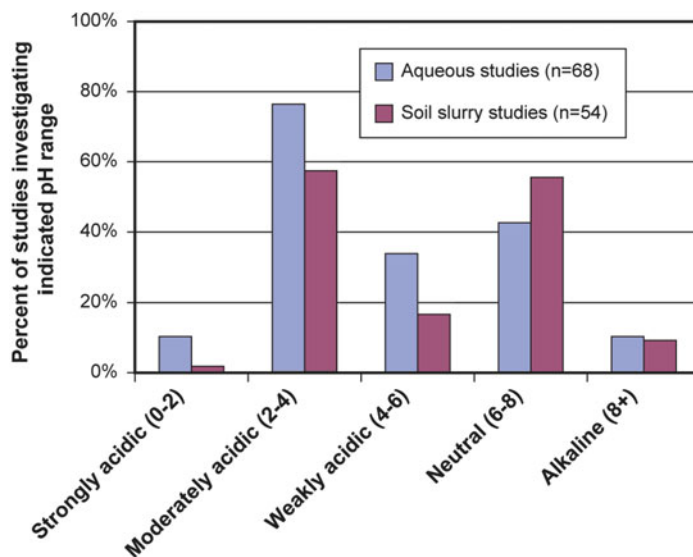


Figure 2.2. Percent of studies investigating certain pH ranges as determined from a comprehensive review of the literature. Note, the totals sum to more than 100% as many studies investigated multiple pH ranges.

surfaces to catalyze the reaction (see Section 2.2.3.2), or to deliver a soluble organic ligand (chelate) with the catalyst [Fe(II) or Fe(III)] which can keep the iron in solution as an organo-metallic complex (see Section 2.2.3.3).

2.2.3.2 Catalysis with Natural Minerals

One of the main differences between traditional hydrogen peroxide applications in water treatment systems and CHP use in ISCO is the fact that the oxidant interacts strongly with minerals present in porous media. The minerals can act as a catalyst similar to aqueous iron species where radicals may be produced by surface reactions. The mineral surfaces can also act as nonproductive oxidant sinks where hydrogen peroxide is decomposed without producing any reactive intermediates. Some reactions may also promote dissolution of minerals releasing a soluble metal, such as iron, which can then act as a soluble catalyst as in the Fenton's reaction. With mineral surface catalyzed reactions, radicals are unlikely to diffuse significant distances (a few nanometers) from the mineral surface prior to reaction due to the high reactivity of the radical.

A number of specific minerals have been investigated in pure systems to determine which common soil minerals have the most effect on hydrogen peroxide persistence and catalysis of reactions (e.g., Valentine and Wang, 1998; Huang et al., 2001; Kwan and Voelker, 2003; Watts et al., 2005b; Teel et al., 2007; Furman et al., 2009). These studies and others have generally found that the iron and manganese minerals have the most pronounced effects on hydrogen peroxide stability and catalysis, while other trace minerals generally have only minor effects on oxidant stability. Given that iron and manganese minerals are very common in soil and groundwater systems, these minerals are generally believed to be the main oxidant sinks for hydrogen peroxide in natural systems. Studies that have compared iron and manganese minerals, particularly Teel et al. (2007), have often found that manganese minerals, especially pyrolusite, decompose hydrogen peroxide faster than the iron minerals. However, iron minerals often tend to be present in soil and groundwater systems at higher concentrations than manganese minerals, so the decomposition activities of both types of minerals are of relevance to ISCO. These reactions with minerals are also pH-dependent. Table 2.4 presents some of the most commonly investigated iron

and manganese minerals and the nature of their reactions for different pH values. Decomposition activity refers to how rapidly the mineral promotes decomposition of the oxidant on a qualitative basis relative to the other minerals, and considers the catalytic ability of the mineral only on a mass basis (e.g., surface area is not factored in). The reactive species column indicates which radicals and reactive species are suspected to form by the reaction with that particular mineral. Finally, the catalytic effectiveness indicates whether or not the mineral was capable of catalyzing degradation of a target organic contaminant. Question marks indicate that the nature of the interaction is currently uncertain or unknown.

Table 2.4 illustrates that the impact of each mineral on hydrogen peroxide chemistry is variable. The variability between minerals involving the same metal is due in part to surface area. For instance, ferrihydrite and pyrolusite have high specific surface areas (Huang et al., 2001; Kwan and Voelker, 2003; Teel et al., 2007), and this may result in a larger number of catalytic sites. This may in part explain why hydrogen peroxide decomposes so rapidly in the presence of these minerals. Indeed a study by Valentine and Wang (1998) compared the decomposition rates of hydrogen peroxide in the presence of ferrihydrite, goethite, and a semi-crystalline iron-oxide at neutral pH; the three iron minerals had very different decomposition rates, but when normalized by specific surface area, the catalytic activities of the three were nearly the same. Another comparative study by Kwan and Voelker (2003) compared ferrihydrite, goethite, and hematite at pH 4 and found that when normalized for surface area and hydrogen peroxide concentration, the OH[•] radical production rate for goethite and ferrihydrite was nearly the same, but for hematite, it was an order of magnitude lower. Thus, the process is not strictly surface area dependent, but area is clearly a factor.

Table 2.4. Mineral Interactions with Hydrogen Peroxide^a

Mineral	Acidic pH (~3)			Neutral pH (~7)		
	Decomposition activity	Reactive species	Catalytic effectiveness	Decomposition activity	Reactive species	Catalytic effectiveness
Ferrihydrite (Fe ₂ O ₃ •0.5H ₂ O)	Rapid	OH [•] O ₂	Effective	Very rapid	? No OH [•] ?	Ineffective
Goethite (α-FeOOH)	Rapid	OH [•] Others?	Effective	Moderate	No OH [•] O ₂ ^{•-} ? Others?	Effective
Hematite (Fe ₂ O ₃)	Moderate	OH [•]	Effective	Very rapid	?	Effective
Magnetite (Fe ₃ O ₄)	Rapid	?	Effective	?	?	?
Siderite (FeCO ₃)	Moderate	?	?	Moderate	?	?
Pyrolusite (β-MnO ₂)	Very rapid	?	?	Very rapid	No OH [•] O ₂ ^{•-}	Effective
Manganite (MnOOH)	Moderate	?	?	Rapid	?	?

^aData from Huang et al. (2001), Kwan and Voelker (2002, 2003), Teel et al. (2001, 2007), Valentine and Wang (1998) and Watts et al. (2005a, b).

"?" indicates that a parameter is uncertain or unknown

pH is also another major factor. Some minerals are more active at one pH than another. For example goethite appears more active at acidic pH than at neutral pH, while hematite is much

more active at neutral pH than acidic pH. However, it appears overall that the rates of decomposition of hydrogen peroxide are higher at neutral pH than acidic pH. Yet even more important to ISCO than the decomposition rates are the changes in catalytic activity that occur at differing pH. With the iron minerals, it appears that they are capable of catalyzing the production of OH^\bullet radicals at acidic pH, analogous to traditional Fe(II) catalyzed systems. Several studies have largely confirmed this through the use of scavenging experiments where an excess of a scavenger compound known to react with hydroxyl radicals is introduced, and then the degradation of a particular organic substrate is compared between systems with and without the scavenger (Teel et al., 2001; Kwan and Voelker, 2003). When reactions were studied at neutral pH, the scavengers had no effect on organic substrate degradation, which implies that degradation in neutral pH systems is occurring via a non-hydroxyl radical pathway. A similar phenomenon is likely occurring in pyrolusite-catalyzed systems at neutral pH. Here it has been shown that a highly oxidized contaminant, carbon tetrachloride (CT), may be degraded although CT is considered recalcitrant to reaction with hydroxyl radicals. It has been shown that the reactive intermediate in these systems is superoxide ($\text{O}_2^{\bullet-}$) (Watts et al., 2005a, b; Furman et al., 2009).

2.2.3.3 Catalysis with Chelated Metals and Impacts of Other Organo–Metallic Complexes

Chelating agents (ligands) are soluble organic compounds that have the ability to bind to metal ions or soil minerals. By binding with metal ions, the chelating agent can maintain the metal ion in solution under redox conditions where the metal would ordinarily precipitate. They may also alter the reactivity of metals and minerals with hydrogen peroxide, as the bound form of the metal or mineral may have different availability for reactions than the unbound form. Chelating agents have been used in CHP oxidation systems as they may promote hydrogen peroxide catalysis under pH conditions that ordinarily pose difficulties because of the low solubility of dissolved iron at neutral pH. Thus, they have been used in some ISCO applications in situations where aquifer acidification is not practical (due to buffer capacity, metal mobilization, etc.). Citric acid, cyclodextrins, ethylenediaminetetraacetic acid (EDTA), and other amino-poly-acetic acids are examples of chelating agents that have been used for chelated-metal activation of CHP (Pignatello and Baehr, 1994; Jazdanian et al., 2004; Kang and Hua, 2005).

Several different kinds of chelating agents have been explored in the literature; depending on the agent, multiple mechanisms may promote the degradation of organic contaminants. Chelating agents have proven effective at slowing the decomposition of hydrogen peroxide in the subsurface, which can promote effective delivery, thereby improving contaminant degradation when compared to systems without chelants (Watts et al., 2007). Several mechanisms may contribute to this improvement in performance. The slowing of the decomposition of hydrogen peroxide may be due in part to the chelating agent binding with active mineral surfaces and dissolved metals, thus reducing their catalytic activity with hydrogen peroxide; this can lead to increased hydrogen peroxide lifetimes in the subsurface. Improved contaminant degradation may be caused by the chelating agent keeping the bound iron in solution and available for catalysis; Fe(III) that is not bound is likely to precipitate out of solution as ferric hydroxide [$\text{Fe}(\text{OH})_3$], which is not as effective of a catalyst. Finally, the chelating agent can enable sustained iron release. Dissolved iron is consumed by CHP reactions, reducing the aqueous concentration of iron. This triggers additional iron release from that bound by chelating agents, which can continue to feed the reaction.

Cyclodextrins are a novel species that have additional functionality over typical chelating agents. These large complex molecules not only bind iron as a ligand, they also enhance the

partitioning of low solubility organic contaminants as well. Cyclodextrins contain a hydrophobic core into which non-polar organic contaminants may partition, while surface sites on the molecule bind iron. When reacted with hydrogen peroxide, the catalysis produces radicals in direct vicinity of the contaminant and thus the degradation activity is enhanced not only by enhanced iron availability but also by bringing the contaminant closer to the site of radical generation. Several studies that have evaluated the addition of cyclodextrins to CHP reactions have noted higher contaminant degradation yields over systems using iron catalysts alone; they have also reported that the impact of scavengers may be reduced (Tarr et al., 2002; Lindsey et al., 2003). One study also evaluated another novel catalyst for CHP using heme, which is the active portion of the hemoglobin molecule, the biochemical compound responsible for transport of oxygen and carbon dioxide in human blood (Chen et al., 1999). Heme is a relatively complex organic molecule, but it is highly soluble and Fe(III) is bonded into the molecule. When reacted with hydrogen peroxide, it has been proposed that the iron is oxidized to Fe(IV), much like the ferryl ion is proposed as an intermediate in Fenton's reaction; the catalyst itself acts as an organic radical that can then degrade organic contaminants. The novel part is that once the heme radical has reacted with organics, the parent catalyst is regenerated.

While chelating agents are generally effective at promoting iron solubility and improving the degradation of the target contaminants, one potential downside is that the chelate, being an organic compound itself, may be degraded by the reaction. For example, if an OH^\bullet or other radical is evolved in direct proximity to the organic ligand, the ligand itself may be degraded. Hence, optimizing the chelated catalyst dose is important because adding too little may result in ineffective catalysis, while adding too much may result in excess scavenging of the oxidant and inefficient reaction.

However, not all organo-metallic complexes are desirable. Low molecular weight organic acids are common byproducts of organic oxidation processes, particularly when the parent contaminant is either aromatic or contains a large number of carbon atoms. These organic acids may act as simple chelating agents similar to citric acid or EDTA and may complex with the iron catalyst. Depending on the organic acids being generated this may be either beneficial or detrimental to oxidation effectiveness. Kwon et al. (1999) reported that valeric, muconic, and propionic acids may promote iron solubilization and catalytic activity with hydrogen peroxide, thus imparting a beneficial impact on reaction. However, multiple investigators have found that oxalic acid, a common organic byproduct and often produced in considerable concentrations, binds so strongly to the iron that the iron is effectively non-reactive with hydrogen peroxide (Li et al., 1997b; Kwon et al., 1999; Lu et al., 2002). Thus, oxalic acid may partially inhibit hydrogen peroxide catalysis if it builds to sufficiently high concentrations.

Some organo-metallic reaction intermediates can support reactivity. When hydroxyl radicals attack aromatic compounds, catechols and other aromatic diols are often formed as intermediates. These diols possess reductive capabilities that may reduce Fe(III) back to Fe(II), which supports continuation of Fenton's reaction. In some investigations of hydrogen peroxide oxidation of chlorinated phenols, it has been noted that there is a lag period at the start of the reaction, followed by an accelerating rate of transformation until finally the contaminant is nearly depleted and the reaction rate slows down. This initial lag and subsequent acceleration is attributed to the role of catechol and hydroquinone intermediates supporting the reaction, and the lag is the period needed for sufficient intermediate concentrations to form to support the reaction (Sedlak and Andren, 1991b; Chen and Pignatello, 1997; Lu, 2000; Chen et al., 2002; Lu et al., 2002; Zazo et al., 2005).

2.2.4 CHP Reaction Kinetics

Reaction kinetics is an important consideration with respect to CHP effectiveness. The stoichiometries presented in Equations 2.4–2.12 represent some of the many reactions that potentially can occur simultaneously in CHP systems. The reactions will generally continue to occur until one of the key reactants is depleted. The limiting reagent in CHP systems is usually hydrogen peroxide, but it may also include the catalyst, particularly if it becomes unavailable due to precipitation or complexation reactions. Because hydrogen peroxide is generally the limiting reagent in these chain reaction systems, it is often desirable to know the rate at which hydrogen peroxide is depleted within the system so that enough oxidant can be effectively delivered into the subsurface. Furthermore, the rate at which target contaminants will degrade is of interest; in order for ISCO to be effective, the chain reactions need to last long enough for the target contaminant to be degraded. The rate of individual reactions that occur within CHP chain reactions (such as radical production reactions or contaminant degradation reactions) have been generally described by a second-order kinetic model. With second-order kinetics, the reaction rate is dependent on the rate constant for the reaction, as well as the concentrations of the reactants in solution. Reaction rate constants for a wide range of organic and inorganic reactants have been measured (Buxton et al., 1988; Haag and Yao, 1992; Waldemer et al., 2009). Despite the availability of these constants, considerable challenges exist in modeling or predicting the concentrations of reactants and byproducts due to the wide range of reactants in heterogeneous subsurface systems.

Modeling of CHP chemistry has been attempted and the results of these efforts are discussed in Section 2.2.4.1. However, because of the extreme difficulty in such modeling approaches, it is often simpler to conduct a treatability test and measure reaction kinetics empirically to fit a pseudo first-order model. This approach is particularly useful to ISCO when trying to predict hydrogen peroxide decomposition, which is termed “oxidant persistence” as described in Section 2.2.4.2.

2.2.4.1 Fundamental Reaction Kinetics and Modeling Approaches

Because of the complexity of hydrogen peroxide chemistry and the many competing reaction mechanisms described in Sections 2.2.2 and 2.2.3, modeling reaction kinetics is difficult. However, kinetic modeling within appropriate bounds does provide benefits, especially in scientific investigations by gaining insight and making predictions without running numerous experiments. The approaches used in the literature include: (1) precise fundamental chemistry models that track the numerous reactions in CHP systems, (2) more simplified models based on competition of several species for a specific radical, and (3) several pseudo first-order approaches. A discussion of these approaches is provided to illustrate the strengths and limitations of each.

Fundamental Chemistry Models

While it is desirable to know the rates of oxidant depletion and contaminant degradation for purposes of ISCO design and performance modeling, these rates are very difficult to predict through chemistry modeling in CHP systems; this is due to the large number of reactions occurring simultaneously that must be included in a chemistry model to get a reasonably accurate representation of the system. To model a CHP system, individual rate constants for significant reactions within the chain need to be determined, and individual mass balances need to be written for each reactive species. These models are difficult to solve because the large number of reactions dictate that a large series of non-linear differential equations need to be solved to get a solution. Thus, mathematical determination of the overall

oxidant and contaminant degradation rates becomes very difficult. In addition, the data needs of such models become very large because the model may require specific knowledge about the reacting species, such as aqueous concentrations, porous media compositions, reaction rate constants and others. An example of this difficulty is presented in the work of De Laat and Gallard (1999), where they successfully modeled rates and radical concentrations in a completely mixed, aqueous-phase-only system (no soil present), involving only hydrogen peroxide, soluble iron catalysts and a range of pH (no contaminants present). Even in this “simple” chemistry system, they found that they had to include no less than 21 reactions (16 kinetic expressions and 5 iron-water-hydrogen peroxide speciation reactions) to obtain an acceptable model to fit the experimental data. This resulted in the need to solve five simultaneous non-linear differential equations using numerical methods. This system has vastly reduced complexity in comparison to CHP applications *in situ*, where a variety of contaminants, soil minerals, dissolved solutes, and natural organic matter (NOM) are present. Typically, data is sparse for these species. For all practical purposes, precise theoretical modeling of CHP chemistry *in situ* remains impractical.

Competition Kinetics Analysis

Competition kinetics analysis is a simplified tool that allows a general assessment of the relative rate of reaction of two or more reactants with OH^\bullet . This method of analysis can be used to evaluate the general order of contaminant degradation, the role of potential scavengers, or to determine whether it is reasonable to expect contaminant transformation altogether given the presence of other targets or scavengers. Because there are many reactions that occur simultaneously in CHP systems, this analysis provides a general indication of possible results. In a simplified laboratory treatment system, however, results may be more specific. For example, the relative rate of reaction (R) is the ratio of reaction rates of a potential reactant relative to the sum of all reactants. For example, consider a system with three compounds that react with OH^\bullet , where compound 1 is the contaminant of interest, and compounds 2 and 3 are OH^\bullet scavengers. Then the relative rate of reaction for compounds

$$R_{C_1/C_1,C_2,C_3} = \left(\frac{k_{C_1}[C_1][\text{OH}^\bullet]}{(k_{C_1}[C_1] + k_{C_2}[C_2] + k_{C_3}[C_3])([\text{OH}^\bullet])} \right) \quad (\text{Eq. 2.19})$$

where:

C_1, C_2, C_3 = concentrations of scavengers and/or target reactants.

$k_{C_1}, k_{C_2}, k_{C_3}$ = second-order reaction rate constant between C_1, C_2, C_3 , and OH^\bullet .

Consider if the reaction rate of compound 1 ($k_{C_1} = 1 \text{ M}^{-1}\text{s}^{-1}$, the concentration C_1 is 1 M, and the scavengers have reaction rates $k_{C_2} = 0.1 \text{ M}^{-1}\text{s}^{-1}$ and $k_{C_3} = 8 \text{ M}^{-1}\text{s}^{-1}$ and concentration $C_2 = 10 \text{ M}$ and $C_3 = 1 \text{ M}$. Then the relative rate of reaction is $1/(1+1+8)$ or $1/10$. If these are the only three reactions present that consume OH^\bullet and the reactant concentrations are not changing appreciably, this model implies 1 out of 10 hydroxyl radicals will be consumed by the contaminant, while the other 9 out of 10 are involved in scavenging reactions. Here, $[\text{OH}^\bullet]$ is assumed to be the same since the reactions take place in the same reaction vessel.

The second-order reaction rate constants for the reaction between OH^\bullet and potential scavengers in CHP treatment systems, or other environmental contaminants vary widely in magnitude (Table 2.5). Several well documented and comprehensive compilations of the second-order reaction rate constants for many environmental contaminants and other reactive species (scavengers) has been published (Buxton et al., 1988; Haag and Yao, 1992).

This method of analysis does not take into consideration other potential complexities of Fenton-driven oxidation systems. For example, there are reaction intermediates that are also responsible for contaminant transformation. Additionally, there may be reactants that

Table 2.5. Reaction Rate Constants^a Between OH[•] and Potential Scavengers, or Environmental Contaminants

Contaminant	Second-order reaction rate constant (L/mol s)
Carbon tetrachloride	$<2 \times 10^6$
Chloroform	$\approx 5.5 \times 10^6$
Methylene chloride	5.8×10^7
2-Chlorophenol	1.2×10^{10}
Chlorobenzene	5.5×10^9
Perchloroethene	2.6×10^9
Trichloroethene	4.2×10^9
Vinyl chloride	1.2×10^{10}
Benzene	7.8×10^9
Ethyl benzene	7.5×10^9
Toluene	3.0×10^9
m-, o-, p-Xylene	$6.7\text{--}7.5 \times 10^9$
PCBs	$5\text{--}6 \times 10^{10}$
Polycyclic aromatic hydrocarbons (PAHs)	1×10^{10}
Methyl tert-butyl ether (MTBE)	1.6×10^9
Tert-butyl alcohol (TBA)	6.0×10^8
Acetone	1.1×10^8
1,4-Dioxane	2.8×10^9
Scavenger	Second-order reaction rate constant (L/mol s)
Chloroacetic acid ^b	4.3×10^7
Malonic acid ^b	2.0×10^7
Oxalic acid ^b	1.4×10^6
Hydroxide ion	1.2×10^{10}
Bicarbonate ion	8.5×10^6
Carbonate ion	3.9×10^8
Ferrous iron	4.3×10^8
Hydrogen peroxide	2.7×10^7

^aRate constants from Buxton et al. (1988) and Haag and Yao (1992).

^bDecomposition products (carboxylic acids) from the oxidation of organic contaminants represent potential scavengers.

are present that are not included in the analysis that could significantly affect results. Results of this analysis should be used as a general assessment of reaction conditions, and in recognition of the simple system it represents.

Other Approaches

Given the complexity of CHP kinetics, many studies typically model kinetics as pseudo first-order using data obtained from laboratory batch testing. This offers the advantage of simple mathematics for modeling or prediction purposes. However, the disadvantage is that the accuracy of extrapolating results from batch to field systems is uncertain because so many factors impact hydrogen peroxide chemistry and kinetics. One pseudo-theoretical approach of simplifying CHP

chemistry to enable more effective modeling was proposed by Miller and Valentine (1995a). They presented a simplified conceptual model of hydrogen peroxide kinetics as being described by three pseudo first-order reactions in two steps. First, hydrogen peroxide reacts with soil minerals and iron to produce a lumped concentration of undefined radicals, followed by two reactions in competition that either degrade the target substrate or go to competing nonproductive reactions. Alternatively, reaction rate kinetics can be used to approximate the steady-state OH^\bullet concentration ($[\text{OH}^\bullet]_{\text{SS}}$). Subsequently, the estimate of $[\text{OH}^\bullet]_{\text{SS}}$ can be used to predict the pseudo first-order transformation rates of other target contaminants in similar CHP systems (Huling et al., 2000a). Limitations of these methods are that treatability studies are needed to produce the kinetic constants, and simplifying assumptions are necessary that overlook the complexity of CHP chemistry. In some cases, these reaction rates may not hold constant over time as the actual substrates, intermediates, and byproducts may be consumed over the course of reaction and may change the kinetic rates. Given the complexity of hydrogen peroxide chemistry, the reliance on laboratory testing, and typically sparse data on system parameters (such as scavenger concentrations), the ability to predict contaminant degradation kinetics with CHP *in situ* remains challenging and the accuracy of prediction is highly uncertain.

2.2.4.2 Hydrogen Peroxide Decomposition Kinetics in Porous Media (Oxidant Persistence)

ISCO involves the use of hydrogen peroxide in the presence of porous media; therefore the impact of the porous media on reaction kinetics is a major factor in hydrogen peroxide decomposition kinetics (hereafter referred to as oxidant persistence). For ISCO using CHP to be effective, the oxidant and its catalysts must be in contact with the target contaminant for a long enough period of time that the oxidation reactions can take place. This also includes time necessary for contaminant desorption or dissolution if necessary. Oxidant persistence also impacts the penetration of hydrogen peroxide into the target treatment zone, as reaction will consume the oxidant as it is forced away from an injection point. While the chemistry of CHP is very complex, studies focusing on the persistence of hydrogen peroxide in porous media batch systems have generally found the oxidant decomposition behavior to fit pseudo first-order kinetics reasonably well. Miller and Valentine (1995a) also reported that pseudo first-order kinetics held for a one-dimensional (1-D) transport column system they investigated. Pseudo first-order decomposition kinetics predicts a simple exponential decay of the oxidant vs. time in the subsurface.

Hydrogen Peroxide Stabilization

Because hydrogen peroxide is typically short lived in the subsurface, it is often desirable to increase its lifetime in the subsurface through the addition of chemical amendments that stabilize the oxidants. Phosphate is one compound that has been used as a stabilizing agent. Phosphate can bind and reduce the activity of mineral and soluble catalysts, and thus make them less available for reaction. Studies evaluating phosphate have noted that oxidant decomposition does slow in response to this anion, confirming its stabilizing effect (Lipczynska-Kochany et al., 1995; Valentine and Wang, 1998; Watts et al., 1999b; Baciocchi et al., 2004; Mecozzi et al., 2006). Phosphate is a weak hydroxyl radical scavenger, so implementing phosphate stabilization is not likely to have detrimental effects to CHP degradation of target organics. However, because phosphate is such a strong complexing agent, the effectiveness of implementing phosphate stabilization at field scale is more uncertain because the transport distances of this anion are expected to be limited.

More recent efforts have focused on using organic ligands as stabilization agents, in part to overcome the limitations of phosphate. Watts et al. (2007) screened more than a dozen organic ligands for their potential to stabilize hydrogen peroxide in the presence of subsurface solids.

They screened the ligands that Sun and Pignatello (1992) found to promote only low reactivity of iron-ligand catalyzed CHP oxidations. Watts et al. (2007) found that the most effective stabilizers are citrate, malonate, and phytate. These results are demonstrated in Figure 2.3. These stabilizers were capable of decreasing hydrogen peroxide decomposition rates by up to 20 times in four soils collected from different regions of the United States. These results suggest that hydrogen peroxide decomposition rates in the subsurface can be decreased dramatically using one of the three stabilizers.

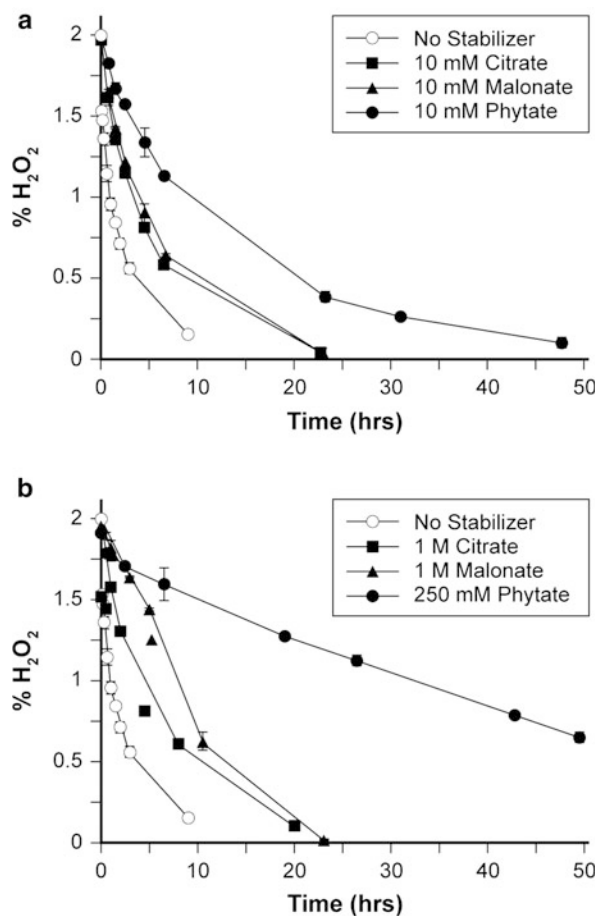


Figure 2.3. Effect of several stabilizers on hydrogen peroxide lifetimes in Georgia sandy clay soil systems. Initial H_2O_2 concentration = 2% and 5 mL solution per 1 g soil. Note: M - molar; mM - millimolar. From Watts et al., 2007; reprinted with permission.

Oxidant Persistence

Of 59 studies that evaluated CHP reactions in porous media, 18 reported either pseudo first-order kinetic rates from experimental systems or provided kinetic data (e.g., H_2O_2 concentration vs. time data) from which rate constants could be estimated (Bacocchi et al., 2003, 2004; Barcelona and Holm, 1991; Bissey et al., 2006; Chen et al., 2001; Crimi and Siegrist, 2005; Leung et al., 1992; Mecozzi et al., 2006; Miller and Valentine, 1995a, b, 1999; Petigara et al., 2002; Tyre et al., 1991; Watts et al., 1990, 1994, 1999b; Yeh et al., 2003, 2004). A total of 139 rate constants were compiled for oxidant persistence in 37 different field porous media. A variety of chemistry parameters, such as varied oxidant concentrations, activation aid types,

pH, and use of various stabilization aids were recorded. Table 2.6 presents the maximum, minimum, median, and first and third quartiles for the 139 oxidant persistence rate constants. To illustrate the effect that oxidant persistence can have on oxidant transport, the table also includes the anticipated effective transport distances for hydrogen peroxide at these decomposition rates. This is predicted using a simple 1-D linear velocity, and the effective transport distance is defined as the distance where the oxidant concentration reaches 10% of the initial concentration. Hence if hydrogen peroxide were to be steadily injected into a system obeying the median rate for oxidant persistence (0.20 h^{-1}) at a linear (1-D) injection velocity of 10 m/day, the concentration at 5 m away would be predicted to be 10% of the injected concentration.

Table 2.6. Decomposition Rate Constants and Estimated Resultant Transport Distances with Groundwater Velocity

First-order rate range	Decomposition rate constant (1/h)	Half life (h)	Effective ^a 1-D transport distance (m) vs. velocity (m/day)		
			0.1 m/day	1.0 m/day	10 m/day
Minimum	0.00097	713	10.7	107	1,070
1st quartile	0.036	19.3	0.27	2.7	27
Median	0.20	3.50	0.05	0.5	5
3rd quartile	1.2	0.60	0.008	0.08	0.8
Maximum	36	0.02	0.0003	0.003	0.03

^aEffective transport distance defined as the distance where the oxidant concentration reaches at least 10% of the injected concentration.

The large spread of oxidant decomposition rates represents the possible range that may be encountered during ISCO with CHP. However, extreme values such as the minimum and maximum rates are often the result of unique circumstances that may not be realistic for ISCO implementation (extreme concentrations of oxidant, catalyst, stabilizers, pH, etc.). Thus practitioners might reasonably anticipate values in the middle of this large range, such as between the first and third quartiles. It is useful to observe that a review of field scale implementations of CHP by Krembs (2008) reported that the median observed radius of influence was about 5 m (about 15 ft).

Additional statistical analysis (ANOVA) of these rate constants revealed at least six major factors that significantly influence oxidant persistence (e.g., >95% confidence) (1) soil mineralogy, including mineral types and their respective surface areas (grain size), (2) oxidant concentration, (3) catalyst type and concentration, (4) pH, (5) the use of stabilization aids, and (6) solids concentration (solids-to-solution ratios used in treatability tests). Several trends were observed with respect to these factors. Oxidant concentration, mineralogy, the addition of a soluble iron catalyst (as opposed to natural iron mineral catalysis), and soil texture (classified by the pipette method) had the most significant effects on decomposition rates. It was unclear whether iron minerals or manganese minerals had more impact; depending on the type of mineral analysis done, one often proved more important than the other. Generally, as the concentration of these minerals increases, the oxidant decomposition rates increase. Higher oxidant concentrations often exhibited slower rates of decomposition, and the addition of any iron catalyst accelerated decomposition. Soil texture had a complex effect in that soils with either a medium loam or sandy loam texture exhibited faster rates of decomposition. Given the small number of soils ($n = 37$) included in the analysis, this may just be an artifact of unique behavior of several specific soils. However, it does potentially indicate a correlation between grain size and catalytic activity; this makes intuitive sense as finer-grained media have more mineral surface area and presumably more catalytic surface sites. However, the effect appears

to be complex, as silty-loams, silty-clay-loams, sands, and loamy-sands all had similar ranges of decomposition activity. Presumably silty-clay loams and silty-loams would have even more surface area than a sandy-loam, but perhaps the parent minerals that form these fine particles have less intrinsic catalytic activity.

Several other parameters were found to influence hydrogen peroxide persistence but at much lower significance (e.g., <95% confidence). Addition of stabilizers such as phosphate decreased rates of decomposition, but the degree of stabilization that is possible seems to be strongly influenced by the other more significant parameters. pH also affects persistence, with generally faster rates of decomposition at higher pH. However, the reduced significance of pH may be due to the complex effects pH may have on iron and mineral complexation reactions, as well as speciation of reactive oxygen species. NOM had little impact on oxidant persistence, possibly due to the complexity of the interactions with NOM (as discussed in Section 2.2.5.3), as NOM may impart mechanisms that both accelerate and moderate oxidant decomposition.

Under field conditions, porous media mineralogy and surface area cannot be controlled. Thus control of oxidant persistence within the subsurface must be derived from careful selection and optimization of the other parameters, including oxidant concentration, catalyst type and concentration, pH, and the use of stabilization aids.

2.2.5 Factors Affecting Efficiency and Effectiveness of Oxidation

A number of factors impact the efficiency and effectiveness of CHP reactions. One consideration is the effect of competing or nonproductive reactions on efficiency. Another is an evaluation of whether the contaminant is fully degraded, and if not determination of the byproducts of organic contaminant oxidation. The impact of natural organic matter on CHP is also discussed in detail, and highlights a complex effect on CHP effectiveness. Finally, other physical factors such as temperature and oxygen gas evolution have the potential to impact CHP efficiency and effectiveness through alteration of reaction pathways.

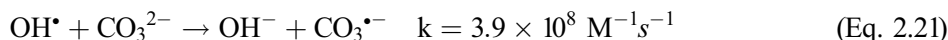
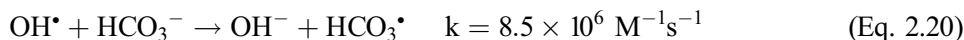
2.2.5.1 Competing Nonproductive Reactions

Nonproductive reactions compete with the organic contaminant for the oxidant. In some situations, contaminant degradation may slow or cease altogether. In the past, these nonproductive reactions were termed “scavenging” reactions, and frequently focused on inorganic solutes (carbonate, chloride, etc) that competed with the contaminant for the hydroxyl radical (OH^\bullet) (Huling et al., 1998). Indeed, data from classical Fenton’s systems support this observation (e.g., Beltrán et al., 1998; Lipczynska-Kochany et al., 1995; Kwon et al., 1999). However, more recent research has not only implicated other radicals in CHP chemistry (e.g., superoxide; Smith et al., 2004), but suggests that some of these classical “scavengers” might actually contribute productively to degradation reactions (Umschlag and Herrmann, 1999). For instance, percarbonate is a novel oxidant that is being used for ISCO and involves hydrogen peroxide chemistry at alkaline pH (e.g., pH 11) and very high carbonate concentrations (Kelley et al., 2006). Thus the role these compounds play in CHP chemistry and their effect on efficiency may in fact be more complex than acting simply as a nonproductive side reaction. The present state of knowledge regarding these various “scavengers” is discussed in the following subsections.

Carbonate and Bicarbonate

Because the carbonate and bicarbonate anions are two of the most common anions in groundwater, their impact on CHP chemistry is important. Traditionally, bicarbonate has been recognized as a scavenger in a hydrogen peroxide system, especially toward hydroxyl radicals.

When hydroxyl radicals react with aqueous carbonate or bicarbonate species, the carbonate or bicarbonate radical is formed. These resulting radicals are thought to have much lower reactivity and propensity to degrade organic contaminants than the hydroxyl radical. As a result, the formation of carbonate or bicarbonate radicals via Equations 2.20 and 2.21 has generally been viewed as inefficiency in CHP systems. Note that the rate of reaction between carbonate and hydroxyl radical is roughly 45 times faster than that of bicarbonate and hydroxyl radical, so this process may become more pronounced as the pH increases into the alkaline range (Buxton et al., 1988).



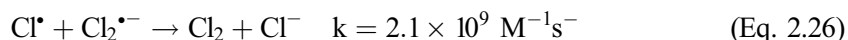
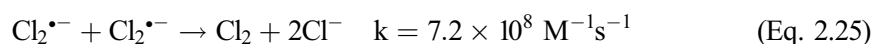
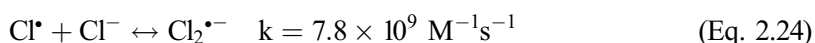
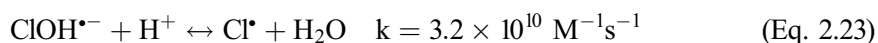
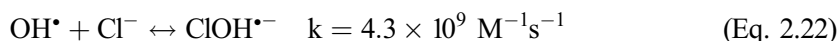
In addition to scavenging hydroxyl radicals, the carbonate radical also has a fast rate of reaction with hydrogen peroxide ($2.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ at pH 11.8) (Zuo et al., 1999); thus, in addition to consuming hydroxyl radicals, carbonate radicals may also consume hydrogen peroxide. When considering the effectiveness of CHP in subsurface systems that contain high levels of carbonate or bicarbonate, the role of radical scavenging should be considered because of the potential impact it could have on ISCO treatment using CHP.

Recently, evidence has emerged that not all carbonate effects are adverse to hydrogen peroxide ISCO. For instance, Umschlag and Herrmann (1999) found that the carbonate and bicarbonate radicals were capable of degrading a series of aromatic contaminants, including benzene. Furthermore, sodium percarbonate ($\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$) is an oxidant that has been recently implemented for ISCO and operates at high hydrogen peroxide and carbonate concentrations (Kelley et al., 2006). The reaction mechanisms behind this novel oxidant are not well known, but it is likely that they include many of the same hydrogen peroxide mechanisms in addition to some possibly unique mechanisms. In addition to reacting with hydroxyl radicals, carbonate may also complex dissolved iron and iron from mineral surfaces and alter their reactivity. Valentine and Wang (1998) found that the presence of carbonate slowed both the decomposition of the oxidant, and the degradation of the contaminant in an iron mineral catalyzed system; however, no adverse impact on reaction efficiency was observed. For aqueous Fe(II) species, the presence of carbonate or bicarbonate appears to even speed the rate of catalysis with hydrogen peroxide, possibly because the reactivity of $\text{FeCO}_3(\text{aq})$ is faster than $\text{Fe}^{2+}(\text{aq})$ or $\text{FeOH}^+(\text{aq})$ with hydrogen peroxide (Lipczynska-Kochany et al., 1995). Many studies have noted adverse effects from this anion (Beltrán et al., 1998; Lipczynska-Kochany et al., 1995), but there is also evidence that it may support CHP reactions. Thus the impact of carbonate on CHP efficiency appears complex.

Chloride

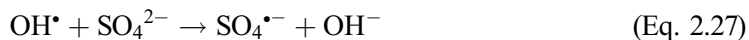
Chloride ion has been found to have significant effects on reaction, typically resulting in a slowing of the degradation of an organic substrate. Chloride affects the reaction of CHP by both scavenging radicals produced by CHP reactions and complexing soluble iron and possibly mineral catalytic sites. De Laat et al. (2004) found that chloride had no apparent effect on the kinetics of a Fe(II)-catalyzed peroxide system, but in an Fe(III)-catalyzed system the kinetics of hydrogen peroxide decomposition and contaminant degradation slowed, which was attributed to complexation of Fe(III) by chloride. Chloride is also known to interact with the radicals produced by CHP. When chloride reacts with hydroxyl radicals, a series of propagation reactions may proceed to form the dichloride radical anion ($\text{Cl}_2^{\bullet-}$) via the reactions in Equations 2.22–2.26 (Yu and Barker, 2003 and references within). The reactivity of the dichloride radical anion with organics is largely unexplored in the present CHP literature. However, the dichloride radical anion has rapid rates of reaction with other chloride species and via the reactions in Equations 2.25 and 2.26 may produce chlorine gas, which can in turn cause halogenation of organic

compounds. This has been observed to occur by Kiwi et al. (2000). However, it is likely that the vigorous reactions during CHP could also break down halogenated daughter products as they are produced. Conditions that favor production of the dichloride radical (which should be avoided) are acidic pH, high chloride concentrations (over 1,000 ppm), and low peroxide concentration (less than 1,000 ppm) (Pignatello, 1992; De Laat et al., 2004). The high concentrations of chloride required to produce this reactivity are unlikely to occur in most normal groundwater environments. Generally, chloride concentrations typical of groundwater (20–100 mg/L) are unlikely to cause significant complexation, scavenging, or halogenation. Nonetheless, when dense nonaqueous phase liquids (DNAPLs) such as perchloroethene (PCE) are present, chloride may accumulate in the aqueous phase from oxidation of DNAPLs and may eventually affect the reaction. The presence of chloride in highly brackish groundwater may also pose a challenge to CHP ISCO.



Sulfate

Sulfate is another common groundwater constituent that can affect CHP reactivity. However, when sulfate reacts with hydroxyl radicals, the reaction is not necessarily unproductive, as the sulfate radical is produced and is known to have significant reactivity with organic contaminants. Thus, the reaction in Equation 2.27 is a useful propagation reaction when sulfate is present. Sulfate is also known to affect CHP kinetics through complexation reactions. De Laat et al. (2004) reported that Fe(II) complexed with sulfate appeared to have faster catalytic activity than Fe(II)-hydroxy complexes. However, for Fe(III), the opposite was true, where the catalytic activity of Fe(III)-sulfate complexes was much lower than Fe(III)-hydroxy complexes. Thus, the presence of a large amount of sulfate in groundwater may have mixed effects on CHP chemistry, increasing kinetics of some reactions, while decreasing others or altering reaction pathways. Sulfate is only likely to be encountered in groundwater in concentrations high enough to be of concern where waters are brackish or sulfur-based remediation technologies have previously been applied (e.g., persulfate ISCO, dithionite *in situ* chemical reduction).



Hydrogen Peroxide

When present at high concentrations, hydrogen peroxide may become its own scavenger. Propagation reactions, such as Equations 2.5, 2.6, and others may become significant as hydrogen peroxide concentrations increase. While the propagation reactions evolve a radical, they also consume a radical and a hydrogen peroxide molecule; if propagation reactions become excessive, the oxidant may catalytically decompose itself, representing an inefficiency in the system. This is more likely to occur at high oxidant concentrations because reactions like Equations 2.5 and 2.6 become more favored due to the high activity of hydrogen peroxide in the system, as well as the higher rate of catalysis and thus higher concentration of radicals. Since high oxidant concentrations are necessary for ISCO to ensure adequate oxidant delivery for degradation of contaminants *in situ*, the optimal oxidant dose for effective contaminant

degradation is best determined experimentally and the amount of oxidant scavenging that is tolerable is often a matter of the economics of delivery.

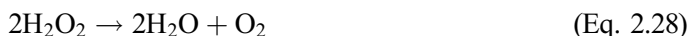
Other Anions

Nitrate is effectively non-reactive towards hydroxyl radicals (Lipczynska-Kochany et al., 1995; De Laat et al., 2004). However, it does have strong scavenging potential toward solvated electrons, which might impact some CHP reaction pathways. Nitrate would generally not be anticipated to be present in groundwater at high concentrations (e.g., >10 mg/L) unless the site to be treated includes explosives [e.g., hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), trinitrotoluene (TNT)] or is affected by agricultural activity.

Perchlorate is effectively inert in CHP systems (Lipczynska-Kochany et al., 1995; De Laat et al., 2004), given its inability to scavenge radicals produced in the system and low affinity for producing complexes with iron. As such, it often has been used in laboratory and theoretical research as an acid or salt for pH and ionic strength control, as well as the conjugate base for soluble iron catalyst salts. However, because perchlorate is itself a severe groundwater pollutant, its use in field applications is precluded. Because CHP is effectively inert toward perchlorate, the presence of a perchlorate plume within a target treatment zone should have no effect on the ability of CHP to degrade organic contaminants.

Biologic Enzymes

Other nonproductive reactions in CHP systems include the reactions with enzymes that decompose hydrogen peroxide. Microorganisms have antioxidant enzymes that serve as protective mechanisms to guard against the damage that may be done to a cell by radicals evolved from hydrogen peroxide, which is present in all natural water systems at very low levels. Two of the major types of enzymes that perform this function are catalase and peroxidase. Catalase is one of the most potent biological enzymes for detoxifying hydrogen peroxide by decomposing it to oxygen and water, as given by the reaction in Equation 2.28. Despite catalase typically being present at very low concentrations in natural systems, it has very high catalytic activity and thus may still influence CHP reaction chemistry (Petigara et al., 2002). Peroxidase enzymes also catalyze decomposition of the oxidant to reaction products that do not include either hydroxyl radical or oxygen production.



2.2.5.2 Contaminant Mineralization and Byproduct Formation

CHP chemistry, as described above, produces a variety of reactive intermediates that attack and degrade organic contaminants. In ideal applications, these reactions proceed to complete mineralization of the contaminants of concern (COCs) to carbon dioxide, water, and salts (such as chloride, bromide or nitrate), but this is not always the case. Many organic contaminants will require multiple oxidation steps, and therefore multiple attacks by radicals to completely mineralize the contaminant, especially if the organic compound is composed of a large or complex chemical structure. Between each oxidation and degradation step, various organic intermediates are produced. If the CHP reaction is vigorous enough and the organic intermediates are susceptible to degradation by the radicals being produced by the reaction, then complete mineralization may occur. However, if the oxidant or radicals are limiting reagents or if the intermediates produced are less susceptible to degradation by CHP, then mineralization may be incomplete and intermediates may remain after CHP treatment. Often, this results from the CHP treatment of large organic contaminants containing aromatic rings or long aliphatic carbon chains. The commonly observed byproducts for a wide range of organic contaminants

include low molecular weight carboxylic acids, such as formic acid, oxalic acid, acetic acid, and others (Koyama et al., 1994; Bier et al., 1999; Huling et al., 2000b; Zazo et al., 2005). Generally these are non-toxic or biodegradable. Heteroatoms (e.g., Cl^- , NO_2^- functional groups) within the parent organic compound are often released as aqueous salts (such as chloride for chlorinated organic compounds or nitrate for nitro-organic compounds), but in some cases, their continued inclusion as intermediates has been observed (Huling et al., 2000b). Changes to system pH have been noted; systems can become more acidic as carbon dioxide and organic acid byproducts release H^+ . However, within porous media, the native mineralogy will likely contain some buffering capacity that may prevent large pH shifts from occurring. Specific byproducts for specific contaminants are discussed in more detail in Section 2.4.

2.2.5.3 Natural Organic Matter

The role of natural organic matter (NOM; also referred to as soil organic matter or SOM) in CHP systems has been investigated in numerous studies, with significant variability in the effects on chemistry observed. This may be partly attributed to the wide array of unique experimental conditions used in these studies. However, these results are likely representative of possible responses that occur under field conditions since a wide range of environmental conditions exist from site to site and within each site. Specifically, NOM can:

- Serve as an adsorbent for the target compound (making it less available in solution)
- Bind with Fe and other inorganic reactants
- Serve as an electron acceptor or donor
- Shuttle electrons
- Scavenge radicals

It is reasonable to assume that the various roles of NOM may occur simultaneously, introducing significant complexity in data interpretation. Through these reactions and mechanisms, NOM can enhance or limit the mass transport, mass transfer, and the reaction kinetics involved in the CHP treatment process. The end result is that the presence of NOM can have either a negative or positive impact on oxidative treatment. Because of the difficulty in characterizing a wide range of site conditions and predicting the role of NOM and other related parameters on treatment performance, site-specific treatability studies may be needed to assess ISCO feasibility.

NOM is a mixture of organic material comprised of various classes of organic matter, often described as a complex mixture of humin, humic acids (HAs), fulvic acids (FAs), and other phenolic and quinone/hydroquinone compounds. These organics have a broad range in molecular weight, are amorphous, and contain large numbers of carboxyl and hydroxyl functional groups, as well as aliphatic hydrocarbon chains and aromatic rings. The specific functional groups impart physical and chemical characteristics to the NOM, which affect soil particles and dissolved solutes in various ways. Polar functional groups may bond the NOM to mineral surfaces and complex dissolved ions, such as metal cations. Non-polar hydrophobic functional groups may adsorb and sequester low solubility hydrophobic contaminants within the soil matrix. Components of NOM are differentiated based on molecular size and solubility in acid or alkaline solutions and have different chemical and physical characteristics. The relative quantity of each component will influence the overall role of NOM in oxidative treatment systems.

NOM adsorption of hydrophobic compounds plays multiple roles in the fate of these compounds in ISCO systems. A dual-mode polycyclic aromatic hydrocarbon (PAH) sequestration process involves sorption onto HA and FA, which is bound at the surface of soil particles, and humin material, which is found in the core of soil particles (i.e., internal surface area) (Bogan and Trbovic, 2003). Sorption onto the humin material requires PAHs to diffuse across

the HA/FA interface on the particle surface to ultimately reach the humin phase. In a similar conceptual model of CHP, intra-particle hydrogen peroxide inward diffusion and contaminant desorption and outward diffusion in activated carbon particles was found to limit the extent of contaminant oxidation (Huling et al., 2009; Kan and Huling, 2009). Similarly, intra-particle desorption and diffusion of PAHs required longer time frames (Bogan and Trbovic, 2003) to be transported from the NOM and required longer diffusion and reaction times for chemical oxidants to diffuse inward. Additionally, the structure of NOM molecules allows the binding of organic contaminants and their sequestration from the bulk solution. The resulting physical separation of sites associated with OH[•] formation and contaminant sorption is partly responsible for the inhibition of contaminant oxidation by OH[•] (Lindsey and Tarr, 2000a, b). It is evident that the role of NOM and contaminant sorption is to slow down mass transport, mass transfer, and reaction kinetics. In several studies, the rate and extent of contaminant degradation declined in soils or water with higher organic matter and was attributed to contaminant sorption and lower availability for oxidative reactions (Tyre et al., 1991; Watts et al., 1991a; Lindsey and Tarr, 2000a, b; Baciocchi et al., 2003; Kanel et al., 2003). This general trend is more pronounced as contaminants become more hydrophobic and as more time has elapsed for contaminant-NOM sorption and equilibrium to occur (Bogan and Trbovic, 2003; Lundstedt et al., 2006).

It has been proposed that oxidation of NOM occurs during ISCO, which results in the release of sorbed PAH contaminants from the active sites (Rivas, 2006) and this effect is not oxidant-specific. A portion of sorbed PAHs were released from the oxidation of NOM by persulfate (Cuyper et al., 2000). Additionally, a lag was observed before the oxidation of trichloroethene (TCE) and trichloroethane (TCA) by persulfate and was attributed to the oxidation of NOM followed by contaminant transformations (Liang et al., 2003). An apparent release of RDX from the sorbed phase was measured during KMnO₄ oxidation (Struse et al., 2002). Similarly, an increase in bioavailability of chlorinated compounds by NOM oxidation was proposed for the observed increased rate of biological reductive dechlorination (Droste et al., 2002). In general, these studies suggest that contaminant oxidation is inversely correlated with NOM, and that NOM oxidation corresponds with a release (desorption) of compounds, especially those less amenable to oxidation.

NOM may bond with available hydrogen peroxide catalytic (Fe) sites on mineral surfaces, as well as form complexes with soluble iron catalysts, much like a chelating agent. In some cases, the addition of NOM to soil or the comparison between high-NOM and low-NOM soils indicates a decrease in the hydrogen peroxide reaction rate (Valentine and Wang, 1998; Tarr et al., 2000; Crimi and Siegrist, 2005; Bissey et al., 2006). A reduction in the hydrogen peroxide reaction rate does not necessarily mean a reduction in oxidation efficiency, however.

NOM and oxidation reaction byproducts may react with hydroxyl radicals and other reactive intermediates and therefore behave as a radical scavenger. For example, the ratio of pentachlorophenol (PCP) and H₂O₂ consumption rates in soil suspensions were inversely related to NOM (Watts et al., 1990). In a different CHP treatment system, the oxidation of benzo(a)pyrene was inhibited by the presence of non-target organics, including glucose, cellulose, and lignin (Kelley et al., 1990). Results suggest that the organic matter may have successfully competed with the target contaminants, although the exact mechanism could not be differentiated. Conversely, the rates of reaction of NOM in other CHP systems were generally slow (Goldstone et al., 2002; Bissey et al., 2006), suggesting that NOM is not a major oxidant sink, especially over the timeframes that CHP reactions occur. Further, activated carbon has extremely high surface area and exhibits many of the same ring structures and functional groups that give NOM its sorption characteristics. However, CHP driven regeneration of spent-activated carbon (i.e., degradation of contaminants sorbed on activated carbon used for water treatment) can be achieved despite the high level of organic carbon content (Huling et al., 2000b, 2007, 2009; Kan and Huling, 2009).

In some treatment systems, NOM enhanced oxidative treatment. OH^\bullet production was enhanced in the presence of peat by one or more peat-dependent mechanisms (Huling et al., 2001). Fe concentration and availability in the peat, reduction of Fe(III) to Fe(II) by the organic matter, and reduction of organic-complexed Fe(III) to Fe(II) were probable causes. Similarly, NOM either served as a reducing agent for Fe(III), or supported the reduction of Fe(III) by H_2O_2 (see Equations 2.11 and 2.12), thus enhancing Fe(II) availability and supporting CHP reaction propagations (Voelker and Sulzberger, 1996; Li et al., 1997b; Vione et al., 2004). CHP degradation of 2,4,6-TNT was greater in a system amended with fulvic acid than in another containing humic acid (Li et al., 1997b). Enhanced kinetics was attributed to accelerated Fe(III) reduction. Humic material can facilitate electron transfer for Fe(III) reduction in microbial systems (Lovley et al., 1996; Scott et al., 1998), and similar redox coupling can occur by quinones and hydroquinones, constituents of humic materials, in CHP systems (Chen and Pignatello, 1997). Overall, these reactions provide an additional mechanism to reduce Fe(III) to Fe(II), resulting in more efficient OH^\bullet production. Contaminated aquifer material containing these types of organic matter may exhibit similar mechanisms that enhance CHP oxidation.

2.2.5.4 Temperature

CHP reactions are exothermic and can raise the temperature of aquifer material and groundwater. Significant and rapid increases in temperature have been observed in some cases, particularly when H_2O_2 concentrations are high, and reaction is fast. For example, Mecozzi et al. (2006) witnessed a rapid temperature increase from 30 to 70°C in a hydrogen peroxide soil slurry batch system. Elevated temperatures from the exothermic CHP reaction have been observed in the field beyond the 70°C observed by Mecozzi et al. (2006) and have even melted polyvinyl chloride (PVC) injection wells. It is beyond the scope of this section to discuss the health and safety concerns raised by such an extreme temperature rise. This section focuses on the fundamental impact of temperature on the reaction chemistry.

Chemical reaction rates increase as temperature increases and obey the relationship established by Arrhenius (Equation 2.29). Kinetic rate constants (either first-order or second-order) are a function of the activation energy (E_a), as well as the frequency factor (A), which is a physical parameter representing collision frequency between reactants.

$$k = Ae^{-\frac{E_a}{RT}} \quad (\text{Eq. 2.29})$$

Because there are many simultaneous reactions that occur within CHP reaction chains and because each reaction may have different activation energies, initial kinetic rates, and frequency factors, the effect of increased temperature on kinetics for each reaction differs in magnitude. Therefore, the dominant or fastest reactions may shift with temperature, causing changes in dominant reaction mechanisms and efficiencies. General trends that have been noted in the literature are that the rate of oxidant decomposition will generally accelerate with higher temperature.

The increases in temperature due to hydrogen peroxide decomposition may or may not improve contaminant degradation rates, as other competing side reactions will also accelerate. Elevation of temperature may accelerate the oxidation of contaminants that are slower to react and less soluble at ambient temperatures, such as TNT (Li et al., 1997a, b). However, higher temperatures may also accelerate oxidant decomposition, reducing oxidant persistence. Other physical and chemical processes also change with temperature, such as solubility, formation of azeotropes with nonaqueous phase liquids (NAPLs), and decomposition reactions. This can make it difficult to extrapolate overall system kinetics, CHP reaction efficiency, and treatment effectiveness from one temperature to another. Because of the complexity of this temperature

dependence, the uncertainty in extrapolating results from treatability studies to the field may be reduced if the studies are conducted at temperatures that are relevant to the field. The majority of studies in the literature have investigated CHP at ambient room temperatures between 20 and 25°C, while ambient groundwater temperature is more often in the range of 10–15°C.

2.2.5.5 Oxygen Gas

Hydrogen peroxide is approximately 94% (by weight) oxygen; therefore, oxygen gas [O₂(g)] can be a significant byproduct of some H₂O₂ reactions. Smaller amounts of carbon dioxide (CO₂) gas may be present as the result of mineralization of organic contaminants and acidification of carbonates. Molecular oxygen may be evolved from reaction of hydrogen peroxide with inorganic minerals, such as goethite and pyrolusite, as well as biologic enzymes, such as catalase. Because oxygen has low solubility in water (8–10 mg/L), oxygen emitted from CHP systems will readily form a gas phase. Watts et al. (1999b) found oxygen evolution from a CHP system in the presence of goethite to follow zero-order kinetics, indicating that the rate of oxidant decomposition to oxygen was constant with time. Rates of oxygen gas evolution increased with increasing pH, as well as higher goethite concentrations. The use of a phosphate stabilizer reduced the rate of oxygen evolution.

When injecting H₂O₂ into the subsurface, the rapid formation and expansion of O₂(g) in the pore space may serve to enhance the transport distance of the oxidant solution through the subsurface than would be accomplished from simple fluid injection. Furthermore, oxygen is a terminal electron acceptor used in the aerobic biodegradation of some compounds. Gas evolution in subsurface may also result in air sparging and stripping effects, resulting in the mobilization of volatile organic contaminants (VOCs). The formation and transport of VOC vapors may represent unacceptable exposure pathways and health risks, in which case, they would need to be monitored and controlled. Furthermore, the displacement of pore space by gas may temporarily reduce the permeability and affect groundwater movement. This is a transient effect as the gas will eventually dissolve into the aqueous phase and restore permeability, but it requires time. Finally, the evolution of O₂(g) in the presence of flammable hydrocarbon contaminants may result in flammable or explosive mixtures, requiring careful management of CHP when targeting these contaminants.

2.3 OXIDANT INTERACTIONS IN THE SUBSURFACE

When hydrogen peroxide is injected into the subsurface, a series of simultaneous chemical reactions occur that result in catalysis and decomposition of the oxidant, degradation of organic contaminants, and changes to the subsurface. Much of the previous section described specific chemical reactions, reactive species, and mechanisms that may occur in subsurface systems. This section describes the combined impact that these effects have on ISCO using CHP, with an emphasis on parameters that may be controlled by ISCO practitioners.

It is worth noting that while the majority of the CHP literature has focused on reaction chemistry and mechanisms, relatively little attention has been given to CHP reagent delivery and transport in subsurface systems. For example, Siegrist et al. (2010) found 74 studies evaluating CHP in batch aqueous systems; another 59 investigated CHP in batch soil-slurry systems. However, only 12 studies investigated the transport of hydrogen peroxide through porous media under conditions that mimic field injection and delivery processes (e.g., 1-D flow-through columns, 1-D diffusion cells, 2-D tanks, and mockups of injection probes). Thus considerable data gaps remain in understanding processes that impact oxidant transport and the magnitude of their effects. One area of uncertainty lies with the formation of O₂(g) from

hydrogen peroxide in the subsurface (see Section 2.2.5.5), and the resulting effect of the gas on oxidant and groundwater transport. Observations from Watts et al (1999b) indicate that under some conditions, substantial gas evolution can occur. Gas evolution can result in groundwater displacement, reductions in permeability, and other transport effects. However, no controlled laboratory- or field-scale investigations have been published that quantify and document these effects, making it difficult to offer detailed information on how they may impact CHP implementation.

This section is divided into two subsections that discuss the subsurface impacts of hydrogen peroxide that are well explored in the literature (1) the impact that oxidant persistence has on transport in the subsurface and (2) the effects that CHP injection may have on the subsurface environment, particularly metal mobility.

2.3.1 Impact of Oxidant Persistence on Oxidant Transport

One of the paramount considerations in implementing ISCO is determining how effectively the oxidant can be distributed in the subsurface. This includes consideration of generic processes that impact any oxidant, such as permeability and heterogeneity and their impacts on delivery of the oxidant solution. However, it also includes considerations specific to hydrogen peroxide, especially with regard to oxidant persistence. Oxidant persistence and the factors that affect it are discussed in Section 2.2.4.2. The following section outlines the impact that oxidant persistence can have on oxidant distribution.

Within a given subsurface environment, hydrogen peroxide is a short lived but vigorously reacting oxidant, with a typical half-life of several hours to several days. The persistence of the oxidant is important because the rate of oxidant decomposition determines (1) the amount of contact time the oxidation reaction will have in the contaminated subsurface and (2) selection and design of the injection method. With low oxidant persistence, there is less time available for the oxidant to transport through porous media and react with contaminants, especially those in either sorbed or NAPL phase. There is likely to be very little transport once the injection has actually stopped (that is, no “drift” due to the transport of the groundwater under natural gradients).

Oxidant persistence affects the transport time and the ability of the oxidant to reach the target zone(s) by advection, dispersion, or diffusive transport mechanisms. This is illustrated conceptually in Figure 2.4, which shows a typical pseudo first-order decomposition of hydrogen peroxide with respect to time. Assuming that forced advection is the primary mechanism responsible for oxidant delivery in porous media, and that dispersion and diffusion are negligible, then the effective transport distance in the subsurface is primarily a function of the solution velocity and the rate of oxidant decay. In some cases, a catalyst or other reagents may be delivered and similar transport and persistence requirements are applicable to these as well.

Shorter effective transport distances necessitate closer injection point spacing; where large NAPL or sorbed mass is present, multiple injection rounds may be necessary to deliver enough oxidant and enable adequate contact time to degrade the target organics. To help alleviate the need for close injection point spacing and to extend the contact time, increasing the oxidant persistence is often a desirable goal. The negative effect of low oxidant persistence on transport has been noted in the literature. For instance, Baciocchi et al. (2004) found that in a column system with a Darcy velocity of 14 m/day, a 2 wt.% solution of hydrogen peroxide declined to only 5–25% of its initial concentration after passing through only 30 cm of porous media. The use of a phosphate stabilizer dramatically improved oxidant transport as the concentration at 30 cm was 90% of its initial concentration when the stabilizer was present (see Figure 2.5).

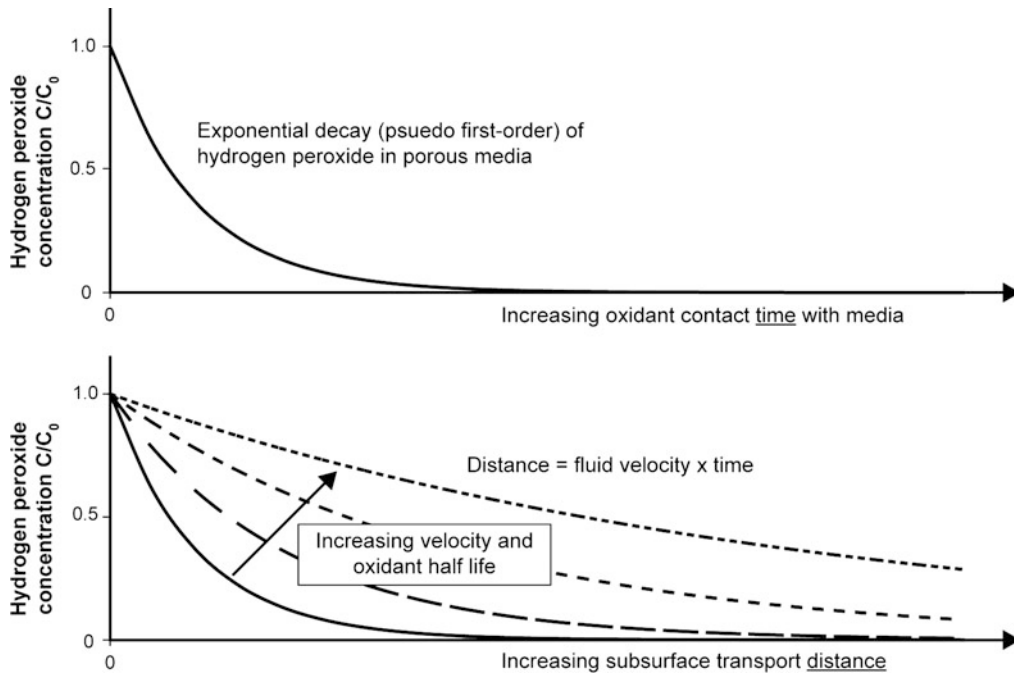


Figure 2.4. Conceptual diagram illustrating how oxidant persistence impacts oxidant transport. Higher injection velocities and longer half lives increase the transport of the oxidant into the porous media.

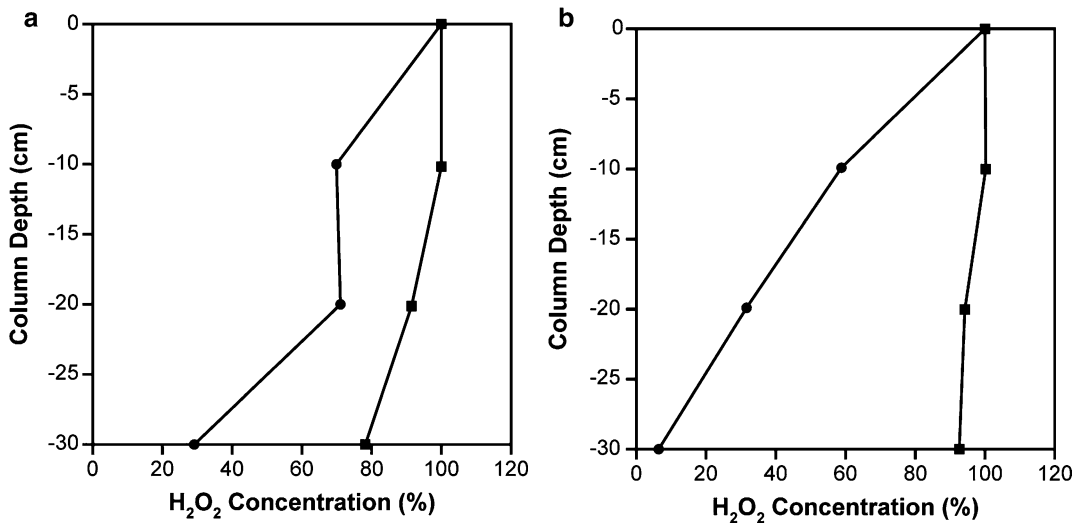


Figure 2.5. Hydrogen peroxide concentration profile in soil columns after (a) 10 min and (b) 180 min flow. Inlet conditions: H₂O₂ concentration = 2%, flow rate = 4.5 mL/min, column diameter = 2.5 cm: (filled circle) H₂O₂ only and (filled square) H₂O₂ + 2.46 g/L phosphate (PO₄). From Baciocchi et al., 2004; reprinted with permission.

In another study of hydrogen peroxide transport, diffusion over long time periods was investigated by Seitz (2004), who reported that a 1 wt.% solution was not able to diffuse through a 2.5-cm-long sandy loam soil core to detectable concentrations within a 50-day time period. However, despite the inability to detect oxidant diffusion through the core, there was

some evidence of diffusive oxidant transport in this system as contaminant and NOM concentrations decreased in the portion of the core closest to the oxidant source, suggesting some degradation was occurring. This system did not have any stabilizers or catalysts added to it, and it is unclear if chemistry optimization may have improved oxidant diffusion.

These studies highlight some of the challenges of low oxidant persistence. As a result, efforts have been made to optimize hydrogen peroxide chemistry for longer transport. As discussed in Section 2.2.4.2, work by Watts et al. (2007) and others has focused on the use of stabilizers which promote hydrogen peroxide lifetimes in subsurface systems, and help to increase transport and effectiveness.

2.3.2 Impacts on Metal Mobility

The use of CHP in the subsurface has the potential to affect metals mobility through several mechanisms. First, oxidation reactions with metals and minerals may change the oxidation states of the metals and alter their mobility and toxicity. Metal mobility also can be altered by the degradation of metal-binding NOM (Sirguy et al., 2008). Finally, the use of activation aids to promote iron solubility, such as pH adjustment (Villa et al., 2008) or the addition of chelators (Siegrist et al., 2006), or stabilizers like phosphate can also affect the mobility of other metals present in solution.

Laboratory studies have provided evidence as to how ISCO using CHP might impact metal mobility. These studies have shown that CHP can promote the release of various metal ions, including those of zinc (Zn), cadmium (Cd), copper (Cu), lead (Pb), cobalt (Co), Mn, chromium (Cr), and nickel (Ni) (Rock et al., 2001; Monahan et al., 2005; Villa et al., 2008). The extent to which each is solubilized can depend greatly on the metal compound, treatment scheme, and chemical conditions in porous media. These studies have generally employed batch reactors with extensive contact between the oxidant and the porous media. In many cases they have not evaluated attenuation mechanisms that might be active after the reaction has ceased or the metals have drifted outside the ISCO reaction zone into untreated media, especially on time-scales relevant to the field-scale. Thus the understanding of the ultimate fate of metals during ISCO with CHP is incomplete. A case study of ISCO sites (all oxidants) by Krembs (2008) found that metals concentrations were monitored at only 23 of the 242 sites reviewed. Most of these were permanganate injection sites, and thus the number of CHP sites was too small to make a significant statement about metals mobility. However, regardless of oxidant, in most cases toxic metals such as chromium, arsenic, or nickel were attenuated within 6 months. The following sections discuss studies that have evaluated metal mobility and the mechanisms involved.

2.3.2.1 Studies of Increased Metal Mobility during CHP treatment

Monahan et al. (2005) found that Fe(III)-catalyzed hydrogen peroxide at pH 3 caused the release of Cd, Cu, and particularly Zn ions from the mineral kaolinite in batch studies. Under neutral pH and the addition of a chelator, total metals release was higher than at pH 3. Lead, which was immobile under acidic conditions, was mobilized at neutral pH. This was attributed to free radicals oxidizing and mobilizing the metals. At low doses of hydrogen peroxide (<7 g/L), no detectable release of metals from kaolinite was observed. However, the behavior of individual metals varied, with some metals rising or falling in concentration depending on pH. The data for zinc from this study (presented in Figure 2.6) illustrate that despite higher total metals concentrations at neutral pH with a chelator, the zinc concentration in solution was lower than at acidic pH.

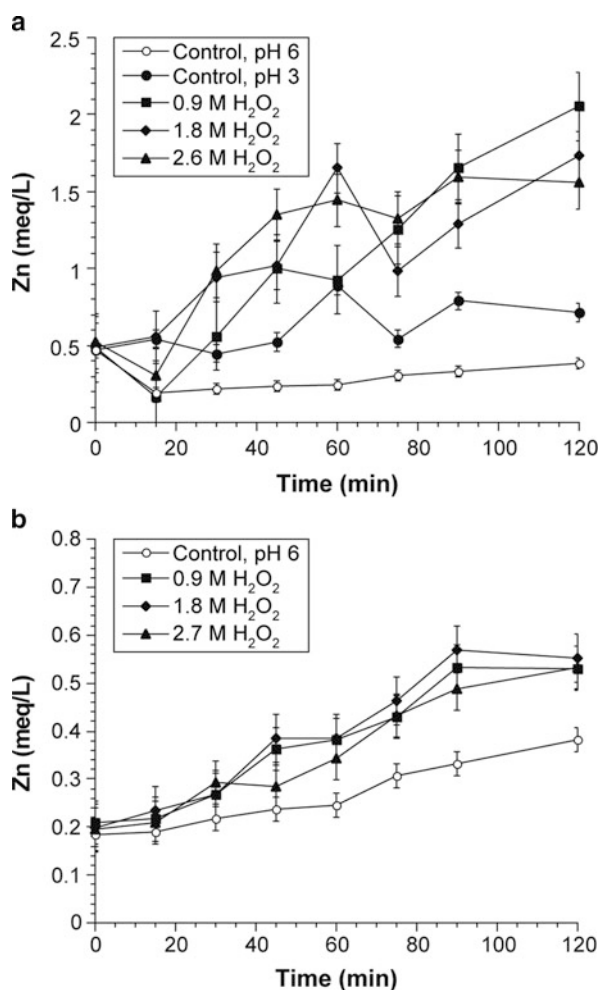


Figure 2.6. Zinc data from (a) Fe(III)-catalyzed hydrogen peroxide system at pH 3 and (b) Fe(III)-chelate catalyzed hydrogen peroxide system at pH 6 (from Monahan et al., 2005). Note different scales on the y-axis. Conditions: soil was kaolinite with sorbed metals; solids to solution ratio = 1 g/35 mL; chelate used as nitrilotriacetic acid (NTA); [Fe(III)] = 1 mM, [Fe(III)-NTA] = 1 mM; oxidant concentration given in figure. Note: meq/L - milliequivalents per liter. Reprinted with permission.

In another study, after 3.5 days of reaction with 1.1 moles of hydrogen peroxide and 3.0 mmol of Fe(II), Villa et al. (2008) found significantly increased metals dissolution from a soil contaminated with diesel fuel: Zn (36%), Cu (12%), Ni (8.9%), Mn (3.1%), Cr (0.9%), and Co (0.4%). Cr, Ni, Cu, and Mn levels increased the most and their concentrations were above accepted levels for groundwater. No increase was observed for Pb or Cd.

Rock et al. (2001) observed hexavalent chromium release from an acidic, oxidizing soil from ore processing and electroplating sites. On addition of hydrogen peroxide, a large amount of Cr(VI) solubilized. The release was attributed to oxidation of Cr(III) in the soil, solubilization of Cr(VI), and oxidation of NOM. However, the elevated levels of Cr(VI) were observed to attenuate several days after hydrogen peroxide had dissipated, possibly due to re-binding to the remaining NOM.

2.3.2.2 Oxidative Alteration or Destruction of NOM

Largely due to the efficiency and non-specificity of hydroxyl radicals formed during its application, CHP can result in significant modification or loss of metal-binding NOM (Sun and Yan, 2007; Sirguy et al., 2008). In batch studies using four different soil types, Sirguy et al. (2008) showed that in addition to destroying a large percentage of the PAH contaminants present in the soils, hydrogen peroxide resulted in a substantial loss of organic carbon (around 75–90%). As in permanganate or ozone ISCO, destruction or modification of NOM can release metals bound to it.

2.3.2.3 Alteration of pH

A reduction in pH is possible with CHP use, especially when acid addition is used to enhance iron catalyst solubility in the subsurface; this approach can increase metal mobility in the subsurface (Huling and Pivetz, 2006). Although acidification in well-buffered groundwater usually abates naturally in a period of days, some researchers have found pH levels as low as 2.3 to persist for longer periods in weakly buffered systems (Villa et al., 2008). The potential binding sites for metals in minerals and organic compounds include hydroxyl, carboxyl, and nitro groups to which abundant hydrogen ions (H^+) can competitively bind, aiding desorption and solubilization of metals (Dewil et al., 2007; Villa et al., 2008). The extremely low pH can also cause increased solubility of certain oxides and hydroxides of metals in the porous media (Villa et al., 2008).

2.4 CONTAMINANT TREATABILITY

Because of the nonselective nature and wide reactivity of CHP chemistry, CHP has been used to treat a variety of organic contaminants. The frequency with which common organic contaminant classes are encountered in the CHP literature has been surveyed and is summarized in Table 2.7. Most of these studies present laboratory data, since there are far fewer rigorous field investigations. Some studies have investigated multiple contaminants and thus the total number of instances does not equal the total number of studies. This review provides a glimpse of the different organic contaminants that have been targeted with CHP. Studies that have investigated CHP in aqueous systems with no porous media present vs. systems involving porous media are distinguished. Typically, soil slurry systems are more representative of CHP-ISCO field conditions with high oxidant concentrations, mineral surfaces, chelates, or soluble catalysts, while the aqueous systems are more representative of traditional Fenton's systems with low oxidant concentrations, low pH, and soluble Fe(II) catalysts.

2.4.1 Halogenated Aliphatic Compounds

ISCO using CHP has been extensively applied to this category of contaminants, especially the chloroethenes, in both source zones and plumes (Krembs, 2008). Sorbed or nonaqueous phase masses are often present at sites where these chemicals have been used and their presence can have serious effects on ISCO effectiveness. The following section reviews the degradability of these contaminants using ISCO. Nearly all of the studies have been conducted at ambient temperatures and in small well-mixed laboratory scale batch apparatus, such as vials or flasks, with the exception of Bergendahl et al. (2003), who used a 55-gallon batch reactor.

Table 2.7. Susceptibility of Different Organic Compounds to Oxidative Degradation by CHP

Contaminant category	Number of aqueous system studies	Number of soil-slurry system studies	Treatability
Chlorinated aliphatic compounds	15	19	
Chloroethenes	3	5	Degradable
Chloroethanes	6	0	Conditionally degradable
Chloromethanes	2	1	Conditionally degradable
Other	14	7	Conditionally degradable
Chlorinated aromatic compounds	24	14	
Chlorophenols	14	7	Degradable
Chlorobenzenes	2	1	Degradable
Polychlorinated biphenyls (PCBs)/dioxins/furans	7	6	Conditionally degradable
Other	1	0	Conditionally degradable
Hydrocarbon compounds	25	22	
Benzene, toluene, ethylbenzene, and total xylenes (BTEX)	1	3	Degradable
Total petroleum hydrocarbons (TPH) and saturated hydrocarbons	0	9	Degradable
Methyl tert-butyl ether (MTBE)	4	1	Conditionally degradable
Phenolic compounds	10	1	Degradable
Polycyclic aromatic hydrocarbons (PAHs)	8	8	Conditionally degradable
Other	2	0	Conditionally degradable
Other organic compounds	37	22	
Explosives and nitroaromatic compounds	8	5	Degradable
Pesticides	8	4	Conditionally degradable
Other	21	13	Conditionally degradable
Total studies	74	59	

2.4.1.1 Chloroethenes

Chloroethenes are the most common COCs treated by ISCO. This class of organic compounds includes those containing a carbon–carbon double bond. Their degradability is well documented in the literature. Studies involving both aqueous and soil-slurry systems indicate that chloroethenes are readily degradable by CHP within a wide range of conditions, including different hydrogen peroxide concentrations, iron catalysts and concentrations, and pH ranges.

Aqueous system studies have largely employed traditional methods for hydroxyl radical (OH^\bullet) generation by using Fe(II) catalysts and low concentrations of hydrogen peroxide. These studies generally found increased chloroethene degradation at lower pH, in part due to the higher availability of soluble iron. However, experiments by Teel et al. (2001) reported that at neutral pH, a non- OH^\bullet mechanism may be responsible for degradation. A number of more recent studies using Fe(III) or mineral catalysts have implicated superoxide ($\text{O}_2^{\bullet -}$) as being a

major reactive species in CHP systems, particularly when H_2O_2 concentrations are high (e.g., 3.5–35 g/L) (Watts et al., 1999a; Teel and Watts, 2002; Smith et al., 2004). Thus, the ease of degradation observed for chloroethenes may be due in part to a susceptibility to a variety of reaction mechanisms, both oxidative and reductive.

Degradation of chloroethenes, particularly TCE and PCE, has been demonstrated in slurry systems using a variety of porous media types. Permeable sands have been investigated most, but some lower permeability media, including loams and even fractured rocks, have been studied. The pH of slurry systems is generally in the neutral to weakly acidic range, reflecting the natural pH of the media. Because of the near-neutral pH, use of an Fe(II)-chelate complex has been attempted to maintain iron availability. Other studies have used the natural mineralogy of the porous media as the only catalyst. The efficacy of this approach appears to be media-specific, depending on what iron and manganese minerals are present. Because chloroethenes have been shown to be degradable by both oxidative and reductive mechanisms, the presence of minerals that catalyze either type of reaction will likely improve performance. Very pure silica sands with little iron or manganese mineralogy may support less degradation, presumably due to the absence of these minerals (Yeh et al., 2003). However, too high of a catalytic mineral content could also lead to excessive oxidant decomposition, making delivery in the subsurface a challenge.

Only a few studies have evaluated intermediates or byproducts of CHP oxidation of chloroethenes. Chen et al. (2001) tracked both total organic carbon (TOC) and chloride and suggested that TCE was completely dechlorinated based on a nearly stoichiometric chloride release; TOC declined accordingly, suggesting that the carbon end product of the reaction was CO_2 . However, not all studies documented such efficient chloride recovery. In an aqueous system Teel et al. (2001) noted a chloride release of only 2 mole Cl^- /mole TCE with CHP at low pH, and only 1 mole Cl^- /mole TCE at neutral pH, suggesting the possibility that chlorinated intermediates might be accumulating. Indeed, an early chemical oxidation study by Leung et al. (1992) detected the formation of dichloroacetic and formic acids during early stages of reaction, but these were subsequently degraded as reaction continued and complete mineralization was attained. Chen et al. (2001) and Gates and Siegrist (1995) also noted a minor pH drop over the course of reaction, suggesting that protons (H^+) were produced as well, though the complex nature of porous media-CHP interactions cannot exclusively attribute this to reaction with chloroethenes.

2.4.1.2 Chloroethanes

Only a few studies have investigated chloroethane degradation in aqueous systems. These have been based on the traditional Fenton's reaction, where OH^\bullet radicals are the primary reactive intermediate present. These systems have shown some reactivity with chloroethanes but at reduced rates of reaction, leading to lower extents of degradation. Results from Bergendahl et al. (2003) seem to suggest a reduced treatment efficiency with higher chlorine content when methods emphasizing OH^\bullet activity are used. However, a very different study by Teel and Watts (2002) using a soluble Fe(III) catalyst at low pH demonstrated substantial degradation of fully chlorinated hexachloroethane (HCA). HCA is a highly oxidized compound, which would make it very resistant to degradation by oxidative mechanisms. However, this study demonstrated degradation of other highly oxidized compounds such as CT, bromotrifluoromethane, and tetranitromethane, thus implicating a reductive mechanism believed to be the superoxide anion ($\text{O}_2^{\bullet -}$). Similar research in slurry systems by Watts et al. (1999a) demonstrated degradation of HCA and evaluated reaction products; approximately 66% of the chlorine was released and the daughter products detected were pentachloroethane, and lesser

amounts of 1,1,2-trichloroethane, PCE, and both *cis*- and *trans*-1,2-dichloroethene (*cis*-DCE, *trans*-DCE). Degradation yield improved with higher hydrogen peroxide concentrations, highlighting the importance of higher oxidant concentrations to promote reductive mechanisms using CHP. Gates-Anderson et al. (2001) seem to support this; they found that in a sand with only natural mineral content to enable reaction some treatment of 1,1,1-TCA was achieved at high oxidant concentrations. The ability of natural minerals to catalyze degradation of chloroethanes appears to vary with media because a sandy loam characterized with a higher free iron oxide content and using the same experimental approach failed to attain any treatment of 1,1,1-TCA. However, treatment of the chloroethenes TCE and PCE was detected in both media, so the reaction pathways present may have differed within the two media. Overall, given the limited number of studies, as well as variable performance demonstrated by CHP treatment of chloroethanes, treatability studies are advisable for sites with these contaminants using high concentrations in the 1–10 wt.% range for hydrogen peroxide and Fe(III) catalysts.

2.4.1.3 Halomethanes

Halomethanes have traditionally been considered to fall outside the realm of ISCO treatment because of their highly oxidized nature, which would make them resistant to oxidative degradation. However, recent work has provided a scientific basis for treatment of these contaminants by CHP. Treatment of halomethanes under field conditions has not been well documented in the literature. Laboratory studies investigating oxidation of halomethanes have been limited to relatively pure systems, involving either aqueous phase alone or with neat mineral or NAPL phases, but not in porous media. Hence, caution is advised in proceeding with ISCO targeting these contaminants. It would be advisable to demonstrate the technology with treatability or pilot studies before proceeding to full-scale implementation.

Halomethane degradation in CHP systems is likely due to reductive mechanisms. Buxton et al. (1988) and Haag and Yao (1992) reported rate constants for OH^\bullet radical reactions with several chlorinated and brominated methanes and found them to be much lower than typical OH^\bullet reaction rates with other radicals or organic and inorganic compounds. In particular, CT, a common DNAPL contaminant, has been found to be essentially unreactive with OH^\bullet radicals.

However, recent research has focused on the possible role that a superoxide anion ($\text{O}_2^{\bullet -}$) may play in these systems (Teel and Watts, 2002; Smith et al., 2004, 2006; Watts et al., 2005b). Considering the catalyst doses reported in the literature, soluble Fe(III) catalysts appear to be the most efficient for these reactions since they promote hydroperoxyl radical (HO_2^\bullet) generation via Equations 2.10–2.12 instead of OH^\bullet generation via the Fenton reaction (Equation 2.1). This then leads to production of $\text{O}_2^{\bullet -}$ via the disassociation reaction in Equation 2.8. However, solubility of Fe(III) must be maintained either through chelating agents or low pH conditions. The use of manganese-based catalysts in both soluble and mineral forms also appears to catalyze degradation of these highly oxidation-resistant compounds. But it appears that very high concentrations of these manganese-based catalysts need to be present in order to promote the reaction. These studies have typically used concentrations of hydrogen peroxide in the 1–7 wt.% range with a variety of catalysts. These higher concentrations of oxidant are important, as demonstrated by Smith et al. (2004), because they not only promote generation of superoxide, but the presence of hydrogen peroxide also increases the reactivity of superoxide by improving its solvation in aqueous systems.

Currently, little information is available with respect to reaction byproducts from CHP treatment of halomethanes. One intermediate that has been observed in off-gas from CHP treatment of CT is phosgene gas (COCl_2). Though this gas is toxic, it is not likely to pose a threat

in groundwater or porous media because in the presence of water, it readily hydrolyzes to CO_2 and hydrochloric acid, with a reported half-life of 0.026 s, so it does not persist in these environments (ACC, 2003). However, if occupational exposure to CHP off-gases were to occur, particularly in enclosed workspaces, this could be of concern. In terms of potential for contaminant mineralization, Watts et al. (2005b) found an average chloride release of 2 mole Cl/mole CT, suggesting incomplete dechlorination. However, the production of phosgene in these systems implies that mineralization may occur after hydrolysis of this product is complete.

2.4.1.4 Other Halogenated Aliphatic Compounds

Little is known about CHP treatment of other halogenated aliphatic compounds such as chlorinated or brominated aliphatic compounds with three or more carbon atoms. These contaminants are not found as frequently at sites that need remediation as the other halogenated aliphatic compounds. Haag and Yao (1992) reported OH^\bullet radical rate constants with 1,2-dibromo-3-chloropropane and 1,2-dichloropropane and found that they were higher than those of chlorinated methanes and ethanes, but still lower than most aromatic and pesticide compounds. This suggests that they may be somewhat more susceptible to oxidative attack, but more research is needed. CHP treatability studies would be advisable for any site containing these compounds.

2.4.2 Chlorinated Aromatic Compounds

Chlorinated aromatic compounds represent another class of groundwater COCs. These compounds include chlorophenols, chlorobenzenes, PCBs, dioxins, and others and are derived from wood preservatives, solvents, hydraulic fluids, dielectric oil, and other materials.

2.4.2.1 Chlorobenzenes and Chlorophenols

Chlorobenzenes and chlorophenols have been extensively studied (Table 2.7). These compounds are grouped for discussion since they generally follow similar reaction pathways and may be expected to co-occur in the environment. These compounds are very degradable by CHP, particularly by hydroxyl radicals.

There are different isomers of chlorinated benzenes and chlorinated phenols. However, most studies on reaction mechanisms have found similar degradation pathways for these compounds. Chlorinated benzenes and chlorinated phenols are attacked by hydroxyl radicals to form intermediate organic radicals [chloro-hydroxy-cyclohexadienyl radicals (ClHCD^\bullet)]. These radicals then undergo transformations with other aqueous reactants to form phenols and benzene-diols (such as catechol or benzoquinone), which may be either chlorinated or dechlorinated. Subsequent hydrolysis reactions then lead to benzene ring cleavage, and the products often include low molecular weight carboxylic acids. Commonly detected carboxylic acids include the fully dechlorinated oxalic and formic acids, but one study reported the formation of 2-chloromaleic acid as well (Huling et al., 2000b). Because of their lower susceptibility to hydroxyl radical attack, accumulation of these acids in solution can occur (Koyama et al., 1994). However, in natural systems, these acids are often important food substrates and are readily biodegraded. In rare cases, especially those where oxidant concentrations are low and contaminant concentrations are high, the ClHCD^\bullet radicals may cause polymerization reactions either with each other or with other organics, leading to the formation of PCBs, hydroxychlorobiphenyls (hydroxy-PCBs), or other phenolic polymers (Sedlak and Andren, 1991b). However, these compounds themselves are subject to attack, and their formation or accumulation is less likely in the vigorously oxidizing systems typical of CHP.

While the reaction pathways are similar for isomers of chlorinated benzenes and chlorinated phenols, the kinetics may vary from one isomer to another. The position of the hydroxy- and chloro- functional groups on the benzene ring influence the kinetics because they direct hydroxyl radicals to attack the ring at positions either ortho- or para- to these functional groups (Tang and Huang, 1995). Thus, different isomers of the same chlorophenols may have different degradation rates because some will have higher susceptibility to hydroxyl radical attack than others. Generally, these differences between isomers of the same compound (e.g., 2,4-dichlorophenol and 3,4-dichlorophenol) appear to be smaller (less than an order of magnitude) when compared to that of two different compounds (e.g., dichlorophenols vs. trichlorophenols), where the differences are generally greater (more than an order of magnitude).

Another important aspect of degradation kinetics with aromatic contaminants is that organic reaction products produced by oxidation can themselves support and accelerate the reaction by regenerating iron as a catalyst (Lu, 2000; Lu et al., 2002). Benzene-diols, especially catechol, have the properties of a reducing agent and may regenerate Fe(II) from Fe(III). This supports the reaction because Fe(II) produced is immediately available to produce more hydroxyl radicals via the Fenton reaction (Equation 2.4). Figure 2.7 gives a typical plot of contaminant concentration vs. time in a batch reactor with these contaminants. The plot shows an initial lag stage where reaction proceeds slowly and the contaminant concentration declines very slowly. This is followed by a stage of accelerating degradation, where the contaminant concentration declines more rapidly with time (the sharp drop). The final stage of reaction is an exponential decay of COC concentration. The acceleration phase is the period of reaction where these diol intermediates are accumulating in solution and regenerating the iron; the lag phase is the period of time required to accumulate suitable concentrations of these intermediates to support the reaction. This lag period is up to several hours long in mineral-catalyzed systems, but it is shorter with soluble Fe(III) systems and not observed with a soluble Fe(II) catalyst (Lu, 2000; Lu et al., 2002).

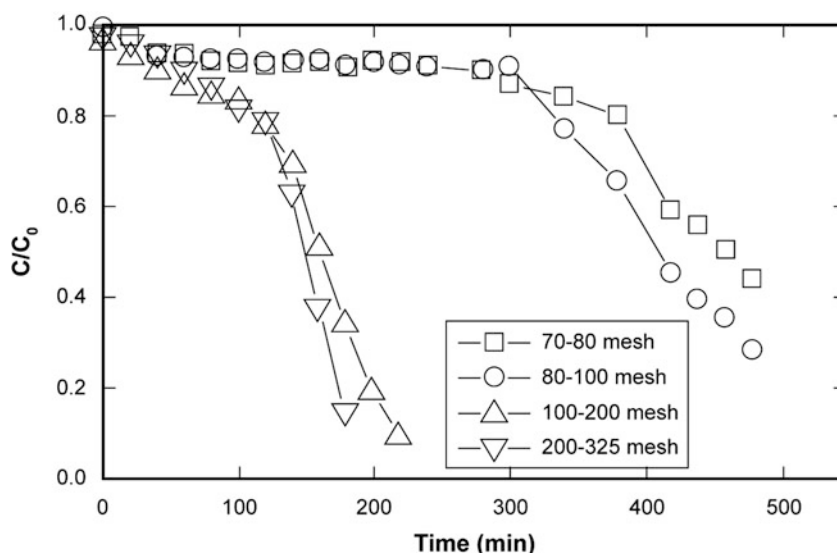


Figure 2.7. Concentrations of 2-chlorophenol (2-CP) vs. time in a catalyzed hydrogen peroxide system (from Lu, 2000). The different curves represent different mesh sizes of the goethite catalyst illustrating the effect of catalytic surface area on reaction. Conditions were [2-CP] = 50 mg/L; [goethite] = 200 mg/L; [H₂O₂] = 75 mg/L; [NaClO₄] = 0.1 M, initial pH = 3, temperature = 30°C. Reprinted with permission.

The reaction pH may also have the potential to affect the mechanisms of CHP degradation of chlorophenols. All phenols are organic contaminants that may act as weak acids. For some phenolic compounds, the pKa of the contaminant is in the neutral to alkaline range (e.g., pKa of phenol = 9.99, 2-chlorophenol = 8.55, 2,3-dichlorophenol = 7.44, Dean, 1999). Because the majority of the CHP research has focused on the acidic range, most of the research on degradation and mechanisms has been under conditions where the protonated form would be expected to be dominant. Generally, the research indicates that CHP at low pH is more effective for degrading chlorophenols than at higher pH, but this may be due to the more effective catalysis and production of hydroxyl radicals at this pH, rather than changes to chlorophenol reactivity or mechanisms. However, at alkaline pH, the ionic form of phenol would be expected to be present, and this may change its sorption (due to higher polarity) as well as potentially change the degradation mechanisms. One major study that did look at hydrogen peroxide degradation of chlorophenols at high pH attributed degradation to a much different reaction mechanism (singlet oxygen) and observed different intermediates than those at low pH (Tai and Jiang, 2005). This study employed a molybdenum catalyst instead of an iron catalyst, so it is unknown if this different mechanism is due to the change of pH range, the different catalyst, or both.

The degradation of these compounds within porous media has been less thoroughly investigated than in aqueous systems. One common trend is that increases in NOM content cause a decline in the degradation kinetics of chlorobenzenes and chlorophenols. The mechanisms behind this have not been thoroughly investigated but are speculated to involve a higher degree of contaminant sorption in systems with higher NOM, as well as the possibility that the NOM is acting as a radical or oxidant sink. Watts et al. (1994, 1999a) reported enhanced desorption of chloroaromatic compounds in the presence of higher concentrations of peroxide, where contaminants were degraded at rates much faster than by mass transfer mechanisms alone, possibly indicating that some of the challenges posed by the lower solubility of these compounds may be partially overcome by the oxidant. Nonetheless, based on data available, high NOM groundwater systems may pose challenges to CHP ISCO of some of these contaminants.

2.4.2.2 Polychlorinated Biphenyls, Dioxins, and Furans

PCBs, dioxins, and furans are persistent organic contaminants that have very low aqueous solubility and a high propensity to sorb to organic substrates in the environment. ISCO treatment of these contaminants has been much less extensively investigated, in part because of their low solubility, which challenges the efficiency of their degradation by an aqueous phase oxidant. However, the literature does provide insight for their treatment by ISCO.

PCBs represent 209 different chemical compounds (congeners) sharing the biphenyl structure and substituted with between 1 and 10 chlorines (homologs) in various positions around the biphenyl structure. In industry, PCBs were generally produced as a mixture of these various compounds, so where subsurface releases have occurred, a variety of congeners will be present.

Studies that have measured reaction rates for hydroxyl radical attack on PCBs have generally found the rates to be quite high (e.g., $10^9 \text{ M}^{-1}\text{s}^{-1}$), which is certainly in the range of treatability of other organic contaminants with CHP. However, the degradation activity is often slow, because the aqueous concentration of PCBs is so low. A novel approach by Lindsey et al. (2003) has used a cyclodextrin ligand in conjunction with soluble iron catalyst and hydrogen peroxide to overcome the solubility problem in treatment of PCBs. Cyclodextrins have hydrophobic cores which strongly hydrophobic compounds like PCBs may partition into,

and the cyclodextrin exterior has a hydrophilic site where dissolved iron may complex. Subsequent reaction with hydrogen peroxide may result in radical generation in direct proximity to the contaminant leading to solubilization and degradation of PCBs, provided effective contact between the cyclodextrin and PCB can be achieved.

Several investigations have examined the reaction byproducts from the treatment of PCBs by CHP. The present understanding of the degradation mechanism is that hydroxyl radical abstracts a hydrogen atom preferentially from one of the non-chlorine substituted positions on the PCB molecule, generating a hydroxy-PCB reaction intermediate. Indeed, hydroxy-PCBs and possibly dihydroxy-PCBs have been observed by Sedlak and Andren (1991a). Further reaction pathways beyond these intermediates or reaction pathways involving other radicals known to be produced by CHP (such as superoxide anion $[O_2^{\bullet-}]$ or perhydroxyl radical $[HO_2^{\bullet}]$) are largely unknown. Koyama et al. (1994) reported the formation of oxalic and formic acids in a system investigating PCB oxidation by hydrogen peroxide, suggesting that further reaction and ring cleavage does occur.

The rate and extent of degradation of a given PCB varies by congener. Sedlak and Andren (1991a) investigated the degradation of Aroclor-1242 and found that the more highly chlorinated homologs degraded more slowly than the less chlorinated homologs. They also found that within each homolog group, the congeners that had chlorines substituted in the ortho- positions degraded more slowly than those with chlorine substituted in the meta- or para- positions. Due to these differing rates of reaction, treatment of a PCB mixture might lead to enrichment of the slower degrading PCBs over time, as the faster reacting PCBs are depleted from the system (Manzano et al., 2004). However, the rates generally seem to vary less than one order of magnitude and the extent of this effect is unknown.

Treatment of PCBs adsorbed to field porous media is less explored than systems evaluating PCB degradation in aqueous systems. Osgerby et al. (2004) reported on the degradation of PCBs from two volcanic field soils and found that the conditions under which CHP would degrade PCBs were different for the two soils, and highly pH-dependent. Fe(III) catalysts were the most effective, and alkaline (~pH 9) to strongly alkaline (~pH 13–14) conditions catalyzed the best degradation, possibly indicating that superoxide is a contributor to the reactivity of these systems. However, CHP implementation at alkaline pH may be difficult because the lifetime of hydrogen peroxide at these pH levels is very short. Under acidic conditions, effective degradation was seen in one soil but not the other, and neither was effective at neutral pH. Manzano et al. (2004) found that in a silica sand river sediment, low catalyst doses, an optimal hydrogen peroxide concentration of 5%, and elevated temperatures led to higher extents of degradation, and up to 82% dechlorination was observed for an Aroclor-1242 mixture.

Dioxins and furans represent a category of contaminants similar in nature to PCBs and are known for their toxicity at very low concentrations. The degradation of these contaminants by CHP has been investigated in only a few studies. Mino et al. (2004) found that Fe(II) catalyzed systems were slow to initiate degradation of 2,7-dichlorodibenzo-p-dioxin (DCDD), but Fe(III) catalysts were able to catalyze degradation and chloride liberation. Presumably, Fe(II) systems only initiated degradation once Fe(III) had been produced by Fenton's reaction. This lack of degradation in an environment where hydroxyl radical activity is expected to be high indicates that the degradation of DCDD proceeds by some other mechanism. Mino et al. (2004) hypothesized that the ferryl ion $[Fe(IV)]$ was responsible for this degradation but did not embark on mechanistic experiments to determine the reactive species. However, the reaction of Fe(III) with hydrogen peroxide would be expected to produce the perhydroxyl radical (HO_2^{\bullet}) based on reactions shown in Equations 2.10–2.12; it is unclear if this species plays a role in the degradation as well. 4-Chlorocatechol was detected as a byproduct, suggesting that the multi-ring dioxin structure was being cleaved. Watts et al. (1991a) investigated the

degradation of octachlorodibenzo-p-dioxin (OCDD) in soil and found that degradation extent was inversely related to the NOM content of a soil. This is a similar trend to that found with the treatment of chlorinated benzenes and phenols and may indicate low treatment efficiency due to either sorption processes or NOM acting as a radical sink.

2.4.3 Fuel Hydrocarbons

Fuel hydrocarbons encompass a wide range of organic contaminants contained in common fuel mixtures such as gasoline, diesel, jet fuel, crude oil, and others, as well as additives made to these mixtures. Because spills into the subsurface often involve light nonaqueous phase liquid (LNAPL) releases, the contaminant mass in nonaqueous and sorbed phases may be high, which can affect CHP treatment. Because of the large variety of compounds that may be encountered at a fuel hydrocarbon release site, regulatory approaches often require reductions of only certain compounds, such as MTBE or BTEX, or a summation of compounds as determined by one method (e.g., TPH). Thus, application of CHP may need to be targeted at a specific contaminant present in the mixture, or some portion of the hydrocarbon mass, depending on the objective of the remediation.

Care should be taken when applying CHP to these contaminants because the application of CHP can result in heat generation and oxygen gas evolution, which in turn can create flammable or explosive mixtures in the subsurface when fuel hydrocarbons are present in large concentrations.

2.4.3.1 Methyl Tert-Butyl Ether

Several investigations have generally found that MTBE is readily transformed (e.g., >90–99%) by CHP treatment, but mineralization of the contaminant (to CO₂ and H₂O) is difficult. Burbano et al. (2005) noted that even under the most effective conditions determined by their study in an aqueous system, only 32% of the carbon content of MTBE was mineralized to CO₂. Instead, a series of intermediate and byproduct compounds have been regularly detected. These include tert-butyl formate (TBF), TBA, acetone, and methyl acetate (Burbano et al., 2002; Neppolian et al., 2002; Ray et al., 2002; Burbano et al., 2005). These intermediates are slower to react with CHP than MTBE and may therefore accumulate in solution over the course of treatment. Subsequent degradation of TBF and TBA appears to lead to acetone formation, which is very slow to react with CHP, while methyl acetate is formed by a different pathway (Burbano et al., 2002). Acetone generation may be significant with concentrations in some systems reaching almost a third of the initial MTBE concentration (molar basis). However, acetone is biodegradable, so it may not be of significant risk if CHP fails to completely mineralize MTBE. CHP at acidic pH appears to be more effective at degrading MTBE than at neutral pH.

2.4.3.2 Benzene, Toluene, Ethylbenzene, and Total Xylenes

BTEX is a common group of COCs targeted for ISCO treatment using CHP. These aromatic compounds have been found to be readily degradable by hydroxyl radicals; phenols, catechols, and quinones are often reactive intermediates detected during their oxidation. Much like the reactions observed in the treatment of chlorobenzenes and chlorophenols, these catechols and quinones may serve to support the CHP reaction by reducing iron to Fe(II), thus regenerating the catalyst. Ring opening occurs and the byproducts often include low molecular weight organic acids, such as formic and oxalic acids (Watts and Teel, 2005). There is evidence that CHP treatment may also improve BTEX desorption by mechanisms other than strictly degradation mechanisms (Watts et al., 1999a).

2.4.3.3 Total Petroleum Hydrocarbons and Fuel Mixtures

The use of CHP to degrade mixtures of fuel hydrocarbons either in LNAPL form or sorbed to soil has been investigated. Fuels are complex mixtures of organic chemicals but often can be characterized as having several major fractions, including an aromatic fraction and an aliphatic fraction. The aliphatic fraction includes chain hydrocarbons, while the aromatic fraction includes benzene-related compounds. In addition to these two fractions, there is often a continuum of molecular weights, ranging from low carbon number molecules (6–10 carbon atoms per molecule) to very high carbon number molecules (30–34 carbon atoms per molecule). The nature of the fuel release will influence the relative abundance of these various compounds, with gasoline and diesel spills having lower carbon fractions than crude or bunker oil releases.

Investigations of CHP treatment of fuel hydrocarbons in soil and groundwater have revealed two major trends. First, the degradation of the aromatic fractions proceeds more rapidly than degradation of the aliphatic fractions. This is not surprising, given the affinity of the hydroxyl radical for attacking electron-rich aromatic rings. Thus, the aromatic fraction will be depleted more rapidly than the aliphatic fraction, representing a potential advantage of CHP treatment of these hydrocarbon wastes because much of the toxicity of fuel spills is associated with the aromatic fraction (e.g., BTEX) (Watts et al., 2000). The other major finding is that low carbon number compounds are more rapidly degraded than higher carbon number compounds; this may be due in part to higher carbon number compounds lower solubility and stronger tendency to sorb to subsurface media. As a result, the reductions in TPH that are achievable with CHP may depend on the type of fuel initially spilled and will generally not lead to complete degradation.

In CHP treatment of a soil with diesel sorbed at 1,000 mg/kg, a 99% reduction in diesel range organics was observed (Watts and Dilly, 1996). Other results have shown a 50% TPH reduction to be typical in the CHP treatment of a diesel–kerosene mixture (Kong et al., 1998). In the CHP treatment of a crude oil mixture, the maximum reduction in TPH obtained under the conditions studied was 31% (Millioli et al., 2003). Mineralization of the fuel hydrocarbon contaminants to CO₂ may lag even further. A system evaluated by Xu et al. (2006) found that while reductions in diesel range organics in porous media could exceed 93%, only 5–12% of the initial contaminant carbon content was mineralized to CO₂.

Because mineralization of TPH contaminants to CO₂ lags behind their degradation by CHP, intermediates and byproducts of CHP treatment of fuel hydrocarbons should be considered. Ndjou'ou and Cassidy (2006) evaluated the physical and chemical properties of byproducts produced during the reaction of CHP with fuel hydrocarbon contaminants and found that a series of alcohols, aldehydes, ketones, and carboxylic acids are produced. These intermediates and byproducts may exhibit the properties of a surfactant, with hydrophilic functional groups imparted by the oxidation reaction and by hydrophobic hydrocarbon chains. They found that the concentrations of these surfactant-like intermediates could become so high that they exceeded the critical micelle concentration (CMC) by as much as a factor of 4. As a result, enhanced solubilization of the fuel hydrocarbon contaminants was observed. These intermediates were also susceptible to further degradation by CHP if suitable oxidant was still available to react. Biodegradation could also occur simultaneously within the system.

2.4.4 Polycyclic Aromatic Hydrocarbons

PAHs represent a category of pollutant that is often associated with creosote, coal tar, manufactured gas plant (MGP) residuals, and other hydrocarbon contaminant releases. These contaminants, like fuel hydrocarbons (and often a minor component of fuel-based wastes)

contain a wide variety of chemical compounds and structures. PAHs share in common multiple aromatic benzene rings bonded to each other. The positions on the exterior may simply be occupied by hydrogen atoms or may be substituted by other hydrocarbon functional groups such as methyl or ethyl. PAHs are compounds of low to very low aqueous solubility, so they partition strongly to the sorbed phase associated with NOM. In addition to containing PAHs, contaminant releases often contain other lighter hydrocarbon components, such as phenols and cresols, as well as aliphatic and aromatic fuel hydrocarbons. In complex mixtures of organic contaminants, one trend often observed with their CHP treatment is that components of the mixture that are either more soluble or more oxidizable are degraded at faster rates than the less soluble or less oxidizable components, leading to enrichment of the remaining components in the contaminant mixture over time (Forsey, 2004).

CHP oxidation of PAHs in aqueous and porous media systems is strongly affected by their sorption to NOM and subsurface solids. The nature and amount of NOM in the contaminated media to be treated has a significant influence on the effectiveness of CHP with PAH wastes. Bogan and Trbovic (2003) observed a complex relationship between the organic carbon (f_{oc}) content of porous media and the extent of PAH degradation. They found that increasing NOM content led to improved PAH degradation and was maximized at a f_{oc} of about 0.05; above that level, increasing NOM decreased performance. They also found that PAHs with a large number of rings (4–5) were more readily degraded in porous media that had not aged and more readily than PAHs with fewer rings (2–3). In all cases, the more the contamination aged, the more treatability was reduced for all PAHs. They hypothesized that the complex relationship between f_{oc} and extent of treatment could be explained since low f_{oc} porous media contain relatively condensed or highly humified NOM fractions that sorb PAHs strongly, while at optimum f_{oc} values, NOM has a larger fraction that is less condensed and may reversibly sorb PAHs, allowing high treatment effectiveness. At very high f_{oc} , the magnitude of sorption is too extreme for the aqueous oxidant to contact the contaminant. To explain the apparent higher treatability of 4- to 5-ring PAHs, which would seem counterintuitive, they hypothesized that rate-limited sorption may play a role, where the larger PAHs take more time to migrate through and sequester themselves in the NOM matrix than the smaller PAHs. This would seem to be the case observed by Lundstedt et al. (2006), where in a highly aged mixture of PAHs, the larger 4- to 5-ring PAHs were treated to a lower degree, presumably because of their lower rates of desorption. Thus, the more highly aged the PAH spill, the more difficult it is to degrade the contaminant mass using hydrogen peroxide. Use of cosolvents, surfactants, or cyclodextrins may improve performance when treating sorbed PAHs (Lindsey et al., 2003; Lundstedt et al., 2006).

Given the complex structures of PAH contaminants, it is not surprising that various intermediates may be formed during oxidation. In theory, it would require numerous oxidation reactions by OH^\bullet to fully mineralize a PAH containing three or more aromatic rings. Lundstedt et al. (2006) monitored for intermediates and found that a number of oxy-PAHs were formed. They also observed a series of quinones and ketones, which is in line with products observed during the oxidation of other aromatic contaminants. Kanel et al. (2003) also observed the generation of salicylic acid from oxidation of phenanthrene. Low molecular weight organic acids, such as acetic, formic, and oxalic acids, are also likely to be produced. Because of their large structure and the inherent inefficiencies associated with oxidizing contaminants with CHP, attaining complete mineralization of PAH contaminants may be quite difficult. This difficulty is illustrated by Watts et al. (2002), where in treating benzo(a)pyrene in a soil slurry system, the stoichiometry of hydrogen peroxide to benzo(a)pyrene needed for 85% mineralization of the contaminant to CO_2 was in the range of 1,000:1–10,000:1.

Phenols and cresols are common contaminants that often co-occur with PAH contaminated wastes, such as coal tar or creosote. The degradation of these compounds by CHP and

their reaction pathways have been extensively documented in the literature, and chlorophenols and nitrophenols follow similar trends. Phenols typically show autocatalytic kinetic behavior when oxidized in CHP systems, especially those using Fe(III) catalysts, as the reaction of hydroxyl radicals with phenols typically produces hydroquinone or catechol, which are both effective complexing and reducing agents for Fe(III). Thus, these systems typically show an initial slow phase of reaction, followed by accelerating rates of reaction as the hydroquinone and catechol concentrations build (see Figure 2.7). The reaction pace then slows as the phenols and their reductive intermediates are depleted from the system (Chen and Pignatello, 1997). The subsequent breakdown of these aromatic intermediates leads to production of a series of carboxylic acids, particularly formic, oxalic, acetic and maleic acids, with lesser amounts of fumaric, malonic, and muconic acids (Zazo et al., 2005). However, if significant numbers of organic radicals are formed during the reaction, polymerization reactions can occur as well, forming aromatic polymer chains, which is more likely to occur if contaminant concentrations are high and oxidant concentrations are low (Zazo et al., 2005). Cresols generally appear to behave similarly to phenol in CHP systems.

2.4.5 High Explosives, Nitro- and Amino-Organic Compounds

High explosives include organic compounds that often contain nitrogen in an oxidized (nitro) form and sometimes in a reduced (amino) form as well. These compounds are common contaminants at munitions sites and places of their manufacture and may be present in pure solid phase or in dissolved and sorbed phases. In comparison to chlorinated solvent and hydrocarbon contaminants, the degradation by CHP of these organic compounds is less well investigated. However, the literature does provide information on the degradability of some of these organic contaminants, especially TNT and RDX. Elevated temperature (40–45°C) instead of ambient temperature dramatically improves both the rate and extent of degradation, especially for TNT. This improved reactivity at elevated temperature may be due in part to the higher solubility of TNT (Li et al., 1997b), in addition to alteration of the kinetic rates of reaction. Bier et al. (1999) reported up to 80% carbon mineralization of RDX in a CHP system, with both nitrate and ammonia detected as byproducts, as well as formic acid and methylenedinitraamine intermediates.

Other nitroaromatics appear to degrade in a similar manner to chlorobenzenes and chlorophenols in terms of both kinetics and reaction pathways. Hydroxyl radicals attack hydroxylate sites on the aromatic ring, giving nitrophenol from nitrobenzene. In addition, a lag phase in the kinetics is noted similar to oxidation reactions involving chlorophenols (see Figure 2.7), for which degradation kinetics are initially slow in a Fe(III) catalyzed system and then accelerates with time followed by exponential decay. In chlorophenol systems, this behavior is attributed to the accumulation of catechols and quinones, which have reducing capabilities and may regenerate Fe(III) to Fe(II). The lag phase is the period of time needed to accumulate a sufficient quantity of Fe(II) to support the reaction. In addition, Rodriguez et al. (2003) reported that when oxygen was present in solution, the perhydroxyl radical was generated as a byproduct of the reaction between CHP and nitrobenzene, providing evidence that dissolved oxygen may support the reaction. Teel and Watts (2002) reported on the degradation of the highly oxidized compound tetranitromethane and found that it was degradable by CHP under conditions where superoxide is expected to form but was not degraded by hydroxyl radicals. Other organic compounds containing nitro or amino groups have not been investigated as extensively. Quinoline and nitrobenzene often have been employed as hydroxyl radical probes because of their known reactivity with hydroxyl radicals.

2.4.6 Pesticides

Pesticides encompass a broad category of compounds with a wide variety of structures and formulas that have been developed exclusively for their toxicity towards certain plants, animals, insects, fungi, or microbes. ISCO has not been used to treat these compounds because the nature of their use often involves large, low level aerial applications for which ISCO is not typically well suited. However, where such compounds have been released to the environment as point sources or in areas where high concentrations are targeted for remediation, ISCO using CHP may be effective. Given the various chemical structures that pesticides exhibit, the transformation pathways and mechanisms for individual compounds may not be well established. Thus, in cases where the chemistry associated with contaminant transformations is not well known, treatability studies will be needed.

One common theme found in studies of CHP degradation of pesticides is that solubility or degree of sorption affects the rate and extent of treatment achievable; higher solubility, less strongly sorbed pesticides may be degraded more rapidly and to greater extents (Tyre et al., 1991; Wang and Lemley, 2004).

Two pesticides that have been more extensively studied with CHP oxidation are the herbicides 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). The oxidation of these related compounds in CHP systems (acidic pH, low oxidant concentration, Fe(II) catalyst) often involves the release of mono-, di-, and tri-chlorophenols, after which the reaction proceeds as described for chlorophenols (Pignatello, 1992; Tarr et al., 2002; Chu et al., 2004). 2,4,5-T has slower kinetics than 2,4-D. Pignatello and Baehr (1994) reported that nearly 100% stoichiometric chloride release could be attained for 2,4-D in a sandy loam using chelated Fe(III) catalysts at neutral pH. However, only a small amount of the contaminant was completely mineralized to CO₂. Little information is available on CHP degradation of other pesticides.

2.4.7 Sorbed or NAPL Contaminants

CHP has demonstrated potential for effectively treating sorbed and NAPL phase organic contaminants both in laboratory studies and in the field. Results indicate that contaminant mass transfer and transport processes may be accelerated by the use of CHP (Watts et al., 1999a; Lindsey et al., 2003; Ndjou'ou and Cassidy, 2006; Smith et al., 2006). However, CHP studies evaluating NAPLs and sorbed phases have utilized experimental conditions not fully representative of subsurface mass transfer and transport processes. Typically, studies have been done in batch reactors that are either completely mixed or stagnant. Dissolution or desorption rates in the literature often have been measured relative to changes in aqueous concentration gradients that are artificially imparted in a batch system, such as by continuous flow of gas through a vial (for volatile contaminants) or by aqueous fill and draw methods. In the subsurface environment, desorption and NAPL dissolution rates tend to be dominated by advective groundwater flow, mechanical dispersion, and molecular diffusion. The magnitude of each of these processes is often controlled by site-specific parameters, such as groundwater gradients, site permeability, and heterogeneity.

Nonetheless, the studies in the literature do provide some insight about how various mass transfer processes may be impacted by CHP. For contaminants present in either sorbed or NAPL phase, CHP has the potential to increase mass transfer by rapidly degrading aqueous phase contamination in pore spaces adjacent to the NAPL-water interface or sorption sites, provided there is effective oxidant delivery. This degradation reaction drives more aqueous dissolution and can significantly enhance NAPL dissolution rates over rates that occur under

ambient conditions of advective transport alone. By analogy to permanganate-based ISCO research, such mass depletion rate enhancements may be significant, as dissolution rates have been observed to increase in response to an oxidant as much as 15 times or more (Reitsma and Dai, 2001; Petri et al., 2008).

Recent studies have demonstrated that reactive species generated during CHP can also actively promote the dissolution of DNAPLs well beyond their maximum natural rates of dissolution. Smith et al. (2006) investigated the enhanced dissolution of carbon tetrachloride and chloroform DNAPLs. By generating hydroxyl radical, superoxide anion, and hydroperoxide anion in separate reactions, they determined that superoxide enhanced DNAPL dissolution (Figure 2.8).

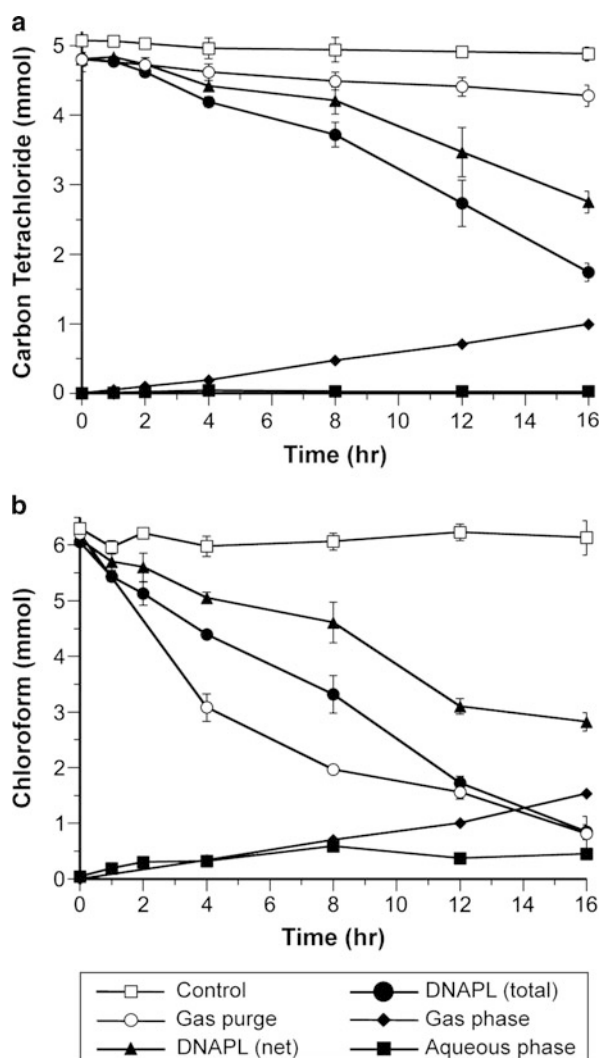


Figure 2.8. Mass balance data demonstrating enhanced DNAPL dissolution by CHP. Data for carbon tetrachloride (a) and chloroform (b) shows that the DNAPL mass declines much faster when CHP is present vs. a gas purge control where CHP is not present. The gas purge control represents the maximum mass transfer rate possible by volatilization. From Smith et al., 2006.

In addition, Watts et al. (1999a) reported that some of the reactive species formed by CHP may enhance the desorption of sorbed contaminants in a manner beyond simply degrading the contaminant in the aqueous phase. Corbin et al. (2007) isolated the reactive species in CHP reactions that is responsible for enhanced contaminant desorption. They conducted reactions that generated one of the following reaction species: hydroxyl radical, hydroperoxide anion, and superoxide anion. Superoxide was the reactive oxygen species responsible for enhanced contaminant desorption. Therefore, some of the reactive oxygen intermediates formed during CHP oxidation, including superoxide, may act as surfactants or have other properties that enhance solubilization of hydrophobic contaminants. Organic intermediates produced by contaminant degradation reactions may contribute as well. Ndjou'ou and Cassidy (2006) reported that the organic intermediates generated from CHP oxidation of some complex organic wastes, such as NAPL phase fuel hydrocarbons, may produce organic surfactants as intermediates during the reaction, and these can even become concentrated enough in solution that they exceed the CMC. These results are presented in Figure 2.9, showing the surface tension, CMC, and enhanced solubilization of total petroleum hydrocarbons. Thus, enhanced solubilization of the remaining contaminant may occur, increasing its availability for aqueous degradation reactions.

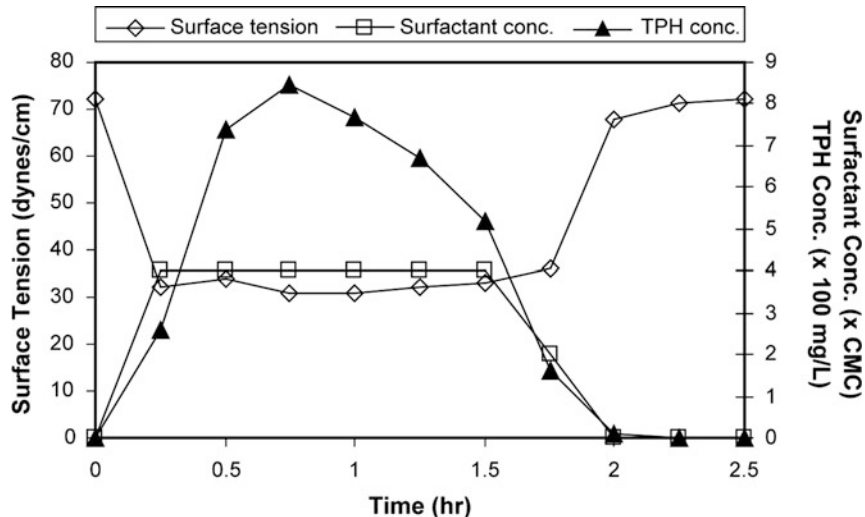


Figure 2.9. Data showing surfactant production and enhanced solubilization of total petroleum hydrocarbons in a Fe(III)-chelate CHP system. Conditions: field soil contaminated with $10,600 \pm 850$ mg/kg TPH; solids to solution ratio of 4 g/10 mL; [Fe(III)] = 40 mg/L, [EDTA] = 6 mg/L; [H₂O₂] = 10 g/L; initial pH = 8. From Ndjou'ou and Cassidy, 2006; reprinted with permission.

Research has shown, however, that for increasing contaminant hydrophobicity and sorption, CHP reaction efficiency will decrease, posing a challenge to effective treatment with CHP (Quan et al., 2003; Lundstedt et al., 2006; Watts et al., 2008). Furthermore, Bogan and Trbovic (2003) found the extent of treatment that can be achieved declines with increased contaminant aging. Thus high organic content media containing contaminants where a spill occurred long ago will probably be treated with lower efficiency and effectiveness than porous media in which spills were recent. Thus, while CHP provides mechanisms in which desorption and degradation are enhanced over ambient groundwater dissolution conditions, the absolute rates of these processes are still strongly site-specific depending on the NOM, the contaminants present, and the amount of time they have had to age.

Byproducts of CHP reactions also have been shown to include heat and off-gassing, which have the potential to influence treatment of sorbed or NAPL contaminants, though the significance of these effects have not been quantified. Because heat can be a significant byproduct of CHP reactions, especially in areas of vigorous reaction, elevation of temperature can occur in subsurface systems. In general, the aqueous solubility limit of organic contaminants generally increases with temperature, as do the kinetics of degradation reactions (see Section 2.2.5.4). While these changes are transient, they have implications for NAPL mass transfer. Furthermore, rapid off-gassing, which is a common attribute of CHP injections, and rapid heat evolution have the potential to increase dispersion in more permeable subsurface formations. Dispersion might further enhance NAPL dissolution. Gas evolution also has the potential to influence NAPL mass transfer and mass depletion rates through volatilization of VOCs and through evolving vapor plumes. Vapor plumes in the subsurface migrate upward, often spreading laterally when they encounter low permeability zones (Tomlinson et al., 2003). VOCs within such gas plumes can then re-dissolve into groundwater that is contacted as the gas rises. The potential for gas evolution should be considered during design of CHP systems. The additional dispersion processes could be beneficial for enhancing contaminant-oxidant contact, but care should be exercised to not generate uncontrolled or hazardous situations.

2.5 SUMMARY

CHP has a complex chemistry that is capable of degrading a wide variety of organic compounds. This wide reactivity is due to the ability of CHP to generate a large number of reactive radicals through propagation reactions, which have both oxidative and reductive capabilities. These radicals are produced via reactions between hydrogen peroxide and catalysts. A wide variety of catalysts have been investigated, including soluble iron salts, soil minerals, and novel iron-organic ligand complexes (chelates). Hydroxyl radicals traditionally have been viewed as the main reactive species in CHP reactions, as they are strong non-specific oxidants that react broadly with organic compounds. Recently, the importance of other radical species has been explored and it has been found that CHP, through the action of superoxide, as well as possibly other intermediates, may degrade highly oxidized organic contaminants (such as halogenated methanes) through reduction reactions. These non-hydroxyl radical species also contribute to the enhanced desorption and NAPL dissolution that can occur in CHP systems. Typically the byproducts of CHP reactions include inorganic salts, carbon dioxide, and other organic compounds, most commonly carboxylic acids.

While CHP has been shown to degrade a wide variety of organic contaminants, the efficiency and effectiveness of CHP treatment is variable. Optimized chemistries can achieve rapid and significant degradation of target contaminants in aqueous, sorbed, and even NAPL phases. However, other systems may be challenged by a number of interactions between CHP and constituents in soil and groundwater. If present in high concentrations, other reactants may out-compete the contaminant for the oxidant and thus cause limited contaminant degradation. Also, sorption of highly hydrophobic contaminants is a challenge in CHP treatment because the oxidant is short lived in the subsurface and there is limited contact time for desorption reactions to occur. Nonetheless, CHP does provide some mechanisms to enhance desorption rates over ambient conditions, which offers an improvement in rate over sites relying on natural attenuation alone to decrease contaminant sorbed masses.

Finally, effective CHP delivery into the subsurface is needed to achieve effective groundwater remediation. Within the subsurface, oxidant persistence is low and is influenced by a

number of site-specific conditions and ISCO design parameters. Longer oxidant persistence is generally desired with CHP to increase reaction time. Use of optimized injection strategies or stabilizers may help improve oxidant persistence and treatment effectiveness.

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CHAPTER 3

FUNDAMENTALS OF ISCO USING PERMANGANATE

Benjamin G. Petri,¹ Neil R. Thomson², and Michael A. Urynowicz³

¹Colorado School of Mines, Golden, CO 80401, USA; ²University of Waterloo, Waterloo, ON, Canada N2L 3G1; ³University of Wyoming, Laramie, WY 82071, USA

Scope

Use of permanganate for *in situ* chemical oxidation of contaminants of concern (COCs) in groundwater, including reactions, kinetic expressions, oxidant interactions with subsurface media, and the effectiveness for common COCs.

Key Concepts

- Permanganate is a selective oxidant and will only oxidize certain types of organic compounds.
- Sodium permanganate is readily miscible in water, while potassium permanganate has a solubility limit of 6.5 wt.% at 20°C.
- For all practical purposes permanganate reactions occur only in the aqueous phase.
- Permanganate chemistry is relatively insensitive to pH over a wide range.
- Permanganate is highly reactive with compounds having alkene bonds and less reactive towards compounds with carbon-carbon single bonds (e.g., saturated hydrocarbons).
- Oxidation reactions follow second-order kinetics overall with respect to the concentration of permanganate and the concentration of target organic compounds.
- Insoluble manganese dioxides and carbon dioxide are the main byproducts of permanganate reactions with organics.
- Under some conditions, manganese dioxide solids or carbon dioxide gas may reduce formation permeability and interfere with oxidant delivery and treatment efficiency.
- Permanganate reacts with naturally occurring reduced materials in subsurface porous media. This is termed natural oxidant demand (NOD). Permanganate NOD is a kinetically controlled process, which can significantly interfere with the destruction of the target COC.
- Permanganate has the potential to affect the mobility of heavy metals through several mechanisms. However, based on field experience, this phenomenon is usually transient, and elevated metals concentrations attenuate with time.

3.1 INTRODUCTION

Permanganate is a common chemical oxidant that has long been used in the treatment of water and wastewater, as well as industrial and organic chemistry applications (e.g., Ladbury and Cullis, 1958; Fatiadi, 1987; Dietrich et al., 1995; Singh and Lee, 2001). Its strong reduction potential, predictable chemistry, stability, and nontoxic byproducts make it an attractive oxidant for applications such as selective oxidation of organics, removal of dissolved manganese, trihalomethane precursor removal, and other processes. Permanganate, along with hydrogen peroxide, was among the first oxidants considered for use with *in situ* chemical oxidation (ISCO) applications, with significant research and development starting in the early and mid 1990s (Gonullu and Farquhar, 1989). From these early applications, much was learned about the processes that control the effectiveness of permanganate in the subsurface; permanganate is now one of the most commonly applied ISCO oxidants. Its relatively simple oxidation chemistry, when compared to that of other ISCO oxidants, is well understood, as are many of the subsurface fate and transport processes. One of the most important properties of permanganate is its stability, which is often regarded as its greatest strength. The high stability of permanganate enables long contact times and transport distances in the subsurface when no excessive natural oxidant sinks are present. This promotes oxidant delivery through advective, dispersive, and diffusive processes within heterogeneous subsurface environments (e.g., Siegrist et al., 1999; Conrad et al., 2002; Struse et al., 2002b; Seitz, 2004; Thomson et al., 2007). However, in part because of this high stability and simple chemistry, its use is restricted to a more limited range of organic contaminants compared to other ISCO oxidants.

Permanganate is classified as a selective oxidant because it will degrade some organic compounds and not others, depending on the chemical structure of the target contaminant and its susceptibility to permanganate attack (Singh and Lee, 2001; Waldemer and Tratnyek, 2006). It also reacts with subsurface aquifer materials, particularly natural organic matter (NOM), which exert a finite but rate controlled natural oxidant demand (NOD) (Mumford et al., 2005). In some cases, this may represent a large oxidant sink and challenge performance and cost effectiveness (Haselow et al., 2003; Crimi and Siegrist, 2004b; Urynowicz et al., 2008; Xu and Thomson, 2008). Finally, the success of oxidant delivery is sometimes impacted by a reaction byproduct, which under typical environmental conditions is an amorphous solid in the form of manganese dioxide (MnO_2). This byproduct forms primarily at or near the point of reaction and has the potential to foul injection devices and impact subsurface permeability and flow pathways, which in turn may impact subsurface permanganate and contaminant transport processes (Schroth et al., 2001; Conrad et al., 2002; MacKinnon and Thomson, 2002; Li and Schwartz, 2004c; Tunnicliffe and Thomson, 2004; Heiderscheidt et al., 2008a). Along with subsurface heterogeneity, these alterations to transport processes can pose significant challenges to permanganate ISCO efficiency and effectiveness as flow bypassing may limit contact between the oxidant and contaminant (Li and Schwartz, 2000; Thomson et al., 2008).

This chapter begins with a description of permanganate chemistry including reaction pathways and kinetics. This is followed by a discussion of NOD and the oxidant interactions in the subsurface environment. The chapter then discusses the types of contaminants that permanganate can degrade during ISCO.

3.2 CHEMISTRY PRINCIPLES

This section describes the properties of permanganate and the chemical reactions and interactions that can occur in the subsurface during ISCO. In comparison to other advanced oxidation processes, permanganate reaction chemistry is relatively simple.

3.2.1 Physical and Chemical Properties

The permanganate ion is a strong chemical oxidant that gives aqueous solutions a distinct pink to dark purple color depending on the concentration. The permanganate ion is a transition metal oxidant with a high reduction potential of 1.68 volts (V) at acidic pH (Lide, 2006) and derives its oxidizing power from manganese in the heptavalent form (Mn[VII]). This valence state of manganese is not favored under the redox conditions of most natural water environments; thus, permanganate is a potent oxidant that will accept electrons from many organic and inorganic substrates. There are two forms of permanganate that are widely available for use in ISCO applications: potassium permanganate (KMnO₄) and sodium permanganate (NaMnO₄). The reactivity of either form with regards to oxidation chemistry is essentially the same, but there are some important physical differences between them that have implications for design of permanganate ISCO systems. Within this chapter, this oxidant is called “permanganate” and refers to the permanganate ion (MnO₄⁻), which is the active oxidizing agent. Distinction between the potassium and sodium salts will only be made in situations where such a distinction is necessary. All permanganate mass concentrations discussed are expressed with respect to the permanganate ion (MnO₄⁻) (e.g., grams MnO₄⁻ per liter (g/L) as opposed to g KMnO₄/L), which allows direct comparison between potassium and sodium forms. Table 3.1 presents important properties for both forms.

Table 3.1. Major Physical and Chemical Properties of Permanganate

Property	Sodium permanganate (NaMnO ₄)	Potassium permanganate (KMnO ₄)
Molecular weight (g/mole)	141.93	158.03
Most common physical form	Aqueous liquid	Crystalline solid
Solubility limit in distilled water (g/L)	Miscible in water (~900 g/L)	65.0 g/L (20°C) 27.8 g/L (0°C)
Specific gravity of solution	1.36–1.39 (40 wt.% solution)	1.039 (6 wt.% solution)
Chemical incompatibilities	Strong acids, organic peroxides, concentrated hydrogen peroxide, organic compounds, reductants and metal powders	

Note: °C - degrees Celsius; wt.% - weight percentage.

Sodium permanganate is readily miscible in water at all concentrations and temperature ranges practical for ISCO. This allows the oxidant to be delivered to the site as a concentrated aqueous liquid, which can then be diluted to the desired injection concentration without any special solids handling equipment. However, differences in the manufacturing process make sodium permanganate more expensive on an equivalent basis than potassium permanganate. In comparison to sodium permanganate, potassium permanganate has comparatively low solubility (6.5 wt.% at 20°C) (Lide, 2006), and even lower at typical subsurface temperatures) but it is frequently cheaper on an equivalent basis. Due to its low solubility, it is usually delivered to a site as a solid; thus, solids handling equipment is needed to enable mixing of the potassium permanganate solids prior to injection and to minimize occupational exposure to airborne chemical dust. Suitable equipment is widely available since the use of permanganate ISCO has grown, and manufacturers of permanganate for ISCO have developed granulated and encapsulated forms of solid potassium permanganate that reduce chemical dust (Kang et al., 2004; Ross et al., 2005). Because of its solubility limit, the highest concentration of potassium

permanganate that may be injected into the subsurface at ambient temperatures using standard liquid injection methods is approximately 4–5 wt.%, while sodium permanganate may be delivered at higher concentrations.

Another consideration that may be important when using standard injection technologies with potassium permanganate is that oxidant precipitation may occur in the subsurface. Since the solubility limit of potassium permanganate drops with temperature, the injection of a saturated solution prepared at ambient or higher temperatures into a cooler subsurface may cause the solution to become supersaturated, possibly promoting formation of a permanganate precipitate. This may cause temporary well plugging in some situations, especially in lower hydraulic conductivity media as the precipitates may aggregate and clog pore throats in the vicinity of the injection well. However, over time the permanganate precipitates should dissolve as less concentrated groundwater migrates into the vicinity of the injection well.

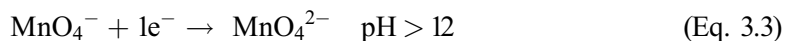
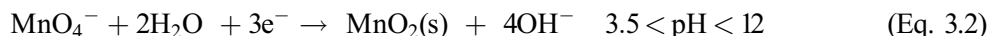
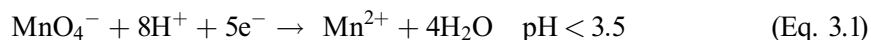
Some innovative injection methods have taken advantage of the low solubility limit of potassium permanganate by injecting solid phase permanganate as a method of sustained oxidant release over long time periods. These methods have utilized the injection of slurries of solid and liquid permanganate into hydraulic fractures (Case, 1997; Siegrist et al., 1999) and encapsulation of solid permanganate in wax or polymer coatings which dissolve in the presence of nonaqueous phase liquid (NAPL) (Kang et al., 2004; Ross et al., 2005). Methods that have been explored for these solid permanganate applications include soil mixing, hydraulic fracturing, surface applications, and the injection of microparticles into wells.

Permanganate is an ion, and like most ions, it may act as a conjugate base. However, the protonated form of permanganate (HMnO_4) is formed only under very acidic conditions and is also chemically unstable. The acid dissociation constant (pK_a) for the permanganate ion has not been measured due to the instability of the protonated form. Thus, the ionic form (MnO_4^-) will be the dominant form of permanganate in solution. Due to its high polarity, the permanganate ion neither volatilizes nor partitions readily into nonpolar organic phases. In ISCO systems, permanganate oxidation reactions are generally limited to the aqueous phase. In organic chemistry applications, phase-transfer catalysts enable organic phase reactions by complexing permanganate with quaternary-ammonium salts, which allow the oxidant to partition into a nonpolar organic phase (Fatiadi, 1987). Some researchers have investigated the use of phase-transfer catalysts as a possible way to accelerate the treatment of NAPL compounds with ISCO by promoting oxidation both in the organic phase and in the bulk aqueous phase (Seol and Schwartz, 2000; Seol et al., 2001). Using these methods, they were able to successfully accelerate the degradation of organic phase trichloroethene (TCE) and perchloroethene (PCE), which are known to be readily degradable by permanganate. However, significant degradation of 1,1,2-trichloroethane (1,1,2-TCA) and 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA) was also achieved, despite these compounds being essentially unreactive with permanganate in aqueous solution. Thus the reactivity and mechanisms of permanganate in organic solvents may differ from those in aqueous solutions. The efficacy of using phase-transfer catalysts for ISCO is largely unknown and application of these catalysts under field conditions has not been documented in the open literature. Thus, for all practical ISCO applications, permanganate reactions occur only in the aqueous phase.

3.2.2 Oxidation Reactions

Permanganate is a transition metal oxidant that reacts primarily through direct electron transfer reactions rather than through radical intermediates, as with other ISCO oxidants. The number of electrons transferred, as well as the reaction mechanisms that dominate, depends on

system pH. Generally, more electrons are transferred under conditions of acidic pH as shown by the following half reactions:



The reaction in Equation 3.2 is the dominant reaction at most natural groundwater pH values. As a result, permanganate typically may be expected to undergo a three electron transfer reaction during *in situ* applications producing a solid manganese dioxide that usually appears as a colloid in aqueous systems (Crimi and Siegrist, 2004c). However, in some cases, particularly during the treatment of highly contaminated zones, such as adjacent to NAPL sources, the pH may undergo significant alteration, as alkalinity or especially acidity may be a product of the reaction. Values as low as pH 1 have been observed in laboratory settings when treating organic phase TCE or PCE (MacKinnon and Thomson, 2002; Petri, 2006). In a field setting, Stewart (2002) observed pH values as low as 2.5 when treating a thin TCE pool, indicating that the 1% carbonate mineral content of the porous media in this area had been effectively depleted. Under such acidic conditions, the reaction in Equation 3.1 may become dominant and alter reaction stoichiometry and mechanisms. Alkaline permanganate oxidation, represented by Equation 3.3, is generally unlikely to occur in ISCO applications because this high pH falls outside the normal range for groundwater environments. However, the formation of the green manganate ion (MnO_4^{2-}), which is itself an oxidant, may occur under highly alkaline conditions.

Permanganate reactions under neutral or slightly acidic pH regimes, which encompass conditions typical of most groundwater systems, entail direct reaction between the permanganate anion (MnO_4^-) and the substrate being oxidized. Under these conditions, free radical reactions such as those involving hydroxyl radicals (OH^\bullet) are not known or presently thought to be involved in the degradation of organics. However, under alkaline conditions, particularly strong alkaline conditions where Equation 3.3 is expected to be dominant, free radicals such as the hydroxyl radical (OH^\bullet) have been implicated in permanganate reactions (Ladbury and Cullis, 1958). These alkaline permanganate oxidation systems undergo different reactions than permanganate oxidation at normal pH ranges, so reaction mechanisms and products may shift. In research investigating the impact of pH on the degradation of ISCO-relevant contaminants, little kinetic effect has been observed under environmentally relevant conditions (Yan and Schwartz, 1999; Damm et al., 2002), suggesting no major shift in the mechanisms.

3.2.3 Reaction Mechanisms and Pathways

Permanganate has been demonstrated to react with a variety of different organic compounds. With aliphatic carbon compounds, the reactivity of permanganate is often a function of the type of carbon bonding within the compound, as well as functional groups on the aliphatic chain. Permanganate is well known to be reactive with alkene bonds, which are carbon-carbon double bonds and contain π electrons. The mechanism behind this oxidation has long been suspected to be an addition of permanganate ion across the carbon-carbon double bond forming a cyclic ester, which may subsequently result in either breaking the carbon-carbon bond altogether or in the addition of hydroxy ($\text{C}-\text{OH}$) or carbonyl ($\text{C}=\text{O}$) functional groups to the molecule (Ladbury and Cullis, 1958; Fatiadi, 1987; Singh and Lee, 2001). This is demonstrated in Figure 3.1, which has been adapted from Arndt (1981).

In aqueous solutions, addition of these polar functional groups to organic compounds may often yield unstable intermediates that further degrade by hydrolysis reactions. Additional discussion of permanganate reactions with ethene compounds, particularly chloroethenes, is provided in Section 3.4.1. Permanganate is also known to be highly reactive with alkyne bonds (Fatiadi, 1987), which are carbon-carbon triple bonds, but these bonds are not as common among contaminants typically targeted for groundwater remediation. With alkane compounds (carbon-carbon single bonds), such as saturated hydrocarbons, permanganate is typically much less reactive. This lower reactivity arises primarily because saturated hydrocarbons lack any π electrons and thus an electrophilic reagent like permanganate has a much lower ability to abstract electrons from carbon-carbon single bonds (σ bonds) in the compound. Substitution of aliphatic compounds with functional groups, such as carboxyl ($-\text{COOH}$) or hydroxyl ($-\text{OH}$) groups, may improve their reactivity as alcohols, and organic acids have been observed to be reactive (Arndt, 1981).

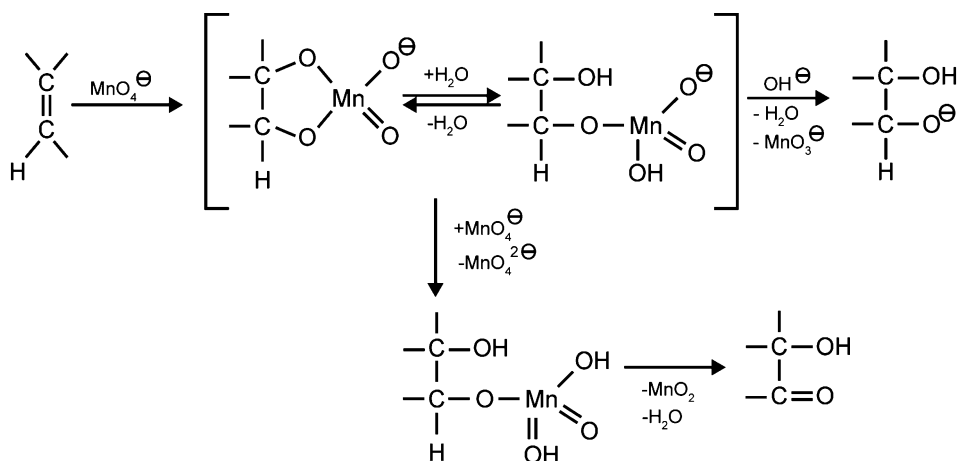


Figure 3.1. Oxidation of alkene (double) bonds by permanganate (after Arndt, 1981).

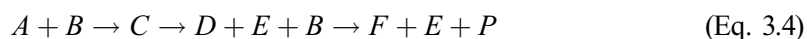
In permanganate oxidation of aromatic chemicals, the reactivity of permanganate has been found to vary greatly due to the presence of different functional groups on the aromatic ring. While all aromatic compounds contain π electrons, permanganate itself is very unreactive with benzene (Waldemer and Tratnyek, 2006), which lacks any functional groups. This lack of reactivity has been attributed to the high degree of aromaticity of benzene, where the π electrons are highly delocalized in the aromatic ring. A high degree of delocalization makes it more difficult for permanganate to abstract an electron via a redox reaction. When methyl, ethyl, or other alkyl functional groups are substituted onto the aromatic ring, such as with toluene, ethylbenzene, or xylene, permanganate may oxidize the compound by abstracting a benzylic hydrogen atom from the functional group (Forsy, 2004; Waldemer and Tratnyek, 2006), often yielding a corresponding benzyl alcohol or benzoic acid (Ladbury and Cullis, 1958; Singh and Lee, 2001). Subsequent oxidation reactions can then break the aromatic ring. The presence of other functional groups can also have a strong effect on permanganate reactivity. Electron-donating functional groups, such as the hydroxyl group (OH), contain unshared electrons that may increase the electron density such that the ring may be more easily attacked by permanganate (Schnitzer and Desjardins, 1970). This may explain why the reaction with phenol is up to seven orders of magnitude faster than with benzene (Waldemer and Tratnyek, 2006). Electron withdrawing functional groups, such as carbonyl ($\text{C}=\text{O}$), carboxyl ($-\text{COOH}$), sulfonate ($-\text{SO}_3\text{H}$), and nitro ($-\text{NO}_2$) groups appear to have the opposite effect because they

decrease electron availability within the aromatic ring and react more slowly with permanganate (Schnitzer and Desjardins, 1970); this may explain why nitrophenols are degraded at much slower rates than phenol (Waldemer and Tratnyek, 2006). Additional discussion on permanganate reactions with aromatic contaminants is provided in Sections 3.4.3 and 3.4.4.

In the oxidation of polycyclic aromatic hydrocarbons (PAHs), which contain multiple aromatic rings, it has been found that the reactivity of permanganate is largely dependent on the degree of aromaticity of the various rings in the PAH, as determined by the Clar model (Brown et al., 2003). Again, this may indicate that the reactivity correlates with the degree of localization of electrons. Because individual aromatic rings within a PAH must share electrons with other rings, the degree of aromaticity of each ring in the compound may differ. The Clar model presents a method for conceptualizing the electron configuration within a given PAH, where the number of rings in the PAH with benzene-like aromaticity (termed aromatic sextets) are maximized (Clar, 1972). The remaining carbon bonds are modeled as either shared double bonds (shared between rings) or “true” double bonds, where the electron behavior is highly localized similar to an alkene bond. Brown et al. (2003) found the reactivity of permanganate with PAHs can be explained by the prevalence of these structures within a given PAH. Those with “true” double bonds reacted the most extensively with permanganate, as would be expected based on the oxidant’s strong reaction with alkene bonds, while the rate of reaction declined where PAHs had large numbers of rings with aromatic sextets. Shared double bonds improved reactivity, but the impact was tertiary to the impacts of true double bonds and stabilizing aromatic sextets. PAHs that are also substituted by functional groups as mentioned above also may be impacted by those reaction mechanisms that apply to single-ring aromatic compounds, such as abstraction of benzylic hydrogen (Forsey, 2004). More discussion on the degradability of PAHs with permanganate is provided in Section 3.4.5.

3.2.4 Permanganate Reaction Kinetics

For chemical oxidation to occur, MnO_4^- must collide with a target contaminant of concern (COC) (e.g., TCE), and consistent with Figure 3.1, 1 mole of MnO_4^- reacts with each mole of TCE to produce an intermediate that further combines with another mole of MnO_4^- to produce products such as carbon dioxide (CO_2), MnO_2 , and salts according to Equation 3.4:



where A = organic compound (e.g., TCE), B = MnO_4^- , C = cyclic ester, D = organic intermediate, E = MnO_2 , F = CO_2 , and P = other products (e.g., chloride [Cl^-]). The first step is the rate-limiting step, so the rate of reaction is controlled by the concentration of both reactants, A and B. The degradation of A can be described as a second-order irreversible bimolecular reaction with the kinetics given by the following rate law:

$$r_a = \frac{d[A]}{dt} = -k[A]^\alpha[B]^\beta \quad (\text{Eq. 3.5})$$

where, k = specific reaction rate constant (units determined by α and β), $[A]$ = concentration of the organic (mole $[\text{mol}] \text{L}^{-1}$), $[B]$ = concentration of the oxidant ($\text{mol} \text{L}^{-1}$), α = reaction order with respect to A, β = reaction order with respect to B, and t = time. For the second-order degradation of a COC such as TCE by MnO_4^- , the general Equation 3.5 can be written as:

$$\frac{d[\text{TCE}]}{dt} = -k_2[\text{TCE}]^1[\text{MnO}_4^-]^1 \quad (\text{Eq. 3.6})$$

where, k_2 = second-order reaction rate constant (molar⁻¹ [M⁻¹] second [s⁻¹]), $[TCE]$ = concentration of TCE (mol L⁻¹), $[MnO_4^-]$ = concentration of the MnO₄⁻ (mol L⁻¹), $\alpha = 1$ for first-order reaction with respect to TCE, and $\beta = 1$ for first-order reaction with respect to MnO₄⁻. Figure 3.2 illustrates the oxidation of TCE following the second-order reaction given in Equation 3.6.

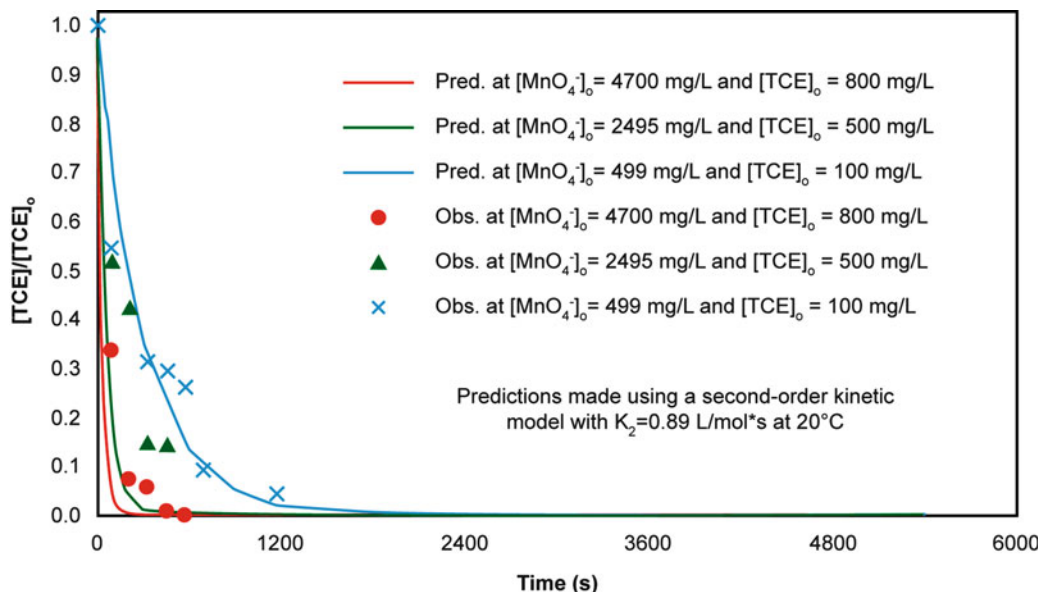


Figure 3.2. Predicted and observed change in concentration of TCE versus time during a second-order reaction with MnO₄⁻ (Siegrist et al., 2001).

If MnO₄⁻ is maintained in excess (e.g., >5× the stoichiometric requirement based on the TCE present), the reaction rate shown in Equation 3.6 can be adequately described as pseudo first-order. This is accomplished by setting the pseudo first-order rate constant, k' (units of T⁻¹), equal to the product of the second-order reaction rate constant, k_{2TCE} , and the initial concentration of MnO₄⁻ (Equations 3.7 and 3.8):

$$\frac{d[TCE]}{dt} = -k'[TCE]^1 \quad (\text{Eq. 3.7})$$

$$k' = k_2[MnO_4^-]^1 \quad (\text{Eq. 3.8})$$

In a similar approach to that just described for the degradation of an organic (e.g., TCE), the second-order depletion of MnO₄⁻ can be described by Equation 3.9:

$$\frac{d[MnO_4^-]}{dt} = -k_{2MnO_4^-}[TCE]^1[MnO_4^-]^1 \quad (\text{Eq. 3.9})$$

Reaction rates can be impacted by temperature as described by the Arrhenius equation (Equation 3.10):

$$k = A_f e^{-\frac{E_a}{RT}} \quad (\text{Eq. 3.10})$$

where A_f is the Arrhenius frequency factor, E_a is the activation energy of the reaction (kilojoules [kJ] mol⁻¹), T is the temperature (Kelvin [K]) and R is the gas constant (8.314 joules [J]

$\text{K}^{-1} \text{mol}^{-1}$). Activation energy, E_a , can be determined from the kinetic rate constants, k , of an elementary reaction at two or more different temperatures. For example, the rate constants determined for KMnO_4 oxidation of TCE by Case (1997) at 20 and 10°C revealed $E_a = 78 \text{ kJ mol}^{-1}$. Yan and Schwartz (1996) determined the reaction rate constants of the KMnO_4 oxidation of 10 milligrams per liter (mg/L) TCE at 25 and 10°C and E_a was calculated to be 73 kJ mol^{-1} . Huang et al. (1999) also studied the kinetics of chemical oxidation of TCE by MnO_4^- and reported an activation energy of $35 \pm 2.9 \text{ kJ mol}^{-1}$.

The temperature dependency of the second-order reaction of TCE with MnO_4^- is given by Equation 3.11, which is a rearrangement of Equation 3.10.

$$\ln K = \ln A_f - \frac{E_a}{R} \left\{ \frac{1}{T} \right\} \quad (\text{Eq. 3.11})$$

The degradation of TCE at several temperatures and the second-order rate constants is illustrated in Figure 3.3. Compared to 10°C, the second-order rate constant can be nearly 3x higher at 20°C.

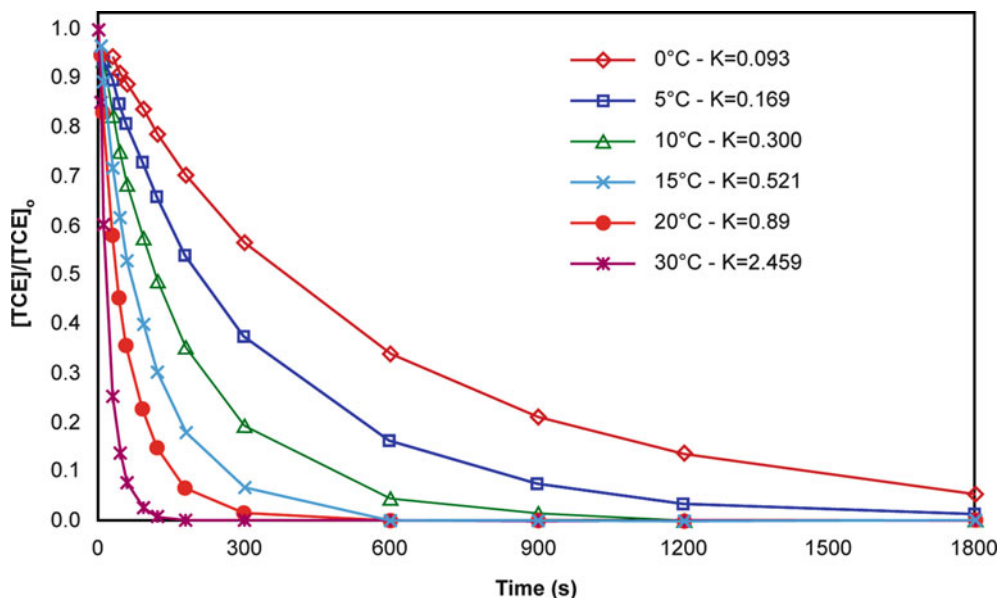


Figure 3.3. Temperature effects on the degradation of TCE during a second-order reaction with MnO_4^- at different temperatures (Siegrist et al., 2001).

Second-order rate constants have been determined for many of the more common COCs that have been shown to be oxidized by permanganate (Waldemer and Tratnyek, 2006). In most cases where the target organic is non-polar and does not dissociate in aqueous systems, these reaction rate constants have been found to be largely insensitive to pH or ionic strength within normal groundwater ranges (Yan and Schwartz, 2000; Damm et al., 2002; Huang et al., 2002).

With permanganate reactions, kinetics can be an important factor for determining whether or not a particular compound will degrade. With a high reduction potential of 1.68 V, permanganate reactions with many organics are thermodynamically favorable, but permanganate will only be effective for oxidation if a reaction proceeds at a rate that is reasonable on the timescale of ISCO applications. In general, reaction rate constants lower than $10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ will have increased difficulty in achieving degradation of contaminants due to kinetic limitations. For example, a compound having a reaction rate constant of $10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ in a permanganate solution with a

concentration of $7.5 \text{ g MnO}_4^-/\text{L}$ (equivalent to 0.063 M) will have a half life of about 30 h. While this may be reasonable in many ISCO applications because the oxidant will typically persist for days, getting this high of a concentration of oxidant uniformly distributed in the subsurface is often difficult, and lower permanganate concentrations will result in slower kinetics. Thus, when considering application of permanganate for oxidation of contaminants with reaction rates slower than this, treatability studies are highly recommended since contaminant degradation may not proceed at a rate fast enough to compete with NOD kinetics. Many rate constants for specific organic contaminants have been compiled in a database called ISCOKIN accessible at <http://www.cgr.ebs.ogi.edu/isco/> (Waldemer et al., 2009).

3.2.5 Manganese Dioxide Production

According to the reaction shown in Equation 3.2 and the speciation diagram presented in Figure 3.4, permanganate will be reduced to manganese dioxide under conditions commonly present during ISCO (i.e., low pH and high redox potential [Eh]). MnO_2 production is visually confirmed by a dark brown to black colored zone within the subsurface (see Figure 3.5) (Schroth et al., 2001; Conrad et al., 2002; MacKinnon and Thomson, 2002). Upon initial production, the MnO_2 solids are colloidal in size though they can agglomerate into larger size particles. MnO_2 solids produced during permanganate ISCO have been observed using scanning electron microscopy (SEM) demonstrating their colloidal nature (Figure 3.6).

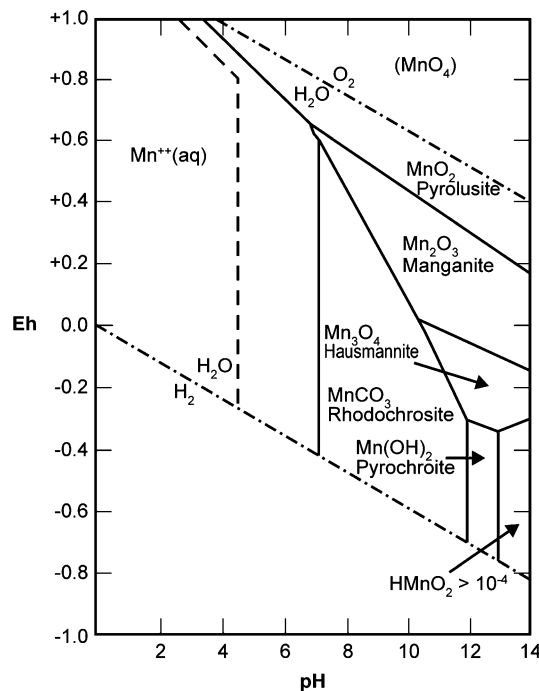


Figure 3.4. Impact of Eh and pH on manganese speciation. Conditions at 25°C and total dissolved carbonate at $10^{-1.4} \text{ M}$ (Duggan et al., 1993).

The manganese dioxides associated with permanganate ISCO are commonly denoted as MnO_2 , where manganese is assumed to be in the Mn (IV) oxidation state. However, Arndt (1981) reported that no manganese dioxide has ever been observed to have the exact mineralogy

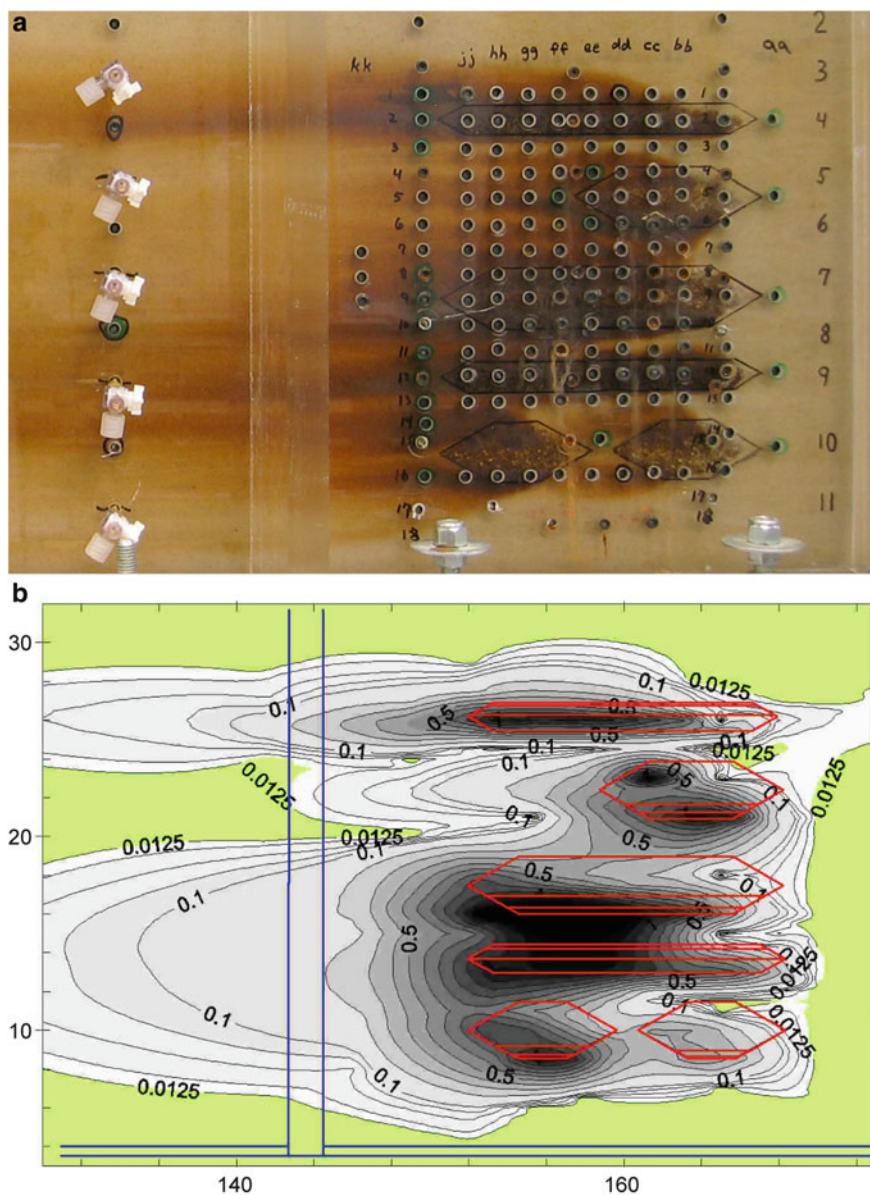


Figure 3.5. Manganese dioxide deposition following potassium permanganate flushing of a two-dimensional (2-D) sand-filled tank with a PCE dense nonaqueous phase liquid (DNAPL) source zone emplaced in it (Heiderscheidt, 2005; Heiderscheidt et al., 2008a). Over 2.5 days, two pore volumes of a 2,120 mg MnO_4^-/L oxidant solution were flushed from right to left. Concentrations of MnO_2 deposited are shown in the bottom image (g $\text{MnO}_2/\text{kilogram (kg)}$ sand) around six discrete PCE sources, which are outlined in red (PCE in a pool, two residuals, one pool and two residuals from top to bottom).

of MnO_2 because there is always water, hydroxide (OH^-), and foreign ions (especially Na^+ if using sodium permanganate, K^+ if using potassium permanganate) entrained in the mineral matrix. This always results in a deficiency of oxygen and the manganese dioxides produced are generally in the range of $\text{MnO}_{1.7}$ to MnO_2 (Arndt, 1981). To simplify the discussion in this section, the formula MnO_2 will be used to represent the manganese dioxides that are produced during permanganate ISCO.

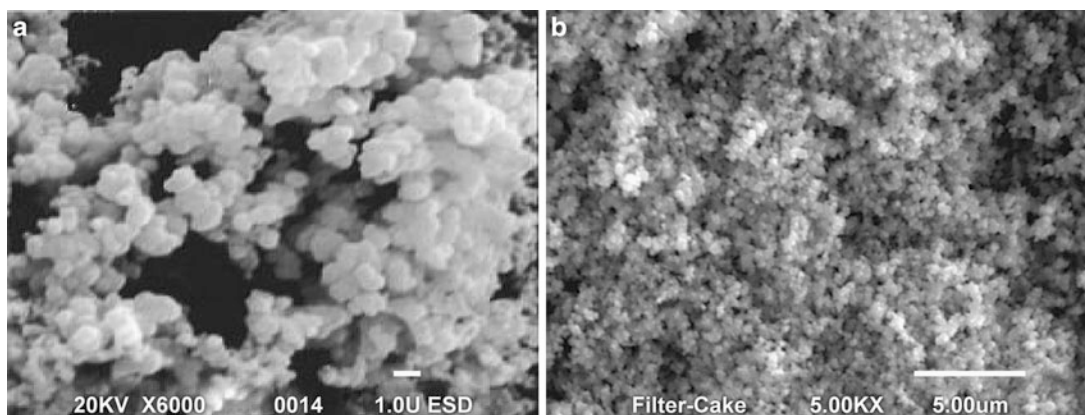


Figure 3.6. Images of MnO_2 under scanning electron microscopy: (a) SEM image ($\times 6,000$) of MnO_2 solids in groundwater collected from an extraction well used in a paired well delivery of 2–4 wt.% KMnO_4 to treat DNAPL contaminated groundwater (West et al., 1997); (b) photomicrograph ($\times 5,000$) of solids retained on a 1-millimeter (mm) cartridge filter from the aboveground piping in a permanganate recirculation system (Siegrist et al., 2000).

Pure MnO_2 can have several crystalline forms as illustrated in Figure 3.7 (Pisarczyk, 1995). In a study that specifically analyzed the manganese precipitate formed during ISCO using X-ray diffraction analysis, the researchers observed that it was generally colloidal in nature and was either amorphous (lacking crystalline structure) or had the signature of the manganese mineral birnessite (Li and Schwartz, 2004b).

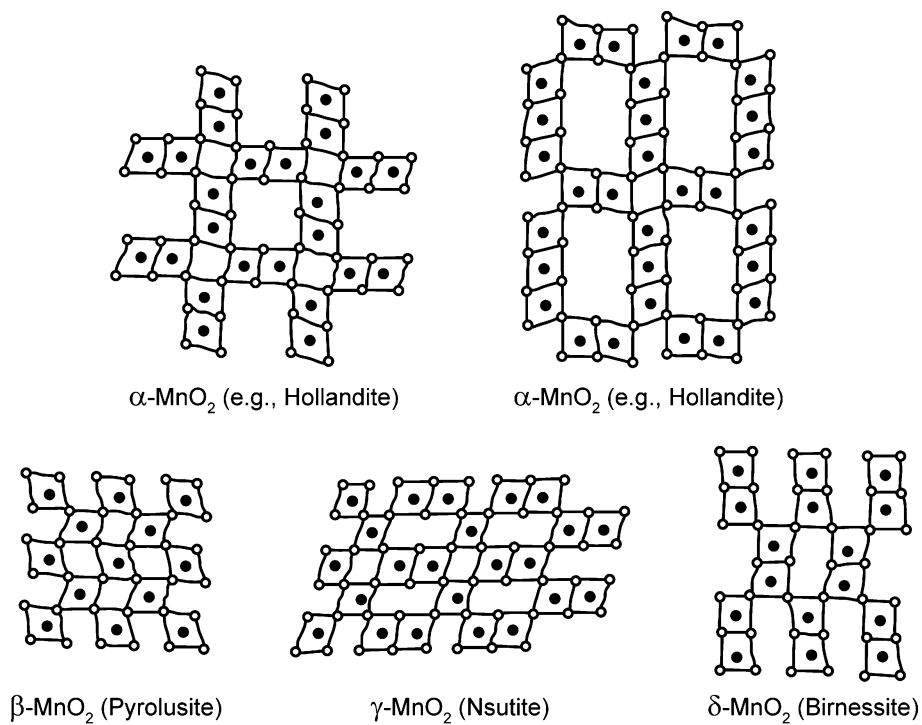


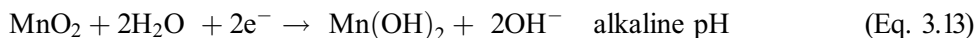
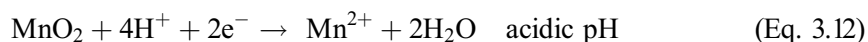
Figure 3.7. Crystalline forms of MnO_2 (adapted from Pisarczyk, 1995).

Neither dissolved Mn^{2+} or MnO_2 solids are toxic except in extremely high concentrations (ATSDR, 2000), so they are normally of little concern from a health risk perspective. However, they can be aesthetically undesirable in water that is a source for both potable and nonpotable uses. When dissolved manganese encounters atmospheric oxygen, as will generally occur in drinking water systems, it slowly oxidizes to again form MnO_2 , imparting a yellow or brown color to water and staining plumbing fixtures. Since this is publicly undesirable, a secondary maximum contaminant level (MCL) of 50 micrograms per liter ($\mu\text{g/L}$) has been established for Mn by the U.S. Environmental Protection Agency (USEPA). While compliance with secondary MCLs is usually voluntary, the presence of high concentrations of dissolved manganese in the subsurface may be of concern at some sites.

Aside from aesthetics, MnO_2 solids produced during permanganate ISCO can have significant physiochemical impacts on the subsurface environment, which can affect ISCO effectiveness. First, and most important, MnO_2 solids have the potential to alter subsurface hydraulic conductivity and permeability near the point of oxidant injection and within a target treatment zone. This, in turn, can alter the reactive transport of permanganate in the subsurface, which may have a profound impact on the remediation of DNAPLs and other contaminants by permanganate (MacKinnon and Thomson, 2002; Siegrist et al., 2002; Li and Schwartz, 2004c). MnO_2 solids also can cause high backpressures and problems with injection equipment if either the subsurface or the equipment clogs with MnO_2 . The impact of MnO_2 on subsurface oxidant and contaminant transport is discussed extensively in Section 3.3.2.

Secondly, while MnO_2 is highly insoluble under oxidizing conditions, under some subsurface conditions, it may undergo reductive dissolution to form the soluble manganese ion (Mn^{2+}). Microbial activity might enhance this dissolution. For example, Sahl (2005) witnessed the complete removal of MnO_2 solids from a biologically-active sand packed column after permanganate had been applied and the system equilibrated, though the exact mechanism was not determined. The long-term fate of MnO_2 in a target treatment zone after ambient redox conditions reestablish themselves is still not well understood.

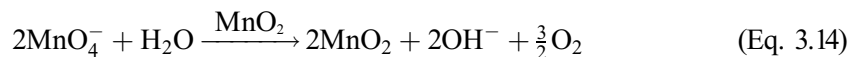
MnO_2 is also an oxidant with a reduction potential of 1.24 V in acidic environments (Arndt, 1981), which is strong enough to make reactions with many organic compounds thermodynamically favorable (Equation 3.12). However, at alkaline pH, this potential is reduced to -0.05 V (Equation 3.13), indicating that manganese dioxides may be quite stable under these conditions.



Arndt (1981) reviewed the reactivity of manganese dioxide minerals, such as pyrolusite and psilomelane, and reported a number of different oxidation reactions and mechanisms that could occur with organic chemicals. However, many of these reactions were carried out in nonpolar solvents. Since polar solvents like water may complex with the mineral surface and alter the mineral's reactivity, it is likely that nonpolar solvents facilitate reaction mechanisms not possible in aqueous systems. Pizzigallo et al. (1995) specifically noted that birnessite and pyrolusite, both manganese minerals with the formula of MnO_2 , could effectively degrade mono-, di-, and tri-chlorophenols at appreciable rates. Although these rates were two to three orders of magnitude slower than the rate for the degradation of these compounds by permanganate oxidation reported by Waldemer and Tratnyek (2006), they are still rapid enough to be important over long time periods. Further evidence for oxidation of chloroethenes by MnO_2 was given by Kim and Gurol (2005), who observed continued chloride production at slow rates from a TCE DNAPL even after the permanganate ion had been depleted from the system. Thus MnO_2

may be involved in continued oxidation and attenuation processes after oxidant injection has ended and after the permanganate ion has been depleted from the system. Under the appropriate conditions, this may result in continued abiotic transformation of organic contaminants.

MnO₂ can also catalyze permanganate autodecomposition and act as a nonproductive oxidant sink, as shown in Equation 3.14 (Stewart, 1965).



This reaction is generally observed to be much slower than contaminant oxidation reactions and is usually not a significant concern in advection controlled ISCO delivery systems. However, in diffusion controlled ISCO delivery systems where permanganate is present for extended periods of time and all other major reductants are depleted, this process may be significant.

MnO₂ may also affect subsequent applications of ISCO using other oxidants. Manganese minerals are extremely active catalysts for hydrogen peroxide (Watts et al., 2005; Teel et al., 2007). While these minerals may catalyze the degradation of organic contaminants, the potentially high concentrations of MnO₂ after a permanganate injection could lead to extremely rapid and perhaps violent decomposition of hydrogen peroxide. Thus, application of catalyzed hydrogen peroxide (CHP) within a zone where permanganate has been previously applied is not recommended, at least not without very careful consideration. The interaction of persulfate with manganese dioxides is not well studied, but based on analogy to hydrogen peroxide, it is conceivable that it may also act as a catalyst.

MnO₂ may act as a sorbent for dissolved solutes, especially metal cations. As a colloidal solid, MnO₂ has a large surface area and sorption sites on the colloid surface may attract and reversibly bond positive cations. Crimi and Siegrist (2004a) specifically noted that these MnO₂ solids could sorb and immobilize cadmium, although the degree of sorption depended on other system parameters. For example, the amount of cadmium sorption was higher at neutral pH than low pH because of competition between protons (H⁺) and cadmium for the available sorption sites. Likewise, the presence of calcium in solution also resulted in lower degrees of cadmium sorption. The nature of oxidant addition might also impact the metal sorption capacities of MnO₂. Since permanganate is injected as either a sodium or potassium salt, a concentrated plume of sodium or potassium ions will also be present. As such, these monovalent cations will initially dominate cation exchange processes within the reaction zone where MnO₂ is formed. However, divalent or higher valence cations typically have stronger cation sorption potential than these monovalent cations; thus, as the subsurface equilibrates after a permanganate injection, these monovalent cations may be replaced by other metals through ion exchange.

3.2.6 Carbon Dioxide Gas Evolution

Carbon dioxide (CO₂) is also a byproduct of the mineralization of organic compounds by permanganate. When permanganate attacks organic compounds, it has the potential to either partially or fully oxidize the compound to inorganic byproducts; in the case of carbon atoms, the end product is CO₂. In aqueous systems, the amount of CO₂ that may be dissolved in water is pH-dependent. At high pH, the aqueous system has the capacity to store large amounts of carbon dioxide as carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻). However, at low pH, carbon dioxide will tend to be expelled from solution as CO₂ gas (Benjamin, 2002). As acidity may be produced by permanganate reactions, especially when degrading some chlorinated organics, the potential exists for CO₂ to be released from solution as gas; this has been observed in a number of systems (Reitsma and Marshall, 2000; Schroth et al., 2001; Li and Schwartz, 2003; Petri et al., 2008).

The fate of the CO₂ gas produced during permanganate ISCO depends on the subsurface conditions. In some cases, the CO₂ gas may remain trapped and allow other dissolved gases to partition into the gas phase. If this discontinuous gas phase is close to a NAPL pool, then its presence could significantly affect the mass transfer from the pool through repeated, spontaneous expansion and mobilization of the gas phase (Mumford et al., 2008). In other cases, the CO₂ gas will eventually redissolve into water again as the pH rebounds. pH rebound may occur either due to the buffering of pH by carbonate minerals or the influx of higher pH water from upgradient locations. However, while this effect is transient, the resulting gas migration or entrapment in groundwater systems has the potential to alter transport mechanisms in the subsurface in a number of ways, which are discussed in more detail in Section 3.3.2.

3.2.7 Oxidation of Natural Organic Matter

Permanganate has long been known to oxidize and degrade NOM, and it is generally accepted that NOM is the largest contributor to natural oxidant demand (NOD – see Section 3.3.1) at ISCO sites (Haselow et al., 2003; Xu et al., 2004; Mumford et al., 2005; Urynowicz et al., 2008). Alkaline permanganate oxidation, especially at elevated temperatures, has been used by many as a method to investigate the structure of humic matter, by degrading NOM and characterizing the byproducts to make determinations about the parent structures of humic matter (Schnitzer and Desjardins, 1970; Ortiz De Serra and Schnitzer, 1973; Griffith and Schnitzer, 1975; Almendros et al., 1989). The use of permanganate at high pH and temperature, which may involve the manganate (MnO₄²⁻) ion (from Equation 3.3) as well as possibly free radicals, results in a chemistry that differs from permanganate chemistry occurring at typical ISCO sites. It is unknown how much error this may impart in extrapolation of results from these high pH and high temperature studies to conditions representative of ISCO. However, these studies are useful particularly in the information they provide about the types of byproducts that may be expected from permanganate oxidation of NOM. These studies have shown that permanganate reacts extensively with humic matter, and many byproducts have been identified, including aliphatic and aromatic carboxylic acids. Griffith and Schnitzer (1975) identified major individual byproducts as being succinic and glutaric acids in the case of aliphatics, while major aromatic acids included benzene substituted with up to four carboxyl or hydroxyl groups. Almendros et al. (1989) noted that temperature had an impact on the nature of the byproducts – more aliphatic byproducts were stripped out of the NOM matrix at low temperatures, while aromatics required higher temperatures before they were released from the NOM. This was attributed to the higher stability of aromatic structures in the NOM matrix.

3.3 OXIDANT INTERACTIONS IN THE SUBSURFACE

When permanganate is injected into the subsurface during an ISCO application, a number of important interactions occur between permanganate, its reaction products, and the subsurface environment. For example, aquifer materials contain natural reductants, such as NOM and reduced minerals that may exert a demand for the oxidant, reducing its transport and persistence. This, in turn, can impact system efficiency in degrading the target organic contaminants. Other impacts include the generation of the solid MnO₂ reaction product, as well as CO₂ gas evolved from organic oxidation, which may further alter the subsurface chemistry and reactive transport processes. These and other impacts all have the potential to affect remediation effectiveness and are therefore important considerations for the design and implementation of ISCO at contaminated sites. These interactions are discussed in further detail below.

3.3.1 Natural Oxidant Demand

3.3.1.1 Process Description

NOD must be considered for every ISCO site that uses permanganate. When permanganate is injected into the subsurface, it is consumed by a series of reactions that occur between subsurface media and the oxidant, including NOM, as well as inorganic minerals and dissolved solutes (Haselow et al., 2003; Mumford et al., 2005; Urynowicz, 2008; Urynowicz et al., 2008; Xu and Thomson, 2008). The permanganate mass that is consumed by these reactions is not available for the degradation of the COCs. Consequently, these reactions can be viewed as a nonproductive oxidant sink. Other terms have evolved to refer to NOD, including soil oxidant demand (SOD) and total oxidant demand (TOD). These terms, described in the glossary, are not used in this chapter.

Nearly all naturally occurring media will have some degree of NOD, but the range of NOD varies widely from one site to another and can also vary considerably across the same site. While many sites have low NOD and are well suited to permanganate ISCO, there are others where NOD reactions can exert an excessive oxidant demand. Under these conditions, NOD may consume so much permanganate that either a cost-prohibitive amount of permanganate must be injected to overwhelm NOD or else treatment effectiveness will be poor because so much permanganate is consumed by NOD that little is available to degrade COCs (Haselow et al., 2003; Mumford et al., 2004). Thus, careful evaluation of permanganate NOD must be a component of the decision-making process for permanganate ISCO.

The initial conceptual model considered NOD to be an instantaneous finite oxidant sink that needed to be satisfied before permanganate was available to oxidize the COCs (Drescher et al., 1998; Zhang and Schwartz, 2000; Siegrist et al., 2001); however, more recent investigations have shown that NOD is a kinetically controlled process (Heiderscheidt et al., 2008b; Mumford et al., 2005; Hönning et al., 2007; Jones, 2007; Urynowicz, 2008; Urynowicz et al., 2008; Xu and Thomson, 2009). Consequently, the rate of permanganate consumption by NOD may have significant implications to ISCO applications. Some of the more recent studies have attempted to represent NOD using both a kinetic rate of reaction and a finite upper NOD limit representing the ultimate NOD. A finite upper limit differs from the nature of oxidant longevity with other oxidants such as hydrogen peroxide, which catalytically decomposes in the presence of aquifer materials; the catalytic activity is largely unaltered by the oxidant, thus rendering eventual total oxidant decomposition with every application (Teel et al., 2007). A finite upper limit on NOD assumes that NOD, like a contaminant, can eventually be completely satisfied, after which no more permanganate will be lost to NOD reactions. However, the slow autocatalytic decomposition of permanganate by MnO_2 in Equation 3.14 indicates that there is no upper limit on oxidant decomposition. However, Xu and Thomson (2008) reported that the autocatalytic decomposition of MnO_2 is generally so slow that it is only of concern over a timeframe of months. Thus, autocatalytic decomposition is generally of more relevance for long-term site monitoring than it is for initial oxidant injection and distribution.

NOM long has been suspected as being the largest contributor to NOD; as such, several correlations between NOD magnitude and fractional organic carbon content (f_{oc}) have been proposed (Hood, 2000; Xu and Thomson, 2008). However, these empirical relationships are only representative of the data used to construct them, so their suitability for aquifer solids with vastly different NOM limits their widespread utility. Reduced inorganic minerals and solutes may also play a significant role at some sites.

The most common way to estimate the NOD magnitude of a specific media remains a laboratory test procedure for determining the mass of permanganate consumed per mass dry soil after a prescribed period of time. A number of factors have been observed to impact the NOD measurements reported from these tests. In theory, neglecting autocatalytic decomposition, the permanganate mass consumed by NOD will increase until it asymptotically reaches an “ultimate” NOD at infinite time. Thus, NOD magnitudes measured in the laboratory increase with the amount of time allowed for reaction. It also has been reported that increased permanganate concentration results in higher NOD values (Siegrist et al., 2002; Crimi and Siegrist, 2005; Hönning et al., 2007; Urynowicz et al., 2008; Xu and Thomson, 2009). Other factors related to the experimental condition (e.g., soil:water ratio, permanganate:soil ratio) can also effect the results.

Because of the effect that reaction time, permanganate concentration, and other experimental conditions have on the magnitude of NOD, it has become desirable to measure NOD with a standardized method that enables direct comparison of results for one material to another. This has resulted in the development of an American Society of Testing and Materials (ASTM) method to assist with the site-specific characterization of NOD for permanganate (ASTM, 2007). Part A of the ASTM method is a 48-h test that enables timely characterization of NOD to support technology screening and early decision-making for permanganate ISCO. Part B of the ASTM method is a 2-week kinetic test that provides additional insight into the rate and extent of permanganate consumption. Another quick and economical alternative to estimate the ultimate NOD for aquifer materials to support site screening for permanganate ISCO and for initial design purposes is to use the modified chemical oxygen demand (COD) test using permanganate as the oxidant (Xu and Thomson, 2008). Initial testing of this 2-hr method showed no statistically significant difference between the permanganate COD test and the maximum NOD obtained from well-mixed batch reactors.

NOD testing is typically performed using disaggregated media in aqueous batch systems that are continuously tumbled or mixed. The agitation continuously scours the surfaces of soil grains, ensuring complete contact with nearly all oxidizable matter. However, in practice, permanganate must be injected into the subsurface and rely on advection, dispersion and diffusion processes to contact the media rather than mechanical agitation. Under field conditions, some portion of the site’s oxidizable matter may be located within dead-end pores, diffusive-limited low permeability media, or trapped within soil grains making it less available to the oxidant. Furthermore, a barrier to further oxidation may develop with time because MnO_2 deposition may inhibit further reaction (Jones, 2007; Xu and Thomson, 2009). In laboratory systems, this barrier may be scoured away by agitation. Thus, NOD values from laboratory batch tests are generally assumed to overestimate the NOD observed in the field. Xu (2006) found that the NOD estimated from column experiments was one half to one tenth that of the maximum NOD from a 7-day batch test, and proposed that a correlation between the two may allow for better up-scaling to predict the *in situ* NOD.

Another way to obtain better estimates of field NOD values is to use a permanganate push-pull test (Struse et al., 2002a; Mumford et al., 2004). This method involves the injection of a known amount of permanganate into the subsurface, followed by a reaction period, and then groundwater extraction from the same injection point. A conservative tracer, such as bromide, is used to evaluate the efficiency of extraction of the original permanganate injection slug. NOD is then calculated by the difference in injected and extracted oxidant masses and the volume of media contacted. Using this method, Mumford et al. (2004) demonstrated that *in situ* NOD could be reliably measured with repeatable results, provided that groundwater drift during the reaction was low.

3.3.1.2 NOD Magnitude

The permanganate demand associated with NOD is often many times greater than the demand expressed by the target compounds (Haselow et al., 2003; Hönning et al., 2007). Consequently, the magnitude of permanganate NOD is one of the most important parameters for screening the viability of a particular site for ISCO with permanganate. In the literature, NOD has been reported as being as low as <0.04 g MnO_4^- /kg media (Haselow et al., 2003) to as high as 98 g MnO_4^- /kg media (Xu and Thomson, 2008).

Hönning et al. (2007) completed a study in Denmark where laboratory batch slurry experiments were completed with 31 sandy and clayey subsurface porous media from 12 Danish sites. At these sites, the NOD (measured over 21 days) was generally higher in clayey compared to sandy media with typical values of 0.5–2 g MnO_4^- /kg (dry wt.) for glacial meltwater sand, 1–8 g MnO_4^- /kg (dry wt.) for sandy till, and 5–20 g MnO_4^- /kg (dry wt.) for clayey till.

Following the recent completion of ASTM 7262-07 (ASTM, 2007), Carus Chemical has compiled a database containing NOD values (measured over 48 h following Part A) for 274 samples collected from 46 sites. These data are summarized in the histogram shown in Figure 3.8.

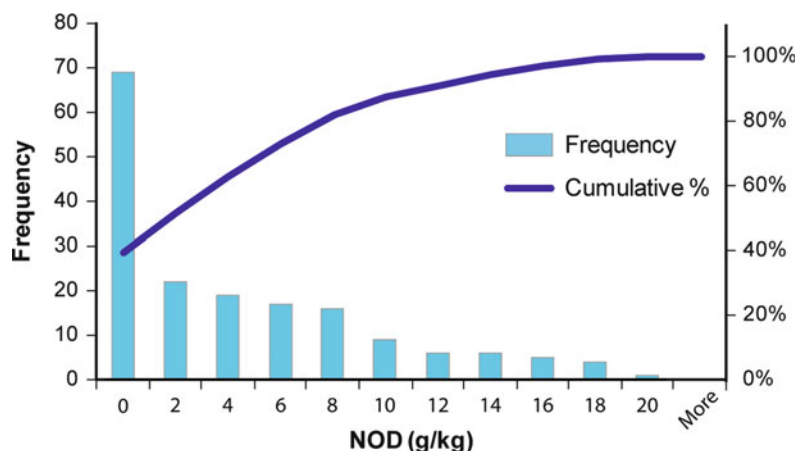
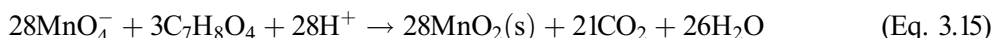


Figure 3.8. Histogram of permanganate NOD values for 174 samples collected from 46 sites (figure provided courtesy of M. Dingens, Carus Chemical Company, June 9, 2009).

Correlating NOD to site-specific porous media properties is difficult due largely to the heterogeneous nature of aquifer solids and the variability in geochemical properties among sites. However, where correlations have been determined, the magnitude of NOD has generally been found to correlate most strongly with NOM content (Hönning et al., 2007; Xu and Thomson, 2008). When permanganate is contacted with NOM, NOM will partially degrade, sometimes quite extensively (Griffith and Schnitzer, 1975; Almendros et al., 1989; Woods, 2008); this reactivity may impart a significant demand for the oxidant (Haselow et al., 2003; Urynowicz et al., 2008; Xu and Thomson, 2008).

A stoichiometric relationship for permanganate oxidation of NOM as represented by a model compound is shown in Equation 3.15 (Hönning et al., 2007):



Equation 3.15 suggests a theoretical ratio equal to 13.2 g MnO_4^- per g of TOC. In the study by Hönning et al. (2007) noted above, for a glacial meltwater sand with a low TOC

(0.01–0.06 wt.%) the researchers observed a linear relationship between permanganate consumption and TOC that was consistent with Equation 3.15. However, the experimental results for sandy and clayey till with a relatively higher TOC (0.4–1.8 wt.%) revealed a range of values between 2 and 20 g MnO_4^- per kg media with no correlation between the NOD and the initial TOC.

Xu and Thomson (2009) also examined the relationship of NOD to TOC. They proposed an empirical relationship (Equation 3.16) for the maximum NOD (150-day test) based on the data shown in Figure 3.9:

$$\text{Avg } NOD_{\max} = 12.2(\text{TOC}) - 3.4 \quad r^2 = 0.78 \quad (\text{Eq. 3.16})$$

where NOD is expressed as g KMnO_4/kg and TOC is in mg/g.

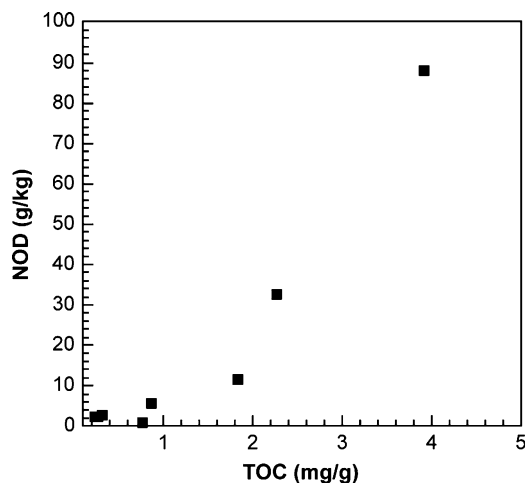


Figure 3.9. NOD as a function of TOC (unpublished data of Xu and Thomson, 2009).

A fair amount of variability in NOD measured by Xu and Thomson (2009) could not be strictly explained based on TOC values alone. The results suggested that some types of NOM might be much more oxidizable by permanganate than others. The two notable outliers in the data set clearly illustrate the limitations of using only TOC to estimate NOD. One media with the fourth-highest value of TOC tested (0.77 mg/g) produced the lowest NOD measured at 0.77 g KMnO_4/kg media, while the highest NOD media had the highest TOC of 3.93 mg/g and a NOD of 87.9 g KMnO_4/kg . Comparing only these two media, a threefold increase in TOC registered a 115-fold increase in NOD measured over the 150 day time period. However, the relationship given by Equation 3.16, based on data from the eight media, would only predict about a 12-fold increase over this range by drastically over-predicting the low NOD sample and slightly under-predicting the high NOD sample. Further characterization of the paradoxical high TOC, low NOD media indicated that at least some of the organic carbon content may be lignitic, similar to low-grade coal, possibly indicating a higher degree of weathering and consolidation of the organic matter than occurs with many humic substances common in soils; this might explain why the soil was more resistant to permanganate oxidation than other porous media used in the study.

The correlation of NOD with media properties other than NOM content has been less successful. For example, reduced minerals have long been suspected to play a role in NOD, especially in soils with low NOM content but inexplicably high NOD. However, Xu

and Thomson (2008) found that including amorphous iron content in the correlation with TOC only mildly improved the correlation coefficient from 0.78 to 0.8. The significance of such a small increase is difficult to discern, especially with only eight media included in the investigation. Hönning et al. (2007) examined the effects of redox state on NOD and found inconclusive results regarding any inverse correlation between NOD and reducing conditions.

Mumford et al. (2005) investigated the impact of particle size on NOD for a single porous media. It would seem logical to hypothesize that oxidation of NOD occurs at particle surfaces; thus, one would expect smaller size fractions that have larger surface areas to exhibit higher NOD. However, Mumford et al. (2005) found the opposite to be true where the coarse-size fraction of the media exhibited almost double the NOD of the other fractions. Further investigation revealed that this coarse fraction also had nearly twice as much NOM associated with it as the other size fractions in the media, so the increase in NOD is understandable. They proposed that the coarse particles were in fact agglomerations of soil particles held together by NOM and that permanganate could freely diffuse into them and react. Thus, the lack of clearly defined relationships between NOD and easily measured subsurface properties, such as organic carbon content, reduced inorganic species, or grain size indicate that NOD must be experimentally determined to predict NOD at a site with any certainty. Consequently, the use of existing literature values to develop correlations of NOD with media properties must be performed with caution.

3.3.1.3 NOD Kinetics

Overview of Considerations

NOD kinetics also may be important to consider during the design and implementation of ISCO with permanganate. However, the importance will depend primarily on the magnitude of the ultimate NOD. For example, the kinetics may not be that important at sites where NOD magnitude is low as the total amount of permanganate lost to NOD is small regardless of time. However, for sites with moderate to high NOD or where delivery of permanganate over large distances is desired, the kinetics may play a very important role because slower rates will allow for longer delivery distances even when the NOD is high. Although several different approaches have been used to represent NOD kinetics, the reaction of permanganate with NOD is generally conceptualized as a continuum of parallel reactions that occur with various minerals and organics in the porous media, and these reactions proceed at a continuum of rates (Mumford et al., 2005; Urynowicz et al., 2008). Thus, the faster reactions quickly deplete the fast reacting species, while the slower reacting constituents continue to react over long time periods (Figure 3.10). This is generally observed as a slowing of the rate of permanganate consumption over time (Figure 3.11). However, Urynowicz et al. (2008) observed that the reaction order with respect to permanganate also decreased with time. For some media, this may occur gradually; for others, a more abrupt change in rate has been observed. To better understand the complex kinetics of NOD, some have advocated separating the rate expression into two parts: a “fast” NOD represented by a rapid rate or an instantaneous demand and a “slow” NOD represented by much slower rates of reaction (Mumford et al., 2005; Urynowicz et al., 2008; Xu and Thomson, 2009).

Instantaneous NOD Approach

Initial attempts at modeling NOD conceptualized it as an oxidant sink with instantaneous demand (Zhang and Schwartz, 2000; Mumford et al., 2002; Haselow et al., 2003). This approach requires that NOD be completely depleted before permanganate can be transported

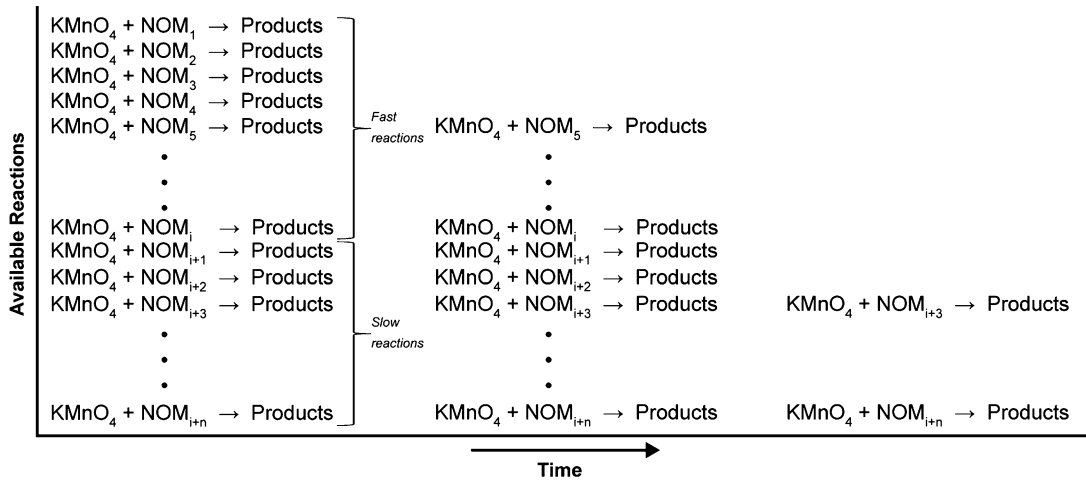


Figure 3.10. Available reactions between permanganate and fast and slow reacting constituents (i.e., NOM) with time (adopted from Urynowicz et al., 2008).

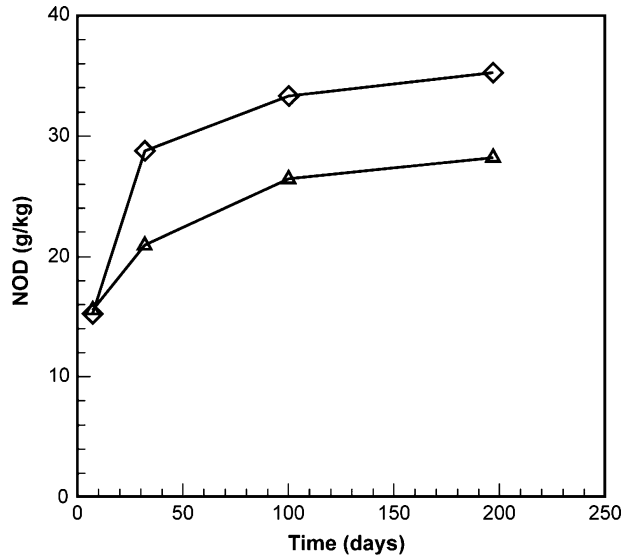


Figure 3.11. NOD profiles showing fast and slow permanganate reactions for an initial permanganate concentration of 10 (triangles) or 20 (diamonds) g KMnO₄/L (adopted from Xu and Thomson, 2009).

further. This is the most conservative approach to modeling permanganate delivery because it essentially assumes that all of the permanganate NOD must be satisfied before contaminant treatment can occur. However, NOD is a kinetically controlled process and NOD and contaminant degradation occur simultaneously. Consequently, the design and implementation of permanganate ISCO using the instantaneous NOD approach may result in using more permanganate than is required for effective contaminant degradation. Furthermore, the total exhaustion of NOD is not always desirable since permanganate can be very stable once reductants are depleted and it may persist in the subsurface for undesirably long timeframes.

Rate-Limited NOD Approaches

A variety of rate-limited approaches have been proposed by various authors to model NOD kinetics for the purpose of analyzing laboratory data or for predicting permanganate subsurface transport. Approaches used include instantaneous, zero-order, first-order, or second-order reaction rates, and combinations thereof. These rate-limited approaches have varying degrees of mathematical complexity associated with them and sometimes account for other processes as well. For instance, one of the rate-limited models proposed by Xu and Thomson (2008) includes a kinetic term for the autocatalytic decomposition process described by the reaction in Equation 3.14, as well as capturing NOD passivation due to the deposition of MnO_2 on the grains of porous media. Other studies have found it useful to break the rate-limited NOD into fast and slow fractions to get a better fit of permanganate consumption with time. However, the breakpoint between fast and slow fractions may be open to interpretation since different cutoff times may be employed. Generally, it appears that the slow fraction accounts for a greater proportion of the ultimate NOD than the fast NOD. The data reported by Xu and Thomson (2008) indicate that about 50% of the ultimate NOD has been realized by 7 days and that much of this occurs in less than 1 day. However, for the two-component first-order model proposed by Urynowicz et al. (2008), the fast fraction on average accounted for 35% of the ultimate NOD for one soil sample, with the fraction of fast NOD trending strongly with oxidant concentration from 18% at high oxidant concentration to 53% at low concentration.

The approach proposed in Chapter 9 for simplified prediction of permanganate transport in porous media approximates a fast and slow fraction by assuming the fast fraction is instantaneous and the slow fraction follows second-order kinetics consistent with Xu and Thomson (2009). A summary of the rate-limited NOD formulations proposed by several authors is included in Table 3.2. Chapter 6 provides additional information about incorporating rate-limited NOD expressions into mathematical models.

The complexity of available models varies from relatively simple to more complex. The zero-order model proposed by Mumford et al. (2005) and the two component pseudo first-order model proposed by Urynowicz et al. (2008) shown in Table 3.2 are mathematically simple enough to be incorporated into site-specific analytical models that include advection-dispersion reaction equations, such as those solved by van Genuchten and Alves (1982). Because of this, it may be possible to incorporate these simple models of rate-limited NOD into spreadsheet tools and design equations. However, the loss of oxidizable aquifer material by reaction with permanganate slows the rate of NOD with time, eventually exhausting NOD at some point. This process cannot be captured by a zero- or first-order model. Failure to account for this may result in significant overestimation of the amount of permanganate lost to NOD, especially as the length of time being modeled increases. Thus, simple mathematical models may be relevant only during an initial oxidant injection episode. To capture processes that take more time, like injection and drift, passive injection, or recirculation, or predictions of the long-term longevity of permanganate in the subsurface may require the use of more complex models. Rate-limited NOD models such as those proposed by Xu and Thomson (2009) require a numerical framework to be solved.

3.3.1.4 Impact of NOD on Permanganate Transport

The magnitude and kinetics of NOD impact permanganate subsurface delivery and transport in a number of ways. For example, many ISCO applications use forced injection for delivery, either through wells or direct push probes. Since initial velocities are often high, the fast-reacting NOD fraction is likely to have a greater impact on permanganate distribution

Table 3.2. Summary of Rate-Limited NOD Models Proposed in the Literature

Type of kinetics	Model formulation	Definition of terms
Mumford et al. (2005)		
Zero-order	$\frac{dC_{MnO_4^-}}{dt} = -k_0$	Where k_0 is a constant (mg MnO_4^- /kg media-day)
Other	$NOD(t) = NOD_{Ultimate}(a \cdot \ln(t) + b)$	Where, a (1/ln(day)) and b (unitless) are constants, $NOD_{ultimate}$ (mg/kg) is the maximum possible NOD
Xu (2006)		
Second-order short-term NOD	$\frac{dC_{MnO_4^-}}{dt} = -k_{MnO_4} (C_{MnO_4^-})^\alpha (C_{OAM})^\beta \text{ and}$ $\frac{dC_{OAM}}{dt} = -k_{oam} (C_{MnO_4^-})^\alpha (C_{OAM})^\beta$	Where, k_{MnO_4} is a second-order reaction rate for permanganate consumption by oxidizable aquifer material (OAM), k_{OAM} is a second-order reaction rate for OAM consumption by permanganate, α and β are constants reflecting the reaction order, and C_{OAM} is the OAM concentration determined by a dichromate COD test. β was held to equal one for solution of the kinetic model
Urynowicz et al. (2008)		
Two component pseudo first-order	$\frac{dC_{MnO_4^-}}{dt} = -k_f a (C_{MnO_4^-}) - k_s b (C_{MnO_4^-})$	Where, k_f (1/time) is a first-order rate constant for the fast reacting fraction of NOD, k_s is a first-order rate constant representing the slow fraction of NOD, and a and b are fractions adding to 1 describing the amount of permanganate reacting with one fraction versus the other
Xu and Thomson (2009), Jones (2007)		
Second-order short-term and long-term NOD	$\frac{d\theta C_{OAM}^{fast} V}{dt} = -k_{ox}^{fast} \theta C_{OAM}^{fast} C_{MnO_4^-} V, \text{ and}$ $\frac{d\theta C_{OAM}^{slow} V}{dt} = -k_{ox}^{slow} \theta C_{OAM}^{slow} C_{MnO_4^-} V, \text{ and}$ $\frac{d\theta C_{MnO_4^-} V}{dt} = -k_{ox}^{fast} \theta C_{OAM}^{fast} C_{MnO_4^-} V - k_{ox}^{slow} \theta C_{OAM}^{slow} C_{MnO_4^-} V - k_{MnO_2} \theta C_{MnO_4^-} V$	Where, θ is porosity, V , is the total volume of the system, k_{ox}^{fast} is the second-order rate constant for the fast OAM fraction, k_{ox}^{slow} is the second-order rate constant for the slow OAM fraction, C_{OAM}^{fast} is the concentration of the fast OAM fraction, C_{OAM}^{slow} is the concentration of the slow OAM fraction, and k_{MnO_2} is a first-order rate constant for autocatalytic decomposition of the oxidant

(continued)

Table 3.2. (continued)

Type of kinetics	Model formulation	Definition of terms
CDISCO (see Chapter 6, Section 6.9.3; also see Siegrist et al., 2010)		
Instantaneous NOD fraction	<p>If $C_{MnO_4}^i > C_{NOD-I}^i \rho_B / n$,</p> <p>then $\left[C_{MnO_4}^{i+1} = C_{MnO_4}^i - N_I^i \rho_B / n \text{ and } N_I^{i+1} = 0 \right]$</p> <p>else $\left[C_{NOD-I}^{i+1} = C_{NOD-I}^i - C_{MnO_4}^i n / \rho_B \text{ and } C_{MnO_4}^{i+1} = 0 \right]$</p>	Where, C_{NOD-I} and C_{MnO_4} are the concentrations of instantaneous NOD and permanganate. The superscript i indicates values at the start of the calculation and the superscript $i + 1$ indicates values at the end of the calculation. n is porosity and ρ_B is soil bulk density
Second-order slow NOD fraction	$\frac{dC_{NOD-S}}{dt} = -k_2^{slow} C_{NOD-S} C_{MnO_4}$	Where, C_{NOD-S} is the concentration of slow NOD volume, k_2^{slow} is the second-order reaction rate of slow NOD with permanganate, and t is time

during the initial phase of injection. However, as velocities decrease and oxidant contact with the media continues under natural groundwater advection, the slow reacting NOD fractions may become more important because of the much longer timeframe needed for these transport processes. Delivery strategies such as injection and drift, which rely on natural advection and dispersion, are likely to be strongly impacted by both the fast- and slow-reacting fractions of NOD.

Because delivery of permanganate into low permeability zones may rely on diffusion as a transport mechanism and because diffusion requires long time periods for effective oxidant transport, the full spectrum of kinetic NOD processes, including fast and slow fractions, may be of interest. Seitz (2004) evaluated the diffusive transport of permanganate in two media that had similar effective diffusion coefficients for permanganate, similar tortuosity, and similar diffusive fluxes for a conservative bromide tracer but much different NOD magnitudes. With the high NOD media, which had an NOD of 24 g MnO_4^- /kg media, permanganate took 80 days to transport by diffusion across a soil core that was 2.5 centimeters (cm) long. However, a low NOD media with similar diffusive properties but with only 3.2 g MnO_4^- /kg media had breakthrough in the same distance in only 24 h. This represents a large retardation of diffusive transport of permanganate and illustrates how NOD may be a controlling factor for treatment of contaminant diffused into low permeability layers.

Monitoring data collected at field sites have documented the impact of NOD on permanganate transport. At one ISCO site, the treatment of a TCE plume fell short of expectations presumably due to high NOD limiting oxidant delivery. Furthermore, high-injection back-pressures were encountered and were hypothesized to be the result of MnO_2 deposition near the injection wells from NOD oxidation. An investigation of these problems by Crimi and Siegrist (2004b) included modeling the site using a numerical transport model developed by Heiderscheidt et al. (2008b), which incorporated fast and slow first-order NOD kinetics. The results from this modeling exercise indicated that extensive MnO_2 deposition could occur

close to the well screen from NOD oxidation, resulting in operational problems. On the basis of the model results, it was predicted that reducing the permanganate concentration and increasing the injection flow rates would improve the oxidant distribution and reduce the plugging problem by dispersing MnO_2 away from the injection wells over a larger region of the subsurface (Heiderscheidt et al., 2008b).

3.3.2 Permanganate Impacts on Subsurface Transport Processes

Subsurface transport processes that potentially can be affected during ISCO with permanganate include changes to subsurface permeability, DNAPL mass-transfer processes, contaminant sorption, and density driven advection. These effects are discussed below.

3.3.2.1 Impact of MnO_2 on Flow and Transport

As described in Section 3.2.5, MnO_2 solids are a product of permanganate oxidation reactions. Substantial deposits of MnO_2 have the potential to alter subsurface transport behavior. While Struse et al. (2002b) demonstrated that MnO_2 had little effect on diffusive transport properties of porous media (such as tortuosity), MnO_2 has been clearly shown to have the potential to reduce permeability for advective flow in porous media (Schroth et al., 2001; Conrad et al., 2002; Li and Schwartz, 2004a; Heiderscheidt et al., 2008a) or fractures (Tunnicliffe and Thomson, 2004). This permeability reduction tends to occur in zones of intense permanganate reaction, such as at NAPL interfaces or where high NOD is encountered (Conrad et al., 2002; Li and Schwartz, 2004a; Heiderscheidt et al., 2008a).

Heiderscheidt et al. (2008a) reported, based on a pressure transducer study, that a concentration of 0.1 g MnO_2 /kg media was needed to alter flow pathways in sandy media. This concentration is significantly below the amount of MnO_2 deposition required to fill the pore space. For instance, if MnO_2 had the same density as the common manganese mineral pyrolusite (5.04 g/cm³), this concentration would reduce the porosity of the formation by only 0.01%, assuming an initial porosity of 0.3 v/v. The fact permeability may be significantly reduced at low MnO_2 concentrations such as this indicates that either the density of MnO_2 solids is either much lower than that of the pure mineral or that the permeability reduction occurs due to MnO_2 deposition at the pore throats rather than pore body filling. Heiderscheidt (2005) developed a model to account for permeability changes from MnO_2 deposition and the resulting impacts to flow fields. The model had to assume that permeability reduction occurred as a result of pore filling over the entire pore space, so the assumed density of MnO_2 solids was a very sensitive parameter. An MnO_2 particle density of 9.5 mg/cm³ best fit pressure transducer and total manganese data collected from a 2-D sand tank experiment. This value is orders of magnitude lower than the density of pyrolusite. It is unknown if the threshold concentrations of MnO_2 needed to have an impact on transport differ for finer media, such as fine sands, silts, or loams. These media have smaller pore throats and may therefore be more sensitive to clogging caused by MnO_2 deposition.

Since the subsurface environment is heterogeneous, the delivery patterns of permanganate solutions and the accompanying deposition of MnO_2 are also heterogeneous. The heterogeneity of MnO_2 deposition may be further affected as a result of the distribution of target and non-target compounds alike. For example, NAPLs represent areas of highly concentrated reductants and when exposed to permanganate can result in intense localized generation and deposition of MnO_2 (Conrad et al., 2002; MacKinnon and Thomson, 2002; Li and Schwartz, 2003, 2004c; Siegrist et al., 2006). The presence of NOD can also result in significant MnO_2 deposition

(Crimi and Siegrist, 2004b; Xu and Thomson, 2009). If NOD is spatially uniform, the resulting MnO_2 deposition from NOD oxidation may be uniform; however, if NOD is spatially variable, then the MnO_2 deposition that may result from its oxidation may likewise be spatially variable. The combination of these factors may impart additional heterogeneity in the MnO_2 distribution beyond that imparted from permanganate delivery alone.

The heterogeneous distribution of MnO_2 has important implications for oxidant and contaminant transport, and the resulting efficiency of ISCO treatment. Because all of these effects result in variability in the magnitude of MnO_2 deposition across the subsurface, the impact to permeability is likely not uniform over the entire target treatment zone. Local reductions in hydraulic conductivity typically manifest themselves as a general slowing of velocity and eventual flow bypassing can occur in areas where large amounts of MnO_2 deposition has occurred (Li and Schwartz, 2000; MacKinnon and Thomson, 2002; Lee et al., 2003; Heiderscheidt et al., 2008a). This may adversely affect the efficacy of permanganate ISCO because with time, an increasing amount of permanganate may effectively bypass the contaminated zones and may therefore not contribute to contaminant treatment (Li and Schwartz, 2000; Lee et al., 2003). The impact of flow bypassing can be especially important when treating DNAPLs. MacKinnon and Thomson (2002) found that manganese oxide “rocks” several centimeters in diameter formed at the permanganate-DNAPL interface during a 5 month sand tank ISCO experiment. The “rocks” were composed of agglomerations of aquifer sand cemented together by MnO_2 . These deposits clearly impeded groundwater flow and mass transfer from the DNAPL pool in this system. These impacts are discussed in greater detail in Section 3.3.2.3.

3.3.2.2 Impact of Gas Evolution on Flow and Transport

Gas evolution during permanganate ISCO has been observed to occur in porous media, especially when DNAPL contaminants are being treated (Reitsma and Marshall, 2000; MacKinnon and Thomson, 2002; Lee et al., 2003; Li and Schwartz, 2003; Petri et al., 2008). The chemical process leading to the evolution of CO_2 in the pore space is described in Section 3.2.6. Although the volumes of gas that might be evolved at a permanganate ISCO site are probably much smaller than those with hydrogen peroxide- or ozone-based ISCO, the presence of gas in groundwater systems has the potential to alter flow and transport in several ways. First, displacement of water within the pore space by a gas reduces the relative permeability of the subsurface; this can temporarily reduce groundwater flow through areas that have been partially water desaturated by a gas (Reitsma and Marshall, 2000; Lee et al., 2003; Li and Schwartz, 2003). Like MnO_2 deposition, this can cause flow bypassing of zones of intensive gas production, which are most likely to occur near DNAPL interfaces. Thus, this may reduce the efficiency of permanganate ISCO as a result of the oxidant bypassing the target contaminant (Lee et al., 2003).

The evolution of gas, especially in a DNAPL source zone containing volatile contaminants, also has the potential to affect contaminant transport. Volatile organic compounds (VOCs) may partition into the gas phase and transport with the gas wherever it migrates. In the saturated zone, gas may migrate upward due to buoyancy. VOCs that have partitioned into gas may then dissolve into groundwater that is either uncontaminated or is contaminated at levels lower than equilibrium concentrations for liquid-gas partitioning (Mumford et al., 2008). Several authors have noted that complete water desaturation of DNAPL source zones is possible if excessive CO_2 evolution occurs, and significant amounts of DNAPL mass may be lost to this process (Reitsma and Marshall, 2000; Petri et al., 2008). If contaminated gas channels are confined to zones where permanganate is present, VOCs may be degraded as they partition into the water phase. Several authors have observed these gas channels and noted that they may become

heavily encrusted in MnO_2 , indicating that oxidation was occurring at the air-water interface with the groundwater (Reitsma and Marshall, 2000; Petri et al., 2008). If vapors containing VOCs migrate into uncontaminated zones that are not contacted with permanganate, then contaminant concentrations in these areas may increase. In the available literature, gas evolution has been reported only in permanganate systems that have targeted a DNAPL. This is because only NAPLs, particularly chlorinated NAPLs, appear to generate sufficient acidity to drive the gas evolution reactions described in Section 3.2.6. Conditions that decrease the likelihood and severity of gas evolution include the presence of a well-buffered aquifer (Schroth et al., 2001), as well as the use of lower oxidant concentrations (Petri et al., 2008). DNAPLs with low solubility and thus slower rates of reaction (for instance, PCE as opposed to TCE) also have a lower likelihood of evolving gas (Petri et al., 2008).

3.3.2.3 Impacts on DNAPL Mass Transfer Processes

Permanganate has been extensively studied for the remediation of DNAPL compounds, particularly the chloroethenes, TCE and PCE. From numerous investigations in batch systems, 1-D columns, 2-D and 3-D tanks, and field investigations, a number of mechanisms and interactions between ISCO and DNAPLs have been identified that may have potential ISCO implications.

To further understand the implications of ISCO for DNAPL mass transfer, it is useful to quickly review the conceptual model for DNAPL mass transfer and transport. The mass transfer of DNAPL compounds is typically theorized as occurring through the diffusion of the contaminant across a thin aqueous stagnant film at the DNAPL interface. A linear concentration gradient across the film drives diffusive transport across the film. At the NAPL phase side of the film, the concentration is assumed to be saturated with respect to the contaminant; at the bulk aqueous phase side of the film, the concentration is assumed to be that of the bulk aqueous phase (e.g., the concentration in the pore space or representative elemental volume). Mass in the bulk aqueous phase is then subjected the subsurface processes of advection, dispersion, bulk diffusion, and reaction. This conceptual model of diffusion across a thin film may be described mathematically using the relationship in Equation 3.17.

$$\frac{\partial C}{\partial t} = k_{La}(C_s - C) \quad (\text{Eq. 3.17})$$

where, C is the aqueous contaminant concentration within the aqueous phase, C_s is the saturation concentration of the DNAPL, t is time and k_{La} is the bulk mass transfer rate coefficient. k_{La} in turn is empirically related to system parameters such as velocity, media grain size, heterogeneity and others (Miller et al., 1990; Powers et al., 1994; Saba and Illangasekare, 2000). This relationship in Equation 3.17, as well as the bulk phase subsurface processes of advection, dispersion, bulk diffusion, and reaction, provides the basis for much of the discussion of impacts of permanganate ISCO on DNAPL mass transfer.

Dissolution Enhancement by COC Oxidation

A number of investigators have reported that DNAPL mass depletion rates in groundwater systems are enhanced by the presence of permanganate over the ambient rate of dissolution in systems without permanganate (Schnarr et al., 1998; Reitsma and Dai, 2001; Jackson, 2004; Heiderscheidt et al., 2008a; Kim and Gurol, 2005; Urynowicz and Siegrist, 2005; Petri et al., 2008). Enhanced dissolution can represent an advantage of ISCO treatment with DNAPLs as the slow rate of depletion of DNAPLs due to dissolution into groundwater flowing by the DNAPL-water interface is the main cause of their longevity in source zones. Acceleration of

DNAPL dissolution and subsequent degradation by chemical reactions in the aqueous phase can result in decreased DNAPL source longevity and may also improve treatment efficiencies with ISCO. This enhanced dissolution is driven by the oxidation reactions in the aqueous phase, which help maintain low contaminant concentrations and high concentration gradients (i.e., high $C_s - C$ in Equation 3.17).

Many investigators have noted varying degrees of dissolution rate enhancement caused by oxidation (Schnarr et al., 1998; Reitsma and Dai, 2001; Schroth et al., 2001; MacKinnon and Thomson, 2002; Jackson, 2004; Heiderscheidt, 2005; Kim and Gurol, 2005; Urynowicz and Siegrist, 2005; Petri et al., 2008). In a theoretical model system of a DNAPL pool interface, Reitsma and Dai (2001) reported that rate enhancements from 5 to 50 times the ambient rates may be possible. Degrees of enhancement were higher for higher oxidant concentrations, but lower for higher velocities. The velocity impact was likely due to this theoretical system being reliant on lateral dispersion as a primary transport mechanism of contaminant away from the DNAPL interface. At higher velocities, lateral dispersion is greater, leading to greater dissolution rates. Apparently, due to the kinetics of oxidation, enhancements of dissolution over non-oxidizing systems only become large when the initial mass-transfer rate is small. In a 1-D experimental system (a porous media filled flow-through tube reactor, see Figure 3.12), Petri et al. (2008) observed dissolution rate enhancements of up to 16 times the initial rate, with the degree of enhancement dependent on oxidant concentration, the DNAPL contaminant type, and flow velocity. Higher enhancements occurred with PCE over TCE, higher oxidant concentrations, and at lower ambient flow velocities.

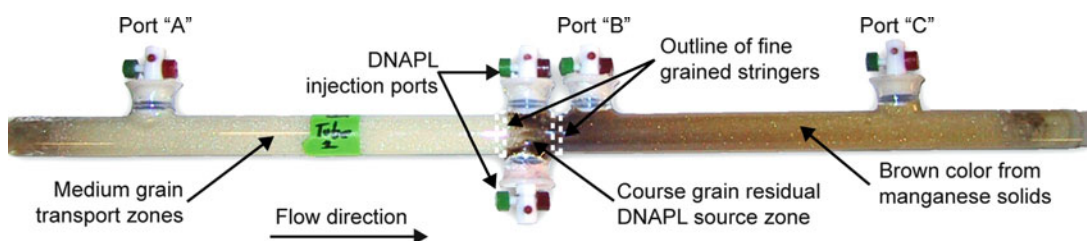


Figure 3.12. Flow-through tube reactor studies of permanganate flushing to examine the interacting effects of oxidant concentration and flushing velocity on DNAPL depletion (Petri, 2006).

The difference in enhancement caused by the type of DNAPL (e.g., PCE over TCE) is probably due to the higher solubility of TCE, where the dissolution rate is inherently higher and the degree of enhancement that is possible may be more limited when high dissolution rates are already present. Flushing velocity also had an impact, where a higher groundwater flow velocity resulted in faster dissolution, but at these high rates, oxidation could not accelerate dissolution to any significant degree. However, where dissolution was initially slow due to a low ambient flow velocity, enhancements could become large with the addition of permanganate. Thus, it appears that there are upper limits on how much dissolution rates can be enhanced by the presence of an oxidant, and these depend on the kinetics of the oxidation reaction relative to the kinetics of dissolution.

To further understand and conceptualize the enhancement behavior observed with permanganate, two mechanisms have been proposed to account for this enhancement behavior. The first assumes that the relationship and parameters in Equation 3.17 are unchanged by the occurrence of the oxidation reaction and that the enhancement in the rate of dissolution is caused by the reduction of the concentration in the bulk phase alone, enhancing the concentration gradient. The other approach, first conceptualized by Schnarr et al. (1998) and

based on Cussler's (1997) theory for diffusion of reactive compounds, is that considerable reaction may actually occur within the thin film. This results in a non-linear concentration gradient that is not captured by Equation 3.17, and is demonstrated by Figure 3.13.

Reitsma and Dai (2001) explored this theoretical non-linear concentration gradient and found that the enhancement from oxidation would not be particularly significant unless the thin film thickness was very large. In relating this theory to real systems, a definite boundary between the thin film and the bulk aqueous phase does not exist. Yet conceptually, this may be thought of as representing a contaminated zone where the DNAPL resides in a location (such as a low permeability zone) where ambient velocities are so slow as to be essentially absent. Thus, the bulk of oxidant delivery may occur via diffusive transport rather than advection. Under these conditions, the conceptual model in Figure 3.13 may be more representative than predicting mass transfer based on Equation 3.17 alone.

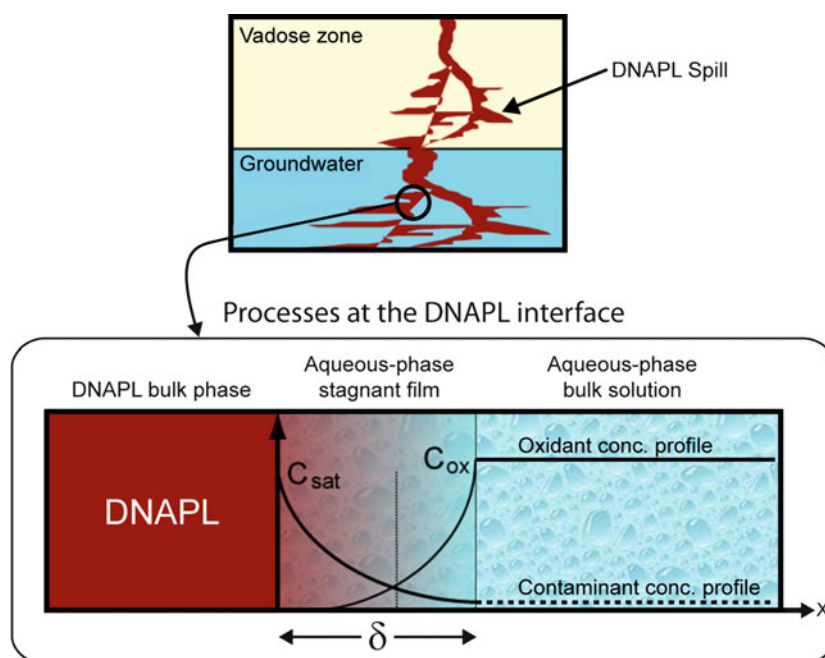


Figure 3.13. Proposed concentration profiles at the DNAPL interface, impacting mass transfer (Siegrist et al., 2001).

Dissolution Inhibition Due to MnO_2 Deposition

When permanganate is used to degrade DNAPL contaminants, the DNAPL-water interface can become a zone of intensive reaction. As a result, the DNAPL-water interface is also a zone of potentially intensive MnO_2 deposition, and therefore may cause a permeability reduction in the porous media at this interface (as discussed in Section 3.3.2.1). Within numerous 2-D tank experiments, the deposition of MnO_2 in the porous media within several cm of a DNAPL-water interface has been observed to effectively reduce permeability and alter the groundwater flow field (Conrad et al., 2002; Heiderscheidt et al., 2008a; Siegrist et al., 2006). In 2-D or 3-D flow fields, this can lead to deflecting groundwater flow around the DNAPL source (Conrad et al., 2002; Lee et al., 2003). Dissolution mass transfer rates for DNAPLs in groundwater are sensitive to flow fields and velocities at the DNAPL-water interface (Miller et al., 1990; Powers

et al., 1994; Saba and Illangasekare, 2000). Thus reductions in permeability and flow bypassing away from the DNAPL-water interface have the ability to reduce mass-transfer from DNAPL pools (MacKinnon and Thomson, 2002; Heiderscheidt et al., 2008a). This local change in permeability also reduces the advective transport of permanganate to the DNAPL-water interface. As the permanganate reaction period increases and more MnO_2 builds up, the reduction in permeability near the DNAPL-water interface becomes more significant.

When applying permanganate ISCO to DNAPLs, some have observed enhanced rates of DNAPL dissolution initially as described in the previous section, but over time the dissolution rate progressively declined, often to much slower rates than the dissolution rates observed prior to permanganate oxidation (Schnarr et al., 1998; Huang et al., 2000; MacKinnon et al., 2002; Li and Schwartz, 2003; Tunnicliffe and Thomson, 2004; Urynowicz and Siegrist, 2005). Although this effect has been observed with various DNAPL architectures, it appears to be magnified when treating DNAPL present in pools (Conrad et al., 2002; Heiderscheidt et al., 2008a). This is probably due to the larger surface area for mass transfer of contaminants present as ganglia compared to pools, as well as to challenges in contacting zones of continuous DNAPL saturation because advective flow is impeded by the DNAPL. Thus, in many pooled systems, the DNAPL mass transfer has been observed to decline with time (Li and Schwartz, 2000; MacKinnon and Thomson, 2002; Lee et al., 2003).

The effects of permeability reduction with time at DNAPL-water interfaces and the reduced mass caused by flow bypassing have important implications for remediation effectiveness. This phenomenon has been considered to be both an advantage and a disadvantage for remediation. The advantage is that encrusting DNAPL pools with a MnO_2 “rind” may effectively encapsulate DNAPLs, immobilizing them and limiting their dissolution. This could impart a permanent reduction in plume loading rates and contaminant mass flux (MacKinnon and Thomson, 2002; Mueller et al., 2006, 2007). The disadvantage is that significant inefficiencies in flushing are encountered; as time progresses, more and more oxidant bypasses the contaminant, leading to reduced treatment effectiveness. Furthermore, a potentially significant contaminant mass may remain in the subsurface. To help prevent or mitigate the effects of flow bypassing with time, some have proposed innovative solutions to either prevent the MnO_2 solids from depositing, or to remove them after they have deposited. These perspectives and the scientific evidence behind them are discussed in more detail below.

Encapsulation of DNAPLs by MnO_2

It has been proposed that deposition of MnO_2 at the DNAPL-water interface may, over time, effectively encapsulate the DNAPL so well that it could limit DNAPL mobilization and inhibit further dissolution, thus reducing groundwater plume concentrations and flux rates. This presumably would mitigate risk and become an effective remediation outcome if the DNAPL could be stabilized in this fashion (Mueller et al., 2007; Thomson et al., 2008). However, for this to be effective, the MnO_2 film that forms a “capsule” around the DNAPL should: (1) have sufficient integrity to prevent DNAPL immiscible phase mobilization, (2) limit or block DNAPL dissolution, and (3) be stable over the long term. Evidence differs on whether these requirements can be met and under what conditions.

MacKinnon and Thomson (2002) reported that after exposure of a PCE pool to permanganate, the MnO_2 deposition zone at the DNAPL interface was so thick and consolidated that the MnO_2 had effectively cemented aquifer sand into MnO_2 “rocks” (Figure 3.14). Such a high degree of consolidation would seem to imply that MnO_2 may be structurally sound enough to prevent a DNAPL from migrating. However, evidence from the experiment of Conrad et al. (2002) points to the contrary, where after MnO_2 had built up on a series of DNAPL residuals and pools in a heterogeneous sand tank, DNAPL was physically observed to have migrated

through one of the MnO_2 rinds after the experiment was finished. However, Conrad et al. (2002) only flushed their heterogeneous tank with two pulses of permanganate at $750 \text{ mg MnO}_4^-/\text{L}$, each pulse lasting about 1.5–2 h, resulting in a total dose equivalent to 0.67 pore volumes. By comparison, MacKinnon and Thomson (2002) flushed their tank with $7,500 \text{ mg MnO}_4^-/\text{L}$ for about 150 days, resulting in an oxidant delivery of about 13 pore volumes. Thus, the difference in time of exposure, concentration of permanganate, and pore volume delivery may explain the apparent difference in the structural integrity of the MnO_2 . In the subsurface, especially at heterogeneous sites, the oxidant solution volume (pore volumes) and concentration (mg/L) as well as the duration of oxidant contact are all likely to be variable at any given point in the aquifer. Thus, DNAPLs within a source zone may have some areas where they are better contained by these MnO_2 rinds than others. In general, it appears that there is the potential for immobilizing DNAPL through the deposition of MnO_2 , but higher oxidant solution volumes, concentrations, and contact times may be required.

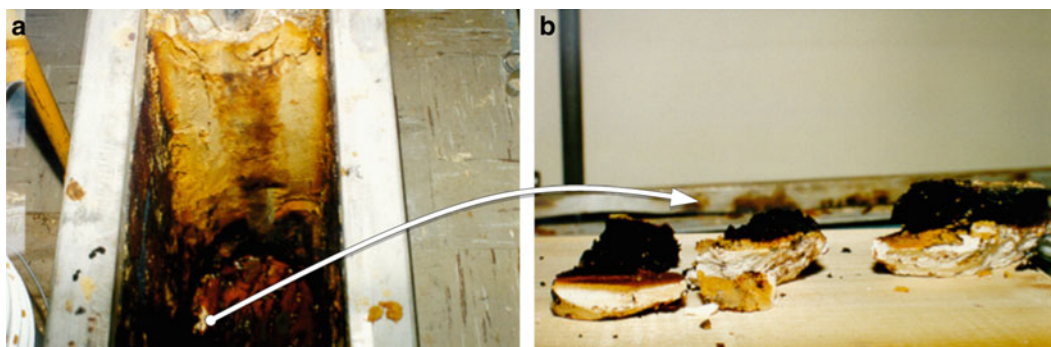


Figure 3.14. MnO_2 crust formation at the interface of a DNAPL pool in a model aquifer system in a 2-D sand tank used to study permanganate flushing to deplete pooled PCE DNAPL: (a) view down into the 2-D tank during the excavation process, and (b) several sections of the sand/silica flour interface removed from the model aquifer showing that the accumulation of MnO_2 had agglomerated, so that rock-like deposits of MnO_2 and sand were formed (MacKinnon and Thomson, 2002).

Many studies have noted declines in dissolution rates with time from DNAPL sources that have MnO_2 films or crusts deposited at the DNAPL-water interface (Li and Schwartz, 2000, 2004c; MacKinnon and Thomson, 2002; Heiderscheidt et al., 2008a; Urynowicz and Siegrist, 2005). MacKinnon and Thomson (2002) demonstrated that while only 45% of a PCE pool mass was destroyed by the oxidation reaction, the contaminant mass flux leaving the tank, and therefore the dissolution rate, declined by more than 75%. It is unclear if MnO_2 can completely inhibit DNAPL dissolution (e.g., prevent diffusion of the contaminant through the “rind”) or if the mass transfer decline is mainly due to changes in permeability in the porous media near the DNAPL-water interface caused by the MnO_2 . For example, Struse et al. (2002b) investigated the diffusive transport of permanganate in fine-grained silty clay soil and noted that permanganate caused virtually no change in diffusive transport properties. This might imply that MnO_2 does not inhibit diffusive transport; however, the study by Struse et al. (2002b) included TCE in both dissolved and sorbed phases but with little or no DNAPL present.

Urynowicz (2000) studied mass transfer of TCE from a droplet of neat TCE suspended in a static aqueous system and explored the effects of permanganate (Figure 3.15). Urynowicz found that the mass transfer from the TCE droplet when exposed to permanganate declined with time and eventually ceased altogether (Urynowicz, 2000; Urynowicz and Siegrist, 2005). As the experiment progressed, a MnO_2 film was observed to encapsulate the DNAPL

(Figure 3.15a, b). After a period of time, SEM analysis revealed a plate-like film with small tears in the film (Figure 3.15c, d). One of the limitations of SEM analysis is that samples are dried prior to or during the analysis so it is unclear if this may have altered the appearance or structure of the MnO_2 film. However, the presence of tears in the film, if not an artifact of sample preparation, might indicate that MnO_2 deposits around NAPLs may not always have sufficient integrity to completely eliminate mass transfer into the aqueous phase. Thus it is questionable whether or not the MnO_2 solids formed *in situ* can form an impervious boundary around a DNAPL that is capable of blocking mass transfer.

The third requirement for effective encapsulation of a DNAPL is that the MnO_2 film or rind must be persistent in the subsurface and not deteriorate over time. This is the least investigated facet of MnO_2 deposition, and more work in this regard is clearly needed. However, there is information that provides some insight into the longevity of MnO_2 deposits. Figure 3.4, adapted from Duggan et al. (1993), shows the dominant manganese species as a function of Eh-pH. Eh-pH diagrams have the disadvantage that assumptions must be made about what species are in solution, and at what concentrations; this may, in turn, impact the predictive results, especially on a quantitative basis. Furthermore, they do not evaluate kinetics of reactions. Some reactions may be thermodynamically favorable, but occur at such slow rates that they are effectively unimportant. However, Eh-pH diagrams are instructive about the nature of the various mineral species. The diagram from Duggan et al. (1993) indicates that solid species of manganese oxides, whether pyrolusite (MnO_2), manganate (Mn_2O_3), hausmannite (Mn_3O_4), rhodochrosite (MnCO_3), or pyrochroite ($\text{Mn}(\text{OH})_2$), are expected to be dominant at neutral to alkaline pH, and the specific mineral phase that was favored was primarily a function of Eh. However, at a neutral to acidic pH and a positive Eh, dissolved Mn^{2+} was by far the most dominant species. As described in Section 3.2.5, MnO_2 functions as an oxidant at acidic pH, and yields Mn^{2+} as a product. Since MnO_2 may effectively act as an oxidant, and a DNAPL is effectively a reductant, and in this application they lie in direct contact with each other, it would appear that there is a strong potential for a reductive dissolution reaction to occur with the MnO_2 rind if acidic pH conditions are present. If alkaline conditions are present, the longevity of MnO_2 appears more likely. However, the potential exists for the conversion from one phase to any of the other mineral phases noted above. It is unknown if conversion reactions would impact the stability of the MnO_2 film. One study by Sahl (2005) noted that in an anaerobic column inoculated with PCE degrading organisms, the MnO_2 that had deposited in the column was completely removed after oxidation ceased and flushing with an anaerobic growth medium was resumed. It was impossible to tell if this conversion was either biotic or abiotic involving components of the anaerobic growth medium, but clearly there are some conditions where MnO_2 is unstable.

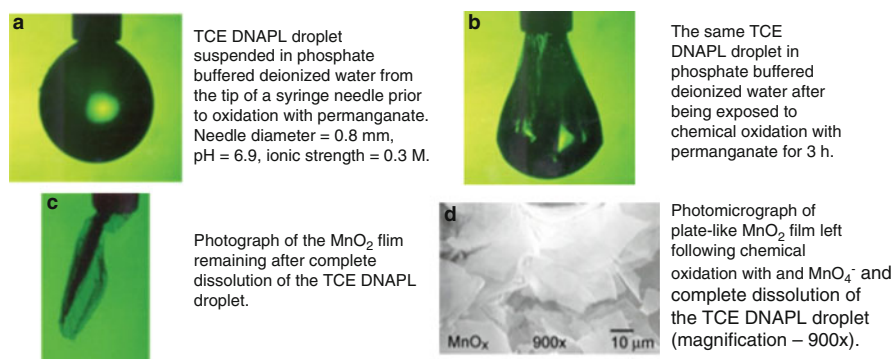


Figure 3.15. Observations of MnO_2 formation on a droplet of TCE DNAPL (Urynowicz, 2000).

Mitigating Efficiency Problems Caused by MnO_2 Deposition

Many investigators have noted declining rates of DNAPL dissolution with time as MnO_2 deposits around sources, and thus rates of contaminant treatment by oxidation decline as well. This results in inherent inefficiencies when using permanganate flushing of DNAPL source zones in aquifers, as often the majority of the injected permanganate may bypass the DNAPL contaminated zones (Li and Schwartz, 2000, 2004c). For example, in the experiment from MacKinnon and Thomson (2002), approximately 45% of the total of 0.7 kg of PCE DNAPL was destroyed and recovered as chloride over the course of the 150-day experiment in a media with virtually no NOD. Yet, this required the addition of about 8.5 kg of potassium permanganate, yielding an effective stoichiometry of ~ 29 moles of permanganate per mole of PCE degraded; this is far higher the theoretical stoichiometry of 4 moles of permanganate to 3 moles PCE degraded (refer to Equation 3.22). This is largely because much of the injected permanganate never contacts the DNAPL to degrade it. Furthermore, the yield of chloride declined with time, indicating that the effective stoichiometry was reducing further as MnO_2 continued to inhibit dissolution. Therefore, many have looked for methods to mitigate or prevent MnO_2 deposition at the DNAPL interface.

To help alleviate the problems of MnO_2 deposition and its negative impacts on flushing efficiency and pore clogging, several methods for solids control, as well as alterations to injection methods, have been proposed. Optimization of injection parameters may be one way of controlling the deposition of MnO_2 in a manner that is less likely to cause permeability reduction and reduced mass transfer. Petri (2006) noted that when treating DNAPL source zones, if either the groundwater velocity was high, or the oxidant concentrations were low to moderate, the MnO_2 deposition was much more dispersed than in slow velocity or high oxidant concentration systems, where deposition was concentrated at the DNAPL-water interface. Deposition of MnO_2 solids away from the interface and over a larger zone in the subsurface (Figure 3.16) might help to reduce the severity of the permeability reduction that can occur with MnO_2 deposition. Dissolution from the DNAPLs was also fast in high velocity systems, leading to rapid depletion of DNAPL mass.

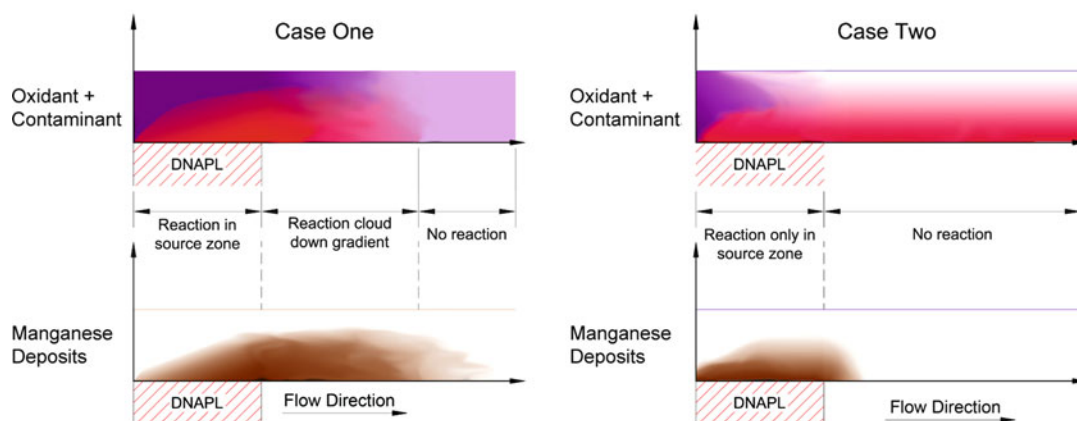


Figure 3.16. Illustration of a reaction cloud during flushing at higher velocity and lower oxidant concentration that evolves away from the DNAPL-water interface resulting in dispersed MnO_2 deposition (Case 1) compared to more localized reaction and deposition (Case 2), which develops under lower velocity and higher oxidant concentrations (Petri, 2006).

Heiderscheidt et al. (2008b) evaluated the permeability loss from MnO_2 deposition at a high NOD field site and model simulations predicted a more favorable dispersed deposition of

MnO₂ when high injection flow rates and moderate oxidant concentrations were used. However, at most field sites, there will be limits to how high a velocity may be achieved, depending on the subsurface hydraulic conductivity in the target treatment zone. Furthermore, moderate oxidant concentrations may require longer injection times to achieve the injection of an equivalent mass of oxidant delivered with a higher oxidant concentration, which may increase costs associated with field time. NOD may be a significant factor as well. Thus, delivery optimization must consider many different factors, in addition to the potential to enhance mass transfer and control MnO₂ deposition.

Several have proposed chemical methods for controlling MnO₂ deposition. Li and Schwartz (2004b, 2004c) proposed a method where organic acid flushes could be cycled with oxidant injections to complex and dissolve MnO₂ after it is deposited in the subsurface. Several biodegradable acids, such as citric acid or oxalic acid, have the ability to reductively dissolve MnO₂ at appreciable rates. Using a method in a 2-D tank that involved cyclic flushing of permanganate followed by organic acid flushes, Li and Schwartz were able to achieve complete removal of a DNAPL source and its associated MnO₂ from a heterogeneous formation. However, a potential disadvantage is that the acid volume requirements to completely remove MnO₂ between each oxidant flush were much larger than the oxidant flush volumes. In addition, though many carboxylic acids are resistant to permanganate oxidation, reaction may still proceed at appreciable rates. Thus, residual oxidant may degrade organic acids injected into the subsurface requiring either an initial water flush or overdosing with the acid to overcome this demand. Likewise, a water flush may be needed with subsequent injections of permanganate to avoid oxidant loss due to reaction with the organic acid.

A chemical amendment approach that has been explored that does not induce an oxidant demand, involves co-injection of chemical additives that act as stabilization aids (Crimi and Ko, 2009; Crimi et al., 2009). Ions such as phosphate can stabilize MnO₂ particles in solution by altering their surface charges as they are produced by the oxidation reaction. In water treatment applications, it is generally desirable to destabilize particles by neutralizing their surface charge, allowing them to flocculate into large particles and settle from solution. However, in controlling MnO₂ to mitigate permeability reduction, the opposite is desired. Imparting a strong surface charge to the MnO₂ colloids inhibits flocculation due to the repellent forces between particles. Thus, with stabilization aids, MnO₂ may remain dispersed in solution as colloids or nano- to micro-sized particles that may be transported considerable distances in the subsurface and thereby reduce the degree of localized permeability reduction associated with standard injections of permanganate.

Crimi and Ko (2009) evaluated a series of potential stabilization agents that are non-toxic, including sodium hexametaphosphate (HMP), xanthan gum, gum arabic, and Dowfax 8390. Their results indicated that HMP had the best performance for stabilizing MnO₂ particles based on studies of particle filtration, size distribution, and zeta-potential (an indicator of surface charge). Further studies by Crimi et al. (2009) investigated simultaneous injection of permanganate and HMP into columns containing DNAPL and four different porous media to observe the impact of HMP on MnO₂ deposition. It was found that HMP significantly reduced the deposition of MnO₂ in the DNAPL source zone by 25–87%, depending on the porous media. Specifically, compared to a control system (permanganate only), inclusion of HMP with permanganate delivered to varied porous media having significant clay content, organic matter, or iron mineral content resulted in the total amount of MnO₂ deposited in the source zone to be reduced by about one-half to one-sixth. This demonstrates the potential of HMP to reduce the negative effects of MnO₂ associated with permeability reduction and reduced DNAPL dissolution.

3.3.2.4 Oxidation Impacts on Contaminant Sorption

Permanganate may have the potential to impact sorption of contaminants to porous media surfaces, possibly enhancing desorption during oxidation. However, the mechanisms and effects of permanganate ISCO on sorption processes are much less investigated than impacts of permanganate on other mass-transfer and transport processes, such as with DNAPLs. With hydrogen peroxide, it has been reported that contaminant desorption rates may be significantly enhanced in oxidation systems, as opposed to baseline or control conditions (Watts et al., 1999). It is conceivable that enhanced desorption rates could result from permanganate reactions via several possible mechanisms:

- Enhanced release of sorbed contaminant due to the degradation of aqueous contaminant, shifting the equilibrium between dissolved and sorbed phases to favor more desorption.
- Enhanced release of sorbed contaminant by destruction of the NOM matrix, releasing and degrading contaminant sorbed to the matrix.
- Alteration of the physical characteristics of NOM, potentially reducing its ability to sorb organic contaminants.
- MnO_2 deposited in the subsurface may sorb contaminants, as well as potentially coat or passivate other organic sorption substrates, impacting their sorption activity.

The nature of changes to NOM resulting from permanganate ISCO may be important to remediation and the consideration of contaminant sorption processes in two ways. Contaminant sorption at many sites is typically modeled with a simple linear relationship given by Equation 3.18.

$$K_d = f_{oc}K_{oc} \quad (\text{Eq. 3.18})$$

where, K_d is the distribution coefficient for contaminant between aqueous and organic matter phases, f_{oc} is the fraction of organic carbon, and K_{oc} is the contaminant organic carbon partition coefficient.

Degradation of NOM mass by permanganate may have an impact on sorption simply by reducing the f_{oc} value and thus reducing the total amount of sorption sites available in the media; this has been demonstrated to occur (Schnitzer and Desjardins, 1970; Ortiz De Serra and Schnitzer, 1973; Griffith and Schnitzer, 1975; Almendros et al., 1989; Seitz, 2004; Woods, 2008). However, the oxidation reaction, especially if it is selective in nature, may have the potential to alter the physiochemical properties of the matrix impacting sorption as well. For instance, K_{oc} values have been shown to be related to the abundance of either hydrophilic or hydrophobic functional groups within the organic matrix, with K_{oc} increasing with the abundance of hydrophobic functional groups (Kile et al., 1999). If permanganate degrades some functional groups preferentially to others, then the hydrophobicity of the organic matter may change, with resulting changes to the K_{oc} value.

Woods (2008) investigated permanganate effects on TCE sorption to porous media. In several different porous media containing TCE that were treated with permanganate at a concentration of 10,700 mg MnO_4^-/L , the f_{oc} was reduced in some by more than 63% of the initial f_{oc} value before oxidation, though reductions of around 20–25% were more common. This provided evidence that significant NOM mass may be lost due to permanganate oxidation reactions. Presumably, contaminant sorbed to the mass that is lost is also subject to degradation. This change to the f_{oc} value also has implications for contaminant sorption after ISCO is applied. If the K_{oc} value of the NOM is unchanged by the oxidation reactions, then the depletion of f_{oc} mass results in a corresponding loss of the media's sorption capacity for the contaminant. If the pre- and post-remediation concentrations of COCs are equal and all other factors are also equal but there is a 50% decline in the f_{oc} , then the total mass of sorbed

contaminant is reduced by a corresponding 50%. However, based on aqueous contaminant concentrations alone, this will not be apparent. Woods (2008) also measured that despite the loss of NOM from soils, the overall K_d partitioning coefficients in the porous media were generally either unchanged or significantly increased as a result of permanganate treatment. This implies that media treated by permanganate may have additional capacity to sorb contaminants though the mechanism responsible for this increased sorption is unclear.

3.3.2.5 Impacts of Permanganate ISCO on Metal Mobility

ISCO using permanganate can affect metal mobility in groundwater by altering pH and Eh, generating MnO_2 solids, changing ionic composition, destroying or altering NOM, or by introducing metals present as impurities in the commercially available permanganate (Siegrist et al., 2001; Crimi and Siegrist, 2004a). Generally, conditions indicating lower risk of metal mobility at a given contaminated site are: high pre-ISCO pH and buffering capacity, highly oxidizing conditions, an abundance of cation exchange sites, and presence of metals less mobile under oxidizing conditions. Concern about metal mobility should be higher at sites where high concentrations ($>1,000$ mg/L) of permanganate are going to be used for longer periods (90 days or more) and at sites already characterized by low pH and buffering capacity, low cation exchange capability, high total dissolved solids content, and presence of natural metals or co-contaminant metals (Siegrist et al., 2001).

Alteration of pH and Eh

Changes in soil and groundwater pH have been shown to greatly affect the mobility of metals (Chuan et al., 1996). Depending on the contaminants present and the pre-ISCO site conditions, permanganate ISCO can drop the pH of a system below 3 (Siegrist et al., 2001; Petri et al., 2008) or raise it above 10 (Nelson et al., 2001; Sirguy et al., 2008). At low pH, the solubility and mobility of metal cations such as lead (Pb), cadmium (Cd), and zinc (Zn) can be markedly increased (Forstner et al., 1991; Chuan et al., 1996). At higher pH, most metals tend to precipitate or adsorb to porous media surfaces.

Permanganate ISCO has also been observed to raise system Eh to as high as +800 millivolts (mV) (Siegrist et al., 2001). Highly oxidizing conditions can increase the mobility of metals of concern through a variety of pathways depending on site conditions (Forstner et al., 1991).

Formation of MnO_2

The MnO_2 formed during permanganate oxidation can adsorb heavy metals, mitigating the effects of increased metal mobility or impurities in $KMnO_4$ (Siegrist et al., 2001). However, the sorption capacity of MnO_2 varies for different metals (Al et al., 2006). Manganese dioxides formed during permanganate ISCO can contribute significantly to the sorption of a number of metals including aluminum (Al), copper (Cu), cobalt (Co), Zn, nickel (Ni), Pb, silver (Ag), titanium (Ti), uranium (U) and Cd in soil (Nelson et al., 2001).

Al et al. (2006) showed at the bench scale that MnO_2 particles have a large capacity to mitigate the metal mobilization induced by other aspects of permanganate ISCO. They introduced a mixture of TCE and $KMnO_4$ (also containing 1 mg/L Cu, Pb, Zn, molybdenum (Mo), Ni, and chromium (Cr(VI))) at the inlet of two soil columns containing different proportions of sand and calcite. Analysis of post-experiment MnO_2 from both columns showed that Mo, Pb, Ni, and Cu were completely attenuated in the column at a wide range of pH levels (2.4–6.25). The attenuation effect was not complete; Zn was not impeded and Cr(VI) was transmitted conservatively through the columns.

Other system parameters such as pH may affect how well MnO_2 attenuates mobile metals during ISCO. Crimi and Siegrist (2004a) showed that cadmium is more highly associated with

particles at pH 7 compared to those at pH 3. Siegrist et al. (2001) reported that at low metals concentration, increasing pH dramatically increases the metal sorption capacity of MnO_2 particles, much as it increases the metal sorption capacity of porous media. At high metal concentrations, however, it appears pH has little or no effect on the sorption of metals by MnO_2 .

Alteration of Ionic Content

Permanganate oxidation has been observed to increase exchangeable ions such as calcium (Ca), magnesium (Mg), and potassium (K) in the subsurface (Nelson et al., 2001; Sirguy et al., 2008). Some of these ions, such as calcium, can compete with heavy metals for sorption sites (Crimi and Siegrist, 2004a). Under some conditions, adsorbed heavy metals could be displaced and be made available for aqueous transport by these exchangeable ions.

Destruction or Alteration of NOM

Permanganate ISCO can change the metal sorption potential of NOM through oxidation (Siegrist et al., 2001). It has been shown that increased permanganate doses can lead to a proportional decline in porous media TOC values (Crimi and Siegrist, 2004a; Woods, 2008). Sirguy et al. (2008) reported that addition of permanganate strongly decreased the amount of organic carbon and nitrogen in a variety of soils. NOM degradation can lead to the release of NOM-associated metals such as Cu or Zn (Brennan, 1991).

Introduction of Metals as Impurities in Permanganate

Another potential cause of elevated concentrations of metals during ISCO with permanganate is the incidental injection of heavy metals present as trace contaminants within the commercially available permanganate products as a result of their manufacture. Generally, chromium and arsenic have been the two metals of most concern as trace impurities. As a result, some early applications of permanganate using technical grades of permanganate have exceeded the low MCLs for these metals. Generally, potassium permanganate contains more trace impurities than sodium permanganate, but the application concentrations with sodium permanganate are also higher, so this may be a concern with both forms of permanganate (Huling and Pivetz, 2006). More recently, chemical manufacturers have tried to address this problem by developing grades of permanganate specifically for ISCO that have lower concentrations of these metals. Permanganate used for remediation should be obtained with a lot analysis that includes data on the concentrations of trace metals, enabling a user to determine if metal impurities will potentially exceed MCLs. If the metals content is high enough that it runs the risk of exceeding MCLs or if a site is particularly sensitive to the metals concentration, this problem might be solved by reducing the concentration of permanganate solution injected into the subsurface (Siegrist et al., 2001).

Metals Mobilization Observed During Permanganate ISCO

Permanganate ISCO at the field scale has been shown to elevate the presence of metals in the subsurface. Crimi and Siegrist (2003) observed significantly elevated levels of Ni, Mn, and Cr in manganese dioxide aggregates present in site groundwater. They attribute the findings largely to site-specific conditions resulting from a significant quantity of permanganate used, a large amount of DNAPL present, and the site geology. Chambers et al. (2000a, b) found elevated levels of Cr(VI) in groundwater at a site treated with permanganate and attributed this to the combination of traces of chromium in the permanganate, as well as oxidation of chromium in the subsurface porous media.

Usually, natural attenuation of metals that might be elevated by permanganate ISCO yields concentrations that reach an acceptable value over a relatively short span in time and space after oxidant injection is terminated (Huling and Pivetz, 2006). In the above research of

Chambers et al. (2000a, b), for example, the increased levels of Cr(VI) dropped back to well below the MCL over a period of 3 months.

Moore (2008) evaluated data from 30 field sites where permanganate ISCO was employed. One parameter evaluated was dissolved chromium concentrations with respect to time. While there were differences in trends as a function of site natural conditions and design features, overall results indicated that chromium concentrations increased immediately after addition of oxidant, but attenuated within 6 months to 1-year post-ISCO. Moore (2008) also considered dissolved Mn concentrations of particular interest as an important potential byproduct of permanganate oxidation that may be expected to persist post-ISCO. Results indicated that levels attenuated within 2 years, and these trends were predictable based on pH and oxidation-reduction potential (ORP) measurements. Moore (2008) also reported that these elevated metals concentrations were found directly within the target treatment zone and were not observed downgradient, except where groundwater velocities exceeded 46 cm/day (1.51 feet [ft]/day).

3.3.2.6 Density-Driven Advection

When dissolved in aqueous solution, any dissolved solute may alter the density of the solution when present in sufficient concentrations. Permanganate ion may behave in this fashion during permanganate ISCO since oxidant concentrations as high as 1 wt.% or more are used, and this increases solution density. The injection of a dense solution into a groundwater matrix of lesser density can cause the dense solution to travel downwards due to gravitational forces. Schincariol and Schwartz (1990) reported that this can happen in subsurface systems when the density difference between fluids is as little as 0.0008 g/cm^3 , equal to the density difference caused by the concentration of 1,000 mg/L of sodium chloride (NaCl). In groundwater systems, fluid movement obeys Darcy's law, so the hydraulic conductivity of the media is a factor in density advection as well.

In media with high hydraulic conductivity, density driven advection can cause appreciable downward velocities of the dense solution. However, low permeability media may effectively limit advection, and thus downward movement may stop when the dense solution encounters an aquiclude. Lateral movement may then occur as the solution ponds on an aquiclude (Schincariol and Schwartz, 1990). The density-driven advection of solutions of permanganate is known to occur and has been reported by several investigators (Nelson, 1999; Stewart, 2002; Siegrist et al., 2006). Stewart (2002) reported on the injection of a 4–5% (wt.%) solution of potassium permanganate into a stagnant aquifer system consisting of a medium sand with a thin TCE DNAPL pool lying on an impermeable sand layer. They observed that the initial radius of oxidant injection was approximately 2 meters (m) (6.6 ft), but the solution migrated downward until it ponded on top of the aquiclude and TCE pool and then migrated laterally. A slight dipping of the aquiclude also encouraged density flow to accelerate in the direction of the dip. Eleven weeks after injection, the permanganate plume had achieved a radius of 3–6 m (9.8–19.7 ft). Post-ISCO monitoring indicated that areas of residual and pooled DNAPL up to 5 cm (2 inches [in]) thick were effectively degraded, and permanganate had diffused up to 15 cm (6 in.) into the aquiclude, while pools up to 13 cm (5 in.) thick still had considerable free product left.

This passive delivery technique would seem to indicate advantages when treating DNAPLs, as the downward migration of the permanganate solution may encourage contact with DNAPL migration pathways. Nelson (1999) noted that significant downward advection could be noted within 2 days of permanganate injection into a sand aquifer and that a unique injection method using direct push technology could create stacked coalescing treatment zones that would enhance oxidant contact with the media over time. Frazer et al. (2006) noted that

density-driven advection was a major process that occurred at a full-scale implementation of ISCO, resulting in improved distribution of the oxidant in a heterogeneous aquifer.

Henderson et al. (2009) investigated density-driven flow as a means to deliver permanganate to DNAPL located in groundwater at the surface of an aquitard. The researchers enhanced a multicomponent reactive transport code (MIN3P) to simulate permanganate-based ISCO. The new code, MIN3P-D, includes a direct coupling between density-dependent fluid flow, solute transport, contaminant treatment, and geochemical reactions. Henderson et al. (2009) used the model to simulate a field trial of TCE oxidation in a sandy aquifer that is underlain by an aquitard. The general spatial and transient evolution in observed concentrations of the oxidant, dissolved TCE, and reaction products were reportedly adequately reproduced by the MIN3P-D simulations. Density-driven movement of permanganate was observed to occur into DNAPL containing regions located at an aquifer–aquitard interface.

3.4 CONTAMINANT TREATABILITY

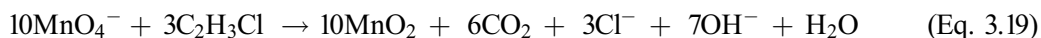
Permanganate is capable of degrading a wide variety of COCs through the reactions described in Section 3.2. The reaction chemistry, kinetics, and products are dependent on the COCs being treated and the conditions within the subsurface. This section describes the degradability of specific contaminant classes by permanganate. There are many different categories of contaminants for which permanganate degradation has been investigated; however, there are also numerous gaps. A generalized assessment of the treatability of different organic compounds during permanganate ISCO is given in Table 3.3. Chapter 9 includes guidance and tools for appropriate selection of permanganate ISCO based on site-specific factors including the COC characteristics, site conditions, and treatment goals.

3.4.1 Chloroethenes

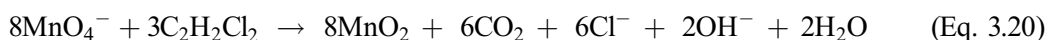
Permanganate has long been known to attack alkene bonds (Ladbury and Cullis, 1958; Arndt, 1981; Fatiadi, 1987), rendering this category of contaminant highly amenable to oxidation by permanganate. The degradation of chloroethenes by permanganate has been extensively investigated; the mechanisms involved and the reaction products are widely understood.

The following stoichiometric relationships have been established for the oxidation of four common chloroethenes by permanganate (Equations 3.19–3.22). These provide a theoretical relationship between reactants and products based on complete mineralization of the contaminant, as well as the assumption that the dominant reaction occurring is the half reaction shown in Equation 3.2 where permanganate ion transfers three electrons yielding MnO_2 as a reaction product.

Vinyl Chloride:



Dichloroethene:



Trichloroethene:



Perchloroethene:

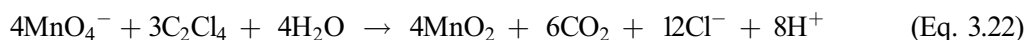


Table 3.3. General Assessment of the Treatability of Different Organic Compounds by Permanganate ISCO

Contaminant group	Section ^a	Contaminant treatability by permanganate?	Comments
Chlorinated aliphatic compounds			
Chloroethenes	3.4.1	High	Chloroethenes are degraded readily with permanganate. Compounds like PCE and TCE have been extensively studied and the mechanisms and products are well understood
Chloroethanes	3.4.2	Negligible	Due to saturated nature of these compounds (e.g., 1,1,1-trichloroethane [1,1,1-TCA]; 1,1-dichloroethane [1,1-DCA]) they do not react readily with permanganate
Chloromethanes	3.4.2	Negligible	Due to the saturated nature of these compounds (e.g., carbon tetrachloride [CT]) they do not react readily with permanganate
Chlorinated aromatic compounds			
Chlorophenols	3.4.4	High	Isomers of chlorophenol react readily with permanganate at rates that are 10 to 100x faster than most chloroethenes
Polychlorinated biphenyls/dioxins/furans	3.4.5	No	Based on compound structure and studies to date, these compounds do not react with permanganate
Hydrocarbon compounds			
Benzene, toluene, ethylbenzene, and total xylenes (BTEX)	3.4.3	Conditional	Benzene is almost nonreactive, but the other BTEX compounds can be degraded but at rates that are 10 to 100x slower than for PCE
Saturated aliphatic hydrocarbons	3.4.3	Negligible	Due to the saturated nature of these compounds and their low aqueous solubility, they do not react readily with permanganate
Methyl tert-butyl ether (MTBE)	3.4.3	Negligible	Reaction rates are much lower than chloroethenes
Phenolic compounds	3.4.4	High	Phenols and isomers of chlorophenol react readily with permanganate at rates that are 10 to 100x faster than most chloroethenes; isomers of nitrophenol react at rates similar to chloroethenes
Polycyclic aromatic hydrocarbons (PAH)	3.4.5	Conditional	Reactivity of PAHs with permanganate varies widely depending on compound structure and conditions
Other organic compounds			
Explosives and nitroaromatic compounds	3.4.6	Conditional	Reactivity with permanganate varies widely depending on compound structure and conditions. For some degradation has been shown, though at very slow rates; nitrophenols are rapidly degraded.
Pesticides	3.4.7	Uncertain	Degradation has been observed for a few compounds, but limited studies have been done

^aThe number refers to the Section within this chapter where information on the treatability of each respective contaminant group is discussed.

As is evident from the stoichiometry, the amount of permanganate required to degrade a chloroethene is inversely related to the degree of chlorination (Table 3.4). This makes intuitive sense because the more chlorinated ethenes are more oxidized; therefore, it should take fewer electron transfers for the oxidant to bring them to mineral reaction products. In addition, the more chlorinated ethenes produce more acidity (H^+), while the less chlorinated ethenes may produce alkalinity (OH^-). This has been observed in laboratory studies where the degree of pH drop with each chloroethene was proportional to the degree of chlorination (Huang et al., 2001).

Table 3.4. Stoichiometric Requirements for Mineralization of Chloroethenes and Several other Organic Compounds by Permanganate^a

Target compound	Molecular weight (g/mol)	Oxidant demand (g MnO_4^- /g of target)	MnO_2 produced (g MnO_2 /g target oxidized)
Perchloroethene	165.6	0.96	0.70
Trichloroethene	131.2	1.81	1.32
Dichloroethene	96.8	3.28	2.39
Vinyl chloride	62.4	6.35	4.64
Phenol	94.1	11.8	8.62
Naphthalene	128.2	14.8	10.8
Phenanthrene	178.2	14.7	10.7
Pyrene	202.3	14.5	10.6

^aMolecular weight of MnO_4^- = 118.9 g, MnO_2 = 86.9 g, $KMnO_4$ = 158 g, and $NaMnO_4$ = 141.9 g.

Although these stoichiometric relationships provide important information, there are limitations to their use in practice. For example, in any *in situ* application, there will be some degree of NOD associated with the aquifer materials, which will compete with the contaminant for the oxidant. As a result, the amount of oxidant needed to degrade the contaminant in the presence of NOD will be much greater than the stoichiometric requirement. Furthermore, the effective stoichiometry can deviate depending on reaction conditions and permanganate delivery. For instance, if the pH drops over the course of reaction to ranges where the half reaction shown in Equation 3.1 becomes dominant, the stoichiometry will change, often reducing the ratio of permanganate to contaminant required due to the stronger oxidation that occurs under these conditions. Furthermore, as discussed in Section 3.2.3 the rate-limiting step is the formation of a cyclic ester, followed by decomposition via various hydrolysis and oxidation reactions to form organic acids or mineralized byproducts. However, in some situations where the contaminant is present well in excess of permanganate, such as may be the case adjacent to NAPLs, there may just be enough permanganate to initiate the reaction but not enough to degrade slower reacting organic acids or subsequent oxidation reactions, in which case the stoichiometry will no longer hold true. Petri et al. (2008) observed that in a 1-D system with TCE and PCE DNAPL present that stoichiometric ratios of permanganate to contaminant were significantly lower than given by reactions in Equations 3.21 and 3.22 for some system conditions.

During the degradation of chloroethenes, the formation of a cyclic hypomanganate ester compound is generally thought to be the rate-limiting step, which can be described by second-order kinetics. The only exception to this is the case of vinyl chloride (VC), which apparently undergoes a two-stage kinetic process since the formation of the cyclic hypomanganate ester with VC is somewhat reversible and different kinetic rates prevail before and after a reversible

equilibrium is established (Huang et al., 2001). Reaction conditions such as pH and ionic strength have largely been found to have little effect on the initial rate-limiting step.

Table 3.5 summarizes the second-order rate constants for each of six chloroethenes that have been determined in multiple studies. These rate constants were all measured at ambient temperature ranges between 20 and 25°C but under a wide range of oxidant concentrations, chloroethene concentrations, and pH conditions. The agreement between the different values across this range of experimental conditions indicates that the rate of chloroethene degradation is not particularly sensitive to any of these parameters. However, the rates do vary substantially in magnitude between chloroethenes, which is largely due to steric effects associated with the number of chlorines and their position within the molecule. For instance, *trans*-1,2-dichloroethene (*trans*-DCE) is the fastest degrading of any of the ethenes, while PCE is the slowest, with over three orders of magnitude difference between the two. Despite this range in rates of oxidation, all the reactions are considered fast enough to enable effective ISCO treatment.

Table 3.5. Summary of Rate Constants for Reaction of Permanganate with Selected Chloroethenes at 20–25°C

Contaminant	pH	MnO ₄ ⁻ concentration (mg/L as MnO ₄)	Contaminant concentration (mg/L)	Rate constant (M ⁻¹ s ⁻¹)	Study
PCE	10.6	150–3,800	0.6–0.8	0.028 ± 0.001	Dai and Reitsma (2004)
	~5.2	3,800–23,000	48–111	0.041 ± 0.011	Hood et al. (2000)
	7	95–750	17	0.035 ± 0.004	Huang et al. (2001)
	7	12	166	0.043	Waldemer and Tratnyek (2006)
	4–8	120	<17	0.045 ± 0.03 ^a	Yan and Schwartz (1999)
	Average:			0.038	
TCE	7	95–750	13	0.80 ± 0.12	Huang et al. (2001)
	7	12	132–525	0.76 ± 0.03	Waldemer and Tratnyek (2006) ^a
	7	12	132–525	0.46 ± 0.05	Waldemer and Tratnyek (2006) ^a
	7	12	132–525	0.67 ± 0.05	Waldemer and Tratnyek (2006) ^b
	4–8	120	<13	0.67 ± 0.03	Yan and Schwartz (1999)
	Average:			0.67	
<i>cis</i> -DCE	7	95–750	9.7	1.52 ± 0.05	Huang et al. (2001)
	7	36	290–1,160	0.71 ± 0.06	Waldemer and Tratnyek (2006)
	4–8	120	<10	0.92 ± 0.5 ^a	Yan and Schwartz (1999)
	Average:			1.05	

(continued)

Table 3.5. (continued)

Contaminant	pH	MnO ₄ ⁻ concentration (mg/L as MnO ₄)	Contaminant concentration (mg/L)	Rate constant (M ⁻¹ s ⁻¹)	Study
<i>trans</i> -DCE	7	95–750	9.7	48.6 ± 0.9	Huang et al. (2001)
	4–8	120	<10	30 ± 2 ^a	Yan and Schwartz (1999)
	Average:			39.3	
1,1-DCE	7	95–750	9.7	2.1 ± 0.2	Huang et al. (2001)
	4–8	120	<10	2.38 ± 0.13 ^a	Yan and Schwartz (1999)
	Average:			2.24	
VC	7	95–750	6.2	Two-step kinetics	Huang et al. (2001)

^aStatic systems – differences between the two values unclear.

^bStopped flow apparatus.

The cyclic hypomanganate esters that form when permanganate reacts with chlorinated ethenes are unstable and decompose rapidly via different pathways depending on pH and the chloroethene being degraded. At low pH, reaction with protons (H⁺) causes the carbon-carbon bond in the ester to break, releasing either formyl chloride (in the case of TCE) or phosgene (in the case of PCE). These, in turn, are both rapidly hydrolyzed releasing the chlorine as hydrogen chloride (HCl), and results in carbon dioxide (in the case of PCE) and formic acid (in the case of TCE) (Yan and Schwartz, 2000; Huang et al., 2002). At neutral and high pH, the cyclic hypomanganate ester is broken down through a series of fast hydrolysis reactions, which result in the complete dechlorination of either PCE or TCE, with the chloride released as HCl; the end products include several organic acids. Oxalic acid was a primary product produced by both, but glycolic and glyoxylic acids have also been observed (Yan and Schwartz, 2000; Huang et al., 2002). All of these organic acids may be further degraded and mineralized to CO₂ by reaction with permanganate, but these reactions have been observed to be slower than the reaction with the original chloroethene, so their accumulation in solution is possible. Because these potential byproducts are fully dechlorinated and they are also common natural substrates that are readily degradable by microbes, their accumulation in solution is not an issue from a risk assessment perspective and may even benefit subsequent bioremediation or natural attenuation efforts.

3.4.2 Chloroethanes and Chloromethanes

In comparison to chloroethenes, chloroethanes and chloromethanes, such as 1,1,1-TCA, 1,1-DCA, CT, and others, do not readily react with permanganate. Waldemer and Tratnyek (2006) attempted to measure kinetic rate constants for the degradation of these and other related compounds and found them to be $<4 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. The saturated nature of these compounds and the lack of a double bond makes them much less susceptible to oxidation in aqueous solution; many authors that have tried to oxidize these compounds and report little or no treatment (Gates-Anderson et al., 2001; Cho et al., 2002; Jazdanian et al., 2004). The sole exception to this trend is chloroform (CHCl₃), which has a unique chemistry that allows it to degrade at slow but appreciable rates in an aqueous solution (Waldemer and Tratnyek, 2006).

Seol et al. (2001) investigated the degradation of 1,1,2-TCA and 1,1,2,2-TeCA DNAPLs using permanganate with a phase transfer catalyst that allowed permanganate to partition directly into the organic phase and they reported high degradation efficiencies. However, it is unknown if the phase transfer catalyst enables reaction mechanisms to occur that cannot occur within aqueous systems.

3.4.3 BTEX, MTBE, and Saturated Aliphatic Compounds

The permanganate oxidation of BTEX compounds has been studied, though not as extensively as that of chloroethenes. BTEX compounds represent a common component of fuel-related contamination, such as light nonaqueous phase liquid (LNAPL) spills of petroleum hydrocarbons. In addition, BTEX is often a minor component of PAH-containing wastes, such as creosote or coal tar. The kinetics of BTEX degradation by permanganate are generally much slower than those of chloroethenes, ranging from 10 to 100 times slower than PCE, the slowest reacting chloroethene (Waldemer and Tratnyek, 2006). Benzene, in particular, degrades so slowly that, for all practical purposes, it is in effect unreactive with permanganate (Forsey, 2004). This presents a major challenge to the application of permanganate to BTEX contamination, as benzene is regulated by the USEPA more strictly than the other BTEX components. For example, the benzene MCL is 5 parts per billion (ppb), as opposed to toluene at 1,000 ppb, ethylbenzene at 700 ppb, and total xylenes of 10,000 ppb.

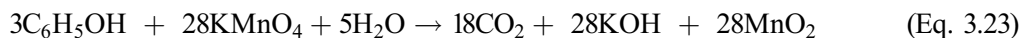
The mechanism of degradation of BTEX compounds, as described by Waldemer and Tratnyek (2006), is different than that of chloroethenes, where instead of forming a cyclic ester, the oxidant attacks a benzylic C–H bond (a hydrocarbon bond on an alkyl side chain of the aromatic ring). Toluene, ethylbenzene, all xylene isomers, and isopropylbenzene all contain benzylic C–H bonds and all react with permanganate at slow but appreciable rates. Since benzene has no benzylic C–H bonds, as well as high aromaticity, it is almost unreactive with permanganate. Forsey (2004) also noted that tert-butyl benzene, which is substituted with an alkyl side chain but lacks a benzylic C–H bond, was also effectively unreactive with permanganate.

The oxidation of MTBE has also been investigated. Damm et al. (2002) found the reaction of MTBE to be much slower than that of typical chloroethenes, with a second-order reaction rate constant of $6.26 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. This is also slower than MTBE degradation rates typically observed with hydrogen peroxide and ozone. The reaction was independent of pH from pH 5–10 and had a mole ratio of 2:1 permanganate to MTBE (Damm et al., 2002). Reaction products that formed include tert-butyl formate (TBF) and tert-butyl alcohol (TBA). These products have also been detected in the oxidation of MTBE by other oxidants, such as hydrogen peroxide (Burbano et al., 2002; Ray et al., 2002). However, permanganate has considerable difficulty in degrading tertiary alcohols, which have also been used as solvents for permanganate reactions in industrial applications. Thus, it is unlikely that TBA produced from MTBE will degrade further by permanganate oxidation (Singh and Lee, 2001). Consequently, TBA accumulation is likely to occur when oxidizing MTBE with permanganate.

To date, the oxidation of saturated aliphatic compounds typical of petroleum hydrocarbons has been much less investigated. The lack of carbon-carbon double bonds in saturated aliphatic hydrocarbons and their extremely low solubility make them poor candidates for oxidation by aqueous permanganate. The reactions between permanganate and saturated hydrocarbons that have been reported in the literature have generally occurred using non-aqueous solvents, phase transfer catalysts, or highly concentrated acids, all of which are unrealistic for most ISCO applications (Arndt, 1981; Fatiadi, 1987). When these oxidation systems were successful in producing reactions, products from these reactions generally included carboxylic acids (Fatiadi, 1987). However, in the permanganate treatment of a fuel mixture, significant degradation of saturated hydrocarbons in the free product is not anticipated.

3.4.4 Phenols

Potassium permanganate has been used for chemical oxidation of phenolic compounds during wastewater treatment. The stoichiometric equation for the oxidation of phenol by KMnO_4 is given by Equation 3.23:



According to Equation 3.23, the mineralization of phenol consumes a relatively large quantity of permanganate, 11.8 g of MnO_4^- per g of phenol (Table 3.4).

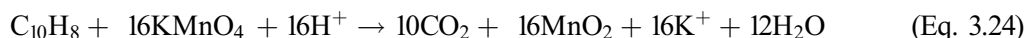
While benzene and other aromatic contaminants containing only hydrocarbon substituted functional groups are slow reacting with permanganate, phenolic contaminants where the benzene ring is substituted with one or more hydroxy groups are among the fastest reacting compounds. Phenol and various isomers of chlorophenol have been observed to have reaction rates 10–100 times faster than most chloroethenes, and nitrophenol isomers have been observed to react at similar rates as chloroethenes (Waldemer and Tratnyek, 2006). This indicates a very strong potential for their successful remediation with permanganate. However, the reaction mechanisms and intermediate products are not as well understood as those of the chloroethenes. Phenols are thought to be degraded by a one-electron transfer reaction with permanganate (Waldemer and Tratnyek, 2006). Byproducts that have been observed have included quinone and other products suggesting ring cleavage. Phenol reactivity is impacted by pH, as phenols may deprotonate depending on their pKa value. The ionic (phenolate) form generally has much faster reactivity than the protonated form (Waldemer and Tratnyek, 2006). Generally, most phenol contaminants have pKa's in the neutral to alkaline pH range, though some nitrophenols and pentachlorophenol are exceptions with pKa's in the acidic range. Thus, when treating phenolic contaminants, faster degradation kinetics may be expected under alkaline conditions.

3.4.5 Polycyclic Aromatic Hydrocarbons

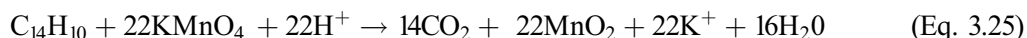
Some PAHs have been shown to be oxidized by permanganate, and several investigations have been made into the reaction kinetics, mechanisms, intermediates, and effectiveness (Gates et al., 1995; Gates-Anderson et al., 2001; Lamarche, 2002; Brown et al., 2003; Forsey, 2004; Thomson et al., 2008). However, there are also some PAH compounds that are refractory toward permanganate oxidation. Among these are biphenyl and dibenzofuran, which do not degrade to any appreciable extent in the presence of permanganate (Siegrist et al., 2001; Forsey, 2004; Thomson et al., 2008).

In early experimental studies, Gates et al. (1995) evaluated the permanganate treatment of sand and silty clay soil contaminated by a mixture of naphthalene, phenanthrene, and pyrene. Equations for the mineralization of these compounds are shown in Equations 3.24–3.26.

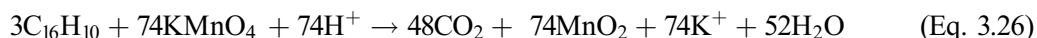
Naphthalene:



Phenanthrene:



Pyrene:



Gates et al. (1995) used batch experiments to examine the relative treatment effects of soil type, oxidant loading rate as well as the use of surfactant or iron amendments and pH adjustment. The initial concentrations of PAHs were: naphthalene = 260–337 mg/kg, phenanthrene = 248–341 mg/kg, and pyrene = 226–331 mg/kg. Prior to oxidant addition, it was estimated that 90–99 wt.% of the PAHs would be in the NAPL phase with only limited mass in the aqueous phase and sorbed to the soil solids. For both soil types, the KMnO_4 treatment efficiencies for naphthalene, phenanthrene, and pyrene were >90% at a 20 g/kg oxidant loading (Figure 3.17).

Brown et al. (2003) evaluated structure activity relationships for the degradation of PAHs sorbed to soil. They found that PAH reactivity varies substantially, but general trends could be explained by the nature of electron distribution within the PAH as determined by Clar diagrams, as discussed in Section 3.2.3. Of the six PAHs they investigated, they found that the extent of treatment declined in the order of benzo(a)pyrene > pyrene > phenanthrene > anthracene \gg fluorine > chrysene, using a zero-order kinetic approach. However, no second-order reaction rates were reported for these PAH compounds.

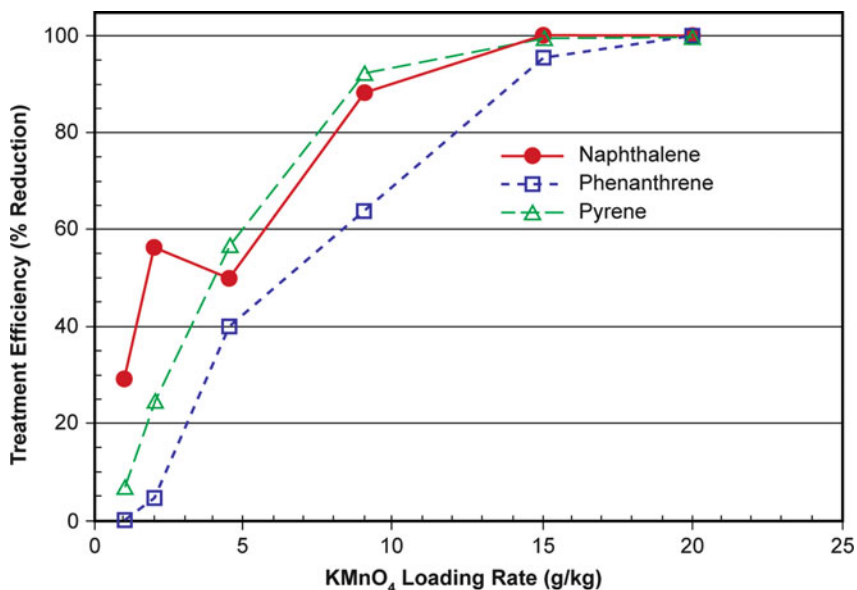


Figure 3.17. Oxidation of PAHs in clay soil slurries during a 48-h period at 20°C as a function of permanganate loading (Siegrist et al., 2001).

Forsey (2004) evaluated the kinetics and intermediates of permanganate degradation of a series of PAH components in DNAPL creosote using batch and 1-D column experiments. The oxidation of most of the PAHs analyzed within the creosote mixture could be modeled using second-order kinetics. For compounds where second-order reaction rate constants were reported, they fell within the range of 10^{-3} to $10^0 \text{ M}^{-1} \text{ s}^{-1}$, making the reaction rates fast enough to allow ISCO to be effective. PAHs specifically noted to be degradable included naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, anthracene, phenanthrene, acenaphthene, fluorene, chrysene, fluoranthene, and pyrene. The conversion of naphthalene to a phthalic acid is detailed in Figure 3.18, as presented by Arndt (1981). Forsey (2004) also demonstrated that indole and carbazole, which are aromatic hydrocarbons containing heteroatoms (nitrogen) within a PAH structure, could be degraded by permanganate.

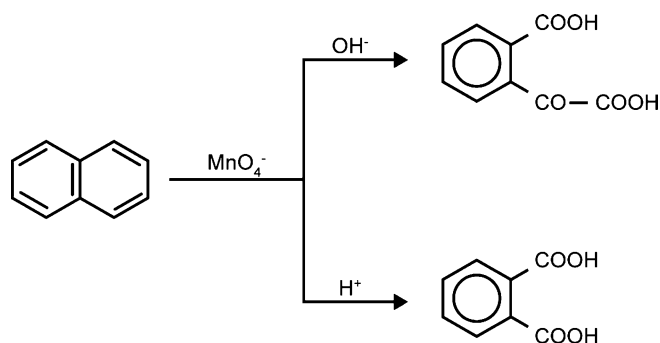


Figure 3.18. Oxidation of naphthalene to aromatic acid byproducts (after Arndt, 1981).

Several intermediate products identified from PAH oxidation included carbonyl ($\text{C}=\text{O}$) group substitution onto the original PAH, resulting in a corresponding polycyclic aromatic ketone (Forsey, 2004). For instance, the oxidation of fluorene resulted in the formation of 9-fluorenone, the oxidation of acenaphthene formed an unstable byproduct, which was identified as acenaphthenone, and the oxidation of anthracene resulted in formation of 9,10-anthraquinone. The former two intermediates were further oxidized by permanganate, and no other hydrophobic intermediates were identified in their subsequent degradation. However, the latter intermediate, 9,10-anthraquinone is known to be very stable in oxidized systems, and a derivative of it is used as a catalyst to manufacture commercial quantities of hydrogen peroxide. Thus accumulation of some stable organic byproducts may occur when treating PAHs with permanganate. Aliphatic and aromatic carboxylic acids may also be included in the byproducts. For example, Arndt (1981) reported high yields of biphenyl-2,2'-dicarboxylic acid from the alkaline permanganate oxidation of phenanthrene.

Because a PAH DNAPL such as creosote or coal tar is typically a mixture of hundreds of different organic compounds (Brown et al., 2006), there are compounds within creosote that are likely resistant to permanganate oxidation. For instance, while PAHs often make up the bulk of creosote or coal tar mass, significant quantities of BTEX and other single-ring aromatic compounds may be present. However, as discussed previously, benzene and tert-butyl benzene are not degraded to any significant degree by permanganate (Forsey, 2004). Furthermore, while wastes such as coal tar or creosote tend to be dominated by aromatic contaminants, there may still be a significant saturated aliphatic hydrocarbon component present (Brown et al., 2006), which is largely inert to permanganate oxidation (Fatiadi, 1987).

The permanganate treatment of a creosote or coal tar DNAPL containing a mixture of degradable and non-degradable components may alter contamination characteristics. One impact observed in the lab experiments reported by Thomson et al. (2008) is that while permanganate treatment may effectively degrade many PAHs and significantly reduce the mass of creosote, the remaining NAPL and sorbed phases will be enriched in the PAHs that are not degradable by permanganate. Thus, aqueous concentrations of these resistant fractions may increase over baseline conditions in accordance with the solubility analog of Raoult's Law, where the effective aqueous solubility limit of a particular compound in a multicomponent NAPL is proportional to that compound's mole fraction within the NAPL (Equation 3.27):

$$C_e = X_n C_s \quad (\text{Eq. 3.27})$$

where, C_e is the effective aqueous solubility limit of a contaminant, X_n is the mole fraction of the contaminant in the NAPL mixture, and C_s is the solubility limit of the contaminant in pure solution. This was observed in batch and column experiments and to some degree in a

pilot-scale experiment, where biphenyl and dibenzofuran concentrations increased in a post-oxidation system indicating enrichment of the DNAPL phase with respect to these resistant PAHs (Forsey, 2004; Thomson et al., 2008).

Given that PAH mixtures have fractions that are oxidizable and not oxidizable, it is unlikely that permanganate ISCO will ever achieve complete destruction of these DNAPLs. However, the research does show potential for the source mass to be reduced with a reduction in the mass loading to a groundwater plume. Thomson et al. (2008) demonstrated that the treatment of a creosote DNAPL in a column experiment with permanganate decreased the total mass of the measured PAH components by 33%, which resulted in a decrease of the total mass discharge of 25%. In a field demonstration at the Canadian Forces Base Borden research site, Thomson et al. (2008) employed a semi-passive pulse injection system to deliver permanganate to treat a creosote source zone. With four upgradient injection wells, a pulse injection system was used to sustain permanganate concentrations in the source zone to maximize the oxidation reaction rates and diffusion related concentration gradients. A total of six pulsing episodes were performed with an average permanganate concentration of about 13 g KMnO₄/L for a total of about 125 kg of KMnO₄. An injection rate of 5 L/min was selected for delivery of the design volume in approximately 10 h, resulting in minimal disturbance to the ambient flow field. Based on an estimated average linear groundwater velocity of 10 cm/day, the tail of each permanganate pulse was expected to migrate sufficiently downgradient of the injection wells in approximately 7 days to necessitate another injection episode to maintain the presence of permanganate within the source zone. Thomson et al. (2008) reported that after 150 days, the mass discharge estimated in groundwater at a downgradient fence line was reduced for all monitored compounds (Table 3.6). This mass discharge reduction (about 2.0 to 1.1 g/day) was observed despite an inability to show a difference in pre- and post-treatment DNAPL masses from soil cores due to source zone heterogeneities. Because many of the PAHs analyzed are among a suite of 16 that are regulated by the USEPA, it is possible that further depletion of these components by permanganate flushing may enable meeting regulatory goals despite leaving a non-reactive fraction (such as saturated hydrocarbons or others) remaining in the subsurface.

Table 3.6. Changes in Mass Discharge in a Groundwater Plume at a Monitoring Fence Line 150 Days After Permanganate ISCO of a Creosote Source Zone (Thomson et al., 2008)

Contaminant	Discharge		Change in mass discharge (%)
	Pre-ISCO (mg/day)	Post-ISCO (mg/day)	
Naphthalene	750	310	-59
1-methylnaphthalene	200	120	-40
Acenaphthalene	15	6	-58
Biphenyl	84	71	-15
Acenaphthene	430	200	-53
Fluorene	110	51	-54
Carbazole	61	18	-70
Dibenzofuran	250	210	-16
Phenanthrene	96	60	-37
Anthracene	31	14	-55
Fluoranthene	13	11	-11
Pyrene	9	3	-63
Total	2,048	1,075	-47

3.4.6 High Explosives and Related Compounds

Several authors have reported success in degrading high explosive compounds, though they are somewhat more challenging to degrade than chloroethenes. For example, permanganate has been applied for the treatment of RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) (Adam et al., 2004; Adam and Comfort, 2005; Waldemer and Tratnyek, 2006). Most explosive compounds targeted for remediation contain nitro groups ($-\text{NO}_2$), which Schnitzer and Desjardins (1970) reported as generally making organic compounds more resistant to oxidation due to their electron withdrawing properties. Nonetheless, degradation may occur.

Adam et al. (2004) conducted extensive treatability studies on the degradation of RDX for use at a field site. They found RDX degradation by permanganate to proceed at a slow rate of reaction, with oxidation continuing at measurable rates up to 30 days or more. Although a second-order reaction rate was not reported, the rates were reported to be considerably slower than the rate of PCE oxidation. The rate of reaction was also found to be insensitive to initial pH over the range of pH 4–11 and RDX concentrations from ~1–10 mg/L. Although the exact reaction pathways and mechanisms are unclear, it was noted that up to 87% RDX carbon release to CO_2 could be achieved, indicating a substantial degree of mineralization. A proportion of the nitrogen content of RDX, about 20–30%, was transformed to N_2O , a common species within the nitrogen cycle. Neither nitrate nor ammonia production were observed, suggesting that N_2O or other nitrogen species were the ultimate fate of RDX nitrogen. This contrasts with products formed during the hydrogen peroxide treatment of RDX, which can include large amounts of ammonia and nitrate (Bier et al., 1999). One organic intermediate suspected to be produced by the reaction was identified as 4-nitro-2,4-diazo butanal. Other intermediates may also be produced, as evidenced by residual organic carbon within the water, but they were not identified. However, microcosm studies suggested that these intermediates were more readily biodegraded than the parent RDX compound, based on CO_2 production rates (Adam et al., 2004; Adam and Comfort, 2005). Thus, given the high degree of mineralization attainable for RDX, it is quite treatable by permanganate. However, the very slow rate of reaction requires extended contact time with permanganate and thus NOD kinetics over long time periods may be a key consideration when treating RDX.

Permanganate oxidation of other contaminants in this category has been investigated to a lesser degree. Nitrophenols, a common co-contaminant that may be found at many explosive-contaminated sites, are observed to have rapid rates of degradation by permanganate like other phenolic contaminants. Waldemer and Tratnyek (2006) reported rate constants for a series of nitrophenols and found them to have reaction rates in similar ranges as chlorinated ethenes, although they were slower than many of the chlorophenol contaminants. 2,4,6-Trinitrotoluene (2,4,6-TNT) also exhibited rates of degradation similar to nitrophenols, although picric acid was found to have a much slower rate of degradation, similar to RDX. However, the reaction pathways and degradation products of many of these other compounds are not well known.

3.4.7 Pesticides

The degradation of some pesticides by permanganate has also been investigated, but again to a much lesser degree than other contaminants. Tollefsrud and Schreier (2002) evaluated the degradation of aldrin, dieldrin, alpha-chlordane and gamma-chlordane in soil and found they all degrade to varying extents, with aldrin degrading the most extensively and dieldrin the least. All four of these pesticides share some structural similarities, but the faster reaction of aldrin may be due in part to the presence of an ethene bond that is not present in the others. Permanganate is well documented for its ability to react with ethene bonds (Ladbury and Cullis,

1958; Fatiadi, 1987). The lower treatment effectiveness for dieldrin might have been due to the fact that in the study by Tollesrud and Schreier (2002) the contaminated soils were aged and dieldrin, which is very hydrophobic, may have been strongly sorbed. Byproducts, intermediates, and reaction pathways were not evaluated, so it is not possible to determine if these compounds were being mineralized in the system evaluated.

3.5 SUMMARY

Many facets of permanganate ISCO have been studied extensively, including the mechanisms of permanganate chemical reactions, the degradability of organic contaminants of concern, and the interactions of permanganate with the subsurface environment. Research has shown that the chemistry of permanganate is quite predictable, involving direct reaction with organic compounds. The degradation of certain contaminant groups, especially chloroethenes and to a lesser extent PAHs, has been extensively investigated and represents the bulk of the knowledge regarding permanganate ISCO. However, there remains operational uncertainty in permanganate ISCO applications, particularly because of the complexity of transport processes controlling delivery of permanganate in the subsurface. Although permanganate transport processes have been widely studied, and there exists a substantial body of knowledge, the magnitude of their impact varies with site-specific conditions. One of the most important factors affecting application of permanganate ISCO is the subsurface NOD. NOD, the nonproductive consumption of permanganate that aquifer materials exert, is known to be widely variable and site-specific and it can strongly influence permanganate ISCO performance. NOD is a kinetically controlled process, but to date, the kinetics elude simple prediction based on easily measurable site-specific characteristics. Thus, the methods for accurate characterization of NOD at a site are based on laboratory test procedures and field push-pull tests.

Other important considerations include the potential impacts of permanganate ISCO on DNAPL dissolution processes and the impacts of the solid phase manganese dioxide (MnO_2) on permeability. Permanganate has been demonstrated to effectively destroy some DNAPLs, especially those present as residual ganglia, at rates far greater than ambient dissolution rates, which leads to more rapid mass depletion. However, DNAPL treatment can also be hindered by the formation of MnO_2 in the source zones, especially where pooled DNAPLs are present. MnO_2 deposits may reduce permeability of porous media near DNAPL source zones, and divert permanganate solution around the sources, which will lead to inefficient oxidant-contaminant contact and reduced DNAPL dissolution. MnO_2 film formation on DNAPLs is generally considered a problem to be avoided because it restricts oxidant-contaminant contact. Operational strategies are needed to prevent MnO_2 precipitation. Permanganate also is believed to affect contaminant sorption processes both by degrading NOM and by altering its sorption characteristics, but this topic has not been investigated extensively. Permanganate itself can act as a dense solution, and this has been proposed for advantageous passive delivery methods by enhancing contact particularly with DNAPLs.

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CHAPTER 4

FUNDAMENTALS OF ISCO USING PERSULFATE

Benjamin G. Petri,¹ Richard J. Watts,² Aikaterini Tsitonaki,³ Michelle Crimi,⁴
Neil R. Thomson⁵ and Amy L. Teel²

¹Colorado School of Mines, Golden, CO 80401, USA; ²Washington State University, Pullman, WA 99164, USA; ³Orbicon A/S, Roskilde, Denmark; ⁴Clarkson University, Potsdam, NY 13699, USA; ⁵University of Waterloo, Waterloo, ON, Canada N2L 3G1

Scope

Chemistry and use of persulfate for *in situ* chemical oxidation of subsurface contaminants, including free radical and other reaction mechanisms, catalysts, subsurface transport, and contaminant treatability.

Key Concepts

- Persulfate reaction chemistry is complex. Persulfate can react through direct electron transfer or free radical reactions. Electron transfer reactions are relatively slow and selective. Upon activation, the free radicals generated have non-specific reactivity that allows for the degradation of a wide range of organic contaminants.
- The radicals that are presently understood to play a major role in reactions are the sulfate radical and the hydroxyl radical. However, there is emerging evidence that the superoxide anion and the perhydroxyl radical also may be important.
- Persulfate activation may be achieved by heat, chelated or non-chelated transition metals (especially iron), hydrogen peroxide, and alkaline pH conditions. The efficiency, effectiveness, and reaction products may vary between contaminants, activation methods, and the porous media to be treated.
- Carbonate, bicarbonate, or chloride ions can act as free radical scavengers and reduce reaction efficiency and effectiveness.
- The kinetics of reaction between persulfate and target compounds is complex. To simplify, pseudo first-order kinetics are often assumed. However, these usually require laboratory estimation because extrapolating between systems is difficult.
- The interaction of aquifer solids and persulfate is not well understood; persulfate does react with aquifer solids resulting in oxidant consumption, but the rate and magnitude of this process are not well characterized. Persistence varies from days to months, depending on conditions.
- The impact of persulfate on metal mobility is not well understood. Conceivably, persulfate could impact metal concentrations in groundwater through modification of pH, oxidation of metals, injection of activation amendments, and other mechanisms.

4.1 INTRODUCTION

Interest in persulfate began in earnest around 2000–2002 when work on persulfate began to appear regularly in conference proceedings and in presentations at major remediation meetings. Because of the relatively short period of time that persulfate has been used for *in situ* chemical oxidation (ISCO) and the fact that persulfate is a less commonly used oxidant in industrial processes and water treatment than hydrogen peroxide, permanganate, or ozone, there is less information available on persulfate. As a result, there is less known about persulfate reaction chemistry, activation methods, contaminant treatability, and subsurface transport. However, the scientific understanding of persulfate for use in ISCO is increasing rapidly and will undoubtedly grow and be refined with time and experience.

4.2 CHEMISTRY PRINCIPLES

To understand the use of persulfate for ISCO and the reasoning behind proper implementation of this technology, it is important to understand the basics of reaction chemistry. Persulfate reaction chemistry is complex, including free radical chain reactions involving initiation, propagation and termination steps; radical scavenging; competing and nonproductive reactions; and oxidation of organic contaminants.

4.2.1 Physical and Chemical Properties

Persulfate, known more formally in the chemistry literature as peroxydisulfate, is a strong oxidant and anion with the formula $S_2O_8^{2-}$. The peroxydisulfate label differentiates this oxidant from peroxymonosulfate, another strong oxidant with the formula SO_5^{2-} . However, peroxymonosulfate is not presently a major ISCO oxidant; for the sake of simplicity, the term persulfate will be used in this volume to refer only to peroxydisulfate. Some important physical and chemical properties of sodium persulfate, the most commonly used form for ISCO, are given in Table 4.1. Persulfate molecular structure is shown in Figure 4.1.

Persulfate is most commonly supplied as a solid sodium salt ($Na_2S_2O_8$). Ammonium persulfate and potassium persulfate solutions are also available but are undesirable for

Table 4.1. Sodium Persulfate Physical and Chemical Properties (from Block, 2006)

Property		Value
Physical form		White crystalline solid
Molecular weight		238.1 g/mol
Solubility limit	0°C	37 wt.%
	25°C	42 wt.%
	50°C	46 wt.%
Solution density	10 wt.%	1.067 g/mL
	20 wt.%	1.146 g/mL
	30 wt.%	1.237 g/mL
	40 wt.%	1.340 g/mL

Note: °C - degrees celsius; g/mL - grams per milliliter; g/mol - grams per mole; wt.% - weight percent.

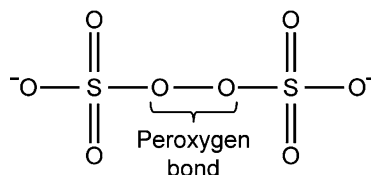


Figure 4.1. Molecular structure of persulfate.

ISCO; the ammonium salt would result in ammonium/nitrate contamination in the subsurface, and potassium persulfate is less soluble and generally more expensive than sodium persulfate. When dissolved in water, sodium persulfate dissociates into sodium cations and persulfate anions. The persulfate ion is quite stable in aqueous solution at room temperature and neutral pH; however, at acidic pH, the persulfate ion slowly hydrolyzes to form peroxymonosulfate (Caro's acid) or hydrogen peroxide (Figure 4.2), with the rate of reaction increasing with decreasing pH (Mariano, 1968). Both of these are highly reactive oxidants that have the potential to oxidize organic compounds (Ball and Edwards, 1956), but their role in persulfate ISCO reactions is unknown.

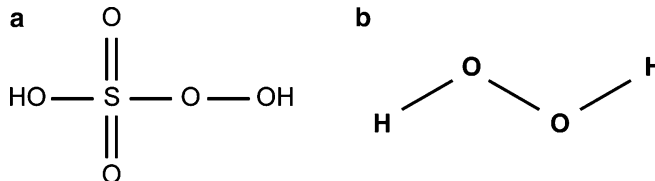


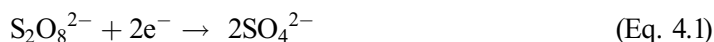
Figure 4.2. Molecular structure of persulfate hydrolysis products: (a) peroxymonosulfate or Caro's acid and (b) hydrogen peroxide.

4.2.2 Oxidation Reactions

Persulfate reaction chemistry is complex – it can involve direct reaction between the target organic and the oxidant, as well as the decomposition of the oxidant into highly reactive free radicals that can then degrade target organic compounds. Persulfate ISCO has similarities to hydrogen peroxide ISCO in that the oxidant is typically “activated” to produce free radicals that have wide non-specific reactivity that allows them to attack a variety of organic contaminants. However, persulfate activation is usually slower than hydrogen peroxide catalysis; therefore, persulfate persistence in the subsurface is typically longer, which can promote more favorable contact times for persulfate to interact with the contaminant. There are a number of activation methods available for persulfate. Each activation method can involve differing reaction mechanisms (Block et al., 2004; Crimi and Taylor, 2007); thus the activation method selected must be matched to the contaminants of concern (COCs) to be treated and the subsurface environment (Block et al., 2004). The chemistry of persulfate may involve a wide variety of free radicals that undergo propagation reactions, including some of the same radicals of importance in hydrogen peroxide chemistry. However, there are radicals that are unique to persulfate chemistry that also serve important roles. Finally, there are a number of reactions between persulfate and aquifer materials that may impact persulfate chemistry and effectiveness, though considerable uncertainty remains in the nature and mechanisms of these reactions.

4.2.2.1 Direct Oxidation

Persulfate is known to react directly with some compounds where no radical intermediates are thought to play a role. House (1962) reported that the standard reduction potential for reaction of persulfate to sulfate anions (Equation 4.1) is 2.01 V.



This high reduction potential indicates that persulfate is a strong aqueous oxidizing agent that makes many oxidation reactions thermodynamically favorable. However, House (1962) indicated that many direct reactions occur at rates that are kinetically slow and that decomposition of the oxidant into free radicals may dramatically improve the rate at which oxidation reactions occur. Recent evidence indicates that direct reaction of the persulfate anion with organics that do not involve radical intermediates also may be significant. For instance, Tsitonaki et al. (2006) reported +99% degradation of methyl tert-butyl ether (MTBE) in a system at ambient temperature, with only MTBE, water, and persulfate ion present (no activators), suggesting that a direct oxidation reaction may be occurring (Figure 4.3). It is also possible that a degree of thermal activation can occur at ambient temperatures.

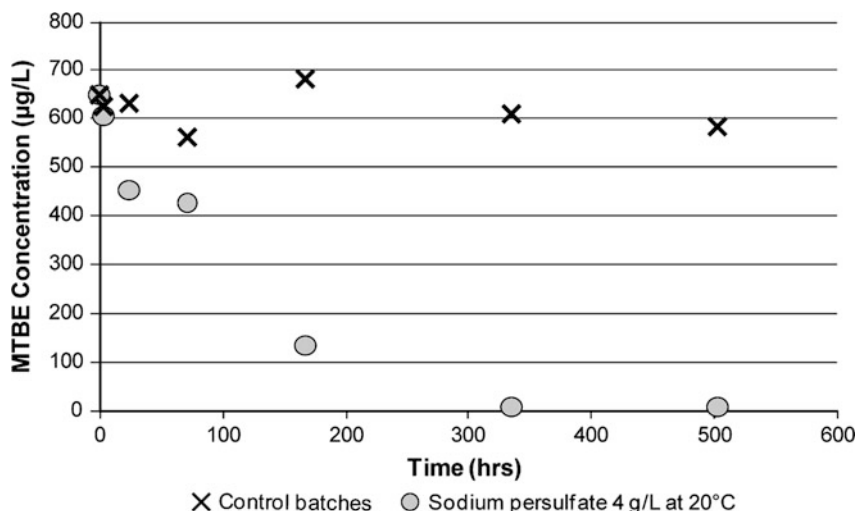
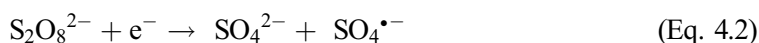


Figure 4.3. Removal of MTBE by sodium persulfate in aqueous systems at ambient temperatures. Experiments performed in headspace free bottles with an aqueous solution of MTBE (650 µg/L) and persulfate (4 g/L). Controls contained no persulfate. Seven replicate bottles were completely mixed at 20°C (68°F), and sacrificially sampled at each time point. From Tsitonaki et al., 2006.

However, probably the most important electron transfer reaction of persulfate appears to occur through a one-electron transfer process, typically with a transition metal, radical, or other reactant, resulting in the production of a sulfate radical ($\text{SO}_4^{\bullet-}$) via the reaction in Equation 4.2.



These reactions are believed to proceed through a one-electron transfer reaction resulting in the cleavage of the peroxygen bond within the persulfate molecule. Typically, a sulfate anion and a sulfate radical are released as products, as well as an oxidized transition metal.

4.2.2.2 Free Radical Oxidation

While direct reaction of persulfate is a potential reaction pathway in ISCO systems, many persulfate reactions occur when the persulfate anion is reacted with another chemical species to form free radicals. This process is termed activation and can provide advantages for persulfate ISCO. Activated persulfate reactions are more rapid and less selective. The trade-off, however, is that persulfate is consumed more rapidly and, potentially, less productively. There are a number of different radicals that are either known or suspected to be formed during persulfate reactions, as well as a wide variety of activation methods. Major radicals known to play a key role in persulfate oxidation systems include the sulfate radical ($\text{SO}_4^{\bullet-}$) and the hydroxyl radical (OH^{\bullet}) (Peyton, 1993; Liang et al., 2007b).

Hydroxyl radicals are strong non-specific oxidants that are common in aqueous free radical systems and have a strong standard reduction potential of 2.59 V in acidic solution (Bossmann et al., 1998). Hydroxyl radicals react through a variety of reaction mechanisms, including direct electron transfer, hydrogen abstraction, and addition to multiple bonds (Bossmann et al., 1998). Reactions with hydroxyl radicals are very fast, often occurring at near diffusion-controlled rates (rates faster than the rate of diffusion can supply the reactants to the site of the reaction), and tend to be in the range of 10^6 – $10^{11} \text{ M}^{-1} \text{ s}^{-1}$ (where M = molar concentration and s = second) (Buxton et al., 1988).

Sulfate radicals are also very powerful non-specific oxidants with a strong standard reduction potential of 2.43 V (Huie et al., 1991) and are a major reaction component of persulfate oxidation systems. However, sulfate radicals react primarily through direct electron transfer, and while their reaction rates with organics are near diffusion controlled rates, they are slightly slower than that of hydroxyl radicals, falling in the range of 10^5 – $10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Neta et al., 1977; Tsitonaki et al., 2010). This slower reactivity may allow for higher concentrations of sulfate radicals to accumulate in solution relative to hydroxyl radicals. Organic oxidation via either hydroxyl radicals or sulfate radicals often results in products that include organic radicals that may then either break down, leading to organic degradation, or react and propagate with other reactants in solution, leading to the formation of new hydroxyl or sulfate radicals.

Thus far, research efforts have mainly focused on the role of sulfate radicals and hydroxyl radicals as the key reactive intermediates in persulfate oxidation systems (e.g., Peyton, 1993; Liang et al., 2006, 2007b). However, there are other radicals in addition to these two that are suspected, but not specifically proven, to play a role in persulfate chemistry as well. These include the superoxide anion ($\text{O}_2^{\bullet-}$) and the perhydroxyl radical (HO_2^{\bullet}), which are also common in hydrogen peroxide systems (De Laat and Gallard, 1999) (see Chapter 2). There are other sulfur-based radicals that have been noted to be important in free radical reactions with sulfite and peroxymonosulfate reaction systems, including $\text{SO}_5^{\bullet-}$ and $\text{SO}_3^{\bullet-}$ radicals (Buxton et al., 1996; Anipsitakis and Dionysiou, 2003), but their occurrence or importance in persulfate-based ISCO systems is not yet known.

Free radical reactions normally involve a series of separate reactions in a reaction chain. Each reaction within the chain can be grouped into three categories: initiation reactions, propagation reactions, and termination reactions. Initiation reactions produce radicals from non-radical species, such as the persulfate anion or hydrogen peroxide. It is these initiation reactions that result in activation of the oxidant. Propagation reactions involve the consumption of one radical and production of another. These reactions can convert one radical species to another, depending on reaction conditions. Termination reactions consume a radical and do not produce any other radicals. Termination reactions represent the final end point of a reaction and may be productive, such as the oxidation of organic contaminants, or nonproductive, such as reaction with non-target organics, minerals, or dissolved solutes.

4.2.2.3 Impact of pH on Radical Intermediates

Persulfate reaction chemistry is pH-dependent. Some of the effects of pH on persulfate activation and chemistry are summarized in Table 4.2. However, assessment of pH effects is complicated by the fact that persulfate reactions affect the pH of the solution. Sulfate is the major inorganic byproduct of persulfate reactions and is an extremely weak conjugate base. Thus, where protons are produced from persulfate reactions, there is potential for a drop in pH; this has been observed in many persulfate systems (Sperry et al., 2002; Block et al., 2004; Waisner et al., 2008). However, the severity of the pH drop is likely a function of the aquifer buffering capacity, as well as the oxidant dose. For instance, Block et al. (2004) noted a pH drop from 7 to nearly 2 in unbuffered batch systems with nearly all activation methods except alkaline activation. Even with alkaline activation, pH changes can occur; Waisner et al. (2008) observed a pH drop from 11 to 9, which could reduce oxidant activation effectiveness. At a field site, Sperry et al. (2002) noted a drop in pH from 5.7 to only 5.3 in monitoring wells, potentially indicating that pH shifts observed under field conditions may be smaller than those in the laboratory. However, this may be partially due to the low resolution of groundwater sampling since strong localized impacts to pH or water quality may be attenuated through mixing/dilution by groundwater from adjacent areas.

Impacts to pH are important to consider because they not only have the ability to shift reaction processes and affect ISCO effectiveness, but they can also affect metal oxidation and mobility. These effects are discussed further in Section 4.3.2.

Table 4.2. Impact of pH on Persulfate Chemistry by Activation Method

Persulfate activation method	Impact of pH on mechanisms and other factors
Alkaline activation	Activation involves raising the pH to 11. At this pH, propagation reactions favor hydroxyl radical as the major reactant over sulfate radical (Liang et al., 2007b). Acid production by the oxidant may cause the pH to drift back down deactivating the oxidant (Waisner et al., 2008).
Iron activation	Iron tends to precipitate at neutral pH and activation can cease. Acidification to pH 3 improves iron availability and activation without chelates (Block et al., 2004).
Chelated-iron activation	Chelated iron improves the ability of iron to stay in solution at neutral pH (Liang et al., 2004b). This in turn improves activation.
Hydrogen peroxide activation	The impact of pH on persulfate-hydrogen peroxide coupled systems has not been extensively reported. However, hydrogen peroxide decomposes at accelerated rates at alkaline and neutral pH, and the free radical chemistry may shift as well.
Heat activation	The impact of pH on heat activation is largely unknown.
Unactivated persulfate	The impact of pH on unactivated persulfate has not been widely investigated. However, data from Block et al. (2004) suggest that unactivated persulfate may be more effective at acidic pH.

4.2.3 Persulfate Activation and Propagation Reactions

Persulfate activation may be achieved by a number of different methods, including the use of heat, chelated or unchelated transition metals, hydrogen peroxide, or strongly alkaline pH; these methods are summarized in Table 4.3 and in text below.

4.2.3.1 Activation Methods

Heat Activation

Persulfate can be decomposed by heat into two sulfate radicals according to the reaction in Equation 4.3. The process is temperature driven, and higher temperatures accelerate the rate of activation dramatically. Heat activation has been studied extensively, at temperatures in the range of 30–60°C (86–140°F) (Huang et al., 2002; Liang et al., 2003; Huang et al., 2005).



Heat activation may result in very aggressive oxidizing conditions. Not only is the rate of activation accelerated, but other reactions between organics, radicals, and other chemical species occur at increased rates as well. The increased rates are typically found to obey the relationship established by Arrhenius (Equation 4.4), where the rate is a function of the activation energy (E_a) and the frequency factor (A), which is a physical parameter representing collision frequency between reactants, and where k is the kinetic reaction rate constant (either first-order or second-order), R is the ideal gas constant, and T is absolute temperature.

$$k = Ae^{-\frac{E_a}{RT}} \quad (\text{Eq. 4.4})$$

Table 4.3. Summary of Key Features of Common Persulfate Activation Approaches

Activation approach	Key features
Heat activation	<ul style="list-style-type: none"> • Higher temperatures accelerate rate of activation • Can result in very aggressive oxidizing conditions • Reaction mechanisms may shift with increasing temperature • Reaction efficiency may shift with increasing temperature (increasing temperature is not always more efficient) • Side reactions (e.g., hydrolysis) can become important with increasing temperature • Temperature may have additional non-reaction impacts such as contaminant volatilization and dissolution
Activation with dissolved metals	<ul style="list-style-type: none"> • Most common persulfate activation approach to date • Ferrous iron [Fe(II)] most common; other transition metals feasible, including ferric iron [Fe(III)] • Fe(II) and Fe(III) can participate in direct redox reactions with contaminant in addition to oxidant activation • Intermediates and products formed vary with pH; low pH conditions tend to be most effective
Activation with chelated metals	<ul style="list-style-type: none"> • Allows for metal catalysis under neutral pH conditions • Fe(II) complexed by ethylenediaminetetraacetic acid (EDTA) or citrate most common to date; others feasible • Optimum ratio of persulfate to metal to chelating agent is key and varies from site-to-site • Chelating agents can be added to porous media systems without additional metal and presumably increase natural metal solubility, making it readily available for activating persulfate • Persulfate may react with chelating agents, affecting their concentration over time

(continued)

Table 4.3. (continued)

Activation approach	Key features
Activation with hydrogen peroxide	<ul style="list-style-type: none"> • Mechanisms are unclear – separate oxidant actions versus combined, interactive impact versus impact of heat generated • Can result in very aggressive and non-specific oxidizing conditions • Optimum ratio of peroxide to persulfate varies site-to-site • Multiple injections of peroxide may be beneficial as it tends to decompose more rapidly than persulfate
Activation with alkaline pH	<ul style="list-style-type: none"> • Sodium hydroxide (NaOH) or potassium hydroxide (KOH) typically used • pH 11 or greater necessary for activation • Several radical species can result from alkaline activation; specific reaction mechanism(s) unclear • Alkaline hydrolysis side reactions with contaminants can be important

Because persulfate oxidation likely involves free radicals that participate in chain reactions with organics and other compounds, there may be many different individual reactions occurring simultaneously. Each reaction within the chain may have different activation energies and frequency factors. Therefore, reaction mechanisms may shift with increasing temperature because some reactions may accelerate more than others. Shifts in mechanism can be important as they affect the overall reaction efficiency.

Generally, when temperature increases, the rate of oxidant decomposition also increases. More often than not, contaminant degradation rates also accelerate. Studies that have evaluated persulfate oxidation of contaminants at multiple temperatures have generally found higher rates and extents of degradation with increasing temperature (Cho et al., 2002; Huang et al., 2002; Liang et al., 2003, 2007b). However, the reaction efficiency may change, sometimes for the worse, because competing side reactions also accelerate (Tsitonaki, 2008). For example, Liang et al. (2006) noted that at 20°C (68°F), scavenging by chloride (see Section 4.2.5.2) became a significant source of inefficiency at a chloride concentration of ~7,000 mg/L; Aiken (1992) noted that at 100°C, the presence of only ~700 mg/L chloride adversely impacted reaction efficiency. Thus, the relative effect of this nonproductive reaction increases with temperature. Data from Tsitonaki (2008) demonstrates the impact of temperature on reaction efficiency, as given in Figure 4.4. Here, the 48-hr degradation of MTBE increases up to a temperature of 35°C (95°F), above which complete oxidation is observed. Yet, for increasing temperatures, the persulfate decomposition continues to increase; thus, for temperatures higher than 35°C, the reaction efficiency in this system is declining as more persulfate is consumed, while the degradation yield remains constant.

At elevated temperatures, other degradation processes beside persulfate chain reactions may also become significant. One potentially important process is contaminant hydrolysis. For common organic contaminants, hydrolysis reactions are generally very slow at ambient temperatures and pH conditions, resulting in the persistence of organic contaminants in groundwater. However, neutral hydrolysis (reaction between the organic and water) and alkaline hydrolysis [reaction between the organic and the hydroxide anion (OH⁻)] both accelerate with temperature. The susceptibility of contaminants to hydrolysis is specific to the organic compound. Some compounds, including some halogenated alkanes, are fairly susceptible to hydrolysis reactions, while others, including chlorinated ethenes, are generally resistant to hydrolysis (Jeffers et al., 1989). Data by Huang et al. (2005) indicate that hydrolysis may be a significant process in heat-activated persulfate systems. For example, in every heat-activated

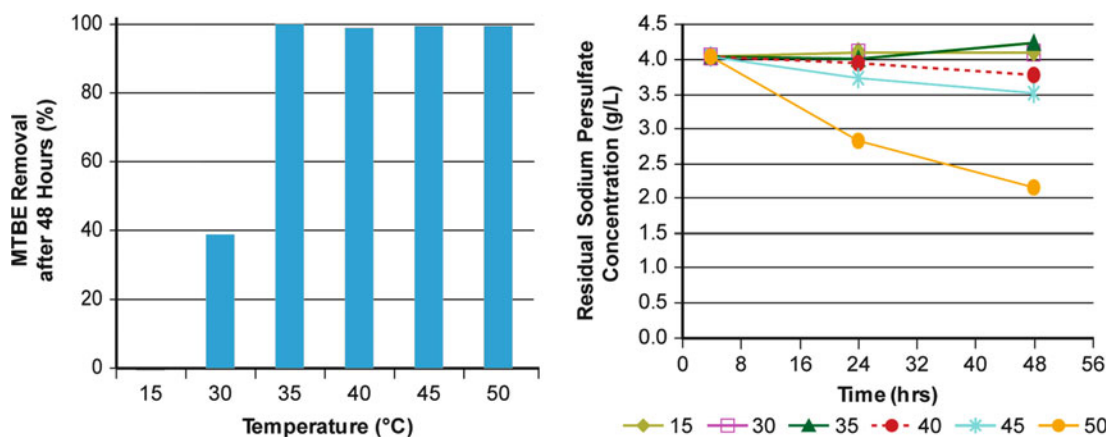


Figure 4.4. Removal of MTBE by sodium persulfate (4 g/L) after 48 h at different activation temperatures (left) and decomposition of persulfate in the same systems (right). Experiments performed in headspace free bottles containing aqueous solution of MTBE (1 mg/L) and sodium persulfate (4 g/L). Experiments were conducted in triplicate and sacrificially sampled at each time point. From Tsitonaki, 2008.

system where temperatures exceeded 30°C (86°F), they noted very rapid degradation of 2,2-dichloropropane regardless of the persulfate concentration. However, nine other halogenated ethanes and propanes were effectively untreated, averaging only 5% removal even under the most aggressive conditions investigated. One would expect that if an oxidative mechanism were responsible for the degradation of 2,2-dichloropropane in this system, then the other nine chemically similar contaminants also would be degraded, at least in part. However, the finding that 2,2-dichloropropane degraded in this system while other halogenated alkanes were resistant makes sense when considering the findings of Jeffers et al. (1989). They investigated the hydrolysis of 16 chlorinated solvents and found that 2,2-dichloropropane had the highest susceptibility to neutral hydrolysis. They found that 2,2-dichloropropane has a half life of approximately 16 h by neutral hydrolysis at 30°C (86°F) and 4 hr at 40°C (104°F), which is well within Huang et al.'s 72-h timeframe. However, while hydrolysis may become a major reaction mechanism for some contaminants at high temperatures, persulfate oxidation reactions may still support degradation of the contaminant via direct attack, as well as by mineralization of byproducts from hydrolysis. For example, alkaline hydrolysis of 1,1,1,2- and 1,1,2,2-tetrachloroethane (1,1,1,2-TeCA and 1,1,2,2-TeCA) yields trichloroethene (TCE) (Jeffers et al., 1989), which is not susceptible to hydrolysis, but is very susceptible to oxidative degradation.

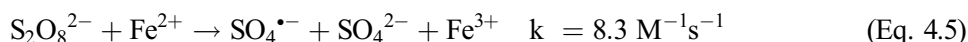
Physical processes may be altered by temperature as well. Many organic contaminants have higher solubility limits at higher temperature, potentially impacting dense nonaqueous phase liquid (DNAPL) dissolution. Volatilization processes also may be accelerated. These processes may further enhance contaminant treatment by promoting DNAPL dissolution or contaminant desorption.

Activation with Dissolved Iron and Other Transition Metals

The use of transition metals is probably the most common activation method reported in the literature. Activation of persulfate by transition metals offers the advantage of accelerating persulfate chemical reactions at ambient temperatures and, through the use of metal-chelate complexes, at ambient pH ranges as well. This may negate the need for alteration of temperature or pH in the subsurface, which could be energy demanding or require large volumes

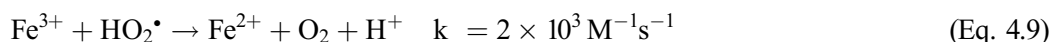
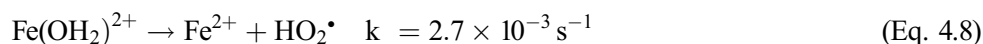
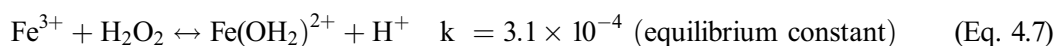
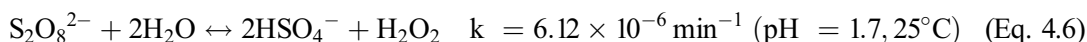
of acids or base. Metal ions that have been explicitly noted to activate persulfate include Fe(II), Fe(III), silver [Ag(I)], and copper [Cu(II)] (Kolthoff et al., 1951; House, 1962; Anipsitakis and Dionysiou, 2004; Block et al., 2004). However, the expense, potential toxicity, and environmental rarity of silver and copper make them unsuitable activators for persulfate ISCO. Thus, Fe(II) and Fe(III) are the two most common transition metal activators used for persulfate ISCO.

The activation of persulfate with Fe(II) is well understood (Kolthoff et al., 1951; Anipsitakis and Dionysiou, 2004; Liang et al., 2004a, b; Crimi and Taylor, 2007). The mechanism is believed to involve a one-electron transfer reaction in which the iron provides the electron to complete the reaction shown in Equation 4.2, yielding the reaction in Equation 4.5 as a result (Kolthoff et al., 1951).



This reaction is in many ways an analog of catalyzed hydrogen peroxide (CHP) reactions (Equations 2.4–2.12 in Chapter 2), where the peroxygen bond within the oxidant is cleaved producing one radical. This radical may then proceed to oxidize target organics or be transformed through propagation reactions.

The mechanism behind Fe(III) activation is much less clear. Liang et al. (2004a) noted that when activating persulfate with Fe(II) the reaction would stall, presumably because the Fe(II) was depleted and, as a result, Fe(III) accumulated in solution. The activity of the system could be revived by either adding more Fe(II) to the system or by adding a thiosulfate reductant to reduce Fe(III) back to Fe(II). This suggests that persulfate activation by Fe(III) may either occur at much slower rates than activation by Fe(II) or possibly be ineffective. Anipsitakis and Dionysiou (2004) reported that Fe(III) had some mild catalytic activity with persulfate, resulting in the degradation of 2,4-dichlorophenol. However, they attributed this to direct reaction between Fe(III) and the aromatic contaminant. Fe(III) is well known to act as an oxidant with some phenolic compounds, particularly catechols and quinones (Chen and Pignatello, 1997; Lu, 2000; Lu et al., 2002), and the product of this reaction is Fe(II), which is then available for persulfate activation. Thus, this apparent activity of Fe(III) as observed by Anipsitakis and Dionysiou (2004) may be an artifact of a slow autocatalytic reaction involving the phenolic contaminant. However, Block et al. (2004) also presented evidence of Fe(III) activation; a persulfate-Fe(III) system was able to achieve significantly higher degradation of chlorinated ethenes, chlorinated benzenes, benzene, toluene, ethylbenzene, and total xylenes (BTEX) and fuel oxygenates, than a persulfate-only control system. While the aromatic contaminants might still promote the iron reduction reaction observed by Anipsitakis and Dionysiou (2004), the degradation of chloroethenes and fuel oxygenates suggests that some catalysis may be occurring. One possibility is the presence of a slow back reaction of Fe(III) to Fe(II) (reactions in Equations 4.6–4.9). Regenerated Fe(II) would then be available for persulfate activation via the reaction in Equation 4.5.



House (1962) reported that the reaction in Equation 4.6 may be promoted under acidic conditions, and the reactions in Equations 4.7 and 4.8 are well known to occur in hydrogen peroxide systems (De Laat and Gallard, 1999). The potential combination of the reactions in Equations 4.5–4.9 indicate that persulfate activation by transition metals might engage in a Haber-Weiss-like catalytic mechanism, where iron is continuously cycled back and forth between Fe(II) and Fe(III) forms, producing radicals until the oxidant is depleted. However, based on current evidence [e.g., reaction stalling seen by Liang et al. (2004a)], this cycle is probably not as robust or strong as the Haber-Weiss cycle observed in hydrogen peroxide systems (Haber and Weiss, 1934). This may be due in part to the reaction in Equation 4.6 being very slow at ambient temperature, which is demonstrated by persulfate's long half life in aqueous solution. For instance, based on first-order rate constants reported by House (1962) for Equation 4.6, a half life of 80 days is predicted in an acidic solution at ambient temperature. Thus, Equation 4.6 may be very slow to occur. Furthermore, hydrogen peroxide may not always be produced from hydrolysis of persulfate. At neutral and alkaline pH, House (1962) observed that oxygen was produced instead of hydrogen peroxide, which would not promote the reaction chain in Equations 4.6–4.9.

Activation with Chelated Metals

Activation of persulfate by dissolved iron also can be affected by iron availability. In water systems, Fe(II) exists in dissolved form [Fe^{2+} or $\text{Fe}(\text{OH})^+$] across a wide range of pH conditions. As oxidant activation proceeds, Fe(II) is oxidized to Fe(III) via Equation 4.5. However, without chelating agents or other solutes present, the soluble forms of Fe(III) [Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$] tend to be prevalent only at acidic pH, while at neutral pH, Fe(III) will tend to precipitate as solid ferric hydroxide [$\text{Fe}(\text{OH})_3$]. When Fe(III) precipitates from the reaction, its activity toward oxidants is reduced or even eliminated (Figure 4.5). Thus, to maintain activation of a persulfate system with iron over extended periods of time, the iron must be present in solution. This may be accomplished by either acidification of a solution (or aquifer) to around pH 3, where Fe(III) becomes soluble, or by the use of organic-iron ligand complexes (or chelates) to maintain iron in solution at neutral pH. The latter approach has been widely employed as a method to enable iron activation at neutral pH (Cho et al., 2002; Block et al., 2004; Jazdanian et al., 2004; Liang et al., 2004b; Nadim et al., 2005; Dahmani et al., 2006; Tsitonaki et al., 2006; Crimi and Taylor, 2007). Block et al. (2004) noted that in a system where the pH was forced to remain neutral (buffered), the chelated-iron system performed much better than an equivalent non-chelated iron system. However, in the unbuffered system where the pH decreased to 2 from the persulfate reaction (Equation 4.7), both systems performed equivalently. Thus, the chelate allowed the system to function at neutral pH, presumably due to improved iron availability.

Studies that have used chelating agents have generally found that iron-chelate complexes improve the treatment effectiveness over equivalent non-chelated iron systems (Block et al., 2004; Liang et al., 2004b; Dahmani et al., 2006). Liang et al. (2004b) presented one of the more comprehensive evaluations of chelated-iron activation and investigated the use of citric acid, EDTA, sodium triphosphate (STPP), and 1-hydroxyethane-1,1-diphosphonic acid (HEDPA). Use of citric acid led to the most extensive contaminant degradation. The others activated persulfate more slowly and thus might promote oxidant persistence. With activation by iron chelates, the molar ratios of oxidant:iron:chelator appear to have a strong impact on overall effectiveness. Liang et al. (2004b) reported that a 1 : 5 molar ratio of chelating agent to iron led to the best performance, though if iron concentrations were low, then comparatively more chelating agent was needed to maintain iron in solution. Similarly, Crimi and Taylor (2007) also investigated chelating agent-to-iron ratios, and also found that a 1 : 5 ratio worked well

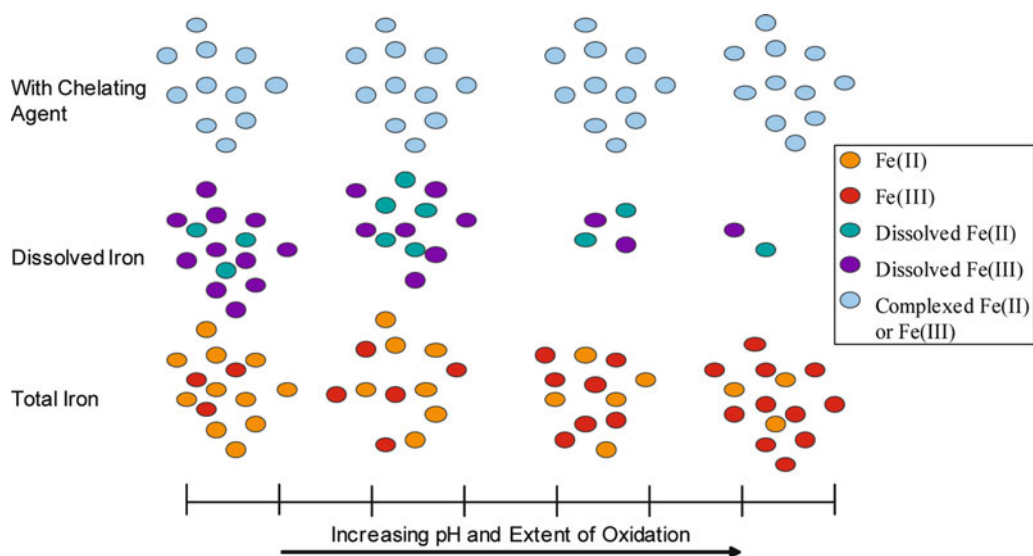


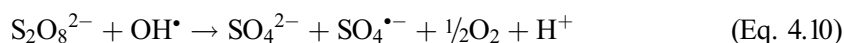
Figure 4.5. Iron availability – total and dissolved as Fe(II) or Fe(III) – and complexed iron using chelating agents as a function of pH and extent of oxidation.

if the iron concentration was high, while again a comparatively higher dose of chelating agent was needed if the iron concentration was low.

One final consideration in the use of chelating agents for activation is that the chelating agent itself might be degraded by the oxidation reaction. Many chelating agents are organic compounds, and thus the potential exists that they may be oxidized by either free radical or direct oxidation reactions. However, studies of chelated iron activation typically do not show changes in the concentration of chelating agents over time, so there is little in the literature to determine the magnitude of this effect.

Activation with Hydrogen Peroxide

The combined application of hydrogen peroxide (H_2O_2) and persulfate has been shown to activate persulfate, even without the addition of a transition metal activator (Block et al., 2004; Robinson et al., 2004; Crimi and Taylor, 2007). The mechanisms behind this activation method are unclear as it is unknown what kind of direct catalytic reaction might occur between hydrogen peroxide and sodium persulfate. However, many soil minerals, especially iron and manganese oxides, are known to be catalytically active toward hydrogen peroxide (Huang et al., 2001a; Kwan and Voelker, 2003; Watts et al., 2005b; Teel et al., 2007). Minerals, such as goethite, pyrolusite, ferrihydrite, and others are ubiquitous in porous media environments; thus, it is anticipated that many field sites will have some catalytic mineral content. Reaction of hydrogen peroxide with the catalytic minerals may initiate the formation of radicals, such as hydroxyl (OH^\bullet) or superoxide ($\text{O}_2^{\bullet-}$) radicals (Kwan and Voelker, 2003; Watts et al., 2005b). Radicals produced from these reactions may then interact with persulfate to form sulfate radicals ($\text{SO}_4^{\bullet-}$) through propagation reactions such as the reaction in Equation 4.10.



Cronk and Cartwright (2006) reported that hydrogen peroxide could support persulfate activation by elevating subsurface temperatures as well. Using controlled dosing of hydrogen peroxide to the subsurface, they were able to elevate subsurface temperatures to the range of

60–80°C (140–176°F) and enable persulfate activation via Equation 4.3. However, it appeared that the hydrogen peroxide and heat dissipated much more quickly than the persulfate decomposed, so periodic application of hydrogen peroxide was necessary to maintain subsurface temperatures that promoted heat activation.

It is worth noting that hydrogen peroxide chemistry probably plays just as important a role in these systems as persulfate chemistry. One common approach in the field is to apply an equal weight percent of both oxidants (e.g., 1 wt.% sodium persulfate and 1 wt.% hydrogen peroxide). However, given the large difference in molecular weights between the two oxidants (34 g/mol for H₂O₂, 238 g/mol for Na₂S₂O₈), application of equal weight concentrations of these two oxidants results in a mole ratio of nearly 7 : 1 hydrogen peroxide to sodium persulfate. Since chemical reactions are driven by molar concentrations, hydrogen peroxide reactions, as discussed in Chapter 2, may be expected to play a major or even dominant role in this chemistry.

Activation with Alkaline pH

Alkaline pH activation of persulfate involves the addition of a concentrated base, often as either sodium hydroxide (NaOH) or potassium hydroxide (KOH), to a persulfate solution to raise the pH into a strongly alkaline range (pH 11–12). This initiates decomposition of the oxidant to form radicals, although the exact nature of the mechanism is unknown. After activation, propagation reactions promote conversion of sulfate radicals to hydroxyl radicals via the reaction in Equation 4.11, due to the high concentration of hydroxide anions (OH[−]) at alkaline pH. Therefore, it is likely that hydroxyl radicals and other radicals derived from their propagation reactions are the primary reactive species in these systems. Furthermore, at high pH, hydroxyl radicals (OH[•]) themselves may dissociate into the oxide radical O^{•−} and H⁺ [dissociation constant (pKa) = 11.9], which can impact their reactivity (Buxton et al., 1988).



For alkaline activation, the pH must typically be raised to 11 or higher. A pH titration evaluation is important, using site-specific media, to evaluate the amount of base necessary to achieve this high of a pH in the subsurface. Alkaline activation was shown by Block et al. (2004) to be very effective at degrading organic contaminants, including the highly oxidized halomethanes and chloroethanes. These contaminants, especially the halomethanes, have largely been understood to have weak reactivity with strong oxidants, including hydroxyl radicals or sulfate radicals (Teel and Watts, 2002; Huang et al., 2005). However, recent research on hydrogen peroxide systems by Watts et al. (2005a, b) and Smith et al. (2004) suggests that the degradation of these highly oxidized contaminants in free radical systems may be occurring through a reductive pathway involving superoxide (O₂^{•−}). It is unknown if there are other unique radicals in these alkaline activation systems that might promote reductive degradation methods or other reaction mechanisms.

Another potentially major degradation process that may occur within alkaline activation systems is alkaline hydrolysis. In strongly alkaline solutions, many organic compounds react with hydroxide anions and decompose or partially degrade independent of the oxidation reactions. The significance and rates of reaction of this process at high pH vary widely for different organic compounds. Rates of reaction generally increase with increasing pH, as well as temperature. Jeffers et al. (1989) studied alkaline and neutral hydrolysis rates for a number of different chlorinated organic solvents across a wide range of pH and temperature conditions. Several, including 1,1,2,2-TeCA, 1,1,1,2-TeCA, 1,1,2-trichloroethane (1,1,2-TCA), and chloroform, were found to have high rates of alkaline hydrolysis at ambient temperatures and

elevated pH ranges that may occur during persulfate oxidation, suggesting that this mechanism might play a major role in the degradation of some organics by alkaline-activated persulfate. However, the products of these hydrolysis reactions in some cases yielded chloroethenes as a byproduct, which were slow to hydrolyze even at high temperatures or high pH; thus, persulfate oxidation reactions may support mineralization by degrading the byproducts of alkaline hydrolysis (see Section 4.4.1).

4.2.3.2 Propagation Reactions

Upon activation of persulfate, several important propagation reactions affect the balance of active radical species within the chain reaction. These propagation reactions are a function of other chemical species present in the aqueous solution. For example, if the pH is high, then a large concentration of hydroxide anions (OH^-) will be present, and reactions between sulfate and OH^- may shift to favor the production of hydroxyl radicals (OH^\bullet), as shown in Equation 4.11; this was observed by Liang et al. (2007b), who conducted scavenging studies to determine the dominant radicals as a function of pH. They found that in persulfate systems, sulfate radicals ($\text{SO}_4^{\bullet-}$) were dominant at low pH (2–4), while hydroxyl radicals (OH^\bullet) dominated at high pH (7–9). Sulfate anion itself is also a species that can propagate radicals. For instance, if a system has high hydroxyl radical activity as well as high sulfate concentrations, then Equation 4.11 may be reversible and sulfate radicals will form. This has been observed in hydrogen peroxide ISCO systems where no persulfate is present, and yet there is evidence that sulfate radicals are forming due to a high background concentration of sulfate (De Laat et al., 2004).

While both sulfate radicals and hydroxyl radicals are known to be strong oxidants, they have different rates of reactions with organics depending on compound properties and functional groups (Neta et al., 1977; Buxton et al., 1988; Haag and Yao, 1992). Some highly oxidized organics, such as carbon tetrachloride (CT), have been noted to be effectively non-reactive with strongly oxidizing radicals, such as hydroxyl or sulfate radicals (Teel and Watts, 2002; Huang et al., 2005). Since these compounds have been observed to break down rapidly under some conditions in persulfate systems (Huang et al., 2005; Root et al., 2005), this highlights the possibility that other unidentified radical species are being formed, possibly including some that promote reductive mechanisms.

Formation of some additional radical species may be supported by the presence of dissolved oxygen. Peyton (1993) investigated thermally activated persulfate for use in total organic carbon (TOC) analysis and found that complete mineralization of organic carbon to carbon dioxide (CO_2) was unlikely to occur unless dissolved oxygen (O_2) was present. One possible propagation reaction involving oxygen is given in the reaction in Equation 4.12:



where R^\bullet is an organic radical, and RO_2^\bullet is an organo-peroxide radical. Organic radicals and organo-peroxide radicals might promote other propagation reactions, as well as degradation of contaminants (Peyton, 1993).

4.2.4 Persulfate Reaction Kinetics

The kinetics of persulfate reactions are another important consideration for the successful degradation of organic contaminants in the subsurface. Given the strong reduction potential of persulfate, and free radical intermediates, many reactions with organic chemicals are thermodynamically favorable. However, these reactions must also occur on a timescale that

is relevant to ISCO remediation to enable effective degradation of COCs. When persulfate is injected into the subsurface, through interaction with contaminant and natural media constituents, it is consumed by a series of catalytic and other reactions until it is eventually depleted from the aqueous solution. This lifetime, or oxidant persistence, is a function of how intensively the oxidant is activated by an activation method, as well as site-specific factors, as oxidant decomposition rates vary from one porous medium to another. In order for effective contaminant degradation to occur, the rate of contaminant degradation by persulfate needs to occur within either a similar or shorter timeframe than the overall lifetime of the oxidant in the subsurface. Furthermore, subsurface processes that affect the transport of the oxidant as well as desorption of sorbed contaminants are time-dependent; therefore, the oxidant must persist long enough for these processes to occur in order to achieve significant contaminant degradation.

4.2.4.1 Persulfate Decomposition Kinetics in Porous Media (Oxidant Persistence)

While oxidant persistence is known to be an important consideration for successful ISCO, the persistence of persulfate in the uncontaminated subsurface environment and the controlling parameters and processes are not yet fully understood. Some of the initial research on this topic attempted to treat the persistence of persulfate in a similar manner as permanganate; these studies assumed a finite persulfate demand for a given porous media and an upper limit on the amount of persulfate that will be consumed by porous media reductants (Hoag et al., 2000; Haselow et al., 2003; Dahmani et al., 2006). Using this approach for design purposes suggests that enough oxidant must be delivered to satisfy this “demand” before effective contaminant degradation can occur. However, Mumford et al. (2005) and Xu and Thomson (2008) showed that permanganate natural oxidant demand (NOD) is not a single-valued instantaneous demand; rather, it is kinetically controlled and hence accommodations for this time-dependent demand must be made. By extension, this kinetic behavior may also apply to persulfate. However, there is some scientific evidence to support the notion that a portion of persulfate consumption by aquifer solids might be due to reaction with a finite number of reductants, which would support a finite demand approach. For instance, persulfate oxidation has long been used in the wet oxidation method for TOC analysis, where natural organic matter (NOM), including humic substances, is presumed to be quantitatively converted to carbon dioxide (Peyton, 1993). Thus, one might expect a finite demand for persulfate from NOM.

More recently it has been observed that the persistence of persulfate appears to differ from permanganate because persulfate loss increases with time with some similarities to the decomposition behavior of peroxide (Brown and Robinson, 2004; Sra et al., 2007, 2010). This suggests that persulfate persistence may be impacted by a catalytic process whereby persulfate will decompose in the presence of naturally occurring catalysts until it is completely depleted. Under these conditions, if the natural catalysts are not altered or depleted by the reaction, then there is no upper limit on how much persulfate mass may eventually be used in this reaction. Sra et al. (2008) evaluated persulfate persistence in multiple porous media and determined that persulfate decomposition did obey pseudo first-order kinetics, suggesting a catalytic decomposition reaction was occurring. Furthermore, they investigated persistence kinetics in batch, column and push-pull field systems and found that oxidant decomposition rates increased from batch to column and field systems by 8 and 50 times, respectively. This increase in decomposition rates is not unexpected because the aquifer materials content increases from batch slurry systems to columns and the field system may encounter heterogeneities (Sra et al., 2010). This behavior may be further complicated if activators or contaminants are present since they can also impact the persistence of persulfate (Crimi and Taylor, 2007; Liang et al., 2008; Sra et al., 2010).

Table 4.4 gives example ranges of persulfate decomposition values reported in the literature. The variability in experimental methods and conditions should be kept in mind when using this information.

Table 4.4. Persulfate Persistence Values Reported in the Literature

Source	Data reported (rate or extent)	Half life	Comments
Liang et al. (2003)	0.75–4.7/day	0.15–0.92 days	First-order persulfate degradation kinetics for 3 soils over 6 h; TCE or TCA present; batch systems; thermal activation (50° or 60°C); 11.7 g of soil in 60-mL reactors
Brown and Robinson (2004)	<0.06–14.3 g- Na ₂ S ₂ O ₈ /kg (wet)	N/A	Persulfate loss increased with time; no threshold observed for 6 uncontaminated soils; data reported after 21 days of exposure; batch systems; no oxidant to solids mass ratio reported
Dahmani et al. (2006)	0.1–0.3 g- Na ₂ S ₂ O ₈ /kg (dry)	N/A	Threshold persulfate consumption observed for 1 soil after 10 days of exposure; batch systems; solution to solids ratio of 5:1 (v/v); persulfate concentration varied from 0.1 to 5 g/L
Liang et al. (2004b)	0.01–1.96/day ^a	0.35–69 days	First-order persulfate degradation kinetics for 1 soil over 24 h; batch systems; TCE present; solution to solids ratio of 5:1 (v/v); different mole ratios of persulfate, chelate (EDTA), iron, and TCE
Crimi and Taylor (2007)	0.02–2.39/day	0.29–35 days	First-order persulfate degradation kinetics for 5 soils; batch systems; solution to solids ratio of 4:1 (v/v); BTEX present; different activators
Liang et al. (2008)	1.39 and 5.98 g- Na ₂ S ₂ O ₈ /kg (dry)	N/A	For one soil over 28 days; batch systems; no temporal data reported; with and without added iron; oxidant to solids mass ratio of 400 g-Na ₂ S ₂ O ₈ /kg
Sra et al. (2010)	0.001–0.34/day	2–700 days	First-order persulfate degradation kinetics for 7 uncontaminated soils; batch systems over 300 days with oxidant to solids mass ratio of 1.0 or 20 g-Na ₂ S ₂ O ₈ /kg; column systems; push-pull field tests over 25 days
Sra et al. (2010)	0.001–0.7/day	1–700 days	First-order persulfate degradation kinetics for 4 uncontaminated soils; batch systems; oxidant to solids mass ratio of 1.0 or 20 g-Na ₂ S ₂ O ₈ /kg; various activators

Note: kg - kilogram.

^aFirst-order rate coefficients estimated by the authors.

4.2.4.2 Fundamental Reaction Kinetics and Modeling Approaches

The rates of reaction between sulfate radicals or hydroxyl radicals and various organic and inorganic reactants are generally reported as following second-order kinetics (dependent on concentration of oxidant and contaminant), while the contaminant destruction rates are

reported as being pseudo first-order (assumes excess oxidant concentration) (Figure 4.6). These rates have been reported in a number of publications, including Neta et al. (1977), and Buxton et al. (1988, 1996, 1999). However, given the complexity of these systems, it is mathematically cumbersome to develop precise analytical models tracking specific reactive species. Table 4.5 summarizes the decay rates of the oxidative species and the observed contaminant destruction rate. The table is a compilation of information from several thorough reviews and experimental studies; the reader is referred to those publications for more information on the initial conditions.

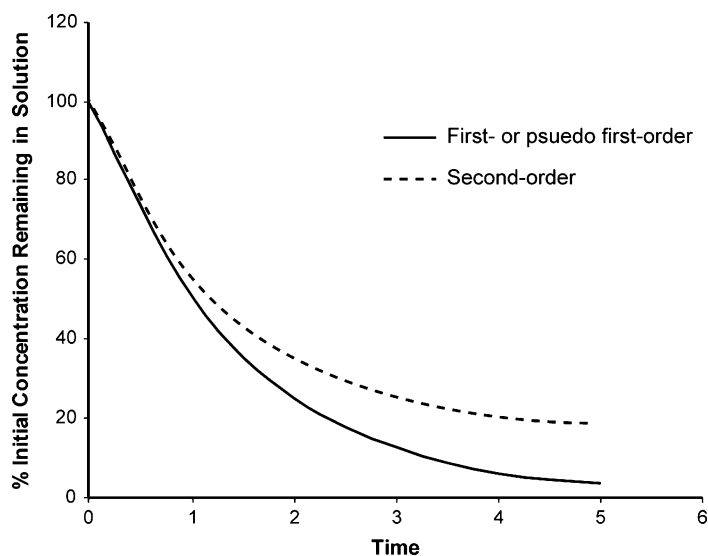


Figure 4.6. Example contaminant data with degradation following first-order, pseudo first-order, or second-order kinetics. Time here is shown as a generic unit change.

A simplified approach using the competition kinetics method allows the estimation of reaction efficiencies when one specific radical species is dominant, but it does not allow estimation of overall kinetic rates. Since the concentration of the radical is the same for all reactions involving it, competition kinetics predicts that the relative dominance of each particular reaction within a system depends on the product of each reactant's concentration with its second-order reaction rate. Those reactants with either faster rates of reaction or higher concentrations tend to dominate. Peyton (1993) demonstrated that this method could be useful for analyzing the persulfate chemistry of TOC analyzers. It may also have some utility for ISCO as well. However, there are a number of unknowns with ISCO that make conclusions with this method more uncertain. For example, the reactivity of persulfate with soil minerals is largely unknown, but with hydrogen peroxide, soil minerals have a major effect on free radical reactions, and failing to include them in competition kinetic calculations could impart significant error. Furthermore, when there are multiple radical species contributing to degradation, competition kinetics cannot easily account for the impact of other radicals.

Because of the multiple and perhaps unclear reaction pathways occurring during persulfate degradation of organic contaminants, modeling persulfate oxidation kinetics at this point in time is plagued by a high degree of uncertainty. Hence, the most common approach for investigating reaction kinetics is to collect relevant laboratory data and then extrapolate these findings to *in situ* conditions. In many cases, pseudo first-order kinetics appear to hold for

contaminants in systems where persulfate is in excess and activators are present (Huang et al., 2002, 2005; Liang et al., 2003, 2004b, 2006, 2007b). However, exceptions have been observed that have resulted in reaction stalling, suggesting other processes are involved (Anipsitakis and Dionysiou, 2004; Liang et al., 2004a). Care must be taken to extrapolate conclusions drawn from well-mixed homogeneous laboratory systems to the complex and heterogeneous subsurface environment encountered in the field.

Table 4.5. Reaction Rates for the Hydroxyl and Sulfate Radicals and the Persulfate Ion

Reactant	Second-order reaction rates for radical decay ($M^{-1} s^{-1}$)		
	$OH^{\bullet a}$	$SO_4^{\bullet - b}$	$S_2O_8^{2-}$
Methanol	9.7×10^8	1.6×10^7	N/R
Ethanol	1.6×10^9	7.8×10^5	N/R
Tetrahydrofuran	4.0×10^9	1.1×10^8	N/R
Methyl tert-butyl ether	1.6×10^9	3.1×10^7	N/R
Chloride ion	4.3×10^9	2.5×10^8	N/R
Carbonate ion	4.0×10^8	1.6×10^6	N/R
Bicarbonate ion	1.0×10^7	6.1×10^6	N/R
Trichloroethene	4.2×10^9	N/A	N/R
Perchloroethene	2.6×10^9	N/A	N/R
Iodide ion	1.1×10^{10}	N/A	N/R
Reactant	Contaminant destruction rate (pseudo first-order) k_{obs} (s^{-1})		
	OH^{\bullet}	$SO_4^{\bullet -}$	$S_2O_8^{2-}$
Methyl tert-butyl ether	0.029 ^c	5.8×10^{4d}	0.13×10^{4d}
Trichloroethene	N/A	2.21 ^e	1.16 ^e
Perchloroethene	N/A	2.69 ^c	0.91 ^c

Note: N/R - not relevant; N/A - not available.

^aBuxton et al. (1988).

^bTsionaki et al. (2010).

^cBurbano et al. (2002).

^dHuang et al. (2002). Based on the assumption that the persulfate ion dominated the reaction at ambient temperature while the sulfate radical dominated the reaction at 50°C.

^eLiang et al. (2007a). Based on the assumption that the persulfate ion dominated reaction with no activator present, while the sulfate radical dominated in activated systems.

4.2.5 Factors Affecting Efficiency and Effectiveness of Oxidation

Once radicals are formed, they react extremely rapidly or almost instantaneously (Neta et al., 1977; Buxton et al., 1988; Haag and Yao, 1992). These reactions include attack on contaminants present in the subsurface, bringing about their degradation, which is the goal of ISCO. However, they are also available to react with other chemical constituents present in solution. Excessive propagation reactions with other radicals, as well as reaction with compounds known to react in a nonproductive fashion, can reduce reaction efficiency and effectiveness. These are sometimes referred to as scavenging reactions. If the concentration of scavengers becomes too high, then the radical to target organic reaction efficiency can be diminished or eliminated altogether. Table 4.6 summarizes the action/impact of key scavengers commonly present in groundwater and further discussion is given in the sections below.

Table 4.6. Summary of Common Free Radical Scavengers Present in Groundwater

Scavenger	Action and impact
Carbonate and bicarbonate	<ul style="list-style-type: none"> • Interact with (scavenge) free radicals and act as metal-complexing agents (important with respect to metal activation) • Can slow down or even inhibit contaminant degradation • Carbonate and bicarbonate free radicals can form – thought to be relatively non-reactive free radical sinks, but may contribute to free radical propagation and possibly contaminant degradation
Chloride	<ul style="list-style-type: none"> • Interacts with (scavenges) free radicals and acts as metal-complexing agent (important with respect to metal activation) • Byproduct of chlorinated solvents oxidation – can accumulate, particularly with DNAPL contamination • Can slow down or even inhibit contaminant degradation • Chloride free radicals can form – thought to be relatively non-reactive free radical sinks • Can potentially result in generation of chlorinated disinfection byproducts (e.g., halomethanes, etc.)
Porous media	<ul style="list-style-type: none"> • Natural organic matter can directly consume persulfate and potentially act as a free radical sink • Activated persulfate may be catalytically active with soil minerals, but mechanisms are currently not understood

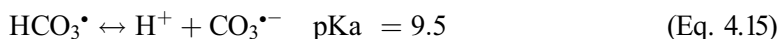
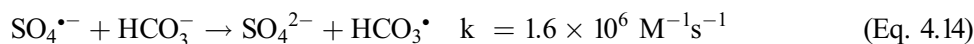
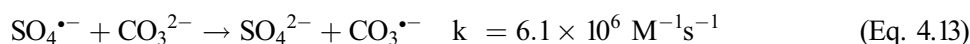
4.2.5.1 Carbonate and Bicarbonate

The impact of these anions on ISCO is important to consider because carbonate and bicarbonate are ubiquitous in the subsurface environment. Carbonate and bicarbonate anions are present in water as a result of absorption of atmospheric carbon dioxide into water, the dissolution of carbonate minerals, and from the degradation of organic compounds by both biotic and abiotic mechanisms. Therefore, many groundwaters have naturally high carbonate and bicarbonate contents; this content can even be increased by ISCO due to the destruction of organics. Carbonate and bicarbonate ions have the potential to affect persulfate reaction efficiency, kinetics, and pathways by both reacting with radicals and acting as a metal-complexing agent.

Carbonate or bicarbonate anions can form aqueous complexes or solid precipitates in aqueous solution with metals or mineral surfaces, decreasing their reactivity (Valentine and Wang, 1998). This effect has not been explored with persulfate specifically; however for comparison purposes, on the basis of reactions involving catalysis of hydrogen peroxide, this complexation process has been noted to significantly slow both the decomposition of hydrogen peroxide and the rate of contaminant degradation. In some cases, this has been observed to slow reaction rates but not reduce reaction efficiency (Valentine and Wang, 1998); in other cases, it has effectively inhibited the reaction (Lipczynska-Kochany et al., 1995; Beltrán et al., 1998).

In persulfate systems, the presence of bicarbonate and carbonate has been noted to reduce the rates of contaminant oxidation and reaction efficiency (Huang et al., 2002; Liang et al., 2006; Waldemer et al., 2007); however, these studies were unable to conclude the mechanism behind these reduced rates and efficiency. Both Peyton (1993) and Liang et al. (2006) noted that the adverse impact of carbonate on persulfate reactions increases with pH, but the mechanism is unclear.

In addition to complexation processes, carbonate and bicarbonate can also form radicals of their own via reactions, as shown in Equations 4.13 and 4.14 (Liang et al., 2006).



This yields the bicarbonate radical HCO_3^{\bullet} and the carbonate radical ($\text{CO}_3^{\bullet-}$), which have their own acid-base chemistry (Equation 4.15) (Zue et al., 1999). The reactivity of these radicals with organic chemicals and their participation in chain reaction propagations are not as well understood as sulfate or hydroxyl radical reactions. Traditionally, they have been viewed as either slow to react or as non-reactive – and therefore nonproductive – radical sinks (Huang et al., 2002; Liang et al., 2006). This view is based largely on the observation that contaminant degradation tends to be less extensive when carbonate is present (Huang et al., 2002; Liang et al., 2006; Waldemer et al., 2007). However, more recent studies have indicated that their formation is not entirely unproductive and that they may actively contribute to both propagation reactions and contaminant degradation. The standard reduction potential for the carbonate radical ($\text{CO}_3^{\bullet-}$) has been reported to be 1.59 V at pH 12 (Huie et al., 1991), which is certainly strong enough to enable many oxidation reactions. Umschlag and Herrmann (1999) investigated carbonate and bicarbonate radical activity with a series of aromatic compounds, including BTEX, and found that carbonate and bicarbonate radicals were able to degrade them. They found the kinetic reaction rates with these radicals were within the range of 10^2 – $10^7 \text{ M}^{-1} \text{ s}^{-1}$; this is slower than that of hydroxyl radicals ($10^9 \text{ M}^{-1} \text{ s}^{-1}$) or sulfate radicals (10^8 – $10^9 \text{ M}^{-1} \text{ s}^{-1}$) with similar aromatic compounds but may still be sufficient to contribute to degradation depending on the concentration of the radicals (Neta et al., 1977; Buxton et al., 1988). Thus, it is possible that carbonate radicals might support some degradation reactions, though the significance of this is unclear.

The above discussion suggests that there may be both complementary and deleterious interactions between persulfate performance and carbonate or bicarbonate; however, the present experimental evidence suggests that these ions have an overall negative impact on operational performance (Huang et al., 2002; Liang et al., 2006). However, identifying specific threshold concentrations where they pose a challenge is difficult because these processes cannot be easily identified, separated, or quantified. Other system variables play a role as well. For example, Liang et al. (2006) noted that at neutral pH, bicarbonate up to approximately 550 mg/L had relatively little effect on efficiency, while at pH 9 or 11, this concentration had large adverse effects on efficiency. Thus, the impact may be system-dependent.

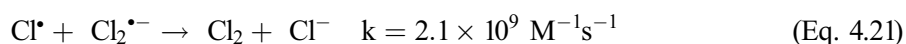
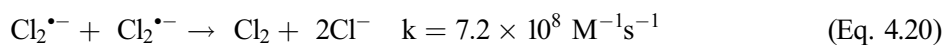
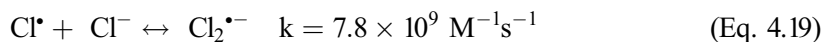
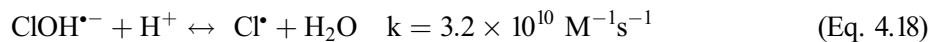
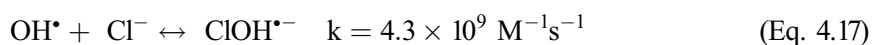
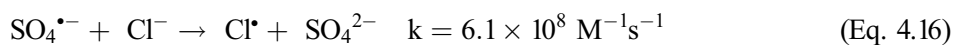
4.2.5.2 Chloride

Chloride is another anion that has the potential to act as a radical scavenger, as well as affect metal availability. Chloride is ubiquitous in natural waters, though its concentrations are typically low unless there is a considerable salinity, such as with marine environments or in highly brackish groundwater. However, like carbonate and bicarbonate, chloride is a potential reaction product when oxidizing chlorinated organic contaminants. Chloride evolution from ISCO reactions can become especially significant when treating DNAPL compounds; concentrations have been noted to locally exceed 3,000 mg/L when treating these contaminants in potassium permanganate systems (Petri, 2006).

Like carbonate and bicarbonate, chloride may also form complexes with metals and minerals (De Laat et al., 2004). Again, this has the ability to impact the rate of catalysis as

the chloridmetal complexes may have different reactivity with persulfate than the hydrated-metal complexes that are dominant in pure aqueous solutions. This phenomena has not been explored in persulfate systems, but has been noted in systems involving iron catalysis of hydrogen peroxide and oxygen. For example, De Laat et al. (2004) noted that chloride had no impact on the kinetics of hydrogen peroxide catalysis by Fe(II), but catalysis was significantly slower with Fe(III) when chloride was present; this resulted in slower rates of oxidant decomposition and slower rates of contaminant degradation. Sung and Morgan (1980) noted a similar slowing effect on the kinetics of Fe(II) oxidation by dissolved oxygen when chloride was present due to iron complexation. However, the degree of this effect on persulfate catalysis by metals or mineral surfaces is not yet known.

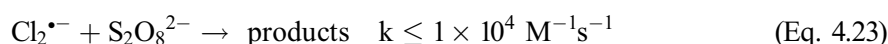
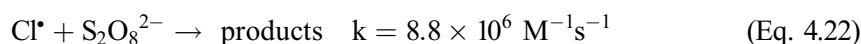
Chloride is well known to react with other radicals, such as hydroxyl or sulfate radicals, to form its own radicals with unique chemistry (Yu and Barker, 2003). The reactions in Equations 4.16–4.18 describe the production of the free chlorine atom (Cl^\bullet) from reactions with sulfate and hydroxyl radicals (Buxton et al., 1999; Yu and Barker, 2003). The chlorine atom is unstable in aqueous systems; if chloride concentrations are sufficiently high, it will complex with a chloride anion to form the dichloride radical (Equation 4.19). Dichloride radicals are generally slower reacting radicals than hydroxyl radicals or sulfate radicals, and thus they may accumulate to higher concentrations in solution. Presently, they are not known to contribute productively to organic compound oxidation, and thus they are often viewed as a nonproductive radical sink. If concentrations of these dichloride radicals are high, they can also react with each other (Equation 4.19) or with the chlorine atom (Equation 4.20) to form chlorine gas (Cl_2) (Yu et al., 2004).



Chlorine gas and its aqueous dissolution products have the potential to form halogenated organics. This was observed by Aiken (1992), who investigated thermal activation of persulfate for TOC analysis in seawater samples; Aiken noted the formation of halogenated organic intermediates when the chloride concentration exceeded 0.1 M (3,500 mg/L). The intermediates included volatile halomethanes and were speculated to also include non-volatile haloacetic acids. Both are well known to form from the oxidation of NOM during chlorine disinfection of drinking water (HDR Engineering, 2001), so speculation of their potential formation is reasonable. In addition, Waldemer et al. (2007) noted that halogenation reactions can occur with the parent contaminant, as traces of hexachloroethane (HCA) were observed when treating perchloroethene (PCE). Presumably, reactive chlorine species produced were reacting with PCE to form HCA. Provided sufficient oxidant contact times, Aiken (1992) noted that the halogenated intermediate yields decreased, suggesting that they could be subsequently broken down. Thus, they may not be of concern in ISCO applications provided oxidant contact is long, and the concentrations remain at trace levels. However, this does indicate that chlorinated compounds

not originally present at an ISCO site might possibly be detected after a persulfate application, especially if background chloride concentrations are high.

The formation of radicals from chloride may not be entirely unproductive. Recent evidence by Yu et al. (2004) suggests that the chlorine atom (Cl^\bullet) and dichloride radical ($\text{Cl}_2^{\bullet-}$) might contribute to propagation reactions with persulfate. They explicitly reported reaction rates for the reactions in Equations 4.22 and 4.23 that may generate radicals from reaction with persulfate ion; however, they did not identify the products of these reactions. Yet the products would likely include other radical intermediates making this a propagation reaction. Yu and Barker (2003) also observed the dichloride radical to initiate production of the perhydroxyl radical (HO_2^\bullet) from hydrogen peroxide. However, it is worth noting that these reactions are slow in comparison to other free radical reactions; their significance in ISCO processes is unknown, but may be minor if other, faster competing reactions dominate.



Despite the evidence that chloride radicals might support reaction propagations, the literature that has reported on chloride scavenging has generally noted that chloride reduces ISCO performance. No distinct threshold concentration for adverse impacts from chloride could be identified from the literature since such a threshold may be temperature- and system-specific. For instance, Aiken (1992) noted that reaction efficiencies declined in systems with chloride concentrations above 700 mg/L; yet, this was in a high-temperature system (100°C or 212°F) that may have resulted in more aggressive oxidant activation than is typical. In contrast, Liang et al. (2006) evaluated the impact of chloride on unactivated persulfate at ambient temperatures and did not find adverse impacts to reaction efficiency until the chloride concentration exceeded 7,000 mg/L.

4.2.5.3 Porous Media

Presently, the impact of aquifer solids, or porous media, on persulfate chemistry is not well understood. For instance, at the time of publication, only four published studies had investigated the effect of different types of porous media on persulfate ISCO, enabling direct comparison between media. Crimi and Taylor (2007) evaluated three different activation methods – alkaline, hydrogen peroxide, chelated iron – in five different porous media and noted that the effectiveness of one method versus another was different in each porous media, implying that media characteristics impact treatment effectiveness. However, it was unclear what mechanisms were causing this variable performance with different activation methods.

The nature of the impact of NOM on persulfate oxidation chemistry and effectiveness is still an area of uncertainty. With hydrogen peroxide, NOM has been observed to have a number of influences on ISCO effectiveness. These have included complexation of dissolved metals and mineral surfaces affecting oxidant catalysis, as well as acting as a sink for radicals and reducing contaminant availability through sorption processes. However, with persulfate, the impact of NOM is much more uncertain, especially with regard to the effect on persulfate catalysis. However, the impact of NOM on oxidant availability and contaminant sorption has been studied to a moderate degree.

Some have postulated that NOM acts as a finite sink for the persulfate oxidant, much like permanganate NOD, and that NOM will be highly depleted by the oxidation reaction (Hoag et al., 2000; Droste et al., 2002; Haselow et al., 2003). This hypothesis is supported by the fact that persulfate has long been used as a wet oxidation method for determining TOC in water

samples, whereby persulfate is used to mineralize the TOC to carbon dioxide, which is then quantified (Aiken, 1992; Peyton, 1993; Koprivnjak et al., 1995). However, these TOC wet oxidation methods tend to use very rigorous reaction conditions, such as very high oxidant doses, acidic pH, and advanced activation methods such as ultraviolet light or very high temperatures; therefore, they may not represent the typical conditions in the subsurface during ISCO. Even under these rigorous conditions, it has been reported that significant TOC content may still remain in solution indicating that some organic carbon content may be effectively non-reactive with persulfate and its free radical chemistry (Koprivnjak et al., 1995). Data by Woods (2008) certainly seems to support this. In her investigation of persulfate treatment of volatile organic compounds (VOCs) in several porous media, the fraction of organic carbon content (f_{oc}) was observed to only decrease by 30% on average, indicating significant NOM may remain after ISCO using persulfate. Others have noted that persulfate reactions in porous media are very different than those involving permanganate NOD, concluding that persulfate reactions with porous media are governed by a rate limited decomposition process and that persulfate does not significantly deplete NOM (Brown and Robinson, 2004). Sra et al. (2010) conducted a series of bench- and pilot-scale studies to estimate persulfate decomposition kinetic parameters in the presence of seven well-characterized aquifer materials. For all of these aquifer solids, the concentration of persulfate was continually depleted at both a low (1 g/L) and high (20 g/L) initial persulfate concentration. This decomposition followed a pseudo first-order kinetic expression indicating that a catalytic process was occurring similar to the behavior of peroxide. However, unlike peroxide, the pseudo first-order reaction rate coefficients for the high-concentration experiments were less than the pseudo first-order reaction rate coefficients for the low concentration experiments, indicating higher persulfate stability at higher concentrations given the same mass of aquifer materials. For some of the aquifer materials, a significant decrease in the chemical oxidant demand (COD) test results were noted following exposure to persulfate for more than 80 days, suggesting that some of the reduction capacity of the solids was indeed depleted.

The impact of porous media minerals on persulfate reaction chemistry is also not well known. Hydrogen peroxide is known to be very catalytically active with certain porous media minerals. Major minerals known to catalyze hydrogen peroxide include oxides of manganese and iron, which can be a major source of radical production in these systems (Kwan and Voelker, 2003; Watts et al., 2005a, b; Teel et al., 2007). However, it is unknown if such catalysis by minerals is also a major process with persulfate. Data from Dahmani et al. (2006) suggest mineral catalysis might occur; extensive degradation of chlorinated ethenes was witnessed in a persulfate system with high manganese and iron content without added activation. However, this study did not conduct experiments to conclude whether a direct reaction between persulfate was occurring or if catalytic production of free radicals was responsible. Therefore, the nature of interactions between porous media minerals and persulfate chemistry is unclear.

4.3 PERSULFATE INTERACTIONS IN THE SUBSURFACE

Within the subsurface, several important objectives must be attained for ISCO to be effective using any oxidant:

- The oxidant must be able to degrade the contaminant.
- The oxidant must effectively contact the contaminant.
- A sufficient quantity of oxidant must contact the contaminant for a long enough time to effectively degrade the contaminant.

While these objectives are generic enough to apply to any oxidant, and often apply to other non-ISCO remediation technologies, there are unique attributes to each oxidant that may impact their ability to meet these three objectives. Ineffective activation may result in a failure to meet the first objective because some of the target contaminants are unlikely to degrade. Meeting the second objective is generally a matter of hydrogeology that is site-specific, with heterogeneous sites presenting the greatest challenges to all *in situ* remediation technologies. However, oxidants also have the unique potential to affect both contaminant and oxidant transport processes within the subsurface which can have important effects on meeting the second objective. To satisfy the final objective, enough oxidant must be delivered and persist long enough that contaminant degradation can occur. Thus, the mass of oxidant delivered and the kinetics of oxidant persistence are important. All of these processes are affected by subsurface transport mechanisms.

The following sections discuss what is known or can be inferred about these important processes as they relate to persulfate ISCO. Only very recently has research attention begun to focus on these processes under conditions more representative of subsurface conditions for persulfate ISCO (Sra et al., 2007; Liang et al., 2008; Liang and Lee, 2008). These have included several one-dimensional (1-D) column studies, as well as a thorough field-pilot investigation in a well-characterized aquifer. However, compared with the transport of other oxidants, there is much less literature to cite in these sections. Thus, the discussion below describes what is known from currently available literature, as well as plausible hypotheses based on intuition and analogies to processes relevant to other oxidants. There is uncertainty in extrapolating results from other oxidants as well, but where little data are available, this approach may assist in anticipating how persulfate might be expected to perform. It should be noted that this is an area where more research is needed, and the understanding of these processes will undoubtedly change with time as more information becomes available.

4.3.1 Impacts on Subsurface Transport Processes

With other ISCO oxidants, such as permanganate or hydrogen peroxide, there are a number of impacts to the subsurface groundwater environment that have the potential to affect transport processes for both the oxidant and the contaminant. For instance, with permanganate, manganese dioxide solids may precipitate, altering formation permeability and flow patterns in the subsurface (Conrad et al., 2002; MacKinnon and Thomson, 2002; Heiderscheidt, 2005). With hydrogen peroxide, significant off-gassing may occur (Watts et al., 1999b), which also can affect permeability and oxidant distribution, as well as transport mechanisms with volatile contaminants. However, with persulfate, the impact of its application to subsurface processes such as advective, dispersive, and diffusive transport, as well as contaminant partitioning between phases has not been extensively explored.

4.3.1.1 Impacts on NAPL

The presence of nonaqueous phase liquid (NAPL) in the subsurface presents unique challenges to all *in situ* remediation technologies. Persulfate has been applied in the field to sites where NAPL contaminants are either known or suspected to exist (Krembs, 2008). However, there is very little direct experimentation between persulfate oxidation and NAPLs noted in the published literature; thus, there are few data from which to interpret the effect of persulfate on NAPL contaminants and their mass transfer and transport processes. Studies from other oxidants, such as permanganate and hydrogen peroxide, do provide some basis for speculation about how persulfate might be expected to interact with NAPL contaminants.

Conceptual Model of NAPLs in the Subsurface During ISCO

Design of ISCO systems typically includes injecting excess oxidant so that the oxidant demand of the COCs is exceeded by many orders of magnitude. This is done in recognition that much of the oxidant may be consumed by other natural oxidant sinks and competing reactions and that some oxidant will fail to contact contaminants due to flushing inefficiencies. However, even assuming that a relatively homogeneous distribution of oxidant can be attained in a subsurface environment, NAPLs pose particular challenges to ISCO because they represent highly concentrated zones of contaminant mass (Figure 4.7). It is likely that the stoichiometric persulfate demand to completely degrade the organics present in NAPL zones will be very large. Thus, it is not uncommon to require multiple injection rounds into such areas to effectively deplete the NAPL (Krembs, 2008).

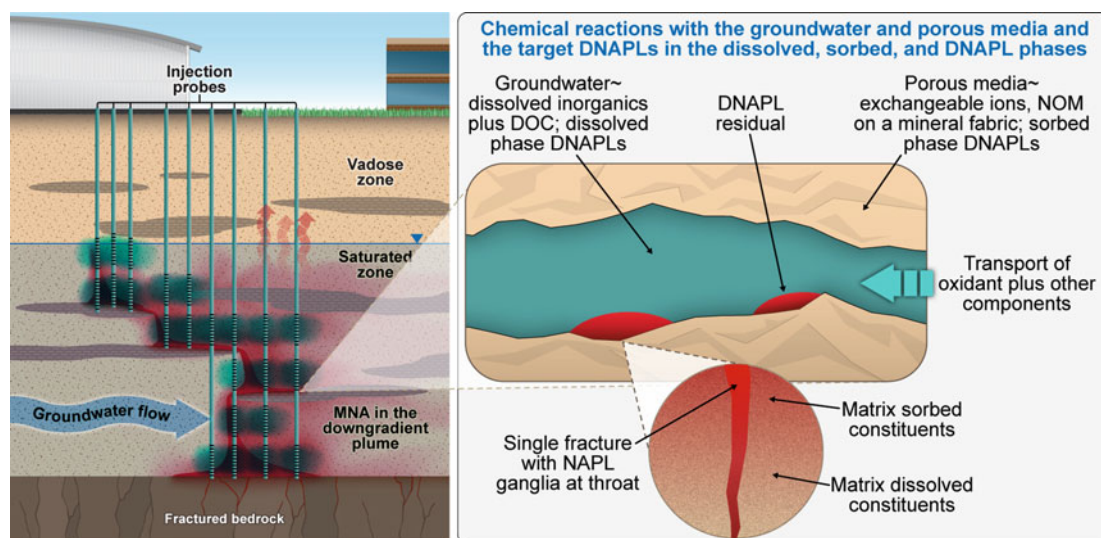


Figure 4.7. Macro- and micro-scale features of contaminated groundwater zones where organic contaminants of concern may exist in the aqueous, sorbed, and nonaqueous phases (adapted from Siegrist et al., 2010). Demand for oxidant in areas of high contaminant mass density (e.g., NAPL) is extensive and reaction at the NAPL/oxidant interface is intensive. DOC - dissolved organic carbon.

Reactions at the NAPL-Water Interface

Based on studies in 1-D columns and 2-D tanks using permanganate, the NAPL-water interface (e.g., Figure 4.7) has typically been observed to be a zone of intensive reaction between the oxidant and the contaminant (Lee et al., 2003; Petri et al., 2008). It therefore seems reasonable to assume that with persulfate, the NAPL interface will still be an intensive reaction zone, as the NAPL effectively represents a reductant, and therefore a vigorous reaction should occur between that reductant and the aqueous oxidant. In this intensive reaction zone, the contaminant is available in excess, while the oxidant must be delivered to it via advective, dispersive, and diffusive transport processes. With permanganate, DNAPL pools and residuals have been observed to become rapidly encrusted with manganese dioxide, the solid, immobile reaction product of permanganate (Conrad et al., 2002; MacKinnon and Thomson, 2002; Heiderscheidt, 2005). The amount of this deposition demonstrates the intensity of reaction that occurs near these DNAPL interfaces. Therefore, it seems likely that with persulfate treatment of NAPLs, persulfate's reaction byproducts of sulfate and a potential pH drop

should also become intensive in the area near a NAPL interface. In addition, dissolved carbon dioxide and chloride produced from organic oxidation should also be generated intensively at this interface. Unlike permanganate's manganese dioxide byproduct, these reaction products from persulfate are generally soluble and therefore may be transported away from the reaction zone. However, they have the potential to affect persulfate chemistry at the interface, as well as affect physical transport processes.

Potential for Impacts to Persulfate Reaction Chemistry

Because the NAPL interface is a zone of presumed reaction intensity, there is also the potential for the evolution of a large amount of the inorganic byproducts from the oxidized contaminant. Most prominent among these may include carbon dioxide, bicarbonate, and carbonate, as well as chloride when chlorinated organic contaminants are treated. With permanganate systems, chloride concentrations have been noted to become quite high, exceeding 3,000 mg/L, when treating TCE and PCE DNAPLs (Petri et al., 2008). As discussed in Section 4.2.5, these ions have the potential to affect reaction chemistry. Many have noted deleterious effects on reaction chemistry when concentrations of these anions become high, such as slower oxidation rates or reduced reaction efficiency (Aiken, 1992; Liang et al., 2006). However, there are also recent lines of evidence that they may contribute to propagation reactions and organic degradation as well (Umschlag and Herrmann, 1999; Yu and Barker, 2003; Yu et al., 2004).

Another potential deleterious effect specific to chlorinated organic compounds is that through free radical propagations involving the chloride ion, halogenation reactions have been observed (Aiken, 1992; Waldemer et al., 2007). For instance, Waldemer et al. (2007) observed production of traces of HCA during the persulfate treatment of PCE. With hydrogen peroxide, the situations that appear most likely to generate such chlorinated intermediates are high chloride concentrations, high contaminant concentrations, and low oxidant concentrations (Pignatello, 1992; De Laat et al., 2004). If this holds true for persulfate as well, such situations seem likely to occur locally at a DNAPL interface. However, since chlorine production is essentially driven by PCE oxidation in this example, it seems that PCE would be degrading at amounts in the tens or hundreds of parts per million range, while HCA, if produced, might be only be evolving at the parts per billion or parts per trillion range. Furthermore, HCA or other intermediates produced would also be subjected to reaction mechanisms from persulfate chemistry and might subsequently degrade. Thus, the risk is presumably posed by the much higher parent contaminant mass and concentrations than traces of intermediate compounds. However, this does raise the possibility that organic compounds that were not detected prior to ISCO remediation might be detected after remediation, and it seems likely that this probability is higher with chlorinated DNAPL contaminants.

These impacts indicate that the complex chemistry of persulfate might change with time and distance at a NAPL interface as byproducts are produced and influence the reaction efficiency and pathways. However, as of yet, there is no detailed experimentation available documenting how chemistry may change with advection, or with dispersive and diffusive transport. Therefore, it is difficult to speculate how significant such impacts may be under field conditions.

Potential for Gas Evolution

Carbon dioxide and its dissolved phase counterparts bicarbonate and carbonate are the primary inorganic carbon-based reaction byproducts derived from oxidation of organic compounds. Water has a lower capacity for storing dissolved carbon dioxide as carbonate and bicarbonate at acidic pH than at alkaline pH (Benjamin, 2002). As a result, the combination of a strong pH drop with high carbonate or bicarbonate concentrations resulting from contaminant oxidation have the potential to evolve carbon dioxide from solution as a gas which can fill pores within porous media. This has implications for the partitioning of contaminants in the

subsurface; it may also reduce the relative permeability of the subsurface. To the authors' knowledge, this phenomenon has not been reported in the literature related to persulfate, and whether this occurs under field conditions is unknown. However, it has been well documented to occur in permanganate ISCO systems involving DNAPLs (Reitsma and Marshall, 2000; Schroth et al., 2001; MacKinnon and Thomson, 2002; Li and Schwartz, 2003; Petri et al., 2008); thus, it is conceivable that gas evolution may occur in persulfate systems as well. Another potential for gas evolution is O₂ generation resulting from hydrogen peroxide decomposition with hydrogen peroxide-activated persulfate. This also can impact contaminant partitioning and subsurface permeability as described above.

4.3.1.2 Impacts on Contaminant Sorption

Persulfate oxidation has the potential to affect contaminant sorption processes. Sorption of organic contaminants is typically attributed to their hydrophobic nature that causes them to partition onto nonpolar NOM over the polar aqueous phase. The most common approach to estimating contaminant sorption is to assume equilibrium between concentrations in the NOM phase and concentrations in the aqueous phase, then relate the two by a partitioning coefficient (Equation 4.24). This coefficient is typically estimated from the NOM content and a contaminant-organic carbon partitioning coefficient (Equation 4.25):

$$K_d = C_{\text{Soil}}/C_{\text{Aqueous}} \quad (\text{Eq. 4.24})$$

$$K_d = f_{oc} K_{oc} \quad (\text{Eq. 4.25})$$

where K_d is the distribution coefficient representing the distribution of sorbed versus aqueous contaminant masses (L/kg), C_{Soil} is the concentration of contaminant sorbed to the soil (mg/kg), C_{Aqueous} is the aqueous phase concentration (mg/L), f_{oc} is the fraction of organic carbon (unitless), and K_{oc} is the contaminant-organic carbon partitioning coefficient (L/kg). Evidence within the literature indicates that oxidation processes that include persulfate can affect the factors in this relationship. Using chelated-iron activated persulfate, Woods (2008) evaluated the impact of ISCO on the quantity of NOM (f_{oc}) and organic carbon sorption behavior (K_{oc}). Experiments were conducted using several porous media from a field site with differing f_{oc} content, with or without a DNAPL contaminant present, and a persulfate dose of 38 g/kg media. In all cases, the K_d value decreased with persulfate, by an average of 15% when DNAPL was present and by nearly 50% when no DNAPL was present. Perhaps the lack of a competing reductant (such as DNAPL) in a persulfate system allows more interaction of the oxidant with a porous media. Analysis indicated changes to the f_{oc} values as well. The f_{oc} decreased by 30% on average and in one case by nearly 60%. Such changes to partitioning characteristics could have implications for how aqueous concentrations respond to ISCO. For instance, if the K_d value were to decrease by 50% site-wide after a persulfate application, then the sorbed mass may also decrease by 50%, but without registering a change in aqueous concentrations. Thus, it may appear that no treatment occurred, when in fact 50% of the mass was degraded but was effectively replaced by the release of additional sorbed mass from the altered porous media.

Cuypers et al. (2000, 2002) attributed enhanced desorption to a different mechanism, where persulfate degraded the NOM matrix, resulting in release of sorbed contaminant, which is then susceptible to oxidation. However, the extent to which this mechanism is possible varied with the nature of the NOM, which is known to be heterogeneous. Cuypers et al. (2000, 2002) evaluated up to 14 different porous media with varied NOM content and noted that persulfate could only degrade components of the NOM matrix that were less condensed and less humified, and could liberate and degrade contaminants sorbed to this portion of the NOM. However, little treatment of contaminants sorbed to highly condensed NOM, representative of

highly weathered organic matter, could be achieved. Since the degree of humification of NOM can vary widely from site to site, and possibly across a site, this implies the effectiveness of treating sorbed contaminants with persulfate may also vary from site to site, as well as spatially within a site, depending on NOM characteristics. Liang et al. (2003) also noted the apparent practical impact of NOM on thermally-activated persulfate treatment effectiveness. They found that for high organic content media, effective treatment required higher oxidant doses, longer contact times, and higher activation temperatures to get the same degree of contaminant degradation as in low organic content media.

Others have investigated treating sorbed phase contamination, and enhancements to contaminant desorption rates and extent have been noted with persulfate (Cuypers et al., 2000, 2002). Watts et al. (1999a) observed enhanced desorption in CHP reactions and attributed this effect to a direct reaction between superoxide and the sorbed contaminant that resulted in the contaminant's desorption into the aqueous phase. Thus, some of the reactive intermediates generated from hydrogen peroxide may have acted as surfactants or cosolvents. Since some overlap is expected between reactive species generated by hydrogen peroxide and those generated by persulfate, this mechanism might have relevance to persulfate systems as well, but it is unclear at this time. Surfactant-like compounds have also been observed to be produced from oxidation reactions and enhance dissolution or desorption (Ndjou'ou and Cassidy, 2006).

4.3.2 Impacts on Metal Mobility

Because the *in situ* treatment of organic contaminants by persulfate oxidation is a relatively new approach, there has not been a lot of investigation of the impact of persulfate on metal mobility. The strong reduction potentials of persulfate anion (2.01 V) (Lide, 2006) and sulfate radicals (2.6 V) (Ebersson, 1987) indicate the potential of these species to directly oxidize metals and minerals. In general, results of monitoring at field sites has indicated that elevated metals concentrations, if observed at all, have attenuated with time and thus may not be a major concern (Huling and Pivetz, 2006; Krembs, 2008). Nonetheless, mechanisms that can lead to increased metal mobility are discussed here for the sake of completeness. Due to the lack of mechanistic research with persulfate in this area, inferences must often be made about metal speciation based on a general understanding of environmental chemistry and analogies to other oxidants.

First, few metal impurities are reported for sodium persulfate. FMC technical data for environmental grade persulfate state 2 ppm of iron, <0.2 ppm of copper and lead, and <0.15 ppm chromium. Data for other metals are not reported.

One aspect of persulfate oxidation with implications for metals is that acidity can be a major reaction product (see Section 4.2.2); thus, a strong pH drop may result if the buffering capacity of the porous media is depleted. Alternatively, alkaline activation (see Section 4.2.3.1) may involve increasing the pH to values of 11 or more. Because metal solubility and speciation are linked to pH, these pH shifts may affect dissolved metal concentrations. These pH effects will be specific to the metal and the system geochemistry; the redox potential and other chemistry species in solution (e.g., sulfate, carbonate and others) interact with pH to determine the final metals concentration.

Persulfate oxidation also uses a variety of activation approaches and amendments; some of these amendments have the potential to affect dissolved metal mobility. As discussed previously, alkaline activation will increase pH and may affect metal mobility. However, others may have an impact as well. For instance, chelating agents are frequently delivered to enhance iron

mobility and availability to promote persulfate activation. However, they are not iron-specific and may complex with and mobilize other metals from the soil matrix. The duration of this mobility has not been investigated, but conceivably it could persist until the chelating agent is degraded or immobilized either by the oxidant itself or other geochemical processes. Increased temperature from heat activation may also affect metal sorption and mobility depending on the metal, the nature of sorption sites, and subsurface conditions. For instance, a rise in temperature has been observed to increase the adsorption of metal cations to soils and catalyst resins and therefore may decrease their mobility (Barrow, 1992; Pehlivan et al., 1995). However, it is unknown how significant this could be in persulfate systems and also unknown whether this decrease in mobility is either transient or permanent once the heat dissipates. Oxidation of NOM represents one final mechanism that could affect metals concentrations and attenuation. The degradation of NOM could result in the release of metals complexed or adsorbed to metal binding NOM.

4.4 CONTAMINANT TREATABILITY

Persulfate is capable of degrading a wide variety of contaminants because of the numerous reactions that occur, as described above. The treatment efficiency, effectiveness, and reaction products may vary by contaminant and activation method. This section describes studies that have evaluated persulfate treatment of different contaminant classes (Table 4.7). Chapter 9 includes tools for appropriate selection of oxidant and oxidant activation approach for different contaminants or contaminant groups.

Table 4.7. General Assessment of the Susceptibility of Classes of Organic Contaminants to Persulfate ISCO

Contaminant group	Susceptible to persulfate oxidation	Notes
Halogenated aliphatics	Yes; dependent on contaminant type	Chloroethenes highly amenable; chloroethanes less amenable; chloromethanes amenable only with very aggressive activation approaches
Chlorinated aromatics	Yes; limited data but highly probable	Little published data, but existing data do indicate high amenability for most chlorinated aromatics; oxidation of aromatics with more complex structures highly dependent on activation approach
Fuel hydrocarbons	Yes; dependent on persulfate activation approach	Oxidation of hydrocarbons with more complex structures highly dependent on activation approach
Polycyclic aromatic hydrocarbons	Yes; dependent on persulfate activation approach	Oxidation of hydrocarbons with more complex structures highly dependent on activation approach; little info available on individual component amenability
Nitroorganics	Yes; some are more amenable than others	2,4,6-Trinitrotoluene (TNT) appears to be more amenable than dinitrotoluene (DNT); limited data
Pesticides	Possibly	Limited data; likely dependent on structural complexity and activation approach

4.4.1 Halogenated Aliphatics

Halogenated aliphatics encompass a variety of organo-halogen compounds, the most environmentally relevant of which include short-chain, chlorinated compounds that have typically been used as solvents. These include chloroethene compounds such as PCE, chloroethanes such as 1,1,1-trichloroethane (1,1,1-TCA), chloromethanes such as CT, and other aliphatics. Brominated and fluorinated contaminants, though less commonly targeted for ISCO remediation, also fall into this general category. The reactivity of persulfate with compounds in this category is variable, and appears to depend primarily on the nature of the carbon bonding (e.g., single versus double bonds), as well as the degree of halogenation.

4.4.1.1 Chloroethenes

Chloroethenes, especially TCE and PCE, are common groundwater contaminants and are among the most frequently targeted COCs by ISCO (Krembs, 2008). As a result, their degradability by persulfate has been more extensively investigated. In general, this category of contaminants is highly amenable to persulfate ISCO. The degradation of all six chloroethenes, PCE, TCE, 1,1-dichloroethene (1,1-DCE), *cis*-DCE, *trans*-DCE, and vinyl chloride (VC), by persulfate has been demonstrated (Huang et al., 2005; Waldemer et al., 2007). Block et al. (2004) investigated the degradation of chloroethenes in aqueous systems with a variety of activation methods, including unactivated persulfate (ambient temperature, neutral pH, no activators), and activation by Fe(II) and Fe(III), chelated Fe(III), hydrogen peroxide, and alkaline pH. They found that chloroethene concentrations were substantially lower relative to controls for each of the activation methods used. The hydrogen peroxide and alkaline activation methods both enabled extensive degradation. However, for unactivated persulfate and Fe(II) or Fe(III) activation, the degradability of chloroethenes was significantly affected by the pH of the system. Although the starting pH was near neutral for these systems, acidity produced by the persulfate reaction caused the pH to drop to near 2 in unbuffered systems, and extensive degradation was observed. Yet, when the pH was forced to remain neutral, as might occur in well-buffered aquifers, the degradation rate was slower and less extensive for iron activation, and unactivated persulfate was almost non-reactive. Liang et al. (2003) conducted investigations with heat-activated persulfate in a porous media slurry at ambient temperature and neutral pH and found that there was limited degradation of TCE. However, heat activation at 40–60°C (104–140°F) led to extensive degradation. These results indicate that non-chelated iron activation and unactivated persulfate may be more challenged by well-buffered systems than heat, hydrogen peroxide, or alkaline activation.

Other interactions with system chemistry have been noted as well. Dahmani et al. (2006) investigated the Fe(II)-chelate activation of persulfate for degrading a series of chloroethenes and noted that the treatment effectiveness declined with increasing contaminant concentration. Liang et al. (2004a) investigated the iron activation of persulfate and found that with Fe(II) activation, the degradation of TCE seemed to stall once all of the Fe(II) was oxidized to Fe(III). The system could be reactivated with the dosing of either more Fe(II) or with thiosulfate, a reductant that would presumably convert Fe(III) to Fe(II). When Liang et al. (2004b) evaluated Fe(II)-chelate activation, much better results were attained, including a 99% reduction of TCE concentration in a porous media slurry system, showing that chelates might help circumvent the challenge of neutral pH.

A recent study by Waldemer et al. (2007) investigated the kinetics of thermal activation of persulfate for chloroethene degradation, as well as reaction products. They found that the kinetic rate of degradation decreased in the order of PCE, TCE, *trans*-DCE, and *cis*-DCE. It is

interesting to note that this is nearly the opposite order found for chloroethene degradation by Huang et al. (2001b) for permanganate oxidation. Waldemer et al. (2007) generally found chloride production to be nearly quantitative, with about 80–90% recovered, but did identify several organic byproducts from chloroethene degradation. When treating either *cis*-DCE or *trans*-DCE, both isomers were detected in major proportions, indicating that isomerization was occurring, converting *cis*-DCE to *trans*-DCE and vice versa. They speculated that this might be caused by the formation of a single-bonded intermediate in the reaction with sulfate radicals, which then decomposes to form a chloroethene again rather than degrading via oxidation and hydrolysis reactions. The only other compound identified when treating TCE and PCE was trace amounts of HCA. The formation of HCA was late in the reaction time, which suggested that a possible halogenation reaction was occurring as chloride accumulated in solution. As discussed in Section 4.2.5, chloride may interact with sulfate or hydroxyl radicals and generate its own radicals, some of which can result in halogenation. Presumably, one of these chlorine radicals reacted with the TCE or PCE parent compound to form HCA.

Huang et al. (2005) reported on the heat activated persulfate treatment of several higher alkene contaminants in a mixture of contaminants, including *cis*-1,3-dichloropropene, *trans*-1,3-dichloropropene, 1,1-dichloropropene and hexachlorobutadiene (HCBD). All of these contaminants were found to be degradable, highlighting the susceptibility of ethene bonds to oxidation reactions. However, HCBD did degrade much more slowly than the others, though it is unknown whether this was due to some inherent resistance to oxidation or to other factors.

Despite this attention to treatment of chloroethenes by persulfate ISCO, there are still aspects of the chemistry that are not well understood. For instance, it is not known what radical species and mechanisms may be the most active in degrading chloroethenes. The role of direct reaction versus free radical reactions is also unknown. Chloroethenes contain a carbon-carbon double bond with π -electrons, and electrons in this configuration are known to be amenable to direct electron transfer reactions. For example, this is the primary mechanism understood to be involved with the degradation of ethene bonds by permanganate (Arndt, 1981). Identification of the major radicals and mechanisms and the conditions under which they are favored may allow for better chemistry optimization with these contaminants.

4.4.1.2 Chloroethanes

Compared with chloroethenes, halogenated alkanes (e.g., 1,1,1-TCA and 1,2,3-trichloropropane) tend to be much more resistant to oxidation by nearly all ISCO oxidants. Studies of their degradation by activated persulfate are no exception to this trend. This resistance is likely due to their lack of π -electrons that are associated with carbon-carbon double bonds and aromatic rings, which promote reactions with electrophilic oxidants. Block et al. (2004), Liang et al. (2003), and Cho et al. (2002) noted that no degradation of chloroethanes occurred in unactivated persulfate systems at ambient temperatures. Instead, significant degradation of 1,1,1-TCA was only observed when either the temperature was raised to 35–60°C (95–140°F) (Cho et al., 2002; Liang et al., 2003; Tsitonaki et al., 2006), or with alkaline or hydrogen peroxide activation (Block et al., 2004). Even then, Liang et al. (2003) observed the rate of 1,1,1-TCA degradation to be slower than the rate of chloroethene degradation at all comparable temperatures, highlighting the resistance of 1,1,1-TCA to oxidation. Jazdanian et al. (2004) noted that despite nearly complete degradation of 1,1,1-TCA in a Fe(II)-chelate activated system, 1,1-dichloroethane (1,1-DCA), a common biodegradation product of 1,1,1-TCA, was not at all degraded, suggesting that among chloroethanes, 1,1-DCA may be even more resistant to oxidation. Huang et al. (2005) investigated heat-activated persulfate treatment of a series of 13 halogenated alkanes, including chloroethanes and higher chlorinated and brominated

alkanes, in the presence of 59 total organic contaminants in one solution. In all systems tested, they found only 2,2-dichloropropane to degrade to non-detectable concentrations. For the other 12 compounds, treatment was better at 30°C (86°F) with an average of 20% removal for all 12 compounds compared to 20°C (68°F) or 40°C (104°F), where removals averaged less than 10%. In the 40°C (104°F) system, chloroethane actually increased in concentration, suggesting that it was a reaction product from other compounds degrading in solution.

In the context of these results, it is worth noting that while many chloroethanes exhibit a resistance to oxidation, several contaminants in this category become susceptible to rapid hydrolysis reactions at high temperatures or strongly alkaline pH values (Jeffers et al., 1989). In particular, 1,1,1-TCA and 2,2-dichloropropane both degrade at rapid rates due to neutral hydrolysis (reaction with H₂O) as temperature increases; therefore, this may be a significant reaction process with heat-activated persulfate. 1,1,2,2-TeCA, 1,1,2-TCA, and 1,1,1,2-TeCA also exhibit rapid alkaline hydrolysis (reaction with OH⁻), suggesting that this might be a major reaction pathway with alkaline activation of persulfate. However, Jeffers et al. (1989) noted that alkaline hydrolysis of several chloroethanes yielded chloroethenes as intermediates, including TCE, VC, and DCE isomers. This is shown in Figure 4.8 as the dehydrochlorination pathway that occurs under reducing conditions and is enhanced at elevated pH. Arnold et al. (2002) also point out that ethanes can yield ethenes via surface-mediated reaction with iron metal or iron-oxide surface. Therefore, even if alkaline conditions or iron-mediated reactions are responsible for initiating degradation of these oxidant-resistant contaminants, persulfate oxidation may support the reaction by degrading the chemical intermediates formed from hydrolysis through the activators employed (e.g., alkaline pH, soluble iron), particularly if introduced prior to persulfate in a sequential approach.

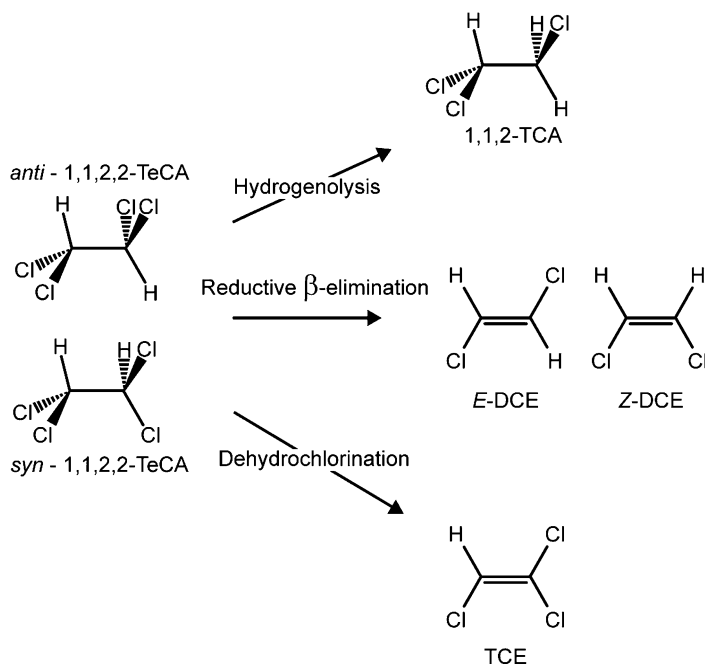


Figure 4.8. Reductive degradation pathways of 1,1,2,2-TeCA (modified from Arnold et al., 2002).

It is likely that if the systems investigated by Huang et al. (2005) had been at higher temperatures such as 60–80°C (140–176°F) and without 59 other contaminants in solution to compete with chloroethanes for persulfate, more extensive degradation would have

been observed as the combination of hydrolysis and persulfate reaction would probably lead to more aggressive treatment. Indeed, a follow-on study by Huang et al. (2005) with just 1,1,2-TCA, and 1,1,1-TCA alone with persulfate at 40°C (104°F) demonstrated that they were more degradable.

It is also worth noting that 1,4-dioxane is commonly found as a co-contaminant with chloroethanes, because it is added to stabilize 1,1,1-TCA. Brown et al. (2004) demonstrated degradation of 1,4-dioxane to non-detectable levels with Fe(II)-activated persulfate, but little information on mechanisms or products is available at this time.

4.4.1.3 Halogenated Methanes

Halomethanes are resistant to oxidation as a result of the high oxidation state of carbon in these compounds. For instance, CT is effectively unreactive with hydroxyl radicals (Haag and Yao, 1992), despite the very strong reduction potential of OH[•]. Because sulfate radicals also react via oxidative mechanisms (Huie et al., 1991), the oxidation of CT by sulfate radical also appears unlikely. However, CT has been demonstrated to be susceptible to degradation via reductive mechanisms, such as with superoxide anion (Watts et al., 1999a; Teel and Watts, 2002; Smith et al., 2004). Other halomethanes, such as chloroform, are likewise not expected to be susceptible to oxidation mechanisms; yet they have shown high degrees of degradation in CHP systems that are suspected to generate superoxide or other reductants (Teel and Watts, 2002; Smith et al., 2006). This resistance to oxidation but susceptibility to reductive reaction pathways suggests that if degradation of halomethanes is to occur in persulfate ISCO systems, then reductive reaction pathways must be present. There is evidence that this might occur, as degradation of halomethanes has also been observed in some persulfate systems (Huang et al., 2005; Root et al., 2005). However, the conditions that lead to the expression of these reductive pathways in persulfate systems are not understood.

The reports of persulfate treatment of halomethanes are somewhat conflicting. The most comprehensive study of persulfate oxidation of halomethanes was conducted by Huang et al. (2005). Using thermal activation of persulfate at temperatures ranging from 20 to 40°C (68–104°F), the objective was to determine the degradability of a wide variety of COCs, including many chlorinated aliphatic and aromatic contaminants. In total, 59 organic contaminants were present in solution, including CT and 11 other halomethanes. In this solution containing all 59 organic contaminants, extensive degradation of CT and three other halomethanes was observed, while others were effectively untreated. This was paradoxical to the hypothesis of Huang et al. (2005) as they did not expect CT to degrade. Follow-on studies were conducted with CT alone that confirmed that thermal activation could not degrade it. Thus, some mechanism may have been present in the complex solution with 59 organics that led to CT and other halomethane degradation that was not present in the CT-only system. What mechanism is responsible is difficult to discern, as it could involve any number of reactive species such as superoxide, solvated electrons, or organic radicals produced by oxidation of the other organic contaminants present (Huang et al., 2005). In contrast, Root et al. (2005) specifically investigated the degradation of CT and chloroform in Fe(II)-chelate-, alkaline-, and peroxide-activated persulfate systems, and found both contaminants to be degraded at rates exceeding controls for all three activation methods. Alkaline activation led to the most extensive degradation, followed by peroxide-activated systems. The evolution of reductive species such as superoxide would seem plausible in these systems given that the presence of either hydroxyl radicals or hydrogen peroxide could yield propagation reactions leading to the formation of reductants. Alkaline or neutral hydrolysis may also play a role since some halomethanes are known to degrade at appreciable rates when either temperature or pH becomes high (Jeffers

et al., 1989), which can occur with alkaline or heat activation. However, the significance of any of these mechanisms leading to the degradation of halomethanes in persulfate systems has yet to be elucidated.

4.4.2 Chlorinated Aromatics

Halogenated aromatics (especially chloroaromatics) are another broad category that contains many contaminants. These compounds also exhibit a range of affinities for chemical oxidation by persulfate, from very reactive to resistant, depending on the compound. This variability in reactivity is understandable; Neta et al. (1977) noted that sulfate radical reactivity is much more selective than hydroxyl radical reactivity.

4.4.2.1 Chlorobenzenes and Chlorophenols

The persulfate oxidation of contaminants within this category is not extensively reported in the literature. However, based on data provided by Huang et al. (2005), these contaminants appear to be very amenable to treatment by persulfate. Huang et al. (2005) investigated the degradation of 8 different chlorinated aromatic contaminants in a complex solution containing 59 different organic contaminants. These included chlorobenzene, all isomers of dichlorobenzene, two isomers of trichlorobenzene, and two isomers of chlorotoluene. All were found to be degradable by thermally activated persulfate, but the rates of degradation decreased with increasing chlorine content on the aromatic ring. Chlorotoluenes had the highest rates of degradation, possibly indicating that the presence of the methyl group on the benzene ring enhances their reactivity relative to chlorobenzene. Barbash et al. (2006) reported that persulfate could enhance the desorption of trichlorobenzene by degrading the NOM matrix, enhancing release of the contaminant. No volatile chlorinated organic daughter products were observed. In comparison to chlorobenzenes, chlorophenols are even less studied. However, phenolic contaminants have in general been observed to be highly amenable to degradation with other oxidants (e.g., Tang and Huang, 1995; Lu, 2000; Waldemer and Tratnyek, 2006); therefore it is anticipated that phenolic contaminants should be highly amenable to persulfate treatment as well. One strong trend observed in hydrogen peroxide systems is that intermediates formed by oxidation, especially benzene-diols such as catechol or quinone, act as reductants to Fe(III) and can actually regenerate the Fe(II) activator (Lu, 2000; Lu et al., 2002). A similar mechanism is conceivable in iron-activated persulfate systems but has not been explored. Presently, the only known study dealing with phenol degradation by persulfate was conducted by Anipsitakis and Dionysiou (2004), who demonstrated that 2,4-dichlorophenol was effectively degraded by both Fe(II) and Fe(III) activated persulfate.

4.4.2.2 Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs), dioxins, and furans are another category of chlorinated aromatic contaminant. There are 209 various congeners of PCBs, and in the environment, they generally occur as mixtures. PCBs tend to be difficult to treat with aqueous oxidants, in part because their hydrophobic nature limits their solubility and as a result, their contact with oxidants in the aqueous phase. Furthermore, there is evidence that achieving complete degradation of PCBs may be difficult even in optimized systems because some of the more highly chlorinated PCB congeners are resistant to oxidation (Sedlak and Andren, 1991).

The treatment of PCBs by persulfate has not been extensively investigated, and until recently, little information was available. Rastogi et al. (2009) investigated the degradation

of 2-chlorobiphenyl (PCB-1) by Fe(II) activated persulfate and peroxymonosulfate. Much of the study focused on peroxymonosulfate, but both were capable of degrading PCB-1. Complete degradation was possible in aqueous systems, but treatment effectiveness was lower in the porous media system, likely due to PCB sorption. Also in the porous media systems, the extent of degradation with persulfate was lower than the extent of degradation with peroxymonosulfate. Radical quenching studies of both oxidants indicated that sulfate radicals ($\text{SO}_4^{\bullet-}$) were the primary reactive species, as opposed to either hydroxyl (OH^{\bullet}) or peroxymonosulfate radicals ($\text{SO}_5^{\bullet-}$). Therefore, slower degradation in the persulfate system than the peroxymonosulfate system may be a catalysis limitation rather than a reactivity limitation. Reaction intermediates were not quantified, but even in one of the most highly treated systems, a 23% TOC content remained, indicating that perhaps some organic byproducts are formed. Waisner et al. (2008) also recently investigated treatment of PCBs in porous media with TNT, DNT, and lead co-contaminants. Heat-activated persulfate at 40°C (104°F) achieved approximately 85% reduction in PCB concentrations, while alkaline activation and alkaline hydrolysis demonstrated only about 70–75% degradation. Byproducts were not investigated. Recently, O'Connell et al. (2009) showed that alkaline-activated persulfate (pH = 13, 60 g/L) in contact for 12 days with porous media spiked with PCB Arochlor-1248 only achieved ~50% reduction in Arochlor-1248 concentration.

4.4.3 Fuel Hydrocarbons

Fuel hydrocarbons represent a broad category of organic contaminants. Hydrocarbon fuels, oils and residues are complex mixtures of organic compounds, including a wide variety of straight and branched chain aliphatics, substituted aromatics, polycyclic aromatic hydrocarbons (PAHs), and additives, such as MTBE. These mixtures may vary widely in composition depending on the hydrocarbon source. This has implications for ISCO because each fraction of the mixture will respond differently to activated persulfate oxidation. The multi-component mixture may even change in composition as a result of ISCO as the more soluble and more oxidizable components are depleted from the mixture and the more resistant or less soluble fractions remain behind. The following section describes the oxidation of each of these sub-categories of fuel hydrocarbons.

4.4.3.1 Methyl Tert-Butyl Ether

Huang et al. (2002) specifically investigated the degradation of MTBE with thermally activated persulfate across a range of pH conditions. They found it to be degradable, with degradation rates increasing with temperature and persulfate concentration. Degradation was less effective at alkaline pH, possibly posing challenges to alkaline activation. A series of organic intermediates were observed to accumulate in solution during oxidation, and included tertiary butyl formate (TBF), tertiary butyl alcohol (TBA), methyl acetate, and acetone. All of these byproducts further degraded, indicating mineralization was possible given sufficient oxidant contact; however, acetone remained in solution much longer than the others, thus indicating that the rate of acetone oxidation was very slow. It is interesting to note that these same organic intermediates are formed during the CHP treatment of MTBE (Burbano et al., 2002, 2005); therefore MTBE degradation by these two oxidants may follow similar mechanisms. Tsitonaki et al. (2006) also investigated MTBE degradation in water and porous media systems, with unactivated, heat activated, and chelated iron activated persulfate. All three activation methods performed well in water only systems. Unactivated persulfate failed in

porous media systems. Iron was effective initially in porous media, but the reaction stalled after several hours. Only heat-activated persulfate achieved 98% degradation.

4.4.3.2 BTEX and Other Aromatic Hydrocarbons

The persulfate treatment of BTEX and other aromatic hydrocarbons has been investigated by several researchers, and in general this category appears very amenable to persulfate oxidation (Huang et al., 2005; Crimi and Taylor, 2007; Sra et al., 2008). Huang et al. (2005) investigated the degradation of BTEX, as well as related aromatic compounds 1,2,4- and 1,3,5-trimethylbenzene (TMB), iso-propylbenzene, n-propylbenzene, tert-butylbenzene, sec-butylbenzene, and n-butylbenzene. All were found to be highly degradable and tended to degrade at faster rates than chlorinated benzenes and many halogenated aliphatic contaminants also present in the same solution. Thus, it appears that aromatic components of fuel hydrocarbons are highly amenable to persulfate ISCO. Acetone concentrations increased significantly in this system, possibly indicating it as a reaction byproduct; because this study was conducted with a total of 59 halogenated and non-halogenated contaminants in solution, it is impossible to determine if this byproduct was formed from the degradation of BTEX or from other contaminants. Sra et al. (2008) investigated BTEX, TMB, and naphthalene degradation as a function of activation methods. In general, BTEX responded well to nearly all activation methods, including alkaline, hydrogen peroxide, and chelated iron activation, as well as unactivated persulfate. However, TMB and naphthalene degradation were more extensive with hydrogen peroxide and alkaline activation. Crimi and Taylor (2007) also investigated the degradation of BTEX contaminants in porous media systems and found the effectiveness and byproducts produced varied by porous media and activation method. One interesting finding was that gas chromatograms with unidentified compounds from the different activation methods yielded radically different patterns, potentially indicating that the organic intermediates and byproducts formed, as well as the reaction pathways involved, are different for the different activation methods.

4.4.3.3 Aliphatic Hydrocarbons

The degradation of aliphatic hydrocarbons by persulfate has not been widely reported. Sra et al. (2008) did evaluate the destruction of specific gasoline fractions (F1 and F2). F1 consists of lower molecular weight hydrocarbons (C6–C10) and F2 consists of higher molecular weight hydrocarbons (C11–C16). In general, it appears that both fractions were treatable by persulfate, but the F1 fraction was more treatable than the F2. Total petroleum hydrocarbons (TPH) could be reduced by more than 93%. Alkaline, hydrogen peroxide, chelated iron, and unactivated persulfate were all evaluated; all showed reductions in TPH, though it appeared that alkaline activation resulted in the highest degree of treatment.

4.4.4 Polycyclic Aromatic Hydrocarbons

PAHs are most commonly associated with residues from coal processing, such as coal tar or creosote, and have also been employed as wood preservatives. The residues are generally complex mixtures of PAHs, which include compounds with various degrees of substitution with aliphatic hydrocarbon chains, as well as heteroatoms such as oxygen, sulfur, or nitrogen. PAHs are generally the dominant component of these mixtures, though generally there is some phenolic, BTEX, and saturated aliphatic component present as well (Brown et al., 2006).

The degradation of PAHs by activated persulfate has been reported in the literature. However, relatively little specific information is available, such as the susceptibility of specific

PAH compounds to degradation, or chemical intermediates that may be formed. Often, just the sum of the 16 U.S. Environmental Protection Agency (USEPA) regulated PAHs are reported as data. However, the very high degree of treatment of non-halogenated aromatic hydrocarbons, such as BTEX, observed by Huang et al. (2005) suggests that these contaminants should be highly susceptible to persulfate oxidation, despite the lack of specific data. Cuyper et al. (2000, 2002) investigated the degradation PAHs sorbed to NOM and found that persulfate could treat a variety of the 16 USEPA PAHs. Persulfate treatment effectiveness after 3 h of oxidation was similar to enhanced biodegradation over 21 days for 2–4 ring PAHs. However, 5–6 ring PAHs were treated to a much higher degree with persulfate than with biodegradation. Furthermore, oxidation of the NOM matrix enhanced their desorption, improving treatment effectiveness. Nadim et al. (2005) also conducted a treatability study on a field porous media and found that the degradation of 16 USEPA PAHs could be achieved using heat and Fe(II)-chelate activated persulfate. Robinson et al. (2004) investigated the treatment of a manufactured gas plant residual with heat and peroxide activated persulfate and found that dicyclopentadiene, a major contaminant at the site, could be degraded by up to 87%. Other semi-volatile organic compounds (SVOCs) results were more variable. Crimi and Taylor (2007) and Huang et al. (2005) both reported the effective degradation of naphthalene in water and porous media using heat, hydrogen peroxide, alkaline, and chelated iron activated persulfate. However, in porous media, the effectiveness of one activation method or another appeared to vary depending on the media, though it was not clear what mechanism might be controlling this performance. Forsey (2004) investigated the degradation of *p*-cresol in a Fe-activated persulfate system by varying the molar ratio of the reactants. When the iron concentration was increased while maintaining a constant molar ratio between *p*-cresol and persulfate (1:8), the amount of *p*-cresol oxidized decreased; however, when the molar ratio of persulfate was increased to 1:10, the amount of *p*-cresol removed increased. When the molar ratio of *p*-cresol:persulfate:Fe²⁺ was adjusted to 1:10:8, 95% of the *p*-cresol was oxidized, indicating an optimal ratio exists and that larger concentrations of iron may inhibit the reaction.

4.4.5 Nitro-Aromatic Compounds

Crimi and Taylor (2007) investigated the activated persulfate treatment of aromatic contaminants in porous media that contained nitrobenzene, BTEX, and naphthalene. The treatment effectiveness for nitrobenzene and the other contaminants of interest was found to vary with porous media type and activation method. In three of the four media tested, chelated iron activation performed better than hydrogen peroxide activation, in some cases, attaining 71 to over 99% degradation of nitrobenzene. However, in the fourth porous medium, hydrogen peroxide activation attained 99% degradation of nitrobenzene, while the chelated iron activation attained no treatment at all. To further complicate results, the BTEX components within the iron chelate-activated systems were degraded, indicating effective persulfate activity. It is unclear why the performance varied with the specific porous media, as the porous media all had similar initial pH values; however, the porous media were not extensively characterized for mineralogy or organic matter, so it is possible that some unknown porous media-dependent mechanism was playing a role. It is interesting to note that Neta et al. (1977) reported that nitrobenzene reacted very slowly with sulfate radicals, if at all. Thus, if the reaction was proceeding via a non-sulfate radical mechanism, that mechanism might depend on porous media type.

Waisner et al. (2008) also investigated the persulfate treatment of a porous media contaminated with high explosives, including TNT, 2,4-DNT and 2,6-DNT, as well as PCBs and lead co-contaminants. Activation methods included heat activated persulfate at 40°C (104°F), alkaline activated persulfate using hydrated lime [Ca(OH)₂], and heat and alkaline activation

combined. They also investigated alkaline hydrolysis alone by adding lime only, without persulfate. Interestingly, all methods led to similar removal of TNT (86–96%), but alkaline hydrolysis alone performed much better on DNT (90%) than any of the persulfate methods, including alkaline activation (39–56%). This might have been due to the pH dropping from 12 to 9 as a result of persulfate oxidation, ceasing alkaline hydrolysis and effective oxidant activation. However, it does indicate that TNT may be somewhat easier to treat than DNT.

4.4.6 Pesticides

Pesticides are a broad category of contaminants that share only the common characteristic of toxicity toward some target organism. They can range in chemical structure from simple to very complex, from insoluble to highly soluble, and from strongly sorbing to highly mobile. The treatment of these compounds by persulfate oxidation is not widely reported in the literature. The persulfate treatment of two specific pesticides, Lindane (γ -hexachlorocyclohexane) and Atrazine, has been reported in the literature.

Crimi (2005) evaluated the effectiveness of various persulfate activation methods for Lindane destruction in two different groundwaters (Groundwater A and Groundwater B), with no porous media present. Persulfate activation methods included heating to 40°C (104°F), alkaline (pH 11), hydrogen peroxide (10:1 mole ratio of hydrogen peroxide to persulfate), chelated iron, and unactivated systems. In Groundwater A, Lindane was degraded from 7 $\mu\text{g/L}$ to below detection limits using all activation methods. However, Groundwater B, which had initial concentrations of 630 $\mu\text{g/L}$ Lindane, had much more variable performance; only alkaline, hydrogen peroxide, and heat activated systems effectively degraded Lindane to non-detectable concentrations (see Figure 4.9). No chlorinated hydrophobic intermediates as determined by gas chromatography (GC)-electron capture detection were observed for these three activation methods. However, iron chelate systems yielded additional peaks on their chromatograms, suggesting that intermediates might be formed. These intermediates corresponded to retention times for chlorophenol and tetrachlorophenol, but compound identities were not confirmed.

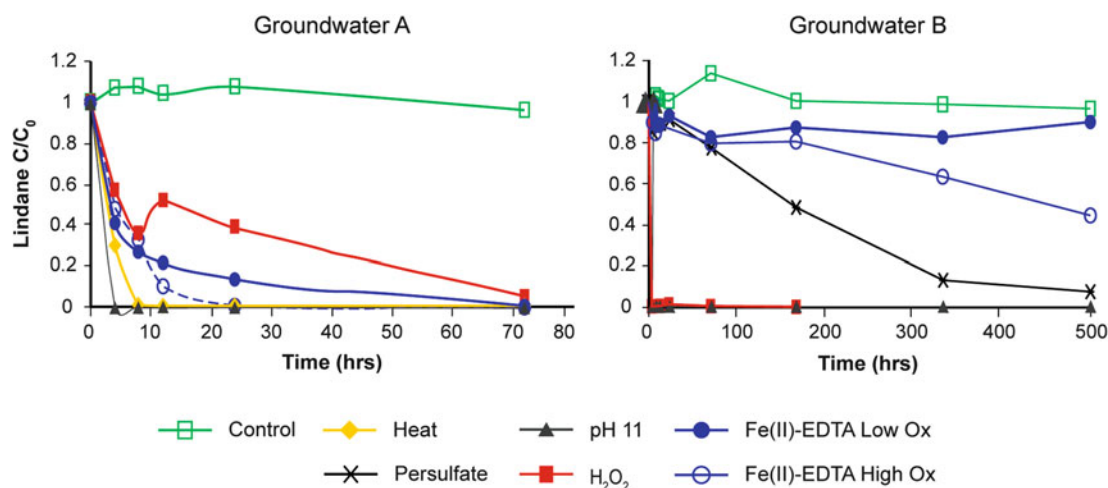


Figure 4.9. Results of Lindane degradation studies by Crimi (2005). Observe the considerable difference between the effectiveness of activation in Groundwater A versus Groundwater B (note change in scale as well). Conditions were identical in both groundwaters, with persulfate at 15 g/L (except the high oxidation condition at 30 g/L). Note: “Heat” line for Groundwater B does not appear – it is “hidden” by the H_2O_2 and pH 11 lines and matches these outcomes.

The degradation of other pesticide compounds has been less thoroughly investigated. Anipsitakis and Dionysiou (2003) investigated the degradation of Atrazine by peroxymonosulfate but found that the sulfate radical was the primary reactive species responsible for Atrazine degradation. Thus, Atrazine may degrade in activated persulfate systems as well.

Huang et al. (2005) investigated the thermally activated persulfate degradation of 59 organics in solution, which included 1,2-dibromo-3-chloropropane and 1,2-dibromoethane, both of which have been used as pesticides. While used as pesticides, these contaminants also fall into the halogenated alkane category discussed in Section 4.4.1.2, and in keeping with the general trends of halogenated alkanes, they were relatively resistant to oxidation. 1,2-Dibromoethane was mostly untreated by persulfate oxidation, while 1,2-dibromo-3-chloropropane experienced some treatment (33% reduction) under the most rigorous conditions investigated [40°C (104°F), 5 g/L persulfate, 72 h contact time].

4.5 SUMMARY

Persulfate has emerged as a viable oxidant for use during ISCO. There are a variety of activation methods available for persulfate that initiate powerful oxidation processes capable of degrading a wide range of organic contaminants. Some mechanisms are well understood, but not with all contaminants or all activation approaches. Some intermediate byproducts have been reported but not for all contaminant categories. There still remain gaps in the knowledge base for persulfate ISCO, particularly regarding optimizing process chemistry to degrade specific contaminants, especially those that are more resistant to oxidation such as halo-methanes and chloroethanes. Finally, there remains large uncertainty in how subsurface interactions impact persulfate chemistry, activation, and effectiveness. Nonetheless, persulfate shows great promise on both the basis of field applications and laboratory studies to be able to efficiently and effectively degrade many organic contaminants of concern.

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CHAPTER 5

FUNDAMENTALS OF ISCO USING OZONE

Wilson S. Clayton,¹ Benjamin G. Petri² and Scott G. Huling³

¹Aquifer Solutions, Inc., Evergreen, CO 80439, USA; ²Colorado School of Mines, Golden, CO 80401, USA; ³U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Center, Ada, OK 74820, USA

Scope

Chemistry and use of ozone gas for *in situ* chemical oxidation, including reaction mechanisms, oxidant interactions with subsurface media, oxidant transport, and effectiveness for different contaminants of concern.

Key Concepts

- Ozone is a very reactive and short-lived oxidant that requires aggressive delivery schemes.
- Ozone is unstable so it must be generated onsite and injected into the subsurface immediately after generation.
- Ozone provides direct oxidation, as well as aggressive radical propagation via catalysis by subsurface solids or by addition of activator.
- Ozone can transform or mineralize a wide variety of organic contaminants, including many hard to treat compounds.
- Ozone is a gaseous oxidant that can be delivered into the vadose zone or sparged into groundwater.
- For ozone sparging, multiphase flow mechanisms and mass transfer limitations dominate ozone delivery.
- Since ozone degrades to oxygen, it can support aerobic biodegradation.

5.1 INTRODUCTION

In situ chemical oxidation (ISCO) using ozone involves the introduction of ozone gas (O₃) into the subsurface to degrade organic contaminants of concern. Ozone is tri-molecular oxygen and a strong oxidant (Figure 5.1) that is a gas under atmospheric conditions. Ozone may react with organic compounds via two predominant reaction pathways: direct reaction between ozone and organic compounds or catalytic decomposition to form free radicals, which may then react with organic contaminants. Direct oxidation may occur in the gas phase (e.g., Reisen and Arey, 2002) and in the aqueous phase by dissolving ozone in water (Hoigné and Bader, 1983a, b; Hoigné et al., 1985). Free radical reactions in the aqueous phase have been documented (Langlais et al., 1991), and others suggest that free radical reactions also may occur in the gas phase (Choi et al., 2002; Reisen and Arey, 2002). Because of this diversity of reaction mechanisms, ozone may degrade a wide array of organic contaminants. Because ozone is a gas, it can be delivered directly into the vadose

(unsaturated) zone, which can be an advantage over liquid-phase oxidants that are limited in their ability to achieve contact with contaminants in unsaturated porous media. Ozone also can be delivered directly to the saturated zone through sparging wells. Here, successful contaminant treatment is a function of effective contact between oxidant and saturated subsurface media, which can be challenging due to complex gas distribution typical of *in situ* sparging technologies (Huling and Pivetz, 2006). Ozone sparging may involve stripping of volatile contaminants of concern (COCs) in addition to COC oxidation. Oxygen (O_2) is a byproduct of ozone decomposition and is also a co-injectant (i.e., air). A gratuitous benefit of introducing O_2 into the subsurface is that it is an important electron acceptor used in aerobic biodegradation processes (Lute et al., 1998; Fogel and Kerfoot, 2004; Ahn et al., 2005; Jung et al., 2008).

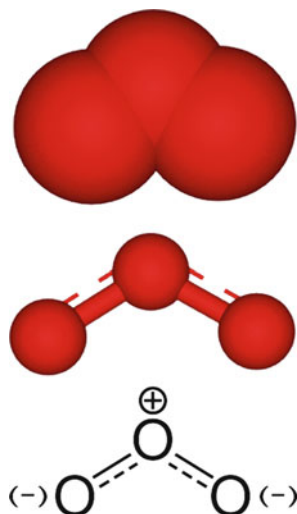


Figure 5.1. Ozone molecular structure.

However, ISCO using ozone also has its limitations. Ozone is too unstable to be manufactured, stored, or transported to a site, so it must be generated onsite and injected into the subsurface immediately after generation. The most common method used to generate large quantities of ozone is the corona discharge method, where ozone is produced from a flow of either air or pure oxygen passed between two electrically charged plates. Pure oxygen gas may also be generated onsite from air. Thus, the reagent costs associated with ISCO using ozone are typically minimal, if any. Instead, the principal costs associated with the oxidant are the equipment and electrical power required to generate the oxidant; electrical power must be available onsite to enable ozonation (Huling and Pivetz, 2006). Another feature of ISCO using ozone that may pose a limitation is the requirement for onsite generation. Large commercial ozone generators are still limited in output, producing in the neighborhood of 50 pounds of ozone per day. Though multiple generators can be employed to generate more oxidant, the ability to dose large masses of oxidant into the subsurface over short timeframes is lower with ozone than with other ISCO oxidants. Thus, sites that require larger oxidant doses will require longer injection durations, which may impact ozone cost effectiveness. Injection durations typically range from 3 to 18 months, depending on the level of contamination and site specific features. However, the fact that ozone injection is conducted over a period of time offers several advantages as well. The ability to focus injection efforts on hot spots that emerge over time as treatment proceeds may help overcome challenges in characterizing contaminant

distributions before treatment. Also, by maintaining aggressive oxidation conditions over a longer duration, more aggressive treatment of high concentrations (including dense nonaqueous phase liquid [DNAPL]) may be achieved relative to other oxidants.

Despite its potential limitations, ISCO using ozone is an effective remediation technology as long as it is carefully matched to site conditions. Effective treatment of the subsurface is linked to effective contact between the oxidant and the contaminant. Like other *in situ* remediation technologies, the effective distribution of ozone is a strong function of permeability and heterogeneity, which may challenge effective contact. This is especially true in the saturated zone, where ozone is sparged into the groundwater, which is especially sensitive to variations in subsurface conditions. Sites that are heterogeneous or dominated by low to moderate permeability will have a more irregular ozone distribution than those that are highly permeable and homogeneous. A more irregular ozone distribution may lead to more variable results. Another consideration is the compatibility of ozone with the media. Like other oxidants, ozone can react with non-target reductants in porous media (e.g., natural organic matter [NOM]), which can affect its stability and transport in the subsurface. If the aquifer materials have high oxidant demand, the efficiency of contaminant oxidation may be low because of competition and nonproductive side reactions. ISCO reaction efficiency will be higher and more cost-effective in aquifers with moderate to low oxidant demand. Thus, proper consideration of hydrogeologic and geochemical considerations when evaluating ISCO using ozone can lead to improved design and performance.

5.2 CHEMISTRY PRINCIPLES

Ozone is a strong oxidant that works via reactions in both the gas and aqueous phases and may act through direct oxidation, as well as free radical intermediates (Staelin et al., 1984; Tomiyasu et al., 1985; Langlais et al., 1991). This creates a variety of different reaction pathways by which an organic contaminant may degrade; as a result, ozone has applicability to a wide range of contaminants. Because reactions can occur in multiple phases (gas and aqueous), as well as through direct and free radical reaction processes, the chemistry of ozone is complex. However, the chemistry is not universal and depending on the specific contaminant, its properties, and other conditions of the system, one pathway may be more favored than another. Some contaminants are sensitive to specific degradation pathways while others are not; thus, geochemical conditions will affect ozone treatment of some contaminants more than others. The following sections describe the chemical properties, reactions, and mechanisms for ozone and how they may be relevant to ISCO.

5.2.1 Physical and Chemical Properties

Ozone is a highly reactive gas composed of oxygen and has the chemical formula of O_3 . Ozone is highly unstable and will decompose with a half life of several hours to several days (DeMore et al., 1997; Hauglustaine et al., 2004; Staelin and Hoigné, 1982). Because ozone is so unstable, it must be generated at the point of use with an ozone generator. These generators work by delivering a steady supply of air or pure oxygen between two ionized plates that ultimately produce ozone. Onsite generators can also be used to produce pure oxygen from air. Generators with air feed generally produce ozone concentrations up to 1–2% by volume and up to 8–10% if using oxygen feed. Air dilution is sometimes used to boost subsurface injection flow rates. The major consumable in ozonation systems is the electric power to generate the ozone.

The physical and chemical properties of ozone gas (Table 5.1) control its mass transfer and transport. The theoretical solubility limit of ozone in water is dependent on both the

temperature and the concentration of ozone in the gas phase. Water solubility increases with higher ozone concentrations in the gas phase and decreases with increasing temperature. Ozone concentrations never reach the solubility limit in the aqueous phase due to decomposition reactions in water, especially under alkaline conditions (Langlais et al., 1991). In environmental systems involving soils and aquifer material, where catalytic minerals and organic compounds react with ozone, decomposition reactions are faster and aqueous phase and gas phase concentrations can be limited.

Table 5.1. Physical and Chemical Properties of Ozone

Property	Value	
Molecular weight ^a	48 g/mol	
Physical form ^a	Light blue to colorless gas	
Standard reduction potential ^a	2.076 V	
Density ^a	2.106 g/L (STP)	
Temperature ^b (°C)	Henry's law constant (atm m ³ /mol)	Solubility limit in water at STP and 5% ozone mass concentration in pure oxygen (mg/L)
0	35.0	46.3
5	44.8	36.2
10	57.4	28.3
15	75.6	21.5
20	93.4	17.4
25	118.0	13.7
30	149.5	10.9
35	186.8	8.69

Note: °C - degrees celsius; atm m³/mol - atmospheres-cubic meter per mole; g - grams; mg/L - milligrams per liter; STP - standard temperature (20°C) and pressure (1 atm); V - volts.

^aLide (2006).

^bLanglais et al. (1991).

5.2.2 Oxidation Reactions

Chemical reactions with ozone involve both direct and free radical oxidation mechanisms, occurring in both the aqueous and gaseous phases. Additionally, ozone reacts with a wide range of organic contaminants and non-target reactants involving an array of pathways and reaction intermediates; as a result, the reaction chemistry of this oxidant is complex.

5.2.2.1 Gas Phase Reactions

Since ozone is a reactive gas and is delivered to the subsurface as a gas, reactions may occur in both the gas phase and aqueous phase. Extensive literature is available that is not reviewed herein relating to gas phase ozone reactions, which are of special interest in atmospheric systems. Some authors have evaluated gas phase ozone reactions in the context of *in situ* ozone treatment. For example, Luster-Teasley et al. (2009) and Hsu and Masten (2001) provide recent examples of investigations into gas phase ozone reactions during *in situ* ozone processes. Luster-Teasley et al. (2009) found that soil pH and moisture content impacted the effectiveness of polycyclic aromatic hydrocarbon (PAH) oxidation in unsaturated soils. In air-dried soils, as pH increased, removal increased, and the removal of pyrene was slower in moisturized soils, with the efficiency decreasing as the moisture content increased. Further

evidence of the importance of gas phase reactions with ozone ISCO exists in the data of Choi et al. (2000), Dunn and Lunn (2002), Goi and Trapido (2004), and Jung et al. (2004), who noted reduced contaminant degradation with increasing moisture content. Higher moisture content reduces the gas-solid phase contact between non-volatile contaminants and ozone and also promotes partitioning of ozone into the aqueous phase.

Gas phase reactions can occur homogeneously with volatile contaminants, where the contaminant partitions into the gas phase followed by reaction with gas phase ozone (e.g., Reisen and Arey, 2002), as well as heterogeneously, where ozone reacts with contaminants in sorbed or nonaqueous phase liquid (NAPL) phases at solid or liquid interfaces (Masten, 1991; Naydenov and Mehandjiev, 1993; Andreozzi et al., 1996). Reisen and Arey (2002) documented the kinetics of degradation of two volatile PAHs. Based on their kinetic rates and the concentrations of ozone used with ISCO, homogeneous reaction could be a significant process for some volatile organic compounds (VOCs). Because phenanthrene is non-volatile at normal temperatures, heterogeneous reaction is likely the process occurring in the system observed by Choi et al. (2000).

The role of free radicals in gas phase reactions in soil and water systems is much less investigated. In atmospheric chemistry, hydroxyl radicals, perhydroxyl radicals, and organic radicals have long been demonstrated to be important to the fate and transport of VOCs in the atmosphere (e.g., Levy, 1971). However, in atmospheric systems, the principal source of radical generations is photolysis of ozone from ultraviolet light from the sun. In the subsurface, this catalyst is not available, but other potential catalysts – such as solid phase minerals or water vapor – may be available. Data from Jung et al. (2004) seems to imply that catalysis of ozone (e.g., formation of radicals) may also occur at solid surfaces in the gas phase; they observed more extensive removal of phenanthrene in dry natural sand systems than in glass bead systems. Natural sands may contain metal oxides that might catalyze radical production, as they are known to do with other reactive peroxygens such as hydrogen peroxide (Teel et al., 2001; Kwan and Voelker, 2003). Several authors have also investigated the use of manganese oxides as a catalyst for organic degradation by ozone (Naydenov and Mehandjiev, 1993; Andreozzi et al., 1996; Li et al., 1998; Li and Oyama, 1998) but have not provided data to indicate whether this occurs by a free radical mechanism or not. At present, the importance of this mechanism in gas phase reactions is difficult to discern.

5.2.2.2 Aqueous Phase Reactions

Aqueous phase reactions are certainly important in the use of ozone ISCO, especially when applied to the saturated zone. Where gas phase ozone is in contact with water in the subsurface, a mass-transfer process occurs, moving ozone mass into the aqueous phase. This process is described in more detail in Section 5.3, but is ultimately driven by the concentration of ozone in the two phases trying to reach equilibrium. However, because ozone is highly reactive in aqueous systems, this equilibrium is never reached. Decomposition processes exert a constant demand for the oxidant and the chemistry parameters that drive these decomposition processes, such as pH, temperature, and organic and inorganic reactants, determine the steady state concentration of ozone in water. In principle, ozone may react with these compounds either via direct reaction or through decomposition to free radicals. Both reaction mechanisms are known to be important in aqueous systems, but depending on the conditions and the contaminants, one mechanism may dominate.

Direct Oxidation Reactions

Ozone is known to react through direct oxidation with a number of organic compounds. Direct reaction entails the oxidation and transformation of an organic without the involvement of free radical intermediates. Two common direct oxidation mechanisms with ozone include cyclo-addition of ozone to an alkene bond (a carbon-carbon double bond), and electrophilic

attack on aromatic hydrocarbons (Langlais et al., 1991). Stopped-flow analysis for measurement of the rate of reaction of ozone with ethene and chloroethene derivatives showed that the rate of reaction is governed by the electron density of the C=C double bond, nearly exclusively following the Criegee mechanism (Dowideit and von Sonntag, 1998). Other direct reaction mechanisms are also likely important depending on the contaminant but these have not been extensively characterized. Overall, these oxidation mechanisms indicate that the nature of direct oxidation of organic compounds by ozone will be selective in nature.

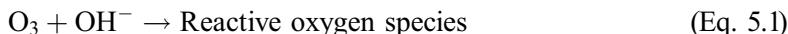
In the first mechanism, cyclo-addition of ozone to an alkene bond, ozone forms a heterocyclic complex as an intermediate, called a primary ozonide. These primary ozonides are unstable and decompose rapidly to cleave the carbon-carbon bond and leave a carbonyl group. The carbonyl compounds left by direct oxidation are unstable and subject to further hydrolysis reactions that may further degrade the compound. Furthermore, hydrogen peroxide (H_2O_2) may be formed as a byproduct of these reactions, which could contribute to other oxidation mechanisms (Langlais et al., 1991; Beltrán, 2004).

The other major reaction mechanism includes electrophilic addition to aromatic rings. This reaction mechanism is driven by ozone withdrawing electrons from electron rich positions on an aromatic ring. Aromatic compounds with electron donating function groups such as hydroxy ($-\text{OH}$) or amino ($-\text{NH}_2$) groups promote this reactivity with ozone, while compounds with electron withdrawing groups – such as nitro ($-\text{NO}_2$), carboxyl ($-\text{COOH}$) or halo ($-\text{Cl}$, $-\text{Br}$, $-\text{I}$) functional groups – tend to slow this reaction (Langlais et al., 1991). The result of this oxidation is typically the addition of a hydroxyl group at the point of attack, with the production of superoxide anion ($\text{O}_2^{\bullet -}$) as a reaction product. In the most common cases, such as with phenolic compounds, the product is either a quinone or catechol, which may then be subsequently attacked by ozone, resulting in ring rupture (Langlais et al., 1991; Beltrán, 2004).

Based on these two well-documented mechanisms, ozone can be anticipated to have high direct reactivity with any contaminant containing alkene bonds, and aromatic contaminants, especially those that are phenolic in nature. However, direct ozone reactivity with other contaminants may be more selective in nature, depending on the characteristics of the particular contaminant. Hoigné and Bader (1983a, b) reported extensively on reaction kinetics for direct oxidation of organics with aqueous ozone and found rate constants could vary by orders of magnitude, with half-lives ranging from 1 to 1,000 seconds (s), depending on the organic and reaction conditions.

Free Radical Reactions

Ozone may also decompose into free radicals, especially when in alkaline aqueous solutions. Some debate exists regarding the exact reaction pathways and radicals that occur in these free radical oxidation systems, but general consensus indicates that initiation of the free radical chain reaction begins with the reaction in Equation 5.1. Various authors have proposed that different products are produced from this reaction, but they are known to include highly reactive oxygen species (Staelin and Hoigné, 1982; Staelin et al., 1984; Tomiyasu et al., 1985).



Noting that Equation 5.1 is initiated by hydroxide (OH^-), the rate of ozone decomposition is directly proportional to pH, with higher pH values increasing the rate of decomposition. Thus, it is known that direct oxidation mechanisms are favored with ozone at acidic pH, where little catalysis occurs, and free radical pathways become dominant at neutral and alkaline pH.

These free radical processes lead to propagation reactions that generate a wide variety of different reactive oxygen species that have been proposed to form under differing conditions.

Some of these free radicals have had their presence confirmed and are widely agreed to play major roles in ozone chemistry, while others are more debatable or theoretical. These radicals, some of proven importance and others more theoretical in nature, are described in Table 5.2.

Table 5.2. Reactive Species Suspected or Known Within Ozone Oxidation Systems

Species	Standard Reduction Potential (V)	Properties
Ozone (O ₃)	2.07 (acid) ^a	Reactive gas and the primary oxidant in ozonation systems. Capable of direct oxidation in addition to the generation of free radicals
Hydroxyl radical (OH [•])	2.59 (acid) ^b 1.64 (alk) ^b	Strongly oxidizing radical that reacts non-specifically with many organic compounds (e.g., Buxton et al., 1988). This radical has traditionally been viewed as the major workhorse of organic oxidation in ozone systems where free radical generation is favored (Langlais et al., 1991; Beltrán, 2004)
Superoxide anion (O ₂ ^{•-})	-0.33 (alk) ^c	Conjugate base of the perhydroxyl radical (HO ₂ [•]), with an acid dissociation constant (pK _a) of 4.8, ^c and is a reductant. It has recently been implicated in the degradation of highly oxidation-resistant organics in hydrogen peroxide systems via reductive mechanisms (Watts et al., 1999)
Perhydroxyl radical (HO ₂ [•])	1.495 (acid) ^a	Dominant form of superoxide at acidic pH with a pK _a of 4.8. ^c It is a weak oxidant but plays a major role in ozone reaction propagations (Langlais et al., 1991)
Hydroperoxide (HO ₂ ⁻)	0.878 (alk) ^a	Conjugate base of hydrogen peroxide, with a pK _a of 11.6. ^a Thus, this ion will largely play a role when the pH is in the alkaline range. Tomiyasu et al. (1985) implicated this as having a major role in ozone free radical propagation reactions
Hydrogen peroxide (H ₂ O ₂)	1.78 (acid) ^a	A reaction product that may be produced by ozone decomposition reactions, though it is also rapidly decomposed. May also be delivered with ozone in the peroxone process. Decomposes to form radicals, especially OH [•] and O ₂ ^{•-}
Molecular oxygen (O ₂)	1.23 (acid) ^a	A major reaction product of ozone decomposition and also present in gas that delivers ozone to the subsurface. Has the ability to react with organic radicals to form organoperoxides and stimulate aerobic biodegradation
Ozonide (O ₃ ⁻)	?	Accepted as a major reaction intermediate in the decomposition of ozone into free radicals (Langlais et al., 1991)
Hydrogen trioxide (HO ₃ [•])	?	Proposed by Staehelin et al. (1984) as a reactive radical intermediate involved in ozone propagations. This is also the protonated form of ozonide (O ₃ ⁻)
Hydrogen tetraoxide (HO ₄ [•])	?	Proposed by Staehelin et al. (1984) as a reactive radical intermediate involved in ozone propagations
Trioxidane (H ₂ O ₃)	?	Highly reactive oxidant that might be formed as an intermediate in the peroxone process. Decomposes in water to form singlet oxygen (Cerkovnik and Plesničar, 1993)
Singlet oxygen (¹ O ₂)	?	A high-energy form of molecular oxygen that may react with certain organics to degrade them (Kanofsky et al., 1988)

^a“Acid” indicates reduction potential under acidic conditions; “alk” indicates reduction potential under alkaline conditions.

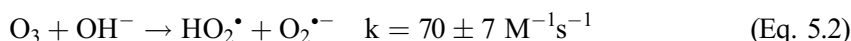
^aProposed reaction chains: Lide (2006).

^bProposed reaction chains: Bossmann et al. (1998).

^cProposed reaction chains: Afanas'ev (1989).

Two major pathways for the decomposition of ozone into free radicals have been proposed (Langlais et al., 1991). These include the mechanism proposed by Hoigné, Staehelin and Bader (the HSB model) (Hoigné and Bader, 1983a, b; Staehelin and Hoigné, 1982) and the mechanism proposed by Tomiyasu et al. (1985). The major differences in these mechanisms is that the HSB model proposes a role for several radicals, specifically hydrogen trioxide (HO_3^\bullet) and hydrogen tetraoxide (HO_4^\bullet), which Tomiyasu, Fukutomi and Gordon dispute. Both pathways are described in the following sections.

Hoigné, Staehelin and Bader Model. With the HSB model, Hoigné, Staehelin and Bader proposed that Equation 5.1 produces a cyclic reaction chain that includes propagation reactions through a number of aqueous free radical intermediates. According to this mechanism, the initiation step begins with Equation 5.1 and produces superoxide anion ($\text{O}_2^{\bullet-}$) and the perhydroxyl radical (HO_2^\bullet), according to the reaction in Equation 5.2 (Staehelin and Hoigné, 1982).



Because the solution is alkaline, the perhydroxyl radical immediately dissociates into superoxide anion (Equation 5.3), and thus two moles of superoxide anion are produced per mole of ozone reacted. The superoxide anions generated then initiate a series of propagation reactions with ozone, where various reactive oxygen species are formed (Equations 5.4–5.8). These have been proposed to include ozonide (O_3^-), hydroxyl radical (OH^\bullet), hydrogen trioxide (HO_3^\bullet) and hydrogen tetraoxide (HO_4^\bullet). This process as proposed by the HSB model is outlined in Equations 5.3–5.8 and Figure 5.2. Reactions 5.9 and 5.10 were proposed as a termination step as well as a mechanism by which hydrogen peroxide may be generated within ozone systems (Staehelin et al., 1984).

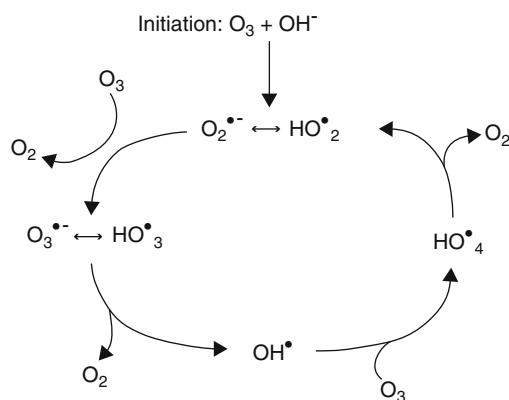
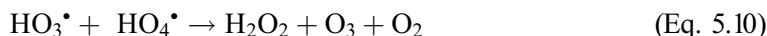
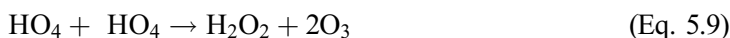
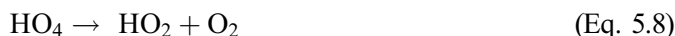
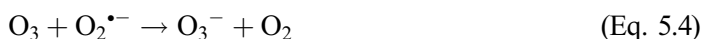
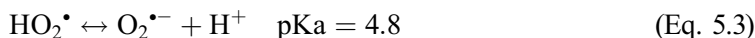
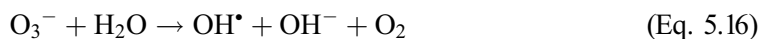


Figure 5.2. Ozone decomposition pathways (adapted from Staehelin et al., 1984).

Tomiyasu, Fukutomi and Gordon Model. Tomiyasu et al. (1985) proposed a different reaction mechanism that proceeds in a more linear fashion and does not include the hydrogen trioxide (HO_3^\bullet) or hydrogen tetraoxide (HO_4^\bullet) radicals as intermediates. Instead, they proposed that either a one-electron transfer process occurred, resulting in the formation of hydroxyl radicals (OH^\bullet) and the ozonide anion (O_3^-) (Equation 5.11) or a two-electron transfer process resulting in the formation of hydroperoxide anion (HO_2^-) and atmospheric oxygen (O_2) (Equation 5.12). Propagation reactions between ozone and the hydroperoxide anion (Equations 5.13–5.19) then yield the formation of hydroxyl radicals, proceeding through ozonide (O_3^-) as a major intermediate.



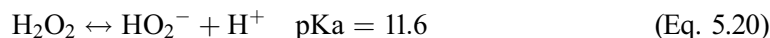
Reaction rates are dependent on pH, with more rapid reaction at elevated pH. Ozone is much more reactive with the hydroperoxide anion than with hydrogen peroxide, with rapid reaction rates above pH 6 (Taube and Bray, 1940; Staehelin and Hoigné, 1982). The Tomiyasu et al. (1985) mechanism emphasizes the role of hydroperoxide (HO_2^-) on the propagation reactions, instead of superoxide, as with the Staehelin, Hoigné, and Bader mechanism. This has particular implications for applications that combine hydrogen peroxide with ozone since low concentrations of hydroperoxide may catalyze a strong reaction.

Impact of pH on Reaction Pathways

Because ozone decomposition and free radical reactions are initiated by the hydroxide anion (Equation 5.1), pH has a strong impact on the oxidation mechanism. At acidic pH, there will be little ozone decomposition unless other catalysts are present, so direct oxidation by ozone will dominate. However, if alkaline conditions are present, then free radical oxidation will likely dominate. Furthermore, ozone stability in water can be expected to be higher in acidic systems, while in alkaline systems, it will decompose rapidly. This has implications for ISCO professionals in two ways. First, direct reaction is a selective process, and thus if acidic conditions are dominant, professionals need to be reasonably sure that direct oxidation is capable of degrading the target contaminant. However, Masten and Hoigné (1992) showed that under alkaline conditions, this may be less of a concern given the non-selective manner of free radical oxidation processes. The other consideration is with respect to ozone deliverability. If strongly alkaline conditions are present, then ozone transport distances in the subsurface may be short due to the rapid reaction of the oxidant. However, under acidic conditions, this is less of a concern. Thus, low pH offers enhanced stability and deliverability while high pH yields oxidation versatility. As a result, pH within a target treatment zone can have implications for application of ozone ISCO.

5.2.2.3 Peroxone Reactions

Peroxone, sometimes referred to as peroxone[®], refers to the simultaneous use of ozone with hydrogen peroxide; it has long been considered an advanced oxidation process (AOP) in water and wastewater treatment. The added benefit of the coapplication of hydrogen peroxide is a higher rate of free radical generation, especially hydroxyl radicals. This is largely achieved through the reaction sequence presented in Equations 5.20 and 5.21. Hydrogen peroxide itself has a slow rate of reaction with ozone (Taube and Bray, 1940), whereas hydroperoxide anion, the conjugate base of hydrogen peroxide, is reactive with ozone (Tomiyasu et al., 1985). This reaction may then propagate to produce hydroxyl radicals through the same reaction sequences outlined above, via the Staehelin, Hoigné, and Bader mechanism or the Tomiyasu, Fukutomi, and Gordon mechanism. Since the dissociation of hydrogen peroxide increases with alkaline pH, the rate of ozone decomposition in peroxone systems will also increase with pH.



The application of peroxone has been demonstrated in some systems to improve the degradation of organic contaminants over the application of ozone alone (Adams and Randtke, 1992; Kuo and Chen, 1996; Bose et al., 1998; Safarzadeh-Amiri, 2001; Mitani et al., 2002). These studies have generally found either more rapid degradation of the contaminant or more extensive mineralization of the contaminant to inorganic byproducts. However, peroxone systems are not always more effective, as a few contaminants may have more susceptibility toward direct reaction with ozone than hydroxyl radicals (e.g., Spanggard et al., 2000) and hydrogen peroxide induced decomposition may serve as a source of inefficiency. Peroxone has been implemented in ISCO field settings though not as often as straight ozone injection (Krembs, 2008; see Chapter 8).

5.2.3 Ozone Reaction Kinetics

Given the strong oxidation potential of ozone and of the reactive oxygen species that may be derived from its decomposition, there are a large number of chemical reactions with organic contaminants, as well as aquifer materials that are thermodynamically favorable. However, the overall effectiveness of ozone oxidation is highly dependent on the kinetic rates of reaction. Direct oxidation reactions between ozone and a particular organic substrate in either gas or water have generally been found to follow second-order reaction kinetics, as shown in Equation 5.22:

$$\frac{\partial C_{ox}}{\partial t} = -k_2 C_{ox} C_{org} \quad (\text{Eq. 5.22})$$

where, C_{ox} is the oxidant concentration (M/L^3), C_{org} is the substrate concentration (M/L^3), k_2 is the second-order rate constant ($\text{M}^{-1}\text{t}^{-1}$), and t is time (the symbols M and L refer to standard units – M is molar and L is Length). Thus, the rate of ozone consumption is a function of the rate constant for reaction with particular substrate, as well as the concentration of that substrate. Similarly, the substrate reaction rate is a function of both the substrate concentration and the ozone concentration. Rate constants for reactions of many specific organic compounds with ozone have been tabulated in the literature. For example, Hoigné and Bader (1983a, b) reported reaction rate constants for many organic and inorganic compounds with aqueous phase ozone (Table 5.3). It is important to recognize that the reported rate constants represent

the disappearance of the parent compound and do not indicate whether daughter products were formed or if complete mineralization occurred. Furthermore, these reaction rates represent only direct oxidation and not COC oxidation by radicals.

Table 5.3. Selected Organic Contaminant Reaction Rates with Ozone

Contaminant	Reaction rate with ozone ($M^{-1} s^{-1}$)	Reference
Nitrobenzene	0.09	Hoigné and Bader (1983a)
Chlorobenzene	0.75	
Benzene	2	
Toluene	14	
Phenol	1,300	
Naphthalene	3,000	
Trichloroethene	17	
Aniline	90	Hoigné and Bader (1983b)
<i>n</i> -Cresol	12–30	
2-Chlorophenol	1.1	
4-Chlorophenol	600	
Nitrophenol	<50	

In addition to direct oxidation reactions, free radical reactions may also play a role. Free radicals derived from ozone decomposition, especially hydroxyl radicals (OH^{\bullet}), also obey second-order reaction kinetics (Equation 5.22). Hydroxyl radical rate constants for numerous organic and inorganic reactants have been reported in the range of 10^9 – $10^{10} M^{-1} s^{-1}$ (Buxton et al., 1988; Haag and Yao, 1992), which represents a half life on the order of 10^{-9} s. However, accounting for contaminant transformation by free radical reaction kinetics can be complex due to the formation of free radical propagation reactions, as well as formation of different radical species and reaction intermediates. In this oxidative treatment system, radicals and other reaction intermediates can be short lived, not often identified nor quantified, yet have significant impact on the reaction. Thus, modeling contaminant transformations under these oxidative conditions can be difficult.

Generally, the faster the kinetic rate of a reaction, the more amenable the compound is to oxidation. However, because ISCO systems are not pure systems – but rather involve complex mixtures of contaminants, NOM, inorganic minerals, and other components, all of which may react with ozone – the kinetics likewise become more complex. These various components all compete for ozone and its free radicals at varied kinetic rates, so it is not possible to easily predict contaminant removal based on kinetics alone. Instead, kinetic models must typically consider multiple simultaneous reactions with these various components in order to effectively predict ozone concentrations and contaminant degradation (Choi et al., 2002; Shin et al., 2004). Due to the complexity of these kinetics, simplified empirical models are often fitted to experimental data using first-order rate approximations for either ozone decomposition or contaminant degradation.

Temperature may also impact the effectiveness of ISCO when using ozone. In general, reaction kinetics accelerate with temperature. This acceleration can have both benefits and drawbacks, as beneficial processes such as contaminant oxidation may increase in rate, but the

rate of nonproductive reactions such as autodecomposition reactions may also accelerate. Although temperatures in the subsurface are fairly constant, there are circumstances where significant temperature increases may occur during ozonation due to exothermic reactions associated with the oxidant. For instance, Dunn and Lunn (2002) noted the progression of a temperature front through a one-dimensional (1-D) column containing dry soil, with temperatures reaching in excess of 200°C, largely attributed to the oxidation of NOM. In moist soils, this temperature front was more modest, with increases of about 10°C observed, indicating that soil moisture likely mitigates the potential for a significant increase in temperature. Thus, in subsurface geologic settings, it is much less likely that large temperature increases may occur. Where a temperature increase did occur, Dunn and Lunn (2002) noted more effective removal of the contaminant.

Temperature also affects ozone solubility. Looking back to Table 5.1, the Henry's Law constant increases strongly with temperature, indicating that lower concentrations of dissolved ozone will be present at elevated temperature (Langlais et al., 1991). Furthermore, because ozone decomposition reactions will likely accelerate with temperature, dissolved concentrations will likely be even lower than the solubility limit would suggest.

5.3 OXIDANT INTERACTIONS IN THE SUBSURFACE

5.3.1 Interactions Affecting Reaction Chemistry

While the reaction chemistry of ozone is complex even in simple aqueous systems or gas phase systems, this complexity is compounded by the interactions of ozone with aquifer solids and groundwater. These interactions may have important implications for effectiveness and efficiency of ISCO using ozone. Some interactions may be productive, such as catalysis to form free radicals, while others may be nonproductive, such as consumption of the oxidant by non-target species. These phenomena are described briefly below.

5.3.1.1 Impact of Metal Oxides

Several authors have reported enhanced degradation of contaminants in field soils over systems involving clean laboratory media, such as glass beads and pure silica sands (Choi et al., 2002; Jung et al., 2004). Some of these experiments involved high-temperature pretreatment of the soil to eliminate NOM to ensure that NOM did not play a role. This provides strong evidence that the presence of naturally occurring soil minerals provides for some mechanism of enhanced contaminant degradation. Several studies of gas phase ozone catalysis provide evidence to support this; Andreozzi et al. (1996) and Naydenov and Mehandjiev (1993) both investigated the degradation of organic contaminants by ozone supported with manganese dioxide (MnO₂) catalysts. Manganese oxides are ubiquitous soil minerals, so they are likely available for catalysis of ozone during ISCO. However, neither of these authors identified the reactive species involved in these oxidation systems, so it is unclear if direct oxidation with ozone dominated or some form of free radical mechanism. Iron and manganese oxides have been extensively investigated for their role in catalysis of hydrogen peroxide and the formation of free radicals (e.g., Teel et al., 2001, 2007; Kwan and Voelker, 2003; Watts et al., 2005b). Thus, there is reasonable scientific evidence to hypothesize that soil minerals play a role in ozone catalysis in gas and possibly aqueous phases. However, the nature and significance of this reaction pathway are presently unknown.

5.3.1.2 Impact of Natural Organic Matter

Ozone is also known to interact with NOM. This seems to be even more the case with gas phase reactions than with aqueous reactions. Hsu and Masten (2001) reported that NOM exerted an extensive demand for ozone, retarding its transport through unsaturated porous media. They reported that roughly 5.4 mg of ozone was consumed per mg of NOM, indicating that ozone was degrading NOM in a consumable fashion. This has implications for ozone reaction efficiency and contaminant treatment effectiveness. Kainulainen et al. (1994) noted that ozone extensively degraded humic substances into smaller components. For example, the average molecular size of humic substances was reduced by an order of magnitude after ozonation. While increased demand for ozone may impact reaction efficiency, this breakdown of organic matter may be advantageous for contaminant treatment. Breakdown of humic substances may make sorbed, hydrophobic contaminants more available for oxidation, leading to higher overall treatment effectiveness. In addition, Lim et al. (2002) hypothesized that hydroxyl radicals (OH^\bullet) can actually be produced by the reaction of ozone with NOM. Thus, there may be some benefit to the oxidation of NOM in terms of contaminant treatment. Ohlenbusch et al. (1998) also noted that breakdown products of humic substances oxidized by ozone were more biodegradable than the parent humic compounds, possibly creating a substrate capable of promoting biodegradation. Thus, the oxidation of NOM may offer tradeoffs, where more ozone is required to treat high NOM media, but they may also promote other reaction and degradation mechanisms capable of destroying contaminants.

5.3.1.3 Impact of Dissolved Solutes

Dissolved solutes such as carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), and chloride (Cl^-) have significant potential to interact with hydroxyl radicals (OH^\bullet) and form reaction intermediates, including radicals. The radicals formed do not degrade organics as effectively as hydroxyl radicals, however. For instance, while the carbonate/bicarbonate radical ($\text{CO}_3^{\bullet-}/\text{HCO}_3^\bullet$) has been shown to have some reactivity with aromatic contaminants (Umschlag and Herrmann, 1999), ozone oxidation experiments carried out in the presence of carbonate or bicarbonate have demonstrated deleterious impacts to reaction efficiency (Adams and Randtke, 1992; Sunder and Hempel, 1997; Bose et al., 1998; Safarzadeh-Amiri, 2001; Zhang et al., 2005). The impact of chloride scavenging has not been extensively investigated, but based on other oxidants, chloride is known to have deleterious effects on reaction efficiency and effectiveness (Lipczynska-Kochany et al., 1995; De Laat et al., 2004). In some cases, interaction with chloride radicals has even been observed to result in halogenation reactions (Aiken, 1992; Kiwi et al., 2000), though this only occurs when excessive chloride concentrations are present with insufficient oxidant doses.

While observations from experiments using other oxidants generally show that concentrations of dissolved solutes must be high before scavenging reactions become significant, it is important to note that many of these scavengers have the potential to be created as products of contaminant oxidation. In water, carbon dioxide dissolves to form carbonate/bicarbonate. Thus, as NOM or organic contaminants are mineralized to carbon dioxide, these constituents may build in concentration until scavenging becomes significant. Similarly, chloride may build in solution if chlorinated organic contaminants are being degraded, especially if they are present in high mass concentrations, such as with DNAPLs. For instance, using permanganate as an oxidant, Petri (2006) noted concentrations of chloride could rapidly exceed 3,000 mg/L at a DNAPL interface as this degradation byproduct accumulated in solution. Thus, there is potential that these scavenging reactions can impact ISCO effectiveness with ozone, especially

where free radical oxidation processes are prevalent. However, it is largely unknown how significant an impact this may have on overall ozone treatment effectiveness in the field.

5.3.2 Interactions Affecting Ozone Transport

5.3.2.1 Ozone Reaction Characteristics

In general, there are two reaction characteristics commonly observed as time progresses that affect ozone transport. The first, at early time, is a “finite demand” mechanism in which ozone consumption diminishes with time; the second is a long-term “kinetic demand” mechanism in which ozone is consumed via catalytic reactions. Natural organic matter, organic contaminants, and reduced inorganics are reactants associated with the finite demand, and water (the hydroxyl anion, OH^-) and metal oxides are reactants controlling the long term “kinetic demand.” The implication of the “finite demand” mechanism is that ozone exhibits breakthrough behavior and gradually travels farther through the porous media over time as the demand becomes exhausted near the point of injection (Lim et al., 2002). This effect is illustrated conceptually below in Figure 5.3, using an analytical model of 2-D radial ozone transport described by Clayton (1998b).

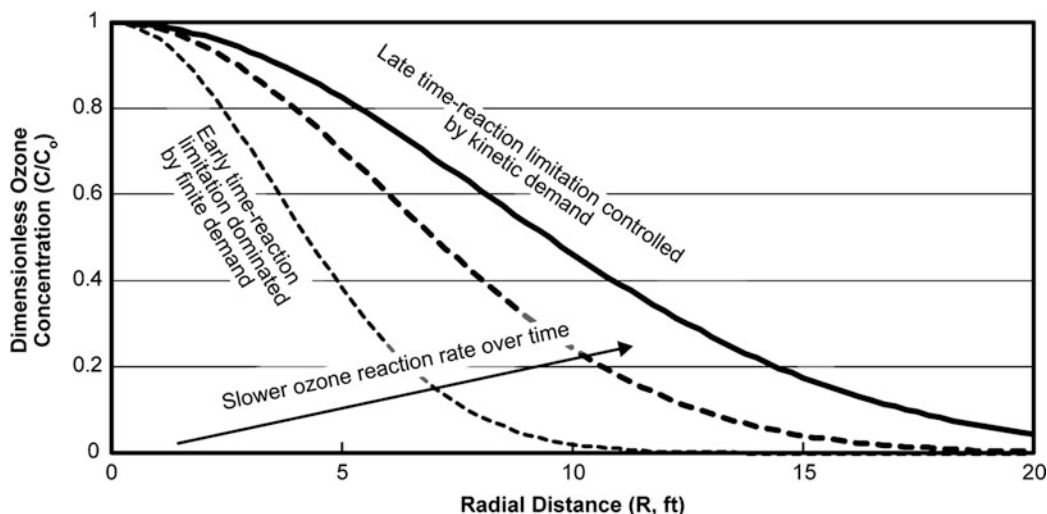


Figure 5.3. Conceptual illustration of increasing ozone radius of influence over time resulting from gradual exhaustion of the finite demand. Ultimately, the ozone radius of influence is controlled by the reaction-limitation imposed by the kinetic demand, which is persistent.

With the “kinetic demand” mechanism, a long term ozone demand resulting from catalytic decomposition persists over time (Lim et al., 2002; Shin et al., 2004) and ultimately controls the late-time ozone transport. Both of these mechanisms were characterized using field soil in laboratory column tests and subsequently used to assess ozone fate and transport under simulated field conditions (Shin et al., 2004). Injection of ozone into the model domain involved a five-spot grid pattern of injection wells and extraction wells with either 2 meter (m) (6.6 feet [ft]) or 1 m (3.3 ft) spacing. Using the same injection rates, simulations predicted complete oxidation of trichloroethene (TCE) and soil inorganic matter within 23–28 h of ozone injection at 1 m (3.3 ft) well spacing, yet with 2 m (6.6 ft) well spacing, only 80% removal was possible after 1,600 h. This result was attributed to the ozone catalysis (the “kinetic demand” mechanism) and its effect on limiting ozone transport.

Interactions between the reactants responsible for the finite and kinetic demands may cause compounding effects. For example, an increase in porous media water content may limit contact between ozone and other reactive species and may increase ozone velocity and transport distance due to the reduced air saturation (Choi et al., 2002). However, high porous media water content and water quality parameters can promote ozone mass transfer to the aqueous phase, which can deplete gas phase concentrations and reduce ozone transport distances (Sung and Huang, 2002).

5.3.2.2 Subsurface Conditions Impacting Ozone Transport

Ozone reaction and transport is affected by several parameters in both the unsaturated and saturated zones. Parameters that impact the reaction rate of ozone mainly include, but are not limited to, the water content, pH, NOM, contaminant concentrations and characteristics, and reactive metals and inorganic species and their concentrations. Further, hydrogeologic and lithologic characteristics of porous media contribute significantly to gas transport processes. It is important to understand potential ozone fate and transport mechanisms for the design of ozone delivery systems.

Porous Media Water Content

Porous media water content impacts O_3 transport in the subsurface in several ways. The presence of water in the pore space reduces the air saturation, and thus increases the velocity of injected ozone (Clayton, 1998b; Choi et al., 2002). Elevated water content (reduced air saturation) also reduces the gas-solid phase contact and provides a greater diffusion-limitation for ozone mass transfer, and thus ozone reactive species associated with the solid surfaces (NOM, metal oxides, contaminants) may become less available for reaction (Choi et al., 2002; Jung et al., 2004). For example, a water content of 75% (of saturation) or more inhibited reaction between ozone and solid phase minerals and organic matter (Jung et al., 2004). Both of these mechanisms increase ozone transport distances.

Ozone decomposition is much more rapid in the aqueous phase than in the gas phase due to the strong catalyzing reaction by the hydroxide ion (OH^-). For example, the typical half-life of gaseous ozone and aqueous ozone (pH 7) at 20°C is 3 days and 20 min, respectively. These values are based on thermal decomposition only; no wall effects, humidity, organic loading, or other catalytic effects are considered. Other dissolved chemical species may also react with ozone. Therefore, ozone gas dissolving into the water phase may undergo catalytic decomposition, effectively decreasing ozone transport.

Assuming the target contaminants are soluble and predominantly found in the aqueous phase, water content plays an important role in assuring contact between ozone and contaminant. Conversely, assuming the target contaminants are predominantly associated with the solid phase material, water content may limit the contact between ozone and contaminants. For example, reduced treatment effectiveness was measured at higher soil moisture content when treating relatively non-volatile contaminants, such as crude oil or PAHs (Dunn and Lunn, 2002; Goi and Trapido, 2004; Zhang et al., 2005; O'Mahony et al., 2006). Overall, an optimal porous media water content is dependent on site-specific conditions.

Natural Organic Matter Content

Ozone oxidation of NOM in the unsaturated zone limits subsurface ozone transport distances (Hsu and Masten, 2001; Choi et al., 2002; Kim and Choi, 2002; Lim et al., 2002; Jung et al., 2004; Zhang et al., 2005). Hsu and Masten (2001) measured a demand of 5.4 mg- O_3 /mg-NOM and determined that NOM oxidation was governed by second-order kinetics, first-order in each reactant. In one study, a 30% reduction of NOM was measured as a result of injecting ozone through a soil column (Shin et al., 2004). This indicates that the total ozone

demand includes partial oxidation of the NOM content in the soil. Highly organic soils or aquifer material are likely to challenge the technical and economic feasibility of ozone ISCO, but still, the feasibility should be based on a site specific evaluation. Limited injection intervals and longer injection timeframes may be needed to successfully overcome the anticipated high ozone demand at sites with high NOM.

Contaminant Concentrations

High contaminant concentrations, in either the form of high sorbed concentrations or NAPLs, may limit ozone transport due to the ozone demand exerted by their reaction (Choi et al., 2002; Kim and Choi, 2002; Zhang et al., 2005). In this case, it is important to plan and design for shorter transport distances, closer injection and monitoring well spacing, longer ozone injection timeframes, and greater ozone loading. A decline in ozone transport was measured during the ozonation of diesel in soils (1,500 milligrams per kilogram [mg/kg]) (Choi et al., 2002) and also at relatively lower concentrations of PAHs (50 mg/kg) (Zhang et al., 2005). These results demonstrate that highly contaminated porous media will likely require a longer ozonation timeframe than lightly contaminated soils to achieve the treatment objective.

Metal Oxides and Other Minerals

Minerals, especially metal oxides of iron and manganese, react with ozone in the subsurface and limit ozone transport (Lin and Gurol, 1998; Jung et al., 2004; Shin et al., 2004). Reduced mineral species react with ozone in non-catalytic reactions (sulfidic compounds) and exert a “finite demand.” Iron and manganese oxides appear to be catalytic in nature and can exert a “kinetic demand” for ozone. In some studies, metal oxides acted as catalysts of ozone and resulted in faster contaminant oxidation, suggesting that enhanced free radical formation improved contaminant degradation (Naydenov and Mehandjiev, 1993; Andreozzi et al., 1996; Choi et al., 2002; Jung et al., 2004). Nonetheless, contaminated sites containing high iron and manganese mineral content or large quantities of reduced minerals may face challenges in achieving sufficient oxidant contact due to these potential oxidant sinks.

5.3.3 Ozone Transport Processes

5.3.3.1 Vadose Zone Processes

Vadose zone transport of injected gases (primarily air) has been evaluated in the context of bioventing (Leeson and Hinchee, 1996a, b). In the vadose zone, soil gas is interconnected within the subsurface pore structure, and gas flows under a pressure gradient regime. Gas flow in the vadose zone is much more controllable than flow of liquids and represents an advantage for *in situ* ozone treatment of the vadose zone. However, vadose zone transport of ozone in air injected to the subsurface is strongly limited by ozone reactions (refer to Section 5.3.2). In general, vadose zone transport and reaction of ozone involves loss of gaseous ozone with time and distance to interphase mass transfer and reaction in the aqueous phase and to gas phase reactions (Clayton, 2000a). The two dominant factors limiting ozone transport are (1) the ozone reaction rates in gas and aqueous phases and (2) the interphase mass transfer rates. Gas phase reactions with the aquifer solids may also be important in the vadose zone ozone transport, especially for low water contents. Simultaneous interphase mass transfer of contaminants between the gas, aqueous, NAPL, and sorbed phases also play a role in ozone transport and reaction processes.

5.3.3.2 Saturated Zone Processes

Air sparging (AS) (Ahfeld et al., 1994; Hein et al., 1997; Johnson, 1998; Brooks et al., 1999) is a technology that has been rigorously investigated, shares similarities with ozone sparging,

and provides insight to mass transport and mass transfer mechanisms with ozone sparging, which has not been rigorously investigated in subsurface systems. During ozone injection into the subsurface, there are ozone mass transport and mass transfer mechanisms that largely determine the fate and transport of ozone, which significantly impacts the success or failure of the treatment process.

Ozone Sparging and Gas Flow

Ozone injection into the saturated zone is carried out using sparging wells where either air or pure oxygen containing ozone is injected under pressure. Ozone sparging in the subsurface is analogous to AS; therefore, it is reasonable to assume that the transport and distribution processes associated with air are applicable to ozone (Huling and Pivetz, 2006). Given the limited number of studies dealing with the fate and transport of ozone gas, a critical analysis of AS can be used to help assess ozone transport and fate in the saturated zone.

In general, AS does not result in a uniform distribution of air extending radially from the injection well. Rather, the air distribution is often non-uniform and highly controlled by subsurface heterogeneity and variation in capillary-hydraulic properties and dependent on subsurface grain size and pore structure characteristics (Dahmani et al., 1994; Clayton, 1998a; Brooks et al., 1999; Elder and Benson, 1999; Chao et al., 2008). Gas transport during AS can occur by three different processes: continuum gas flow in partially saturated porous media, gas flow in discrete partially saturated air channels, and gas bubbles.

In porous media with very large grain sizes that results in large pore sizes, air bubbles may move upward by buoyancy because the buoyant force of a discrete bubble can exceed the capillary air entry pressure (Dahmani et al., 1994; Clayton, 1998a). Bubble flow only occurs in very coarse sand or gravel formations with very low air entry pressures. Dahmani et al. (1994) observed in a laboratory study that when the grain size exceeds 4 millimeters (mm), consistent with the particle size of gravel, AS resulted in the transport of bubbles. However, when the grain size was reduced to 0.75 mm, gas channels dominated and bubbles were not observed. Similar particle size ranges were reported where bubbles dominated in a media with a median grain diameter of 1.7 mm, and gas channels dominated in media with particle diameter of 0.4 mm (Chao et al., 2008). Chao et al. (2008) used a finer diffuser (an AS method) than Dahmani et al. (1994), which may partially explain differences in reported particle size ranges. In extremely coarse media, where bubbles form, their implications for transport and sweep efficiency are much different. Bubbles migrate upward and outward in a cone-shaped pattern in coarse homogeneous media, resulting in higher degrees of contact with the aquifer materials (Chao et al., 2008). However, where bubble flow does occur, coalescing of small bubbles forms larger bubbles and eventually a continuum of gas (air channels) occurs that limits the transport of bubbles laterally and vertically.

At intermediate grain sizes and pore size distributions that are typical of most sites, air flow is expected to occur in a limited number of air channels. The differences between bubble flow and air channel flow are depicted conceptually in Figure 5.4, which shows a simplified representation absent subsurface heterogeneity. Currently, a rigorous field-scale investigation that demonstrates and documents sustained lateral bubble transport does not appear to exist.

Air-channel flow occurs at subsurface air-water capillary pressures that are near the air entry pressure for the subsurface media. In an ideal system, as conceptualized in Figure 5.5, the air channels form a V-shaped network of interconnected air channels (Elder and Benson, 1999 and references therein; Chao et al., 2008). However, gas transport (injected air or ozone) in the saturated zone at most sites is characterized as a non-ideal transport system where air channels are heterogeneously distributed, difficult to characterize and predict (Ahfeld et al., 1994; Hein et al., 1997) and allow the air to bypass a significant cross-section of the aquifer into which it is

injected. Since air-channel flow is expected at intermediate grain sizes and smaller, this is the dominant air-flow regime anticipated at the majority of air or ozone sparging sites (Huling and Pivetz, 2006). Clayton (1998a) showed that field measured air saturations in this case are low ($<10\%$), consistent with the formation of discrete channels. Clayton and Nelson (1995) described field measurement of subsurface gas saturation and dissolved ozone during ozone sparging and found that air saturations and dissolved ozone concentrations were highest within 20 min of initiating ozone sparging. Clayton and Nelson (1995) suggested this resulted from the greater air penetration that would occur at higher air injection pressures prior to breakthrough to the water table. They, as well as Johnson et al. (2001), and other authors have suggested pulsed sparging is generally beneficial for this and other reasons.

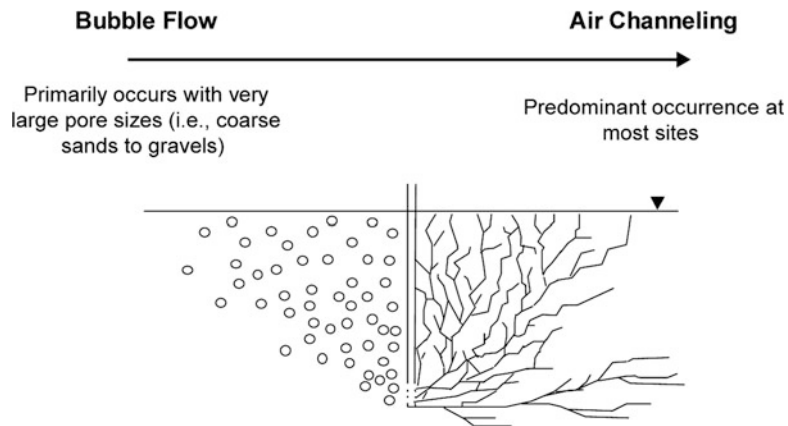


Figure 5.4. Idealized differences between bubble flow and air channeling (modified from Clayton, 1998a).

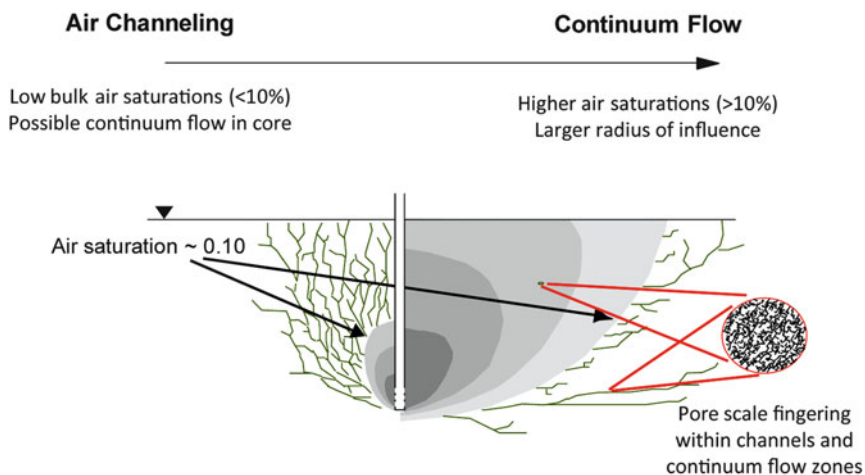


Figure 5.5. Idealized air channeling and continuum flow regimes (modified from Clayton, 1998a).

For a field case study in highly uniform very fine sand (hydraulic fill), Clayton (1998a) showed that the air injection pressures required to propagate subsurface air flow increased well above the air entry capillary pressure and that a region of uniform air flow and high air saturations developed as opposed to a network of discrete channels. This is shown conceptually in Figure 5.5, which is a simplified representation absent subsurface heterogeneity.

In the presence of subsurface heterogeneity, it would be expected that differences in porous media properties would lead to regions of preferential airflow consisting of a heterogeneity-bounded regions of continuum flow. Clayton (1998a) found that field and laboratory measured air saturations for continuum flow conditions were much higher (<10–30%) consistent with the formation of a region of relatively more uniform air saturation as opposed to discrete channels separated by completely water saturated regions. In the field, air saturations of 30% were measured at distances up to 7 m (23 ft) from the injection point in a fine sand. This result implies that while heterogeneity-controlled air channeling is still expected, ozone sparging may be most efficient at finer grained sites, because the higher air saturations will result in greater ozone mass transfer and more uniform ozone contact with contaminants. However, at low permeability clayey sites, the subsurface permeability may be too limiting for ozone sparging.

In reality, subsurface heterogeneity will strongly control the air distribution. The radius of influence in the context of AS is ambiguous because in the three possible airflow regimes, air flow is not uniformly or radially symmetric about a sparge injection point. Further, for air channel flow, which is most typical, heterogeneously distributed air channels leave large volumes of water in between the air channels untouched by the air stripping (volatilization) mass transfer mechanisms (Ahfeld et al., 1994). Given the similarities between air sparging and ozone sparging, it is reasonable to assume that AS and oxidative treatment is also not uniform between sparging wells. Dissolved ozone in groundwater measured by Clayton and Nelson (1995) in a medium sand aquifer did not indicate a uniform spatial pattern. Overall, the radius of influence of ozone in groundwater during *in situ* ozone sparging is not well documented or well understood. At the time of this publication, no case study or examples were available that conclusively demonstrated the radius of influence for ozone sparging.

Ozone Mass Transfer and Reaction

It is generally assumed that mass transfer of ozone and volatile organics between the aqueous phase and the gas phase occurs by diffusion at the gas-aqueous interface. The spacing between air channels, whether at the pore scale (continuum flow) or at a macro scale (air channels), defines the diffusion path length for mass transfer, which controls the mass transfer rate. Mass transfer of ozone from the gas phase to the aqueous phase is driven by the ozone concentration in the gaseous phase and the concentration of dissolved ozone in the aqueous phase. The mass transfer of ozone from the gas phase into the water increases with higher ozone concentration in the gas, and low aqueous concentrations. For air channeling, AS removal of volatiles was shown to treat regions very near the air channels more rapidly than the water-saturated regions in between the channels (Johnson, 1998). It is reasonable to assume that contaminant oxidation occurs by similar mass transfer mechanisms: (1) the diffusion and volatilization of contaminants into the air/ozone channels where gas-phase oxidation reactions occur and (2) the diffusion of ozone into the aqueous phase where contaminant oxidation reactions occur.

The complexity of gas sparging mass transport and transfer processes under most, if not all, subsurface environments makes direct prediction of ozone sparging effectiveness in the saturated zone challenging. In one AS study, contaminant volatilization during AS was limited to a localized zone in the vicinity of a gas channel, and the concentration of VOCs just outside the mass transfer zone remained fairly constant (Braidia and Ong, 2001). This result was attributed to diffusion limitations as affected by diffusivity of the contaminant, the particle size, and the uniformity of the media. The Henry's Law constant and ozone flow rate through the air channel was reported to have little impact. In contrast, with respect to oxygen mass transfer in AS systems, air flow and Henry's Law constants were reported to have a significant

effect (Chao et al., 2008). In these cases, it is unclear to what extent the density of gas channels varied with gas flow rate. The density of gas channels would impact overall mass transfer. Given the rapid reaction rate of ozone in the aqueous phase and limited time of diffusion, it is unlikely that ozone would diffuse significant distances outside of the gas channel.

Ozone reaction rates are a primary factor controlling the subsurface transport of ozone. The rate of aqueous decomposition of ozone has been shown to be a function of pH (Langlais et al., 1991), as well as metal oxides contaminant concentrations and NOM (Choi et al., 2002; Lim et al., 2002). As these quantities increase, ozone reaction increases and transport distances decrease.

Impact of Ozone on Contaminant Transport

Volatilization of organic contaminants may result from *in situ* ozone sparging. With ozone, volatile emissions are ideally mitigated due to the reaction between ozone and VOCs. However, volatile emissions should be evaluated on a site-specific basis and controlled if needed. This is generally addressed through the use of soil vapor extraction (SVE) wells and activated carbon adsorption treatment. Enhanced volatilization, if controlled, is desirable because it contributes to contaminant mass reduction, and for volatile COCs at moderate concentrations, AS alone may be adequate to achieve remedial goals. Entrapment of gas in the pore space may potentially reduce post-ISCO groundwater transport due to air or oxygen gas blockage of the pore water. Additionally, gas sparging in the saturated zone may displace groundwater, and entrapped gas may re-direct groundwater flow around the injection zone. The potential alteration of groundwater and contaminant transport as a result of these factors should be evaluated on a site-specific basis.

5.3.4 Modeling of ISCO Using Ozone

Modeling of ISCO using ozone offers the advantages of enabling predictions of ozone effectiveness and design optimization prior to implementing ozonation in the field. However, modeling of ISCO using ozone is challenging because models are often based on limited field data, collection of additional data may be costly, and many simplifying assumptions must be made, all of which may introduce uncertainty to results. As a result, modeling ozone injection is not widely performed and reported. Nonetheless, several studies have made predictions of ozone transport and remediation using analytical and numerical methods. These findings may be useful to remediation professionals. Most of these have focused on ozone transport and treatment in simplistic systems, especially with low water saturation, such as may be encountered in the vadose (unsaturated) zone (Clayton, 1998b; Hsu and Masten, 2001; Kim and Choi, 2002; Sung and Huang, 2002; Shin et al., 2004). However, several have looked at more complicated systems, dealing with mass transfer of ozone from the gas phase to the aqueous phase, as well as reactions in both phases, which may be more representative of sparging ozone below the water table (Clayton, 1998b; Kim and Choi, 2002; Sung and Huang, 2002).

Table 5.4 presents a series of models proposed by various authors for ozone reactive transport and the processes they considered. These studies do provide useful insight into aspects of ozone ISCO, especially ozone transport behavior. For instance, many of these studies have observed, and confirmed via validation against experimental data, that NOM and soil minerals significantly retard ozone transport through media due to the consumption of ozone with these reactive phases (Hsu and Masten, 2001; Kim and Choi, 2002; Shin et al., 2004). Thus, injection point spacing is an important design consideration because the media properties determine the effective transport distances that may be achieved. Several have also explored the impact of ozone mass transfer into the aqueous phase on ozone transport, which has important

implications for treatment of saturated zone systems (Clayton, 1998b; Kim and Choi, 2002; Sung and Huang, 2002). However, as of yet, all of these models consider only a single mobile phase (gas); in most cases, they assume immobile (e.g., non-volatile) contaminants and focus on highly theoretical systems.

Table 5.4. Studies Describing Mathematical Modeling of ISCO Using Ozone

Study	Domain	Model type	Processes included	Findings
Clayton (1998b)	2-D	Analytical	<ul style="list-style-type: none"> • Radial gas flow from injection point • First-order ozone decay 	Simple model may offer conservative prediction of ozone radius of influence
	1-D	Numerical	<ul style="list-style-type: none"> • Gas phase advection of ozone and volatile contaminants • Rate-limited mass transfer between gas and aqueous phases for contaminant and ozone • Rate-limited desorption of contaminant from soil • Second-order reaction between ozone and contaminant in both gas and aqueous phases 	Theoretical model of ozone transport through a 1-D gas channel with volatile or semi-volatile contaminants. Initially, reaction near the injection point limits distribution, but ozone transport increases with time as reactive substrates are depleted. However, decomposition reactions probably impart an upper limit on ozone transport. Some volatile contaminant mass escaped treatment as fugitive emissions
Hsu and Masten (2001)	1-D	Numerical	<ul style="list-style-type: none"> • Gas phase advection of ozone only including compressible gas flow • Contaminant assumed non-mobile • Second-order reaction between ozone, contaminants and NOM • Phases were lumped^a • Contaminant and NOM reactions modeled as occurring sequentially or simultaneously 	Model limited to non-mobile contaminants. No significant difference in ozone transport between sequential or simultaneous reaction models, as contaminant demand is minor compared with NOM demand. NOM significantly retards ozone transport
Kim and Choi (2002)	1-D	Numerical	<ul style="list-style-type: none"> • Gas phase advection and dispersion for ozone only • Contaminant assumed non-mobile • Second-order reaction between ozone, contaminant and NOM • First-order ozone autodecomposition • Mass transfer of ozone to aqueous phase using three approaches: equilibrium 	The steady-state ozone concentration after breakthrough was well predicted by all three approaches, but breakthrough times were over-predicted. Equilibrium approach was sensitive to the Henry's Law constant, while the rate-limited approach was sensitive to the k_{La} coefficient. The lump

(continued)

Table 5.4. (continued)

Study	Domain	Model type	Processes included	Findings
			model, rate-limited absorption model, and lumped ^a phase model	model predicted reaching steady state faster than the other two, due to the assumption of total contact with all reactive species
Shin et al. (2004)	1-D and 3-D	Numerical	<ul style="list-style-type: none"> • Gas phase advection and dispersion for ozone only • Contaminant assumed non-mobile • Second-order reaction between ozone, NOM, inorganic minerals and contaminants • First-order ozone autodecomposition • Phases were lumped^a 	Estimated model parameters from experimental results and created a 3-D simulation illustrating that NOM, autodecomposition, and inorganic material significantly retard ozone transport. Showed that a twofold decrease in injection point spacing resulted in a 1,000-fold decrease in treatment time to remove a non-mobile contaminant
Sung and Huang (2002)	1-D	Numerical	<ul style="list-style-type: none"> • Gas phase advection and dispersion for ozone only • Contaminant assumed non-mobile • Second-order reaction with contaminant in aqueous phase • Rate-limited ozone mass transfer to the aqueous phase • Enhanced ozone mass-transfer due to reaction within aqueous boundary layer • Rate limited contaminant desorption to aqueous phase 	Theoretical model of ozone transport and non-volatile contaminant degradation in a water wet unsaturated soil. No competing reactions with matrix considered. Found that the Péclet (Pe) and Stanton (St) numbers had significant effects on ozone transport behavior in a 1-D column. Specifically, when St is much less than 1, the systems is mass transfer controlled, and when St is much greater than 1, the system is ozone delivery controlled

^aLumped phases indicates that reaction in gas, liquid or soil phases were not separated, but treated as one with an empirical reaction rate coefficient.

5.3.5 Ozone Impacts on Metal Mobility

ISCO with ozone can affect the mobility of metals in the subsurface through changes in pH and redox potential (Eh), oxidative modification or destruction of metal-sorbing NOM, and changes to the water content within a target treatment zone.

5.3.5.1 Changes in Subsurface Conditions

Alteration of pH and Eh

It has been reported that changes in pH during ozonation is caused by the oxidative transformation of media NOM into organic acids (Huling and Pivetz, 2006). Shin et al. (2005)

concluded that the resultant pH drop is generally proportional to media NOM content. In a 3-D test cell, they saw pH decrease over 20 days from 6.1 to 5.6. Since this was in a medium containing relatively little NOM, extrapolation to media with higher NOM contents would suggest that ozonation of some sites may result in pH values dropping precipitously enough to encourage the enhanced metal mobility prevalent at low pH (Siegrist et al., 2001).

Ozone is a strong oxidizer whose decomposition also produces hydroxyl radicals (OH^{\bullet}), which are even stronger oxidants. These two species can oxidize ORP (oxidation-reduction potential)-sensitive metals, such as chromium and selenium into more mobile states (Jung et al., 2005).

Alteration or Destruction of NOM

Ozone can affect metal-sorbing NOM in two major ways: it can cleave larger NOM molecules into smaller sizes, and it can increase polarity and decrease aromaticity of NOM oxidation byproducts (Kerc et al., 2004). Higher molecular weight organic matter tends to have higher electrostatic potential, more available ligands per molecule, and stronger sorption affinity resulting in increased metal capacity and decreased metal mobility (Kerc et al., 2004). It was concluded that the increased extractability of copper from soil samples pretreated with ozone was due to degradation of NOM binding the copper (Finzgar et al., 2006). In another study, similar results were reported for lead, although they found no effect on the extractability of zinc (Leštan et al., 2005). It should be noted that the increased extractability of lead was observed during the subsequent addition of ethylenediaminetetraacetic acid (EDTA) as a chelator and that ozone alone did not influence lead bioavailability or mobility.

Largely due to the high demand by nonspecific oxidation of NOM and other reactive (reduced) species, ozone may have a short retention time in the subsurface. Consequently, long term injection of ozone may be required to meet the treatment objectives. This may result in significant NOM oxidation and possibly undesirable levels of metal release, assuming significant quantities of metals are bound to the NOM and represent a health risk.

Changes in Water Content

Injected ozone gas is typically dried of all moisture. Therefore, depending on site hydrology, the injection of ozone gas and/or air can lead to evaporation of soil water (Shin et al., 2005). Water content at an ozone injection site is important because it can shield both contaminants and metal-sorbing NOM from gas-phase oxidation by ozone (Jung et al., 2005). Decreased water content due to prolonged ozone exposure could result in greater access of the ozone to metal oxides that promote the formation of OH^{\bullet} and greater availability of metal-binding NOM to oxidation (Choi et al., 2002). Sites with low pre-ISCO water contents, sites vulnerable to changes in water content, and sites with high amounts of NOM-sorbed metals in these conditions may be more susceptible to metal mobilization.

5.3.5.2 Assessing Metal Mobility Under Field Conditions

As noted in the preceding section, ozone has the potential to increase metal mobility through several processes. Field data concerning mobilization of metals during ozonation are limited. If mobilization of metals could be a concern at a particular site, a site-specific analysis of the potential for mobilization should be completed and, based on the exposure pathways, the associated health or ecologic risks should be assessed. This analysis should include careful consideration of factors such as previous waste management activities involving heavy metals, soil and aquifer material with known heavy metals concentrations, pre-existing low pH or vulnerability to pH and ORP changes, high levels of NOM-sorbed metals, and low water content or water content subject to decline through long term ozone/air injection.

5.4 CONTAMINANT TREATABILITY

A wide range of organic contaminants are degradable by ozone because of the high reactivity of ozone in the gaseous and aqueous phase by either the direct reaction with organic contaminants or through the formation and reaction of free radicals. Some contaminant groups have been more widely investigated than others, owing to the continued development of ozone oxidation. For instance, early applications of ozone were typically applied at petroleum sites where SVE or AS had been implemented to remove fuel hydrocarbons. In these cases, ozone was used to target the residual contaminant mass. In these investigations, the hydrocarbon contaminants were less volatile, recalcitrant to biodegradation, and were not removed by AS. These contaminants included total petroleum hydrocarbons (TPH), aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes (BTEX), fuel oxygenates (such as methyl tert-butyl ether [MTBE]), and PAHs. A generalized assessment of the treatability of different organic compounds during ozone ISCO is given in Table 5.5. Chapter 9 includes guidance and tools for appropriate selection of ozone ISCO based on site-specific factors including the COC characteristics, site conditions, and treatment goals.

5.4.1 Chlorinated Aliphatics

Chlorinated aliphatic contaminants are a broad category that includes the most common chlorinated solvents. The most prevalent among these are chloroethenes, due to the widespread use of TCE and perchloroethene (PCE) in industry. Chloroethenes contain a carbon-carbon double bond; given ozone's high direct reactivity with alkene bonds, all chloroethenes have high rates of reaction with ozone. This category has been widely investigated in laboratory and field studies, and many have noted the effective degradation of chloroethenes by ozone (e.g., Sunder and Hempel, 1997; Kerfoot, 2000; Schaal and Hey, 2002; Dablow and Rowland, 2004). These studies have not rigorously investigated reaction mechanisms even though chloroethenes are among the more common contaminants targeted by ISCO. However, ozone oxidation of alkene bonds (e.g., Langlais et al., 1991) strongly suggests that chloroethenes are degradable. The degradation of alkenes by ozone is believed to occur through direct oxidation, where ozone adds to the alkene bond to form a cyclic ozonide. This ozonide is unstable and rapidly breaks down, breaking the carbon-carbon bond altogether, and yields oxygenated intermediates. This mechanism, as presented by Langlais et al. (1991), strongly indicates that phosgene (COCl_2) should be one of the primary intermediates produced by this oxidation reaction. However, phosgene is known to rapidly decompose in water due to hydrolysis reactions, so chloride and carbon dioxide should be the primary products produced by ozonation of chloroethenes. Evidence from experiments by Sunder and Hempel (1997) support this hypothesis; they observed quantitative chloride release during the treatment of TCE and PCE. Free radical oxidation might also play a role as hydroxyl radicals may attack ethene bonds as well. In a peroxone system investigated by Sunder and Hempel (1997), higher hydrogen peroxide doses resulted in increased degradation, suggesting that hydroxyl radicals played a role.

Other major contaminants within the chlorinated aliphatic group include chloroethanes, such as 1,1,1-TCA, as well as chloromethanes, such as carbon tetrachloride. These are also ubiquitous contaminants at industrial sites and have been the subject of some research. However, given their saturated nature (lack of double bonds), these compounds are much less reactive with either ozone or hydroxyl radicals and thus are more resistant to *in situ* ozonation. However, recent studies by Watts et al. (1999, 2005a) have demonstrated that chloroethanes and chloromethanes are susceptible to reductive degradation mechanisms, such

as reaction with superoxide anion ($O_2^{\bullet -}$). Superoxide may be produced through ozone decomposition reactions (e.g., Equations 5.2 and 5.3). However, the extent to which this degradation is possible in ozone systems remains to be demonstrated. Kerfoot (2000) investigated the treatment of a series of chlorinated aliphatics, and found that chloroethanes and chloromethanes were treated to much lower degrees than chloroethenes in the same systems.

Table 5.5. General Assessment of the Treatability of Different Organic Compounds by Ozone ISCO

Contaminant group	Section ^a	Contaminant treatability by ozone?	Comments
Chlorinated aliphatics (e.g., PCE, TCE, 1,1,1-trichloroethane [1,1,1-TCA])	5.4.1	Yes	Mechanisms, rates, and products well-understood and documented
1,4-Dioxane	5.4.1	Yes	Potential for organic acid and alcohol intermediates, depending on radical propagation mechanisms involved
Chlorinated aromatics (e.g., chlorobenzene, dichlorobenzene, chlorophenol)	5.4.2	Yes	Mechanisms, rates, and products well-understood and documented
Fuel hydrocarbons (e.g., BTEX, TPH)	5.4.3	Yes	Mechanisms, rates, and products well-understood and documented
MTBE	5.4.3	Yes	Transient production of tert-butyl alcohol (TBA), which is subsequently treated at a slower rate than MTBE
PAHs (e.g., benz[a]anthracene, benzo[a]pyrene, pyrene, anthracene)	5.4.4	Yes	Mechanisms, rates, and products well-understood and documented
Nitroamine and nitroaromatic explosives (e.g., hexahydro-1,3,5-trinitro-1,3,5-triazine [RDX], nitrotoluene, 2,4,6-trinitrotoluene (TNT), nitrobenzene)	5.4.5	Yes	Mechanisms, rates, and products well-understood and documented
Pesticides (e.g., organochlorines, organophosphates)	5.4.6	Potentially	Fairly limited data available, although encouraging preliminary results

^aThe number refers to the section within this chapter where information on the treatability of each respective contaminant group is discussed.

While not a chlorinated solvent, another contaminant of interest that is often present at chlorinated solvent sites as a co-contaminant is 1,4-dioxane. 1,4-Dioxane was added to chlorinated solvents as a stabilization agent to prevent them from breaking down during their use in

industry. Several authors have looked at the treatment of 1,4-dioxane with ozone. Brown et al. (2004) demonstrated that 1,4-dioxane in contaminated groundwater could be fully degraded by ozone, though the treatment efficiency could not be easily determined due to the long ozonation time in this system. Suh and Mohseni (2004) conducted a more thorough investigation of kinetics, mechanisms, and byproducts with respect to 1,4-dioxane and found that while 1,4-dioxane was extensively oxidized to non-detectable levels, the mineralization of the contaminant to carbon dioxide (CO₂) was relatively low, indicating that organic intermediates were likely being formed. They speculated that these intermediates consisted of low molecular weight organic acids and alcohols but did not identify them. However, they investigated the extent of mineralization when biodegradation processes were included subsequent to ozone oxidation, and found that these byproducts were more biodegradable than the 1,4-dioxane parent compound. Interestingly, they found that the byproducts produced at alkaline pH or with moderate doses of hydrogen peroxide (peroxone) were more readily biodegradable than those produced at acidic pH and with no hydrogen peroxide. Peroxone systems, as well as ozone systems at alkaline pH, are more likely to involve oxidation by free radicals, while ozone systems at low pH are more likely to involve direct oxidation by ozone. Thus, it appears that the products produced from hydroxyl radical reactions for this contaminant may be more biodegradable than those produced by direct reaction with ozone, based on the data of Suh and Mohseni (2004).

5.4.2 Chlorinated Aromatics

Chlorinated aromatics are a contaminant group that includes a wide variety of compounds that have been used as solvents, wood preservatives, pesticides and for other purposes. This group includes chlorinated phenols, chlorinated benzenes, and chlorinated polyaromatic compounds such as polychlorinated biphenyls (PCBs), dibenzo-*p*-dioxins and dibenzo-*p*-furans. A number of studies have investigated the degradation of these compounds by ozone, though the majority of these studies have focused on chlorinated phenols in particular.

In general, phenolic contaminants are susceptible to oxidation processes with nearly every oxidant because the hydroxyl group enriches the aromatic ring with electrons, which are readily abstracted by oxidants. As a result, chlorophenols are treatable by ozone reactions, including both direct reaction with dissolved ozone (Hoigné and Bader, 1983b; Hong and Zeng, 2002) and reaction with hydroxyl radicals (Sedlak and Andren, 1991; Tang and Huang, 1995). Because phenolic contaminants contain a hydroxyl group, they can also dissociate into a hydrogen ion (H⁺) and a phenolate ion, much like a weak acid, and will have a pK_a value at which they dissociate. Thus, ozone may react with either the phenol (non-dissociated) form or the phenolate ion. Studies in the literature have consistently shown that direct oxidation by ozone exhibits much faster kinetics (orders of magnitude) with the phenolate form than the non-dissociated form (Gurol and Nekouinaini, 1984; Qiu et al., 1999, 2001; Benitez et al., 2000; Hirvonen et al., 2000; Haapea and Tuhkanen, 2005). As a result, the kinetics of phenol degradation are much higher with ozone at neutral or high pH, where the phenolate form is dominant, rather than acidic pH where the phenol form dominates.

The main mechanism for direct oxidation of phenol by ozone is likely electrophilic addition of ozone to the aromatic ring, generally resulting in the addition of a hydroxyl group at the point of attack, resulting in a benzene-diol (Langlais et al., 1991). The most common point of attack is at positions either ortho- or para- to the hydroxyl group on the phenol; therefore either chlorinated or dechlorinated catechols and benzoquinones tend to be the primary organic intermediates observed (Hirvonen et al., 2000; Hong and Zeng, 2002; Qiu et al., 2004). These intermediates tend to be even more reactive with ozone and other compounds. Their subsequent

reactions with ozone or aqueous free radicals lead to ring rupture, and the formation of organic acids. Some of these acids may retain chlorine from the parent organic, but given suitable oxidant doses, they degrade and chloride liberation becomes quantitative (Hong and Zeng, 2002). However, because degradation of phenols proceeds through these intermediate compounds, dechlorination may lag behind the initial degradation of the contaminant (Qiu et al., 1999, 2004; Hirvonen et al., 2000; Hong and Zeng, 2002). Although generally a minor reaction pathway, in some cases, the reaction of ozone and its radicals with chlorinated aromatics results in dimerization reactions. This can result in the formation of low levels of biphenyl-like compounds, especially hydroxylated PCBs. This was found to be more of a problem when treating phenols at acidic pH than alkaline pH, probably due to the faster decomposition of the dissociated form (Hirvonen et al., 2000).

When it comes to degrading other chlorinated aromatics with ozone, including chlorobenzenes, PCBs, dioxins and furans, the degradation mechanisms and kinetics are much less investigated in the literature. Several studies have reported varying degrees of removal of PCBs, dioxins, and furans sorbed to soils (Schaal and Hey, 2002; Goi et al., 2006), but they have not provided specific data on degradation kinetics or mechanisms.

5.4.3 Fuel Components and Total Petroleum Hydrocarbons

Fuel hydrocarbons encompass probably the largest and most commonly encountered group of organic contaminants in soil and groundwater. Fuel hydrocarbons, quantified by a gas-chromatographic method as TPH, represent a broad variety of organic contaminants associated with spills of petroleum products. Fuels such as gasoline and diesel fuel are not pure substances; they are mixtures of a wide variety of hydrocarbon compounds. Generally, these compounds may be subcategorized into two major groups, which include aliphatic hydrocarbons and aromatic hydrocarbons. More minor components of fuel hydrocarbon mixtures may include PAHs, as well as fuel additives, such as MTBE.

Ozone has been extensively investigated and applied to treat fuel hydrocarbons associated with fuel spills, and this oxidant generally has excellent reactivity with contaminants in this group. The evolution of the use of ozone for ISCO has many of its roots in treating hydrocarbon-contaminated soils. SVE and AS have long been used as removal methods for treating light nonaqueous phase liquid (LNAPL) fuel spills by recovering volatile contaminants from extracted vapors and by stimulating aerobic biodegradation. However, because fuels are mixtures of organic contaminants, with AS and SVE, the remaining fuel in the subsurface becomes enriched over time in the less volatile or non-volatile components of the mixture. Thus, the introduction of an oxidizing gas such as ozone has been valuable because it has the ability to destroy these residuals. At AS and SVE sites, much of the infrastructure needed for *in situ* ozonation (e.g., sparge wells) is already installed, making ozone ISCO even more economic. Thus there is an extensive body of knowledge regarding the application of ozone to these sites.

5.4.3.1 Aliphatic Hydrocarbons

Generally, aliphatic hydrocarbons are composed of branched chain, straight chain, and cyclic saturated hydrocarbons with varying numbers of carbon atoms. These saturated hydrocarbons have low aqueous solubility, making their oxidation by aqueous oxidants problematic. However, their potential volatility may make them more susceptible to degradation by ozone gas. Remediation goals as applied to these contaminants typically involve meeting reductions of bulk contaminant mass as determined by methods that sum together the large number of organic compounds. Such methods most commonly measure TPH, diesel-range organics

(DRO), and oil and grease content (O&G). As a result, investigations of ozone treatment of hydrocarbon wastes often include measurements of these indicators. In general, it has been demonstrated that large reductions in contaminant masses, as determined by these methods, may be achieved. Table 5.6 summarizes some of the results achieved by studies injecting ozone into soil columns contaminated with fuel hydrocarbons.

Table 5.6. Results of Fuel Hydrocarbon Degradation in Soil Columns as Reported in the Literature

Fuel type	Metric	Concentration (mg/kg)	Percent reduction (%)	Reference
Diesel	DRO	1,485	80	Choi et al. (2000)
Crude oil	O&G	20,600	95	Dunn and Lunn (2002)
Shale oil	TPH	5,500	80	Goi et al. (2006)
Diesel	TPH	2,700	50	Jung et al. (2005)
Diesel	DRO	1,485	94	Yu et al. (2007)

All of these systems were investigated in unsaturated soils with minimal water content. These results demonstrate that gas phase ozone reaction must play a considerable role in the degradation of these contaminants rather than the partitioning of ozone into water and subsequent reaction in the aqueous phase. In particular, Dunn and Lunn (2002) noted that removal of fuel hydrocarbons with ozone was more effective in dry soils than in moist soils, in part because the partitioning of ozone into water acted as an oxidant sink. Ozone must be capable of degrading these organics via reaction within the gas phase, reaction at contaminant-phase interfaces, or partitioning of ozone into the organic phase for reaction. Choi et al. (2000) noted that the presence of metal oxides in soil also apparently catalyzed degradation of TPH as they observed higher TPH degradation in test columns containing field soils with high manganese and iron content than in columns containing pure sands or glass beads. Thus, a heterogeneous catalytic mechanism in the gas phase might also contribute to TPH degradation.

The reaction of ozone with aliphatic hydrocarbons forms organic intermediate compounds. Yu et al. (2007) estimated from soil column studies that a demand of 32 mg-O₃/mg-DRO was needed to fully degrade these contaminants to the point where they no longer were detected as DRO. They also noted that while the kinetic rates of reaction of the various hydrocarbon fractions with gas phase ozone did not differ significantly, lower carbon fractions such as the C₁₀ fraction took longer to disappear with ozonation. Jung et al. (2005) and Choi et al. (2000) noted a similar effect, where the high carbon fraction was reduced in proportion with time while low carbon fractions increased in proportion. This led the authors to conclude that the degradation mechanism for saturated aliphatics involves first the breakdown of high-carbon fractions into low-carbon fractions, followed by further degradation of these low-carbon fractions to carbon dioxide and other low molecular weight organics. However, actual mineralization yields may be low. For instance, while Dunn and Lunn (2002) found that the O&G content of soil contaminated with crude oil at a 20 g/kg concentration could be reduced by up to 95% with ozonation, only 30% of the carbon from this LNAPL could be recovered as CO₂. Their characterization of the residual TPH after ozonation revealed that the remaining hydrocarbon content was more oxygenated after ozonation. Thus, the products likely include lower molecular weight, biodegradable aliphatics containing oxygen groups, such as carboxylic acids, alcohols, ketones, and others.

5.4.3.2 Aromatic Hydrocarbons

Aromatic hydrocarbons are another common fuel component and include a large variety of contaminants that have a benzene ring as the defining structure of the molecule. The positions on the aromatic ring are substituted by a variety of functional groups. In fuels, these substitutions are usually short alkane chains. The most commonly regulated aromatic hydrocarbons are the BTEX components: benzene, toluene, ethylbenzene, and total xylenes. Unlike saturated aliphatic hydrocarbons, aromatic hydrocarbons have higher water solubility, are more mobile, and are measured at higher concentrations in groundwater. Thus, aqueous reaction processes may be more significant with these contaminants, as opposed to the treatment of saturated aliphatics, where gas phase reactions seem to play a dominant role. PAHs and phenolic contaminants are also aromatic hydrocarbons, but they are often found as contaminants at sites not involving fuel spills (see Section 5.4.4).

Degradation of BTEX contaminants with ozone is not as widely documented in the literature as degradation of saturated aliphatics or MTBE. However, they are known to be quite degradable, and their successful removal with ozone ISCO at the laboratory- and field-scale has been demonstrated (Dey et al., 2002; Garoma et al., 2008). Kuo and Chen (1996) extensively investigated the degradation of toluene and the kinetics and mechanisms involved. They found that the direct oxidation by ozone was slow. However, as the pH increased or as hydrogen peroxide was added as in a peroxone system, the degradation of toluene rapidly increased. This is likely due to the production of hydroxyl radicals, as they are known to form in ozone systems at high pH or in peroxone systems. Hydroxyl radicals have been extensively documented to rapidly degrade BTEX and other aromatic compounds (Buxton et al., 1988). It has also been demonstrated that benzene may be degraded by gas phase ozone using manganese dioxide as a catalyst (Naydenov and Mehandjiev, 1993), indicating that soil minerals might play a catalytic role in their degradation.

5.4.3.3 Methyl Tert-Butyl Ether

MTBE is a fuel additive that has been extensively used in gasoline as a fuel oxygenate. However, it has attracted regulatory attention due to its low odor threshold and emerging evidence of its toxicity. Because of its low volatility and biological recalcitrance, MTBE is unlikely to be significantly removed by conventional SVE or AS technologies. As a result, the treatment of MTBE with ISCO using ozone has been a strong focus of recent research. As such, there are a number of studies that have demonstrated the degradability of MTBE.

The degradation of MTBE to innocuous products, such as carbon dioxide (CO₂) and water, has been demonstrated. However, it proceeds through a stepwise process of organic intermediates and has noticeably slower kinetics than oxidation of other hydrocarbon contaminants, such as BTEX (Garoma et al., 2008). Thus, the full mineralization of MTBE to carbon dioxide by oxidation alone may require extensive oxidant dosing. Mitani et al. (2002) conducted an extensive investigation on MTBE degradation reaction rates, mechanisms, and products by ozone. They suggested that degradation of MTBE followed two separate reaction pathways, each with its own intermediates. The dominant pathway proceeded through ozone attack on the methyl group resulting in tert-butyl formate (TBF), which degrades to tert-butyl alcohol (TBA). Under continued ozone dosing, TBA oxidizes to acetone, then to acetic acid. The reaction step from TBF to TBA is relatively rapid, but the conversion of TBA to acetone and from acetone to acetic acid is much slower than the reaction with the parent MTBE. As a result, TBA and acetone are generally observed to accumulate in solution over time and require longer ozone

contact times and doses to degrade them (Mitani et al., 2002; Schreier et al., 2004). The secondary reaction pathway results from oxidative attack on the tertiary butyl group, resulting in the formation of methyl acetate. Again, methyl acetate reacts slower than the parent MTBE compound, though its lower generation rate keeps its concentrations lower than that of TBA and acetone. Methyl acetate degrades to acetic acid (Mitani et al., 2002). Mitani et al. (2002) also found that both direct oxidation with ozone as well as hydroxyl radical (OH^\bullet) attack on MTBE played significant roles in MTBE degradation. This contrasts with the findings of Safarzadeh-Amiri (2001), who attributed the degradation of MTBE by ozone to mainly hydroxyl radical attack. The addition of hydrogen peroxide as in a peroxone system rapidly increased the rate of reaction and extent of degradation (Mitani et al., 2002). Results from field applications of ISCO using ozone at MTBE-contaminated sites have shown promising results in the ability of ozone to degrade MTBE (Dey et al., 2002; Krembs 2008).

5.4.4 Coal Tars, Creosote, and Hydrocarbon Wastes

PAHs are organic contaminants that include multiple benzene rings bonded together. PAHs are commonly present in creosote and coal tar wastes, although they can be present as residuals in some petroleum products as well. Where they are released to the environment, PAH wastes are generally not pure compounds, but rather complex mixtures of numerous PAH compounds. Petroleum wastes such as creosote and coal tar also contain other non-PAH components, such as phenols and cresols, as well as BTEX and non-aromatic compounds (e.g., saturated aliphatics) (Brown et al., 2006). There is extensive documentation in the literature concerning the ability of ozone to treat PAHs and these other waste components.

5.4.4.1 Polycyclic Aromatic Hydrocarbons

Of the groups of organic compounds that have been studied for treatment by ozone oxidation, PAHs have been the most widely investigated. Many studies have observed that when ozone is applied to PAH wastes, the various compounds within the PAH mixture do not degrade at the same rate. Rather, PAHs with fewer aromatic rings (e.g., two or three) degrade to a much higher extent than those with more aromatic rings (e.g., four to six) (Masten and Davies, 1997; Nam and Kukor, 2000; Goi and Trapido, 2004). For instance, Nam and Kukor (2000) observed that with combined oxidation and biodegradation of a PAH waste sorbed to soil, they could achieve 95% removal of the two- to three-ring PAHs, 65% removal of the four-ring PAHs, and only 16% removal of the five-ring PAHs. This may be due in part to the increasing hydrophobicity of PAH contaminants with increasing ring numbers, as more hydrophobic contaminants may be more strongly sorbed to NOM and thus less available to oxidation. This effect has been noted with liquid phase oxidants, such as hydrogen peroxide (Bogan and Trbovic, 2003). However, it is interesting to note that Masten and Davies (1997) also observed this effect even in an unsaturated soil column, where little soil moisture was present. Thus, these more strongly sorbed contaminants may pose challenges to gas phase oxidants just as they do liquid phase oxidants. However, this may not always be the case. Clayton (2000b) observed >95% treatment of mixed three-, four-, and five-ring PAHs. In this study, PAH treatment was nonselective, with equal treatment of three-, four-, and five-ring PAHs.

A number of studies have investigated the degradation mechanisms, pathways, and intermediates formed from the ozone oxidation of PAHs. From the information in the literature, this oxidation can apparently occur in the homogeneous gas phase for more volatile PAHs (Reisen and Arey, 2002), heterogeneously with reaction between ozone gas and PAHs sorbed to

soil particles (Jung et al., 2004), and in the aqueous phase (Hoigné and Bader, 1983a). A large number of intermediate compounds may be formed during the process. The intermediate compounds produced depend on the parent PAH, as well as the reaction conditions. Because PAH compounds contain multiple rings with multiple carbon atoms in a reduced state, multiple oxidation steps by ozone are required to fully mineralize the PAH carbon content to carbon dioxide (CO₂). As a result, with larger oxidant doses, the extent of degradation increases. This is illustrated by Yao et al. (1998), who investigated the products produced by ozonation of pyrene, a four-ring PAH. Low ozone doses yielded intermediates with the three-ring structure of phenanthrene, while higher doses yielded intermediates with a two-ring structure of biphenyl. Thus, progressively higher ozone doses ruptured more rings of the original PAH. While investigating the degradation of phenanthrene, Stehr et al. (2001) observed that some of these intermediates could be further broken down to one-ring aromatic acids, such as salicylic acid and phthalic acid; presumably, they may eventually yield non-aromatic organic compounds with continued ozone dosing.

The number and variety of intermediates that may be produced from a single PAH parent compound can be quite striking and highlights the complexity of oxidation mechanisms. For instance, Zeng et al. (2000) identified up to 61 organic intermediates from benzo(a)pyrene oxidation, including both aromatic and aliphatic intermediates. Many were either straight or branched-chain hydrocarbons, as well as various organic acids and aldehydes. However, not all PAHs are widely susceptible to complete degradation with ozone, even with extensive oxidant dosing. Zhang et al. (2005) investigated the degradation of anthracene, a three-ring PAH, and noted extensive production of 9,10-anthraquinone as a reaction product. The intermediates yielded may have different properties than those of the parent PAH. Oxidation reactions by either direct oxidation with ozone or by free radical oxidation with hydroxyl and other radicals result not only in the cleavage of aromatic rings but also the entrainment of different functional groups on the PAH compounds. The most commonly entrained functional group during the ozone oxidation of PAHs is the carbonyl group (C=O) and varying derivatives of it, such as the aldehyde group, the carboxyl group, and the ketone group (Yao et al., 1998; Zeng et al., 2000). Other functional groups can include ozonides and hydroxy groups. All of these result in the entrainment of oxygen onto the PAH structures, yielding oxy-PAHs as intermediates (Yao et al., 1998; Zeng et al., 2000; Stehr et al., 2001). These functional groups may impact factors such as the compound's hydrophobicity, as well as toxicity. As some of these functional groups impart more polarity on the PAH intermediate than the parent compound, the intermediates may have higher solubility and may be more available for biological transformation reactions. This has led to observations of extensive degradation when oxidation and biodegradation are coupled together, as the oxidized intermediates are more bioavailable and biodegradable than their parent compounds (Nam and Kukor, 2000; Zeng et al., 2000; Goi and Trapido, 2004; Goi et al., 2006; Haapea and Tuhkanen, 2006). However, not all intermediates may be more biodegradable. Stehr et al. (2001) observed evidence of some increased microbial toxicity from the intermediates of pyrene oxidation. Nonetheless, in contaminants such as creosote or coal tar, pyrene merely represents one PAH out of a mixture of many, and those who have investigated the oxidation of these mixtures have generally noted enhanced biodegradability (Nam and Kukor, 2000; Haapea and Tuhkanen, 2006).

Given the extent of intermediates produced by ozonation of PAHs, it seems unlikely that complete mineralization to carbon dioxide will occur by ozone oxidation alone. However, in general, ozonation of PAHs coupled with subsequent biodegradation and natural attenuation mechanisms appears to be quite promising in terms of the mass removal and detoxification of these contaminants.

5.4.4.2 Phenolic Compounds

Phenolic contaminants include phenol, cresols, and other aromatics that are substituted with a least one hydroxyl group. Phenolic contaminants often form a component of PAH based wastes (Brown et al., 2006). As a result, their degradation by ozone is of interest. In general, ozone has rapid and extensive reactivity with phenol and related contaminants, including both direct reaction mechanisms, and free radical mechanisms (Huang and Shu, 1995). Oxidation of phenol proceeds through attack by either ozone or a hydroxyl radical at a point on the aromatic ring either ortho or para to the hydroxyl functional group. The result is generally the formation of a catechol or quinone, which then undergoes ring cleavage to form aliphatic carboxylic acids (Langlais et al., 1991). As discussed in Section 5.4.2 relating to chlorophenols, these contaminants may dissociate into an ionic form at alkaline pH, much like a weak acid. It has been extensively documented that the ionic form of a phenol is much faster reacting with ozone than the non-ionic form (Hoigné and Bader, 1983b); thus alkaline conditions may lead to more rapid and extensive degradation of these contaminants. Oxidation of cresols may yield both aromatic and aliphatic acid intermediates, such as salicylic acid, as well as formic acid, oxalic acid, and others (Wang, 1992).

5.4.5 Nitroaromatics and Nitroamine Explosives

Nitroaromatics and nitroamine explosives contain a nitro group ($-\text{NO}_2$) on a ring structure. Groundwater contaminants within this category include TNT, RDX, nitrobenzene, and nitrophenols. Related compounds include daughter products of these compounds, as well as chloro-nitro-aromatics such as chloronitrobenzene. Ozone has been used to successfully treat explosives compounds in the laboratory (Adam et al., 2006) and in the field (Marvin et al., 2008). Adam et al. (2006) reported the results of a laboratory study involving radiolabeled RDX, and measured $>90\%$ mineralization of RDX to CO_2 , indicating complete ring cleavage. Marvin et al. (2008) reported complete treatment of RDX, tetrahexamine tetranitramine (HMX), TNT, and 2,4-dinitrotoluene without the generation of reaction byproducts. They also noted a limited ozone radius of influence in the vadose zone of 3.4–4.3 m (11–14 ft) due to low permeability clay soils.

Gilmore et al. (2002) evaluated the degradation of TNT with ozone and noted that it could be effectively mineralized based on a nitrogen mass balance. The only intermediate observed included traces of dinitrobenzene. Research by Spangord et al. (2000) indicated that the two isomers of aminodinitrotoluene (metabolites of TNT biodegradation) are even more treatable as they display extremely rapid direct reaction kinetics with ozone. On the basis of these studies, it appears that TNT and its byproducts are degradable by ozone.

RDX degradation mechanisms were evaluated by Bose et al. (1998), who suggested that hydroxyl radicals (OH^\bullet) were necessary to degrade RDX. This was based on the observation that ozonation at high pH or in the presence of hydrogen peroxide resulted in higher degradation yields than ozone alone. Furthermore, even in systems with high hydroxyl radical activity, it appears that complete mineralization of ring carbon within RDX is dependent on yet even more factors. Bose et al. (1998) observed little or no liberation of the ring carbon and only 50% of the nitrogen content in their peroxone system. They speculated that the three nitro groups of RDX were being cleaved, yielding nitrate, but that the organic carbon and half of the organic nitrogen content remained. This is interesting to note in light of findings by Adams and Randtke (1992), who investigated ozonation of Atrazine, a contaminant with an s-triazine ring similar to RDX but with different functional groups. They noted that the functional groups were easily oxidized, but the s-triazine ring was difficult to break down. However, Adam et al. (2006)

was able to achieve extensive (>90%) mineralization of radiolabeled RDX in their experimental systems. These apparent discrepancies may relate to experiment conditions, where Bose et al. (1998) and Adams and Randtke (1992) investigated ozonation in pure aqueous solutions, while Adam et al. (2006) evaluated RDX degradation in soil slurries and soil columns and specifically noted that the presence of the soil enhanced the RDX mineralization. Thus, the soil may have some important catalytic effect on RDX degradation. Nonetheless, it appears that organic byproducts may be formed by RDX treatment by ozone. Adam et al. detected and identified 4-nitro-2,4-diaza-butanal as a byproduct, which has also been detected in the permanganate oxidation of RDX (Adam et al., 2004), and tentatively identified some others. However, in microcosm studies, Adam et al. (2006) found that these intermediates were much more biodegradable than the parent RDX compound by native microorganisms, so their formation might not be a concern from a risk perspective.

Other nitroaromatics include nitrophenols, which are not as extensively investigated. Wang (1992) investigated the detoxification of 2,4-dinitrophenol with ozonation. The toxicity of this contaminant was reduced by 50% based on microbial assays after ozonation and organic acid byproducts were observed.

5.4.6 Pesticides

Pesticides are not often targeted with ISCO, due to their typically dispersed distribution over large areas in the environment. Nonetheless, there is some research available on ozone treatment of several common pesticides in the literature. Adams and Randtke (1992) investigated the degradation of Atrazine by ozone and the byproducts produced. Atrazine contains an s-triazine ring as its core, and several functional groups bonded to that ring. They found that while ozone could fully oxidize the functional groups on that ring, low mineralization yields were attained because it appeared that ozone was unable to cleave the s-triazine ring. Thus, s-triazine byproducts would accumulate in solution as Atrazine is degraded. Pierpoint et al. (2003) looked at two different pesticides, Trifluralin and Aniline. Both contain a benzene ring at their core, and they found that extensive mineralization of the ring carbon to carbon dioxide could be attained (70–97% for Aniline, 72–88% for Trifluralin). This indicates promise for their complete treatment by ozone. Several reaction intermediates were observed, including nitrobenzene and nitrosobenzene in the case of Aniline and several aromatic intermediates that retained the trifluoromethyl group in the case of Trifluralin.

5.5 SUMMARY

ISCO using ozone is a viable technology with potentially wide applicability to many contaminants of concern. Ozone ISCO can benefit from a unique combination of both gas phase and aqueous phase reactions, and can be deployed under unsaturated and saturated subsurface conditions. However, *in situ* ozone application involves significant engineering and safety management, as well as significant subsurface process complexity. Because ozone reacts quickly with a half-life of hours or less, it must be generated onsite and thus requires available electrical power. Limited availability in electrical power may limit the size of the ozone generator, ozone production, and dosing capabilities. This may ultimately limit the size of the site for which *in situ* ozonation can be used. Ozone delivery and distribution to the targeted zone(s) is critical for effective remediation and is strongly influenced by the design of the oxidant delivery system (size, injection pressure, ozone concentration, etc.). Oxidant transport and delivery is limited by numerous ozone reactions that occur in the subsurface, as well as hydrologic parameters including permeability, heterogeneity, and grain size. Within the

saturated zone, ozone sparging involves complex transport processes and reaction mechanisms that may make uniform contact with contaminants challenging. The technology must be carefully matched to site conditions and where appropriately implemented has been successful in treating a wide range of COCs.

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CHAPTER 6

PRINCIPLES OF ISCO RELATED SUBSURFACE TRANSPORT AND MODELING

Jeffrey L. Heiderscheidt,¹ Tissa H. Illangasekare,² Robert C. Borden³ and Neil R. Thomson⁴

¹United States Air Force Academy, Colorado Springs, CO 80840, USA; ²Colorado School of Mines, Golden, CO 80401, USA; ³North Carolina State University, Raleigh, NC 27695, USA;

⁴University of Waterloo, Waterloo, ON Canada, N2L 3G1

Scope

Subsurface transport processes and conditions that affect *in situ* chemical oxidation (ISCO), including source zone architecture, mass transfer, reaction kinetics, and natural oxidant demand (NOD), and modeling methods and tools for process simulation.

Key Concepts

- ISCO effectiveness depends on delivering oxidant to the contaminant which is controlled by subsurface transport processes, including advection, dispersion, and diffusion. These processes are affected by contaminant source zone architecture and dissolution, contaminant sorption and desorption, and oxidant reactions with the contaminants and the porous media.
- Modeling can provide improved understanding of subsurface conditions and help focus remedial selection and design or optimization of an existing remedial system. Modeling can also inform the need for additional site characterization, but model input values frequently have to be extrapolated from limited observed data.
- During design of an ISCO system, transport modeling is helpful in understanding the impacts of NOD, site heterogeneity, and source zone architecture.
- There are few readily available ISCO mathematical modeling tools. Modeling of an oxidant other than permanganate will require adapting an existing tool.
- Conceptual Design for ISCO (CDISCO) and Chemical Oxidation Reactive Transport in 3-Dimensions (CORT3D) are design tools that are useful for determining the potential for implementing ISCO. CDISCO focuses on oxidant transport during the injection phase, oxidant interaction with porous media, and facilitates quick comparisons between injection conditions. CORT3D incorporates these plus other potentially important processes, but takes longer to set up and execute simulations.

6.1 INTRODUCTION

Previous chapters have highlighted a variety of oxidants used during *in situ* chemical oxidation (ISCO) applications. Successful ISCO implementation depends on bringing the oxidant and contaminant into contact in the subsurface. Achieving this reliably and effectively depends upon design factors such as oxidant dosing and the delivery method. Equally important to

successful ISCO implementation are subsurface hydrogeologic/geochemical and contaminant source conditions, including the impact of natural occurring reductants, the mass and architecture of free-phase contaminant, and physical and geochemical heterogeneity. The interaction of these factors and their resultant effect on ISCO performance is often difficult to predict. Additionally, the areal extent of contaminated sites tends to be very large compared to the number of samples that can be obtained to characterize the site hydrogeology, contaminant source zone, and contaminant plume extents.

Modeling is a tool with the potential to provide an improved understanding of subsurface conditions (Clement et al., 2000), as well as insights into complex processes. By simulating possible processes and matching observed data (e.g., hydraulic head, aqueous contaminant concentrations, natural oxidant demand (NOD) mass fractions, and sorbed or nonaqueous phase liquid (NAPL) contaminant mass fractions), potential source zone locations and architectures can be estimated. Such simulations help focus the remedial selection and design process toward oxidants and delivery methods expected to be effective given the likely source architecture and site hydrogeology. By performing simulations using expected upper and lower limits for site parameters the effect of uncertainty can also be examined. These simulations provide insight into the benefits of potential additional site characterization activities, which oxidants are likely to be effective, and how an oxidant should be delivered into the subsurface (Heiderscheidt, 2005). While the complexities and uncertainties involved make true predictive modeling nearly impossible, models can play an important role in site investigations, conceptualization, and data collection. As will become apparent later in this chapter, the ability to model the complex reactions and processes of ISCO in the uncertain subsurface environment is still in its infancy.

ISCO is commonly applied for treatment of organic contamination in source zones, including NAPLs. Hence this chapter begins by describing the characteristics of contaminant source zones and mass transfer processes in the subsurface. This is followed by a discussion of the current understanding and mathematical representations of the primary processes controlling transport of the ISCO reagent. These are the processes that will determine whether the oxidant can be effectively delivered to the target treatment zone (TTZ). A brief discussion is then given to the processes that can affect the hydraulic conditions in the subsurface. Detailed discussion of the oxidation/contaminant reactions and their kinetic expressions is then provided followed by a discussion of oxidant reactions other than those with the target contaminants. This chapter ends with a description of previously published ISCO modeling efforts and discusses the availability of ISCO modeling tools.

6.2 SOURCE ZONE ARCHITECTURE

The physical and geochemical nature of the area of a site where NAPL contamination was originally released (the source zone) is often referred to as the architecture of the source zone. The source zone architecture can impact the nature of the downgradient groundwater plume, as well as the ability of an *in situ* remediation technology to remediate the source zone as well as the plume. This section provides a brief discussion of source zone architecture.

Researchers have demonstrated through mathematical modeling, laboratory experiments and field-scale demonstrations that site heterogeneity has a significant impact on NAPL migration and trapping, resulting in complex, persistent source zones (Schwille, 1988; Kueper et al., 1993). Even in a relatively homogeneous porous media contaminated by NAPLs, micro-scale heterogeneities typically exist, resulting in large zones of residual NAPL saturation [Dekker and Abriola, 2000a; USEPA (U.S. Environmental Protection Agency), 2004].

When initially released into the environment, dense nonaqueous phase liquids (DNAPLs) will sink below the water table (as depicted in Figure 6.1), spreading laterally upon contact with finer

grained layers (Pinder and Abriola, 1986; Kueper et al., 1989; Illangasekare et al., 1995a, b). In addition to this lateral spreading, some DNAPL may enter the finer grained material as a result of fingering caused by pore-scale heterogeneities at the interface of the two layers (Kueper and Frind, 1991a, b; Poulsen and Kueper, 1992; Held and Illangasekare, 1995a, b). Conversely, the presence of coarser grained lenses, especially when overlying lenses of low permeability media, can act as a trap and results in high DNAPL saturations or pooling (Illangasekare et al., 1995b).

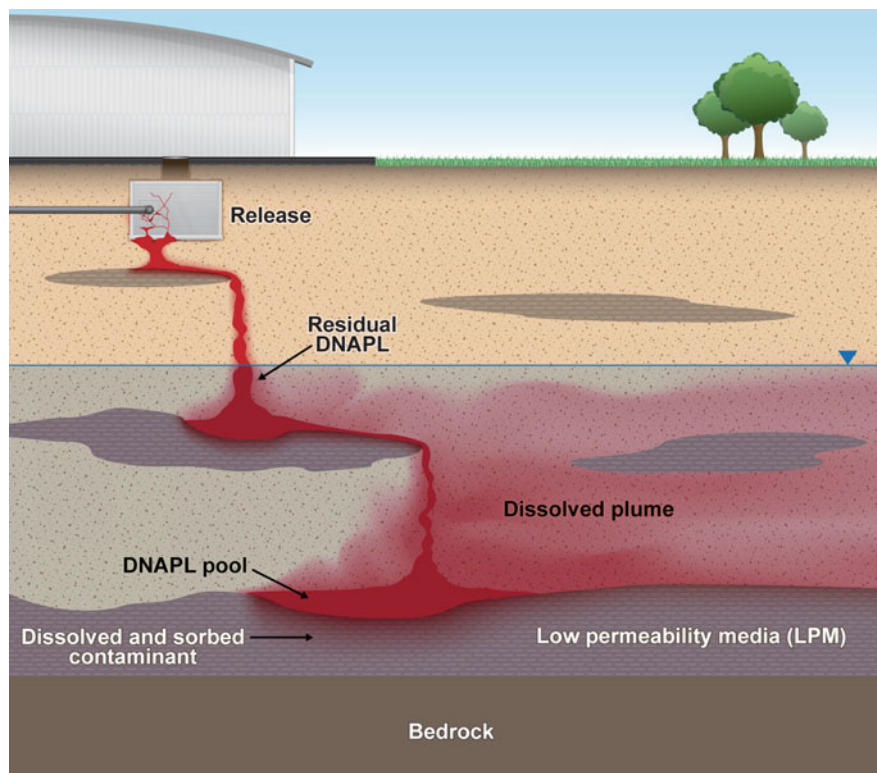


Figure 6.1. Generic contaminated site conceptual site model for a DNAPL source (DNAPL contamination is shown in red).

Light nonaqueous phase liquids (LNAPLs) behave similarly to DNAPLs (such as spreading laterally upon contact with finer grained layers), migrating downward through the vadose zone until they reach the water table. Upon reaching the water table, LNAPLs tend to float on top of the water table, with some possible depression of the water table depending upon the thickness of the LNAPL layer. Additionally, because the LNAPLs float on top of the water table, they tend to move up and down with changes in the water table. This upward and downward movement of the LNAPL layer can result in a large “smear” zone of residual LNAPL saturation in the vicinity just above and below the water table level.

The subsurface environment frequently contains regions of low permeability media within, or as an aquitard beneath, aquifers as depicted in Figure 6.2a. Observations at sites contaminated with NAPL products suggest that over time a significant fraction of dissolved chemical may diffuse into low permeability media (Figure 6.2b), which can become a sink for relatively high amounts of contaminant mass in the dissolved and sorbed phases (Mackay and Cherry, 1989; Johnson and Pankow, 1992; Ball et al., 1997; Liu and Ball, 2002; Sale et al., 2007). For example, Johnson et al. (1989) found that in only 5 years, organic contaminants [including trichloroethene

(TCE)] had diffused 15–20 cm (5.9–7.9 in.) into the extremely low permeability clay liner beneath a hazardous waste dump containing DNAPL. Conversely, waste generated chloride had diffused up to 83 cm (32.7 in.) in that time. The different distances were attributed to different molecular diffusion rates as well as sorption of the organics retarding diffusion. Similarly, Ball et al. (1997) studied a soil core from the aquitard beneath a TCE/perchloroethene (PCE) plume at Dover Air Force Base (AFB), Delaware. They found that PCE and TCE had diffused approximately 80–100 cm (31.5–39.4 in.) into the aquitard in the estimated 15–20 years since the plume arrived above the core location, confirming that an underlying confining layer can be contaminated by an overlying plume of aqueous contamination. Once the NAPL phase is depleted by natural dissolution or an aggressive source removal technology, plume concentrations are likely to rebound as diffused mass is returned from the low permeability media regions back into the surrounding, higher permeability flow zone as illustrated in Figure 6.2c, d (Parker et al., 1994, 1997; Freeze and McWhorter, 1997; Liu and Ball, 2002; Reynolds and Kueper, 2002; Polak et al., 2003).

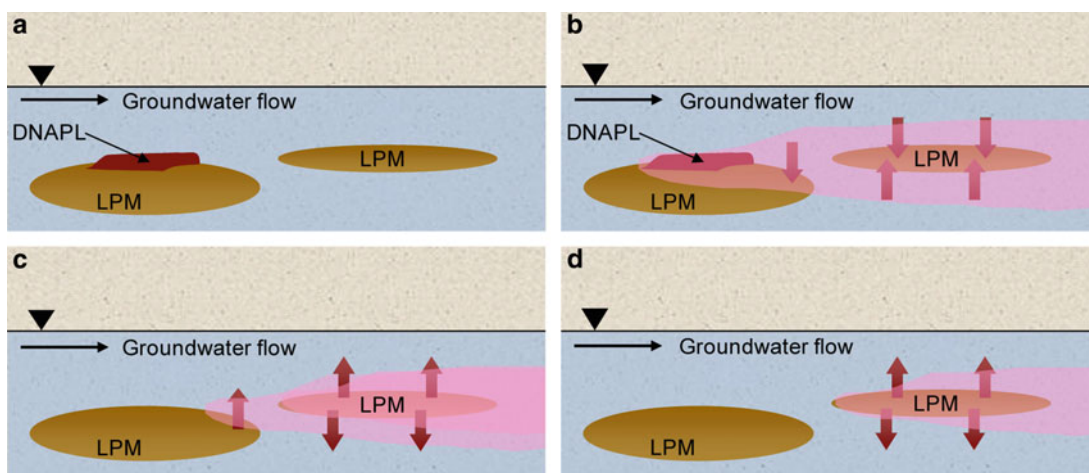


Figure 6.2. Conceptual model of dissolved contaminant diffusion: (a) DNAPL pool overlying low permeability media (LPM), (b) diffusion into LPM, (c) back diffusion from LPM once DNAPL pool is depleted (d) cessation of back diffusion from large LPM region once diffused mass is depleted.

6.3 CONTAMINANT MASS TRANSFER

Contaminant mass transfer refers to the exchange of contaminant mass from one phase to another. There are a number of important mass transfer processes to consider.

6.3.1 NAPL Dissolution

NAPL dissolution, or mass transfer from the nonaqueous to the aqueous phase, is important because it is often the origin of the dissolved contaminant plume in groundwater driving the need to undertake remediation (Illangasekare et al., 2006). The rate at which contaminant is dissolving determines plume concentrations, how quickly contaminant enters the aqueous phase where most of the oxidation reaction is thought to occur, and the longevity of the NAPL source. Aqueous concentrations then affect how much contaminant mass ends up sorbed to aquifer material, where it can become a secondary source of aqueous contamination once the NAPL source is depleted. Further, the degree to which NAPL is filling pore space will affect hydraulic conditions around and through the source zone, impacting fluid flow and affecting delivery of oxidant to the source zone.

The rate of NAPL mass transfer depends upon the configuration and size (i.e., architecture) of the NAPL source. Residual NAPL is present as disconnected blobs and ganglia partially filling the pore space. It is typically left behind as NAPL migrates downward during the initial introduction to the aquifer, as subsurface conditions change to remobilize a large NAPL pool or body, or as a NAPL pool is depleted. Conversely, NAPL pools are regions where the NAPL fills a large fraction of the porous media pore space. A pool of NAPL typically has less interfacial area than the same volume distributed as residual, so the rate of mass transfer from a residual is expected to be greater than that from a pool, resulting in higher aqueous concentrations and faster source depletion (Johnson and Pankow, 1992).

Mass transfer or dissolution of NAPL into the aqueous phase is generally presented as a linear model based on the well known stagnant film model (Sherwood et al., 1975) using a first-order linear driving force:

$$\frac{dc_{\infty}}{dt} = -k_{La}(c_{\infty} - c^*) \quad (\text{Eq. 6.1})$$

where dc_{∞}/dt is the rate of change of aqueous concentration per time ($\text{M L}^{-3} \text{T}^{-1}$), c_{∞} is the aqueous solute concentration (M L^{-3}) of the bulk solution, c^* is the aqueous solubility limit of the soluble component (M L^{-3}), and k_{La} is the NAPL dissolution rate or lumped mass transfer coefficient (T^{-1}). The symbols L, T and M refer to standard units – L is length (generally expressed in centimeters [cm] or meters [m]), T is time (generally expressed in seconds [s] or days [d]) and M is mass (generally expressed in milligrams [mg] or micrograms [μg]). Because k_{La} cannot be measured directly, a considerable amount of research has been devoted to developing methods to estimate k_{La} from measurable system parameters, including pore size and NAPL saturation (Miller et al., 1990; Imhoff et al., 1994; Powers et al., 1994a, b; Ewing, 1996; Nambi, 1999; Saba and Illangasekare, 2000; Clement et al., 2004b).

The general approach is to use an empirically determined Gilland-Sherwood correlation as given by Welty et al. (1976):

$$Sh = a + bRe^c Sc^d \quad (\text{Eq. 6.2})$$

to estimate the modified Sherwood number (Sh) from other dimensionless numbers describing the system (e.g., Reynolds number, Re , and Schmidt number, Sc), where a , b , c , and d are empirically determined constants. The modified Sherwood number relates the mass transport in a system to the diffusive forces, the Reynolds number relates system inertial forces to viscous forces, and the Schmidt number relates viscous forces to diffusive forces. Mathematical equations for these three dimensionless numbers are:

$$Sh = \frac{k_{La}d_{50}^2}{D_m} \quad (\text{Eq. 6.3})$$

$$Re = \frac{\rho_w \bar{v} d_{50}}{\mu_w} \quad (\text{Eq. 6.4})$$

$$Sc = \frac{\mu_w}{\rho_w D_m} \quad (\text{Eq. 6.5})$$

where d_{50} is the representative (median) grain size (L), D_m is the molecular diffusion coefficient ($\text{L}^2 \text{T}^{-1}$), ρ_w is the aqueous phase density (M L^{-3}), \bar{v} is the average linear groundwater velocity (L T^{-1}), and μ_w is the aqueous phase dynamic viscosity ($\text{M L}^{-1} \text{T}^{-1}$). The Sherwood number determined from the empirical correlation (Equation 6.2) is then used in Equation 6.3 to estimate k_{La} . Most correlations incorporate volumetric NAPL content (θ_n) in some form to

account for the changing NAPL-water interfacial area as dissolution proceeds (Miller et al., 1990; Powers et al., 1994b).

Example Gilland-Sherwood relations are shown in Table 6.1. Differences in empirical coefficients and formulations are at least partly due to differences in experimental conditions. For example Powers et al. (1994a) used a one-dimensional (1-D) system with spherical dissolving organic media and Powers et al. (1994b) used a 1-D homogeneous system, while Saba and Illangasekare (2000) were considering a 2-D system with heterogeneity-induced flow-bypassing. Miller et al. (1990) and Imhoff et al. (1994) both used 1-D systems. Ewing (1996) and Saba et al. (2001) considered a 2-D system with surfactant flushing. Nambi and Powers (2003) further expanded the available choices by looking at 2-D systems with high NAPL saturations resulting in slower mass transfer characterized by a significantly increased exponent on the NAPL saturation term. These correlations have been found to be effective for modified Sherwood numbers ranging from 0.01 to over 25.0 (Miller et al., 1990; Imhoff et al., 1994; Nambi and Powers, 2003).

If the NAPL dissolution rate is nearly equal to the fluid transport rate, then the local equilibrium assumption (LEA) is valid and estimating mass removal rates from a NAPL source is simplified and can be accomplished by assuming that the aqueous phase contacting the NAPL has a contaminant concentration equal to the contaminant's aqueous solubility (Powers et al., 1998). The validity of the LEA can be determined using the first Damkohler number, $Da(I)$ shown in Equation 6.6. It is a dimensionless number relating the characteristic time of fluid motion or hydraulic retention time (L/\bar{v}) to the characteristic time of NAPL mass transfer or dissolution ($1/k_{La}$).

$$Da(I) = \frac{k_{La}L}{\bar{v}} \quad (\text{Eq. 6.6})$$

Generally, a $Da(I) \geq 100$ indicates equilibrium, $10 \leq Da(I) < 100$ indicates near equilibrium, and $Da(I) < 10$ indicates rate-limited mass transfer (Brusseu, 1992). Because the mass transfer rate is dependent upon the water velocity, as represented by the Reynolds number (typically to a power other than one) in the correlations, the first Damkohler number may be useful in optimizing the mass transfer of a given system depending on what mass transfer correlation best describes the system (Mayer et al., 1999).

In order to optimize oxidation, it is desirable for the NAPL mass transfer rate to be as close to the oxidation rate as possible. The second Damkohler number, $Da(II)$, shown in Equation 6.7, which relates the characteristic time of NAPL mass transfer or dissolution ($1/k_{La}$) to the characteristic time of chemical reaction ($1/k_1$) is useful for comparing these rates.

$$Da(II) = \frac{k_1}{k_{La}} \quad (\text{Eq. 6.7})$$

A $Da(II) \ll 1$ indicates contaminant mass is transferring into the aqueous phase faster than the chemical reaction can destroy it, while a $Da(II) \gg 1$ suggests that the chemical reaction is faster than the mass transfer.

One possible goal of ISCO is to speed up remediation of a contaminant source zone by inducing increased mass transfer (and subsequent destruction) from a NAPL source. Based on experimental results, Schnarr et al. (1998) suggest that NAPL dissolution and oxidation are processes that occur in parallel with increased mass transfer during oxidation occurring primarily as a result of an increased aqueous concentration gradient. Urynowicz (2000) demonstrated the ability for permanganate to increase dissolution of NAPL TCE in batch and flow-through experiments without porous media present; however, the rate decreased as a manganese dioxide [$\text{MnO}_2(\text{s})$] film formed at the NAPL-water interface. Reitsma and Dai (2001) performed a theoretical study to estimate the maximum expected NAPL mass transfer

enhancement resulting from chemical oxidation. They estimated a maximum five times increase in dispersive mass transport from a PCE NAPL pool resulting from the increased concentration gradient; however, they predict little enhancement in local-scale mass transfer from NAPL to aqueous phase, suggesting no change in dissolution mass transfer parameters. Further, they suggest that actual enhancement is likely to be less because permeability reduction and decreased interfacial contact area were not accounted for in the estimate. On the contrary, MacKinnon and Thomson (2002) calculated a tenfold initial increase in PCE mass transfer from a NAPL pool during a 2-D oxidation experiment, with decreasing mass flux over time attributed to $\text{MnO}_2(\text{s})$ formation.

Table 6.1. Gilliland-Sherwood Mass Transfer Correlations for NAPL-Water Systems

Mass transfer correlation	References
$Sh = 37.15 \left(\frac{\theta_n}{\phi} \right)^{1.24} \text{Re}^{0.61}$ (for $\theta_n/\phi < 0.35$)	Nambi and Powers (2003)
$Sh = 0.4727 \text{Re}^{0.2793} \text{Sc}^{0.33} \left(\frac{\theta_n}{1 - \theta_n} \right)^{1.642} \left(\frac{d_{50}}{\tau L} \right)^{0.1457}$	Saba et al. (2001)
$Sh = 11.34 \text{Re}^{0.2767} \text{Sc}^{0.33} \left(\frac{\theta_n d_{50}}{\tau L} \right)^{1.037}$	Saba and Illangasekare (2000)
$Sh = 4.84 \text{Re}^{0.219} \theta_n^{1.32}$	Ewing (1996)
$Sh = 36.8 \text{Re}^{0.654}$	Powers et al. (1994a)
$Sh = 4.13 \text{Re}^{0.598} \left(\frac{d_{50}}{d_M} \right)^{0.673} U^{0.369} \left(\frac{\theta_n}{\theta_{n0}} \right)^\beta$; $\beta = 0.518 + 0.114 \left(\frac{d_{50}}{d_M} \right) + 0.10U$	Powers et al. (1994b)
$Sh = 340 \theta_n^{0.87} \text{Re}^{0.71} \left(\frac{d_{50}}{x} \right)^{0.31}$	Imhoff et al. (1994)
$Sh = 12 \text{Re}^{0.75} \theta_n^{0.60} \text{Sc}^{0.5}$	Miller et al. (1990)

Definitions of terms and variables are as follows: Sh - Sherwood number; Re - Reynolds number; Sc - Schmidt number; θ_n - volumetric NAPL content; θ_{n0} - initial volumetric NAPL content; ϕ - soil porosity; τ - soil tortuosity; U - soil uniformity index; d_{50} - representative (median) grain size (L); d_M - diameter of a "medium" sand grain (defined by U.S. Department of Agriculture as 0.05 cm [0.02 in]); β - NAPL geometry coefficient; L - characteristic or dissolution length in the flow direction (L); x - distance into the residual NAPL source in the direction of flow (L).

As an alternative to using a Gilliland-Sherwood relation, a simplification can be made to represent NAPL dissolution using a source term or function. For example, Zhu and Sykes (2004) proposed three different pseudo-equilibrium functions to describe source zone concentrations, based upon the mass of NAPL residual remaining in the source zone. Similarly, Basu et al. (2008) proposed and evaluated four simplified source zone functions, relating the flux-averaged aqueous concentration leaving the source zone to various source depletion terms. Using source functions such as these greatly reduces the complexity of the simulation but does not allow changes to the system during the simulation to fundamentally affect the source zone. Specifically, using a source term function lumps the entire NAPL source zone together, paying no attention to the spatial distribution of NAPL within the source zone (Zhu and Sykes, 2004) and ignores subsurface heterogeneities (Willson et al., 2006). Consequently, it may be difficult or impossible for such source terms to simulate potential mass transfer increases or decreases resulting from oxidation within and in close proximity to the source zone.

6.3.2 Contaminant Sorption/Desorption

Sorption is a mass transfer process whereby an aqueous phase solute becomes either absorbed into (Figure 6.3a) or adsorbed onto (Figure 6.3b) the subsurface porous media, removing chemical mass from the aqueous phase. It has the effect of retarding chemical transport through the subsurface compared to the bulk fluid flow because the mass that becomes sorbed is no longer being transported via advection, dispersion, or diffusion (Mackay and Cherry, 1989). Once the aqueous concentration begins to decline, the reversibly sorbed chemical mass will begin to desorb and be returned to the aqueous phase for continued transport.

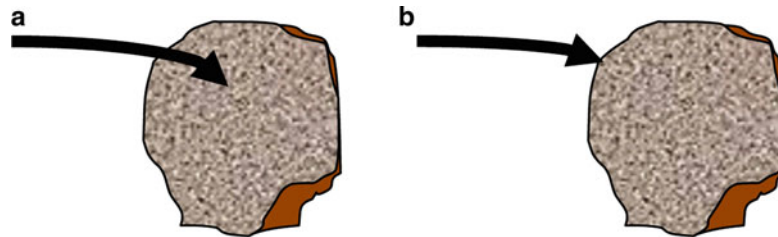


Figure 6.3. Conceptual model of components of sorption: (a) aqueous chemical being absorbed into porous media, (b) aqueous chemical being adsorbed onto the surface of porous media.

Perhaps the greatest impact of sorption is as a contaminant sink and eventually as another source zone of aqueous contamination. In many cases, the pure-phase contaminant originally entered the subsurface years before the remedial effort (Freeze and McWhorter, 1997). As a result, in groundwater with appreciable organic matter associated with the porous media, there have been sufficiently high concentrations over a long enough time for a considerable mass of contaminant to become sorbed to porous media. This sorbed contaminant is generally not readily accessible for oxidation until it desorbs and re-enters the aqueous phase. However, just as with diffusion from low permeability media, desorption is often slow compared to the bulk fluid flow rate (Heyse et al., 2002). Consequently, the sorbed contaminant mass can act as a relatively long-term source of groundwater contamination, with the rate of desorption potentially limiting how quickly the site can be cleaned up.

Sorption may be represented mathematically in equilibrium with aqueous concentrations, meaning that the mass of sorbed contaminant changes instantaneously with changes in aqueous contaminant concentration. Equilibrium sorption is typically implemented using a retardation factor, R_f . The retardation factor is multiplied by the rate of aqueous concentration change, eliminating the need to track and compute sorbed contaminant mass. If implementing sorption this way, a choice must be also be made regarding what type of equilibrium sorption to implement: linear, Langmuir, Freundlich, or some other equilibrium sorption isotherm. This decision determines the equation to use in implementing the retardation factor. Refer to Zheng and Wang (1999) for a more detailed discussion.

Alternately, sorption may be modeled as a rate-limited process where changes in sorbed contaminant mass change more slowly than aqueous concentrations. Haggerty and Gorelick (1994) proposed the following relation for modeling sorption that can simulate either equilibrium or rate-limited sorption of contaminant.

$$\frac{dX_{sorb}}{dt} = \frac{\phi}{\rho_B} \xi \left(C_{cont} - \frac{X_{sorb}}{\lambda_{cont}} \right) \quad (\text{Eq. 6.8})$$

In this relation, ϕ is the soil porosity, ρ_B is the soil bulk density (M L^{-3}), x is the rate-limited sorption mass transfer coefficient (T^{-1}), C_{cont} is the dissolved contaminant concentration (M L^{-3}), X_{sorb} is the mass fraction of sorbed contaminant in the porous media (M M^{-1}), and l_{cont} is the linear sorption coefficient ($\text{L}^3 \text{M}^{-1}$). As ξ gets larger, the non-equilibrium sorption approaches equilibrium sorption; conversely, as ξ gets very small sorption becomes negligible. Modeling sorption in this way allows the rate of sorption/desorption to change at each model location as a function of the local sorbed mass and aqueous concentration.

6.4 PRIMARY REAGENT TRANSPORT PROCESSES

This section describes the primary subsurface transport processes affecting the delivery of injected reagents to the target treatment zone. The importance of each process to a particular ISCO application depends upon site conditions, the selected oxidant, and the oxidant delivery scenario. Discussion of NAPL movement and the ultimate formation of a NAPL source zone is beyond the scope of this Volume because ISCO is typically undertaken at sites where the NAPL is assumed to be immobile due to the length of time between the NAPL release and the start of remediation. An overview of physical transport processes, related to chemical delivery in general, can be found in Kitanidis and McCarty (2011).

6.4.1 Advection

Advection is perhaps the most important process that physically moves the oxidant and dissolved contaminant through the subsurface. Advection refers to the movement of reagent or dissolved contaminant along with the bulk fluid movement from one location to another as depicted in Figure 6.4a. Based on Darcy's Law, advective flow velocities, v (L T^{-1}), for saturated subsurface materials can be estimated from the average (bulk) subsurface hydraulic conductivity, K (L T^{-1}), and porosity (ϕ) along with the average hydraulic gradient ($\Delta h/\Delta x$) causing flow (Equation 6.9).

$$v = -\frac{K}{\phi} \left(\frac{\Delta h}{\Delta x} \right) \quad (\text{Eq. 6.9})$$

In most oxidant delivery scenarios, advection is the dominant transport mechanism and processes altering the subsurface hydraulic gradient, permeability, or porosity are important because they will impact advection. Natural variability of subsurface permeability can vary several orders of magnitude between regions of high and low permeability. In addition, entrapment of NAPLs or air can greatly reduce permeability in affected regions (see Section 6.5 for more information). Reduced permeability can result in flow bypassing around zones that may contain significant amounts of contaminant. Flow bypassing reduces reagent delivery efficiency, prolonging the time to achieve the desired remediation end point. In some extreme cases, the injected reagent may completely bypass the targeted source zones. Further, Soga et al. (2004) reviewed source-depletion technologies and performed numerical simulations confirming that soil heterogeneity and complexity of NAPL source zone morphology are critical factors controlling source reduction effectiveness.

During active injection, a very high pressure (hydraulic gradient) can be applied so that high velocities are temporarily imparted on the groundwater. After injections end, hydraulic gradients return to normal so that the ambient flow field controls further oxidant transport. Refer to Chapter 11 for more discussion and comparison of advective oxidant transport during active injection compared to post injection.

In order to represent advective transport mathematically, the change in subsurface fluid storage must first be described. This is done using the basic flow equation (Equation 6.10), where S_s is the specific storage of the porous medium (L^{-1}), h is the hydraulic head (L), t is the time (T), K_{xx} , K_{yy} , and K_{zz} are the hydraulic conductivity along the x, y, and z coordinate axes corresponding to the x, y, and z axes of hydraulic conductivity ($L T^{-1}$), and W is the volumetric flux per unit volume representing sources and sinks of fluid (T^{-1}). Fetter (1999) and Schwartz and Zhang (2003) provide additional information about the basic flow equation.

$$S_s \frac{\partial h}{\partial t} = \frac{\partial}{\partial x} \left(K_{xx} \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_{yy} \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_{zz} \frac{\partial h}{\partial z} \right) - W \quad (\text{Eq. 6.10})$$

The advection equation (Equation 6.11) describes the change in concentration of species k with time, $\partial C^k / \partial t$ ($M L^{-3} T^{-1}$), as a result of advective transport, where x_{ij} is the distance along the respective Cartesian coordinate axis (L). This equation is applicable to single-phase transport of multiple species. However, in practical terms solute transport in the subsurface does not occur by advection alone. As a minimum, dispersion is generally included as described in the next section. In fact, for many practical applications, additional terms are included to represent solute sources, sinks, and reactions.

$$\phi \frac{\partial C^k}{\partial t} = - \frac{\partial}{\partial x_i} (\phi \bar{v}_i C^k) \quad (\text{Eq. 6.11})$$

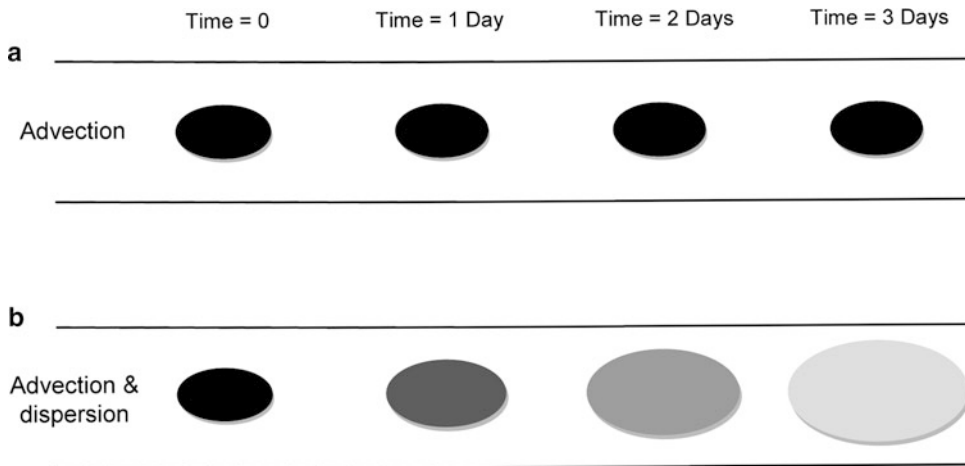


Figure 6.4. Comparison of chemical transport versus time, due to (a) advection and (b) advection and dispersion. Lighter shades indicate lower average concentration as mass spreads out.

6.4.2 Dispersion

Dispersion occurs as a result of the physical mixing caused by variations in advective subsurface fluid velocity through the many disparate porous medium pore paths (Freeze and Cherry, 1979). In fact, dispersion at practical scales of interest is controlled by the subsurface heterogeneity. Dispersion will cause enhanced spreading of the injected oxidant as it moves downgradient resulting in some of the oxidant chemical arriving earlier and some later than under advective transport alone (Figure 6.4b). It will also result in mixing of the oxidant with the dissolved contaminant. If the subsurface fluid velocities are high, either naturally or during reagent injection, or if the subsurface is not homogeneous, then consideration of dispersive

processes will be very important. In general, dispersive mixing is much higher coincident with the direction of groundwater flow than transverse to the groundwater flow direction. Because dispersion is largely dependent upon subsurface fluid velocities, anything altering the subsurface hydraulic gradient, permeability, or porosity is again important.

The combination of advective and dispersive transport is represented using the advection-dispersion equation (Equation 6.12). Specifically, Equation 6.12 describes the change in concentration of species k with time, $\partial C^k/\partial t$ ($M L^{-3} T^{-1}$), as a result of hydrodynamic dispersive transport (first term on the right-hand side), advective transport (second term on the right-hand side), sinks or sources (third term on the right-hand side), and reactions (last term on the right-hand side). Just as with the advection equation (Equation 6.11), this equation is applicable to single-phase transport of multiple species. D_{ij} is the hydrodynamic dispersion coefficient tensor ($L^2 T^{-1}$) and accounts for dispersion and diffusion, q_s is the volumetric flow rate per unit volume of aquifer representing fluid sources (positive) and sinks (negative) (T^{-1}), C_s^k is the concentration of the source or sink flux of species k ($M L^{-3}$), and R_n is the reaction term ($M L^{-3} T^{-1}$). Refer to Fetter (1999) and Zheng and Bennett (2002) for additional details on the advection-dispersion equation.

$$\phi \frac{\partial C^k}{\partial t} = \frac{\partial}{\partial x_i} \left(\phi D_{ij} \frac{\partial C^k}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (\phi \bar{v}_i C^k) - q_s C_s^k + \sum R_n \quad (\text{Eq. 6.12})$$

6.4.3 Diffusion

Diffusion is a relatively slow process in many subsurface environments, compared to advective and dispersive transport. As a result, groundwater carrying the oxidant cannot easily access low permeability media zones (Dekker and Abriola, 2000b; Stroo et al., 2003). For this reason, it can be an important process to consider when there is contaminant mass in the low permeability media. Because different chemicals have different molecular diffusion coefficients and different sorptive properties, it may be possible to exploit these differences in remediating contaminant mass located in some low permeability media, especially with permanganate (Siegrist et al., 1999; Struse et al., 2002b).

Based on the small number of studies reported in the literature, diffusive transport of permanganate during ISCO can occur. Struse et al. (2002b) studied the transport of permanganate by diffusion through 2.54 cm long, intact cores of low permeability silty clay loam soil. Permanganate diffused through the uncontaminated core in approximately 15 days. When TCE was emplaced in the center of the core, it took twice as long for the permanganate to get all the way through the core; however, nearly all of the TCE was successfully oxidized with none diffusing out of the core despite having only half the distance to travel. These results indicate the permanganate can effectively diffuse into a low permeability media and oxidize contaminant mass located there. Further, the effective diffusion coefficients correlated well to the porosities, using the Millington-Quirk relation. Similarly, Siegrist et al. (1999) tested the ability of permanganate to diffuse into silty clay low permeability media at a field site in Ohio. The permanganate was emplaced via hydraulic fracturing, and continuous cores were extracted at several times over 15 months. After 10 months, the permanganate had visibly diffused over 15 cm above and below the emplacement, and batch tests showed that this zone still sustained a high degradation potential. However, few additional studies have been reported in the literature and there has been insufficient study of how the low permeability media characteristics and configuration will impact the effectiveness of ISCO using different oxidants within a target treatment zone.

As demonstrated by Johnson et al. (1989), different solutes diffuse at different rates through a porous medium. To account for the more tortuous path a solute must travel through

in a porous medium, Millington and Quirk (1959, 1961), proposed that the effective diffusion coefficient, D_e , ($L^2 T^{-1}$) of an aqueous solute through a porous medium can be estimated from the molecular diffusion coefficient for a bulk solution of the solute (at an infinitely dilute concentration), D_m , ($L^2 T^{-1}$) and the effective porosity, ϕ_{eff} .

$$D_e = D_m \phi_{eff}^{\frac{4}{3}} \quad (\text{Eq. 6.13})$$

In order to account for the reduced effective porosity in a multiphase system (such as when NAPL is present), Jury et al. (1991) modified the Millington-Quirk relationship, relating it to water content (θ_w) as well as effective porosity (Equation 6.14). In the fully water saturated case, the water content (θ_w) is equal to effective porosity (ϕ_{eff}), and Equation 6.14 simplifies to the Millington-Quirk relation of Equation 6.13.

$$D_e = D_m \frac{\theta_w^{\frac{10}{3}}}{\phi_{eff}^2} \quad (\text{Eq. 6.14})$$

6.4.4 Density-Induced Flow

When a concentrated aqueous oxidant solution is injected into a groundwater zone, the density difference may give rise to a body force that will cause the oxidant solution to migrate downwards, as in Figure 6.5. Appreciation of this density dependent transport of the injected oxidant solution is important. Schincariol and Schwartz (1990) show that significant instabilities in flow can occur even at density differences as low as 0.0008 g/mL. Equations 6.10 and 6.12 are not suitable to capture density dependant transport and alternative formulations are required, such as those described by Guo and Langevin (2002), Langevin et al. (2003), Langevin and Guo (2006), and Henderson et al. (2009).

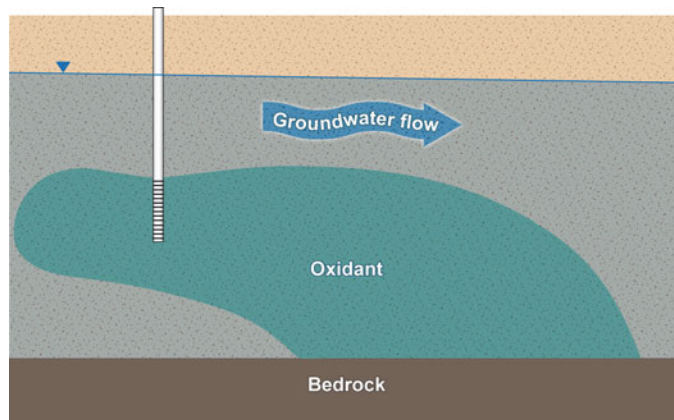


Figure 6.5. Conceptual model of oxidant transport when oxidant density is notably greater than groundwater density.

6.4.5 Sorption

Background on sorption and its impacts on contaminant transport was discussed in Section 6.3.2. During an oxidation injection event, the aqueous contaminant will travel more slowly than the oxidant being delivered, and sorption can increase the potential for the oxidant to reach the aqueous contaminant.

If the sorption reaction is fast enough compared to the subsurface fluid velocity, it can be treated as instantaneous and incorporated into Equation 6.12 by adding the dimensionless retardation factor, R , to the left-hand side of the equation, as in Equation 6.15. Refer to Zheng and Wang (1999) for a discussion of the available instantaneous or equilibrium representations of sorption. When the fluid velocity is fast compared to the sorption reaction, the sorption reaction is represented by a kinetic expression as one of the R_n terms.

$$R\phi \frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} \left(\phi D_{ij} \frac{\partial C}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (\phi \bar{v}_i C) - q_s C_s + \sum R_n \quad (\text{Eq. 6.15})$$

6.4.6 Gas Injection

Ozone is unique among typical ISCO oxidants, as described in detail in Chapter 5, in that it is commonly injected as a gas, often resulting in a continuous supply of gas to the injection point. The injection of gases below the water table has been the focus of numerous studies looking into the subsurface air distribution during *in situ* air sparging. Evidence suggests that macroscopic channel flow (Figure 6.6) will dominate in sands, silts, and clays; while bubble dominated flow will only occur in uniform gravel aquifers (Brooks et al., 1999).

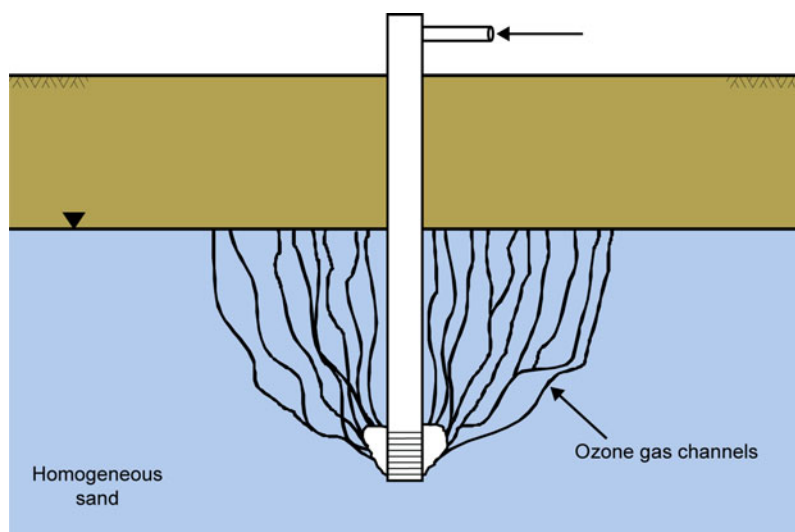


Figure 6.6. Conceptual model of macroscopic channel formation during ozone injection.

The distribution of air that results from air sparging is controlled by both microscopic and macroscopic processes. At the microscopic scale, it is the pore air entry pressure that will govern the migration of the injected ozone; at the macroscale, it is the presence of heterogeneities (e.g., lower permeability zones) that will alter the bulk ozone migration patterns. The actual mechanisms that control ozone channel formation at a particular site will represent a coupling of the processes at these two scales, and thus will dictate the distribution of ozone. Since large pores are associated with higher permeability zones the injected ozone will be concentrated along pathways of relatively higher permeability (Thomson and Johnson, 2000; Tomlinson et al., 2003).

6.5 PROCESSES IMPACTING HYDRAULIC CONDITIONS

At sites implementing ISCO, the groundwater velocity is typically not negligible, so advection and dispersion are important processes in the spread of dissolved contaminant and/or the delivery of oxidant to the target treatment zone. Consequently, it is important to consider processes that can cause changes in the hydraulic conditions spatially, temporally, or both.

6.5.1 Permeability Reductions Caused by Immobile Components

Various methods have been proposed to relate permeability reductions to reductions in porosity caused by immobile components (e.g., NAPL, microbial growth, inorganic precipitates) in pore spaces. These include power law models as in Equations 6.16 (Wyllie, 1962) and 6.17 (Reis and Acock, 1994) or capillary-tube models like the Kozeny-Carman equation in Equation 6.18 (Bear, 1972)

$$k_{r,w} = \left(\frac{1 - S_n - S_{r,w}}{1 - S_{r,w}} \right)^3 \quad (\text{Eq. 6.16})$$

$$k_{r,w} = \left(1 - \frac{\phi - \phi_{eff}}{\phi} \right)^b \quad (\text{Eq. 6.17})$$

$$k_{r,w} = \frac{\phi^3}{K_s(1 - \phi)^2} \left(\frac{d_{50}^2}{180} \right) \quad (\text{Eq. 6.18})$$

where $k_{r,w}$ is the relative water permeability, S_n is the saturation of immobile component in the pore space, $S_{r,w}$ is the residual water saturation for the porous media, ϕ is the porous media porosity, ϕ_{eff} is the effective porous media porosity, b is an empirical exponent related to the type of porous media, K_s is the saturated hydraulic conductivity ($L T^{-1}$) and d_{50} is the representative (median) grain size (L).

The following sections discuss the permeability impacts caused by key immobile components including NAPL, generated solids, and generated gas. Refer to Figure 6.7 for conceptual models of potential pore-blocking mechanisms related to NAPL and solids. The applicability of Equations 6.16 through 6.18 for estimating permeability reduction due to immobile components is also described, along with the potential for underprediction of permeability reduction in relation to solids formation.

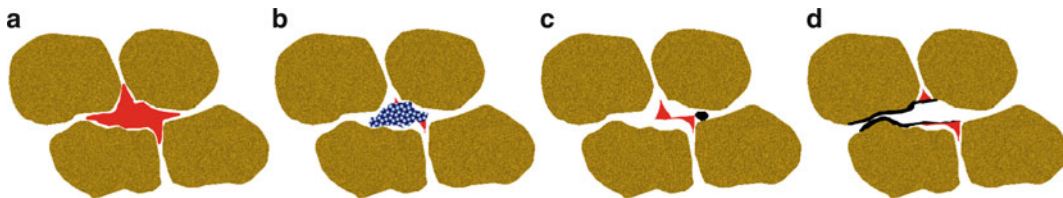


Figure 6.7. Conceptual models of pore-blocking: (a) NAPL filling pore space, (b) microbial growth or amorphous, gel-like precipitate and NAPL, (c) generated solid in pore throat and NAPL (d) generated solid film decreasing pore throat diameter and encapsulating NAPL.

6.5.1.1 NAPL Content

Groundwater flow through a source zone of high NAPL saturation is greatly reduced by the reduction in effective permeability due to NAPL filling most of the pore space when compared

to otherwise similar subsurface regions outside the source zone (Powers et al., 1998; Saba and Illangasekare, 2000). Ostrom et al. (1999) and Taylor et al. (2001) both performed 2-D tank experiments of reagent flushing of NAPLs in heterogeneous systems. In both studies, injected reagents did not considerably reduce NAPL mass from highly saturated NAPL pools overlying low permeability media due to flow bypassing. Similarly, the modeling work of Saenton et al. (2002) showed that flow bypassing can reduce the reagent delivery efficiency, prolonging the time to achieve the desired remediation end-point. In these studies, in some extreme cases, the injected surfactant completely bypassed the NAPL source zones. Conversely, as NAPL is removed from pore space, either through dissolution or remediation, it is logical that an increasing amount of pore space will become available to hydraulic fluid flow, increasing hydraulic permeability and, therefore, increasing fluid velocities through these zones.

Saenton (2003) and Illangasekare et al. (2006) found Equation 6.16 to provide good agreement with experimentally derived permeability data (Saba, 1999) for NAPL in the pore space of silica sands, such as may be visualized in Figure 6.7a.

6.5.1.2 Solids Formation

When using permanganate to oxidize a high saturation NAPL source zone, researchers have shown that permeability reductions may occur due to formation of manganese dioxide thereby reducing the ability for oxidant to be transported to the source (Schroth et al., 2001; Siegrist et al., 2002; Lee et al., 2003). Research into permeability effects from permanganate oxidation of NAPL source zones at lower saturations is a bit more ambiguous. Nelson et al. (2001) concluded that the manganese dioxide produced during oxidation of a PCE NAPL present at approximately 4–7% saturation had negligible effect on the permeability, despite the system remaining at a neutral pH due to natural buffering from the carbonate mineral-containing sands. On the contrary, Lee et al. (2003) found that permanganate oxidation of a TCE NAPL source zone at 8% saturation resulted in generation of up to 4,900 mg $\text{MnO}_2(\text{s})/\text{kg}$ porous media, in an unbuffered silica sand system using deionized water. Further, they witnessed a sixfold decrease in velocity of the oxidation front over the 2-month experiment. They attributed this decrease in oxidation front velocity to decreased oxidation delivery resulting from reductions in permeability. Further, Heiderscheidt et al. (2008b) found that $\text{MnO}_2(\text{s})$ formation exceeding 100 mg $\text{MnO}_2(\text{s})/\text{kg}$ porous media resulted in hydraulic permeability reductions during a 2-D intermediate-scale tank experiment with PCE sources ranging from 6% residual NAPL saturation to >40% saturation pools.

Clement et al. (1996) proposed Equation 6.17 (with $b = 19/6$) for pore clogging due to microbial growth, like that conceptualized in Figure 6.7b. Conversely, Reis and Acock (1994) concluded that the various forms of the Kozeny-Carman equation are not generally a good model for the reduction in permeability following chemical precipitation in a porous media because they significantly under predict permeability reductions. Further, they pointed out that power law models also suffer from underprediction of permeability reductions, especially at high levels of plugging, as may occur when the pore throat becomes blocked long before the pore space is filled, as in Figure 6.7c, d. The underprediction potential for power law models is demonstrated by using them to analyze the results of a 3-D tank experiment by Lee et al. (2003), where a TCE NAPL source zone of approximately 8% residual NAPL saturation was oxidized by permanganate. If a $\text{MnO}_2(\text{s})$ density of 5,040 g/L (CRC, 2001) is used, along with either Equation 6.16 or Equation 6.17 [with $b = 3.5$ from studies using similar sand (Reis and Acock, 1994)], the calculated permeability reduction is only 1.6%. However, it is important to note that the CRC (2001) density is for a dry, aged mineral pyrolusite form of $\text{MnO}_2(\text{s})$ similar to Figure 6.7c or d, while the generated $\text{MnO}_2(\text{s})$ is a hydrous, possibly gel-like, birnessite-like

form expected to have a much lower density (Nelson et al., 2001; Conrad et al., 2002; Li and Schwartz, 2004; Al et al., 2006) similar to Figure 6.7b. Consequently, if an effective $\text{MnO}_2(\text{s})$ density of 1,000 g/L is used, the calculated permeability reduction increases to 7.5%. However, an even greater reduction is needed to account for the experimental results, such as would occur if manganese oxides block the pore throats before the entire pore space is filled. For example, Heiderscheidt (2005) estimated the effective $\text{MnO}_2(\text{s})$ density to be less than 100 g/L to account for the measured permeability reduction in the intermediate-scale, 2-D tank system being studied.

Reitsma and Randhawa (2002) performed 1-D column experiments oxidizing aqueous PCE (approximately 50 mg/L) with 2,000 mg/L potassium permanganate (KMnO_4) [Darcy velocity of 3.0 m/day (9.8 ft/day)] in silica sand. They determined that with $\text{MnO}_2(\text{s})$ filling as little as 1% of pore space (assuming solid $\text{MnO}_2(\text{s})$ with density of 5,040 g/L), permeability was reduced by 98%. However, more pore space may actually have been filled, because it has already been pointed out that a lower density should probably be used for generated $\text{MnO}_2(\text{s})$. Even if the density of the generated $\text{MnO}_2(\text{s})$ is estimated at 1,000 g/L, the predicted permeability reduction (by Equation 6.16 or 6.17) would only be 15%. Reitsma and Randhawa (2002) concluded that the increased permeability reduction must be due to pore-clogging. They also found higher flow rates resulted in slower permeability reduction, possibly because the higher flow rate dislodges some $\text{MnO}_2(\text{s})$ particles as they begin to get lodged in pore throats.

Schroth et al. (2001) performed 1-D column experiments to study the effects of $\text{MnO}_2(\text{s})$ formation on permeability. Their study differed from that of Reitsma and Randhawa (2002) in that residual NAPL TCE was emplaced in two-thirds of the column length, the KMnO_4 concentration was 790 mg/L (790 ppm), and the Darcy velocity was 15.8 m/day (51.8 ft/day). They estimated a permeability reduction of 96% in 24 h. Based on the mass of TCE destroyed, the mass of $\text{MnO}_2(\text{s})$ generated can be estimated as 66.2 g. Assuming it was evenly distributed throughout the NAPL source zone, with a $\text{MnO}_2(\text{s})$ density of 5,040 g/L, the estimated permeability reduction (by Equation 6.16 or 6.17) would only be 10%. However, if the $\text{MnO}_2(\text{s})$ is considered to be located primarily in the first 25% of the source zone, as visually observed by Schroth et al. (2001), the estimated permeability reduction becomes 33.6%. Further, if the generated $\text{MnO}_2(\text{s})$ effective density is taken as 1,000 g/L and it is considered to be located in the first 25% of the source zone, the estimated permeability reduction (at 95.2%) is quite close to the observed reduction. The column used by Schroth et al. (2001) had twice the cross-sectional area and 33 times the length of that used by Reitsma and Randhawa (2002), suggesting that even if throat clogging is occurring at the pore scale, the permeability relations of Equations 6.16 and 6.17 can still be effective at larger scales, as long as an appropriate effective density is used for the generated $\text{MnO}_2(\text{s})$.

While the previous discussion focused on estimating permeability reductions resulting from manganese oxide generation during oxidation using permanganate, it should be equally suitable for permeability reductions caused by solids production using either hydrogen peroxide or persulfate as the oxidant, catalyzed by dissolved iron [Jazdanian et al., 2004; ITRC (Interstate Technology and Regulatory Council), 2005]. In neutral and alkaline pH environments, ferric iron [Fe(III)] tends to precipitate as solid ferric hydroxide [$\text{Fe}(\text{OH})_3$]. However, such impacts can generally be avoided when Fe(III) is the catalyst, as discussed in the hydrogen peroxide and persulfate chapters (Chapters 2 and 4, respectively), by either acidifying the subsurface treatment zone or using a chelating agent to keep iron in solution.

6.5.2 Gas Formation

Just because some oxidants do not generate solids as a byproduct of oxidation, does not mean they are immune from causing reductions in permeability. The production of gases may

also be an issue. One potential source of gas formation is the formation of carbon dioxide when mineralizing organic matter.

A much greater source of gas generation is the formation of oxygen, which has a lower solubility in water than carbon dioxide. Oxygen is generated from the reduction of hydrogen peroxide. Under various site conditions, hydrogen peroxide tends to degrade quickly in the subsurface, so there is a significant potential to impact permeability.

Gas formation has the potential to partially or completely desaturate some pore space. As a result of this desaturation, the available pore space for liquid transport is decreased, resulting in a reduction in permeability. Using Equations 6.16 through 6.18 in response to gas formation requires two major assumptions: the gas formed does not dissolve into the aqueous phase and the gas is immobile, staying where it is formed. These may be reasonable assumptions for particular systems but may be unreasonable for others. For example, if the volume of gas formed is large, resulting air bubbles may become large enough that buoyant forces exceed capillary forces and the air bubble will begin migrating upward, becoming a multi-phase transport problem requiring a multi-phase, multi-component, reactive transport model. In this case, these equations would not be suitable and it may not be possible to reasonably simulate the permeability reductions.

6.6 OXIDANT/CONTAMINANT KINETIC REACTION EXPRESSIONS

The rate of contaminant oxidation varies by oxidant, as does the complexity of the oxidation reaction mechanisms and pathways. The contaminant oxidation rate can vary from being dependent upon just the aqueous contaminant concentration and the oxidant concentration to also depending upon the temperature, activation method, and concentrations of natural organic matter, reduced minerals, and free radical scavengers. The following is a brief synopsis of the important factors determining the oxidation reaction rate for each of the oxidants. Please refer to the oxidant specific Chapters (2–5) for additional details.

Mathematical representation of contaminant oxidation varies by oxidant, but generally involves tracking concentrations of the contaminant, and each species involved in the oxidation. For permanganate, this means the contaminant and permanganate. However, for other oxidants, it can mean tracking the contaminant and each of the important free radicals or reactive species generated from the primary oxidant, along with the appropriate activators or catalysts. Tracking all of these components is a difficult undertaking.

In general the oxidation kinetics for a given contaminant of concern (COC) is a second-order reaction implying that the contaminant concentration (resulting from the oxidation reaction) can be calculated using Equation 6.19, where C_i is the concentration of component i (M L^{-3}), dC_i/dt is the rate of change in concentration of component i with time, and k_2 is the second-order reaction coefficient for degradation of the contaminant by the particular oxidative species ($\text{L}^3 \text{M}^{-1} \text{T}^{-1}$).

$$\frac{dC_{cont}}{dt} = -k_2 C_{cont} C_{oxidant} \quad (\text{Eq. 6.19})$$

Alternately, a first-order reaction expression can be used if either the oxidant or contaminant concentration is in excess, so that the concentration of the excess component will remain essentially constant. In this case, if the oxidant is in excess Equation 6.19 becomes:

$$\frac{dC_{cont}}{dt} = -k C_{cont} \quad (\text{Eq. 6.20})$$

where k is a pseudo first-order reaction coefficient that is equal to the second-order reaction coefficient times the molar concentration of oxidant since that is in excess. Similarly, if the contaminant is in excess and the oxidant is being tracked, Equation 6.19 becomes:

$$\frac{dC_{oxidant}}{dt} = -kC_{oxidant} \quad (\text{Eq. 6.21})$$

with k now being equal to the second-order reaction coefficient times the molar concentration of contaminant since that is in excess. These first-order forms are especially important when using an analytical solution because such solutions are often limited to first-order reaction formulations.

Oxidant and aqueous byproduct concentrations (such as Cl^- for oxidation of chlorinated solvents) are estimated based on the reaction stoichiometry. In generic terms, the reaction for each oxidant species and aqueous byproduct species can be represented by Equations 6.22 and 6.23, respectively:

$$\frac{dC_{oxidant}}{dt} = Y_{oxidant/cont} \frac{dC_{cont}}{dt} - k_j C_{oxidant} - k_{2k} C_k C_{oxidant} + k_y C_y \quad (\text{Eq. 6.22})$$

$$\frac{dC_{by-product}}{dt} = -Y_{by-product/cont} (k_2 C_{cont} C_{oxidant}) \quad (\text{Eq. 6.23})$$

where $C_{oxidant}$ is the particular oxidant component (e.g., free radical or reactive species), $Y_{i/j}$ is the stoichiometric molar mass ratio of component i to component j from the applicable reaction stoichiometry, k_j is the first-order oxidant depletion rate for the j^{th} oxidant depletion reaction (e.g., autodecomposition), k_{2k} is the second-order oxidant depletion rate for the reaction of oxidant with the k^{th} aqueous component (e.g., a component causing a scavenging reaction), C_k is the aqueous concentration of the k^{th} component that is depleting oxidant, k_y is the first-order oxidant generation rate for the y^{th} oxidant generation reaction (e.g., a first-order catalytic generation of free radical species y), and C_y is the aqueous concentration of the species being decomposed to generate the particular oxidant component.

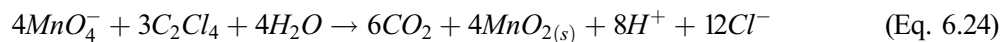
If a second-order reaction is generating the particular oxidant component, another C_k term can be included in Equation 6.22, with a positive sign instead of the negative shown. In this case, the k_{2k} term is the second-order oxidant generation rate and C_k is the aqueous concentration of the k^{th} component that is being decomposed to generate the oxidant.

6.6.1 Permanganate Reaction

As discussed in greater detail in Chapter 3, the oxidation rate for amenable contaminants using permanganate is dependent upon the aqueous contaminant concentration and the oxidant concentration, with the reaction generally being first-order with respect to each concentration and second-order overall. Ladbury and Cullis (1958) reviewed and summarized the various reaction pathways and kinetics for permanganate oxidation of aromatic hydrocarbons, phenols, aromatic alcohols, sugars, aliphatic acids, aldehydes, and ketones, as well as a number of inorganic compounds. More recent research has elucidated the reaction pathways and kinetics of permanganate oxidation of alkenyl halides, specifically chlorinated ethenes, such as PCE and TCE (Schnarr et al., 1998; Huang et al., 1999; Yan and Schwartz, 1999, 2000; Huang et al., 2001, 2002). Further, Huang et al. (2002) found that the rate of PCE oxidation did not significantly change over a pH range of 3–10. These results support and expand on previous research by Yan and Schwartz (1999) showing the oxidation rate for TCE by permanganate was independent of pH in the range of 4–8. Damm et al. (2002) found similar results for the permanganate

oxidation of methyl tert-butyl ether (MTBE) between pH 5.3–9.9. Huang et al. (2002) also found that the reaction rate was independent of ionic strength over the range of 0–0.2 M that is commonly encountered in natural groundwater; however, they did find the reaction rate increased with increasing temperature.

For example, the reaction stoichiometry for oxidation of PCE by permanganate is shown in the reaction in Equation 6.24 and the reaction equations for permanganate and chloride are shown in Equations 6.25 and 6.26.



$$\frac{dC_{MnO_4^-}}{dt} = Y_{MnO_4^-/cont} \frac{dC_{cont}}{dt} \quad (\text{Eq. 6.25})$$

$$\frac{dC_{Cl^-}}{dt} = -Y_{Cl^-/cont} \left(k_2 C_{cont} C_{MnO_4^-} \right) \quad (\text{Eq. 6.26})$$

where $Y_{i/j}$ is the stoichiometric molar mass ratio of component i to component j from Equation 6.24 and the component molecular weights.

6.6.2 Ozone Reaction

Ozone reaction chemistry is much more complex (refer to Chapter 5 for more detail). Ozone can directly oxidize contaminants, in a manner similar to permanganate. However, it can also decompose to form free radicals (hydroxyl, superoxide anion, perhydroxyl), as well as an assortment of other reactive oxygen species that then oxidize contaminants – each having different kinetic reaction rates (Staehelin and Hoigné, 1982; Staehelin et al., 1984; Tomiyasu et al., 1985). Another potential complication is that, unlike the other oxidants, direct (and possibly free radical) oxidation using ozone has been shown to occur in both the gas phase and the aqueous phase (Choi et al., 2002; Reisen and Arey, 2002). Further, the rate of ozone decomposition in the aqueous phase is strongly dependent upon pH, with little decomposition (and free radical formation) at acidic pH and rapid decomposition at alkaline pH.

6.6.3 Hydrogen Peroxide Reaction

Hydrogen peroxide reaction chemistry is slightly less complex than ozone, but still quite complicated, especially when compared to permanganate (refer to Chapter 2 for additional details). Hydrogen peroxide is typically used for ISCO in conjunction with a catalyst, and sometimes a stabilizer, to promote or control its reactivity (e.g., dissolved iron, iron and manganese minerals, organic ligand or chelating agents). When catalyzed, hydrogen peroxide generates free radicals (i.e., hydroxyl, super oxide anion, perhydroxyl) that have rapid reaction rates with many organic contaminants. However, the generation of these radicals involves a large number of chain reactions, creating many intermediate species – some of which are too short lived for measurement. Further, the species and amount of free radicals formed depend upon what catalyst is used, along with the pH.

6.6.4 Persulfate Reaction

Persulfate reaction chemistry is also quite complex as described in Chapter 4. Persulfate oxidation can occur through direct reaction, sulfate radical formation and reaction, hydroxyl radical formation and reaction, and potentially other (superoxide, perhydroxyl, and additional sulfur-based) radical formation and reactions (Peyton, 1993; Buxton et al., 1996; De Laat and Gallard, 1999; Tsitonaki et al., 2006; Liang et al., 2007). Further, the amount and rate of radical

formation is dependent upon using some form of activation. Different activation methods result in different degradation mechanisms, so selection of the activation method may depend upon the contaminant and environment to be treated (Block et al., 2004; Crimi and Taylor, 2007).

6.7 OXIDANT CONSUMPTION BY NONPRODUCTIVE REACTIONS

In addition to destroying target COCs, each oxidant is susceptible to being consumed in nonproductive reactions including NOD, catalysis, and autodecomposition. NOD involves reactions with non-target subsurface materials, including natural organic matter (NOM) as well as inorganic minerals and dissolved solutes. Catalysis refers to the decomposition of oxidant in the presence of a catalyst. Autodecomposition is the spontaneous decomposition of oxidant. These nonproductive reactions compete with the target reaction, reducing the amount of oxidant available to destroy target contaminants. The sources of oxidant consumption by nonproductive reactions and their reaction rates vary by oxidant. Refer to the oxidant-specific chapters (Chapters 2–5) for in-depth information. The following is a brief discussion of the oxidant consumption by nonproductive reactions.

Regardless of the oxidant being used, when NOD is an important factor, it is typically modeled as an immobile phase, which is reasonable because batch studies so far have suggested the porous media NOD is typically far greater than any NOD exerted by dissolved constituents in the groundwater. NOD can be simulated in the model as one or more components using the following first-order equation:

$$\frac{dX_{NOD_i}}{dt} = -k_{NOD_i}X_{NOD_i} \quad (\text{Eq. 6.27})$$

where dX_{NOD_i}/dt is the rate of change in mass of NOD component i with time, X_{NOD_i} is the mass fraction of NOD component i ($M M^{-1}$) and k_{NOD_i} is the first-order oxidation rate for NOD component i (T^{-1}). When Equation 6.27 is used to simulate NOD, a first-order term (circled in Equation 6.28) needs to be inserted into Equation 6.22 to account for oxidant depletion due to the NOD:

$$\frac{dC_{oxidant}}{dt} = Y_{oxidant/cont} \frac{dC_{cont}}{dt} - \left((k_i X_i) \frac{\rho_B}{\phi} \right) k_j C_{oxidant} - k_{2k} C_k C_{oxidant} + k_y C_y \quad (\text{Eq. 6.28})$$

where k_i is the first-order oxidant depletion rate for the reaction of oxidant with the i^{th} NOD component depleting oxidant, X_i is the mass fraction of the i^{th} NOD component depleting oxidant, ρ_B is the porous media bulk density, and ϕ is the porous media porosity. Chapter 3 provides a discussion of several alternative formulations for NOD kinetics, in terms of ISCO using permanganate. In Chapter 3, the amount of NOD or organic aquifer material, as the case may be, is specified as a concentration whereas it is specified as a mass fraction here. Mass fraction is used here because the preponderance of NOD is present in the porous media which is a solid phase. However, concentration and mass fraction of NOD are actually equivalent and are related by the following equation:

$$C_{NOD} = X_{NOD_i} \left(\frac{\rho_B}{\phi} \right) \quad (\text{Eq. 6.29})$$

Alternately, second-order NOD oxidation can be simulated by modifying Equation 6.27 to become:

$$\frac{dX_{NOD_i}}{dt} = -k_{2_NOD_i} X_{NOD_i} C_{oxidant} \quad (\text{Eq. 6.30})$$

where $k_{2_NOD_i}$ is the second-order oxidation rate for NOD component i ($L^3 M^{-1} T^{-1}$) and $C_{oxidant}$ is the concentration of oxidant ($M L^{-3}$). In this case, a second-order term (circled in Equation 6.31) needs to be inserted into Equation 6.22 to account for oxidant depletion due to the NOD:

$$\frac{dC_{oxidant}}{dt} = Y_{oxidant/cont} \frac{dC_{cont}}{dt} \left((k_{2i} X_i) \frac{\rho_B}{\phi} C_{oxidant} \right) - k_j C_{oxidant} - k_{2k} C_k C_{oxidant} + k_y C_y \quad (\text{Eq. 6.31})$$

where k_{2i} is the appropriate second-order oxidant depletion rate for the reaction of oxidant with the i^{th} NOD component depleting oxidant.

When NOD oxidation is actually second- (or higher) order instead of first-order, it can be treated as first-order with the understanding that simulations will overestimate oxidant depletion from NOD oxidation. Overestimation occurs because in a higher order reaction, the kinetic constant is dependent on the concentration of the oxidant, as well as the amount of NOD, so that as oxidant is consumed, the rate of NOD oxidation will decrease. Consequently, the simulation will be conservative in that overestimating oxidant depletion results in further underestimation of contaminant oxidation.

Generally, the volume of NOD oxidized can be assumed to be negligible compared to the pore space so that removal of NOD does not increase permeability; however, if this is not the case, an appropriate density can be used for the NOD volume, and pseudo-saturation for NOD added to the top of the hydraulic permeability equation (Equation 6.16). Including the NOD pseudo-saturation will incorporate changes in NOD volume into calculation of updated hydraulic permeabilities.

Other forms of nonproductive oxidant demand, such as autodecomposition were included in Equation 6.22. Those non-COC oxidant demand terms are demonstrated again in Equations 6.28 and 6.31. Specifically, the first term to the right of the circled term demonstrates autodecomposition of oxidant. The second term to the right of the circled term demonstrates a possible oxidant scavenging reaction.

6.7.1 Permanganate Nonproductive Oxidant Demand

The greatest source of nonproductive permanganate depletion is from reaction with organic matter, reduced metals, and other reductants typically present in field porous media and aquifer solids. The demand for oxidant these porous media constituents exert is referred to as NOD and is often present through the entire site at mass levels greater than the contaminant mass to be remediated. This NOD competes with target contaminants for available oxidant. Though Zhang and Schwartz (2000) proposed that components comprising NOD have a much faster reaction rate with permanganate (MnO_4^-) than do chlorinated contaminants, there is evidence that not all NOD components are oxidized faster than the contaminant (Siegrist et al., 1999; Yan and Schwartz, 1999; Mumford et al., 2002, 2005; Struse et al., 2002a). Because NOD is generally exerted by a complex mixture of components whose surface area available for oxidant contact varies, it is generally accepted that permanganate NOD oxidation is a

kinetically controlled process (refer to Chapter 3, Section 3.3.1). Therefore, oxidation of NOD and contaminant occur simultaneously, with relative rates of oxidation controlling depletion of each. Further, because NOD results from a mixture of constituents, the kinetic rate for NOD oxidation can vary widely for different porous media. While the kinetic rates for some NOD constituents of a particular porous media are often higher than that of the target contaminant, research suggests NOD frequently consists of at least two components with markedly different oxidation rates (Crimi and Siegrist, 2004; Jackson, 2004; Mumford et al., 2005).

6.7.2 Ozone Nonproductive Oxidant Demand

Research indicates that ozone is susceptible to being consumed by reactions with NOM similar to permanganate reactions associated with NOD (Hsu and Masten, 2001; Choi et al., 2002; Kim and Choi, 2002; Lim et al., 2002; Jung et al., 2004; Zhang et al., 2005) (refer to Chapter 5, Section 5.3.2). Additionally, it appears that there is a slow rate of loss of the ozone that is never satisfied with time, likely due to catalytic ozone decomposition due to factors such as pH or porous media mineral content (Clayton, 1998; Lim et al., 2002; Shin et al., 2004), implying that there is an ultimate maximum distance the oxidant will be transported.

6.7.3 Hydrogen Peroxide Nonproductive Oxidant Demand

Compared to the other oxidants being discussed, hydrogen peroxide is probably the most unstable in the subsurface environment (refer to Chapter 2, Section 2.2.4.2). Unlike ozone and permanganate, NOM is not considered a major oxidant sink for hydrogen peroxide because the reaction rates between hydrogen peroxide and NOM are generally quite slow (Goldstone et al., 2002; Bissey et al., 2006). The greatest source of nonproductive oxidant demand for hydrogen peroxide comes from mineral catalysis resulting from the types of minerals present in the porous media and their respective surface areas (i.e., grain size). Additionally, scavenging reactions can occur between radical intermediates and dissolved aqueous species, which interrupt the further propagation of radicals. For example, carbonate and bicarbonate anions are strong scavengers consuming hydroxyl radicals and forming carbonate and bicarbonate radicals (Buxton et al., 1988) that are much weaker oxidants.

6.7.4 Persulfate Nonproductive Oxidant Demand

Some research suggests that NOM acts as an oxidant sink for persulfate just as it does with ozone or permanganate (Hoag et al., 2000; Haselow et al., 2003; Dahmani et al., 2006; Liang et al., 2008) (refer to Chapter 4, Section 4.2.4.1). Other research indicates that persulfate may also undergo catalytic decomposition similar to ozone (Liang et al., 2003; Crimi and Taylor, 2007; Sra et al., 2007). However, there is much less fundamental research on persulfate compared to the other oxidants, making it unclear if one of these processes is more important than the other, or if both occur depending upon subsurface conditions.

6.8 PUBLISHED ISCO MODELING STUDIES

Most prior modeling studies have focused on ISCO using ozone for vadose zone treatment and permanganate for saturated zone treatment. The lack of work on modeling ISCO using persulfate and hydrogen peroxide may be due to the more complex nature of these oxidation reactions and more recent development of the persulfate technology. Additional information on hydrogeochemical models, in general, can be found in Kitanidis and McCarty (2011).

6.8.1 Ozone Modeling

Several different modeling and experimental studies have been conducted to evaluate the use of gaseous ozone injection for treatment of non-volatile organic contaminants in the vadose zone (Hsu and Masten, 2001; Kim and Choi, 2002; Sung and Huang, 2002; Shin et al., 2004). Table 6.2 presents a series of models proposed by various authors for ozone reactive transport, and the processes they considered.

Table 6.2. Studies Modeling ISCO Using Ozone

Study	Domain	Model type ^a	Processes included	Findings
Clayton (1998)	2-D	Analytical	<ul style="list-style-type: none"> • Radial gas flow from injection point • First-order ozone (O₃) decay 	Simple model may offer conservative prediction of O ₃ radius of influence
	1-D	Numerical	<ul style="list-style-type: none"> • Gas phase advection of O₃ and volatile contaminants • Rate-limited mass transfer between gas and aqueous phases for contaminant and O₃ • Rate-limited desorption of contaminant from soil • Second-order reaction between O₃ and contaminant in both gas and aqueous phases 	Theoretical model of O ₃ transport through a 1-D gas channel with volatile or semi-volatile contaminants. Initially, reaction near the injection point limits distribution, but O ₃ transport increases with time as reactive substrates are depleted. However, decomposition reactions probably impart an upper limit on O ₃ transport. Some volatile contaminant mass escaped treatment as fugitive emissions
Hsu and Masten (2001)	1-D	Numerical	<ul style="list-style-type: none"> • Gas phase advection of O₃ only including compressible gas flow • Contaminant assumed non-mobile • Second-order reaction between O₃, contaminants and soil organic matter • Phases were lumped^b • Contaminant and NOM reactions modeled as occurring sequentially or simultaneously 	Model limited to non-mobile contaminants. No significant difference in O ₃ transport between sequential or simultaneous reaction models, as contaminant demand is minor compared with NOM demand. NOM significantly retards O ₃ transport
Kim and Choi (2002)	1-D	Numerical	<ul style="list-style-type: none"> • Gas phase advection and dispersion for O₃ only • Contaminant assumed non-mobile • Second-order reaction between O₃, contaminant and NOM • First-order O₃ autodecomposition • Mass transfer of O₃ to aqueous phase using three 	The steady-state O ₃ concentration after breakthrough was well predicted by all three approaches, but breakthrough times were often over-predicted. Equilibrium approach was very sensitive to the Henry's Law constant, while the rate-limited approach was very sensitive to the k_{La}

(continued)

Table 6.2. (continued)

Study	Domain	Model type ^a	Processes included	Findings
			approaches: (1) equilibrium model, (2) rate-limited absorption model, (3) lumped ^a phase model	coefficient. The lump model predicted reaching steady state faster than the other two, due to the assumption of total contact with all reactive species
Shin et al. (2004)	1-D and 3-D	Numerical	<ul style="list-style-type: none"> • Gas phase advection and dispersion for O₃ only • Contaminant assumed non-mobile • Second-order reaction between O₃, NOM, inorganic minerals and contaminants • First-order O₃ autodecomposition • Phases were lumped^b 	By estimating parameters from experimental results, the authors made a 3-D simulation, finding that NOM, autodecomposition, and inorganic material significantly retard O ₃ transport. This retardation was highlighted for design considerations for parameters estimated from a soil, a twofold decrease in injection point spacing resulted in a 1,000-fold decrease in treatment time to remove a non-mobile contaminant
Sung and Huang (2002)	1-D	Numerical	<ul style="list-style-type: none"> • Gas phase advection and dispersion for O₃ only • Contaminant assumed non-mobile • Second-order reaction with contaminant in aqueous phase • Rate-limited O₃ mass transfer to the aqueous phase • Enhanced O₃ mass-transfer due to reaction within aqueous boundary layer • Rate limited contaminant desorption to aqueous phase 	Theoretical model of O ₃ transport and non-volatile contaminant degradation in a water wet unsaturated soil. No competing reactions with matrix considered. Found that the Péclet (Pe) and Stanton (St) numbers had significant effects on ozone transport behavior in a 1-D column. Specifically, when St is much less than 1, the systems is mass transfer controlled, and when St is much greater than 1, the system is O ₃ delivery controlled

^aModel type refers to whether the mathematical model was based on an analytical solution or a numerical solution.

^bLumped phases indicate that reaction in gas, liquid or soil phases were not separated, but treated as one with an empirical reaction rate coefficient.

Several of these studies showed that ozone transport was limited by reaction with NOM and soil minerals (Hsu and Masten, 2001; Kim and Choi, 2002; Shin et al., 2004). Thus, injection point spacing is an important design consideration as the media properties determine the effective transport distances that may be achieved. Several have also explored the impact of ozone mass-transfer into the aqueous phase on ozone transport, which has important implications for treatment of saturated zone systems (Clayton, 1998; Kim and Choi, 2002; Sung and Huang, 2002). Currently, these models only consider a single mobile gas phase and immobile (e.g., non-volatile) contaminants.

6.8.2 Permanganate Modeling

A number of different models have been developed and applied to help understand the effects of ISCO treatment with permanganate on permanganate movement, and on aqueous contaminant and NAPL removal (Hood, 2000; Zhang and Schwartz, 2000; Reitsma and Dai, 2001; Forsey, 2004; Heiderscheidt, 2005; Mundle et al., 2007; Henderson et al., 2009). Standard approaches for modeling ISCO treatment of contaminants with permanganate include: (1) advective-dispersive transport of dissolved permanganate and a dissolved contaminant; (2) NAPL dissolution is simulated using a linear driving force model with a mass transfer coefficient estimated from a published correlation (Miller et al., 1990; Imhoff et al., 1994; Powers et al., 1994b; or others as described in Section 6.3.1); (3) contaminant sorption to the solid phase is simulated either assuming linear equilibrium partitioning or a rate-limited mass transfer approach; and (4) contaminant degradation is simulated with a second-order relationship where contamination oxidation rate is linearly proportional to the aqueous permanganate concentration and aqueous contaminant concentration. The major differences in these studies include: (1) the simulation conditions examined (1-D versus 3-D, field versus lab, homogeneous versus heterogeneous); (2) kinetics of permanganate consumption by NOD; (3) effect of clogging by generation of $\text{MnO}_2(\text{s})$; and (4) impacts of injection fluid density on solute transport.

In an early study, Zhang and Schwartz (2000) developed a model to simulate ISCO treatment of chlorinated ethenes using the standard approaches described above. Their model was first validated by comparing simulation results to experimental data from 1-D laboratory columns and a 3-D test cell, both of which contained NAPL. During this early work, NOD kinetics were poorly understood and permanganate consumption by NOD was modeled using a second-order function with a very high reaction rate coefficient. The high rate coefficient resulted in an effectively instantaneous reaction, preventing permanganate migration until the NOD had been depleted. The validated model was then applied to simulate a large-scale field test of permanganate treatment. NOD was used as a fitting parameter for model calibration. Permanganate distribution and resulting remediation system performance were found to be sensitive to NOD.

Hood (2000) simulated ISCO treatment of chlorinated ethenes using a 3-D numerical model with the standard approaches described above. Permanganate consumption by NOD was modeled as a second-order reaction between the oxidant and the background organic carbon. However, in this system, oxidant consumption by NAPL was much greater than oxidant consumption by NOD, so the kinetics of the NOD reaction were less significant. Numerical model simulations for a 2-D spatially heterogeneous aquifer showed that the rate of contaminant removal was sensitive to the DNAPL mass transfer rate, oxidant concentration, and groundwater flow velocity. In contrast, contaminant removal rate was not sensitive to the transverse dispersivity and rate constant for contaminant oxidation by permanganate. These results are consistent with analytical modeling results by Reitsma and Dai (2001), which showed the rate of NAPL removal is mainly dependent on NAPL solubility and oxidant concentration and to a lesser extent on reaction rate, stoichiometry, and transverse dispersion coefficients. Higher NAPL solubility and/or lower oxidant concentration reduces the maximum expected enhancement. Reitsma and Dai (2001) concluded that assuming an instantaneous reaction between the contaminant and permanganate may be appropriate for dispersive mass transport from NAPL zones.

Heiderscheidt (2005) developed the CORT3D (chemical oxidation reactive transport in three dimensions) model code by modifying RT3D (reactive transport in three dimensions) (Clement, 1997; Clement et al., 1998) to simulate ISCO treatment with permanganate using the standard approaches described above. In addition, CORT3D includes permeability increases resulting from NAPL dissolution and permeability losses from $\text{MnO}_2(\text{s})$ deposition. Permanganate consumption

by NOD was simulated assuming NOD is composed of separate fast and slow fractions where the rate of permanganate consumption is first-order with respect to NOD. Comparison of CORT3D simulations with results from a 2-D sand tank experiment showed that oxidant enhancement of NAPL dissolution slowed over time as the small PCE ganglia were depleted and $\text{MnO}_2(\text{s})$ formed causing flow bypassing around larger sources. CORT3D was then used to examine the effect of site conditions and injection system operating parameters on ISCO treatment of a fine sand aquifer with a high organic carbon content (up to 0.5%) and NOD (0.2–7 g KMnO_4/kg) (Heiderscheidt et al., 2008a). Comparison of model simulations and field monitoring data showed that the high NOD of the aquifer had a dramatic impact on the resulting oxidant (permanganate) distribution (Figure 6.8). Model sensitivity analyses indicated that permanganate distribution could potentially be increased for this site by injecting lower concentrations of oxidant at a higher flow rate.

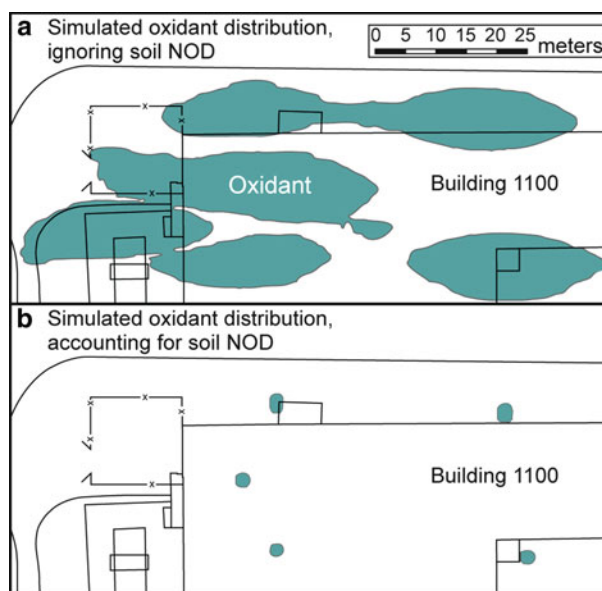


Figure 6.8. Impact of high initial NOD (7 g KMnO_4/kg) on oxidant distribution (*shaded area*) in an aquifer (reprinted from Heiderscheidt et al., 2008a; with permission of the National Ground Water Association and Blackwell Publishing).

Mundle et al. (2007) modified RT3D (Clement, 1997; Clement et al., 1998) to simulate ISCO treatment with permanganate in fractured clay using the standard approaches described above. The model domain was a 2-D vertical slice of one horizontal fracture within a symmetric 3-D fractured clay aquitard. The fracture initially contained a 5-m long TCE NAPL source zone with a saturation of 0.34 and underwent 2 years of natural dissolution and matrix diffusion prior to oxidant flushing. Permanganate consumption by NOD was modeled as a second-order reaction between the oxidant and NOM. Solute transport was influenced by multispecies diffusion and linear equilibrium partitioning of the contaminant (PCE or TCE) to NOM. Model simulations followed the initial dissolution of NAPL in a fracture followed by permanganate flushing through the fracture to remove any residual NAPL and contaminants that had already diffused into the clay matrix. Model simulations showed that (1) ISCO will destroy contaminant mass located in both the fractures and the matrix, (2) dissolved contaminant concentrations will decrease throughout the fracture during active permanganate injection, and (3) concentration

rebound occurs once ISCO is terminated (Figure 6.9). Sensitivity analyses showed that hydrogeologic parameters (initial NAPL saturation, aperture width and spacing, matrix porosity, fractional organic carbon content, NOD kinetics, etc.) and design variables (hydraulic gradient, oxidant dosage, etc.) influenced the amount of contaminant degraded and the extent of rebound. In many cases, maximum rebound concentrations varied from 5 to 10% of the peak concentration prior to permanganate injection and were not correlated with the contaminant mass destroyed.

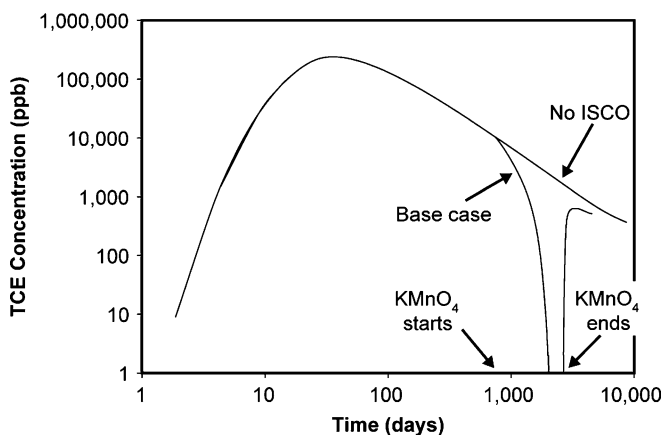


Figure 6.9. Model simulations of contaminant (TCE) concentration versus time 5 m downgradient of a NAPL source zone within a fracture for ISCO treatment with KMnO_4 and without ISCO treatment (reprinted from Mundle et al., 2007; with permission of the National Ground Water Association and Blackwell Publishing).

Henderson et al. (2009) performed a mathematical modeling study to assess the role of density contrasts for the delivery of oxidant. They modified the MIN3P reactive transport code (Mayer et al., 2002) to couple density-dependent flow, transport, and reaction processes, permeability loss associated with $\text{MnO}_2(\text{s})$ formation, and geochemical reactions with the aquifer matrix. A model, built using the modified code was then calibrated to match the spatial and temporal distribution of permanganate, chloride and TCE observed during a detailed field pilot test of DNAPL treatment with permanganate. During the pilot test, a 4,000 L (1,057 gal) slug of 38–48 g/L (38,000–48,000 ppm) KMnO_4 was injected near the center of a 28×32 m (91.9×105.0 ft) sheet pile enclosure. The higher density of the injection solution caused the KMnO_4 solution to sink downward and spread over the surface of a clay aquitard. TCE DNAPL was present in the lower portion of the aquifer near the aquifer-aquitard interface. The calibrated model was able to accurately reproduce the major processes observed in the field, including the density induced sinking of the injection solution, and the decline in pH in some locations associated with hydrogen chloride (HCl) release from TCE oxidation. Figure 6.10 shows the simulated velocity vector field at 15 days after KMnO_4 injection. Simulation results indicate that, following injection, the gradients in fluid density provided the main driving mechanism for the movement of groundwater at later time. Further, solution density and resulting flow patterns were not significantly influenced by reactions with the aquifer matrix. $\text{MnO}_2(\text{s})$ formation appeared to have modest impact on permeability, presumably due to the relatively small amount of KMnO_4 injected (152–192 kg) [335.1–423.3 pound-mass (lbm)]. Though simulation results indicate density induced flow was very effective in enhancing permanganate-contaminant contact during the field test, it may have been due to the specific

conditions of the test where most of the DNAPL was perched near the top of a lower permeability clay layer and the background hydraulic gradient was zero because the pilot test was conducted within a sheetpile enclosure. Density effects are most important when flow associated with density differences is greater than flow associated with the background hydraulic gradient (Ibaraki and Schwartz, 2001).

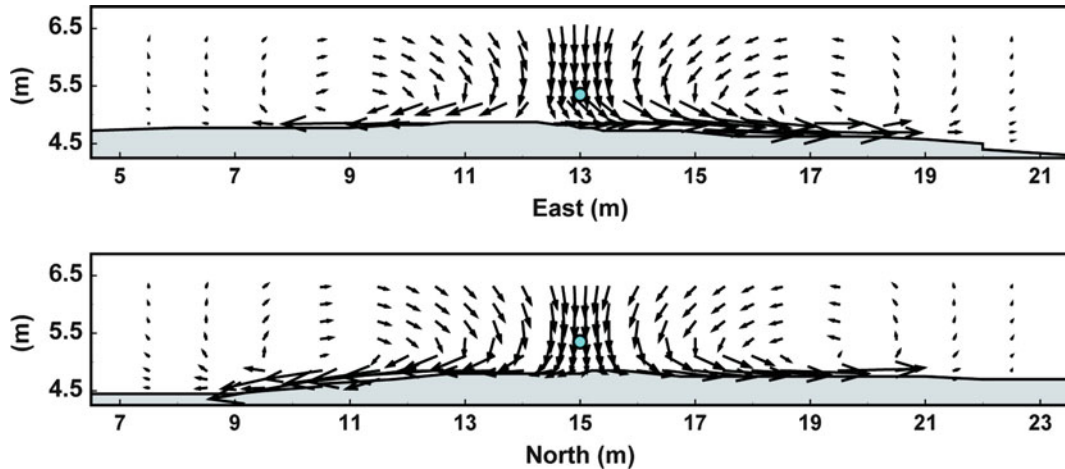


Figure 6.10. Model simulations of the velocity field resulting from injection of a higher density KMnO_4 (38–48 g/L) (38,000–48,000 ppm) solution near the center of a sheetpile test cell (reprinted from Henderson et al., 2009; with permission of Elsevier). Injection point represented by blue circle in center. Shaded layer at bottom is clay aquitard.

6.9 AVAILABILITY OF ISCO MODELING TOOLS

Undertaking a modeling effort can be beneficial for feasibility studies, remedial design, system optimization, and even testing or validating new model codes. Modeling can help with feasibility studies by simulating various remediation options under the range of expected site and source conditions. Although model input values frequently have to be extrapolated from limited observed data, because there is no way to know exactly what the subsurface conditions are, multiple simulations allow for the examination of potential conditions to determine if particular remedial options are feasible.

Once a feasible remediation option has been selected, modeling can be used to vary the system configuration (well locations, flow rates, concentrations, etc.) and determine which configuration is expected to be most effective based on site-specific goals (least expensive to install, least expensive to operate, shortest time to site closure, etc.). Although it is not recommended to use simulation results as a prediction of actual performance, it is quite valid to compare simulation results for relative performance.

If an existing remediation system is not working as originally expected, modeling can be very useful in performing system optimization. Just as with remedial design, simulations can compare modifications to the existing system and determine what changes may be more effective. Such simulations are especially beneficial if no transport modeling was performed during the initial design. Further, modeling can help identify detrimental site or source conditions that were not considered during the initial design.

Despite the utility of modeling, it is apparent from the fairly comprehensive summary of ISCO modeling efforts described in Section 6.8 that few ISCO modeling tools presently exist

and even fewer are readily available. Those that are will be discussed in this section. Because there are so few readily available modeling tools, this section begins with a review of appropriate model dimensionality and applicable analytical solutions. In the absence of a readily available, robust numerical modeling tool, an appropriate analytical solution may be implemented to provide a rough order of magnitude estimate. Analytical solutions are exact mathematical solutions to the flow and solute transport equations. Such solutions must be derived for specific conditions to be studied. They can generally be executed quickly, but are limited to simple flow systems with relatively uniform hydrologic properties. Conversely, numerical solutions are actually approximations, determined using numerical analysis methods (within specified error bounds) of the solution to the solute transport equations. Numerical solutions provide great flexibility in simulating varied and/or dynamically changing conditions, where a closed-form analytical solution cannot be derived, but typically take much longer to execute and usually require a great deal more input data compared to an analytical solution.

6.9.1 Model Dimensions (1-D/2-D/3-D)

One can choose to model the subsurface as a 1-D, 2-D, or 3-D system. Depending on the system to be modeled and the modeling objectives, a 2-D or 1-D model may be suitable and will be easier and quicker to implement. A 1-D model is appropriate if the concentration is uniform over the entire inflow boundary, such as in a porous media column or through the center of a plume or source zone. A 2-D model can be used for a thin (vertically) aquifer that is uniformly mixed throughout the thickness of the aquifer so that vertical concentration gradients are negligible. A 2-D model can also be used to simulate a vertical section along the centerline of a contaminant plume in a thick aquifer if the source is wide enough that transverse horizontal concentration gradients are negligible and will not cause solute movement perpendicular to the centerline.

6.9.2 Analytical Solutions

Analytical solutions provide an exact solution to the underlying mathematical problem and can be solved quickly. A significant drawback of analytical solutions is that they can only be used to model relatively simple flow systems with relatively uniform hydraulic properties. Additionally, each analytical solution is for specific solute/source conditions and boundary conditions. Analytical solutions have already been derived for many simple flow and transport scenarios potentially applicable to ISCO (Gershon and Nir, 1969; Bear, 1972, 1979; Cleary and Unga, 1978; Yeh, 1981; van Genuchten and Alves, 1982; Domenico, 1987; Wexler, 1992; Tartakovsky and Di Federico, 1997; Sun et al., 1999; Leij et al., 2000; Tartakovsky, 2000; Clement, 2001). However, knowledge of higher math is necessary in order to derive a solution for conditions not already tackled. The same holds true if existing solutions are for a 1-D problem and it is desired to develop a 2-D or 3-D solution. Further, it may not be possible to derive an analytical solution for some conditions such as second-order reactions or changing hydraulic conductivity.

Many existing analytical solutions, such as those presented by Wexler (1992) are derived for idealized systems. Groundwater velocity is usually assumed to be uniform, aligned with the principal axis, and of constant magnitude. The porosity and coefficients of hydrodynamic dispersion are also usually assumed to be constant. Consequently, analytical solutions are unable to simulate hydraulic affects such as flow bypassing. Analytical solutions are also limited to simulating equilibrium sorption kinetics in the form of a retardation factor. If simulation of non-equilibrium sorption is necessary, such as if the sorption process occurs slowly relative to

groundwater velocities under pumping conditions, then a numerical solution is necessary. Another limitation of analytical solutions is that they can only be derived for first-order kinetic reactions even though contaminant oxidation reactions are typically second-order. However, as discussed previously, contaminant oxidation can be simulated as a first-order reaction if either the contaminant or oxidant concentration remains approximately constant throughout the simulation. Finally, analytical solutions are mostly limited to single component transport. However, recent efforts have shown how to extend single species analytical solutions to multiple species as long as the reactions are sequential and not simultaneous (Sun et al., 1999; Clement, 2001; Quezada et al., 2004; Srinivasan and Clement, 2008). If simultaneous reactions are to be simulated, as is often the case with real-world oxidation scenarios, then a numerical solution is required.

Through the principle of superposition, analytical solutions can be applied to slightly more realistic scenarios. For example, it can be used to simulate systems where inflow boundary concentrations vary over time, in stepwise fashion. Superposition can also be used to simulate inflow boundary concentrations that vary spatially (again in stepwise fashion) for 2-D and 3-D systems (Domenico, 1987; Aziz et al., 2000; Clement et al., 2002; Srinivasan et al., 2007). Wexler (1992) provides good examples of applying the principle of superposition. Potentially useful solutions from Wexler (1992), that might be applied for simulating ISCO, are listed in Table 6.3, along with their applicable conditions/processes.

Table 6.3. Potentially Useful Analytical Solutions for ISCO (Wexler, 1992)

Dimensions	Conditions/processes
1-D	Finite system, specified concentration at the inlet boundary, constant water velocity, constant longitudinal dispersion coefficient, first-order decay, and linear equilibrium sorption (by dividing dispersion coefficients and velocity by retardation factor)
	Finite system, specified flux across the inlet boundary, constant water velocity, constant longitudinal dispersion coefficient, first-order decay, and linear equilibrium sorption (by dividing dispersion coefficients and velocity by retardation factor)
	Semi-infinite system, specified concentration at the inlet boundary, constant water velocity, constant longitudinal dispersion coefficient, first-order decay, and linear equilibrium sorption (by dividing dispersion coefficients and velocity by retardation factor)
	Semi-infinite system, specified flux across the inlet boundary, constant water velocity, constant longitudinal dispersion coefficient, first-order decay, and linear equilibrium sorption (by dividing dispersion coefficients and velocity by retardation factor)
2-D	Aquifer of infinite areal extent, continuous point source where fluid is injected at constant rate and concentration (injection rate is low and does not disturb the flow field), constant water velocity, constant longitudinal and transverse dispersion coefficients, first-order decay, and linear equilibrium sorption (by dividing dispersion coefficients and velocity by retardation factor)
	Semi-infinite aquifer of finite width, finite-width strip source, constant water velocity, constant longitudinal and transverse dispersion coefficients, first-order decay, and linear equilibrium sorption (by dividing dispersion coefficients and velocity by retardation factor)
	Semi-infinite aquifer of infinite width, finite-width strip source, constant water velocity, constant longitudinal and transverse dispersion coefficients, first-order decay, and linear equilibrium sorption (by dividing dispersion coefficients and velocity by retardation factor)
	Semi-infinite aquifer of infinite width, Gaussian source, constant water velocity, constant longitudinal and transverse dispersion coefficients, first-order decay, and linear equilibrium sorption (by dividing dispersion coefficients and velocity by retardation factor)

(continued)

Table 6.3. (continued)

Dimensions	Conditions/processes
	Aquifer of infinite extent, continuous point source where fluid is injected at constant rate and concentration (injection rate is low and does not disturb the flow field), constant water velocity, constant longitudinal and transverse (lateral and vertical) dispersion coefficients, first-order decay, and linear equilibrium sorption (by dividing dispersion coefficients and velocity by retardation factor)
3-D	Aquifer of semi-infinite length but finite width and finite height, finite width and finite height “patch” source at inlet boundary, constant water velocity, constant longitudinal and transverse (lateral and vertical) dispersion coefficients, first-order decay, and linear equilibrium sorption (by dividing dispersion coefficients and velocity by retardation factor)
	Aquifer of semi-infinite length but infinite width and infinite height, finite width and finite height “patch” source at inlet boundary, constant water velocity, constant longitudinal and transverse (lateral and vertical) dispersion coefficients, first-order decay, and linear equilibrium sorption (by dividing dispersion coefficients and velocity by retardation factor)

Despite their limitations, analytical models are important tools. First and foremost, as exact solutions, they are the standard to test numerical solutions. They can also be used to quickly simulate a simplified scenario to estimate rates of solute spread to guide data collection and water-quality-monitoring efforts (Wexler, 1992). Conversely, numerical models (though actually approximations) such as those to be discussed next, are the only alternative for simulating second-order reactions, non-equilibrium sorption, and/or simultaneous multiple component reactions. They are also the only way to simulate non-uniform and/or changing hydrodynamic conditions. Incorporation of all these processes allows a numerical model to simulate very realistic conditions. However, it is critical to remember that many of the numerical model input values have to be extrapolated from extremely limited observed data. Although numerical models can provide a much better range of possible system responses than an analytical solution, they should not normally be used to make predictions of system performance.

6.9.3 Conceptual Design for ISCO

The Conceptual Design for ISCO (CDISCO) tool was developed with support from the Environmental Security Technology Certification Program (ESTCP) under Projects ER-0626 (Borden et al., 2009) and ER-0623 (Siegrist et al., 2010) and is intended to assist with the conceptual design of injection systems for ISCO using permanganate. The tool is intended to simulate the transport and degradation of permanganate during the injection period and for a short time after injection. It does not model downgradient advective drift of oxidant after the injection period. Additionally, it does not model the contaminant concentrations because of the complexities of the various phases of the contaminants that may be present.

The model consists of two major components.

- A numerical model for simulating the 1-D radial transport and consumption of permanganate following injection into a single well. This model allows users to easily evaluate the effect of aquifer parameters (effective thickness, permeability, total NOD, NOD kinetics) and injection conditions (permanganate concentration, injection flow rate and duration) on the effective radius of influence (ROI) of an individual injection well and required well spacing based on a user defined overlap factor.

- A procedure which allows designers to quickly calculate a preliminary cost estimate to evaluate the effect of injection conditions (permanganate concentration, injection flow rate and duration) on total project costs. Input parameters include reinjection frequency, total fixed costs and unit costs for injection point installation, chemical reagents, and labor for injection.

The tool allows the user to enter site-specific data or assumed values of key site and design parameters. Design parameters, such as injection method (well versus direct push point), duration of oxidant injection, mass of oxidant injected, and volume of oxidant solution injected can be varied; the tool will estimate well/point spacing and generate a preliminary cost estimate. These simulations allow a preliminary design optimization to be performed by quickly executing various model runs with varied inputs and comparing the resulting cost. Graphical representations of the effect of the design parameters on project costs are generated.

The tool was designed primarily for permanganate; however, with modification to the kinetic input parameters, it is possible that CDISCO can approximate pseudo first-order kinetics applied to oxidant persistence, as often observed with hydrogen peroxide and sodium persulfate under some conditions. Thus, CDISCO may have some applicability to the conceptual design of these oxidants, including consideration of their decomposition kinetics. One major limitation on the use of CDISCO for simulating persulfate and catalyzed hydrogen peroxide (CHP) distribution is that it does not consider the transport of an activator (iron, base, another oxidant, heat, etc.). Because the subsurface transport of the activator may be very different than the primary oxidant, the pseudo first-order rate may vary spatially and with time. Under these conditions, it would not be appropriate to use CDISCO to model persulfate and CHP distribution. Any user attempting to use the CDISCO tool for oxidants other than permanganate should be aware that there is considerable uncertainty in how accurately the tool output will match real field processes, and caution is advised. Users should have a good understanding of ISCO before using this tool.

6.9.3.1 CDISCO Permanganate Transport Model

Advective-dispersive transport of permanganate away from a central injection well is represented as flow through a series of continuously stirred tank reactors (CSTR). Numerical dispersion associated with evaluation of the time derivative is negligible (van Genuchten and Wierenga, 1974), so longitudinal dispersion is simulated by setting the length of each reactor to two times the longitudinal dispersivity. Permanganate consumption by the target contaminant is simulated as an instantaneous reaction. NOD is assumed to be composed of two fractions: NOD_I, which reacts instantaneously with permanganate and NOD_S, which reacts more slowly. The rate of permanganate (M) loss with time (dM/dt) is proportional to the oxidant concentration times the NOD_S concentration:

$$\frac{dM}{dt} = -k_s NOD_S M \rho_B / \phi \quad (\text{Eq. 6.32})$$

where NOD_S is the concentration of slow NOD ($M L^{-3}$), M is the concentration of oxidant ($M L^{-3}$), k_s is the second-order slow NOD consumption rate ($L^3 M^{-1} T^{-1}$), ρ_B is the soil bulk density ($M L^{-3}$), and ϕ is the soil porosity. Separation of the NOD into instantaneous (or very fast) and slow fractions is consistent with experimental results from Mumford et al. (2005), Xu (2006), Urynowicz et al. (2008), and others.

The CSTR model is implemented within a Microsoft Excel* spreadsheet. The user first enters information on aquifer characteristics (porosity, hydraulic conductivity, injection interval, NOD, contaminant concentrations, etc.), injection conditions (permanganate injection

concentration, flow rate, and duration), and target conditions (minimum oxidant concentration and duration to calculate ROI). Based on this information, the spreadsheet establishes a series of reactors. The volume of each reactor increases outward as injected water migrates radially outward from the injection well, simulating the reduced velocity as flow radiates out from the injection well. The actual computations to determine spatial and temporal variations in permanganate concentration are performed in a Visual Basic Macro embedded in the CDISCO spreadsheet (Borden et al., 2009). The time step for each computation is automatically determined within Excel to minimize computational error.

Figure 6.11 shows typical output from the permanganate transport model simulations. The graph shows the variation in permanganate concentration versus distance at several different times (15, 30, 45, and 60 days for this simulation). The table at the bottom shows input parameters and computed ROI for a series of prior simulations. The effective ROI is computed based on a user specified contact time and minimum oxidant concentration.

6.9.3.2 CDISCO Cost Estimating Procedure

The cost estimating procedure generates a preliminary cost estimate based on the user specified treatment area dimensions, injection ROI overlap (%), number of injection events planned, fixed cost, and unit costs for injection point installation, chemical reagents, and labor for injection. Two injection approaches are possible: injection through direct push rods or injection through wells. Cost factors are included for mobilization, labor, materials, equipment rental, travel, and subcontractor costs.

Figure 6.12 shows typical output from the cost estimating procedure comparing preliminary estimates for several different design alternatives. Aquifer parameters, treatment area dimensions (100 ft × 100 ft), ROI overlap (25%), time to calculate ROI (30 days), minimum oxidant concentration (50 mg/L), and number of injection events (5) are constant for all alternatives. Alternative 1 has a relatively high cost because the short injection duration (3 days) required a large number of injection points. Alternative 5 has a lower cost because the longer injection duration (10 days) and higher oxidant concentration (20,000 mg/L KMnO_4) (20,000 ppm KMnO_4) reduced number of injection points required.

6.9.3.3 Application of CDISCO to Persulfate and CHP

Though CDISCO was specifically developed to assist in the design of permanganate injection systems, it may be possible to simulate some elements of CHP and persulfate distribution with appropriate modifications to the CDISCO input parameters. The decomposition of hydrogen peroxide in well-mixed batch systems is often observed to follow pseudo first-order kinetics. CDISCO can be forced to simulate pseudo first-order decay of the oxidant by setting the contaminant concentration and instantaneous NOD equal to zero and setting the slow NOD (NOD_s) much greater than the maximum oxidant concentration. Under these conditions, the effective first-order decay rate will be equal to the second-order slow NOD decay rate times NOD_s . Where persulfate loss is first-order, this same approach could potentially be applied.

However, in practice, the use of these oxidants usually involves the injection of an activator (iron, base, another oxidant, heat, etc.), often in sequential order; this impacts kinetics and delivery in ways CDISCO does not consider. For instance, CDISCO cannot account for separate tracking of an oxidant and an activator. In general, the only situation where CDISCO may approximate the kinetics of oxidant persistence is where the activator and oxidant are mixed simultaneously at the injection point, and then the assumption must be made that the first-order rate stays constant from that time onward. It is also important

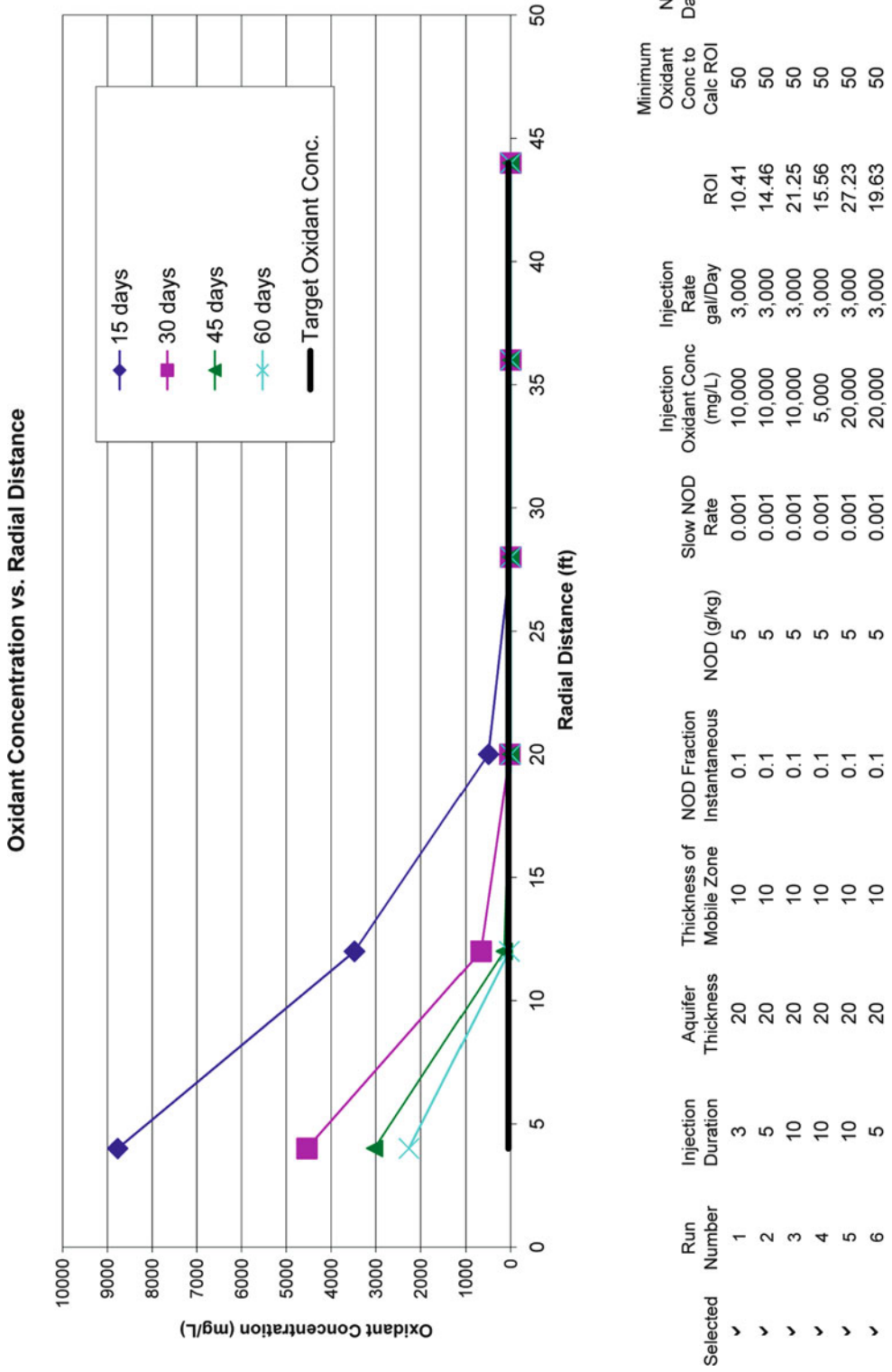


Figure 6.11. Typical output from CDISCO during a permanganate transport model simulation.

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

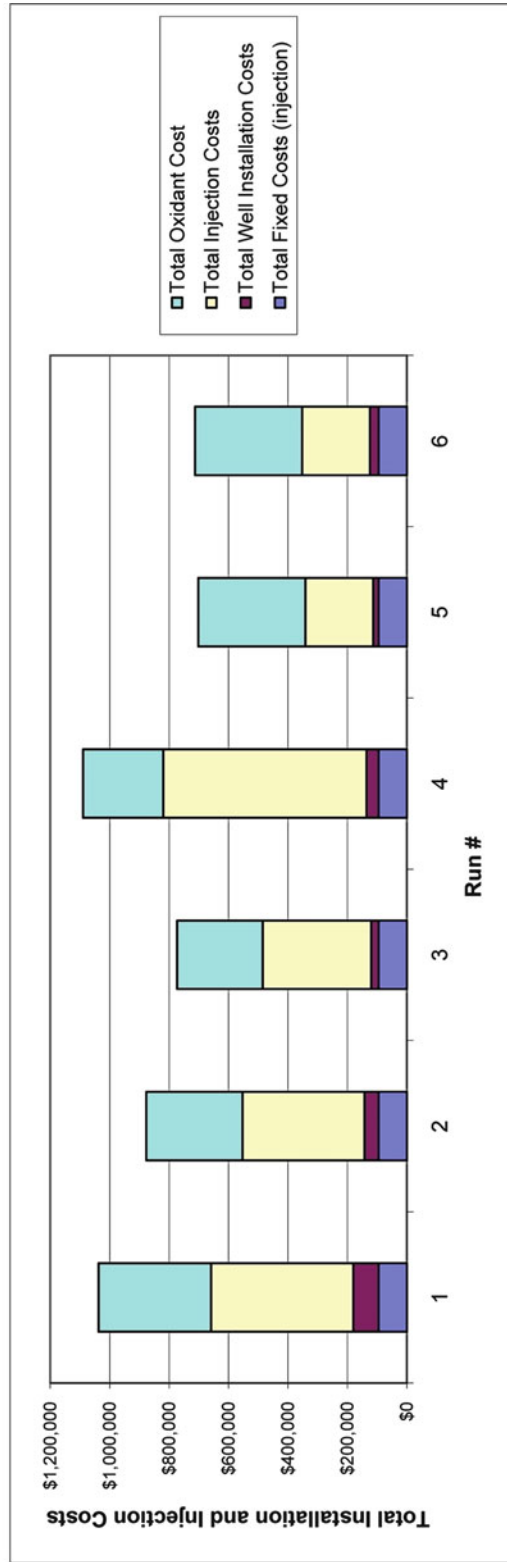


Figure 6.12. Typical output from CDISCO used for an injection scenario cost comparison.

to note that the reactive transport of these oxidants is also not as well documented as with permanganate, and thus there may be phenomena that affect their transport that CDISCO cannot simulate. For example, with hydrogen peroxide, an observed ROI is often larger than what would be expected based on fluid addition alone, in part because evolution of oxygen gas in the pore space increases the fluid displacement. Since the reactive transport of persulfate and CHP is not well documented, there is a lack of datasets suitable for verifying CDISCO with hydrogen peroxide or persulfate. Consequently, it is challenging to determine the accuracy of CDISCO in these applications. Thus, in most cases, it will not be practical to use CDISCO for predicting persulfate or hydrogen peroxide transport and persistence. Any user attempting to use the CDISCO tool for oxidants aside from permanganate should be forewarned that there is considerable uncertainty in how accurately the tool output will match real field processes, and caution is advised.

6.9.4 Chemical Oxidation Reactive Transport in Three-Dimensions

This tool was developed with support from the Strategic Environmental Research and Development Program (SERDP) under Projects ER-1290 (Siegrist et al., 2006) and ER-1294 (Illangasekare et al., 2006); it provides for simulation of 3-D ISCO reactive transport in groundwater (Heiderscheidt, 2005). CORT3D is based on a modified form of RT3D version 2.5 (Clement, 1997, 2001; Clement et al., 1998, 2000; Clement and Johnson, 2002; Johnson et al., 2006) and MODFLOW, 2000 (McDonald and Harbaugh, 1988; Harbaugh and McDonald, 1996a, b; Harbaugh et al., 2000).

RT3D is a general purpose finite-difference numerical code that can be used to simulate various types of multi-species reactive transport in 3-D groundwater aquifers (Lu et al., 1999; Clement et al., 2000, 2004a; Lee et al., 2006; Lim et al., 2007; Rolle et al., 2008). RT3D is based on MT3D (Zheng, 1990) and was developed at the Pacific Northwest National Laboratory (PNNL) for use in design of accelerated *in situ* bioremediation systems and for evaluation of natural attenuation, but it is not limited to those scenarios. Instead, RT3D provides the flexibility to simulate reaction kinetics for any chemical system of interest (including a mixture of mobile and immobile components) via the user-defined reaction package feature. CORT3D uses this feature to incorporate an oxidation-specific reaction package. Additionally, a number of executables are used by CORT3D to incorporate changing permeability and NAPL dissolution as the simulation progresses.

Because dissolution and oxidation are transient processes where NAPL saturation decreases with time and manganese oxide solids (a byproduct of the chemical oxidation process when using permanganate) increase with time (i.e., effective porosity and permeability change), the groundwater flow pattern needs to be updated over time. The more frequent the update of the flow solution (through changes of effective hydraulic conductivity, porosity, NAPL saturation, and manganese oxide volume), the closer the simulation approaches a transient solution.

CORT3D offers a great deal of flexibility incorporating subsurface processes. It includes NAPL dissolution, equilibrium or rate-limited sorption, second-order kinetic contaminant oxidation, kinetic oxidation of NOD – both a fast kinetic portion and a slow kinetic portion, and different diffusion coefficients for each aqueous species. The code tracks three aqueous mobile components (contaminant, aqueous chloride, and aqueous oxidant) and five immobile components (NAPL, sorbed contaminant, manganese oxide, fast NOD, and slow NOD).

As with CDISCO, the code was developed for ISCO using permanganate. However, with the proper assumptions and rate data, users may be able to use it for investigating suitability and performing conceptual design with other oxidants.

6.9.4.1 CORT3D Model Formulation

Mass transfer or dissolution of the NAPL into the aqueous phase is implemented using a general form of the Gilland-Sherwood correlation of Saba and Illangasekare (2000) to estimate the lumped mass transfer coefficient described in Section 6.3.1. Saenton (2003) used this same correlation for intermediate-scale 2-D PCE natural dissolution and surfactant enhanced dissolution experiments; it was found to be flexible and effective. The generic correlation is:

$$Sh = \alpha_1 Re^{\alpha_2} Sc^{\alpha_3} \left(\frac{\theta_n d_m}{\tau L} \right)^{\alpha_4} \quad (\text{Eq. 6.33})$$

where the empirical coefficients α_1 , α_2 , α_3 , α_4 , τ are unique for a given system and are determined through calibration or inverse modeling. The model code does not directly account for potential ISCO effects on mass transfer when calculating the lumped mass transfer coefficient because doing so requires knowledge of the intrinsic mass transfer coefficient, which cannot be calculated. Instead, if the intrinsic mass transfer is expected to increase (more than can be accounted for by the increased concentration gradient during oxidation) due to fast chemical reaction, the Gilland-Sherwood parameters need to be estimated for dissolution during chemical reaction through inverse modeling. A forward simulation is then run in phases, using the appropriate Gilland-Sherwood parameters for each phase.

Although numerical finite difference model codes tend to introduce artificial numerical dispersion under highly diffusion-dominated conditions, models using these codes are still useful for comparing different scenarios. To that end, CORT3D permits different effective diffusion coefficients to be simulated for each mobile species, and the effective diffusion coefficient for each species varies spatially based on porous media properties. This modification is important for simulating diffusive transport of permanganate into low permeability media, where transport is dominated by diffusion (Siegrist et al., 1999; Struse et al., 2002b). Effective diffusion coefficients, D_e , ($L^2 T^{-1}$) are estimated using the modified Millington-Quirk relationship (Jury et al., 1991) from Section 6.4.3, relating effective diffusion to molecular diffusion coefficient, D_m ($L^2 T^{-1}$), water content, θ_w , and effective soil porosity, ϕ_{eff} .

$$D_e = D_m \frac{\theta_w^{10}}{\phi_{eff}^2} \quad (\text{Eq. 6.34})$$

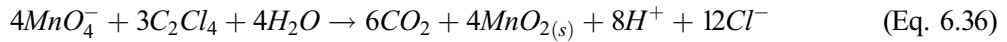
A new chemical oxidation reaction module was developed for use with the modified RT3D code. The new module tracks three mobile species: aqueous phase contaminant (cont), permanganate (MnO_4^-), and chloride (Cl^-). Contaminant concentrations (resulting from the oxidation reaction) are calculated using the second-order reaction (Huang et al., 1999; Siegrist et al., 2001):

$$\frac{dC_{cont}}{dt} = -k_2 C_{cont} C_{MnO_4^-} \quad (\text{Eq. 6.35})$$

where C_i is the concentration of component i ($M L^{-3}$), dC_i/dt is the rate of change in concentration of component i with time, and k_2 is the second-order reaction coefficient for degradation of the contaminant by MnO_4^- ($L^3 M^{-1} T^{-1}$).

MnO_4^- and Cl^- concentrations are calculated based on the reaction stoichiometry, but the MnO_4^- equation also includes NOD terms. The reaction module was written so the stoichiometric ratios are adjustable to accommodate modeling oxidation of different contaminants; for oxidation of PCE, the stoichiometric reaction given by the reaction in Equation 6.36

applies. The reaction equations for permanganate and chloride are shown in Equations 6.37 and 6.38:



$$\frac{dC_{MnO_4^-}}{dt} = Y_{MnO_4^-/cont} \frac{dC_{cont}}{dt} - (k_{NOD_f} X_{NOD_f} + k_{NOD_s} X_{NOD_s}) \frac{\rho_B}{\phi} \quad (\text{Eq. 6.37})$$

$$\frac{dC_{Cl^-}}{dt} = -Y_{Cl^-/cont} \left(k_2 C_{cont} C_{MnO_4^-} \right) \quad (\text{Eq. 6.38})$$

where $Y_{i/j}$ is the stoichiometric molar mass ratio of component i to component j from Equation 6.36 and the component molecular weights. In Equation 6.37, X_{NOD_f} is the mass fraction of NOD sites with a faster oxidation rate ($M M^{-1}$), X_{NOD_s} is the mass fraction of NOD sites with a slower oxidation rate ($M M^{-1}$), k_{NOD_f} is the first-order oxidation rate for fast NOD sites (T^{-1}), and k_{NOD_s} is the first-order oxidation rate for slow NOD sites (T^{-1}).

The reaction module also tracks five immobile species: NAPL phase contaminant, sorbed contaminant, $MnO_{2(s)}$, fast NOD, and slow NOD. Generation of $MnO_{2(s)}$ is simulated using Equation 6.39:

$$\frac{dX_{MnO_2}}{dt} = \frac{\phi}{\rho_B} \left[Y_{MnO_2/MnO_4^-} \right] \left(-\frac{dC_{MnO_4^-}}{dt} \right) \quad (\text{Eq. 6.39})$$

where, X_{MnO_2} is the mass fraction of $MnO_{2(s)}$ solids in the soil ($M M^{-1}$) and dX_i/dt is the rate of change in mass fraction for component i with time. Treating all generated $MnO_{2(s)}$ as immobile provides a worst-case simulation of generated solids filling pore-space and potentially altering permeability.

The reaction module can also simulate either equilibrium or rate-limited sorption of contaminant using the following equation (Haggerty and Gorelick, 1994):

$$\frac{dX_{sorb}}{dt} = \frac{\phi}{\rho_B} \xi \left(C_{cont} - \frac{X_{sorb}}{\lambda_{cont}} \right) \quad (\text{Eq. 6.40})$$

where ξ is the rate-limited sorption mass transfer coefficient (T^{-1}), X_{sorb} is the mass fraction of sorbed contaminant in the soil ($M M^{-1}$), and λ_{cont} is the linear sorption coefficient ($L^3 M^{-1}$). As ξ gets larger, the non-equilibrium sorption approaches equilibrium sorption; as ξ gets very small sorption becomes negligible. Clement et al. (2004a) used and verified the functionality of this formulation in their modeling study of the coupling of NAPL dissolution with rate-limited sorption and kinetic biological degradation.

CORT3D uses the first-order Equations 6.41 and 6.42 at locations where oxidant is present to simulate changes to the mass fraction of fast and slow NOD, respectively.

$$\frac{dX_{nod_f}}{dt} = -k_{nod_f} X_{nod_f} \quad (\text{Eq. 6.41})$$

$$\frac{dX_{nod_s}}{dt} = -k_{nod_s} X_{nod_s} \quad (\text{Eq. 6.42})$$

NOD is assumed to be immobile because batch studies so far have suggested the soil NOD is typically far greater than any NOD exerted by dissolved constituents in the groundwater. Further, the volume of NOD oxidized is assumed to be negligible compared to the pore space, so removal of NOD does not increase permeability; however, the oxidation of NOD does consume permanganate generating $MnO_{2(s)}$ which in turn reduces permeability.

Permeability changes due to decreasing NAPL volume and $\text{MnO}_2(\text{s})$ generation are estimated using Equation 6.43, which was generated for unconsolidated sand with well-sorted grains and non-wetting NAPL (Wyllie, 1962).

$$k_{r,w} = \left(\frac{1 - S_{\text{MnO}_2} - S_n - S_{r,w}}{1 - S_{r,w}} \right)^3 \quad (\text{Eq. 6.43})$$

In this equation, S_{MnO_2} is a pseudo-saturation representing the volume of total pore space filled with manganese oxide solids. This pseudo-saturation is estimated by converting the mass fraction of solids produced to a volume using an effective manganese oxide density. The effective density is essentially a fitting parameter and not an actual density of manganese oxide particles generated. This is because $\text{MnO}_2(\text{s})$ formed during oxidation using permanganate may take different forms depending on porous media and water conditions, as well as where it forms, as discussed in Section 6.5.1. The magnitude of permeability reduction attributed to each of the potential pore blocking mechanisms is expected to be site specific, depending on porous media and water conditions. As a result, it is expected that the effective density parameter may vary between simulations of different site conditions, but it should be a constant for all similar conditions within a single simulation.

Because dissolution and oxidation are transient processes where NAPL saturation decreases with time and manganese oxide solids increase with time (i.e., effective porosity and permeability change), the groundwater flow pattern needs to be updated periodically. The more frequent the update of the flow solution (through changes of effective hydraulic conductivity, porosity, NAPL saturation, and manganese oxide volume), the closer the simulation approaches the transient solution. Because the flow and transport solutions are not coupled in this model code, long (time) simulations are broken down to a number of short steady-state flow and transient transport runs that are executed in sequence. Similar to the model code of Saenton (2003) for simulating surfactant enhanced aquifer remediation, effective hydraulic conductivities are used within MODFLOW to generate the velocity field. This velocity field is then used in estimating the NAPL dissolution mass transfer coefficient. Then, the transport model code simulates the NAPL dissolution, oxidation, and other relevant reactions over a relatively short time interval. If overall simulation time is not over, the transport results are used to generate new porosities and hydraulic conductivities and the process is repeated.

6.9.4.2 CORT3D Model Code Verification

An important step in developing CORT3D was verification by comparing results from this model code against analytical solutions and other (previously verified) numerical codes. After the code was verified, the next step was testing to demonstrate that a model (using the code) of specific experimental conditions was able to reproduce important processes and effects after being calibrated with an independent set of observations. A summary of the verification process follows. Refer to Heiderscheidt (2005) for a detailed discussion.

The chemical oxidation reactions in CORT3D were verified against analytical solutions in several steps. First, oxidation of PCE (without NOD present) was simulated using a 1-D homogeneous system under no-flow conditions, using both the CORT3D model and an analytical solution to the PCE oxidation rate law (Hood, 2000). The agreement between the CORT3D and analytical results indicated that the contaminant oxidation kinetics were operating correctly. The NOD oxidation kinetics were similarly tested, using the model to simulate oxidation of fast NOD (without PCE present) under no-flow conditions and comparing it to the analytical

solution for first-order degradation. Again, the CORT3D and analytical results were in agreement, indicating that the model kinetics were operating correctly.

CORT3D was next verified against analytical solutions incorporating advection, dispersion, and chemical reaction. Although the CORT3D computer model incorporates second-order chemical oxidation, available analytical solutions were for homogeneous systems under uniform flow in the direction of the primary axis incorporating only first-order reactions. Consequently, CORT3D simulations were set up so that either contaminant or oxidant was present in excess making the reaction pseudo first-order with a first-order rate constant (k_1) equal to the second-order rate constant (k_2) times the molar concentration of the species in excess (C_{Excess}) (Equation 6.44). Results from CORT3D were compared to those from the analytical solution to the 1-D solute-transport equation for a finite system with a third-type (or Cauchy) flux boundary at the inlet (Wexler, 1992). A specified concentration gradient of zero was established for the outlet boundary. Initially, the concentration of the species of interest was zero at all locations in the column.

$$k_1 = k_2[C_{Excess}] \quad (\text{Eq. 6.44})$$

Two comparisons were performed using a short, 40-cm (15.7-in.) column: one with oxidant in excess and one with PCE in excess. In both cases, the CORT3D model results were identical to the analytical solution, indicating the model is working correctly. An additional comparison was made for a much larger 1-D case holding oxidant in excess, with a 40-m (15.7-in.) long column and different conditions to verify the model code works at larger scales. Again, the model exactly reproduced the analytical solution results.

The model code was also verified against a 2-D analytical solution for a semi-infinite length, finite width aquifer containing homogenous medium, with constant and uniform groundwater velocity in the x-direction only, and a constant line contaminant source of a finite width at the inlet (Wexler, 1992), as illustrated in Figure 6.13. Again, the simulation was set up with oxidant in excess to approximate a pseudo first-order reaction because the analytical solution was first-order. The outlet and side boundaries were all specified concentration gradient boundaries equal to zero. Despite using a 1-m (3.3-ft) square cell size in the CORT3D simulations, the numerical results were nearly identical to the analytical results with an $R^2 = 0.995$ for the 10 m (32.8 ft) off-centerline locations and 0.999 for the centerline locations.

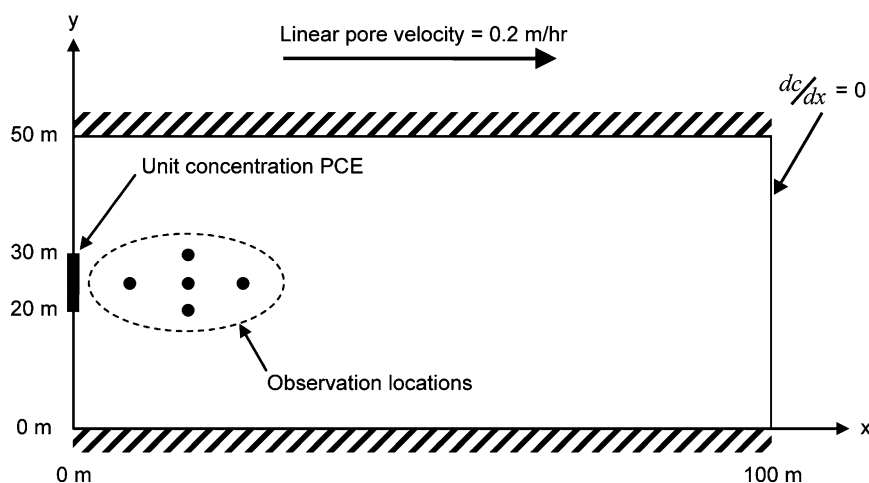


Figure 6.13. Schematic of 2-D aquifer scenario used in a CORT3D simulation (reprinted with permission from Heiderscheidt, 2005).

A series of simulations were also performed to verify that the revised RT3D diffusion code worked as expected. The new code was used to simultaneously simulate both pure diffusion (without a hydraulic gradient, hence absence of advection and mechanical mixing) of three components (PCE, MnO_4^- , and Cl^-), and again under combined advective and dispersive/diffusive conditions. The results were compared to those of running the original RT3D code individually for each of condition. Identical results indicated that the new effective diffusion code works properly.

After verifying that the model code worked as expected, it was used to simulate a series of 1-D laboratory experiments, documented in the literature, highlighting important ISCO related processes, such as decreasing permeability due to $\text{MnO}_2(\text{s})$ generation since there is no analytical solution for this. The goal of these tests was not to universally validate the modeling code for all conditions since it is recognized that models of specific scenarios must be individually validated for the specific boundary conditions, performance criteria, and application (Refsgaard and Knudsen, 1996; Van Waveren et al., 1999; Refsgaard and Henriksen, 2004). Instead, the purpose of this testing was to demonstrate that models created using the modeling code capture specific important ISCO-related processes and effects observed in experiments. Where sufficient data was available, the model was calibrated using one set of data and then used to predict observed effects from an independent set of data.

Experiments highlighting permeability reduction due to $\text{MnO}_2(\text{s})$ generation, NAPL dissolution and oxidation, enhanced mass transfer during oxidation, and NOD oxidation were each simulated using CORT3D. In some cases, the available data set was too small to permit model calibration followed by prediction of a separate data set. Additionally, since the experiments were extracted from literature, important data that would permit full model calibration was sometimes missing. However, despite data limitations, the simulations of Heiderscheidt (2005) were able to capture the salient features of each process observed in the experiments.

6.9.4.3 CORT3D Simulation of Navy Training Center Site, Florida

Following verification, numerical model simulations were conducted using CORT3D to examine site conditions and system features that may have adversely affected ISCO performance at the Naval Training Center's (NTC) Operable Unit 4 located in Orlando, Florida (Figure 6.14), as part of an effort to identify potential ISCO system modifications to achieve the desired remediation performance. At the NTC site, ISCO was implemented using vertical injection wells in a continuous recirculation approach to deliver potassium permanganate into a groundwater zone for treatment of PCE and its breakdown products. However, observed oxidant distribution was much more limited than anticipated.

After performing characterization studies of the site groundwater and subsurface porous media, CORT3D modeling was performed for a variety of conditions (injection/extraction well flow rates, injected oxidant concentration, amount of NOD present, and NOD oxidation rate). Figure 6.8 demonstrates the significant affect that NOD can have on oxidant transport, underscoring the need to account for NOD when designing an ISCO system. Table 6.4 summarizes simulation results for the base scenario (1,000 mg/L at 56.8 L/min), and scenarios with high and low oxidant concentration and high and low flow rate for comparison. Remaining scenarios (not shown) fell within the ranges of those shown. For each scenario, the table lists the area of oxidant transport and extent of $\text{MnO}_2(\text{s})$ generation, along with percent change from the base scenario. The ratio of oxidant transport to $\text{MnO}_2(\text{s})$ extent is a measure of the expected effectiveness for each condition (with respect to maximizing the extent of oxidant transport while minimizing the extent of $\text{MnO}_2(\text{s})$ deposition). The highest ratio indicates the best oxidant delivery scenario. Specifically, for the NTC site, low concentration injection at a high flow rate

is a more effective method than the base case or other scenarios for delivering the required mass of oxidant to the target treatment zone while minimizing unproductive oxidant consumption by NOD and the level of $MnO_2(s)$ deposition (Heiderscheidt et al., 2008a).

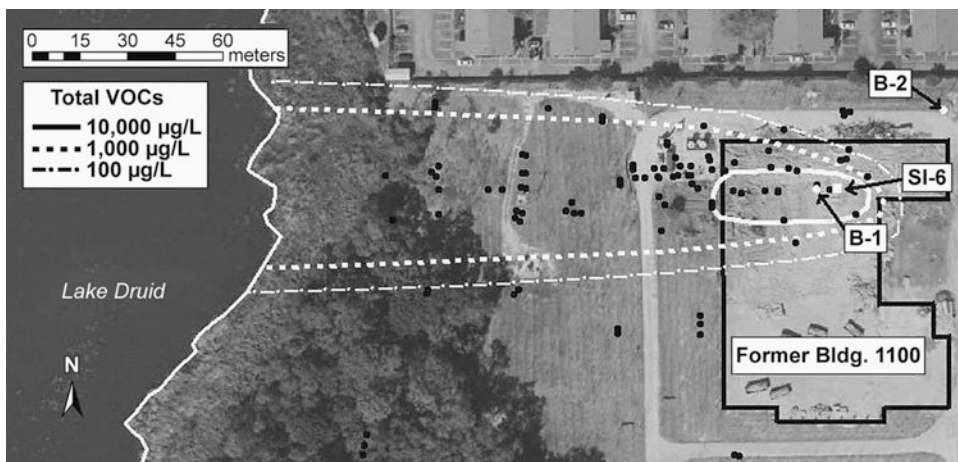


Figure 6.14. Naval Training Center site location map (reprinted from Heiderscheidt et al., 2008a; with permission of the National Ground Water Association and Blackwell Publishing).

Table 6.4. Simulation Results for Determining Optimal Oxidant Delivery Scenario

Simulation conditions		Oxidant transport		MnO ₂ extent		Ratio of oxidant transport/MnO ₂ extent
Oxidant concentrations (mg/L)	Flow (L/min)	m ²	% Change	m ²	% Change	
250	18.9	5.4	-78	6.6	-76	0.81
250	56.8	8.6	-66	11.2	-59	0.76
250	181.7	46.8	87	40.4	48	1.16
1,000	56.8	25.5	0	28.0	0	0.91
1,000	181.7	58.3	123	52.2	92	1.12
4,000	56.8	79.2	216	113.0	306	0.70
4,000	181.7	177.4	623	175.0	560	1.01

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Note: % change measured against base scenario (1.00 mg/mL at 56.8 L/min).

6.10 SUMMARY

Successful implementation of ISCO frequently depends upon appropriate consideration of a variety of relevant transport and reaction processes. All of the usual transport processes such as advection, dispersion, diffusion, and sorption are important in implementing ISCO. Additionally, density driven transport can be important when injecting high concentrations of certain oxidants. Other important considerations are oxidant/contaminant reactions, mass transfer, non-COC oxidant demand, and hydraulic impacts resulting from contaminant source removal and oxidation byproduct formation. The relative importance of some of these factors varies depending upon the oxidant being considered for a particular set of site conditions.

Because of the large number of important factors, and their interdependence, modeling is a powerful tool that can facilitate investigation of subsurface conditions, help focus remediation selection on oxidants and delivery methods that are expected to be effective given the likely source zone architecture and site hydrogeology, and improve the design process. Though existing modeling tools primarily focus on permanganate, it may be possible to adapt them to other oxidants under certain conditions and with certain assumptions. Doing so effectively depends upon adequately framing the question to be answered, or the modeling objective, and then selecting an appropriate model, and implementing it correctly.

Disclaimer: The views expressed in this chapter are those of the authors and do not necessarily reflect the official policy or position of the United States Air Force Academy, the Air Force, the Department of Defense or the U.S. Government.

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CHAPTER 7

PRINCIPLES OF COMBINING ISCO WITH OTHER *IN SITU* REMEDIAL APPROACHES

Junko Munakata-Marr,¹ Kent S. Sorenson Jr.,² Benjamin G. Petri¹ and James B. Cummings³

¹Colorado School of Mines, Golden, CO 80401, USA; ²CDM, Denver, CO 80202, USA; ³U.S. Environmental Protection Agency, Office of Solid Waste Emergency Response, Washington, DC 20460, USA

Scope

Interactions between *in situ* chemical oxidation (ISCO) and other *in situ* remediation technologies, and optional approaches for coupling ISCO with bioremediation, surfactant/cosolvent flushing, air sparging, or thermal treatment.

Key Concepts

- ISCO applied in combination with other remedial technologies, particularly when plans are formulated prior to implementing a remedy, may provide significant benefit over ISCO alone.
- Enhanced *in situ* bioremediation and monitored natural attenuation are most frequently combined with ISCO.
- ISCO may temporarily decrease aerobic and anaerobic microbial abundance and diversity, but these typically rebound with time.
- ISCO combined with surfactants or cosolvents may enhance contaminant removal, though chemical compatibility of remedial agents must be considered.
- Air sparging and thermal methods may interact synergistically with ISCO, while *in situ* chemical reduction acts in opposition to ISCO.

7.1 INTRODUCTION

This chapter focuses on the integration and synergistic coupling of *in situ* chemical oxidation (ISCO) with other remediation technologies and approaches to provide a combined remedy and achieve more effective and efficient cleanup. This coupling may be accomplished simultaneously, or be temporally or spatially distinct. Temporally, ISCO and other technologies are applied sequentially to the same target treatment zone (TTZ), such as ISCO followed by *in situ* bioremediation. Spatially, ISCO can be used to treat a portion of the site, with different technologies or approaches applied to other portions. For example, ISCO may be used to treat the source zone and *in situ* chemical reduction (ISCR) with a zero-valent iron (ZVI) permeable reactive barrier (PRB) may be used to contain the plume.

Treatment of contaminants of concern (COCs) with ISCO applied proactively in conjunction with other remediation techniques may provide significant benefit. For example, pretreatment with ISCO (“priming”) may increase susceptibility of target COCs to subsequent treatment by bioremediation, while post-treatment with ISCO (“polishing”) may have significantly decreased

oxidant requirements to treat residual contamination left behind by prior treatment techniques. This proactive coupled approach may be the only method by which remediation objectives may be achieved in situations where ISCO alone is deemed to be insufficient (e.g., stringent treatment goals for a site with high contaminant mass density in challenging lithology).

Combined approaches may result from changes in remediation strategy over time as new information is gathered. For example, at contaminated sites where other remediation methods have been implemented, subsequent application of ISCO is de facto a combined approach and must consider interactions between prior and planned treatments. Such prior treatments may influence ISCO applied in the same location or adjacent to previous treatments. Many technologies are suitable for coupling, though their particular interactions with ISCO should be carefully evaluated.

The case study data presented in Krembs (2008) (also in Chapter 8) revealed that of 135 ISCO sites where combined approaches were considered, 76% coupled ISCO with other remediation techniques; 60% applied another treatment pre-ISCO, 22% coupled during ISCO, and 30% coupled post-ISCO (Table 7.1). Some sites reported combining remedies with ISCO multiple times (e.g., both before and after ISCO application), thus the total of these percentages exceeds 100%. The reported frequency of post-ISCO coupling is likely an underestimate because post-ISCO coupling may have been initiated after the case study documents were written (often shortly after completion of ISCO).

Table 7.1. Percentage of 135 Sites Using ISCO Combined with Other Remedies at Different Scales (Krembs, 2008)

Type of coupling	All scales	Full-scale only	Pilot-scale only
All sites where ISCO is coupled in a combined remedy	76%	89%	44%
Where ISCO is applied after another method	60%	68%	36%
Where ISCO is applied simultaneously with another method	22%	30%	3%
Where ISCO is applied before another method	30%	38%	15%
Total number of sites	135	90	39

As shown in Table 7.2, the most common pre-ISCO remedy was excavation (50%), followed by pump-and-treat (P&T; 22%); ISCO was likely implemented after such techniques proved ineffective at reaching remediation goals. P&T (11%) and soil vapor extraction (SVE) (9%) were chosen most frequently to apply concurrently with ISCO, while monitored natural attenuation (MNA) (19%) and enhanced *in situ* bioremediation (EISB) (17%) were the most common post-ISCO “polishing” approaches (Table 7.2). Sites with dense nonaqueous phase liquids (DNAPLs) were more likely to have ISCO coupled with other technologies, especially post-ISCO technologies such as EISB and MNA, which were implemented after ISCO at 45% of DNAPL sites ($n = 49$). Coupling was applied at high rates ($\geq 67\%$) with all contaminant types, with all oxidants, and in all geological settings reviewed, with the exceptions of percarbonate (only two case studies total, with one coupling) and impermeable, heterogeneous media (8 of 14 case-study sites used coupling).

This chapter summarizes the available published literature on interactions between ISCO and other *in situ* remediation techniques, focusing on those technologies and approaches that have the potential for significant interactions. The purpose of this chapter is *not* to provide a complete overview of all of the factors that impact other technologies but instead to report important areas where ISCO has unique impacts to other technologies and vice versa. Some

aspects of coupling ISCO with other technologies and approaches have been reviewed previously (Sahl and Munakata-Marr, 2006; Scott and Ollis, 1995; Waddell and Mayer, 2003); this chapter includes key literature described in those reviews and adds more detailed descriptions of studies not included in the reviews. Considerations for site-specific engineering of combined treatment technologies and approaches are presented in Chapter 9.

Table 7.2. Summary of Techniques Coupled Before, During, and After ISCO (Krembs, 2008)

Technology or approach	Percent of sites (<i>n</i> = 103)		
	Technology used before ISCO	Technology used concurrently with ISCO	Technology used after ISCO
Air sparging (AS)	8	3	1
Biosparging	–	–	1
Bioventing	1	–	–
Dual-phase extraction (DPE)	1	2	2
Enhanced fluid recovery (EFR)	2	–	–
Enhanced <i>in situ</i> bioremediation (EISB)	3	2	17
Excavation	50	4	8
Monitored natural attenuation (MNA)	–	–	19
Pump-and-treat (P&T)	22	11	8
Surfactant/cosolvent	–	3	4
Soil vapor extraction (SVE)	18	9	–

Notes: Percentages sum to greater than 100% because multiple techniques were combined at some sites. MNA was only entered as a coupling technique after ISCO when specifically called out that it was used after ISCO, so use of MNA after ISCO is likely underestimated.

7.2 *IN SITU* BIOLOGICAL METHODS

At many ISCO sites, either MNA or EISB are integral parts of the remediation strategy. Thus, it is important to consider the potential impacts that ISCO oxidants may have on subsurface biological communities and geochemical conditions before ISCO is used at these sites. Process interactions may be complementary, such that ISCO enhances biological activity, or deleterious, where ISCO may inhibit biological processes. Overall, the available literature suggests that ISCO does not sterilize the subsurface, though it may temporarily disrupt bioprocesses, which typically recover with time. This section discusses these specific interactions, some of the mechanisms behind them, and their potential implications for MNA and EISB.

7.2.1 Impacts of Oxidants on Geochemistry and Bioprocesses

Several reports (Sahl and Munakata-Marr, 2006; Scott and Ollis, 1995; Waddell and Mayer, 2003) have summarized effects of chemical oxidants on microbial abundance or diversity. These effects can be caused directly (interaction between oxidant and microorganisms) or indirectly (e.g., by changes in redox, pH, substrate availability). Generally, microbial concentrations and diversity decrease during exposure to chemical oxidants, but both may rebound, sometimes to higher levels than prior to oxidation. The literature describing direct and indirect microbial effects is summarized in this section; information related specifically to microbial

impacts of ISCO combined with MNA and enhanced bioremediation efforts is presented in Sections 7.2.3 and 7.2.4, respectively.

Strong oxidants, often used for disinfection, can obviously have direct deleterious effects on microbes. However, microorganisms may defend against reactive oxidants by producing antioxidative enzymes such as catalase and superoxide dismutase; many aerobic and facultative microbes found in soil and groundwater (Pardieck et al., 1992), as well as some environmentally relevant anaerobes (Brioukhanov et al., 2002; Hewitt and Morris, 1975), may express these protective enzymes. For example, one microbial strain expressing catalase was protected from a high concentration of hydrogen peroxide (H_2O_2) (34 g/L; 1 M), while a strain lacking catalase was completely inhibited by a lower hydrogen peroxide concentration (0.34 g/L; 10 mM) (Schlegel, 1977).

Microbial activity with concurrent chemical oxidation has been observed, further demonstrating microbial resistance to oxidants. Based on results from aqueous batch microcosms, simultaneous mineralization by catalyzed hydrogen peroxide (CHP) oxidation of perchloroethene (PCE) with aerobic biodegradation of byproducts was predicted to be optimal (62%) at 77 mg/L (2.3 mM) hydrogen peroxide, $10^{4.2}$ cells/mL and 18 mg/L (0.33 mM) ferrous iron (Fe(II)) (Büyüksönmez et al., 1999). Simultaneous CHP oxidation of PCE and aerobic biodegradation of oxalate were observed in aqueous batch microcosms (Howsawkeng et al., 2001) and soil slurry reactors (Ndjou'ou et al., 2006). PCE oxidation rate and extent by CHP increased with increasing CHP concentration, though oxalate assimilation decreased (Howsawkeng et al., 2001) or lagged (Ndjou'ou et al., 2006) with increasing CHP.

Tsitonaki et al. (2008) reported inhibitory effects of heat-activated persulfate. Controls (no persulfate) at temperatures between 15 and 50°C showed no effect of temperature on total numbers or live/dead cell ratios as measured by BacLight™. Exposure to persulfate (activated at 40°C) for 2 days did not impact indigenous live cell concentrations but significantly lowered numbers of bioaugmented *Pseudomonas putida*, possibly due to differences in growth phase (stationary vs. exponential, respectively). Cells remained intact at all persulfate doses tested, but despite the similar cell numbers, acetate uptake was severely inhibited at the highest persulfate dose (10 g/L; 50 mM), suggesting that intact cells were inactivated, perhaps by the observed drop in pH to <4. Acetate uptake at the lowest doses of persulfate (0.1 and 1 g/L; 0.5 and 5 mM), at which the pH remained >7, was comparable to the control.

Indirectly, addition of chemical oxidants may influence the principal terminal electron acceptor (TEA) present in the system. The amount of energy available to microbes depends on the TEA; the most energetic TEAs must be virtually depleted before a lower energy TEA may dominate, as presented in Table 7.3.

Table 7.3. Hierarchy of Terminal Electron Acceptors in Microbial Metabolisms

	Terminal electron acceptor	Reduced counterpart	Bioprocesses
↓ More Reducing	Oxygen (O_2)	Carbon dioxide (CO_2)	Aerobic respiration
	Nitrate (NO_3^-)	Ammonium (NH_4^+) Nitrogen (N_2) Nitrous oxide (N_2O)	Nitrate reduction
	Ferric iron (Fe(III))	Ferrous iron (Fe(II))	Iron reduction
	Manganese oxide (MnO_2)	Dissolved manganese (Mn^{2+})	Manganese reduction
	Sulfate (SO_4^-)	Bisulfide (HS^-)	Sulfate reduction
	Carbon dioxide (CO_2)	Methane (CH_4)	Methanogenesis

Depending on the oxidant, all of the above TEAs, with the sole exception of nitrate, may be products of ISCO reactions. ISCO using hydrogen peroxide, ozone, or percarbonate has the potential to evolve significant amounts of oxygen (as dissolved O₂), so the subsurface may become aerobic during ISCO applications with these oxidants, enhancing aerobic microbial activity (Bittkau et al., 2004). Sulfate is a major byproduct of persulfate reactions. In addition, Fe(II) and Fe(III) are catalysts for both hydrogen peroxide and persulfate ISCO approaches and may be delivered into the subsurface at substantial concentrations in some cases. Manganese dioxide is the typical inorganic byproduct of permanganate oxidation systems, so it may also be present in significant amounts. Finally, many ISCO reactions result in the oxidation of organic contaminants, as well as soil organic matter, to form carbon dioxide, which dissolves in water to form carbonate and bicarbonate. Such ISCO byproduct TEAs have the potential to shift microbial community dynamics from their pre-ISCO equilibrium. This can have beneficial and detrimental impacts to biodegradation. For instance, aerobic biodegradation of petroleum hydrocarbons may be enhanced by the presence of oxygen; at the same time, oxygen will generally inhibit reductive dechlorination processes. Similarly, sulfate may enhance the activity of sulfate-reducing bacteria that may be involved in benzene, toluene, ethylbenzene, and total xylenes (BTEX) or polycyclic aromatic hydrocarbon (PAH) degradation yet may interfere with reductive dechlorination processes. MnO₂ produced in the permanganate process may act as a terminal electron acceptor for degradation of compounds such as 1,2-dichloroethene (DCE) (Bradley et al., 1998). Such impacts are generally transient, and after the oxidant and resulting TEAs are depleted, subsurface geochemical effects generally attenuate over time and the geochemistry returns to pre-ISCO conditions.

In addition to ISCO effects on available TEAs, under some conditions, ISCO can substantially alter pH, which in turn can impact microbial activity. As described in Chapters 2 to 5, in some situations, pH can decline to near 2 or rise to near 11 based on the reaction chemistry and the buffering capacity of the groundwater system. Though microorganisms have been found to grow in extreme pH environments, microbes generally do not have a high tolerance for rapid changes in pH and could thus be negatively impacted by some ISCO applications. In the permanganate reaction, the pH may drop as the permanganate ion reacts with organic contaminants as well as natural organic matter. Persulfate may also decrease pH (Block et al., 2004). Additionally, persulfate may be activated by alkaline conditions (Block et al., 2004) while peroxide may be introduced at acidic pH (Watts and Dilly, 1996). Such extreme pH (highly acidic or alkaline pH) can significantly reduce microbial growth rates, possibly altering the diversity of the microbes in areas of oxidant application (Landa et al., 1994). For example, anecdotal evidence suggests that complete reductive dechlorination of chlorinated solvents such as PCE and trichloroethene (TCE) to ethene is optimal near circumneutral pH (Fogel et al., 2009; Zhuang and Pavlostathis, 1995), while partial reductive dechlorination has been observed over a wider pH range, with transformation to *cis*-DCE observed down to a pH of at least 5.5 (Macbeth and Sorenson, 2009). Laboratory studies have shown that a specific strain of *Dehalococcoides*, the only organisms shown to grow using DCE and vinyl chloride (VC) as an electron acceptor, has an optimal pH range between 6.8 and 7.5 (Maymó-Gatell, 1997). Furthermore, Magnuson et al. (1998) showed that the PCE dehalogenase enzyme (which transforms PCE to TCE) from *D. ethenogenes* strain 195 was unstable below pH 5 and above pH 8.

7.2.2 Enhanced Biodegradability of Contaminants by Pre-oxidation

Many studies have investigated pre-oxidation of target compounds prior to (and typically applied separately from) microbial transformation. *Ex situ* wastewater or aqueous-phase treatment has been the focus of many pre-oxidation studies (see Scott and Ollis, 1995 for review), which, while relevant, represents a significantly different system and will not be discussed further

here. *Ex situ* oxidant pretreatment of soils for PAH removal has also been reviewed (Mohan et al., 2006; Rivas et al., 2000) and is described in other literature (Haapea and Tuhkanen, 2006). Polychlorinated biphenyls (PCBs) have also been treated *ex situ* by combined oxidation and biological treatment (Cassidy et al., 2002). Pre-oxidation of recalcitrant compounds to more bioavailable substrates has been used for years to enhance biodegradation in contaminated soils. As summarized in other reviews (Sahl and Munakata-Marr, 2006; Waddell and Mayer, 2003), biodegradability generally increased after chemical oxidation, suggesting that ISCO may enhance subsequent biotransformation. ISCO may also enhance microbial activity by producing substrates through oxidation of humic and fulvic acids in natural organic matter (Almendros et al., 1989; Griffith and Schnitzer, 1975; Ortiz De Serra and Schnitzer, 1973).

Table 7.4 summarizes key conditions and findings from additional studies investigating enhanced biodegradation after oxidation, in the context of MNA or EISB (with bioaugmentation). PAH has been the primary target contaminant, with numerous studies demonstrating enhanced aerobic biodegradation after pre-oxidation with CHP (Kulik et al., 2006; Lee and Hosomi, 2001; Piskonen and Itävaara, 2004) or ozone (Kulik et al., 2006; Nam and Kukor, 2000; O'Mahony et al., 2006) to more biodegradable byproducts. Additional studies have demonstrated biodegradation of CHP reaction products of the dioxin isomer 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (Kao and Wu, 2000) and aerobic biodegradation of permanganate-oxidized cyclotrimethylenetrinitramine (RDX or Royal Demolition eXplosive) and its byproducts (Adam et al., 2005).

While most investigations have focused on enhanced biodegradation following oxidation, one study (Nam et al., 2001) reported greatest removals in PAH-contaminated soil by applying CHP after biodegradation. Naphthalene was completely removed by the biodegradation/CHP sequence compared to 94% removed by the CHP/biodegradation sequence. Similarly, CHP applied after biodegradation removed 56–68% benzo(a)pyrene vs. 25% when applied before biodegradation.

7.2.3 Monitored Natural Attenuation

MNA that relies on indigenous microbial activity may be temporarily diminished by chemical oxidation, though microbial populations typically recover (Sections 7.2.1 and 7.2.4). Indeed, chemical oxidants may be specifically chosen to stimulate indigenous bacteria under the dominant natural attenuation processes. For example, if sulfate reduction is the dominant natural attenuation process at a site, persulfate may be a better oxidant choice to stimulate this microbial population rather than CHP or ozone, assuming similar oxidant effectiveness against the target contaminants. Conversely, CHP or ozone may be more appropriate to apply in aerobic treatment zones, potentially resulting in fewer changes to the geochemistry and microbiology during treatment. In addition, MNA may be enhanced due to decreased concentrations or increased biodegradability of contaminants as a result of ISCO (Section 7.2.2).

Numerous microcosm- and column-based studies have investigated impacts of ISCO on microorganisms in native soil or aquifer solids in the context of MNA by biodegradation. Details of some of these studies are summarized in Table 7.5. Generally, microcosm- and column-based studies have demonstrated decreases in microbial biomass with oxidation but increased contaminant removal with the combination of oxidation and biodegradation. For example, in studies investigating ozonation for different time periods (Ahn et al., 2005; Jung et al., 2008), greater decreases in heterotrophic plate counts (typically one to three orders of magnitude) were observed in soils exposed to ozone for longer periods of time. Highest extents of contaminant removal by ozone followed by biodegradation were observed in soils exposed to ozone for intermediate time periods suggesting that high exposures were inhibitory to microbes while low exposures provided suboptimal pretreatment.

Table 7.4. Summary of Laboratory Studies Investigating Chemical Oxidation Combined with Biodegradation in the Context of MNA and EISB (These Studies Did Not Describe Microbial Effects; Those that Did Are Provided in Tables 7.5 and 7.6)

Oxidant	Experimental setup	Target contaminants	Contaminant removal
Monitored natural attenuation			
Goi et al. (2006)			
CHP H ₂ O ₂ applied to Fe-containing soil at different H ₂ O ₂ /contaminant ratios once per day for 3 days	<ul style="list-style-type: none"> • CHP in batch slurries (and quenched) • Oxidation followed by aerobic incubation of unamended soil (no pH adjustment, no inoculation) samples for 30 days 	Sand and peat spiked with transformer and shale oils <ul style="list-style-type: none"> • 5.6 and 5.5 g/kg shale oil in sand and peat, respectively • 17.4 and 19.0 g/kg transformer oil in sand and peat, respectively 	<ul style="list-style-type: none"> • CHP followed by biotreatment achieved 80% and complete removal of shale and transformer oils, respectively, in sand, while in peat, 53 and 75% removals were respectively achieved • Greater removal was achieved with combined treatments than with either individual treatment: biodegradation alone removed 52 and 50% of shale and transformer oils in sand and 42 and 33% in peat
Ozone (0.2% v/v)	<ul style="list-style-type: none"> • Ozone applied for 1, 2 or 5 hr to soil or peat in columns • Oxidation followed by aerobic incubation of unamended soil samples for 30 days 		<ul style="list-style-type: none"> • Transformer oil degradation using ozonation followed by biotreatment was less effective (70% removal) than CHP in sand, but other removals were comparable to CHP • Greater removal was achieved with combined treatments than with either individual treatment
Kulik et al. (2006)			
CHP H ₂ O ₂ /Fe applied to soil at different H ₂ O ₂ /soil ratios	<ul style="list-style-type: none"> • 24-hr slurries with 10 g sand or 3 g peat and 100 mL distilled water with H₂O₂/Fe(II) in 10:1 molar ratio • H₂O₂:sand mass ratios 0.043, 0.086, 0.172 • H₂O₂:peat mass ratios 0.133, 0.266 • Followed by aerobic bio with no inoculation or pH adjustment 	<ul style="list-style-type: none"> • Sand spiked with seven different PAH compounds to a concentration of 1,420 mg total PAH/kg sand • Peat spiked with seven different PAH compounds to a concentration of 2,370 mg total PAH/kg sand 	<ul style="list-style-type: none"> • Highest PAH removals (88.5% in sand, 70% in peat) at highest H₂O₂/Fe(II) doses • After 8-week incubation, overall 94% removal (20% increase) in sand that received the lowest dose of H₂O₂/Fe(II) • After 8-week incubation, overall removal (59%) in peat that received the lowest dose of H₂O₂/Fe(II) comparable to removal (55%) in control that received no H₂O₂/Fe(II)
Ozone (0.05% v/v)	<ul style="list-style-type: none"> • Two-phase ozonation in semi-continuous bubble columns followed by aerobic bio with no inoculation or pH adjustment 		<ul style="list-style-type: none"> • 64% PAH removal in 120 min in sand • 41% PAH removal in 300 min in peat • Although PAH degradation by ozone was higher in sand than in peat, combining ozonation with subsequent 8-week biodegradation resulted in similar removal (70–75%) of PAH in both soils

(continued)

Table 7.4. (continued)

Oxidant	Experimental setup	Target contaminants	Contaminant removal
Piskonen and Itävaara (2004)			
CHP 0.006 g H ₂ O ₂ and 0.35 mg Fe(II) per g soil or 0.0015 g H ₂ O ₂ and 0.087 mg Fe(II) per g soil	<ul style="list-style-type: none"> • Oxidation in beakers of PAH-contaminated soil (with indigenous PAH-degrading microorganisms, enriched by addition of 250 mg/kg soil of PHE, PYR and BaP) • Biodegradation in oxidized soil evaluated in 96-well microtiter plates by radiolabelled CO₂ generation 	Radiolabelled PHE, PYR and BaP (5 nCi) added to microtiter plates	<ul style="list-style-type: none"> • In 170-day incubation, CHP increased PHE mineralization significantly (12%) over that in unoxidized soil at lower but not higher CHP concentration • 52 and 61% of PYR mineralized in 170 days at lower and higher CHP concentrations, respectively; 27% mineralized in unoxidized control • No mineralization of BaP observed • Addition of surfactants Tween 80, Brij 35, Tergitol NP-10 or Triton X-100 with CHP did not enhance mineralization over CHP alone
Bioaugmentation			
Adam et al. (2005)			
KMnO ₄ 4,000 mg/L	Spiked aquifer material oxidized in flasks until RDX depleted, some reactions quenched with MnSO ₄ , supernatant transferred to aerobic microcosms containing aquifer material	Aquifer material spiked with 5 mg/L aqueous RDX for oxidation	<ul style="list-style-type: none"> • RDX oxidation products biodegraded more quickly than RDX, and more quickly in quenched than unquenched microcosms, but extent of mineralization (CO₂ production) after 77 days incubation did not differ significantly, with 47, 49 and 57% mineralization in unoxidized, unquenched and quenched microcosms, respectively
Kao and Wu (2000)			
CHP 20 mg/L H ₂ O ₂ and 28 mg/L Fe(II) at pH 3.5 (applied three times in sequence)	Sandy soil spiked with TCDD oxidized in soil slurry reactor (500 g soil + 500 mL DI water), pH adjusted to pH 7 and bioaugmented with aerobic activated sludge at >10 ⁷ heterotrophic cells/g soil	125 µg TCDD/kg soil	<ul style="list-style-type: none"> • CHP removed 99% of TCDD; numerous degradation products identified • All degradation products were biodegraded within 35 days
Lee and Hosomi (2001)			
CHP 0.03–0.1 g H ₂ O ₂ and 2.7–7.0 mg Fe(II) per g soil	Simulated soil (andosol) spiked with BaA, oxidized in reactor, moved to aerobic flask containing nutrients and river sediment containing PAH-degrading microorganisms	500 mg BaA/kg soil	<ul style="list-style-type: none"> • 97% BaA removal in 24 hr at >0.085 g H₂O₂ and >5.6 mg Fe(II) per g soil, with BaA-7,12-dione identified as primary product • Aerobic biodegradation removed 98% BaA-7,12-dione but minimal BaA removal in 63 days

(continued)

Table 7.4. (continued)

Oxidant	Experimental setup	Target contaminants	Contaminant removal		
Nam and Kukor (2000)					
Ozone 0.00015% v/v	Silt loam (2.94% organic carbon) or sand (0.03% organic carbon) spiked with seven PAHs and coal tar-contaminated loamy sand, ozonated, then inoculated with PAH-degrading consortium at $>10^8$ cells/g soil	600 mg total PAH/kg in spiked soil: <ul style="list-style-type: none"> • 100 mg each of NAP, FLU, PHE, ANT and PYR per kg soil • 50 mg each of CHR and BaP per kg soil Initial concentrations in coal tar-contaminated sand were (mg/kg soil) <ul style="list-style-type: none"> • 1205 NAP • 252 FLU • 921 PHE • 524 PYR • 454 CHR • 366 BaP 	<ul style="list-style-type: none"> • Ozonation completely removed NAP in 2 days in spiked silt loam and sand • Ozonation removal of other compounds in spiked sand ranged from 73.5% (FLU) to 32.4% (BaP) in 2 days • Ozonation removal of other compounds in spiked silt loam ranged from 95.1% (FLU) to 10.3% (PYR) in 4 days • In spiked silt loam, 2 days ozonation followed by 4 weeks biodegradation increased removal over ozonation alone of PHE (36.8% additional removal), ANT (64.3%), PYR (37.5%) and CHR (39.3%) but 4 weeks biodegradation followed by 2 days ozonation removed 25–50% less • In coal tar-contaminated soil, 2 days ozonation followed by 4 weeks biodegradation increased removal of PYR and CHR about 60% over biodegradation alone, which removed 95% of NAP, FLU and PHE but little else • BaP removal not enhanced by combined techniques 		
Nam et al. (2001)					
CHP 2 g H ₂ O ₂ and 323 mg Fe (ClO ₄) ₃ ·6H ₂ O 82.5 mg of catechol or 141.0 mg of gallic acid (chelating agent) and 1 g CaCO ₃ (pH control) added to soil before CHP	Coal tar-contaminated loamy sand, oxidized, inoculated with PAH-degrading consortium at $0.4\text{--}1.2 \times 10^8$ cells/g soil	Initial concentrations in coal tar-contaminated sand were (mg/kg soil) <ul style="list-style-type: none"> • 1,205 NAP • 252 FLU • 921 PHE • 524 PYR • 454 CHR • 366 BaP 	Target	CHP → Bio ^a	Bio → CHP ^a
			NAP	94%	100%
			FLU	67%	98%
			PHE	64%	99%
			PYR	32%	81%
			CHR	16%	59%
			BaP	25%	62%
O'Mahony et al. (2006)					
Ozone 0.001% v/v	Loamy sand (2.07% carbon, pH 3.61) and clay loam (4.29% carbon, pH 6.03) ozonated, transferred to flask and inoculated with <i>Pseudomonas alcaligenes</i> PA-10 at 3×10^9 CFU/g dry weight soil	Soil spiked with 200 mg PHE/kg soil for combined treatment, 100 mg PHE/kg soil for biodegradation alone	<ul style="list-style-type: none"> • 6 h ozonation removed 45–55% PHE in both soils • Unozonated inoculated soil completely degraded PHE in 1 day, while uninoculated soil (ozonated or not) degraded $\geq 70\%$ PHE in 9 days • Combined treatment did not enhance PHE removal in clay loam, and ozonation slowed PHE removal in bioaugmented loamy sand 		

(continued)

Table 7.4. (continued)

Oxidant	Experimental setup	Target contaminants	Contaminant removal
Valderrama et al. (2009)			
CHP 1,574–8,862 mM H ₂ O ₂ and 47–180 mM Fe(II), at H ₂ O ₂ :Fe ratios of 10:1, 20:1, 40:1 and 60:1	Contaminated soil oxidized in batch slurry reactors followed by biodegradation in aerobic sequencing batch reactor bioaugmented with activated sludge	Initial concentrations in contaminated soil were (mg/kg soil) 258 PHE 228 FLA 165 ACE 153 PYR 124 FLU 58 CHR 68 ANT 44 BbF 41 BaA 40 BaP 25 BkF	<ul style="list-style-type: none"> Overall PAH removal after 30 min CHP treatment was 42, 43, 61 and 71% at respective H₂O₂:Fe ratios of 10:1, 20:1, 40:1 and 60:1 Subsequent biodegradation increased overall removal by 20, 32, 9 and 0% at respective H₂O₂:Fe ratios of 10:1, 20:1, 40:1 and 60:1 Highest overall PAH removal by CHP + biodegradation was 75% compared to 45 and 71% by biodegradation and CHP alone

Note: µg - microgram, ACE - acenaphthene, ANT - anthracene, BaA - benz(a)anthracene, BaP - benzo(a)pyrene, BbF - benzo(b)fluoranthene, BkF - benzo(k)fluoranthene, CaCO₃ - calcium carbonate, CFU - colony forming units, CHR - chrysene, DI - deionized, FLA - fluoranthene, FLU - fluorine, g/kg - grams per kilogram, hr - hour, KMnO₄ - potassium permanganate, MnSO₄ - manganese sulfate, NAP - naphthalene, nCi - nanocuries, PHE - phenanthrene, PYR - pyrene, TCDD - 2,3,7,8-tetrachlorodibenzo-p-dioxin, v/v - volume to volume ratio.

^aAverage removal with two chelators.

Table 7.5. Summary of Laboratory Studies Investigating Chemical Oxidation Combined with Biodegradation, Including Microbial Impacts, in the Context of MNA

Experimental setup	Target contaminants	Contaminant removal	Microbial community observations
Aerobic bio			
Ahn et al. (2005)			
Ozone applied to soil columns for 0, 10, 30, 60, 180, 300, or 900 min followed by biodegradation in aerobic beakers	2,651.5 mg TPH/kg soil 278.6 mg aromatics/kg soil	<ul style="list-style-type: none"> Greatest ozonation removals at 900 min: 47.6% TPH and 11.3% aromatics After 9-week incubation, highest biological removals of TPH (25.4%) and aromatics (4.7%) observed in 180- and 0-min ozonated soils, respectively Negligible biological removal of 3.6% TPH and 0.5% aromatics in 900-min ozonated soil during the incubation period 	Oxidant: Ozone (1.4% v/v) <ul style="list-style-type: none"> Initial CFU/g unozonated soil: <ul style="list-style-type: none"> Total heterotrophic bacteria, 1.6×10^8 Hexadecane degraders, 1.3×10^7 Phenanthrene degraders, 1.2×10^6 After ozonation, heterotrophic bacteria CFU decreased by the following orders of magnitude: 0.5 (10-min ozonated soil); 1 (30-min); 2 (60- and 180-min); and 3 (300- and 900-min). Number of hexadecane degraders decreased similarly.

(continued)

Table 7.5. (continued)

Experimental setup	Target contaminants	Contaminant removal	Microbial community observations
			<p>Phenanthrene degraders not detected in soils ozonated ≥ 60 min</p> <ul style="list-style-type: none"> • After 9-week incubation, total heterotrophic and hexadecane-degrading CFU increased by 0.5–1.5 orders of magnitude. Phenanthrene degraders increased by 1.5 and 2.5 orders of magnitude for 10- and 30-min ozonated soils, respectively, and were detected at 8.2×10^5 and 4.2×10^4 CFU/g in 60- and 180-min ozonated soils • DNA-based population estimates were 1–2 orders of magnitude higher • Whole-cell hybridization demonstrated little difference in community composition after 9-week incubation of 300- and 900-min ozonated soil and unozonated control
Fogel and Kerfoot (2004)		Oxidant: Ozone (0.001, 0.01 and 0.03% v/v); H ₂ O ₂ (5%)	
Aerobic microcosms with groundwater from site where ozone and peroxide applied, treated for 30 min	Petroleum hydrocarbons expected in water but not reported	Increase in short-chain (C9–C16) and decrease in long-chain (C18–C36) aliphatic hydrocarbons with ozonation and ozone/peroxide addition	<ul style="list-style-type: none"> • 0.001 and 0.01% ozone in air increased total heterotrophic bacteria numbers by 4–5 and 3–4 orders of magnitude, respectively, over background, with similar increases in hexadecane degraders • 0.03% ozone with or without peroxide appeared toxic, as heterotrophic and hexadecane numbers were below detection limit
Jung et al. (2005)		Oxidant: Ozone (1.4% v/v)	
Ozone applied to soil columns for 0, 10, 30, 60, 180, 300, or	2,600 mg TPH/kg soil	<ul style="list-style-type: none"> • Greatest TPH removal by ozonation (50%) after 900 min but no additional 	<ul style="list-style-type: none"> • Heterotrophic bacteria were reduced from 10^8 to 10^6, 10^5 and 10^4 CFU/g soil after 60, 300 and

(continued)

Table 7.5. (continued)

Experimental setup	Target contaminants	Contaminant removal	Microbial community observations
900 min followed by biodegradation in aerobic beakers		removal after 9-week incubation <ul style="list-style-type: none"> • Greatest overall TPH removal in soil ozonated for 180 min (40% TPH removal) followed by biodegradation of an additional 15% TPH during 9-week incubation 	900 min ozonation, respectively <ul style="list-style-type: none"> • Similar reductions in alkane-degrading bacteria, with reductions from 10^7 to 10^3 CFU/g soil after 900 min of ozonation • Phenanthrene-degrading bacteria decreased from 10^6 CFU/g soil to 10^4 after 30 min ozonation and to below detection limit at ≥ 60 min ozonation • During 9-week incubation, counts of heterotrophic, alkane-degrading and phenanthrene-degrading bacteria increased up to two orders of magnitude, with greatest increases observed in phenanthrene degraders in soils ozonated for 10 min or unozonated
Jung et al. (2008)			Oxidant: Ozone (0.9% v/v)
Ozone applied to soil columns for 0, 30, 90, 180, or 360 min followed by biodegradation in aerobic beakers; seven soils and commercial sand tested	750 mg hexadecane/kg soil	<ul style="list-style-type: none"> • Greatest hexadecane removals in sand (45–80%) over other soils tested (20–40%), with increasing removals at longer ozonation times • After 4-week incubation, additional hexadecane removal but smaller decreases in soils ozonated longer 	<ul style="list-style-type: none"> • Ozonation for 30 min decreased heterotrophic plate counts >87% in all soils • Kill varied with soil texture (soil organic and water content, particle size) • After 4-week incubation, heterotrophic numbers increased inversely proportionally to ozonation time: 1 order of magnitude in soils ozonated for 30 min, minimal change in soils ozonated 360 min
Lute et al. (1998)			Oxidant: Ozone (5–6% v/v)
<ul style="list-style-type: none"> • Soil slurry with continuous ozone application • Soil column with continuous 	3,300 ppm total PAH in slurry 200 ppm total PAH in soil column	<ul style="list-style-type: none"> • 99% removal in slurry within 50 h • 70% removal in column in 10 weeks 	<ul style="list-style-type: none"> • Three and five order of magnitude decreases in slurry heterotrophic plate counts in 1 and 8 h, respectively

(continued)

Table 7.5. (continued)

Experimental setup	Target contaminants	Contaminant removal	Microbial community observations
air flow, ozone applied 15 min every other day			<ul style="list-style-type: none"> PLFA analysis indicated that a diverse microbial community was maintained during the 10-week column operation; 1–2 order magnitude increase in density reported
Martens and Frankenberger (1995)			
		Oxidant: CHP; 0.016 g H ₂ O ₂ and 0.93 mg Fe(II) per g soil	
Microcosms containing soil (with indigenous PAH-degrading microorganisms) from MGP spiked with PAH	400 mg/kg soil of each: Acenaphthene Anthracene Benzo(a)pyrene Chrysene Fluoranthene Fluorene Naphthalene Phenanthrene Pyrene	<ul style="list-style-type: none"> During 56-day incubation, CHP plus biodegradation significantly enhanced mineralization to CO₂ over biodegradation alone of fluorene (35 vs. 13%), phenanthrene (29 vs. 3%), anthracene (24 vs. <1%), and benzo (a)pyrene (17 vs. 2%); mineralization comparable between two treatments for other PAH Treatment with SDS prior to CHP increased % removal of phenanthrene, fluoranthrene and pyrene 38, 39 and 30%, respectively, though chrysene removal was not enhanced 	<ul style="list-style-type: none"> Not reported in this study, but authors mention their previous study (Martens and Frankenberger, 1994) that reported initial decrease in bacterial and fungal populations with CHP application, followed by recovery in 5–7 days
Palmroth et al. (2006)			
		Oxidant: CHP; 0.4 g H ₂ O ₂ per g Fe-rich soil	
CHP in soil columns followed by biodegradation in soil microcosms	4,000 mg PAH/kg soil	<ul style="list-style-type: none"> 44% in 4 days by CHP in fully saturated soil column Subsequent incubation of soil in aerobic microcosms increased removal up to 15% during 16-week incubation, though similar removal (12%) occurred during incubation of unoxidized soil 	In CHP-treated columns: <ul style="list-style-type: none"> Lower viable cell counts Lower activities of microbial extracellular enzymes Higher toxicity of leachate toward <i>Vibrio fischeri</i>
Anaerobic bio			
Bittkau et al. (2004)			
		Oxidant: CHP; 68 mg/L H ₂ O ₂ and 112 mg/L Fe(II) [2 mM each] for MCB oxidation; 34 mg/L H ₂ O ₂ and 56 mg/L Fe(II) [1 mM each] for PLFA analysis	
Anaerobic groundwater microcosms	CHP: 15 mg/L [130 μM] MCB	<ul style="list-style-type: none"> MCB: complete removal within 70 days 	<ul style="list-style-type: none"> Lower viable cell counts and PLFA in CHP-treated than in air-treated

(continued)

Table 7.5. (continued)

Experimental setup	Target contaminants	Contaminant removal	Microbial community observations
	Anaerobic Bio: (MCB removed) 8 mg/L [100 µM] benzene 50 µM each chlorohydroquinone [7 mg/L], hydroquinone [6 mg/L], phenol [5 mg/L], catechol [6 mg/L] and resorcinol [6 mg/L]	<ul style="list-style-type: none"> • Benzene: negligible • Chlorohydroquinone: 68% in 70 days • Hydroquinone: 72% in 70 days • Phenol: 74% in 70 days • Catechol: 66% in 41 days • Resorcinol: 76% in 41 days 	microcosms, though higher than in untreated controls <ul style="list-style-type: none"> • Lower diversity in CHP-treated microcosms than in air-treated or untreated control microcosms, as determined by PLFA

Note: µM - micromolar, DNA - deoxyribonucleic acid, MCB - monochlorobenzene, MGP - manufactured gas plant, PLFA - phospholipid fatty acids, ppm - part(s) per million, SDS - sodium dodecyl sulfate, TPH - total petroleum hydrocarbons.

Several field studies have investigated the impacts of ISCO on microbial populations in the specific context of MNA. No adverse impacts (Gardner et al., 1996) on microbial biomass as measured by aerobic and anaerobic culturing were observed immediately following permanganate application (3–5 wt.%) at a field site. Two weeks after injection of a 0.7% solution of KMnO_4 in a field pilot test, diminished but viable populations of aerobic and anaerobic heterotrophs, nitrate reducers, sulfate reducers, and methanogens were cultured from the soil (Klens et al., 2001). Aerobic heterotroph counts in groundwater increased substantially within 6 months, but no sulfate reducers or methanogens were detected in groundwater samples 3 months after oxidation. Increased biomass without significant changes in diversity as measured by phospholipid analyses was observed in field plots 1 month after permanganate oxidation at Cape Canaveral Air Station (Azadpour-Keeley et al., 2004). Biomass levels decreased during the 12 months after treatment to near pre-oxidation values. Oxidation of lignin and humics was suggested to release bio-available carbon, stimulating growth. Droste et al. (2002) applied a combination of persulfate and permanganate at a field site contaminated with residual DNAPL and aqueous-phase TCE. Enhanced reductive dechlorination of TCE was observed in and downgradient of the injection area during 22 months of post-injection monitoring. Geochemical and phospholipid data suggested that the persulfate stimulated sulfate-reducing bacteria, which did not appear to significantly interfere with post-oxidation biodegradation of TCE. At two field sites receiving potassium and/or sodium permanganate, PLFA analysis indicated significant increases in biomass levels post-oxidation, with complex microbial communities present in wells impacted by permanganate (Luhrs et al., 2006).

MNA was accepted as the final remedy for Site 11 at the Naval Submarine Base (NSB) Kings Bay, Georgia, following CHP application (Maughon et al., 2000). Total chlorinated volatile organic compound (CVOC) concentrations decreased to <100 µg/L (average reduction of 99%) within the target treatment area after 30 days following treatment, and remained there for at least 13 months at the most contaminated monitoring well.

After CHP treatment was applied in 1998–1999 at Naval Air Station (NAS) Pensacola, FL, wastewater treatment plant, samples collected from the low-pH groundwater plume in 2003–2005 indicated biotic and abiotic reductive dechlorination activity (Bradley et al., 2007).

Within a 60 m (197 ft) distance along the groundwater flow path, total chloroethene concentrations decreased by >98% and the makeup of the chloroethene contaminants shifted from 90% TCE to primarily reductive dechlorination daughter products, DCE (50%) and VC (25%). Reductive dechlorination was observed in some, though not all, sediment microcosms incubated for 228 days. Quantitative polymerase chain reaction (qPCR) analysis demonstrated presence of *Dehalococcoides*-like organisms in groundwater, though at lower levels than in water outside of the plume. MNA has been approved as a formal part of the remedy at NAS Pensacola.¹

Permanganate was applied at the Savage Municipal Water Supply Well Site, Milford, New Hampshire, where bioaugmentation was under consideration as a polishing step (Macbeth et al., 2005). Key results from a microbiology investigation at this site are highlighted in the sidebar below and presented in further detail in Appendix E, Section E.4.1. At this site ISCO resulted in increased microbial DNA concentrations but also decreased microbial diversity (measured by genetic analyses) in groundwater samples 1 year after ISCO was implemented. The investigators suggest that while high oxidant concentrations may decrease overall biomass and diversity, as oxidant concentrations decrease below a certain threshold, a few microbial populations are stimulated; as oxidant concentrations decrease further, additional populations are stimulated such that both biomass and diversity increase, and eventually diversity recovers to pre-ISCO levels.

Depending on factors such as effectiveness of the ISCO remedy, remedial action objectives, and site conditions, MNA following ISCO may be sufficient to achieve remediation objectives in a timely manner. However, if MNA is unable to achieve remediation objectives, more aggressive approaches such as EISB (Section 7.2.4) may be required.

7.2.4 Enhanced *In Situ* Bioremediation

Impacts of ISCO on contaminant biodegradability and microbial communities can affect any biologically based treatment, as described above. As summarized below, studies generally indicate that EISB may be successful following ISCO and the cessation of active oxidation.

One potential consideration in coupling ISCO with all EISB remediation methods is that if EISB has been applied to a site prior to ISCO, and ISCO is to be applied within the same TTZ as EISB, then the potential exists for a reaction between the oxidants and any EISB remedial amendments remaining within the TTZ. Many EISB approaches involve the injection of electron donor substrates, such as lactate or emulsified oil, to help enhance the microbial activity of a site. However, these substrates are essentially reductants that may exert a strong demand for an injected oxidant, more so than expected based on an oxidant persistence or oxidant demand test on native media from the TTZ alone. In addition, these substrates may also promote growth of significant biomass, which may also increase the oxidant demand. Thus, residual electron donor or biomass generation in the subsurface may require delivery of additional oxidant to overcome this demand. This must be considered in the ISCO design due to the implications for remediation economics and effectiveness.

¹ Personal communication with M.A. Singletary, Naval Facilities Southeast, Jacksonville, FL, September 25, 2009.

Savage Municipal Water Supply Well Site, Milford, New Hampshire
<p>Setting</p> <p>The Savage Municipal Water Supply Well Site, Operable Unit 1, in Milford, New Hampshire has a small PCE DNAPL source zone that created a larger dissolved PCE plume in groundwater. The source zone had been contained by a slurry wall, but ISCO was selected several years later to provide mass destruction in the vicinity of the DNAPL. It was recognized, however, that polishing following ISCO would be required, and EISB, via reductive dechlorination, was thought likely to be the most appropriate technology for this application. As such, an effort was undertaken to characterize the microbial community structure thoroughly prior to performing ISCO, 1 year after initial ISCO injections (8,500 lb potassium permanganate in two injection wells), and then 1 year after a larger, second round of ISCO injections (24,000 lb potassium permanganate in eight wells; Macbeth et al., 2005; Macbeth, 2006; Weidhaas and Macbeth, 2006). In addition, specific sampling for <i>Dehalococcoides</i> spp. organisms was performed to determine whether bioaugmentation might be required as part of an EISB polishing strategy.</p>
<p>Key Results</p> <ul style="list-style-type: none"> • Between 2003 and 2005, PCE concentrations decreased between slightly less than 90% to over two orders of magnitude in the treatment zone monitoring wells, with final concentrations ranging from 17 to 190 µg/L. • The oxidation–reduction potential (ORP) increased steadily in all of these wells from 2003 to 2004 to 2005, ranging from 889 to 925 mV in 2005. • Dissolved organic carbon (DOC) content was fairly low throughout, but increased slightly from 2003 to 2005. • Microbial diversity as measured by species “richness,” or number of species, was fairly high in baseline samples from all of the wells, though it was somewhat lower in the treatment zone wells, presumably due to the higher PCE concentrations. The species richness dropped dramatically in the treatment zone wells in 2004, and remained at similar levels in 2005. Species richness was fairly constant in all wells outside the treatment zone in all three sampling events. • Microbial community structure and diversity as measured by “evenness,” which represents the extent to which the relative abundance of species is “even” (i.e., similar abundance for various species or predominance of a few species) was similar between treatment zone and downgradient wells in 2003. However, evenness dropped substantially in treatment zone wells in 2004 as the community became dominated by a very small number of species that could tolerate the high permanganate concentrations. The evenness recovered somewhat in treatment zone wells in 2005, and was unchanged in downgradient wells throughout. • Clone library analysis provided similar insights, showing a wide range of bacteria with only distant relationships in downgradient wells, while sequences from the treatment zone in 2004 were mostly very closely related fermentative bacteria (<i>Desulfosporosinus</i>). In 2005, the number and range of genera increased in the treatment zone, though most were still closely related to <i>Clostridia</i>. • Based on these results, a conceptual model for the microbial community dynamics before, during and after permanganate treatment was developed (Macbeth et al., 2005; Macbeth, 2006) and is detailed in Appendix E.4.1.

7.2.4.1 Anaerobic Processes

Use of chemical oxidants at contaminated sites dominated by anaerobic conditions can lead to a significant change in the redox conditions. Many anaerobic microorganisms are extremely sensitive to such changes, but several studies have demonstrated that anaerobic EISB microorganisms may persist in the subsurface during oxidant application and may even be enhanced afterward.

Hrapovic et al. (2005) observed no dechlorination activity following potassium permanganate oxidation when distilled water was fed through columns containing soil from a field site undergoing natural attenuation. The dechlorination activity before oxidation was not determined, therefore the relative impact of oxidation on the dechlorination activity of the native soil

microbes cannot be established. Subsequent bioaugmentation with a culture capable of reductive dechlorination followed by ethanol amendment resulted in eventual resumption of reductive dechlorination activity. One of two columns that received site groundwater containing microbes eventually generated very low levels (average 23 $\mu\text{g/L}$) of reductive dechlorination byproducts.

Sahl et al. (2007) observed a rebound in reductive dechlorination activity of an anaerobic mixed culture following partial permanganate oxidation of pure-phase PCE in one-dimensional (1-D) columns. During oxidation, permanganate was applied to the columns at a range of concentrations and application velocities. After oxidation, columns were fed nutrient medium containing methanol but were not reinoculated. The recovery in activity, sometimes to levels above those achieved prior to oxidation, was observed in all columns despite the prevalence of MnO_2 solids generated by the permanganate reaction. Molecular analysis of dissected columns verified the presence of *Dehalococcoides* microorganisms capable of reductive dechlorination within the columns, indicating that dechlorinating organisms can survive permanganate oxidation and live among MnO_2 solids generated from permanganate reaction.

At a field site where TCE and DCE were almost completely removed by permanganate, molasses or lactate injection used to stimulate reductive dechlorination after permanganate application did not stimulate sufficient microbial activity to remove oxidant-resistant 1,1-dichloroethane (1,1-DCA) (Pac et al., 2004). Dissolved oxygen levels decreased to <0.5 mg/L in application wells, and ORP declined to <150 mV except in one well with residual permanganate. The residual permanganate as well as the short monitoring period (fall application through spring monitoring) may have impacted the lack of 1,1-DCA biodegradation. Conversely, at another field site where TCE levels rebounded after application of 450 gallons (gal) (1,700 L) of 20% sodium permanganate, increasing concentrations of reductive dechlorination products *cis*-DCE and VC were observed following lactate injection (Luhrs et al., 2006).

7.2.4.2 Aerobic Processes

Though aerobic microorganisms are also subject to oxidant effects (Section 7.2.1), they grow under more positive redox conditions than anaerobic microbes and thus may be less inhibited by the redox changes imparted by ISCO. Several microcosm-based studies have investigated the effects of ISCO on biodegradation in aerobic EISB contexts. The results, summarized in Table 7.6, are consistent with those described in other sections, showing lower microbial numbers and greater inhibition of biodegradation with increasing oxidant dose, but with rebound in numbers over time after the oxidant is depleted.

7.3 SURFACTANT/COSOLVENT FLUSHING METHODS

Surfactant and cosolvent flushing are remediation techniques that involve injection of an aqueous surfactant or cosolvent mixture into the subsurface to increase the apparent or real solubility of low solubility contaminants and enhance the mobility of nonaqueous phase liquids (NAPLs). These techniques have traditionally been applied to enhance the efficiency and shorten the timeframe of a contaminant mass removal technology, especially P&T, as more contaminant is removed per volume of water extracted than with groundwater flushing alone. Generally, this approach is targeted at immiscible (NAPL) phase contaminants, especially DNAPLs, as these pose one of the most persistent challenges to conventional mass removal technologies (Lowe et al., 1999; Kavanaugh et al., 2003).

Table 7.6. Summary of Laboratory Studies Investigating Chemical Oxidation Combined with Aerobic Enhanced *In Situ* Bioremediation, Including Microbial Impacts

Experimental setup	Target contaminants	Contaminant removal	Microbial community observations
Bioaugmentation			
Miller et al. (1996) Oxidant: CHP; 0.15–0.36 g H ₂ O ₂ and 2 mg Fe(II) per g soil			
CHP in soil slurry microcosms followed by biodegradation in soil microcosms and leachate microcosms, both inoculated with untreated soil	Soil spiked with 100 mg of the pesticide, pendimethalin/kg soil	<ul style="list-style-type: none"> • 65–99% in 2 days for soils at pH 3–4; <25% for soil at pH 7 • Organic material released by CHP treatment was biodegradable, as measured by optical density of leachate 	<ul style="list-style-type: none"> • No colony growth on tryptic soy agar (TSA) after CHP treatment • Leachate (neutralized to pH 7) stimulated microbial growth, including microbes capable of bioremediation, but decreased microbial diversity, as measured by number of colony types cultured on TSA and <i>Pseudomonas</i> isolation agar
Stehr et al. (2001) Oxidant: Ozone; 1.2% v/v			
Low (0.1%) total organic carbon (TOC) sand and high (3.5%) TOC soil ozonated, soil transferred to aerobic slurry bioreactor and bioaugmented with <i>Sphingomonas yanoikuyae</i> DSM 6900	Soil spiked with 1,000 mg phenanthrene/kg soil	<ul style="list-style-type: none"> • Phenanthrene readily biodegraded in unoxidized sand, with 90% removal in 24 h and 95% removal in 48 h • Ozonation inhibited aerobic biodegradation, with removals of only 50 and 65% in sands receiving 0.188 and 1.214 mg O₃/kg sand, respectively, in 24 h; 95% removal required 96 h in both sands 	<ul style="list-style-type: none"> • Increased inhibition of dehydrogenase activity in <i>Sphingomonas yanoikuyae</i> and <i>Bacillus subtilis</i> with increasing ozone dose, even in the absence of phenanthrene
Biostimulation			
Kastner et al. (2000) Oxidant: CHP (field site received six 1-day batch injections in three wells of 50% H ₂ O ₂ , 50 mg/L FeSO ₄ , pH adjusted with H ₂ SO ₄)			
Aerobic microcosms with groundwater from site where CHP applied	<ul style="list-style-type: none"> • 0.7 mg/L (5 μM) aqueous TCE in control microcosm • 5 mg/L (40 μM) aqueous TCE in test microcosm with groundwater from treated zone 	<ul style="list-style-type: none"> • Insignificant TCE degradation by groundwater methanotrophic enrichments within 140 days, even in untreated control • Phenol (50 mg/L; 0.5 mM) stimulated TCE degradation in control microcosm but not in others; toluene (50 mg/L; 0.5 mM) did not stimulate degradation 	<ul style="list-style-type: none"> • Methane addition stimulated methanotrophs in groundwater from treated zone • No significant differences in microbial direct counts were observed between CHP-treated and untreated control groundwater and soil samples taken 10 months after treatment • The authors suggest that low pH resulting from CHP application inhibited microbial TCE degradation but that

(continued)

Table 7.6. (continued)

Experimental setup	Target contaminants	Contaminant removal	Microbial community observations
			viable aerobic, co-metabolic processes existed post-treatment in areas with a higher pH, though background or control levels of activity were not compared
Ndjou'ou et al. (2006)		Oxidant: CHP; 0.00085–0.017 g H ₂ O ₂ per g soil, with molar ratio H ₂ O ₂ :Fe(III) of 50	
CHP in silt loam slurry reactors	<ul style="list-style-type: none"> • Soil spiked to 200 mg PCE/kg soil • Slurry spiked to 200 mg/L oxalate 	<ul style="list-style-type: none"> • All CHP doses oxidized >95% PCE within 600 min • Aerobic biodegradation of oxalate occurred simultaneously with CHP oxidation of PCE at low CHP doses, but higher CHP doses progressively delayed oxalate metabolism until after PCE oxidation complete • Decomposition of H₂O₂ to oxygen provided oxygen to support oxalate biodegradation, keeping dissolved oxygen (DO) levels relatively constant despite bioconsumption 	<ul style="list-style-type: none"> • Increasing CHP dose progressively decreased log (heterotrophic plate counts)/g soil from 7.5 with no CHP to 6.0 at the highest CHP dose after 600 min • Temporary inactivation of live cells suggested by lag in oxalate degradation at highest CHP doses

Coupling surfactant/cosolvent flushing with ISCO can improve performance, as typically surfactant or cosolvent flushing alone does not achieve complete contaminant removal. Usually some residual contamination remains; therefore, elevated contaminant concentrations may persist despite large mass reductions attained by surfactant/cosolvent flushing (Lowe et al., 1999). Application of ISCO after surfactant/cosolvent flushing may be effective at degrading this residual contamination, making attainment of remediation objectives more likely. Research by Dugan (2008) demonstrates this behavior, as flushing with surfactants removed about 90% of the PCE mass from a relatively homogeneous DNAPL source zone in a 2-D flow cell. The residual DNAPL remaining after the surfactant flush maintained elevated effluent TCE concentrations. Subsequent flushing with permanganate achieved an additional 90% removal of the remaining mass, resulting in a greater than 99% overall contaminant mass reduction.

More recent applications of surfactants have also evaluated their ability to improve *in situ* treatment technologies by making low solubility organic contaminants more available to aqueous treatment reagents (Dugan, 2008; Li, 2004; Lundstedt et al., 2006; Xu et al., 2004). The co-application of an oxidant and surfactants simultaneously may have benefits by enhancing contaminant contact with oxidants. Enhanced solubilization effectively increases the amount of contaminant present in solution that the oxidant may target, and thus may increase the rate and extent of oxidation. This represents a change from traditional surfactant applications as the emphasis shifts to contaminant degradation *in situ*, rather than traditionally

required (and sometimes difficult and expensive) *ex situ* recovery and treatment. Experimentation by Dugan (2008) revealed promise that co-application of surfactants and permanganate could result in extensive depletion of DNAPL mass, though Dugan was unable to exactly quantify the amount of treatment enhancement enabled by the surfactant over the oxidant alone.

For coupled application of ISCO with surfactants to be effective, whether as a sequential mass removal method or as a simultaneous ISCO treatment enhancement, several key factors specific to ISCO/surfactant coupling need to be considered. These include establishing the chemical compatibility of oxidants with surfactants or cosolvents, as well as understanding what benefits may be expected from enhanced solubilization. The published literature provides a basis for several of these mechanisms, though more work would be beneficial to enable more quantitative evaluation of the advantages of ISCO/surfactant coupling, especially with regard to co-application. In the field practice, coupling of ISCO with surfactants has been implemented. For instance, three of the ISCO sites reviewed by Krembs (2008) indicated that they had coupled the two technologies together; all three were applications of co-injection. Undoubtedly more sites have applied this approach but were not included in the review. Because this approach is relatively recent, little information is currently available on the overall long-term effectiveness of this approach, though this knowledge base may grow with time and increasing frequency of application.

7.3.1 Oxidation in the Presence of Surfactants or Cosolvents

Studies investigating the simultaneous use of oxidants and surfactants or cosolvents have generally noted that the enhanced solubilization of hydrophobic contaminants improved the rate and extent of their degradation by oxidants (Dugan, 2008; Li, 2004; Lundstedt et al., 2006; Xu et al., 2004). This provides scientific support for the presumed benefits of simultaneous application. For instance, Zhai et al. (2006) investigated the treatment of PCE by permanganate in the presence of cosolvents. They found contaminant degradation and chloride production rates increased due to the higher contaminant concentrations in solution, despite a slower second-order rate constant for permanganate reaction within a cosolvent. Similarly, Xu et al. (2006) also noted that surfactants applied in conjunction with CHP improved the degradation of a diesel light nonaqueous phase liquid (LNAPL) in soil over treatment with CHP alone. Li (2004) noted apparently higher chloride generation rates in presence of a surfactant than without, when treating DNAPL-phase TCE with permanganate. Collectively, these studies provide evidence of enhanced solubilization increasing the rate of oxidation by permanganate. However, translating the results from these studies (most batch systems) to the field may be difficult. Additional fundamental research in more representative (complex, flow-through) systems is desirable to determine the magnitude of enhanced mass removal that may occur under field conditions.

Not technically surfactants, cyclodextrins are unique polysaccharides that have hydrophobic interiors into which organic contaminants may partition and hydrophilic exteriors that promote their suspension in solution and can bind aqueous iron. If persulfate with iron is used, the activation of persulfate can then occur in a zone close to the contaminant and increase treatment efficiencies and mass transfer from DNAPL compounds. Liang et al. (2007) experimented with the enhancement of persulfate ISCO for DNAPL treatment by coupling persulfate with hydroxypropyl- β -cyclodextrin (HBCD) as an activator and solubility enhancement agent. Cyclodextrins have also been investigated for use in hydrogen peroxide ISCO systems and have also shown promise (Lindsey et al., 2003; Tarr et al., 2002). Liang

and Lee (2008) later investigated HBCD at about 5.5 g/L for treatment of a DNAPL source zone in a 1-D column, and noted that it enhanced the solubility by 47%, which in a 1-D column would also increase the effective DNAPL mass depletion rate by a corresponding amount. The addition of Fe(II) to the mixture had no impact on the ability of HBCD to enhance solubility, indicating that iron and HBCD could be delivered together as an activator.

In contrast, Liang and Lee (2008) noted relatively little difference in persulfate treatment extent in terms of the amount of contaminant degraded in the HBCD system versus an iron-only control system. Instead of injecting persulfate into the column base so that both HBCD and persulfate contacted each other in the DNAPL source zone, Liang and Lee (2008) injected persulfate into a sparging curtain downgradient of the DNAPL source. The activated persulfate oxidation was therefore contained to a zone downgradient of the source and did not directly contact the DNAPL. Furthermore, the high velocity in the column indicated that the contact time between the oxidant and contaminant was only 18 min before it reached the sampling port. Thus, it is difficult to anticipate how treatment effectiveness would change should persulfate, activation aid (iron), and HBCD contact the DNAPL source all at once or in succession as might occur under field conditions. It is unknown if cyclodextrins have been applied under field conditions in conjunction with an oxidant and thus their efficacy for field-scale remediation is still uncertain.

7.3.2 Oxidation Mechanism Shifts in the Presence of Cosolvents

With cosolvents, reaction mechanisms and products may shift by coupling with ISCO. Arndt (1981) reported extensively on oxidation reactions with permanganate in both aqueous and nonaqueous solvents. It is noteworthy that the reported reaction products and pathways of reactions depended not just on the oxidant or contaminant but also on the solvent. This dependence is also evident in the coupling literature between cosolvents and oxidants. For instance, Zhai et al. (2006) noted that the chloride mass balance in treating PCE with permanganate was 100% in aqueous solution, while it was only 70% with either *tert*-butanol or acetone cosolvents, raising the possibility that chlorinated intermediates are formed with the cosolvent that are not formed in the purely aqueous system. Likewise, Lundstedt et al. (2006) evaluated the degradation of PAHs by CHP in the presence and absence of a 33% ethanol solution as a cosolvent. The use of ethanol provided for effective solubilization of PAHs, and the extent of PAH degradation was higher than in a water-CHP only system. However, oxy-PAH byproducts were formed in greater amounts in the cosolvent solution than aqueous solution, possibly indicating a shift in mechanism. Another possibility is that oxy-PAHs may have been degraded in aqueous solutions while competition between the cosolvent and the intermediate for the oxidant inhibited degradation of the intermediate in cosolvent solutions.

7.3.3 Oxidant Compatibility with Surfactants and Cosolvents

Another key interaction that must be considered prior to coupling surfactants or cosolvents with ISCO is the potential for a reaction between the remedial agents. Surfactants and cosolvents are organic compounds, and oxidants may react with them, exerting a nonproductive oxidant demand and also destroying the surfactant. Water flushes are often used to recover residual surfactants and cosolvents after application. If such water flushes have removed most of the residual surfactant or cosolvent before ISCO application (as in an unplanned coupled application), then compatibility may not be of much concern. However, if

surfactant or cosolvent concentrations remain high in the subsurface prior to ISCO, or if ISCO is to be conducted simultaneously with surfactant/cosolvent flushing, then compatibility of the oxidant and surfactant/cosolvent may significantly impact the efficiency of the approach.

Chemical compatibility between some oxidants and some surfactants or cosolvents has been reported in the literature; indeed several ISCO vendors market surfactants/cosolvents compatible with oxidants. Dugan (2008) investigated the chemical compatibility of up to 72 surfactants and 8 cosolvents with potassium permanganate, while Zhai et al. (2006) reported on the compatibility of permanganate with 17 cosolvents. Between both studies, despite screening a large number of surfactants and cosolvents, only a few were reasonably compatible with permanganate. Of the 72 surfactants investigated by Dugan (2008), only eight were found to be sufficiently resistant to permanganate oxidation at high surfactant concentrations (greater than critical micelle concentration [$>CMC$]) that would merit possible consideration for co-application. Of the cosolvents tested by both authors, many of the more biodegradable and environmentally benign cosolvents, such as primary alcohols (e.g., ethanol) or secondary alcohols (e.g., isopropyl alcohol), were noted to be very reactive with permanganate, indicating that they would make for unfavorable couplings, especially for co-application. Only acetone and *tert*-butyl alcohol (TBA) demonstrated sufficient resistance to permanganate oxidation that they could be considered for co-application. Indeed, these compounds are known to be resistant to permanganate oxidation and have been used as solvents in permanganate chemistry applications (Arndt, 1981; Damm et al., 2002; Singh and Lee, 2001). TBA has been injected as a cosolvent (Falta et al., 1999). However, acetone is considered hazardous and therefore an unlikely candidate for subsurface injection (ATSDR, 1994).

With other oxidants such as persulfate, CHP, or ozone, the likelihood for strong chemical compatibility between the oxidant and the surfactant is also questionable. These oxidants generate radicals with non-specific reactivity in contrast to the selective reactivity of permanganate; thus, the likelihood of reaction between the various radicals produced and organic surfactants and cosolvents would seem to be high. Hydroxyl radicals are known to be reactive with primary alcohols (Buxton et al., 1988), and hydrogen peroxide ISCO is known to degrade the permanganate-resistant acetone and TBA (Burbano et al., 2005; Neppolian et al., 2002). With persulfate, TBA may have potential for coupling because TBA is known to scavenge sulfate radicals at a much slower rate than hydroxyl radicals (Anipsitakis and Dionysiou, 2004), but the efficacy of this coupling has not been explicitly investigated. Dugan (2008) evaluated a large series of surfactants coupled with Fe(II)-CHP and noted that many systems generated excessive foam and heat, highlighting the potential for operational challenges to their coupling with CHP. However, despite the potential reactivity of surfactants or cosolvents with these oxidants, their use in conjunction with ISCO is not altogether precluded. Lundstedt et al. (2006) investigated the use of CHP in conjunction with ethanol (33%) as a cosolvent, and noted that enhanced contaminant desorption and degradation occurred. However, reaction efficiencies were reduced, most likely due to competition between the contaminant and the cosolvent for reaction with the oxidant.

7.3.4 Surfactant Production by Oxidation Reactions

Literature suggests that ISCO may also produce surfactant-like reaction intermediates from certain contaminants, which may be exploited as a coupled approach. Ndjou'ou and Cassidy (2006) noted in slurry reactors that the reaction of CHP with fuel hydrocarbons present as LNAPL produced organic intermediates with surfactant-like properties. Initial concentrations of surfactant-like intermediates were very low, but they accumulated in

solution with time to produce concentrations that exceeded the CMC by a factor of 4 and resulted in enhanced solubilization. Provided that oxidant was dosed in excess and sufficient contact time was provided, these surfactant-like intermediates were subsequently degraded along with the petroleum hydrocarbons mobilized within their micelles. Millioli et al. (2003) may have also observed evidence of enhanced solubilization; they targeted LNAPL crude oil in soils with CHP and noted that much of the oil and grease content was suspended and removed via the creation of an emulsion. This finding highlights the possibility of a mechanism that might lead to temporary increases in contaminant concentrations during oxidation even when no surfactant is injected.

Because reports of surfactant generation from ISCO are limited in the literature, the significance of this process in field-scale applications is uncertain. The potential for surfactant production to occur in a subsurface environment is likely closely related to the type of contaminant present, as well as the mass levels present. Given that this effect has not been reported in the extensive knowledge base with ISCO and DNAPL-phase chlorinated solvents (Siegrist et al., 2006), it seems unlikely that oxidation reactions with typical chlorinated solvents may generate these surfactant-like intermediates. However, LNAPLs containing TPH and PAH typically involve mixtures of high molecular weight aliphatic and aromatic hydrocarbons, the oxidation of which would likely result in multiple organic intermediate compounds prior to complete mineralization to carbon dioxide. Thus, it seems that these surfactant-like intermediates are more likely to be formed from petroleum hydrocarbons than other contaminants, although this has yet to be proven.

7.4 ABIOTIC REDUCTION METHODS

Abiotic reduction technologies can be broadly construed to include any remediation technique where a chemical reductant is introduced to the subsurface to degrade a contaminant of concern via a reductive pathway. Reduction reactions can result in dehalogenation of chlorinated or brominated organics, as well as other degradation reactions through the donation of electrons. In this way, *in situ* chemical reduction (ISCR) is much the opposite counterpart to ISCO.

Because abiotic reduction technologies involve the introduction of reductants to the subsurface and a corresponding alteration of the ORP, they have a strong potential to interact with ISCO. Reductants reduce the subsurface ORP while oxidants raise it. If a large amount of reductant is present in the subsurface during an ISCO application, then a large amount of oxidant might be needed to neutralize the reductant and raise the ORP before effective oxidation reactions may occur. Likewise, if ISCR is to be applied after ISCO, injection of large amounts of reductants may be needed to neutralize excess oxidant and reduce the ORP before reduction reactions may occur. Thus, coupling these two technologies within the same target treatment zone may be challenging because in this respect they act in opposition to each other. Further discussion follows regarding the potential coupling with zero-valent iron (ZVI) and other ISCR technologies.

7.4.1 Zero-Valent Iron

The most common form of ISCR is the use of ZVI, in which the oxidation of metallic iron produces electrons that are available for reduction reactions with organic contaminants. ZVI can be delivered in granular form to construct PRBs that may intersect a contaminant plume. It can also be injected as nanoscale ZVI, where the particles are sufficiently small that they may be injected and distributed into permeable formations for source zone treatment.

Relatively little literature has investigated the impact of ISCO on ZVI and vice versa. One study of the direct interaction between ZVI and permanganate ISCO found that the ZVI exerted a significant demand for the permanganate oxidant (Okwi et al., 2005). In addition, they found that the MnO_2 that deposited on the ZVI surfaces as a byproduct of permanganate oxidation effectively deactivated the iron, inhibiting further reductive dechlorination reactions. Thus, a ZVI reactive barrier intercepting a permanganate plume from an ISCO application would be undesirable, as the oxidant would likely be depleted by the PRB, and the PRB might also be deactivated by the oxidant. In the case of nanoscale iron injected within a source zone, again, oxidant demand may be high and the iron may be partially or fully deactivated. Thus, to maintain effectiveness of both permanganate ISCO and ZVI ISCR, it appears that contact between the oxidant and reductant should be avoided.

As for the interaction between ZVI and hydrogen peroxide, no direct research has been reported in the literature. However, based on the literature about hydrogen peroxide catalysis, rapid reaction and oxidant decomposition should probably be anticipated. The oxidation of ZVI produces Fe(II) and Fe(III), both in aqueous solution and as solid hydroxides and oxides. All of these iron species are well known to be catalytically active toward hydrogen peroxide (Fenton, 1894; Haber and Weiss, 1934; Kwan and Voelker, 2003; Li et al., 1999; Teel et al., 2007). These catalytic reactions may produce radicals that could then degrade organic contaminants (Kwan and Voelker, 2003). Thus, the catalytic decomposition of hydrogen peroxide by ZVI and its byproducts may have productive influences on remediation. However, at the same time, the application of ZVI often involves either very large masses of ZVI (e.g., a PRB) or very large surface areas of it (e.g., nanoscale iron), so the catalysis could be rapid and vigorous. This could make oxidant delivery a challenge, and thus have negative implications for ISCO performance, especially in terms of oxidant longevity. Oxygen produced by the decomposition of hydrogen peroxide could also contribute to the oxidation of iron. Presently, it is unknown what, if any, impact hydrogen peroxide ISCO could have on the contaminant degradation activity of the ZVI. Unlike permanganate, there is no solid reaction byproduct to coat the ZVI surface, so it seems unlikely that hydrogen peroxide would deactivate the iron. However, excessive oxidant exposure might deplete ZVI mass, decreasing its longevity.

Likewise, interactions between ZVI and persulfate are not reported. Again, however, ZVI reactions produce dissolved Fe(II) and Fe(III), as well as iron oxides. Fe(II) is well known to activate persulfate reactions (Kolthoff et al., 1951), and Fe(III) is suspected to catalyze reactions (Anipsitakis and Dionysiou, 2004; Block et al., 2004). The catalytic reactivity between solid iron oxides and hydroxide or iron metal is unknown but might also play a role. However, another important effect of persulfate is a potentially large pH drop (Block et al., 2004). Acidic conditions are known to be corrosive to iron metal, and thus persulfate may speed the corrosion of ZVI. As with hydrogen peroxide, the impact of persulfate on ZVI reactivity is unknown. Again, it seems plausible that as no solid reaction product is produced by persulfate reactions, the surface of the ZVI should still have some catalytic activity to it, but excessive reaction with oxidants may deplete ZVI mass or longevity.

7.4.2 Other *In Situ* Chemical Reduction Technologies

Other ISCR technologies are not as common as ZVI but include the use of some aqueous reducing agents to enable similar reactions. Other chemical reductants reported in the literature include dissolved Fe(II), sodium dithionite, and calcium polysulfide (Brown et al., 2006; Chemburkar et al., 2006; Szecsody et al., 2006). These reductants work through mechanisms similar to ZVI whereby the reductant donates electrons to stimulate degradation of an organic

contaminant. Sometimes, the term *in situ* chemical reduction is used to describe a method that includes the addition of electron donor amendments to stimulate microbial anaerobic reductive dechlorination; for the purposes of this document, these technologies are discussed in Section 7.2.4.1 on anaerobic bioremediation.

Very little if any information is available in the literature regarding the interactions between ISCO oxidants and these other reductants, aside from Fe(II). Fe(II) is certainly catalytically active toward hydrogen peroxide and sodium persulfate (Fenton, 1894; Kolthoff et al., 1969) and is often delivered with these oxidants as an activation aid. Thus, any Fe(II) delivered as part of an *in situ* chemical reduction technology would contribute to the catalysis of these oxidants. Reactions between oxidants and the other reductants would probably result in extensive oxidant decomposition and consumption. However, the free radical oxidants may have some potential to generate various free radicals via initiation and propagation reactions, especially with sulfur-based reductants such as dithionite and calcium polysulfide. Buxton et al. (1996) reported that a number of oxy-sulfur radicals may be formed when differing oxidation states of sulfur are present in the same solution, including $\text{SO}_3^{\cdot-}$ and $\text{SO}_5^{\cdot-}$ radicals. However, it is purely speculative at this point whether or not these play any role in the interactions between ISCO oxidants and sulfur-based reductants.

7.5 AIR SPARGING METHODS

Air sparging (AS) is a mass removal technology for volatile contaminants. Its use has been extensive at ISCO sites, generally having been applied prior to ISCO to remove source zone contamination (Krembs, 2008). However, despite this extensive prevalence of use at ISCO sites, limited literature is available on interactions between ISCO and AS. Siegal et al. (2009) reported enhanced distribution of persulfate, increased dissolution of LNAPL, and decreased concentrations of BTEX, petroleum hydrocarbons, acetone and *cis*-DCE with the addition of AS at Edwards Air Force Base, CA. Decreased contaminant concentrations were observed despite the fact that the persulfate was not activated when AS was added, due to insufficient sodium hydroxide (NaOH) levels at a distance from the chemical injection well. Beyond the interactions described in the above report, the authors of this chapter can only speculate about general information regarding site-specific considerations or interactions between these two technologies, due to limited additional published literature. For example, prior installation of AS equipment may offer an economic benefit to ozone-based ISCO, as infrastructure for ozone sparging and vadose zone emissions capture would already be in place. Residual air in the saturated zone may impact subsurface permeability and oxidant distribution, or AS may stimulate aerobic biological activity and thus affect permeability and oxidant demand. However, the significance of any of these potential processes is difficult to assess given the lack of literature describing direct interactions between ISCO and AS.

7.6 THERMAL METHODS

Thermal remediation methods involve the heating of the subsurface to induce a number of physical and chemical processes that allow for the removal or degradation of organic contaminants. The addition of heat for thermal remediation is generally achieved with one of three methods: steam injection, electrical resistance heating, or thermal conductive heating. In general, higher temperatures increase the rate and magnitude of a number of physiochemical processes, including contaminant solubilization, volatilization, desorption, thermal decomposition, oxidation (with atmospheric oxygen and oxidants), hydrolysis, and others (USEPA, 2004). With thermal remediation, contaminant removal may occur via physical extraction, such as with

soil vapor extraction (SVE), or contaminants may be degraded by the acceleration of aforementioned chemical processes. Temperature increases can be quite high, more than 500°C in some cases (USEPA, 2004). While thermal remediation is a very aggressive remediation method that is often capable of meeting remediation goals, coupling with ISCO may offer some benefits. With thermal remediation, a considerable expense is often the thermal energy required to increase temperatures in the subsurface. Some contaminants, such as semi-volatile organic contaminants (SVOCs), may require very high temperatures to volatilize or degrade and thus necessitate high-energy inputs to attain effective treatment with thermal remediation. However, because coupling with oxidants introduces additional chemical degradation mechanisms in these systems, the amount of heating required to attain effective degradation might be reduced. Thus, coupling of ISCO with thermal remediation may result in some cost savings or better treatment effectiveness. Likewise, some contaminants that are resistant to oxidation by ISCO at ambient temperatures may be more readily degradable by oxidants at elevated temperatures. Thus, ISCO may be enhanced by thermal remediation, and the two technologies may have synergistic benefits.

However, several key considerations need to be made prior to coupling ISCO with thermal remediation. Very little published literature is available regarding direct coupling of ISCO with thermal remediation, especially in the field. For instance, of the 242 ISCO case studies identified by Krembs (2008), none reported coupling with thermal remediation. Heat may be used to activate persulfate (Huang et al., 2005), so the combination of persulfate with thermal remediation seems obvious; however, evaluation of the effectiveness of such coupling has been limited (Waldemer et al., 2007). Many studies have, however, evaluated the impact of temperature on chemical reaction kinetics and mechanisms. Chemical reaction rates increase as temperature increases, typically obeying the Arrhenius relationship (refer to Chapters 2–5).

With ISCO systems, the oxidation reactions may vary in complexity from comparatively simple direct reaction with permanganate to complex chain reactions with hydrogen peroxide and persulfate. Because chain reactions represent a series of simultaneous reactions, it can be difficult to predict the impact of an increase in temperature on reaction efficiency because different reactions in the chain may accelerate at different rates depending on their activation energy. For instance, if competing side reactions accelerate more with temperature than contaminant degradation reactions, then either contaminant degradation or oxidant efficiency might decrease as temperature increases. Likewise, if a contaminant is very resistant to oxidation at low temperatures, increasing temperature might increase the degradation rate considerably. A general acceleration of kinetics may be expected independent of which oxidant is used. However, with persulfate, which is slow to react at ambient temperature unless activated, heat may catalyze the oxidant to produce free radicals (Peyton, 1993), which means that temperature increases with persulfate may result in larger performance enhancements than with other oxidants.

The coupling of ISCO with thermal remediation also allows ISCO to gain from the benefits of thermal remediation mechanisms. For instance, with thermal remediation, hydrolysis reactions (reaction with water) accelerate with some contaminants to the point that contaminant concentrations are significantly reduced. This may result in rapid degradation of some contaminants, such as chlorinated ethanes (Jeffers et al., 1989), which tend to be resistant to oxidation. However, the hydrolysis reactions of some of these contaminants may yield chlorinated intermediates, so the presence of an oxidant may promote contaminant mineralization by degrading intermediate compounds.

However, a potential downside to coupling with thermal remediation is that other deleterious processes involving the oxidant may also increase in rate. For example, with free radical oxidants, catalysis at elevated temperature may be so strong that oxidant decomposition is

rapid, limiting oxidant distribution. Furthermore, propagation reactions may become excessive, reducing reaction efficiency. Nonetheless, combining the physiochemical processes of thermal remediation with ISCO has potential to strongly improve treatment extent and effectiveness.

7.7 FIELD APPLICATIONS OF COMBINED APPROACHES

While numerous field sites have applied combined approaches (evidenced in Tables 7.1 and 7.2), few sites have collected sufficient data to provide insight into the fundamental interactions occurring at the field scale. Table 7.2 indicates that MNA and EISB have been the most common technologies applied as post-ISCO polishing technologies in the field. In addition, as noted in Section 7.2, coupling MNA and EISB with ISCO has also received the most attention in laboratory research to date. Three field applications of ISCO and its interactions with other remediation technologies and approaches are presented in Appendix E, Section 4. One application, which is highlighted in the sidebar presented in Section 7.2, included a rigorous evaluation of the impacts of ISCO on the microbial community in the field (Appendix E, Section E.4.1). As part of this application, a hypothesized conceptual model was developed that was consistent with the field application as well as with the other studies summarized in Section 7.2. In addition, two field applications that demonstrate the versatility of ISCO in combined approaches are presented in Appendix E: one study demonstrates the utility of increased temperatures and pressures associated with CHP to enhance product recovery and the second describes sequential application of CHP and permanganate.

7.8 SUMMARY

Coupling different remediation technologies and approaches together can improve the probability of meeting remediation objectives, especially at sites with unique challenges or aggressive cleanup goals. ISCO is compatible with a number of other remediation technologies and approaches, including bioremediation, MNA, and other active *in situ* remediation methods. However, to optimize the performance of ISCO and the combined remedy, careful consideration of potential interactions is recommended prior to implementation. Though oxidants have the potential to inhibit and temporarily disrupt subsurface biological processes, these effects are typically transient and activity rebounds with time. In some cases, bioremediation and MNA may actually be enhanced by ISCO as the oxidant may add terminal electron acceptors or partially oxidize contaminants making them more amenable to biodegradation. Interactions of ISCO with other remediation technologies are more oxidant- and technology-specific and are, in general, less investigated.

Based on the literature documenting fundamental interactions between ISCO and other remediation techniques, as well as evidence from field applications, ISCO has demonstrated compatibility for coupling with enhanced aerobic and anaerobic bioremediation, MNA, and surfactant/cosolvent flushing. ISCO also has potential for coupling with AS, *in situ* chemical reduction, and thermal remediation. Pretreatment with ISCO to reduce mass, co-treatment with ISCO and amendments such as surfactants to enhance treatment effectiveness, and/or post-treatment with ISCO to polish residual contaminants may increase the likelihood of meeting treatment goals, reducing treatment times, and reducing treatment costs. Treatment of contaminants by ISCO in conjunction with other remediation techniques should therefore be proactively considered at all sites except those relatively few sites where ISCO is clearly capable of achieving remediation goals in a cost-effective manner as a standalone remedy.

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CHAPTER 8

EVALUATION OF ISCO FIELD APPLICATIONS AND PERFORMANCE

Friedrich J. Krembs,¹ Wilson S. Clayton¹ and Michael C. Marley²

¹Aquifer Solutions, Inc., Evergreen, CO 80439, USA; ²XDD, Stratham, NH 03885, USA

Scope

Analysis of field-scale *in situ* chemical oxidation (ISCO) case studies to evaluate site conditions and design parameters affecting performance.

Key Concepts

- ISCO has been applied to many different types of sites, at a wide range of project scales, and using a variety of design approaches.
- Most projects attempted to remediate volatile organic compounds (VOCs), especially chlorinated ethenes.
- The majority of applications were at sites where ISCO was used to treat permeable, unconsolidated media, though there were also applications in impermeable unconsolidated media and fractured rock.
- Half of the applications met the goals specified for the ISCO project. The success rate was highly correlated with the stringency of the goals attempted. Very few sites were successful in meeting maximum contaminant levels (MCLs); No sites with known or suspected dense nonaqueous phase liquid (DNAPL) met MCLs.
- ISCO has been more successful treating fuel-related compounds than chlorinated compounds.
- Median project cost was \$220,000, and the median unit cost was \$94 per cubic yard treated. Project scale, the presence of DNAPL, and delivery method appeared to directly influence these costs.
- No lasting reductions in microbial activity were noted among the 15 case studies that monitored microbial populations.
- Half of the projects that monitored aqueous phase metals concentrations noted transient increases. The duration and severity of these increases was highly site specific. Only two sites reported off-site impacts; these two used constant injection systems, and the off-site impacts abated after injection system modification.

8.1 INTRODUCTION

This chapter presents the methods and results of the compilation and analysis of a database of field applications of *in situ* chemical oxidation (ISCO) (case studies). The case study database preparation and analysis was performed as part of Environmental Security Technology Certification Program (ESTCP) Project ER-0623, and is presented in Krembs (2008) and in Siegrist et al. (2010).

The ISCO case study database was prepared to enable use of information from past field-scale ISCO projects to examine when this remediation technique was most successful, identify inherent limitations of the technology, and determine what system designs seemed to be most effective. This analysis considered the situations in which ISCO was performed, the methods through which it was implemented, and the results achieved. This work was carried out in a systematic fashion to record relevant data for each case study in a way that was consistent and allowed meaningful comparisons between case studies. The final goal was to examine the case studies collectively and provide an unbiased assessment of what results ISCO could reasonably be expected to achieve depending on site and design conditions. The case study data reported in this chapter span projects that were completed between 1995 and 2007, including some of the first ISCO projects implemented. The state of the practice advanced considerably during this period. This caveat should be kept in mind as some of the projects may have used ISCO in a manner that is not consistent with what would currently be considered best practices.

In order to be as comprehensive as possible, the database included data from as many field projects as possible. The sites included had differing levels of quality assurance, overall design quality, and monitoring approaches. For example, at many sites the ISCO treatment goal was a reduction in the aqueous phase concentration of contaminants of concern (COCs) and samples of aquifer solids were not analyzed. This is a limitation that may have prevented conclusions regarding COC mass reduction at many sites in the database. Despite the technical limitations in evaluating data from ISCO field projects, the compilation and analysis of a large number of projects provides a representative overview of the state of industry practice and ISCO performance achieved during the period from 1995 to 2007.

8.2 PREVIOUS CASE STUDY REVIEWS

Numerous case study reviews have been conducted on environmental remediation at field sites. Several previous case study reviews have focused on ISCO, or contained a significant number of ISCO case studies. Attempts were made to leverage these earlier works by including their findings within the database and also following up with the site contacts when such information was available. The methods used in quantitative analyses and metrics developed by these case study authors were also examined, and incorporated to varying degrees within the database. These case study documents are summarized in Table 8.1, and discussed further below.

Table 8.1. Summary of Prior Case Study Reviews

Name	Author	Year	No. of sites	Type	Comments
<i>In situ</i> remediation technology: <i>in situ</i> chemical oxidation	USEPA	1998	14	D	Focused exclusively on ISCO case studies and showed examples of its use.
Technology status review: <i>in situ</i> oxidation	ESTCP	1999	42	B	Focused exclusively on ISCO and included quantitative analysis, e.g., the percentage of sites that were successful versus those that were not and total project costs.
Technical and regulatory guidance for <i>in situ</i> chemical oxidation of contaminated soil and groundwater	ITRC	2001	8	D	Used case studies as supporting appendix to ISCO guidance document.

(continued)

Table 8.1. (continued)

Name	Author	Year	No. of sites	Type	Comments
Assessing the feasibility of DNAPL source zone remediation: review of case studies	Geosyntec Consultants, Inc.	2004	28	B	Focused on DNAPL source zone remediation including ISCO and other technologies. Performed quantitative analyses of results.
DNAPL remediation: selected projects approaching regulatory closure	USEPA	2004	4	D	Examined selected case studies of DNAPL sites at or near regulatory closure, including what remediation technologies were used as well as regulatory framework.
Technical and regulatory guidance for <i>in situ</i> chemical oxidation of contaminated soil and groundwater (2nd ed)	ITRC	2005	14	D	Used case studies as supporting appendix to ISCO guidance document.
Analysis of DNAPL source-depletion costs at 36 sites	McDade et al.	2005	13	B	Examined remediation cost data for 36 DNAPL sites, including ISCO as well as other technologies.
Performance of DNAPL source depletion technologies at 59 chlorinated solvent impacted sites	McGuire et al.	2006	23	B	Examined remediation performance at 59 DNAPL sites, including ISCO and other technologies. Developed numerical metrics to assess success and rebound. Companion paper to McDade et al. (2005).

Notes: No. of Sites - number of ISCO case studies included in case study review, DNAPL - dense nonaqueous phase liquid, D - demonstration type case study review, which generally use a relatively small number of examples to demonstrate that at these few sites a given result has been achieved (e.g., some DNAPL sites can approach regulatory closure), B - broad-scale type case study review, which generally use a relatively large sample size and statistical analysis to examine trends (e.g., among DNAPL source depletion sites, average costs have been this). The State of Colorado Division of Oil and Public Safety's *Petroleum Hydrocarbon Remediation by In-situ Chemical Oxidation at Colorado Sites* (2007) is another useful ISCO case study document, but it was unpublished at the time the data was collected for this work.

The case study documents listed in Table 8.1 were reviewed to obtain information on case study data collection and analysis methods and as a means of populating an updated ISCO database from existing ISCO case studies. This review provided insights into what project parameters to consider, metrics to assess performance, and fruitful data collection methods. Specifically, the broad-scale analyses (ESTCP, 1999; Geosyntec Consultants Inc., 2004; McDade et al., 2005; McGuire et al., 2006) showed the merits of attempting to gather a relatively large dataset and performing statistical analyses to examine trends. These case study reviews also demonstrated the need to develop meaningful metrics with which to assess the case studies and also the requirement that these be calculated or analyzed in a consistent manner. Section 8.4 describes the metrics used to assess case study data.

8.3 DEVELOPMENT OF AN ISCO CASE STUDY DATABASE

This section presents an overview of the methods used in the preparation of the ISCO case study database, including conceptual design of the database, definitions of key parameters, data collection methods, and normalization of the data into a consistent format through treatment and reduction. Finally, this section addresses some limitations of the methods that had to be employed. Additional details on methods and definitions may be found in Krembs (2008).

8.3.1 Key Database Parameter Definitions

The definitions of several of the parameters developed during the database design are discussed briefly here because they will be featured prominently in later sections where the results are presented. These include classification systems developed for site geology, COC groups, project goals, and types of treatability studies, as well as calculations of the volume of the target treatment zone (TTZ), number of pore volumes of fluid delivered, the oxidant mass loading rate (or oxidant dose), percent reduction of COC concentration, and whether or not contaminant rebound occurred.

8.3.1.1 Site Geology

Each site was assigned to a Geology Group A through F, based on the subsurface geologic conditions, including permeability, heterogeneity, and consolidation of the geologic media (ESTCP, 2007 after NRC, 2004). The boundary between permeable and impermeable unconsolidated media is reported as a saturated hydraulic conductivity (K) of greater than or less than 10^{-5} cm/s (0.028 ft/day), respectively. For unconsolidated media, the boundary between heterogeneous and homogenous material is a range of hydraulic conductivity (maximum/minimum) of greater than or less than 1,000, respectively. Note that the maximum and minimum hydraulic conductivity values used to assess heterogeneity are those that are present in a particular stratum, even if the stratum is too thin to have its hydraulic conductivity measured directly in the field. For example, a site underlain by sand with intermittent clay stringers would be considered heterogeneous even if the results of slug testing in wells with 10-ft screens did not differ by a factor of 1,000. The consolidated (rock) material is subdivided based on the matrix porosity, which is inferred from the description of the rock type in project reports rather than a reported porosity value. A list of the six Geology Groups is shown in Table 8.2.

Table 8.2. Hydrogeology Characteristics for the Site Groups

Site group	Permeability	Morphology
Group A	Permeable ($K > 10^{-5}$ cm/s)	Homogeneous ($K_{\max}/K_{\min} < 1,000$)
Group B	Impermeable ($K < 10^{-5}$ cm/s)	Homogeneous ($K_{\max}/K_{\min} < 1,000$)
Group C	Permeable ($K > 10^{-5}$ cm/s)	Heterogeneous ($K_{\max}/K_{\min} > 1,000$)
Group D	Impermeable ($K < 10^{-5}$ cm/s)	Heterogeneous ($K_{\max}/K_{\min} > 1,000$)
Group E	Consolidated material with low matrix porosity	Generally igneous and metamorphic rocks
Group F	Consolidated material with high matrix porosity	Generally sedimentary rocks

Sites were assigned to the above groupings based on the TTZ the ISCO system was applied to. For example, a site underlain by a thick deposit of clay with a 1-ft thick sand aquifer overlying bedrock would be assigned to Group C if the sand layer bounded by clay (above) and rock (below) was the zone to be treated during ISCO application. The site would not be assigned to Group A because of the likely interaction between the permeable sand comprising the bulk of the TTZ and the less permeable materials above and below. It would not be assigned to Group D because the majority of the TTZ is permeable even though the bulk of the site's subsurface geologic media is impermeable.

8.3.1.2 Oxidants

The oxidants used during ISCO remediation projects were placed into six groups based on the oxidizing agent used:

- Permanganate (MnO_4^-), including potassium and sodium forms
- Catalyzed hydrogen peroxide (CHP) (hydrogen peroxide [H_2O_2] with ferrous iron (Fe (II)) or Fe(II)-chelates), also known as modified Fenton's reagent
- Ozone (O_3)
- Persulfate ($\text{S}_2\text{O}_8^{2-}$)
- Percarbonate (e.g., $[\text{Na}_2\text{CO}_3]_2 \cdot 3\text{H}_2\text{O}_2$)
- Peroxone, ozone with hydrogen peroxide catalyst

The activator was also recorded for those oxidants that require activation.

8.3.1.3 COC Groups

The major COCs present at the sites were recorded in the database, as both broad classes of COCs (such as volatile organic compounds [VOCs]), as well as specific compounds (such as benzene). These variables were not mutually exclusive, so if multiple contaminants were present at a site, this information was captured in the database. The maximum concentrations of individual COCs in groundwater and subsurface solids (when available) were also recorded.

8.3.1.4 Treatability Studies

Laboratory-scale treatability studies conducted during design of an ISCO system were placed into two distinct groups: batch studies (e.g., neat chemistry studies, slurry reactors); and transport studies (e.g., columns, tanks). Projects that were referred to as treatability studies but were conducted at the field-scale were classified as pilot studies, which were analyzed separately from laboratory treatability studies as defined above.

The type of information that a treatability study produced was also recorded in the database; brief descriptions are listed in Table 8.3. In many cases, a treatability study provided information that fit into more than one category; for this reason, the five categories in Table 8.3 are not mutually exclusive.

8.3.1.5 Project Goals

Five general types of goals were attempted by the projects in the case study review. These goals are identified in Table 8.4, listed from most to least stringent. Goals were important to include in the database because they provide the context against which success and failure were judged for each of the projects.

Table 8.3. Types of Treatability Studies

Type of treatability study	Description
COC degradation	The study demonstrated that the site's COCs could be degraded by ISCO oxidant(s)
Optimization	The study examined multiple oxidant and/or activator concentrations to determine ideal ISCO chemistry conditions for field-scale application
Secondary groundwater impacts	The study evaluated the potential for adverse impacts to secondary groundwater standards (e.g., mobilization of metals)
Natural activators/buffers	The study evaluated whether naturally occurring minerals (most commonly iron) could activate ISCO reagents without the addition of other activators. Also included in this group were studies that evaluated the presence of naturally occurring minerals (e.g., carbonates) that could hinder the ability to modify the subsurface pH during ISCO
Natural oxidant demand (NOD)/soil oxidant demand (SOD) ^a	The study quantified the degree to which the subsurface media would consume oxidants. This group of studies included those performed on either contaminated or uncontaminated media, and also both kinetic studies in which the laboratory measured oxidant concentrations versus time and ultimate demand studies in which the laboratory measured the concentration of oxidant remaining after a predetermined amount of time

^aNOD is used in this chapter though the two terms are generally used interchangeably.

Table 8.4. Remediation Goals in the Database

Goal of remediation	Description
Meet maximum contaminant levels (MCLs)	The project team attempted to meet the most stringent regulatory groundwater criteria for COC concentrations
Meet alternative cleanup levels (ACLs)	The project team attempted to meet ACLs in groundwater. ACLs are a numerical concentration to be met that are by definition higher than MCLs. Their use was often associated with a site-specific risk evaluation and/or a regulatory framework in which low-yield aquifers are not required to meet MCLs
Reduce mass/concentration by predetermined percent	A set percent reduction in COC mass or concentration was targeted prior to remediation
Reduce mass/concentration/time to cleanup	This goal differs from the above in that there was not a predetermined numerical percent reduction that was to be met, but rather the goal was just to generally reduce contaminant mass and/or concentration, thereby reducing the time to cleanup
Evaluate effectiveness or optimize future work	This goal is most common in pilot studies, and includes a field-scale evaluation of effectiveness as well as remedial design analysis, such as well spacing, oxidant persistence, etc.

8.3.1.6 Design Parameters

The database was designed to capture the complicated design of a remediation system that was tailored to site-specific conditions through the use of several parameters that would allow comparison between diverse ISCO projects. For this reason, metrics were defined to

calculate the values of these parameters in a systematic, meaningful, and consistent way that would describe the data under a host of different circumstances. Explanations of these ISCO design metrics are listed below. The metrics can be visualized using the schematic diagram presented in Figure 8.1. This diagram shows a direct push rig delivering reagents (e.g., teal color) to the subsurface below the site. The distance the oxidant has traveled from the injection point is the radius of influence (ROI). Each of the cylinders is the zone of influence of one particular injection point. Collectively, these overlapping cylinders define the TTZ, shown with the dashed lines.

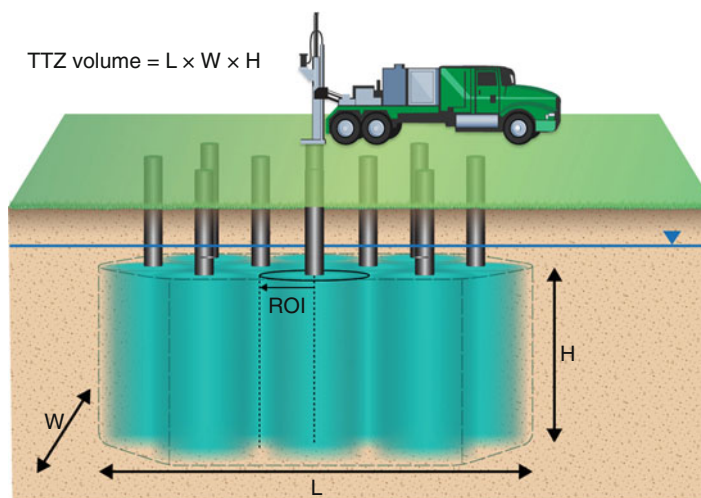


Figure 8.1. Schematic drawing of an idealized representation of oxidant injection. The oxidant is shown traveling an even distance in all horizontal directions from the injection point. Due to variations in subsurface geology, the distribution of oxidants is likely never this uniform in field applications.

Number of Pore Volumes Delivered

The term “number of pore volumes” generally refers to a dimensionless number that relates the volume of solution introduced during remediation to a volume of pore space in a given volume of geologic media. In the case of the database, the ISCO design’s number of pore volumes is calculated as:

$$\# \text{ Pore Volumes } [-] = \frac{\text{Volume of Oxidant Injected } [L^3]}{(\text{TTZ Volume } [L^3])(\text{porosity } [-])} \quad (\text{Eq. 8.1})$$

where [L] = length; [-] = dimensionless, and where the volume of oxidant injected includes only solutions that contain the oxidant, either with or without a catalyst. Catalysts and pH adjusters are not included in the calculation unless they are injected simultaneously with the oxidant. The TTZ, when not stated explicitly in the source document, is defined in areal extent as the outer edge of the injection location array with the design ROI considered in estimating the lateral extent of the TTZ (the hexagonal shape surrounding the ten ovals in Figure 8.1). The TTZ volume is calculated from the TTZ aerial extent by multiplying the thickness of the interval over which oxidant is injected (see Figure 8.1). The injection solution

is assumed to flow horizontally from the injection point as hydraulic conductivity is generally considerably greater in the horizontal direction than the vertical direction (Freeze and Cherry, 1979; Cleary, 2004). When not given in the source text, the porosity is assumed to be 0.35. While an assumed porosity of 0.35 may not be correct in all cases, a total range of variation between 0.1 (glacial till) and 0.6 (clay) is the maximum reported for most unconsolidated media (Fetter, 2001). The number of pore volumes calculated in the database vary by over four orders of magnitude.

Oxidant Loading Rate

This parameter is a ratio of the mass of the oxidant injected to the total mass of geologic media in the TTZ and is also referred to as the oxidant dosing or oxidant dose. This value is calculated by:

$$\text{Oxidant Loading Rate [g/kg]} = \frac{\text{Mass of Oxidant Injected [m]}}{(\text{Volume TTZ [L}^3\text{)}) (\text{Bulk Density [m/L}^3\text{)])} \quad (\text{Eq. 8.2})$$

where [L] = length, [m] = mass.

The units for oxidant loading rate (grams [g] oxidant/kilogram [kg] bulk subsurface media), based on industry standards, allow easier comparison with total organic carbon (TOC) and NOD during design analysis. When permanganate was used as the oxidant, the oxidant loading rate is calculated based on the mass of permanganate anion introduced.

8.3.1.7 Percent Reduction in Maximum Groundwater Concentration

Percent change is calculated in the database (for this and other metrics) as:

$$\text{Percent Change [-]} = \frac{\text{Max. Conc. Before [m/L}^3\text{]} - \text{Max. Conc. After [m/L}^3\text{]}}{\text{Max. Conc. Before [m/L}^3\text{]}} \quad (\text{Eq. 8.3})$$

The percent change in maximum values was calculated based upon data collected within the TTZ before the start of ISCO compared to data collected within the TTZ collected within a period of 1 year after the end of the last oxidant injection during ISCO implementation. The post-ISCO period of 1 year was selected to allow the oxidant to become depleted and the subsurface contaminant phase distribution to re-equilibrate. Therefore, the metric was designed so that the percent change calculations would reflect a rebound effect if any occurred. The post-ISCO monitoring period was also kept relatively short to avoid influences of any non-ISCO processes, such as other remediation technologies being used at the site. This calculation may be based on the same single location before and after ISCO (e.g., a persistent hot spot) or on two different sampling locations (e.g., the highest reported concentration after ISCO was not at the same location as before ISCO).

8.3.1.8 Cost

Total cost refers to the price of the remediation; these values were intended to be as inclusive as possible (design, implementation, and performance monitoring phases). The cost values do not include costs for site characterization, which is required for use with any remediation technology. These data should be used with caution, as there was likely significant variation in what costs were included within a reported total cost (e.g., well installation or performance monitoring omitted). Unit cost is the total cost divided by the volume of the TTZ.

8.3.1.9 Coupling

Coupling refers to the use of multiple remediation technologies, the premise being that two technologies could achieve a synergy or cost savings that each on their own could not. Coupling of ISCO with other technologies is described in detail in Chapter 7.

As it applies to the case study analysis, coupling means that another remediation technology was applied to treat the same source or plume at a particular site. This included both spatial and temporal coupling. An example of spatial coupling is using soil vapor extraction (SVE) in the vadose zone and ISCO in the saturated zone. Examples of temporal coupling are air sparging followed by ISCO treatment in the same target treatment zone, or of ISCO treatment of a source zone followed by monitored natural attenuation (MNA) of the remaining contaminants.

8.3.1.10 Rebound

Rebound represents an initial decrease in groundwater COC concentrations immediately after site remediation followed by an increase in groundwater COC concentrations during the post-treatment monitoring period. The issue of contaminant rebound has been a perceived performance deficiency associated with the use of ISCO to remediate groundwater because it indicates that only a partial treatment has been achieved. However, rebound is an expected aspect of *in situ* treatments that function predominantly within the aqueous phase, including ISCO, as well as bioremediation, chemical reduction, and others. In many instances, the occurrence of rebound may reflect an inadequate ISCO design for the site conditions or treatment goals, or it may indicate that further ISCO treatment applications are needed to achieve the treatment goals.

Rebound can occur when oxidants degrade the COCs that are present in the aqueous phase but do not entirely degrade contaminants that are present in the sorbed, nonaqueous phase liquid (NAPL), or inaccessible aqueous phases. Once the oxidant is depleted, any remaining sorbed or NAPL phase COCs can re-equilibrate with the groundwater, resulting in an increase in aqueous phase contamination observed during the post-ISCO monitoring period. Another potential mechanism for contaminant rebound is back-diffusion from low permeability media that were not completely treated during ISCO implementation. A third mechanism is incomplete delineation of the source zone resulting in ISCO applications not targeting the source zone as intended. Increases in contaminant concentrations may also occur as the result of an influx of contaminated groundwater from untreated upgradient locations at the site. This type of concentration increase could happen with any *in situ* remediation technology if it is not successfully applied to the entire contaminated zone and is therefore not considered rebound as used in this project; the purpose here is to examine the ISCO-specific incidence of rebound.

Rebound in groundwater COC concentrations does not directly reflect changes in total COC mass in the TTZ. For example, if DNAPL or sorbed COC mass is partially destroyed, then the change in groundwater COC concentrations may not be reduced proportionally. For this reason, if only aqueous phase COC concentrations are measured (as were most often the case in the ISCO case studies evaluated), overall COC mass reductions cannot be readily assessed. This is an inherent limitation with a majority of the project case studies included in the database.

Incidence of rebound should not necessarily be equated with failure of an ISCO project. Rebound has the positive attributes of marking the transfer of contaminants to the more treatable aqueous phase and can also help locate previously unknown areas of NAPL or high sorbed-phase concentrations. Rebound is included in the database to allow those considering

ISCO to have a fair assessment of the likelihood that contaminant concentrations in groundwater within the TTZ may increase to a degree during the post-ISCO monitoring period. However, in instances when rebound is observed at an individual site, project teams are strongly urged to consider the likely physical mechanism(s) that may be occurring and how such mechanisms would respond to additional treatments. For example, if rebound occurs at a site due to incomplete characterization of the COCs in the TTZ, then repeated injections at the same location will likely not result in the desired reductions in COC concentration.

Now that rebound as it is used in this context has been defined, the metric through which it is evaluated can be described. An increase in post-ISCO COC concentrations must be placed in the appropriate context when considering its importance. For example, a post-ISCO increase from 0.5 to 5.5 µg/L represents a 1,000% increase during that period. However, the relative importance of this increase will vary depending on what the MCL is and also if the initial concentrations were 10 or 1,000 µg/L. For this reason, the rebound metric used in this study will compare post-ISCO increases to pre-ISCO baseline values; this is a departure from previous case study works. GeoSyntec (2004) left the definition of rebound up to those who responded to their survey. McGuire et al. (2006) only examined concentration changes in the post-remediation monitoring period and stated that rebound occurred when there was an increase of 25% or more in the second half of the post-treatment monitoring period relative to the first half regardless of pretreatment concentrations. McGuire et al. (2006) also examined only parent compounds and omitted degradation products. In this study, rebound is said to occur at a monitoring location if post-ISCO concentrations increase greater than 25% relative to baseline values, or if the inequality below holds:

$$\frac{\text{Most Recent Post ISCO} - \text{Lowest Post ISCO}}{\text{Baseline}} \geq 0.25 \quad (\text{Eq. 8.4})$$

“Most Recent Post ISCO” is the most recent (closest to present day) analytical result collected within 1 year after the completion of oxidant delivery. “Lowest Post ISCO” is the lowest recorded value in the post-ISCO monitoring period. In the event that concentrations continually decline at a monitoring location after ISCO, then rebound clearly did not occur; the most recent and lowest concentration would be the same, and the above inequality would not hold. “Baseline” values are ideally an arithmetic mean of all sampling results at that location collected within the year prior to ISCO’s application unless a temporal trend was observed or if only a single value was available.

In order to perform an evaluation of rebound using the above technique, at least 1 year of post-ISCO performance monitoring data collected in three or more sampling events is required. This amount of time is necessary to allow the oxidant to be depleted in the TTZ and for the subsurface to re-equilibrate. In situations in which the oxidant is particularly persistent (e.g., purple color is observed in wells over 1 year after a permanganate application) then the monitoring period on which the rebound metric was based was extended to include the next two sampling events after oxidant depletion.

Once again, the above rebound calculation was performed at each well in the TTZ. The percentage of well locations in the TTZ experiencing rebound as defined above were also calculated and recorded. This is a second metric that provides information on the site-wide prevalence of rebound at a given field site.

8.3.2 Case Study Database Development Construction

The database development process included the collection of case study source documents, followed by data entry and normalization. Because a general goal of this work was to generate as large a sample size as possible, the case studies used to populate the database were collected

from many different sources. Table 8.5 lists the different categories of data sources, a general assessment of the thoroughness and reliability of these sources, and additional commentary.

The data entry was performed by a single individual, reducing the introduction of “operator influence” on the classification schemes used. When data on a particular parameter was not available in source documents for a site, that field was left blank in the database. The data were entered in a consistent set of units.

8.3.3 Potential Limitations

The methods described in the previous subsections have certain limitations that should be appreciated.

8.3.3.1 Data Collection Limitations

There were several potential sources of bias that may limit how representative the collection of ISCO sites contained in the database were to the larger population of all field-scale ISCO sites. These biases stem from how the data were collected. First, an effort was made to collect as much data as possible; for this reason data were gathered from existing, easily accessible sources. These existing sources may not be completely representative of ISCO as a whole. For example, the State Coalition for the Remediation of Drycleaners has an online database of thorough case studies, many of which pertain to sites where ISCO was used. For this reason, dry cleaners may be an over-represented facility type in the database, and chloroethenes may be an over-represented contaminant group. However, experiences at dry cleaners remediated with ISCO are applicable to other sites contaminated with similar contaminants. Federal facilities may have dry cleaners on site, such as the Naval Training Center in Orlando, FL, which had a chlorinated solvent plume – the result of dry-cleaning operations – that was remediated using ISCO.

Table 8.5. Summary of Data Sources

Type	Received from	Reliability of data	Thoroughness of data	Comments
Regulatory project files	Internal Project Team, State and Federal Regulators, Consultants, Project Owners	Very good	Very good to good	These documents were the preferred source of information, and consist of reports submitted to regulators by environmental professionals. Thoroughness was sometimes less than desired if multiple consultants produced multiple reports and only one report could be obtained for review. The USEPA and many state regulatory agencies have websites from which these reports may be downloaded
Science and engineering journals	Library searches	Very good	Good to fair	These journal articles were a reliable source of information, but in many cases did not provide all the desired details because they represent a several page distillation of what would be reported to regulators in a more lengthy report

(continued)

Table 8.5. (continued)

Type	Received from	Reliability of data	Thoroughness of data	Comments
Technical bulletins and guidance documents	Online and library searches	Very good to fair	Very good to fair	Case studies were often included within these documents as supporting materials. In many cases the materials were less thorough than needed for this work. However, even brief case studies allowed for the collection of data on that site though other means, such as contacting site regulators. The authors' quality assurance/ quality control (QA/QC) measures taken during case study compilation were not always included in these reports
Case study reviews	Online and library searches	Very good	Very good to fair	These case study reviews included both demonstration and broad-scale type studies. The former's data is generally quite thorough regarding a limited number of sites. Broad-scale studies reported relatively few details on a larger number of projects. Both types of case study review were valuable in that they provided the names of sites so that further information could be gathered through other means
Online databases	Online searches	Very good to fair	Good to fair	There are several online databases devoted to remediation case studies, including ISCO sites. The content varies significantly among the case studies, and the QA/QC measures taken by the database managers to verify the data are unclear
Conference proceedings	Conference host	Good	Very good to fair	Case study summaries of ISCO remediations reported in conference proceedings contain data of varying quality. This source provides limited ability to acquire further information as the project owner has often allowed only a limited amount of information be released and removed the site name and city from the reported material

(continued)

Table 8.5. (continued)

Type	Received from	Reliability of data	Thoroughness of data	Comments
Technology vendor information	Vendor webpages	Fair	Fair	Many technology vendors have brief case study summaries available on their websites. These are intended to provide an overview of the work rather than specific details

Notes: Reliability of data refers to the credibility of the data source as assessed from the level of peer review to which the documents were subjected and the degree to which the documents represent marketing materials as opposed to technical reports. Thoroughness of data refers to the number of parameters for which the source documents contained the desired data. USEPA - U.S. Environmental Protection Agency.

Secondly, there may have been a bias towards successful studies. As stated previously, conference proceedings and promotional literature were both sources of data. Given that a site owner, project engineer, or technology vendor is voluntarily sharing information on a case study, they may consider it to be in their best interest to choose case studies that were successful. This is particularly true when the individual reporting the case study has a financial incentive in the form of future work to portray their past work in as favorable a light as possible. However, if such a bias towards good sites does in fact exist, it would have a positive aspect as well. One of the purposes of this work is to examine under what sets of conditions ISCO is successful, so having as many successful sites as possible will help serve this purpose of the work.

Another set of limitations was associated with the difficulty that was encountered in gathering ISCO project data. This occurred for several reasons, including the reluctance of site owners to release information on a site. If a site owner views discussion of environmental impacts to their property as a potential liability and sees no benefit to releasing the information, they will often keep it to themselves.

8.3.3.2 Data Reduction and Analysis Limitations

There are also limitations to the methods used to reduce and analyze the data; these limitations are summarized briefly below with additional discussion in Krembs (2008).

Oxidant persistence in the subsurface has significant impacts on the cost and success of an ISCO remediation. However, in the reports reviewed, there were many different means through which practitioners measured the persistence of the oxidant at their sites. For more persistent oxidants, the duration for which oxidant persisted before being consumed was generally determined to an accuracy on the order of months (e.g., report language such as “the oxidant persisted for 5 months in the TTZ and was not present during the site visit conducted 8 months after ISCO was completed”). Due to these constraints, it was not possible to input data on oxidant persistence into the database.

Oxidant persistence during permanganate applications is largely dependent on NOD, though in highly contaminated source zones COC demand may dominate this effect. However, in the reports reviewed, there are many ways in which practitioners determined the NOD through bench-scale testing. The main variations were the amounts of oxidant and site subsurface solids used in the test and how frequently and over what duration of time the oxidant concentrations were measured during the test. Due to this wide variation in testing protocols, the data could not be compared in a consistent way; thus, the case studies offer little guidance with respect to ranges of NOD at permanganate sites.

The success of all remediation technologies is partly dependent upon the understanding of the COC mass distribution in the subsurface, and also the relationship between the mass distribution and the permeability field distribution. The understanding of these issues, in turn, depends on the methods and intensity of subsurface sampling programs. Attempts were made to quantify the rigor of subsurface characterization methods by calculating parameters such as sampling density (e.g., samples collected per cubic yard). However, very few projects had enough data to calculate such metrics. Among those projects whose datasets did support such calculations, the results appeared to be generally driven by the size of the sampling network (e.g., a relatively dense network might end up with a low samples per volume because one well was installed a great distance downgradient adjacent to a receptor). The end result is that the database is not able to screen out ISCO implementations that failed to produce the desired result because of the incomplete understanding of the distribution of COCs in the subsurface treatment zone.

The use of groundwater concentrations as proxy for contaminant concentrations in other phases (sorbed and NAPL) has significant limitations. Groundwater COC concentrations are reported on a far more frequent basis than concentrations in aquifer solids in the reports reviewed. A major reason for this is that groundwater is nearly always the regulatory driver for the projects included in the database.¹ However, at sites with NAPL or significant sorbed phase concentrations of COCs, only a small percentage of the total contaminant mass is present in the aqueous phase. In addition, the manner in which the COCs partition between the aqueous phase and other phases is difficult to predict in source zones without analytical data and may change after ISCO because naturally occurring organic matter, which can serve as a sorption site for COCs, may be destroyed during ISCO² (Siegrist et al., 2001; Siegrist and Satijn, 2002). Due to these issues, ISCO may result in a significant reduction in total COC mass, including sorbed and NAPL phases, even though groundwater concentrations are similar before and after ISCO.

8.4 OVERVIEW OF ISCO CASE STUDY DATABASE CONTENTS

This section presents an overview of the data contained in the case study database. All of the data are discussed together in this section, which includes a general overview followed by the subdivisions based on COCs, geology, and oxidant. Analysis of what site conditions appear to impact the ISCO design used are presented in Sections 8.5 and the conditions impacting treatment performance are discussed in 8.6.

Unless otherwise noted, these data include both full-scale and pilot-scale applications. The breadth of data varied widely among the case study sources, resulting in many parameters remaining blank during data entry due to a lack of data. For this reason, the number of sites in each analysis fluctuates greatly, as shown by the n values associated with each analysis. The n values reported are the number of sites in the database that have data for all of the parameters being analyzed (the fields for all parameters in the analysis are non-blank).

¹ Sites where ISCO was used to treat subsurface solids with no consideration of mitigating groundwater impacts were deemed to be outside the scope of this project and are therefore not included in the database.

² The extent of interactions between oxidants and natural organic matter varies considerably based upon the oxidant. Permanganate is the most reactive, followed by persulfate. Catalyzed hydrogen peroxide and ozone are less selective, meaning that they may react with other inorganic constituents of the subsurface solids or auto-decompose prior to reacting with subsurface organic matter.

The database contains 242 sites from seven nations and 42 states in the USA. There are 19 different site types represented. The bulk of sites are federal, manufacturing/industrial, and dry-cleaning facilities. An appreciable number of chemical production, former manufactured gas plants (MGP), service stations, waste disposal, and wood treatment sites are included as well.

A wide range of contaminants have been treated at the field-scale using ISCO. However, the majority of sites in the database were contaminated with chloroethenes (70%). Benzene, toluene, ethylbenzene, and total xylenes (BTEX) (18%), total petroleum hydrocarbons (TPH) (11%), chloroethanes (8%), methyl tert-butyl ether (MTBE) (7%), SVOCs (7%), and chlorobenzenes (5%) were present as well. Other contaminants were present at less than 3% of the sites. Approximately half of the sites were reported to be contaminated with DNAPL (or contaminant levels potentially indicative of DNAPL), and approximately one-tenth were contaminated with light nonaqueous phase liquid (LNAPL).

The scope of this work was to analyze the use of ISCO to treat contaminated groundwater; for this reason, only sites where the project team reportedly sampled groundwater are included. Approximately one quarter of sites also measured or estimated (from aqueous concentrations and TOC data in subsurface solids) COC concentrations in subsurface solids to supplement their conceptual site model (CSM) and ISCO performance analysis. Total contaminant mass and mass flux were estimated at only 6 and 2% of the sites, respectively.

Six oxidants are represented in the database. The overall frequency of their use is shown over time in Figure 8.2. The trend over time shows that permanganate and CHP are the most commonly applied, followed by ozone, and that persulfate, perozone, and percarbonate are the more recently developed of the oxidants. The overall trends in field-scale oxidant use over time are similar to the results of a similar analysis from a literature review of laboratory studies of ISCO oxidants conducted by Petri et al. (2008) in that permanganate and CHP are the most commonly used/studied, though ozone and persulfate are prevalent as well (refer to Chapter 1, Figures 1.7 and 1.8).

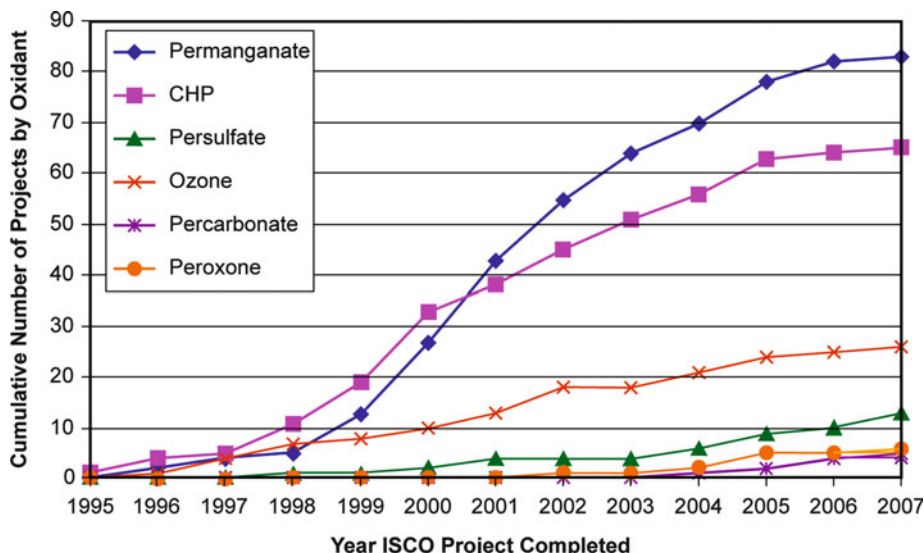


Figure 8.2. Cumulative frequency of oxidants used over time ($n = 182$). The apparent decline in the frequency of the use of ISCO (the slope of the curves at more recent time) is an artifact of the fact that there is a lag time between when a project is finished and when the results are made available to the public.

ISCO has been used in a wide variety of geologic media, including unconsolidated sediments and fractured bedrock. The average saturated hydraulic conductivities reported among sites varied between 10^{-4} ft/day (3.5×10^{-8} cm/s) (a silty clay) and 2,400 ft/day (0.85 cm/s) (a karst system), with a median of 4.5 ft/day (1.6×10^{-3} cm/s) ($n = 87$). The depth to groundwater varied between 1 and 150 ft (0.3–46 m) below ground surface (bgs) with a median of 10 ft (3.0 m) bgs ($n = 124$). The range of reported and calculated (using Darcy's Law and assuming an effective porosity of 0.3 if none was provided) groundwater flow velocity was 0.002 to 5 ft/day (7.0×10^{-7} to 1.8×10^{-3} cm/s), with a median of 0.2 ft/day (7.0×10^{-5} cm/s) ($n = 58$). The TOC in subsurface solids ranged between 0.0013 and 280 g/kg, with a median of 4.1 g/kg ($n = 23$). The degree of heterogeneity in unconsolidated subsurface solids varied considerably, with descriptions ranging from "homogeneous fine sand, trace silt" to "highly heterogeneous sand, gravel, and silt." The ratio between the maximum to minimum hydraulic conductivity values recorded at a single site (another measure of heterogeneity) ranged between 1.25 to nearly 4,000 ($n = 12$). The distribution of applications among the six Geology Groups is shown in Table 8.6.

The goals of an ISCO project vary between reducing COC concentrations to below MCLs to evaluating the effectiveness of the remediation technology at the field-scale. As described in the Section 8.3.1.5, the goals of an ISCO remediation were placed into five categories, and some projects had multiple goals for the remediation technology. MCLs were the most common goal (37%), followed by general mass or time to cleanup reduction (31%), technology evaluation or optimization (27%), ACLs (25%), and lastly mass reduction by a predetermined percentage (9%) ($n = 112$).

Table 8.6. Summary of Geology Group Distribution

Geology groups	Description	Percent of sites ($n = 209$)
Group A	Permeable ($K > 10^{-5}$ cm/s) and homogeneous ($K_{\max}/K_{\min} < 1,000$)	21
Group B	Impermeable ($K < 10^{-5}$ cm/s) and homogeneous ($K_{\max}/K_{\min} < 1,000$)	3
Group C	Permeable ($K > 10^{-5}$ cm/s) and heterogeneous ($K_{\max}/K_{\min} > 1,000$)	47
Group D	Impermeable ($K < 10^{-5}$ cm/s) and heterogeneous ($K_{\max}/K_{\min} > 1,000$)	15
Group E	Consolidated material with low matrix porosity (generally igneous and metamorphic rocks)	7
Group F	Consolidated material with high matrix porosity (generally sedimentary rocks)	7

ISCO reagents have been delivered using many techniques. However, well injections, direct push points, and sparge points (applicable only to ozone and peroxone) are the most commonly used (Table 8.7).

The ISCO system designs within the case studies reviewed were predominantly full-scale applications (65%) with a lesser amount of pilot tests (35%). Over half (52%) of ISCO designs targeted both sorbed and aqueous phase contaminants, slightly less than half (45%) targeted aqueous phase contaminants only, and a few sites (2%) treated both aqueous phase contamination and contamination trapped within a bedrock matrix ($n = 164$). [The distinction between

Table 8.7. Summary of Oxidant Delivery Method

Delivery method	Percent of sites (<i>n</i> = 181)
Injection wells	47
Direct push	23
Sparge points	14
Infiltration	10
Recirculation	7
Fracturing	6
Mechanical mixing	2
Horizontal wells	1

Notes: Percentages sum to greater than 100% because multiple delivery techniques were used at some sites. "Infiltration" refers to trenches, galleries, or vertical wellpoints installed in the vadose zone so that the oxidant will migrate vertically through the treatment zone.

aqueous only and the other categories was based on the text description of the CSMs and the TOC content of the subsurface solids if reported. The latter category does not mean that sorbed phase contamination did not exist, just that it was considered negligible relative to the aqueous phase contamination.]

Most designs (52%) targeted the source zone only, while 19% targeted both the source and the plume, 14% targeted the plume only, and 14% were pilot tests and only targeted a smaller portion of the source or plume (*n* = 170). The areal extent of the TTZ ranged from 80 to 260,000 sf (7.4–24,000 m²), with a median of 8,100 sf (750 m²) (*n* = 110). The volume of the TTZ ranged from, 7.4 to 337,000 cy (5.7–260,000 m³), with a median of 5,000 cy (3,800 m³) (*n* = 110).

Oxidant loading rates (mass oxidant/mass subsurface solids treated) varied between 0.004 and 60 g/kg, with a median of 1.1 g/kg (*n* = 68). The number of pore volumes varied between 0.004 and 56, with a median of 0.12 (*n* = 65). The number of delivery events varied between 1 and 10, with a median of 2 (*n* = 159).

A majority of sites (78%) performed a treatability study (*n* = 121). However, this may be an overestimate because it was difficult to ascertain that a treatability study was *not* performed in many cases simply because no mention was made of treatability studies in project documents. When treatability studies were not mentioned, no assumption was made (the field was left blank, and was not included in analyses such as the calculation of the 78% frequency above). Note that this is not the same as assuming that no treatability study was performed. Treatability studies were determined not to have been performed by correspondence with the site contacts and from report language indicating that a treatability study was deemed unnecessary. A majority of full-scale sites (60%) performed a pilot test (*n* = 87).

The ISCO technology approach was modified during field implementation at 58% of the sites (*n* = 78). Such modification was tracked to evaluate the frequency with which practitioners are using the Observational Method. This theory of environmental remediation has been adapted from geotechnical engineering (Peck, 1969) and follows the philosophy that a relatively higher degree of uncertainty may be acceptable during the initial implementation but that performance results should be continually monitored and the CSM and ISCO system design updated based upon observations made during implementation (see additional description in Chapter 11). Examples of such modifications included changes to oxidant concentration, number and spacing of injection points, number of delivery events, and injection pressure and flow rate.

Most sites utilized ISCO in a combined remedy (76%), with 60% using a pre-ISCO couple, 22% coupling during ISCO implementation, and 30% coupling post-ISCO ($n = 135$). The frequency of post-ISCO coupling is likely an underestimate because many of the source documents that were reviewed were written shortly after ISCO was completed, and post-ISCO coupling may have been initiated after the writing of those documents. Excavation was the most common pre-ISCO couple (50%), followed by SVE (18%). Pump-and-treat (P&T) (11%) and SVE (9%) were used most frequently during ISCO, while MNA (19%) and enhanced *in situ* bioremediation (EISB) (17%) were the most common post-ISCO couples.

Mass reduction was calculated for only nine implementations; among these, the minimum mass reduction was 73%, the median was 84%, and the maximum 94%. Of the sites with performance data, 24% reported results for both subsurface solids and groundwater, while the remainder reported groundwater concentrations only ($n = 120$). At some sites, ISCO achieved greater than 99.99% reduction in maximum COC concentrations in groundwater. Six sites have met and maintained MCLs, including three chlorinated solvent sites where ozone sparging (two sites) or CHP (one site) were used to treat low concentration plumes (less than 70 $\mu\text{g/L}$ trichloroethene [TCE]). One site with a known DNAPL release reduced concentrations of TCE from near its solubility limit to risk-based levels (300 $\mu\text{g/L}$) using ISCO (Sun Belt Precision Products, reported by B.L. Parker in USEPA, 2003 and ITRC, 2005). However, other sites have shown negligible changes, or even increases, in groundwater COC concentrations following ISCO. While there are many confounding factors that impact the percent reductions in groundwater noted in the database, non-chlorinated compounds generally showed greater decreases than chlorinated compounds.

About half (52%, $n = 121$) of the projects achieved their performance goals, with the percentage of projects meeting a particular goal inversely related to the stringency of that goal. The six sites that met MCLs represent 15% of the sites in the database that attempted to meet MCLs ($n = 39$). ACLs were met by 39% of projects attempting to do so ($n = 28$), while 46% successfully reduced mass or concentration by the targeted percentage ($n = 11$). A general mass reduction goal was attained at 80% ($n = 40$) of sites and technology evaluation was successful at 95% of sites ($n = 37$).³ Site closure was attained at 24% of the full-scale sites ($n = 74$). Site closure as defined here means that the project met whatever regulatory criteria were required (e.g., MCLs, ACLs, implementation of institutional controls) such that remediation and monitoring were no longer required. Of the sites that did attain closure, 89% were coupled with another technology, with 58% using another technology prior to ISCO, 37% using another co-located technology during ISCO implementation, and 21% using another technology after ISCO. It is likely that some of the sites that had not met the site closure requirements when these data were collected may have done so subsequently.

The median total project cost was \$220,000 ($n = 55$) and the median unit cost was \$94/cy ($\$120/\text{m}^3$) ($n = 33$). These costs are slightly below those reported for ISCO sites by McDade et al. (2005).

Overall, rebound occurred at over half (62%) of sites in the database ($n = 71$). Among those sites that experienced rebound, it occurred at nearly half (49%) of the monitoring wells

³ The two sites that failed to successfully evaluate ISCO technology at the field scale did not monitor oxidant distribution and did not collect samples of subsurface solids for COC analyses. Groundwater concentrations did not decline after ISCO injections, and none of the data collected indicated why no reductions were observed.

within the TTZ ($n = 26$). Rebound occurred less frequently at sites with fuel related contaminants than at sites contaminated with chlorinated VOCs (CVOCs). In addition, when rebound did occur at sites with fuel related contaminants, it did so at a lower percentage of monitoring locations than at CVOC sites.

8.5 ANALYSIS OF CONDITIONS IMPACTING ISCO DESIGNS

This section presents more detailed summary statistics investigating how COCs and geology affected design and results, and also presents differences in design strategies between applications using the various oxidants.

8.5.1 COCs Treated

ISCO designs depended on the COCs present at a site. The analysis presented in this section will focus on differences between treatment of chloroethenes and fuel-related compounds. Other chlorinated compounds and SVOCs are omitted in this section because of the relatively smaller number of case studies for these compounds. The data for chloroethanes and chlorinated benzene compounds are more similar to chloroethenes than they are to fuel-related compounds. More practitioners attempted to meet MCLs at fuel-related (BTEX, TPH, and MTBE) sites than at sites contaminated with chloroethenes (Table 8.8).

Table 8.8. Goals Attempted for ISCO Remediation by COC Group

Goals of remediation	Percent of sites			
	Chloroethenes ($n = 110$)	BTEX ($n = 21$)	TPH ($n = 15$)	MTBE ($n = 12$)
Meet MCLs	28	48	67	75
Meet ACLs	28	19	13	8
Reduce mass by a given %	10	5	0	0
Reduce mass and/or time to cleanup	34	33	20	17
Evaluate effectiveness/optimize	32	5	7	0

Notes: Vertical summation may yield greater than 100% because some sites had more than one of the above goals. The n value presented is the total number of sites in that COC group whose source data had clearly stated goals.

The selection of oxidant also varied by COC group. Permanganate was the most commonly selected oxidant for the chloroethenes, whereas CHP and ozone were the more commonly selected for the fuel related compounds (Table 8.9). The other COC groups have also been included in this table for reference. Note that the COC groups are not mutually exclusive – a site may have contained COCs in multiple categories – and that the high percentage of chloroethane sites treated with permanganate may have been situations in which the chloroethane was a co-contaminant and the primary goal of the remediation was to treat chloroethenes.

The approach in the remediation design with respect to pre-design testing and use of coupled approaches varied between the chloroethenes and the fuel related compounds,

particularly MTBE. All three groups of fuel related sites used a coupled approach more frequently, most often excavation. MTBE sites used treatability studies less often and used pilot-scale studies more often than the other groups. These results are shown in Table 8.10.

Table 8.9. Oxidant Used by COC Group

Oxidant used	Percent of sites						
	Chloroethenes (<i>n</i> = 154)	Chloroethanes (<i>n</i> = 18)	Chlorobenzenes (<i>n</i> = 11)	BTEX (<i>n</i> = 38)	TPH (<i>n</i> = 24)	MTBE (<i>n</i> = 15)	SVOCs (<i>n</i> = 20)
Permanganate	58	50	18	8	13	7	15
CHP	31	33	64	50	46	20	45
Persulfate	6	28	27	13	8	13	5
Ozone	8	6	9	21	25	53	40
Peroxone	1	6	0	3	4	13	5
Percarbonate	1	6	0	11	8	0	5

Notes: Vertical summation may yield greater than 100% because some sites used more than one oxidant. Horizontal summation of *n* values is greater than the total number of sites because multiple COC groups were present at many sites.

Table 8.10. ISCO Pre-design Testing and Coupling by COC Group

	Chloroethenes	BTEX	TPH	MTBE
Percent using treatability study	67 (<i>n</i> = 51)	70 (<i>n</i> = 10)	56 (<i>n</i> = 9)	33 (<i>n</i> = 3)
Percent using pilot study – full scale sites only	58 (<i>n</i> = 60)	67 (<i>n</i> = 12)	55 (<i>n</i> = 11)	83 (<i>n</i> = 6)
Percent of sites using coupling	71 (<i>n</i> = 95)	94 (<i>n</i> = 18)	93 (<i>n</i> = 14)	92 (<i>n</i> = 12)
Percent coupled before ISCO	53	83	64	83
Percent coupled during ISCO	19	33	21	33
Percent coupled after ISCO	33	17	43	8

The results of ISCO remediation were different for sites contaminated by chloroethenes and for sites contaminated by fuel related compounds. Sites contaminated with chloroethenes did not show, on average, results that were as positive as ISCO implementations conducted at sites contaminated with fuel related compounds. These results are shown in Table 8.11. The low incidence (0%) of meeting MCLs at BTEX sites may be confounded by the stringent data collection methods used to construct the database. This metric was not entered in the affirmative unless the fact that MCLs were met and maintained could be confirmed by contacting the regulatory official responsible for the project. Such confirmation was attempted but unsuccessful for the BTEX sites. The result in the table should not be interpreted as meaning that no ISCO remediation has ever reduced BTEX concentrations to MCLs; it means that the regulatory officials could not be contacted during the course of this case study review to confirm that MCLs had been met.

8.5.2 Hydrogeologic Conditions

This section presents selected statistics based on the six Geology Groups into which the sites were placed, as shown in Table 8.12. The classification system that was used to group the sites based on geologic media is repeated below and described thoroughly in Section 8.3.1.1.

Table 8.11. Selected Performance Results by COC Group

	Chloroethenes	BTEX	TPH	MTBE
Percent attaining closure	20 (<i>n</i> = 50)	43 (<i>n</i> = 7)	38 (<i>n</i> = 8)	63 (<i>n</i> = 8)
Percent attaining MCLs among all sites	3 (<i>n</i> = 105)	0 ^a (<i>n</i> = 12)	25 (<i>n</i> = 12)	60 (<i>n</i> = 5)
Percent of sites with rebound	72 (<i>n</i> = 54)	38 (<i>n</i> = 8)	43 (<i>n</i> = 7)	29 (<i>n</i> = 7)
For rebound sites, percentage of monitoring wells (MWs) w/rebound	50 (<i>n</i> = 22)	29 (<i>n</i> = 2)	25 (<i>n</i> = 1)	29 (<i>n</i> = 2)

^aThe incidence of meeting MCLs was only entered in the affirmative after attempting to discuss the case study with the regulatory official. This percentage shown should not be interpreted to mean that ISCO has never reached MCLs at a BTEX site. Site closure is defined as the completion of active remediation and monitoring, and includes the attainment of MCLs, risk-based standards, and may include requirements of institutional and engineering controls. Some of the sites that had not attained closure or met MCLs as of the collection of the case study data may have done so subsequently. The percentage attaining MCLs is based on those attaining that concentration standard irrespective of the project's goals.

Table 8.12. Hydrogeology Characteristics for the Site Groups

Site group	Permeability	Morphology
Group A	Permeable ($K > 10^{-5}$ cm/s)	Homogeneous ($K_{\max}/K_{\min} < 1,000$)
Group B	Impermeable ($K < 10^{-5}$ cm/s)	Homogeneous ($K_{\max}/K_{\min} < 1,000$)
Group C	Permeable ($K > 10^{-5}$ cm/s)	Heterogeneous ($K_{\max}/K_{\min} > 1,000$)
Group D	Impermeable ($K < 10^{-5}$ cm/s)	Heterogeneous ($K_{\max}/K_{\min} > 1,000$)
Group E	Low matrix porosity	Generally igneous and metamorphic rocks
Group F	High matrix porosity	Generally sedimentary rocks

Geology Groups A and C collectively make up 69% of the case studies in the database. Groups B, E, and F make up another 17% collectively. These latter three groups are actually similar physically in that they are dominated by flow through fractures that are interconnected to varying degrees but also have an interaction between the generally immobile matrix porosity and the more mobile fracture zones. For this reason, they are combined in the tables that follow. The combining of these three groups is based on the assumption that the homogeneous, impermeable sites that make up Group B are in fact fractured. Fractures in clay materials were reported at many clay sites in the database. The presence of contamination within clay materials, including concentrations of COCs indicative of DNAPL, is further evidence that these systems are fractured because the contamination must have permeated the clay somehow. These two lines of evidence support the combining of Geology Groups B, E, and F – termed Group BEF – for analysis.

There are some differences between the ways in which practitioners approach sites based upon the geologic media to be treated. The projects in Group A attempted to meet the most stringent remediation goal of meeting MCLs most often, as shown in Table 8.13.

ISCO system design varied with respect to the geologic media treated. Permanganate was the selected oxidant with greater frequency in the lower permeability Groups D and BEF, whereas CHP is selected relatively less frequently at these types of sites (Table 8.14). Group A sites performed treatability and pilot studies less frequently than the other Geology Groups (Table 8.15). However, the difference in the use of coupling was not nearly as marked, as

Table 8.13. Goals Attempted for ISCO Remediation by Geology Group

Goal of remediation	Percent of sites			
	Group A (<i>n</i> = 30)	Group C (<i>n</i> = 78)	Group D (<i>n</i> = 16)	Group BEF (<i>n</i> = 21)
Meet MCLs	43	35	31	29
Meet ACLs	27	22	56	10
Reduce mass by X%	3	12	6	10
Reduce mass and/or time to cleanup	20	37	13	43
Evaluate effectiveness/optimize	20	31	13	38

Note: Group BEF is the aggregate of Groups B, E and F. Vertical summation of the columns may yield greater than 100% because some sites had multiple treatment goals.

77% of both Groups A (*n* = 30) and C (*n* = 66) sites used a coupled approach, while 57% of Group D sites (*n* = 14) and 94% of Group BEF sites (*n* = 16) coupled ISCO with another technology. These trends are similar when considering whether the coupled technology was implemented before, during, or after ISCO.

Table 8.14. Oxidant Used by Geology Group

Oxidant	Percent of sites			
	Group A (<i>n</i> = 42)	Group C (<i>n</i> = 98)	Group D (<i>n</i> = 31)	Group BEF (<i>n</i> = 14)
Permanganate	33	38	68	50
CHP	41	40	32	29
Persulfate	5	6	0	7
Ozone	12	17	3	14
Peroxone	7	2	0	0
Percarbonate	5	3	0	0

Note: Group BEF is the aggregate of Groups B, E, and F.

Table 8.15. ISCO Pre-treatment Testing by Geology Group

Type of pre-treatment test	Group A	Group C	Group D	Group BEF
Percent using treatability study – all scales	55 (<i>n</i> = 20)	83 (<i>n</i> = 64)	80 (<i>n</i> = 15)	75 (<i>n</i> = 16)
Percent using treatability study – full scale only	25 (<i>n</i> = 12)	40 (<i>n</i> = 75)	70 (<i>n</i> = 10)	75 (<i>n</i> = 8)
Percent using pilot study – full scale only	29 (<i>n</i> = 17)	59 (<i>n</i> = 44)	85 (<i>n</i> = 13)	78 (<i>n</i> = 9)

Note: Group BEF is the aggregate of Groups B, E, and F.

The performance results of ISCO projects also vary with the type of geologic media treated. Using the attainment of site closure as the performance metric, Group A sites were closed 47% of the time (*n* = 15), whereas 13% of Group C sites attained closure (*n* = 38). Using the attainment of MCLs as the performance metric, among sites that attempted to meet this goal, 33% of Group A sites were successful (*n* = 24) as opposed to 13% of Group C sites

($n = 38$) (Table 8.16). No (0%) sites in other categories attained MCLs. When examining the percent reduction of maximum total COC concentrations, Group A sites had a median percent reduction of 77% ($n = 11$), compared to 58% for Group C ($n = 39$), 43% for Group D ($n = 9$), and 43% for Group BEF. Rebound occurred least frequently at Group A sites, and most frequently in Group BEF sites (Table 8.17). The number of wells experiencing rebound at sites where rebound did occur shows the opposite trend, with rebound occurring over a larger percentage of the site's monitoring wells at Group A sites, and less at Group BEF sites (Table 8.17).

Table 8.16. Selected Performance Metrics at ISCO Sites by Geology Group

Performance result	Group A	Group C	Group D	Group BEF
Percent attaining closure – full scale only	47 ($n = 15$)	13 ($n = 38$)	29 ($n = 7$)	20 ($n = 10$)
Percent attempting and meeting MCLs	33 ($n = 9$)	11 ($n = 19$)	0 ($n = 3$)	0 ($n = 4$)
Percent attempting and meeting ACLs	29 ($n = 7$)	50 ($n = 12$)	33 ($n = 6$)	50 ($n = 2$)

Note: Group BEF is the aggregate of Groups B, E, and F.

Table 8.17. Incidence of Rebound by at ISCO Sites Geology Group

	Group A	Group C	Group D	Group BEF
Percent of sites with rebound	35 ($n = 17$)	65 ($n = 34$)	75 ($n = 8$)	89 ($n = 9$)
For rebound sites, percentage of MWs w/ rebound	56 ($n = 3$)	49 ($n = 15$)	52 ($n = 4$)	36 ($n = 3$)

Note: Group BEF is the aggregate of Groups B, E, and F.

8.5.3 Oxidant

Differences in the results when the entire dataset is subdivided by oxidant are discussed in this section. Among the projects contained in the database, permanganate was used to treat predominantly chloroethenes; this group of COCs was present at 95% of the sites at which permanganate was applied ($n = 87$). Among sites at which CHP was applied, chloroethenes were present at 61%, while BTEX, TPH, and SVOCs were present at 26, 15, and 11% of the sites, respectively ($n = 72$). Note that the percentages of this and other analyses in which COC groups are analyzed may exceed 100% because multiple contaminant groups were present at some sites. Among ozone sites, chloroethenes were present at 44%, BTEX at 30%, TPH at 22%, MTBE at 30%, and SVOCs present at 26% ($n = 27$).

The goals of remediation varied somewhat by oxidant. Among ozone sites, 71% attempted to meet MCLs ($n = 21$), and 50% of peroxone sites attempted to meet MCLs ($n = 4$). The other four oxidants attempted to meet MCLs between 20 and 33% of the time.

The TTZ of ISCO systems varied between the different oxidants. Ozone and peroxone were used to treat only the contaminant plume (as opposed to the source zone) at 35% ($n = 20$) and 50% ($n = 4$) of the sites at which those two technologies were applied, respectively. The other oxidants only targeted the plume for between 0 and 13% of sites. Ozone and peroxone systems generally targeted larger TTZ areas and volumes than the other four oxidants. The oxidant concentration injected was lower for permanganate than for CHP and persulfate, both as injected and after *in situ* mixing with activators and injected water (Table 8.18).

Table 8.18. Oxidant Concentration Injected

	Permanganate	CHP	Persulfate
Median injected oxidant concentration (g/L)	24 ($n = 59$)	190 ($n = 37$)	160 ($n = 8$)
Median oxidant concentration after <i>in situ</i> mixing of oxidant solution and activator and/or flush water solution (g/L)	23 ($n = 40$)	90 ($n = 23$)	100 ($n = 5$)

Notes: Other oxidants omitted due to small sample size. The second measure of concentration above was calculated for each site by reducing the injected oxidant concentration to account for the injection of activator and/or water, assuming complete mixing *in situ*. Permanganate and persulfate concentrations are for those anions only, while CHP is the concentration of hydrogen peroxide.

Design parameters also differ between the oxidants, including ROI, the number of pore volumes delivered, the number of delivery events, and the duration of those delivery events (Table 8.19). The design ROI (planned ROI), as determined from project reports' text descriptions or injection spacing, is consistent between the aqueous phase oxidants (permanganate, CHP, and persulfate) and greater for ozone. The observed ROI, as determined from project documents' results of injection monitoring, showed that CHP generally attained the design ROI, while permanganate, persulfate, and ozone observed greater oxidant distribution than anticipated. Permanganate was delivered at a lower oxidant-loading rate (g oxidant/kg media treated) and higher number of pore volumes than CHP, while persulfate was introduced at a higher median dose and number of pore volumes. The number of delivery events and their duration was similar for the aqueous phase oxidants, and the duration of delivery events was much longer for ozone.

Table 8.19. Design Parameters by Oxidant Used

	Permanganate	CHP	Persulfate	Ozone
Median design ROI – ft (m)	14 (4.3) ($n = 29$)	15 (4.8) ($n = 30$)	13 (4.0) ($n = 6$)	25 (7.6) ($n = 5$)
Median observed ROI (ft)	25 (7.6) ($n = 11$)	15 (4.8) ($n = 6$)	20 (6.1) ($n = 3$)	No data
Median oxidant dose (g/kg)	0.4 ($n = 36$)	1.2 ($n = 19$)	5.1 ($n = 6$)	0.1 ($n = 4$)
Median number of pore volumes delivered	0.16 ($n = 32$)	0.073 ($n = 26$)	0.57 ($n = 6$)	No data
Median number of delivery events	2 ($n = 65$)	2 ($n = 57$)	1 ($n = 10$)	1 ($n = 15$)
Median duration of delivery events (days)	4 ($n = 45$)	6 ($n = 42$)	4 ($n = 7$)	210 ($n = 15$)

Note: Peroxone and percarbonate omitted due to the small sample size.

Treatability studies were used for 78% of permanganate sites ($n = 50$), 78% of CHP sites ($n = 45$), 100% of persulfate sites ($n = 8$), 100% of percarbonate sites ($n = 2$), 43% of ozone sites ($n = 7$), and 33% of peroxone sites ($n = 3$). The frequency of pilot testing among full-scale applications ranged between 50 and 65% for permanganate, CHP, ozone, and peroxone, while 100% of persulfate sites used a pilot test ($n = 4$) and 0% of percarbonate sites used a pilot test ($n = 1$).

The performance achieved by ISCO varied within the database depending on the oxidant used (Table 8.20). This table includes all contaminants and sites with and without NAPL, and

also does not consider the cost of the remediation. These confounding factors have not been accounted for in this table; therefore, this table should not be interpreted to mean that one oxidant is universally preferable to another.

Table 8.20. Selected Performance Results by Oxidant

	Permanganate	CHP	Ozone	Persulfate	Peroxone
Percent of sites attaining closure	16 (<i>n</i> = 32)	27 (<i>n</i> = 22)	50 (<i>n</i> = 12)	0 (<i>n</i> = 4)	50 (<i>n</i> = 2)
Percent of sites attaining MCLs	0 (<i>n</i> = 55)	2 (<i>n</i> = 45)	31 (<i>n</i> = 13)	0 (<i>n</i> = 8)	50 (<i>n</i> = 2)
Median percent total COC reduction in groundwater	51 (<i>n</i> = 27)	56 (<i>n</i> = 26)	96 (<i>n</i> = 5)	24 (<i>n</i> = 5)	No data
Median total cost (1,000 U.S. \$)	240 (<i>n</i> = 25)	270 (<i>n</i> = 14)	160 (<i>n</i> = 10)	No data	270 (<i>n</i> = 3)
Median unit cost (\$/cy)	130 (<i>n</i> = 17)	130 (<i>n</i> = 10)	44 (<i>n</i> = 2)	No data	32 (<i>n</i> = 2)
Percent of sites with rebound observed	78 (<i>n</i> = 32)	57 (<i>n</i> = 21)	27 (<i>n</i> = 11)	50 (<i>n</i> = 2)	No data
For rebound sites, percentage of MWs w/rebound	48 (<i>n</i> = 11)	53 (<i>n</i> = 10)	28 (<i>n</i> = 3)	No data	na

Notes: na - not applicable. Percarbonate omitted due to a lack of data. This table includes all contaminants, Geology Groups, and sites with and without NAPL. The percentage of sites listed in the attaining MCLs category includes all sites irrespective of their remediation goals.

8.6 ANALYSIS OF CONDITIONS IMPACTING ISCO TREATMENT PERFORMANCE

This section presents the results of the case study data with respect to the treatment effectiveness that ISCO was able to achieve and also what site conditions appear to be driving these results. Prior to detailing these results, some additional discussion is presented regarding the value of various performance metrics for use as a response variable in statistical analysis.

8.6.1 Use of Performance Metrics

The percentage of sites that achieve a given remediation goal depends on the difficulty of the goal attempted – MCLs is the most difficult goal to achieve, while general evaluation of the remediation technology is the easiest (Section 8.4). The attainment of site closure is highly dependent upon the regulatory context. Regulatory context refers to the particular endpoint requirement that must be met depending on who is providing regulatory oversight. Many of the case studies were overseen by state regulators, and the regulatory requirements vary considerably from state to state. Some regulatory programs allow “treatment to the extent practicable” or site-specific risk assessment, whereas others require attainment of specific concentrations. Therefore, while the goals and regulatory context are highly important from a qualitative perspective in assessing the likelihood of success, these performance outcomes are too site-specific to allow their use in a statistical analysis assessing the impacts of various other geological or contaminant constraints on success or failure.

As opposed to the above qualitative metrics, quantitative metrics can be compared between different sites and are independent of regulatory context. Percent reduction in maximum

contaminant concentrations in groundwater is the most prevalent quantitative metric in the case study database, primarily because it can be calculated with a modest amount of data. As stated in the Section 8.3.1.7, this metric was calculated as the percent change in the highest concentration of a COC (or group of COCs) in the TTZ before ISCO versus after ISCO. This metric suffers from the major limitation that groundwater samples alone do not provide significant insights into the total mass of COCs present in source zones.

8.6.2 Performance Experiences and Effects of Design and Environmental Conditions

Based on the case studies in the database, ISCO remediation achieves a larger percent reduction in maximum contaminant concentration when fuel related compounds are being treated compared to chlorinated compounds. This is likely not due to differences in reaction kinetics between oxidants and these two groups of COCs. Huling and Pivetz (2006) document that kinetic rates between oxidants and chloroethenes and chlorobenzenes are as fast as those between oxidants and petroleum hydrocarbons, BTEX, and MTBE. Since oxidation kinetics are not the reason for this difference in performance, this difference is likely attributable to differences in how these various COCs migrate through the subsurface. MTBE is more soluble than the other COCs and is therefore more available to be oxidized in the aqueous phase during ISCO treatment. The solubility and sorption characteristics as predicted by the octanol–water partitioning coefficient (K_{ow}) are not greatly different for chloroethenes and selected fuel components (benzene, ethylbenzene, and toluene) (Hemond and Fechner-Levy, 2000).

Based on the data in the database, there are no apparent differences in performance in terms of percent reduction of maximum groundwater concentrations among the various CVOCs. Based on the reaction kinetics, it should be expected that chloroethanes would generally not achieve percent reductions as great as other CVOCs (Huling and Pivetz, 2006). However, the mean reduction in maximum 1,1,1-trichloroethane (1,1,1-TCA) concentration in the database is 65% ($n = 4$), which is greater than the mean of other CVOCs. It is postulated that this unexpected result is due to the relatively smaller sample size of the 1,1,1-TCA sites. However, based on the four sites that are available, ISCO appears to be able to achieve reduction of this COC in some situations. [These four sites included permanganate, CHP, persulfate, and percarbonate applications. The permanganate application was intended to treat chloroethenes that were also present.]

The total cost of ISCO projects performed to treat fuel related COCs is also lower than those treating CVOCs. This difference does not appear to be an issue of project size; unit costs, areal extent, and volume of the TTZ did not differ significantly between fuel related and CVOC sites. One possible explanation for this difference in cost is that fuel related compounds are more accessible for treatment due to their migration characteristics. Another possibility is that the ISCO projects at fuel-related sites were targeting a smaller total mass of COCs relative to CVOC sites.

There are several ways in which ISCO system designs differ depending on what oxidant is being applied. This is anticipated because of the differences in reactivity and persistence among the various oxidants. This may also be attributable to personal preference, as many practitioners specialize in applications of one type of oxidant, and they may have developed their own specialized techniques based on experience gained in the field.

CHP practitioners appear to use a higher concentration, a lower injection volume, and a greater number of delivery events approach relative to permanganate practitioners (Tables 8.18 and 8.19). These differences should be expected given that permanganate is a more persistent

oxidant that CHP. The authors believe that this result also arises because many CHP practitioners routinely plan on delivering oxidants during multiple treatment events. The differences in the total number of pore volumes delivered between CHP and permanganate applications may also be due to the means through which this calculation was performed at CHP sites; only the hydrogen peroxide volume and not the separately added activator solution was included in the calculation.

Use of pre-design testing (pilot testing or treatability studies) also varied among the different oxidants (Section 8.5.3). Half of the ozone projects performed treatability studies as a pre-design test, a frequency significantly lower than that of other oxidants. All of the persulfate projects performed a treatability study, a frequency significantly greater than projects using the other oxidants. Treatability studies were used as a pre-design test at approximately 80% of CHP and permanganate sites. The fact that treatability studies were performed for all persulfate sites is not surprising because there are multiple activation methods that may be used with this oxidant. The fact that CHP and permanganate were similar is somewhat surprising – CHP requires activators of some sort (naturally occurring or injected) while permanganate does not. However, the degree of permanganate consumption due to NOD is an important design consideration, and 71% of permanganate sites for which there was sufficient data to determine what type of treatability study was performed ($n = 39$) used a treatability study to determine the NOD. The use of pilot-scale testing did not vary depending on the oxidant selected for ISCO remediation. This result is not surprising, because pilot tests are generally designed to evaluate oxidant distribution and delivery issues (as well as other issues); these issues are more dependent upon subsurface geology than oxidant characteristics. An exception to this statement might be the gaseous oxidants ozone and peroxone. However, pilot studies that consisted of installing a single delivery point and monitoring the distribution were frequently used with these oxidants. The purpose of these tests was generally to optimize full-scale well spacing and also to evaluate the impact of these continuous oxidation systems on aqueous metals concentrations.

There was no difference in the mean reductions of maximum perchloroethene (PCE) or TCE concentrations depending on which oxidant was selected. These are the only two contaminants for which there were enough data to perform statistical testing. This result is not surprising given that some of these oxidants have been used in ISCO for over 10 years. If one oxidant were definitively better (or worse) than the others, practitioners would use it more exclusively (or not use it at all). No differences were noted between total costs or unit costs of ISCO projects depending on the oxidant selected. While the cost per pound or electron equivalent varies significantly by oxidant, many other factors besides chemical costs have an impact on the total cost of ISCO projects (see Chapter 13).

The geologic conditions within the TTZ being treated has an important impact on both the design of ISCO systems and the results achieved. Conventional thinking is that permeable materials are more amenable to ISCO treatment, as are homogeneous materials. This thinking is supported by the data in the database, as homogeneous and permeable sites (Group A) achieved better performance with respect to many indicators, such as attainment of site closure and incidence of rebound (Tables 8.16 and 8.17). However, there was not a significantly greater reduction in the maximum PCE or TCE concentration achieved at Group A sites relative to other geologic media.

The Group A sites also performed treatability and pilot studies less frequently than other Geology Groups (Table 8.15), yet still achieved good results. The result with respect to pilot studies is expected, as this type of pre-design test is primarily aimed at gathering information on oxidant deliverability issues, and oxidant delivery is less problematic in homogeneous, permeable materials relative to other geologic media.

When considering the attainment of ACLs as a performance metric, the conventional wisdom is contradicted by the results of the database. ACLs were met more frequently at Group C (permeable and heterogeneous) sites than at Group A sites (Table 8.16). This result is significant at the 90% confidence level for all sites and at the 95% confidence level when considering only chloroethene sites that had concentrations present greater than the 1% solubility criterion. [Statistical significance was assessed using the non-parametric randomization test following the methods of Lunneborg (2000).] One possible explanation for this seemingly anomalous result is variations in regulatory context.⁴

There were also no statistically significant differences noted between Group A and Group C (the two groups for which there was the most data) with respect to the percent reduction in maximum PCE or TCE concentrations; this appears to be due to practitioners using a higher oxidant dose at Group C sites. These statistical tests were conducted both with and without accounting for the presence of DNAPL. This analysis examines consistent contaminants and a metric whose result is independent of regulatory context. This result is contrary to the conventional wisdom that homogeneous sites are more amenable to ISCO than heterogeneous ones. One possible explanation for this is that ISCO remediation designers are compensating for the increased challenges posed by heterogeneous sites and are therefore able to achieve good results in heterogeneous, permeable materials (Group C). This theory was evaluated by examining the number of pore volumes, the number of delivery events, and the duration of delivery events between Group A and Group C sites contaminated with chloroethenes above the 1% of solubility criterion. This analysis did not note significant differences in these three parameters between these two Geology Groups, holding oxidant and DNAPL presence constant. When considering the oxidant dose (g oxidant applied/kg media treated), there are differences between the designs of both CHP and permanganate remediations performed at chloroethene sites depending on whether Group A or Group C materials are being treated. In the case of both oxidants, the oxidant dose was greater for Group C materials. Though these results were not statistically significant (p value = 0.155, n = 9 for CHP and p value = 0.222, n = 12 for permanganate), the lack of significance is postulated to be due to the small sample size for these two analyses.

The suspected presence of free phase (NAPL) contamination has important implications for environmental remediation. As shown in the preceding sections, suspected DNAPL sites are treated using ISCO with considerably more regularity relative to LNAPL sites. The presence of DNAPL affects ISCO goals, design, and performance results. When DNAPL is suspected of being present, practitioners are less likely to attempt to meet MCLs immediately after ISCO (20 versus 51%, n = 120). ISCO applications at DNAPL sites also targeted a smaller volume TTZ than sites without DNAPL (median 3,000 cy versus 7,000 cy, n = 95). ISCO systems were designed to deliver a greater number of pore volumes of reagents and a higher oxidant dose at sites where DNAPL was present relative to sites where DNAPL was not present. The average duration of delivery events was also longer for DNAPL sites.

ISCO applications at DNAPL sites were no more likely to be modified during implementation than sites without DNAPL. However, remedies applied at DNAPL sites were more likely

⁴ As stated above, regulatory context refers to what endpoint was acceptable to the regulatory agency overseeing the project. A majority of the projects were performed under the jurisdiction of state regulatory agencies, and the requirements were highly variable from state to state. One particular regulatory issue that may have confounded the data was that the state of Texas allows ACLs of 100 times the standard MCL for sites with low yield aquifers. The state of Texas considers low yield aquifers to be those with yields of less than 150 gallons per day.

to couple ISCO with other technologies, especially post-ISCO technologies such as EISB and MNA (80 versus 73% for all types of coupling, and 45 versus 22% for post-ISCO coupled technologies, $n = 113$).

ISCO applications at DNAPL sites also differed with respect to their performance results, being significantly less likely to meet MCLs (0 versus 25%, $n = 36$) or attain site closure (9 versus 37%, $n = 62$) relative to sites without DNAPL. However, they are no less likely to meet ACLs. Returning to the issue of goals of ISCO application, these last statistics point to the importance of setting realistic expectations for ISCO applications for DNAPL treatment. If possible, ACLs should be negotiated for the site. If MCLs are an absolute requirement, a post-ISCO coupled technology will likely be required. Several sites in the database used computer models to estimate the length of time required after ISCO was completed to reach MCLs based on site-specific estimates of natural biodegradation of contaminants (Chapelle and Bradley, 1998; Chapelle et al., 2005). These estimates were predicated upon two assumptions (1) ISCO will achieve a reduction to a specified concentration and (2) natural biodegradation rates will return to baseline levels sometime after ISCO is completed. This first assumption depends on proper ISCO design and implementation and is similar to sites that have a regulatory ACL framework in place because ISCO must meet a specific groundwater concentration that is higher than MCLs. The latter assumption is reasonable because none of the case studies in the database noted lasting reductions in microbial populations and because EISB and MNA were frequently used after ISCO, especially at DNAPL sites (see Section 8.7).

ISCO projects at DNAPL sites had a higher total cost of treatment relative to other sites. This is expected given that DNAPL sites are generally considered to be more difficult to remediate and also that DNAPL sites used a greater duration of delivery events, greater number of pore volumes of reagents, and a greater amount of oxidant, as shown above.

Pilot-scale testing led to improved performance of full-scale ISCO projects that were implemented in permeable, heterogeneous materials (Group C) but did not seem to improve performance in permeable, homogeneous materials (Group A). One of the primary reasons that practitioners perform pilot tests is to assess issues related to oxidant delivery (transport distance, changes in concentration over time, preferential flow, etc.). The frequency of success of Group A sites that did not perform pilot tests indicates that oxidant delivery may be predicted with an acceptable level of certainty based on data available after general site characterization (grain size, extent of contamination, etc.). Conversely, the level of uncertainty regarding oxidant distribution in permeable and heterogeneous materials (Group C) appears to be great enough that pilot testing is of particular importance when treating this type of material.

Although it appears initially counterintuitive, based on the statistical tests that were performed, treatability studies did not appear to increase the success of ISCO projects. However, as stated earlier, there are caveats to this statement. First, because the database is based on field-scale ISCO projects, it does not include any treatability studies that showed unfavorable results that caused the project designer to select another remediation technology or approach. These types of situations highlight the value of treatability studies because if the results of laboratory-scale work are not promising, the likelihood of success at the field-scale is low. Unsuccessful laboratory studies are considerably less costly than unsuccessful field-scale ISCO implementations.

A second caveat is that it was difficult to determine that a treatability study was not performed based upon the materials reviewed. If no mention of treatability studies was made in project documents, this field was left blank unless it could be confirmed that a treatability study was not performed. This may result in an overestimate of the frequency of treatability study use.

8.7 SECONDARY ISCO IMPACTS

Microbial communities, before and after ISCO, were examined in 15 case studies and none showed a lasting decrease in microbial populations.⁵ Some studies showed an initial decrease immediately after ISCO implementation; however, the microbial populations rebounded to baseline levels in all situations. EISB was used as a post-ISCO coupled technology at 19 sites in the database. MNA was explicitly used post-ISCO at 20 sites in the database. The use of MNA after ISCO is likely underestimated because (1) it was only entered as a post-ISCO couple when project documents explicitly stated it was to be used and (2) because many of the project documents reviewed were written shortly after ISCO and the need for and selection of a post-ISCO technology had not been assessed at that time.

Of the 23 sites that tested for metals, 10 (43%) reported that metals concentrations remained within background ranges during and after ISCO. The remaining 13 sites (57%) reported metals concentrations during and after ISCO that were elevated relative to baseline concentrations. Arsenic, chromium, manganese, and nickel were the metals whose concentrations most commonly increased. The duration of the increases were highly site-specific and varied between less than 1 month and greater than 36 months. This is not to state that regulatory criteria were exceeded for this duration, just that concentrations remained above the pre-treatment values. Metals increases were limited to within the ISCO TIZ in all instances except two. The two sites with downgradient metals increases were both continuous ozone/peroxone sparge applications. In both cases, the metals attenuated within 1 month of system shutdown. In one case, the system was restarted at a lower oxidant dose that treated the COCs but did not mobilize metals. In the other case, the system remained shut down because the COC compliance goal had been met.

Aquifer permeability was reduced at 17% of the 36 sites that described this parameter before and after ISCO. Among CHP sites, permeability reductions were noted at 9% ($n = 11$). This was a situation in which gas generation in low permeability media resulted in higher injection pressures than desired. This situation was remedied by changing from a pressurized injection system to a gravity feed injection system. Among permanganate sites, 26% reported permeability reductions ($n = 19$). One of these was a demonstration study in which the authors attempted to demonstrate that permanganate remediation could serve the dual purpose of oxidizing contaminants (in this case, creosote) and encapsulating the unoxidized residual COCs in manganese dioxide (Lamarche et al., 2002). The incidence of permeability reduction reported above may overstate the frequency with which this occurs, because a lack of permeability reduction was only entered when the project documents specifically stated that it did not occur. Several projects reported measures taken to improve injection well performance, having shown decreases in permeability after permanganate injection. These included surging and redevelopment and also addition of acids and dilute hydrogen peroxide. In some situations well performance improved; in others it did not.

⁵ Nine of these case studies were permanganate sites, five were CHP, and one each were persulfate and ozone. Each of these oxidants performs through different reaction chemistries and vary in the degree to which their end products may stimulate microbial populations. However, due to the small percentage of sites that monitored microbial communities, and the different techniques through which they did so, no differences between oxidants were noted in this study with respect to microbial impacts.

8.8 SUMMARY OF KEY FINDINGS

Key findings drawn from the analysis of the 242 ISCO case studies collected are listed below:

- ISCO projects as a whole met their intended goals slightly more than half of the time (52%, $n = 121$). Success rates were highly dependent upon the stringency of the goals attempted. Very few that attempted to meet MCLs were successful in doing so (15%, $n = 39$). 39% ($n = 28$) of sites that attempted to meet ACLs were successful. Nearly all sites that attempted mass reduction and technology evaluation were successful in doing so (80%, $n = 40$ and 95%, $n = 37$, respectively).
- The majority of the sites did not have enough implementation and performance monitoring data in the project documents reviewed to definitively state the reason for success or failure. Subsurface solids laboratory analytical results, quantitative monitoring of oxidant distribution during injection, and complete site characterization results were potentially valuable data that were most commonly unavailable.
- The sites that did meet MCLs were low concentration chlorinated solvent plume applications (three sites) and MTBE sparge curtains (three sites). No sites with known or suspected DNAPL met MCLs.
- 24% of full-scale sites attained site closure ($n = 74$). The majority of these site closures involved attainment of ACLs or cleanup to the extent practicable. Of the sites that attained closure, 89% coupled ISCO with another technology, including 58% using a coupled technology before ISCO (e.g., excavation or SVE), 37% using a co-located technology during ISCO, and 21% using another technology after ISCO (e.g., MNA).
- Very few sites calculated COC mass before and after ISCO, reflecting prevalent commercial project constraints. Of those that did, the median percent reduction in mass was 84% ($n = 9$).
- Subsurface solids and groundwater sampling results were reported as a means of assessing performance at one quarter of the sites, while the remainder relied on changes in groundwater concentration only ($n = 120$). Given that approximately three quarters of the sites attempted to treat source zones, the lack of subsurface solids sampling indicates that many of the projects did not have an appropriately designed monitoring program to assess progress toward defined goals.
- ISCO has been used to treat a wide variety of organic compounds, though a majority of case studies targeted PCE and TCE.
- ISCO has been used most frequently in permeable subsurface solids, though an appreciable number of sites with impermeable subsurface solids or fractured rock have been treated as well.
- ISCO has been used to treat sites contaminated with DNAPL and sites without NAPL with approximately equal frequency. LNAPL sites have been treated with ISCO as well, though with relatively less frequency.
- Rebound occurred in at least one monitoring location at 62% of sites. In those situations when rebound did occur, it occurred in approximately half of the monitoring wells within the treatment zone. Physical mechanisms for this phenomenon could have included mass transfer limitations from the sorbed/NAPL phases to the aqueous phase, back diffusion of COCs from low permeability media, or incomplete characterization of baseline COC concentrations which led to improper placement of injection locations, resulting in incomplete treatment. It was not possible to distinguish the relative frequency

of each of these mechanisms with the data available. At many sites, an inadequate oxidant dose, injection well spacing, or injection volume may have led to the partial treatment results. Repeated treatments using the same approach may be successful under some of these conditions but not under others.

- The median total cost of ISCO remediation is \$220,000, and the median unit cost is \$94/cy treated.
- ISCO has achieved a significantly better performance for treatment of fuel related compounds, particularly MTBE, relative to chlorinated compounds. In particular, ozone and peroxone sparging systems have demonstrated a high success rate at MTBE and other fuel related sites, both in terms of the frequency with which they meet MCLs and also the consistently high percentage decreases in maximum contaminant concentrations.
- ISCO has achieved up to 99.9% reductions in maximum chlorinated compound concentrations in groundwater. However, this was the exception, and an equal number of sites did not observe any reduction in maximum groundwater concentration, and the median percent reduction was 54% ($n = 56$). The performance of ISCO with respect to this metric is more variable at sites contaminated with chlorinated compounds, particularly at sites with significant sorbed or DNAPL phase contaminants. These data are confounded by the lack of subsurface solids sampling at many of these sites.
- The degree of heterogeneity in permeable subsurface solids affects both the success of remediation and the incidence of rebound. Homogeneous and permeable sites (Group A) are more likely to meet MCLs and attain site closure and have a higher mean percent reduction in maximum contaminant concentrations; they are less likely to experience rebound relative to permeable, heterogeneous sites (Group C). However, ACLs are met with consistent frequency after ISCO remediation conducted in permeable subsurface solids independent of the amount of heterogeneity. Practitioners use a higher oxidant dose when treating heterogeneous materials.
- The use of pilot testing improves performance results in heterogeneous, permeable materials (Group C) but does not have an impact on performance in homogeneous, permeable materials (Group A).
- The presence of DNAPL is as much of a challenge to ISCO as it is to other remediation technologies. No DNAPL sites in the database attained MCLs. However, ACLs and site closure were attained for some DNAPL sites. ISCO practitioners use longer delivery events, greater injection volumes, and a higher oxidant dose for DNAPL sites. DNAPL sites are more likely to use a coupled post-ISCO technology, particularly EISB and MNA. Rebound is more prevalent at suspected DNAPL sites, with 78% of DNAPL sites observing this phenomenon in at least one well ($n = 36$) versus 56% at sites where DNAPL was not suspected ($n = 34$).
- Microbial populations are not permanently reduced through the use of ISCO and may be unaffected by ISCO or even flourish as a result of ISCO treatment. ISCO is compatible with EISB and MNA when these two technologies are used after ISCO.
- Approximately half of the case studies that monitored metals concentrations noted transient increases as a result of ISCO. The duration and severity of increases is highly site-specific. All metals impacts were localized to the ISCO treatment zone except for two projects that noted increases in chromium concentrations downgradient.

- Permeability reductions were noted in approximately one-fifth of case studies, including one quarter of permanganate case studies. These numbers may overstate the incidence of these issues because some project documents did not discuss permeability changes, most likely because they did not occur. The causes of permeability reduction are highly site-specific and could not be correlated with any of the data in the database. In some cases, well performance was improved by redevelopment or addition of acids or hydrogen peroxide.

8.9 SUMMARY

This chapter provides a comprehensive summary of a quantitative analysis performed using data contained within an ISCO case study database. The database was prepared to enable use of information from past field-scale ISCO projects to examine when it is most successful, identify inherent limitations to the technology, and determine what system designs seem to be most effective. The purpose of the quantitative analysis was to relate ISCO successes and failures to key design and site conditions toward advancing the standard of practice by identifying key design attributes that can improve the probability of success under challenging site-specific conditions. A careful review of the findings will allow practitioners to better focus and optimize their designs based on site conditions and treatment goals. Even though there are some limitations with the data within the database, the results of the analysis can lead to more cost-effective ISCO treatment.

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CHAPTER 9

SYSTEMATIC APPROACH FOR SITE-SPECIFIC ENGINEERING OF ISCO

Michelle Crimi,¹ Thomas J. Simpkin,² Tom Palaia,² Benjamin G. Petri³ and Robert L. Siegrist³

¹Clarkson University, Potsdam, NY 13699, USA; ²CH2M HILL, Englewood, CO 80112, USA;

³Colorado School of Mines, Golden, CO 80401, USA

Scope

A systematic engineering approach for effective screening, design, and implementation of *in situ* chemical oxidation (ISCO).

Key Concepts

- A systematic engineering approach can increase the probability that an ISCO project will achieve remediation goals and objectives in a successful manner.
- The applicability of ISCO to a contaminated site, as well as the appropriate oxidant and delivery approaches, depend on site conditions and treatment goals, for which ISCO can be screened accordingly. A well-defined Conceptual Site Model will help guide ISCO Screening.
- To improve treatment efficiency and effectiveness, coupling ISCO with other technologies and approaches with respect to space (e.g., downgradient approaches) or time (e.g., post-ISCO natural attenuation) should be considered for most ISCO applications.
- A tiered approach to the Conceptual Design of an ISCO system can guide site-specific data collection to optimize treatment and cost effectiveness.
- Final system design and implementation planning will depend on the contracting approach employed.
- Using the Observational Method for ISCO operations and performance monitoring will guide design optimization and can improve treatment effectiveness.

9.1 INTRODUCTION

Effective design and implementation of *in situ* chemical oxidation (ISCO) is the result of informed decision making throughout the application of ISCO, beginning with initial technology screening and ending with field implementation and performance monitoring. Decisions that must be made throughout an ISCO application are generally consistent with those for other *in situ* groundwater remediation technologies, with some technology-specific details. The systematic engineering approach outlined in this chapter presents one methodology for applying ISCO within a larger environmental cleanup process. Figure 9.1 shows on the left-hand side the general, commonly followed approach to environmental cleanup, while the right-hand side of the figure shows how the approach described in this chapter matches up to the traditional

process. The ISCO approach is divided into four major components: Screening, Conceptual Design, Detailed Design and Planning, and Implementation and Performance Monitoring.

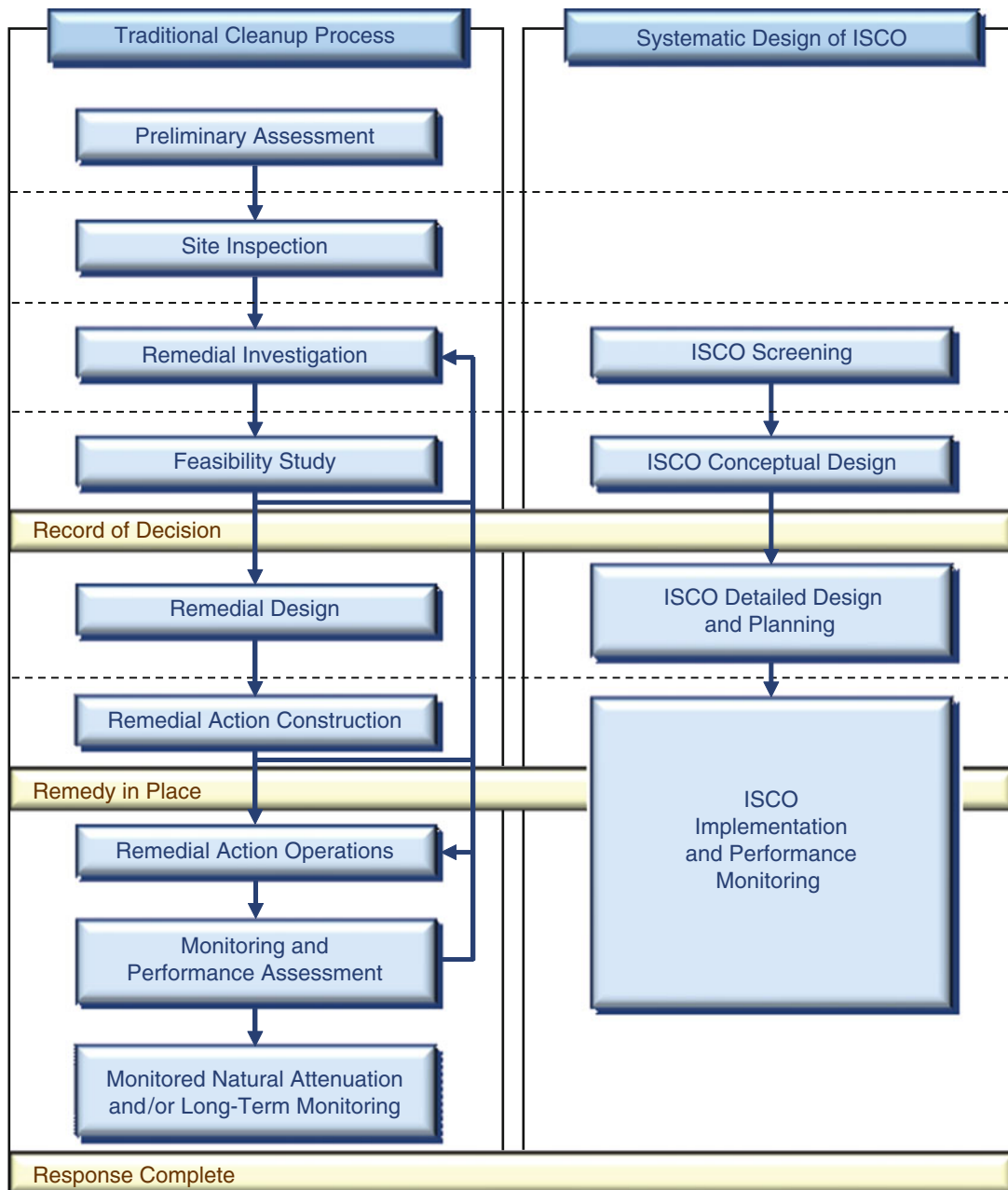


Figure 9.1. The typical approach to the environmental cleanup process (left-hand side) as it relates to the ISCO-specific systematic engineering approach describe herein (right-hand side).

Table 9.1 introduces the general content of each of these components. While Figure 9.1 presents these components in a linear decision mode, it is important to note that often design and implementation of a technology is an iterative process as information about site conditions and design effectiveness is gained throughout the application.

The core components of an ISCO systematic engineering approach are summarized below, and are described in detail in their respective sections in this chapter, with major chapter subsections dedicated to each. This chapter provides examples of procedures and processes for successful ISCO design and implementation within the context of the above four components. These examples are based on review of literature, case histories (lessons learned from both successes and failures), and professional experience. There is some redundancy with material presented in other chapters; the other chapters should be consulted for further detail on specific facets of ISCO technology. For instance, for details relevant to specific oxidants reference is made to Chapters 2–5, corresponding to the particular oxidant of interest, while for specific details on mathematical modeling of ISCO reference is made to Chapter 6.

Table 9.1. Components of a Systematic Approach for Site-Specific Engineering of ISCO

ISCO approach component	Scope
ISCO Screening Process	<ul style="list-style-type: none"> • Defines the data needed to evaluate the applicability of ISCO for a site • Describes key factors that impact oxidant selection and delivery approach selection • Addresses the need for and value of coupling ISCO with other remediation technologies and approaches (e.g., monitored natural attenuation (MNA) post-ISCO)
ISCO Conceptual Design Process	<ul style="list-style-type: none"> • Includes two phases of design for promising ISCO approaches identified during ISCO Screening <ul style="list-style-type: none"> – Initial Conceptual Design phase (Tier 1 design) is used to rapidly narrow ISCO options in terms of cost and implementation viability, using already available data – The second, more thorough Conceptual Design phase (Tier 2) refines promising Tier 1 designs using additional data from site-specific laboratory, field, or modeling studies with the goal of reducing cost uncertainty and design effectiveness • Presents example procedures/processes for conducting lab and/or field pilot tests, and cost estimation criteria
ISCO Detailed Design and Planning Process	<ul style="list-style-type: none"> • Three separate phases; preliminary design, final design, and planning <ul style="list-style-type: none"> – Preliminary design covers development of a Preliminary Basis of Design Report, along with development of an Operation and Contingency Plan – Final design covers contracting approaches, design and performance specifications, value engineering and design optimization, construction costing, and cost optimization – Planning focuses on procurement; the bid process; contract selection; and issues of quality assurance, health and safety, and performance monitoring
ISCO Implementation and Performance Monitoring Process	<ul style="list-style-type: none"> • Three separate phases; implementation, delivery performance monitoring, and treatment performance monitoring <ul style="list-style-type: none"> – Implementation focuses on infrastructure construction and baseline contaminant and geochemical monitoring – Monitoring prescribes appropriate approaches, including response actions to take when observed site conditions are different than anticipated – Oxidant delivery performance and treatment effectiveness performance are discussed in the context of measuring results against performance criteria and implementing contingency plans as necessary

9.2 SCREENING OF ISCO APPLICABILITY

9.2.1 Introduction

The ISCO Screening Process, shown in Figure 9.2, is a multi-step, iterative process to determine if ISCO is applicable to a site based on contaminant characteristics, site conditions, and remediation objectives. The general process is described as follows. The first level of ISCO Screening is to determine if ISCO should be eliminated immediately from consideration based on key site attributes that dictate that ISCO will likely not be effective. Appropriate site characterization data must exist to determine if there are clear reasons why ISCO is not applicable. Tools are provided herein to guide these data collection efforts and decisions. If there are no clear indications that ISCO is impracticable, the next step is to determine if a coupled approach (ISCO plus an appropriate pre- and/or post-ISCO remediation technology or approach) deserves consideration based on necessity and/or to improve cost-effectiveness. This is followed by a systematic, integrated evaluation of oxidants and delivery techniques based on multiple critical site characteristics. A series of lookup tables can then be referred to for selecting appropriate ISCO approaches (a set of specific oxidant and delivery method combinations) that are based on contaminant characteristics and porous media/groundwater conditions. The output of the evaluation is a set of viable ISCO options for site-specific ISCO application that are scored and ranked with consideration of three major factors: effectiveness, implementability, and user preference.

It is important to note that while many of the processes and decisions throughout ISCO Screening are depicted in a linear fashion with some feedback loops incorporated, ISCO should be applied using the Observational Method. The Observational Method acknowledges that decisions must be made based on data that contains some degree of uncertainty, and that data collected throughout a remediation project are used to reduce uncertainty and refine a remedy application in an iterative fashion. The general steps of the Observational Method for site remediation, also discussed in Chapter 11, are as follows:

- Conduct an investigation to establish the general characteristics of a site
- Establish the most probable site conditions and potential deviations from these conditions
- Develop a design based on these most probable conditions
- Determine courses of action if conditions deviate from those predicted (contingency plans)
- Measure and evaluate actual conditions during technology implementation
- Modify the design and implementation as needed to suit actual site conditions

Decisions during the ISCO Screening component are made to continuously address and reduce uncertainty. ISCO Screening decisions and processes are depicted in Figure 9.2. The numbers in Figure 9.2 refer to process steps, while the letters refer to decision points. Process steps and decision points are described in the sections below and illustrated with a case study.

9.2.2 Site Characterization Data Needed for CSM Development and Screening of ISCO

To consider any remediation technology, a conceptual site model (CSM) should first be developed. CSM development is discussed in Chapter 10. Additionally, guidance is offered as

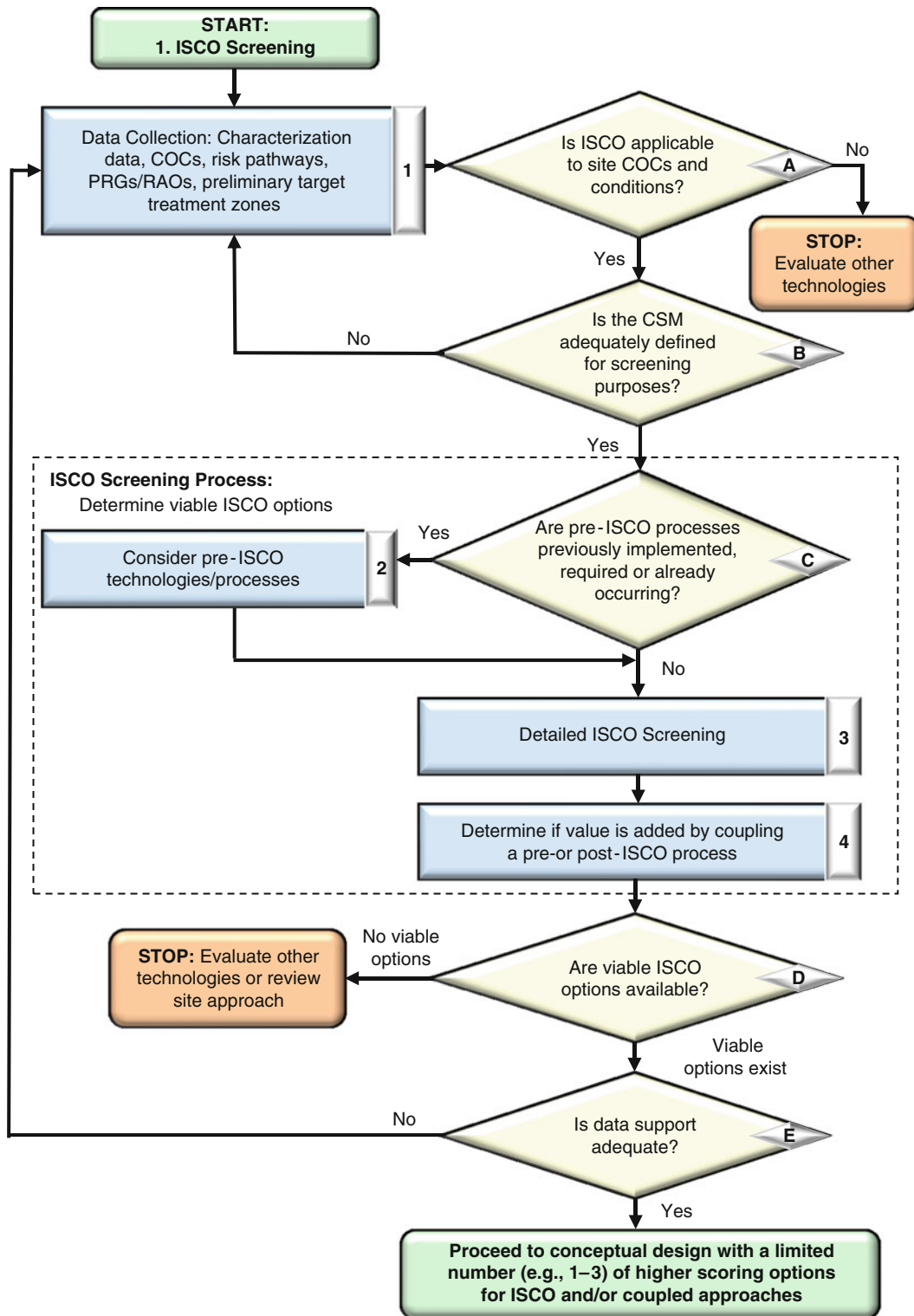


Figure 9.2. Decision logic diagram for Screening ISCO applicability to a site. Note: COC - contaminant of concern, CSM - conceptual site model, PRG - preliminary remedial goal, RAO - remedial action objective.

part of the U.S. Environmental Protection Agency's Soil Screening Guidance: User's Guide document in their Appendix A (USEPA, 1996). The CSM will typically be based on:

- Site history considering past, current and future uses
- Age, type, and location of release(s)
- Site geology and hydrology
- Previous remediation activities and remedial progress made at the site
- Applicable regulatory program under which remediation is being conducted
- Current site management plan and exit strategy

Screening Process 1 (shown as Box 1 in Figure 9.2) involves consideration of ISCO site characterization data needs, through use of a checklist of typical CSM data and ISCO-specific site characterization information (Table 9.2). The checklist includes parameters that are needed for design of almost any *in situ* remediation technology, in addition to a few ISCO-specific parameters.

Data gaps in the CSM can introduce uncertainty in the selection of ISCO as a viable technology to meet remediation objectives for a site (see Chapter 10). The acceptable level of uncertainty will vary from site to site depending upon many factors including the stringency of the remedial objectives. For example, if treatment to maximum contaminant levels (MCLs) is required for the site by a regulating body, then high CSM certainty is needed and higher costs of data collection are warranted. If, however, the goal is to reduce contaminant mass and budget is seriously constrained, then less certainty in the CSM may be acceptable. Additionally, if the Observational Method is followed throughout the ISCO technology screening, design, and implementation phases much of the additional data can be collected on an as-needed basis to fill important data gaps and address the related uncertainty. It may be in the project team's best interest to collect excess porous media and groundwater (and store using proper procedures) from the site for later analyses in case ISCO emerges as a viable remedy. This will save costs for future mobilizations for sample collection. For example, enough porous media for a natural oxidant demand (NOD) test could be collected during the remedial investigation (RI) if chlorinated solvents are presumed to be present. Samples could be stored and NOD tests run later should permanganate emerge from the screening stage as the preferred oxidant. The number of samples to collect, along with their collection procedure (s), handling, and storage should be guided by standard practices (e.g., see USEPA, 1989, 1991 and references therein).

9.2.3 Screening ISCO for Site-Specific Contaminants, Site Conditions, and Treatment Goals

ISCO can be an effective remediation technology for treating some organic COCs in the subsurface and for meeting risk-based or performance-based remediation goals and objectives. However, ISCO cannot be applied universally to all contaminated sites, and the ease and effectiveness of ISCO depends significantly on site-specific conditions. This section provides example procedures and precautions to help determine if ISCO should be considered during the preliminary technology screening process.

From the information provided in Screening Process 1, ISCO Site Characterization Data Needs, the next step is to determine if ISCO is clearly not viable (Decision A, Figure 9.2). There are four considerations that help make this decision: (1) ability of oxidants to react with COCs, (2) site hydrogeology, (3) nature and extent of contamination (e.g., presence of NAPL

Table 9.2. Checklist of Information Needed to Develop a CSM and Enable Screening of ISCO

<u>Contaminant of concern (COC) data</u>
<input type="checkbox"/> Identification of COCs
<input type="checkbox"/> Estimate of lateral and vertical extent of contamination (source and plume areas)
<input type="checkbox"/> Approximate information on source mass and/or phase distribution (dissolved phase only, significant sorbed mass, nonaqueous phase liquid (NAPL) suspected or known to exist, pooled NAPL, etc.)
<input type="checkbox"/> Approximate age of the spill or release
<u>Hydrogeology data</u>
<input type="checkbox"/> Identification (e.g., continuous log) of all significant lithologic layers present within and immediately adjacent to the contaminated zone
<input type="checkbox"/> Identification of prominent confining or semi-confining layers that govern groundwater flow
<input type="checkbox"/> Aquifer material characteristics
<i>If site is consolidated:</i>
<input type="checkbox"/> Estimate of permeability (primary/secondary)
<i>If site is unconsolidated:</i>
<input type="checkbox"/> Hydraulic conductivity as measured by field tests (if hydraulic conductivity is obviously high (e.g., coarse uniform sand) or obviously low (e.g., clay), measurement is not necessary for screening)
<input type="checkbox"/> Characterization of heterogeneity (e.g., is formation primarily permeable or impermeable, assessment of likely variation in saturated hydraulic conductivity (K) between distinct strata, evaluation of interconnection of high K zones, evaluation of whether fractures or other preferential pathways exist)
<input type="checkbox"/> Depth to confining layer
<input type="checkbox"/> Estimation of groundwater elevations, hydraulic gradients (horizontal and vertical), flow direction
<u>Geochemistry data</u>
<input type="checkbox"/> Groundwater oxidation-reduction potential (ORP)/redox potential (Eh)
<input type="checkbox"/> Porous media/groundwater pH
<input type="checkbox"/> Dissolved oxygen (DO)
<input type="checkbox"/> Temperature
<u>Goals and objectives</u>
<input type="checkbox"/> Analysis of applicable regulations
<input type="checkbox"/> Identification of numeric and non-numeric goals/objectives
<input type="checkbox"/> Identification of numeric objectives to meet primary goals
<input type="checkbox"/> Determination of the necessary endpoint to be achieved using ISCO
<u>Site plan</u>
<input type="checkbox"/> Plan is to scale
<input type="checkbox"/> Topography and ground surface elevations
<input type="checkbox"/> Lateral extent of contaminant source zone(s) and plume(s) delineated
<input type="checkbox"/> Location of major site infrastructure identified with emphasis on implications for site access (e.g., buildings, roadways, utilities, fencing, tanks, etc.)
<input type="checkbox"/> Locations of monitoring wells, soil cores, or other characterization activities clearly identified
<u>Cross section of hydrogeology and contamination</u>
<input type="checkbox"/> Profile to scale and located along the primary source/plume core alignment
<input type="checkbox"/> Contaminant source zones and plumes delineated laterally and vertically
<input type="checkbox"/> Major site surface and subsurface infrastructure identified with emphasis on implications for site access (e.g., buildings, roadways, utilities, fencing, tanks, etc.)
<input type="checkbox"/> Prominent geologic layers identified to the base of the contaminant plume
<input type="checkbox"/> Confining or semi-confining lithologic layers identified
<input type="checkbox"/> Piezometric surface for aquifer(s) of concern
<input type="checkbox"/> Risk receptors (e.g., wells, surface water bodies, residences, etc.)
<input type="checkbox"/> Regulatory compliance locations (e.g., property lines, etc.)
<input type="checkbox"/> Locations of monitoring wells, soil cores, or other characterization activities clearly identified
<u>ISCO-specific data</u>
<input type="checkbox"/> Health and safety, and other issues
<input type="checkbox"/> Permanganate NOD (e.g., 48-h test in American Society for Testing and Materials (ASTM) method D7262-07) for chlorinated ethene-contaminated sites (i.e., where permanganate is a likely candidate) ^a

^aA similar evaluation at this screening stage is not necessarily recommended for other oxidants because there will not be a limit to the extent of oxidant consumption. With oxidants that autodecompose when activated (via contact with natural minerals in porous media or via engineered activation), 100% of the oxidant will be depleted, albeit at varied rates of decomposition. It is prudent and economical, however, to collect enough media for later kinetic tests with oxidants for any site where ISCO may be viable.

vs. low dissolved concentrations) and (4) remediation objectives. Each of these considerations is discussed below.

9.2.3.1 Determine ISCO Applicability for COCs

ISCO should be considered for sites where groundwater and/or porous media are contaminated with organic COCs that are degradable (i.e., complete mineralization to carbon dioxide (CO₂) and/or other innocuous byproducts) by common ISCO oxidants. Table 9.3 presents a list of major contaminant classes divided into three categories. These findings are based upon cumulative experience with ISCO oxidants, but specific contaminants and site conditions may be more amenable to one oxidant than another, necessitating additional screening beyond this process (presented later). Table 9.3 is based on the information available in the literature at the time of this writing that is also referred to in other chapters (Chapters 2–5). Research continues on many of these oxidants, so new information is likely to evolve in the future. This table is only intended to help establish whether or not ISCO should be considered, and to give some insight into the level of experience of using ISCO with specific contaminant types.

Table 9.3. Categorization of Contaminant Classes by ISCO Treatability^a

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

Sources: Hoigné and Bader (1983a, b), Huang et al. (2005), ITRC (2005), Huling and Pivetz (2006), Waldemer and Tratnyek (2006). Note: BTEX - benzene, toluene, ethyl benzene, and total xylenes; MTBE - methyl tert-butyl ether; NDMA - *N*-nitrosodimethylamine; PAHs - polycyclic aromatic hydrocarbons; PCBs - polychlorinated biphenyls; RDX - hexahydro-1,3,5-trinitro-1,3,5-triazine; TAME - tert-amyl methyl ether; TNT - trinitrotoluene; TPH - total petroleum hydrocarbons.

^aDegradability of contaminants will vary by the oxidant used, so additional evaluation is required to select the most appropriate oxidant; see Section 9.2.6.

Category 1 contains organic contaminant classes that common ISCO oxidants can readily degrade. In general, the bulk of ISCO applications and experience have been in treating sites with Category 1 contaminants. **Category 2** contains organic contaminants that are degradable by ISCO oxidants, but their degradability is much more site- and process-specific. These contaminants will often either exhibit more resistance to oxidation and reduced degradation efficiency, or their degradability and cost-effective treatment by ISCO oxidants is less proven and more uncertain. If the site's primary risk-driver COCs are in Category 2 contaminant classes, more caution should be exercised in screening ISCO for these contaminants because the science and engineering knowledge base regarding ISCO application to these COCs is less defined. **Category 3** contains contaminant classes for which ISCO should NOT be considered for COC treatment. Generally, these are inorganic contaminants where ISCO will be either

ineffective, or potentially worsen a situation by altering contaminant behavior in the subsurface. Furthermore, if redox-sensitive heavy metals or radionuclides are present as co-contaminants at a site where target COCs are in Categories 1 or 2, ISCO Screening should consider the potential for affecting risk due to impacts of ISCO on co-contaminant concentrations and/or mobility. CSM uncertainty should be low at such sites before proceeding with ISCO Screening.

Even when the COCs are amenable to oxidation, ISCO treatment goals may be unachievable under some site conditions and subsurface settings because of the difficulty in delivering the oxidant throughout the target treatment zone (TTZ). Table 9.4 presents a matrix to further guide ISCO Screening and summarizes recommendations for whether the ISCO Screening Process should proceed based on the ISCO treatment goals that might be established and for generic hydrogeologic conditions and contamination levels. Recommendations are categorized as follows:

- “1” – Further screening of ISCO technologies is highly recommended. The combination of ISCO treatment goals, site conditions, and COC characteristics indicate that ISCO options may exist that have a high potential for meeting remediation objectives.
- “2” – Further screening of ISCO technologies is suggested. The combination of ISCO treatment goals, site conditions, and COC characteristics indicate that ISCO options might exist that offer potential for success, but with higher uncertainty. Consideration of coupling ISCO with other technologies (bioremediation, thermal, etc.) or use of advanced delivery techniques (e.g., mixing, fracturing, etc.) is also suggested because this may improve the chances of meeting treatment goals.
- “3” – Further screening of ISCO technologies is optional. The combination of ISCO treatment goals, site conditions, and COC characteristics presents a challenge to successful application of ISCO. However, it is anticipated that these same goals and characteristics would pose a challenge to many other remediation technologies as well. As such, consideration of ISCO may still proceed, but with recognition that there is low certainty with respect to performance. Consideration of coupling with other technologies and/or use of advanced delivery techniques is strongly recommended.

To use Table 9.4, the general level of contamination for a site must first be assessed (discussed further in Chapter 10, Section 10.4.2). Often, low concentrations/masses of organic contaminants are assumed if concentrations in groundwater are <1% of contaminant aqueous solubility, and high contaminant concentrations/masses are assumed if greater than this value (this value corresponds to the standard rule of thumb used in assessing dense nonaqueous phase liquid (DNAPL) presence based on aqueous phase COC concentrations (USEPA, 1992). However, sites with high organic carbon content would likely have significant sorbed contaminant mass, yet concentrations may be below this 1% threshold. Low contaminant concentrations/masses are addressed in the top portion of Table 9.4, and high levels in the lower portion.

Next, the ISCO treatment efficiency needed to meet a remediation goal is determined. For example, if a site contains perchloroethene (PCE) concentrations of 5 mg/L, and the remediation goal is to meet the MCL for PCE at 5 µg/L, then a 99.9% concentration reduction is needed. The percent reduction is located across the top row of each portion of the table for high and low contaminant levels.

Once the percent reduction needed is selected, the site characteristics that most closely match actual site conditions are considered (left-hand column of Table 9.4). The box corresponding with the appropriate ISCO treatment goal, site conditions, and COC characteristics in the table provides a recommendation for further screening of ISCO for the site. In general, but especially regarding

the site hydrogeology characterization, it is important to note that the recommendations provided in Table 9.4 relate to the decision to continue screening ISCO for a site and do not convey any finding related to probability of success. The recommendations are generally optimistic, to avoid eliminating ISCO as a potentially viable technology too early, when it may prove challenging yet

Table 9.4. Recommendation for Further Screening of ISCO Technologies Based on COC Levels, Site Hydrogeology, and ISCO Treatment Goals

Type of ISCO treatment goal: Removal magnitude (%):	Concentration reduction			Mass reduction			Mass flux reduction		
	50–90	90–99	99–99.9	50–90	90–99	99–99.9	50–90	90–99	99–99.9
Low contaminant concentration/mass									
Unconsolidated media									
Homogeneous permeable	1	1	2	1	1	2	1	1	2
Heterogeneous permeable	1	2	2	1	1	2	1	1	2
Homogeneous low permeability	1	2	2	1	1	2	1	1	2
Heterogeneous low permeability	1	2	2	1	1	2	1	1	2
Consolidated media (fractured)									
Sedimentary	1	2	2	1	1	2	1	1	2
Igneous/metamorphic	1	2	3	1	2	3	1	1	2
Karst	1	2	3	2	2	3	1	2	3
High contaminant concentration/mass									
Unconsolidated media									
Homogeneous permeable	1	1	2	1	1	2	1	1	2
Heterogeneous permeable	1	2	3	1	1	2	1	2	3
Homogeneous low permeability	1	2	3	1	2	3	1	2	3
Heterogeneous low permeability	1	2	3	1	2	3	1	2	3
Consolidated media (fractured)									
Sedimentary	1	2	3	1	2	3	1	1	2
Igneous/metamorphic	2	2	3	2	3	3	1	2	3
Karst	2	3	3	3	3	3	2	3	3

Notes: Key terms are defined in the box below. Recommendations relate to the decision to continue screening ISCO for a site and do not convey any finding related to probability of success. Values in the table are based on literature review, field experience, and case studies evaluated by the authors.

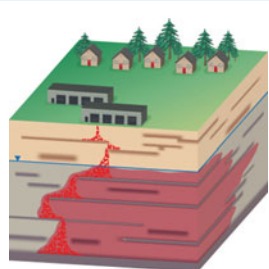
The numbers in each cell have the following meaning: "1" - Further screening of ISCO technologies is highly recommended. "2" - Further screening of ISCO technologies is suggested. "3" - Further screening of ISCO technologies is optional.

Definition of key terms used in Table 9.4.

- **Low contaminant concentration/mass.** COCs present in dissolved phases significantly below contaminant solubility limits (e.g., <1% solubility) or low levels of sorbed contaminant mass are present (e.g., conditions often found in groundwater plumes).
- **High contaminant concentration/mass.** COCs concentrations indicative of large sorbed masses or residual NAPL contamination; typical of conditions found in or near contaminant source zones. Includes pooled NAPL although NAPL pools should normally be pretreated therefore values do not apply to pooled NAPL unless pools are removed or reduced to residual-phase levels prior to ISCO.
- **Type of ISCO treatment goal.** Type of groundwater remediation goal being pursued as the desired post-ISCO end point at a given site. Three types include:
 - **Concentration reduction goals.** Sites where the remediation goal is either a specific porous media or groundwater contaminant concentration reduction (e.g., 95%), or target concentration value. Success or failure may be determined by whether a set percent reduction or threshold concentration is met or exceeded at a point, at a boundary, or site wide.
 - **Mass reduction goals.** Sites where the goal is to reduce contaminant mass (e.g., to reduce source or plume longevity). Sometimes, mass reduction goals are the target, but no performance estimate is made, and ISCO is just applied to enable a follow-up process, such as MNA or bioremediation. Typically, these goals are applied across an entire site or source zone and use geospatial methods and routine monitoring data for estimation.
 - **Mass flux reduction goals.** Considers the flow of groundwater contaminant mass across a two-dimensional (2-D) compliance plane—account for reductions in concentrations across the two-dimensional plane, as well as impacts to the groundwater flow field that may result from remediation. Values for this category are based on authors' judgment, research and experience, rather than actual case study performance, which are currently unavailable for this goal.
- **Unconsolidated media.** Sites where contaminant TTZs are located within unconsolidated porous media (uncemented sands, silts, clays, and tills)—divided into four subcategories:
 - **Permeability.** A site is considered permeable for ISCO application if the average hydraulic conductivity is greater than 10^{-4} cm/s and low permeability if it is less than 10^{-4} cm/s.
 - **Heterogeneity.** A site is considered heterogeneous if the hydraulic conductivity varies spatially by more than a factor of 1,000, and homogeneous if it varies by less than a factor of 1,000. Determination of such a factor is often based on idealized estimates based on presence of sands, silts, and clays rather than measured K values.
- **Consolidated media.** A site where the contaminant TTZ is in a consolidated fractured rock formation. Divisions are made based on the standard geologic definitions of sedimentary, igneous, and metamorphic rock formations, with the sole exception of karst formations. Karst formations pose unique problems to groundwater remediation using ISCO and thus must be evaluated separately.

viable compared to other remediation alternatives. For example, if the majority of COCs present at a heterogeneous site are present in a mobile, accessible zone, then the probability of success is significantly greater than if the COCs are present in lower permeability, low transmissivity zones. Further screening may still be recommended in the latter case because most technologies will experience limitations in contacting these less accessible fractions of COCs.

The information in Table 9.4 has been assembled based on published findings (summarized in Chapters 2–5), remediation experience documented in case studies (summarized in Chapter 8), results from a survey of ISCO experts, and the collective experience of the authors. Example 9.1 demonstrates the applied use of Tables 9.3 and 9.4.

Example 9.1. Screening ISCO for Site-Specific Contaminants, Geology, and Treatment Goals	
<p>Is ISCO viable for Site X? Site X contains chlorobenzenes where total chlorinated volatile organic compounds (CVOCs) in groundwater are present in concentrations up to 30,500 µg/L and are present in porous media in concentrations up to 40,000 µg/kg. DNAPL is suspected in some areas. Through site characterization activities, it has been determined the greatest contaminant impact is between 10 and 30 ft below ground surface (bgs) over an area 100 ft by 100 ft. This site is permeable and heterogeneous glacial till with an average hydraulic conductivity of approximately 50 ft/day. The treatment goal at the site is simply to achieve some mass reduction.</p>	<p>Contaminants:</p> <ul style="list-style-type: none"> • Chlorobenzenes • Concentrations up to 30,500 µg/L total CVOCs in groundwater and 40,000 µg/kg in soil • DNAPL suspected in some areas • Greatest impact at 10–30 ft bgs <p>Geology/Hydrology:</p> <ul style="list-style-type: none"> • Glacial till • Permeable and heterogeneous • K = 50 ft/day <p>ISCO Treatment Goal:</p> <ul style="list-style-type: none"> • Reduce contaminant mass 
<p>Response: Table 9.3 indicates that ISCO is a viable option for chlorobenzenes as the contaminant group appears in Category 1, highly amenable to effective degradation. Next, Table 9.4 is consulted. The lower half of the table is used due to the high contaminant mass at the site. The “50–90” column is then consulted under the header “mass reduction” to reflect the site’s ISCO treatment goal. Within that column, the media category to consult is the “heterogeneous permeable” row. The corresponding response is that it is worthwhile to continue the ISCO Screening Process (Table 9.4 recommendation = 1).</p>	

Reductions of greater than 99.9% are rarely achieved with source zone remediation technologies, and ISCO is generally no exception. Based on a review of ISCO field scale applications (see Chapter 8 for further details), concentration reductions greater than 99.9% have been reportedly achieved by ISCO in some situations, but they are the exception rather than the rule. As a result, a particularly robust ISCO design (e.g., high-density injection networks, several delivery events, multiple pore volumes [PVs] of ISCO reagents) is typically developed for sites attempting to reach such high levels of COC destruction. A Contingency Plan including a post-ISCO coupled technology (e.g., enhanced bioremediation or MNA) is often required and should be integrated with the design. Consider, for example, an unconsolidated homogeneous permeable site with residual trichloroethene (TCE) DNAPL, groundwater TCE concentrations measured at 200 mg/L, and where a risk-based concentration goal of 20 µg/L site wide is the remedial objective. A 99.99% concentration reduction is required, but it is highly unlikely this can be achieved with ISCO alone. In such a situation, ISCO might be applied to achieve a treatment goal equivalent to TCE mass reduction in a TTZ (e.g., 90%). ISCO could then be followed with either enhanced *in situ* bioremediation or MNA to achieve additional TCE treatment and eventually meet the 20 µg/L remediation objective.

9.2.4 The Conceptual Site Model for ISCO Screening

Throughout ISCO selection and design, and consistent with the Observational Method applied to site remediation, the CSM is revisited to help make sure that a sufficient amount of appropriate quality data has been collected and the CSM is adequately defined to support the decisions at hand. This step is Decision Process B in Figure 9.2.

Chapter 10 highlights the site characteristics typically described in a CSM. Depending on the stage of ISCO remediation, the approach used, and the remediation objective, higher or lower degrees of uncertainty may be acceptable. For instance, less information is needed about the site at the screening stage than at the Detailed Design and Planning stage to enable a

good outcome. Likewise, a relatively homogeneous site with dissolved phase contamination and an alternative cleanup level (ACL) objective will allow for greater uncertainty than a relatively homogeneous site with a DNAPL source zone and MCLs as a clean-up objective. The degree of uncertainty that is allowable in the CSM is subject to stakeholder agreement, and should be openly discussed. While this level of engagement with stakeholders is recommended here, this approach to site management is not widely practiced and may not be appropriate at all sites.

To assist in analyzing “uncertainty,” one approach can involve assigning semi-quantitative scores to important criteria. For example, if the weight-of-evidence unanimously indicates DNAPL presence, a HIGH certainty score can be assigned to this related criterion. If the dissolved-phase contaminant plume is poorly delineated (unbounded) on two sides, then a MODERATE certainty score would be assigned to this criterion. Additionally, a relative degree of “importance” can be assigned to each of the criterion to account for different weights certain criteria may carry. Each may have a relative degree of importance that is specific to site conditions and stakeholder perspectives. Furthermore, the importance of understanding the particular site conditions may change with time during ISCO project implementation (from screening through design and implementation). Project stakeholders should collectively decide on appropriate importance values and these may be revisited periodically throughout the project.

The acceptable level of certainty will be project-specific and should be based on project-team consensus. It will also depend upon the phase of the ISCO site-specific engineering within which decisions are being made. For example, a lower level of certainty may be acceptable during the ISCO Screening Process, but an increased level of certainty is preferred during the ISCO Conceptual Design Process. Finally, during ISCO Detailed Design and Planning, a high degree of certainty is important to maximize the potential for successful implementation. The goal of establishing CSM certainty is to assure appropriate data gaps are addressed and uncertainty is reduced and/or acceptable. This in turn can result in increased probability of treatment success.

If the outcome of Screening Decision B is that CSM certainty is deemed too low, then Screening Process 1 (ISCO-Specific Site Characterization) should be revisited to identify and close data gaps to help make sure that adequate site characterization data are collected to support the subsequent decisions (see Figure 9.2). If CSM certainty is deemed adequate, the next step is to evaluate ISCO compatibility with previously implemented remediation technologies and ongoing natural attenuation processes, or if a pre-ISCO coupled approach is necessary.

9.2.5 Consideration of Pre-ISCO Remediation

Screening Decision C (Figure 9.2) assesses the viability and benefits of conducting a pre-ISCO treatment step. Furthermore, pre-ISCO processes may be already occurring (naturally, such as biological degradation, or by design) or have been implemented in the past, resulting in site conditions that must be considered while screening ISCO.

In some cases, coupling ISCO with other remediation technologies or processes is a deliberate, pro-active decision (see Chapter 7). For example, it is possible to (1) benefit from synergistic, naturally-occurring biotic or abiotic COC attenuation processes, (2) improve chances for success because ISCO alone may not be capable of reliably achieving the desired remediation objectives due to high contaminant levels (e.g., NAPL) or other technically challenging conditions (e.g., low permeability formation), or (3) increase cost-effectiveness. If a site falls into a “2” or “3” category in Table 9.4, coupling may improve upon the performance achieved by using ISCO alone.

ISCO is often considered for a site where pre-ISCO processes are already occurring, resulting in a *de facto* coupled approach. This results in a “YES” response to Decision C in Figure 9.2. Some examples may include:

- Another technology has already been implemented at the site and the effects of prior remedial actions must be considered, or
- Natural biotic or abiotic processes are evident at the site and resumption (and enhancement) of these processes post-ISCO may be desired.

If a “YES” outcome is decided, the next step is to screen for pre-ISCO coupling to identify possible synergistic or deleterious interactions with ISCO (Process 2 in Figure 9.2). These interactions are summarized in Table 9.5, while detailed discussion of the interactions between ISCO and other technologies is included in Chapter 7. This list presented in Table 9.5 includes a variety of treatment technologies and approaches that may have already taken place, are currently ongoing, or may be necessary to improve the potential to reach remediation objectives. The information provided in Table 9.5 offers considerations for enhancing the coupling approach and/or cautions to consider in ISCO design and implementation. If a “NO” outcome is decided, then the next step (Process 3 in Figure 9.2) is to identify ISCO approaches as described in Section 9.2.6.

9.2.6 Detailed Screening of ISCO

Detailed ISCO Screening (Screening Process 3 of Figure 9.2) is an integrated set of steps for completing the screening and identification of appropriate ISCO approaches. It includes selection of oxidant chemicals and delivery method combinations. These steps are discussed below and presented in Tables 9.6–9.9.

The first step is to determine which oxidants and activation approaches (if needed) are most appropriate for destruction of the site COCs. While earlier screening processes (Table 9.3) evaluated the amenability of a contaminant class to chemical oxidation, a more detailed analysis is needed at this stage of screening. Table 9.6 provides further detail for evaluating contaminant amenability to degradation by *specific* oxidants including: permanganate, hydrogen peroxide, percarbonate, persulfate, and ozone. The table provides a scaled “grading” system of relative effectiveness of treating the contaminant with a particular oxidant. These grades have been assigned based on literature and case study review, as well as professional experience and expert opinion. The grades are meant as guidance and are subject to refinement as new knowledge evolves through research and experience. It is no surprise that many different contaminants are amenable to oxidation by several oxidants, and specific stakeholders may have a preference for one oxidant over others based on personal experiences. It is not appropriate to “down-select” ISCO options at this point based on preference; rather, it may be worthwhile to retain all or most of the viable options identified at this point and defer the down-select process until later when site conditions are considered in more detail (next step described below) or even for the Conceptual Design phase where costs can be preliminarily considered (Section 9.3).

The second step of Detailed ISCO Screening is to consider the oxidant’s applicability under the site-specific geochemical conditions, using Table 9.7, which follows the same type of scaled “grading” system presented in Table 9.6. For details on how and why the condition(s) of interest may impact oxidant viability, reference is made to Chapters 2–5 where details of oxidant chemistry and subsurface interactions are described. Again, the information presented in Table 9.7 should be viewed as guidance and subject to refinement. Where a site condition is of concern, but is not addressed in Table 9.7, the recommended approach is to retain the oxidant for consideration. The result of evaluating contaminant characteristics and site conditions using Tables 9.6 and 9.7 should be selection of at least one, more likely a number, of oxidants and/or oxidant activation/catalysis approaches that appear generally viable for the site under consideration.

The third step is to consider appropriate delivery approaches that are matched to the characteristics of the oxidant(s) under consideration (Table 9.8). The principles underpinning the

Table 9.5. Pre-ISCO Remediation Technologies That May be Applied *Within* the ISCO TTZ

Pre-ISCO technology	Advantages	Disadvantages
Excavation	<ul style="list-style-type: none"> • Rapid implementation • Easy to apply oxidant at the infiltrative surface • Soil mixing approaches may be more easily implemented 	<ul style="list-style-type: none"> • Hotspots may remain • Preferential flow may occur through backfill • Contaminated or highly organic backfill may cause excessive oxidant demand • Oxidant treatment of clean backfill represents inefficient oxidant use
Enhanced product recovery/ multiphase extraction	<ul style="list-style-type: none"> • Potential to reduce large mass of contaminants, which may reduce the mass of oxidant required • Removal of pooled or high NAPL saturation zones improves advective oxidant transport and likelihood of ISCO's success 	<ul style="list-style-type: none"> • Smear zone thicknesses may be increased • Residual NAPL will likely remain
Surfactant enhanced aquifer remediation (SEAR)	<ul style="list-style-type: none"> • Potential to reduce large mass of contaminants, which may reduce the mass of oxidant required • Surfactants may improve the reactivity of some oxidants • Enhanced solubilization and desorption may occur improving oxidation efficiency in the aqueous phase 	<ul style="list-style-type: none"> • Incompatible surfactants may cause excessive oxidant decomposition • Gas evolution may cause foaming and permeability loss • Some NAPL mass is likely to remain after SEAR
Soil vapor extraction/air sparging	<ul style="list-style-type: none"> • Potential to reduce large mass of contaminants, which may reduce the mass of oxidant required. • Infrastructure may already be in place for <i>in situ</i> ozonation • Contaminated vapors may be captured when using oxidants that evolve significant amounts of gas • May oxidize some reduced minerals, lowering the media NOD for ISCO 	
Thermal remediation	<ul style="list-style-type: none"> • Potential to reduce large mass of contaminants, which may reduce the mass of oxidant required • Elevated temperature may effectively activate some oxidants • For some oxidants and resistant contaminants, kinetic rates of degradation may be tremendously improved at elevated temperature 	<ul style="list-style-type: none"> • Elevated temperatures may pose health and safety concerns for some oxidants and contaminants with exothermic reactions • Solidification of silt and clay materials may occur, challenging subsequent oxidant delivery • At elevated temperature, excessive oxidant decomposition may challenge effective delivery
Intrinsic or enhanced bioremediation	<ul style="list-style-type: none"> • Biological degradation processes (if any) may be anticipated to return to baseline (e.g., unamended natural levels) after ISCO, and these may be used as a polishing step 	<ul style="list-style-type: none"> • Reducing conditions associated with anaerobic conditions may require excessive oxidant dosing • Elevated biomass and/or organic substrate concentrations in the treatment zone may cause excessive competition for oxidant and lead to poor treatment efficiencies

Note: Advantages and disadvantages listed are specific to coupling them to ISCO, not to the general use of the pre-ISCO technology listed.

Table 9.6. Amenability of Common COCs to Oxidation by Commonly Employed Oxidants

Oxidant and activation technique	Permanganate	Hydrogen peroxide			Persulfate				Ozone				
		Chelated iron	None ^a	Iron/acid	Percarbonate	Alkaline pH	Thermal	Iron	Chelated iron	None	Peroxide	Ozone only	With peroxide
Common contaminant mixtures													
Light hydrocarbon fuels ^b	Fair	Good	Good	Good	Good	Excellent	Excellent	Excellent	Excellent	Good	Excellent	Good	Good
Heavy hydrocarbon fuels ^c	Poor	Fair	Fair	Fair	Fair	Good	Good	Poor	Fair	Poor	Good	Fair	Fair
Creosote, coal tar, manufactured gas plant (MGP) residuals, other PAHs	Good	Good	Good	Good	Good	Good	Good	Fair	Fair	Poor	Good	Good	Good
PCBs or PBBs ^d	N/R ^e	Fair	Poor	Fair	Fair	Fair	Good	Poor	Poor	N/R	Fair	N/R	N/R
Dioxins or furans	N/R	Fair	Poor	Fair	Fair	Fair	Good	Poor	Poor	N/R	Fair	N/R	N/R
Common specific fuel contaminants and breakdown products													
Benzene	N/R	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Toluene	Good	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Ethylbenzene	Good	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Xylenes (<i>o</i> -, <i>p</i> - or <i>m</i> -)	Good	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Methyl- <i>tert</i> -butyl ether (MTBE)	Poor	Good	Good	Good	Good	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Good	Good
<i>Tert</i> -butyl alcohol (TBA)	N/R	Fair	Fair	Fair	Fair	Good	Good	Fair	Fair	Poor	Good	Fair	Fair
Common chlorinated solvents, stabilizers and their breakdown products													
Perchloroethene (PCE)	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Trichloroethene (TCE)	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Dichloroethenes ^f	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Vinyl chloride	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Tetrachloroethanes ^g	N/R	Fair	Fair	Fair	Fair	Fair	Fair	Fair	Fair	Fair	Fair	Fair	Fair
Trichloroethanes ^h	N/R	Good	Good	Good	Good	Good	Good	Fair	Fair	Poor	Good	Good	Good
Dichloroethanes ⁱ	N/R	Good	Good	Fair	Fair	Good	Good	Fair	Fair	Poor	Good	Good	Good
Chloroethane	N/R	Good	Good	Fair	Fair	Good	Good	Fair	Fair	Poor	Good	Good	Good
Carbon tetrachloride	N/R	Excellent	Good	Good	Fair	Excellent	Fair	N/R	N/R	N/R	Excellent	N/R	N/R
Chloroform	N/R	Good	Good	Good	Fair	Good	Good	N/R	N/R	N/R	Good	Poor	Poor
Dichloromethane	N/R	Good	Good	Fair	Fair	Fair	Fair	N/R	N/R	N/R	Fair	Poor	Poor
Methylene chloride	N/R	Good	Good	Fair	Fair	Good	Good	Fair	Fair	Poor	Good	Poor	Poor
1-4-Dioxane	Good	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Good	Good

(continued)

Table 9.6. (continued)

Oxidant and activation technique	Permanganate	Hydrogen peroxide		Percarbonate	Persulfate				Ozone			
		Chelated iron	None ^a		Iron/acid	Alkaline pH	Thermal	Iron	Chelated iron	None	Peroxide	Ozone only
Chlorinated aromatic contaminants												
Pentachlorophenol (PCP)	Good	Good	Good	Good	Good	Good	Fair	Fair	Good	Good	Good	Good
Tri- and tetrachlorophenols	Good	Good	Good	Good	Excellent	Excellent	Good	Good	Excellent	Excellent	Good	Good
Chloro- and dichlorophenols	Good	Good	Good	Good	Excellent	Excellent	Good	Good	Excellent	Excellent	Good	Good
Chlorobenzene	Poor	Fair	Fair	Fair	Excellent	Excellent	Good	Good	Excellent	Excellent	Good	Fair
Di- and trichlorobenzenes	Poor	Fair	Fair	Fair	Excellent	Excellent	Good	Good	Excellent	Excellent	Good	Fair
Hexachlorobenzene	N/R	Fair	Fair	Fair	Good	Good	Fair	Fair	Good	Good	Fair	Fair
Explosives, energetics and breakdown products												
RDX and HMX	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good
TNT and DNT	Poor	Poor	Poor	Poor	Good	Poor	Poor	Poor	Poor	Good	Poor	Poor
Di- and trinitrobenzenes	Fair	Fair	Fair	Fair	Fair	Fair	Fair	Fair	Fair	Good	Good	Fair
Mono- and dinitrophenols	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good
DNT dinitrotoluene, HMX tetrahexamine tetranitramine												

^aMineral catalysis.
^bGasoline, diesel, kerosene, jet fuel, etc.
^cFuel oils, bunker oil, etc.
^dPolychlorinated biphenyls (PCBs) or polybrominated biphenyls (PBBs).
^eN/R = not recommended.
^f1,1-, *cis*-1,2-, and *trans*-1,2-dichloroethane (1,1,1-, *cis*-1,2-, *trans*-1,2-DCE).
^g1,1,1,2- and 1,1,2,2-tetrachloroethane (1,1,1,2- and 1,1,2,2-TeCA).
^h1,1,1,1- and 1,1,2-trichloroethane (1,1,1,- and 1,1,2-TCA).
ⁱ1,1- and 1,2-dichloroethane (1,1,- and 1,2-DCA).

Table 9.7. Applicability of Oxidants to Common Geochemical Conditions

Oxidant and activation technique	Permanganate	Hydrogen peroxide			Persulfate				Ozone				
		Chelated iron	None ^a	Iron/acid	Percarbonate	Alkaline pH	Thermal	Iron	Chelated iron	None	Peroxide	Ozone only	With peroxide
pH range													
<5	Excellent	Excellent	Excellent	Excellent	N/R ^b	N/R	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
5-6	Excellent	Excellent	Excellent	Excellent	Fair	Poor	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
6-7	Excellent	Excellent	Good	Good	Good	Fair	Excellent	Good	Excellent	Excellent	Excellent	Excellent	Excellent
7-8	Excellent	Good	Fair	Fair	Excellent	Good	Excellent	Fair	Good	Good	Good	Good	Good
8-9	Excellent	Good	Poor	Poor	Excellent	Excellent	Good	Poor	Good	Fair	Fair	Good	Fair
>9	Good	Poor	N/R	N/R	Excellent	Excellent	Fair	N/R	Poor	Poor	Poor	Fair	Poor
Alkalinity (mg/L as calcium carbonate [CaCO ₃])													
0-300	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
300-1,000	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
1,000-3,000	Excellent	Good	Good	Good	Excellent	Excellent	Good	Good	Good	Good	Good	Good	Good
>3,000	Excellent	Fair	Fair	Fair	Excellent	Excellent	Fair	Fair	Fair	Fair	Fair	Good	Fair
Chloride concentration (mg/L) ^c													
0-300	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
300-1,000	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Good	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
1,000-3,000	Excellent	Good	Good	Good	Good	Good	Fair	Good	Good	Good	Good	Good	Good
3,000-10,000	Excellent	Fair	Fair	Fair	Fair	Fair	Poor	Fair	Fair	Fair	Fair	Fair	Fair
>10,000	Good	Poor	Poor	Poor	Poor	Poor	Poor	Poor	Poor	Poor	Poor	Poor	Poor
Amenability to saturated zone fraction organic carbon content (<i>f_{oc}</i>)													
<i>f_{oc}</i> > 3.0%	N/R	N/R	N/R	N/R	N/R	N/R	Poor	Poor	Poor	Poor	Poor	Poor	N/R
1.0% > <i>f_{oc}</i> < 3.0%	Poor	Poor	Poor	Poor	Poor	Poor	Fair	Fair	Fair	Fair	Fair	Fair	Poor
0.3% > <i>f_{oc}</i> < 1.0%	Good	Good	Good	Good	Good	Good	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Good
0.1% > <i>f_{oc}</i> < 0.3%	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
<i>f_{oc}</i> < 0.1%	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Contaminant concentration ^d													
Very low	Good	Excellent	Excellent	Excellent	Excellent	Excellent	Good	Good	Good	Good	Good	Good	Excellent
Low	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Moderate	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
High	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Fair
Very high	Good	Fair	Fair	Fair	Fair	Fair	Fair	Fair	Fair	Fair	Fair	Fair	Poor

^aMineral catalysis.
^bNot recommended.
^cShould include chloride equivalent based on contaminant concentrations as appropriate.
^dVery low = <10 mg/kg or <100 µg/L; Low = 10-100 mg/kg or 0.1-1 mg/L; Moderate = 100-1,000 mg/kg or 1-10 mg/L; High = 1,000-10,000 mg/kg or 10-100 mg/L; Very high = >10,000 mg/kg or >100 mg/L.

Table 9.8. Appropriateness of Delivery Methods for Different Oxidants

Delivery method	Permanganate	Hydrogen peroxide	Ozone	Persulfate
<i>Direct-push probe injection</i>				
	Frequently implemented	Frequently implemented	Technically impractical	Frequently implemented
<i>Well injection</i>				
Vertical wells	Frequently implemented	Less frequently implemented	Frequently implemented (sparge wells)	Frequently implemented
Horizontal wells	Implemented, but rarely	Technically possible	Implemented, but rarely	Implemented, but rarely
<i>Recirculation</i>				
Vertical wells	Less frequently implemented	Technically impractical	Frequently implemented (sparge wells)	Technically possible
Horizontal wells	Technically possible	Technically impractical	Technically possible (SVE) ^a	Technically possible
<i>Trench or curtain Injection (i.e., intercept a plume)</i>				
	Technically possible	Technically impractical	Less frequently implemented	Technically possible
<i>Soil mixing</i>				
	Implemented, but rarely	Implemented, but rarely	Technically impractical	Implemented, but rarely
<i>Fracture emplaced ISCO amendment^b</i>				
Pneumatic	Implemented, but rarely	Technically impractical	Technically impractical	Technically possible
Hydraulic	Implemented, but rarely	Technically impractical	Technically impractical	Technically possible
<i>Surface application or infiltration gallery</i>				
	Frequently implemented	Technically impractical	Technically impractical	Implemented, but rarely

^aISCO using ozone will frequently involve using soil vapor extraction (SVE) to capture and control gas flow in the subsurface. This air is treated and released, not reinjected.

^bIn addition to fracturing improving delivery, some sites have injected oxidant in a solid form during the fracturing process. Values given in the table reflect general level of usage for groundwater remediation as of 2009.

Legend:

- Frequently implemented (e.g., >15% of sites treated)
- Less frequently implemented (e.g., <15% of sites treated)
- Implemented, but rarely (e.g., <5% of sites treated)
- Technically possible, but may not have been used yet, or is in a demonstration phase
- Technically impractical (e.g., cannot be implemented)

viability of different delivery approaches for specific oxidants can be found in Chapters 2–5. Details regarding oxidant transport processes can be found in Chapter 6 and a discussion of oxidant delivery methods can be found in Chapter 11. In general, an effective delivery method accounts for oxidant persistence and decomposition characteristics during transport in the TTZ.

The final step is to then compare the applicability of the viable delivery approaches for specific oxidants based on general site hydrogeology as shown in Table 9.9. The objective of

Table 9.9. Applicability of Delivery Methods to Common Hydrogeological Conditions

Parameter	Vertical injection wells	Vertical wells recirculation	Horizontal wells	Direct-push probe	Soil mixing	Hydraulic – fracture emplaced ISCO amendment	Pneumatic – fracture emplaced ISCO amendment	Trench or curtain injection (i.e., a plume)	Surface application or infiltration gallery
Amenability to media type									
Unconsolidated media	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Consolidated media	Excellent	Good	Excellent	N/R ^a	N/R	Excellent	Excellent	Fair	Good
Consolidated media properties									
Fracture continuity									
Good fracture continuity	Good	Good	Fair	N/R	N/R	Good	Good	Fair	Good
Poor fracture continuity	Fair	Poor	Poor	N/R	N/R	Good	Good	N/R	Poor
Permeability (both primary and secondary)									
Low	Good	Good	Fair	N/R	N/R	Good	Good	Fair	Good
High	Fair	Poor	Poor	N/R	N/R	Good	Good	N/R	Poor
Transmissivity									
Low	Good	Good	Fair	N/R	N/R	Good	Good	Fair	Good
High	Fair	Poor	Poor	N/R	N/R	Good	Good	N/R	Poor
Unconsolidated media properties									
Hydraulic conductivity (cm/s)									
$>10^{-3}$	Excellent	Excellent	Excellent	Excellent	Excellent	Poor	Poor	Excellent	Excellent
$<10^{-3}$ but $>10^{-4}$	Good	Fair	Fair	Excellent	Excellent	Fair	Fair	Good	Good
$<10^{-4}$ but $>10^{-5}$	Fair	Poor	Poor	Good	Excellent	Good	Good	Fair	Fair
$<10^{-5}$ but $>10^{-6}$	Poor	N/R	N/R	Fair	Excellent	Excellent	Excellent	N/R	Poor
$<10^{-6}$	N/R	N/R	N/R	N/R	Excellent	Excellent	Excellent	N/R	N/R
Magnitude of heterogeneity (K_{max}/K_{min})									
$<1,000$	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Fair	Excellent	Excellent
$>1,000$	Fair	Fair	poor	Good	Excellent	Fair	Fair	Fair	Poor
Type of heterogeneity (if $K_{max}/K_{min} > 1,000$)									
Layered	Fair	Fair	Poor	Good	Excellent	Good	Good	Good	Fair
Random	Fair	Fair	Fair	Good	Excellent	Fair	Fair	Good	Fair

(continued)

Table 9.9. (continued)

Parameter	Vertical injection wells	Vertical wells recirculation	Horizontal wells	Direct-push probe	Soil mixing	Hydraulic – fracture employed ISCO amendment	Pneumatic – fracture employed ISCO amendment	Trench or curtain injection (i.e., intercept a plume)	Surface application or infiltration gallery
Unconsolidated media properties									
Scale of heterogeneities ^b									
Small (<0.3 m)	Good	Good	Poor	Good	Excellent	Poor	Poor	Good	Good
Medium (0.3–1 m)	Fair	Fair	Poor	Fair	Excellent	Fair	Good	Fair	Fair
Large (>1 m)	Fair	Fair	Fair	Good	Excellent	Good	Good	Poor	Poor
Other important delivery parameters									
Depth of delivery (m bgs)									
<5	Excellent	Excellent	Excellent	Excellent	Excellent	Fair	Fair	Excellent	Excellent
<10 m but >5	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Poor
<25 m but >10	Excellent	Excellent	Good	Fair	Poor	Excellent	Excellent	Good	N/R
<50 m but >25	Good	Good	Poor	Poor	N/R	Excellent	Good	Fair	N/R
>50	Good	Good	N/R	N/R	N/R	Fair	Fair	Poor	N/R
Site activity disruption intensity									
Disruption of surface activities ^c	Light	Moderate	Very light	Moderate	Intense	Light	Light	Light	Intense
Disruption of subsurface activities ^d	Light	Light	Light	Moderate	Intense	Moderate	Moderate	Light	Moderate
Ability to treat contaminant mass distribution ^e									
Very low	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Low	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Moderate	Good	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Good	Excellent
High	Good	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Fair	Good
Very high	Fair	Good	Good	Good	Excellent	Excellent	Excellent	Poor	Fair

^aNot recommended.

^bDistance between lenses of alternating materials.

^cBuildings, active roads, restricted areas, etc.

^dFoundations, utilities, etc.

^eVery low = <10 mg/kg or <100 µg/L; Low = 10–100 mg/kg or 0.1–1 mg/L; Moderate = 100–1,000 mg/kg or 1–10 mg/L; High = 1,000–10,000 mg/kg or 10–100 mg/L; Very high = >10,000 mg/kg or >100 mg/L.

completing the Detailed ISCO Screening Process using Tables 9.6 through 9.9 is to emerge with a number of viable oxidant and delivery options that are deemed to be applicable to the COC characteristics and site conditions.

Example 9.2 is based on an actual field site where the option selected was delivery of persulfate via vertical wells (chelated iron activation). Use of these screening tables would have more likely returned direct-push as a more favorable delivery option, however reasonable success could have been expected for the approach chosen. In fact, the approach achieved 75% mass removal and 90% concentration reduction. Follow-on MNA was selected as part of the site’s long-term “polishing” strategy capable of meeting goals. Example 9.3 was also based on a real field site where, unfortunately, well injection was selected as the delivery approach (for permanganate). The approach achieved only a 40% PCE concentration reduction, high delivery back-pressures were reported, and the treatment was considered unsuccessful.

Examples 9.2 and 9.3 highlight the use of these Screening tables.

Example 9.2. Detailed ISCO Screening
Looking again at the characteristics presented for Site X in Example 9.1: Which oxidant(s) and delivery approach(es) is/are most favorable for Site X conditions?

<p>Contaminants:</p> <ul style="list-style-type: none"> • Chlorobenzenes • Concentrations up to 30,500 µg/L total CVOCs in groundwater and 40,000 µg/kg in soil • DNAPL suspected in some areas • Greatest impact at 10–30 ft bgs <p>Geology/Hydrology:</p> <ul style="list-style-type: none"> • Glacial till • Permeable and heterogeneous • K = 50 ft/day <p>Remedial Action Objectives:</p> <ul style="list-style-type: none"> • Reduce contaminant mass 		<p>Response: In consulting Table 9.6, under the “Chlorinated aromatic contaminants” category, it appears that persulfate activated by alkaline pH, heat, or hydrogen peroxide is the most viable option for chlorobenzenes. The method to activate or catalyze the oxidant, if needed, would be further evaluated against site geochemical characteristics (not provided in this example) using Table 9.7. Under typical or average site conditions, most approaches are viable with a solid expectation for success. Table 9.8 indicates the most successful delivery approaches for persulfate include direct-push probe, vertical well injection, or infiltration. Finally, Table 9.9 matches site-specific hydrogeology conditions to viable delivery approaches. The matrix below summarizes the findings from Table 9.9 as a function of the options selected using Table 9.8.</p>	
	Vertical wells	Direct-push probe	Surface application or infiltration
Unconsolidated media	Excellent	Excellent	Excellent
High hydraulic conductivity	Excellent	Excellent	Excellent
Magnitude of heterogeneity >1,000	Fair	Good	Poor
Random heterogeneity	Fair	Good	Fair
Low to moderate delivery depth	Excellent	Excellent	Poor
Ability to treat very high contaminant mass density	Fair	Good	Fair

Example 9.3. Detailed ISCO Screening

Looking at an additional, contrasting site, Site Y: Which oxidant(s) and delivery approach(es) is/are most favorable for Site Y conditions?

Site Y: Contains PCE at a maximum concentration in groundwater of 6,500 µg/L and 4,900 mg/kg in porous media. DNAPL is not suspected. Through site characterization activities, it has been determined the greatest contaminant impact is between 5 and 12 ft bgs. This site is primarily impermeable (clay) and homogeneous with an average hydraulic conductivity of approximately 0.001 ft/day. The treatment goal at the site is to reduce PCE concentrations to 500 µg/L.

Contaminants:

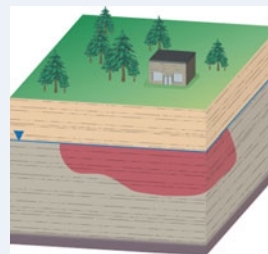
- PCE at maximum of 6,500 µg/L in groundwater and 4,900 mg/kg in aquifer solids
- DNAPL not mentioned in project documents
- Contamination limited to 5–12 ft bgs
- Porous media would be Resource Conservation and Recovery Act (RCRA) F-listed if excavated

Geology/Hydrology:

- Clay
- Homogeneous and impermeable
- $K = 0.001$ ft/day

Remedial Action Objectives:

- Reduce PCE concentration in groundwater to 500 µg/L



Response: In consulting Table 9.6, under the “Common chlorinated solvents” category, it appears that all four of the oxidants listed could be expected to have high PCE treatment effectiveness. Like the previous example, the method to activate or catalyze the oxidant, if needed, would be further evaluated against site geochemical characteristics (not provided in this example) using Table 9.7. Under typical or average site conditions, most approaches are viable with a high expectation for success. Table 9.8 indicates virtually all delivery approaches have some viability based on the wide oxidant applicability. Table 9.9, however, narrows options. An enabling approach such as soil mixing, or hydraulic or pneumatic fracturing would be recommended for such a low permeability site, and soil mixing might be preferable for the shallow delivery depth.

9.2.7 Consideration of ISCO Coupling

If many of the options retained following the Detailed ISCO Screening Process described above in Section 9.2.6 are considered only “fair” or less favorable, adding another pre- or post-ISCO remediation technology or approach may add significant value to the project and increase the overall likelihood of success. Chapter 7 presents a detailed discussion of the fundamentals of coupling ISCO with other technologies and approaches so only a summary is presented in this chapter.

ISCO can feasibly be coupled concurrently (same time and location) with other technologies to improve the ability to reach site remediation objectives. While there is limited information available in the literature and in field case histories, there is a theoretical basis for coupling ISCO with other technologies concurrently including:

- Surfactant/cosolvent flushing to enhance contaminant dissolution, hence making COCs more available for destruction by oxidants in the aqueous phase
- Thermal technologies which may act as an activator (e.g., for heat-activated persulfate) or improve reaction kinetics during ISCO
- Pump and treat, which may use existing infrastructure in recirculation systems or to induce gradients to impact oxidant movement through the subsurface

Tables 9.10 and 9.11 include considerations for ISCO applied adjacent to other technologies or before other technologies, respectively (and, as mentioned, Section 9.2.5 along with Table 9.5 describes considerations for ISCO applied after other technologies).

Table 9.10. Considerations for ISCO Applied at the Same Time as Other Remediation Technologies and Approaches in Adjacent Zones with Low Contaminant Levels

Treatment downgradient of or adjacent to ISCO treatment in zones of low contaminant concentration					
Oxidant used	Enhanced bioremediation		Permeable reactive barrier	ISCO	MNA
	Aerobic	Anaerobic			
Catalyzed hydrogen peroxide	+ Partially oxidized dissolved organics (e.g., dissolved organic carbon [DOC]) mobilized during ISCO process may enhance aerobic bio in down-gradient areas	- While oxidation process will not sterilize subsurface, oxidation process will create highly oxidized and aerobic conditions that may counteract desirable conditions for anaerobic bio + Partially oxidized dissolved organics (e.g., DOC) mobilized during ISCO process may enhance anaerobic bio in downgradient areas	- Sulfate released may cause detrimental geochemical conditions and cause fouling of an iron PRB, though only a few examples of this exist and the fouling can be chemically treated	- If low pH conditions are sustained after treatment, then may be detrimental for persulfate treatment which requires basic conditions for activation • Peroxide does not create problems for subsequent application of permanganate + Is generally very compatible with peroxide because peroxide can be used to catalyze persulfate - If caustic activator is used and high pH is sustained after treatment, then may be detrimental for catalyzed hydrogen peroxide (CHP) process	• ISCO will generally not affect biological mechanisms for downgradient MNA - Metals liberated by ISCO may cause exceedance of groundwater cleanup criteria if downgradient geochemical conditions are not suitable for sorption/precipitation of dissolved metals + Oxidation of reduced metals may improve biological treatment by increasing the electron acceptor pool + ISCO may assist downgradient MNA by liberation of partially oxidized organics (e.g., DOC)
	+ Aerobic bioactivity may be enhanced during peroxide application		• Sulfate may enhance or inhibit anaerobic bio in downgradient areas depending on respiratory pathways involved		
Persulfate			- Residual manganese dioxide may cause problems for subsequent application of peroxide reducing reactivity		+ Oxygen produced may assist downgradient MNA
Permanganate					
Ozone	+ Aerobic bioactivity may be enhanced during ozone application				

Notes: The plus symbol (+) denotes positive impacts, the minus symbol (-) denotes negative impacts, and the dot (•) denotes points of interest. The impacts of a coupled treatment method can apply to all oxidants listed or to some more specifically, as designated by the cell boundaries.

Table 9.11. Considerations for Remediation Technologies and Approaches Applied to the Same TTZ after ISCO

Contaminant level	Post-ISCO treatment	ISCO applied prior to subsequent treatment			
		Catalyzed hydrogen peroxide	Persulfate	Permanganate	Ozone
High	Excavation	+ ISCO may be used to decrease concentrations of RCRA-regulated compounds, thus decreasing landfill/disposal costs + Residual partially oxidized dissolved organics (e.g., DOC) may enhance aerobic bioactivity + Residual oxygen may enhance aerobic bioactivity + Residual DOC may enhance anaerobic bioactivity – While oxidation process will not sterilize subsurface, oxidation process will create highly oxidized and aerobic conditions that may counteract desirable conditions for anaerobic bioactivity			
High or low	Enhanced bio	Aerobic	<ul style="list-style-type: none"> Residual sulfate may enhance or inhibit anaerobic bio in downgradient on respiratory pathways involved 	<ul style="list-style-type: none"> Manganese dioxide solids may decrease transport and sustain elevated redox potential, though evidence suggests that they do not inhibit reductive dechlorination Bioactivity can dissolve manganese dioxide, perhaps allowing better transport 	+ Residual oxygen may enhance aerobic bioactivity
	Anaerobic		<ul style="list-style-type: none"> Residual sulfate may be detrimental to iron reaction 	<ul style="list-style-type: none"> Residual permanganate may passivate iron surfaces 	
Low	Iron-reducing zone or permeable reactive barrier	<ul style="list-style-type: none"> Effects take time to manifest themselves and may be vary depending on site-specific conditions such as indigenous microbial community, geochemistry, and hydrology Reduction in mass flux from the source zone may enhance effectiveness of MNA and cause plume to collapse Residual DOC may enhance bioactivity 			
Low	Monitored natural attenuation	<ul style="list-style-type: none"> Sulfate may enhance or inhibit anaerobic bio in downgradient areas depending on respiratory pathways involved 			

Notes: The plus symbol (+) denotes positive impacts, the minus symbol (–) denotes negative impacts, and the dot (•) denotes points of interest. The impacts of a coupled treatment method can apply to all oxidants listed or to some more specifically, as designated by the cell boundaries.

Each of the ISCO coupling tables should be consulted, as appropriate, to determine if there are opportunities to synergistically combine ISCO with other technologies and approaches. The tables offer considerations for enhancing a coupled approach and/or cautions that must be considered in ISCO design and implementation.

9.2.8 Outcomes of the ISCO Screening Process

This section covers Decision Processes D and E in Figure 9.2. The basic decision process for Screening Decision D is straightforward. If the outcome of Screening Process 3 (Detailed ISCO Screening) and/or Screening Process 4 (Coupling Considerations) is that there are no viable ISCO or coupled-ISCO options, then other remediation alternatives must be considered. When there are viable ISCO options, the next step is to revisit the CSM to evaluate data adequacy in preparation for the ISCO Conceptual Design Process. When the CSM uncertainty is acceptable to the project team, the Conceptual Design process is initiated. When the CSM uncertainty is unacceptably high, stakeholders should consider what aspects of the CSM are not well understood, and work to collect additional data to reduce the uncertainty to an acceptable level prior to proceeding. Where viable ISCO options emerge and adequate data support exists, it is recommended to proceed to Conceptual Design with the top several options identified during screening. Where options are otherwise equal or near equal, stakeholder preference is an appropriate criterion to narrow down the number of options that will be further evaluated during Conceptual Design.

9.3 CONCEPTUAL DESIGN OF AN ISCO SYSTEM

9.3.1 Introduction

The ISCO Conceptual Design Process provides an opportunity to evaluate in more detail the specific ISCO options retained following ISCO Screening so that informed decisions can be made about their viability. The Conceptual Design process consists of analyzing various attributes of each ISCO option with the objective of honing in on a specific design. At this stage, design factors such as oxidant injection point spacing, number of injection points, injection volume and others are taken into consideration.

The process for Conceptual Design outlined here consists of two tiers. The first tier involves analysis of existing information from the site, making informed assumptions where necessary, with the objective of rapidly evaluating various ISCO designs and narrowing the range of options. An uncertainty analysis is then performed to determine if a second tier of Conceptual Design is necessary. If so, the second tier is implemented where additional information can be collected concerning the site via laboratory testing, field pilot testing, or modeling with the goal of reducing the uncertainty in the ISCO system design required to achieve ISCO treatment goals to acceptable limits.

The following sections describe an example process that can be followed to develop a site-specific Conceptual Design for an ISCO technology. The information below corresponds to the processes and decision points depicted in Figure 9.3, and like ISCO Screening (Figure 9.2) the numbers in the figure refer to process steps, while the letters refer to decision points.

9.3.2 The Target Treatment Zone

The TTZ can be defined as the 3-D region of the subsurface that will be treated by ISCO. It should be defined both horizontally (e.g., boundaries on a map) and vertically (depth

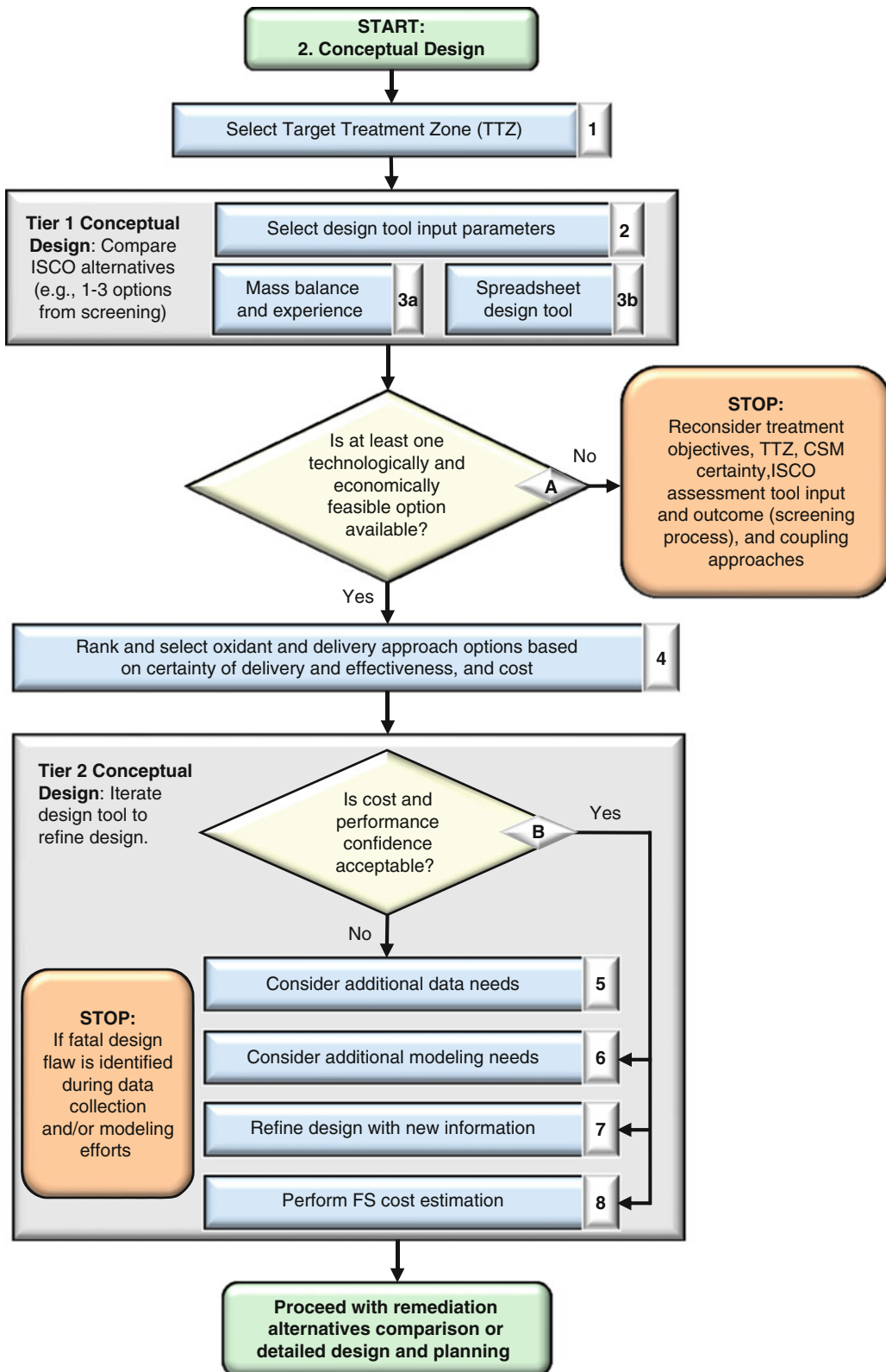


Figure 9.3. Decision logic diagram for ISCO Conceptual Design development.

interval(s) to be targeted). Defining the TTZ is not necessarily an easy or straightforward exercise. The overall site remediation objectives and the timeframe available to achieve them are often the driving factors in defining the TTZ. The following are possible considerations:

- If reaching MCLs or a risk-based cleanup criterion in a short time period is the objective, then the TTZ should be defined based on the best available information on the extent of groundwater exceeding MCLs.
- If reaching MCLs or a risk-based cleanup criterion is a long term goal, then the TTZ can be defined as something smaller, with an approach like MNA used to manage the contaminated zone(s) outside of the ISCO-specific TTZ (see Section 9.2.7).
- If mass removal is the ISCO treatment goal, the extent of mass removal that is desired must be defined. Then the TTZ from which this mass must be removed can be defined.
- Reducing mass flux is a relatively new objective that also may be used (see Chapter 10, Section 10.4.2.2). If mass flux reduction is the ISCO treatment goal, the TTZ should be based on estimates (including simple or complex modeling) of ISCO treatment effectiveness and the subsequent movement of any untreated COCs out of the TTZ.

Defining the depth interval(s) of the TTZ can be done by depth-discrete subsurface profiling (including porous media and groundwater), from which the layer(s) of the subsurface with the majority of the contamination can be targeted. Membrane interface probes (MIP) or similar in-field tools may also be used to help understand the variation of the contamination with depth and/or the presence of the COC mass in different types of lithology (i.e., if the COC mass is entrained in clay or is present in a higher permeability sand) (see Chapter 10, Section 10.4.2).

It is very unusual to have a perfect set of data from which to define the TTZ. There will always be some uncertainty. Additional data could be collected during later phases of the ISCO Conceptual Design Process, as described below in Section 9.3.5. An alternative is to follow the Observational Method and perform the first ISCO injection with the information available. The TTZ for a second injection could be adjusted based on what is learned during the first injection and subsequent performance monitoring (see Chapter 12).

9.3.3 Tier 1 Conceptual Design

Tier 1 Conceptual Design is completed using the current CSM and results of ISCO Screening to provide:

- A preliminary evaluation of the applicability of an ISCO system and an estimate of cost
- A basis for comparison of the ISCO options retained following ISCO Screening (Section 9.2.8)
- Information on the sensitivity of ISCO performance (e.g., oxidant delivery ROI) and cost to various design parameters (e.g., oxidant concentration and injection volume)

9.3.3.1 Design Considerations

The first step in Tier 1 Conceptual Design is to select appropriate design parameters. Key design parameters regardless of the specific design approach followed are related to:

- TTZ
 - Treatment area
 - Saturated zone thickness
 - Percent mobile zone of saturated zone thickness (typically from 5–80% volume to volume ratio (v/v); tracer or pilot tests can be used to evaluate; further explanation provided below)
 - Total porosity (typically $n = 0.15\text{--}0.40$ v/v)
 - Bulk density (typically 1.4–1.8 kg/L)
- Contaminant concentrations and distribution profile (spatial delineation with depth discrete data representing the TTZ)
- Desired oxidant concentration and desired duration of that concentration (based on contaminant mass present, oxidant behavior such as persistence accounting for decomposition, and NOD)
- NOD (typically expressed as mass oxidant consumed/mass media): applicable primarily to permanganate systems (further explanation provided below)
- Number of injections/deliveries of oxidant planned (typically 1–3 but further explanation provided below)

A key design parameter is the “thickness of the mobile zone” in the groundwater system within the TTZ. This is the fractional volume of the TTZ through which the injected oxidant chemicals will actually migrate. Because of the heterogeneities in the subsurface and variability in porous media hydraulic properties, injected oxidant solution is typically only advectively transported through a fraction of the saturated zone formation. At some sites, this fraction is obvious from boring logs (e.g., flow will go predominantly through coarse-grained layers [e.g., sands] and less so in finer-grained layers [e.g., silts and clays]). But even in what appear to be relatively homogeneous subsurface zones, only small differences in hydraulic conductivities are required to cause flow to preferentially go through different portions of the subsurface. These differences may not be apparent from reviewing boring logs. Having a small mobile zone compared to the total thickness of the TTZ may negatively impact performance. For example, if there is contamination in lower permeability layers due to longer term exposure to COCs prior to remediation, the oxidant is not likely to contact this contamination and back diffusion might sustain COC concentrations in groundwater above a remediation objective. But having a low thickness of mobile zone is likely to result in a larger ROI since the injected fluid is likely to move out further from an injection probe or well than radial plug-flow might indicate. This may result in a lower cost for achieving a given ROI. Information from boring logs can provide a reasonable first estimate to use for the thickness of the mobile zone. However, the uncertainty associated with this design parameter should be taken into account, and the sensitivity to it should be evaluated in the Conceptual Design (Payne et al., 2008).

With permanganate, one of the most important design parameters is the NOD (refer to Chapter 3, Section 3.3.1). The NOD, in the absence of NAPL, typically far exceeds the consumption of an oxidant during reaction with the COCs at a site. During the Tier 1 Conceptual Design, actual NOD measurements may not be available. They can vary widely from site to site, as they have been found to be below 0.1 g-MnO₄⁻/kg at some sites, and near 100 g-MnO₄⁻/kg at others. High porous media organic matter content will generally increase NOD significantly, as will substantial biomass, organic growth substrates, or reduced minerals. In the absence of site-specific NOD data, a range of values may be employed to

determine how sensitive the design is to NOD. To reduce uncertainty, an NOD test of the TTZ is strongly recommended as it is presently the only reliable way to quantitatively evaluate NOD.

Typically an NOD value for persulfate, CHP, and ozone isn't applicable due to the reaction chemistry of these oxidants (Chapters 2, 4, and 5). That is, as long as the oxidant is in contact with an agent in the subsurface (e.g., delivered activator, reduced mineral) that affects its desired decomposition to create free radical species, 100% of the oxidant will be consumed over time. Rather than NOD, for persulfate, CHP and ozone, oxidant persistence over time is a more physically appropriate design parameter.

An additional key ISCO design parameter is the number of injections to be used to deliver the oxidant chemicals and achieve the ISCO treatment goals. Among 88 full-scale case studies of ISCO projects containing data on the number of injection events, 75% used more than one delivery event, 45% used two or three delivery events, and 58% used between two and four delivery events. The mean number of delivery events was 2.8 (these statistics do not include ozone or peroxone applications which deliver oxidant continuously for an extended period in one long delivery event). Additional details can be found in Chapter 8. Multiple injection events can add to the cost, but they provide the opportunity to modify and optimize the design based on what is learned in the first injection. This concept of apply, measure, and readjust the design is consistent with the Observational Method.

9.3.3.2 Tier 1 Design Approaches

A number of approaches can be used to complete a Tier 1 Conceptual Design for ISCO. Two are mentioned here and the more complex of these two is described in further detail in Chapter 6. Which approach is used will depend on the ISCO option under consideration, the information available, and the objectives of the design team. In some cases a hybrid approach is followed where a simple approach is used first followed by a more complex approach. This can be appropriate because it can help identify and prioritize the typical design outputs that the design team aims to address early on including:

- Spacing between injection wells and/or spacing between rows of delivery points
- Mass and concentration of oxidant to be delivered at each injection location
- Flow rate and total volume of oxidant solution to inject (and therefore delivery duration)
- Number of injection events

Tier 1 Mass Balance Design Approach

A mass balance approach, demonstrated in Example 9.4, coupled with experience is a commonly used approach. The major components of this approach are (1) specifying the delivery method to be evaluated based on the delivery outcome of the ISCO Screening Process; (2) selecting injection well/point spacing based on experience with similar sites or conditions (normally this depends on formation characteristics and oxidant used); (3) selecting the appropriate oxidant flow rate and concentration, also based on experience and/or specific known chemical properties; and (4) using a mass balance to calculate the mass of oxidant required. The mass balance for oxidants that can be slowly depleted, such as permanganate or unactivated persulfate, should account for NOD (discussed in detail in Chapter 3, Section 3.3.1) and contaminant stoichiometric demand. In contrast, the mass balance of oxidants that undergo rapid

decomposition such as CHP, activated persulfate and ozone should include at least some estimate of how rapidly the oxidant is depleted as described in Chapters 2, 4, and 5, respectively. Or very often, the mass of oxidant used is based on the volume of the TTZ and experience with mass loading ratio (mass of oxidant to mass of aquifer solids).

The designs of some CHP, persulfate, and other oxidant systems depends on the distribution of activators as well as the oxidant chemical (hydrogen peroxide or persulfate). Oxidant and activators/catalysts can be added sequentially as is the case most frequently with heat or alkaline pH activated persulfate or with CHP; they can also be added simultaneously, as is the case most frequently with iron-citrate activated persulfate, for example. Experience is often used to complete these designs and the art and science of their application is constantly evolving. In addition, in support of Tier 1 Conceptual Design, laboratory studies may be used to select optimal chemistry parameters to maximize oxidant distribution, contaminant degradation, and avoid operational problems such as excessive heat or gas evolution. Many factors impact the effectiveness of these oxidants; specific factors examined in an optimization study may include the activator type, activator concentration, stabilizing amendments, oxidant concentration, and pH. Many reasons and procedures for optimizing these factors are discussed in more detail in Appendix D.2. Additional details about appropriate catalysts, activators, and conditioning agents can be found in Chapters 2, 4 and 5 for hydrogen peroxide, persulfate, and ozone, respectively.

Table 9.12, based on a review of case histories describing field applications of ISCO, provides a summary of the median values for the design parameters reported in these case studies (additional details may be found in Chapter 8). While this information is of interest, it does not necessarily suggest that these are the “correct” values for any particular application. Not all of these case studies were successful. “Good” design practices and site-specific considerations should be taken into account prior to selecting values for these design parameters.

At contaminated sites, which have reportedly met ISCO treatment goals, there is a tendency to have a longer injection duration per injection event and a greater total volume of oxidant delivered (see Chapter 8). A review of 68 ISCO case histories revealed that the average volume of oxidant solution delivered into the TTZ at these sites is equivalent to only about 0.10 PV. A survey of professionals (Cooper et al., 2006) indicates that the average volume of oxidant solution injected is equivalent to about 0.10–0.30 PV within the TTZ. Interestingly, in the review of 68 ISCO case histories noted above, it was observed that approximately 0.50 PV of oxidant was delivered into a TTZ, on average, at sites that met a 90% or greater COC concentration reduction metric.

Tier 1 Analytical Model Design Approach

A relatively simple modeling approach can add substantial insight for decision-making compared to the mass balance approach, primarily by allowing for direct comparison of different design choices for ISCO design parameters. Features that a Conceptual Design based on an analytical model may consider above and beyond that possible with a mass balance approach include:

- Hydraulic conductivity variations
- Quantitative or semi-quantitative understanding of subsurface heterogeneities
- Oxidant demand/decomposition kinetics and reactive transport (typically determined in laboratory or field pilot studies)
- Desired percent overlap of oxidant ROI

Example 9.4. Using the Mass Balance Approach for ISCO Design
What is the appropriate spacing for oxidant delivery, concentration and mass of oxidant to deliver, the appropriate flow rate and volume with which to deliver oxidant, and number of times to deliver oxidant to the site?

Referring back to Site X characteristics in Examples 9.1 and 9.2: Site X contains high concentrations of chlorobenzenes in porous media and groundwater, with suspected DNAPL. The ISCO Screening Process was followed and delivery of persulfate via direct-push probe or wells was deemed most viable for the site. Since multiple injections will likely be required, wells were selected. Contamination is between 10–30 ft bgs over an area 100 ft in length by 100 ft wide.

Contaminants:

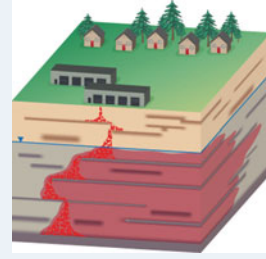
- Chlorobenzenes
- Concentrations up to 30,500 µg/L total CVOCs in groundwater and 40,000 µg/kg in soil
- DNAPL suspected in some areas
- Greatest impact at 10–30 ft bgs

Geology/Hydrology:

- Glacial till
- Permeable and heterogeneous
- $K = 50$ ft/day

Remedial Action Objectives:

- Reduce contaminant mass



Response: A common spacing used for injection wells is about 20 ft, translating to a 5×5 grid of injection points, or 25 total injection wells. If an oxidant dose of 4 g persulfate/kg-media (just above median shown in Table 9.12) is employed, then the approximate mass of oxidant needed is 88,000 pounds (lbs) of oxidant. Note the following assumptions:

- 200,000 ft³ TTZ (100 ft wide \times 100 ft long \times 20 ft deep)
- Bulk density = 110 lb/ft³; therefore media mass is approximately 22,000,000 lb

A delivery of oxidant solution equivalent to about 1 PV within the TTZ should be considered (above median value shown in Table 9.12) due to the high contaminant mass present at the site. One PV is approximately equal to 80,000 ft³ (assuming $n = 0.40$), or 600,000 gallons, of solution delivered. Based on the 29,500,000 g of persulfate needed to be delivered in the 23,000,000 L of solution, a persulfate concentration of 1.7 g/L may be employed. If the budget allows, an uncertainty factor of 2–10 may be employed, resulting in a delivery concentration of 3.4–17 g/L within the “normal” range for persulfate delivery. For this example, alkaline activated persulfate can be assumed to be effective. Aboveground activation may be used. A mass ratio of activator to persulfate of 1:2 was assumed. If oxidant is delivered at a reasonable delivery volume of approximately 10 gallons per minute (gpm)/well simultaneously into eight wells, for 8 h per day, the anticipated time on site per injection event is approximately 16 days. At least two or more injection events could be anticipated for this site based on the high contaminant mass present to achieve significant mass removal, but it is important to keep the target goal in mind. The goal for this site was to achieve some mass removal, therefore one initial injection event could be assumed, with targeted follow-on injections in portions of the TTZ. If additional mass removal was desirable, the Observational Method could be employed to focus subsequent injections on hot spots, reducing the number of injection points, increasing injection spacing, decreasing injection volume, and decreasing the time on site per injection. For example, a second injection with 75% of the mass and volume of the first injection is reasonable to assume. Chapter 13 presents an example cost estimate using this example scenario.

The trade-off for implementing an analytical modeling approach for Tier 1 Conceptual Design rather than (or in addition to) a mass balance approach is the greater need for accurate site data for use in the model (although some parameters can be assumed for initial comparison of options and can then later be refined as warranted). Also, it is important to be cautious in noting uncertainties associated with the model. Model formulations and input values are imperfect and model outputs should not be relied on more heavily than appropriate.

Chapter 6 (Section 6.9.3) describes in greater detail an analytical model design approach that has been developed to allow for a relatively quick and straightforward comparison of ISCO design options; it is named Conceptual Design for ISCO, or CDISCO. CDISCO is based on modeling the subsurface around an injection probe or well as a series of completely mixed

Table 9.12. Median Values Reportedly Used for ISCO Design Parameters for Common Oxidants Based on a Review of Case Studies (from Chapter 8)

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

n = number of sites fitting category.

reaction zones expanding radially from the point of oxidant delivery and it is implemented through a spreadsheet tool. The model is a mathematically simplified version of subsurface transport of reactive solutions, but has the advantage over the mass balance approach of explicitly including key parameters as mentioned above. The output of this particular modeling approach is a design ROI for either a well or probe injection delivery of oxidant solution (the two most common delivery approaches). Estimation of the ROI allows for an initial cost-comparison of the different design approaches and site-characteristics that govern the ROI. It also allows evaluation of the site-specific characteristics to which the ROI is most sensitive (e.g., oxidant type, oxidant demand/kinetics, percent mobile zone, etc.). As explained later in Section 9.3.6, this insight can be used to focus expenditures on collecting key site data to reduce design and cost uncertainty.

As part of Tier 1 Conceptual Design Process 3a or 3b shown in Figure 9.3, costs are considered on a preliminary basis to help optimize the design approach and compare options. For example, CDISCO has a cost estimating procedure which generates a preliminary cost estimate based on the user specified TTZ dimensions, injection ROI overlap (%), number of injection events planned, fixed cost, and unit costs for injection point installation, chemical reagents, and labor for injection. Two injection approaches are possible: injection through temporary direct push probes or injection through permanent wells. Cost factors are included for mobilization, labor, materials, equipment rental, travel, and subcontractor costs. Costs are considered in more detail later after a full analysis of design and design certainty (shown as Process 8 in Figure 9.3).

9.3.4 Feasibility of Conceptual Design Options

The next step of ISCO Conceptual Design is shown as Decision A in Figure 9.3. This decision is based on a judgment of the technical and economic feasibility of viable ISCO options that emerge from Tier 1 Conceptual Design. The decision is based on:

- Ability to implement the design; with considerations including
 - Practicality of delivery point spacing
 - Practicality of the volume and mass of oxidant required
 - Potential interference due to above or below ground infrastructure
 - Safe handling of design oxidant concentrations
- Project budget constraints

Stakeholders should discuss these considerations at this point. If none of the ISCO options evaluated so far are deemed feasible, then the following options should be considered:

- Re-defining the TTZ
- Re-evaluating the Tier 1 Conceptual Design input parameter values
- Re-evaluating the CSM certainty and collecting additional data as needed (see Table 9.1 for a suggested list of data needs)
- Revisiting the ISCO Screening Process, with particular attention to coupled approaches (Section 9.2.5) or more aggressive delivery methods such as soil mixing or recirculation systems (Section 9.2.6)

If more than one ISCO approach is deemed to be technically and economically feasible then the ISCO Conceptual Design Process continues with ranking all feasible oxidant and delivery options.

9.3.5 Ranking Oxidant and Delivery Approach Options

Conceptual Design Process 4 (Figure 9.3) involves a comparison of all viable ISCO approaches (i.e., oxidant/delivery approach combinations) that were carried forward from the Tier 1 Conceptual Design (e.g., 1 to 3 ISCO approaches). This is demonstrated in Example 9.5. It should be reiterated that by this stage of the ISCO selection and design process, it has already been established that ISCO is a suitable remedial approach based on the site-specific conditions and contaminant characterization used in the ISCO Screening Process 1 (i.e., if you can achieve oxidant-contaminant contact, you will presumably achieve degradation of target COCs). Therefore the ranking criteria for this process focus specifically on the effectiveness of and factors related to the oxidant delivery approaches evaluated during ISCO Screening. These criteria are described below:

- **Delivery effectiveness.** This criterion concerns the ability of the delivery method to achieve oxidant-contaminant contact, given the injection design factors evaluated in the Tier 1 Conceptual Design. Basically this can be assessed by evaluating the resulting injection point ROI and other design features by iteratively performing the Tier 1 Conceptual Design process using a range of feasible parameter values. The simpler the approach (i.e., mass balance approach vs. analytical model approach), the less certainty there typically will be in predicting delivery effectiveness.
- **Treatment performance certainty.** Treatment performance certainty is the likelihood that an ISCO design will achieve ISCO treatment goals given site factors that can affect COC levels in the TTZ after oxidant delivery and reaction, such as rebound due to the presence of DNAPL or back diffusion of contaminants out of lower permeability layers. When evaluating this criterion, the primary question for the project team to consider is, “Is the injection design aggressive enough (i.e., accounting for the appropriate injection ROI overlap and sufficient number of injection events) such that ISCO treatment goals will likely be achieved given the CSM uncertainties?” This evaluation process also will be affected by factors beyond the CSM, such as regulatory cleanup requirements, the post-ISCO site management approach, and whether post-ISCO coupled technologies or approaches are feasible and could be implemented.
- **Cost.** Screening-level costs are compared for this criterion. These order-of-magnitude costs should be compared to project budgets to ensure financial sustainability of the ISCO delivery strategies.
- **Cost certainty.** Cost certainty is the likelihood that an ISCO approach can be successfully implemented with minimal risk of unforeseen costs and change orders. Unforeseen costs can stem from the need for additional injection points, more aggressive

injection approaches, higher oxidant dosage, and/or more injection events than planned. As with performance certainty, cost certainty will be based on design factors such as NOD, contaminant mass/distribution, subsurface heterogeneity (i.e., thickness of the mobile zone during injection), and the aggressiveness of the injection design.

- **Implementability.** This criterion is evaluated in the context of actual site conditions, such as access for well placement, interference with site activities, the presence of underground and aboveground infrastructure, and space constraints for temporary placement/storage of injection equipment.
- **Public and worker safety.** This criterion considers potential hazards during the field implementation of an alternative. Safety factors considered include the potential for exposure to the oxidant during oxidant handling, potential for exposure to the oxidant during injection (e.g., through surfacing or travel along utilities), potential for explosive conditions due to accidental mixing of oxidant with combustible/flammable materials and due to byproduct generation (such as oxygen from high concentrations of hydrogen peroxide) and self-accelerated decomposition (and resultant combustion of surrounding materials) when stored oxidants are exposed to heat and moisture (e.g., persulfate).

Different stakeholders may have different priorities with respect to these criteria. For example, for some sites and stakeholders, ISCO treatment performance certainty is of the highest priority. This may be because of the regulatory environment and the ISCO treatment goals that have to be met in order to satisfy site remediation objectives. At other sites, implementability will be key because of complex infrastructure. Stakeholders should agree on the relative importance or weighting of each of these criteria first. Then, each option can be ranked with respect to its potential ability to meet the criteria. The assigned weight times the ranking score can be integrated to come up with an overall score for each ISCO design option.

Example 9.5. Ranking ISCO Options Developed During Conceptual Design
Which oxidant and delivery approach is the most favorable given the site-specific issues affecting effectiveness and implementability presented below?

Two treatment options emerged from ISCO Conceptual Design as viable for treatment of a site in an open field with road and water access. The site has a high and fast natural demand for oxidant. The budget has not yet been established for the site, but the stakeholders desire and anticipate a quick, high-profit sale.

Response: The stakeholders, including the design team, have generated the following table to guide the comparison of the two options. The weighting factors were based on the need for quick treatment with no existing budget constraints or significant implementation challenges. The team worked together to establish estimates of how well options are able to meet the criteria. A value of 1 was assigned for a low probability result and a 5 was assigned to a high probability result. The weighting factors were multiplied by the score, which were then summed for an overall weighted score. The highest scoring option, Option 1, was selected for further design.

ISCO Design Options: Ranking

Criteria	Weighting factor (%)	Option 1	Option 2
Delivery effectiveness	40	5	2
Treatment performance certainty	30	1	2
Cost	0	3	3
Cost certainty	0	1	5
Implementability	10	2	3
Public and worker safety	20	2	3
Overall score (user weighted)	100	2.9	2.3

9.3.6 Tier 2 Conceptual Design

9.3.6.1 Cost and Performance Confidence

The objectives of the Tier 2 Conceptual Design are to: (1) refine the design, possibly with new data; (2) provide information to feed into a feasibility study (FS) (to compare ISCO against other alternatives); and (3) provide a foundation for a refined design if ISCO is selected.

The first step of Tier 2 design is to determine if the cost and performance confidence that is understood leaving Tier 1 design is acceptable, or if there is need to collect additional site-specific data (Decision B in Figure 9.3). As discussed previously, during Tier 1 Conceptual Design, a number of iterations of design options should have been considered with the range of possible input parameters and the range of outcomes evaluated for uncertainty.

Contingency evaluation assists with quantification of the magnitude of uncertainty in the Conceptual Design and helps determine if the cost and performance confidence of the ISCO design is acceptable. The results of the contingency evaluation can be used to assess whether to proceed with the existing Conceptual Design or revisit the data and design basis. The results also can be used later for preliminary detailed design during the ISCO Detailed Design and Planning Process (described in Section 9.4). The contingency evaluation provides a general framework for a project team to consider the range of potential treatment performance outcomes and estimate the cost and schedule impacts that may result if they occur. Details on how to perform the contingency planning process to assess cost and performance confidence are discussed in Chapter 11.

While not common, performance and cost confidence can be acceptable with only Tier 1 Conceptual Design. Examples of site attributes that are conducive to an acceptable confidence level at this stage include:

- When a large amount of data (e.g., related to oxidant persistence) is initially available
- The Observational Method is to be used and the level of uncertainty is acceptable
- The schedule is very tight and the stakeholders are willing to accept high levels of uncertainty
- Low levels of dissolved COCs exist in a well-defined treatment zone
- A relatively small TTZ (e.g., less than 2,000 ft³)
- Highly homogeneous and permeable porous media
- High certainty in the ability to achieve treatment goals
- Extensive experience with both site-specific conditions and design attributes
- Flexible budget, or a project budget that exceeds expected costs

Acceptable performance and cost certainty may be the case in Example 9.5 above where the budget is flexible; however, the project team responsible for this site would likely opt for additional data collection to improve performance certainty as this is a high priority for the site.

Where there is a significant amount of uncertainty in the performance and cost associated with the Tier 1 Conceptual Design, additional data should be collected (Figure 9.3, Process 5). Where performance and cost certainty are judged acceptable, then additional modeling needs (Figure 9.3, Process 6) or design refinements (Figure 9.3, Process 7) should be considered prior to preparing an FS level cost estimate (Figure 9.3, Process 8).

9.3.6.2 Consider Additional Data Needs

The purpose of collecting additional data is to refine ISCO design and reduce performance and cost uncertainty associated with the design. Process 5 in Figure 9.3, data collection, occurs until performance and cost confidence is acceptable and is thus an iterative step with Decision B (described in Section 9.3.6.1 above). It should be kept in mind that if the Observational Method is used for the full-scale application, additional data will be collected during the first full-scale injection completed as part of the ISCO implementation. In other words, the first full-scale injection could be considered as part of this data collection process.

Data collection can support refinements to the CSM and can also narrow the range of values used as input parameters during the Conceptual Design. Data regarding the following may be collected under site-specific conditions relevant to the ISCO design:

- Oxidant demand and persistence (e.g., NOD extent and rate)
- Contaminant or co-contaminant degradability
- Contaminant desorption/dissolution
- Appearance of intermediates and/or byproducts
- Metals mobilization
- Oxidant deliverability and fraction of formation through which oxidant will flow

Data may be collected through different methods at different scales ranging from simple laboratory bench-scale tests, to flow-through column tests at the laboratory pilot scale, to field performance evaluations through testing at the field pilot scale. Figure 9.4 includes a decision process to aid in selecting the appropriate level of testing. In general, where uncertainty surrounds chemical processes (e.g., oxidant persistence, contaminant degradability, variation in outcome with different oxidant activation approaches, etc.), laboratory scale testing may be sufficient. Where uncertainty surrounds delivery and transport processes, field pilot scale testing is recommended.

Guidance for conducting laboratory tests for oxidant persistence as well as for contaminant treatability and byproduct assessment are included in Appendices D.1 and D.2. Appendix D.2 includes examples of contaminant degradability, desorption/dissolution, intermediates/byproducts, and metals solubilization assessment procedures. It is important to note that the oxidant persistence and contaminant treatability/byproducts determinations described in these two Appendices are not to be considered stand-alone, consecutive processes. They may be conducted side-by-side concurrently or consecutively in either order depending on the site-specific data needs. Field pilot-scale testing guidance is provided in Appendix D.4 and addresses field scale means of assessing oxidant persistence, contaminant degradability, byproducts formation, etc.; along with assessment of oxidant deliverability. Related to these laboratory and field pilot tests, Appendix D.3 includes a summary of common analytical methods used to measure occurrence and concentrations of oxidants in environmental samples.

9.3.6.3 Consider Additional Modeling Needs

More complex modeling approaches may involve additional parameters than those considered in Tier 1 Conceptual Design if the level of certainty in design performance and cost is not acceptable. These parameters and their applicability are discussed in more detail in Chapter 6.

Prior to proceeding with additional modeling, data objectives should be carefully reviewed by project stakeholders. Site hydrogeologic and geochemical conditions also should be assessed

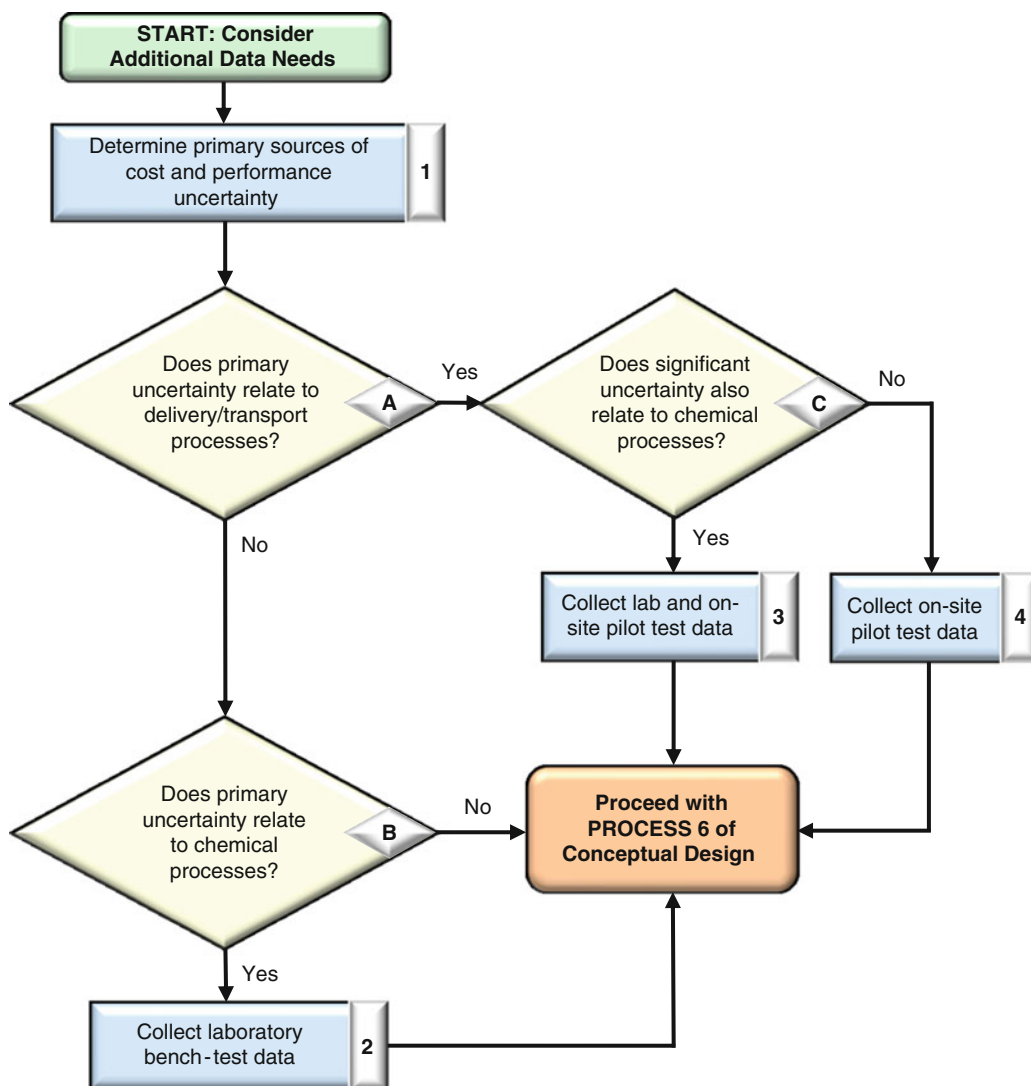


Figure 9.4. Data collection decision logic diagram for Tier 2 Conceptual Design.

to determine if they are amenable to detailed modeling. Additionally, the data needed to increase performance and cost certainty should be carefully considered. Examples of issues for design refinement that can be addressed with more advanced modeling under Process 7 shown in Figure 9.3 include:

- Impact of presence of NAPL
- Effects of contaminant source architecture/geometry
- Oxidant contact efficiency
- Effects of porous media heterogeneity
- Impacts of oxidation byproducts (e.g., manganese dioxide [MnO₂] generation with permanganate)
- Refined delivery approach (injection pattern, volume, and timeframe)

- Effects of oxidant depletion rates, such as NOD kinetics (fast and slow)
- Refined oxidant load and concentration
- Design input sensitivity analysis

Figure 9.5 includes a decision logic diagram to help determine if it is appropriate or feasible to perform more complex ISCO modeling. The following describes each step of the modeling decision process:

- **Define data objectives.** The primary goal of complex modeling at this stage of the Conceptual Design process should be to increase performance and/or cost certainty. The specific design elements driving uncertainty should be determined prior to considering and selecting a model.
- **Amenability of hydrogeologic/geochemical conditions to modeling.** The site-specific hydrogeologic/geochemical conditions should be considered.
- **Budget.** Is the project budget able to support an intensive modeling effort and what is the cost-benefit of performing modeling during the Conceptual Design phase? The project team should consider that additional site data also will be obtained during initial ISCO implementation if the Observational Method is adopted. However, the up-front labor and cost invested in setting up a model can be leveraged during latter phases of a remediation project if the ISCO system is to be expanded (at which time data collected during the first phase of implementation can be used to refine the model). The scale of the ISCO design will ultimately be a large factor in evaluating the benefits of modeling during the Conceptual Design phase.
- **Conceptual site model completeness.** The CSM should be revisited, taking into consideration data collected as part of Conceptual Design Process 5 (described in Section 9.3.6.2) to help make sure that model input will be adequately refined to meet data objectives.

At this stage, it is possible that a numerical model can be used with data from additional site investigations, laboratory treatability studies, and/or field pilot studies that have been completed by this stage of ISCO Conceptual Design. Model simulations specific to the site conditions can be conducted using all the available site data. However, it is necessary to recognize that the available data may not be sufficient to properly calibrate a particular model. Consequently, the utility of the model may be limited to preliminary analyses, to include: comparing and evaluating alternative strategies (this does not need fully calibrated models) and evaluating the feasibility of delivery schemes. Chapter 6 describes and provides examples of more complex modeling approaches, their value, and their limitations.

9.3.6.4 Refining the Tier 1 Conceptual Design

Once additional data have been collected and modeling needs have been addressed, the ISCO design developed in the Tier 1 Conceptual Design phase can be refined to optimize performance and cost (Figure 9.3, Process 7). This may involve:

- Reconsidering ISCO treatment goals where there is low probability of achieving them
- Redefining the TTZ
- Repeating the full Tier 1 Conceptual Design process based on a refined CSM and/or design approach set of input values/ranges
- Incorporating sophisticated modeling output information into the design tool
- Reconsidering coupled ISCO treatment approaches

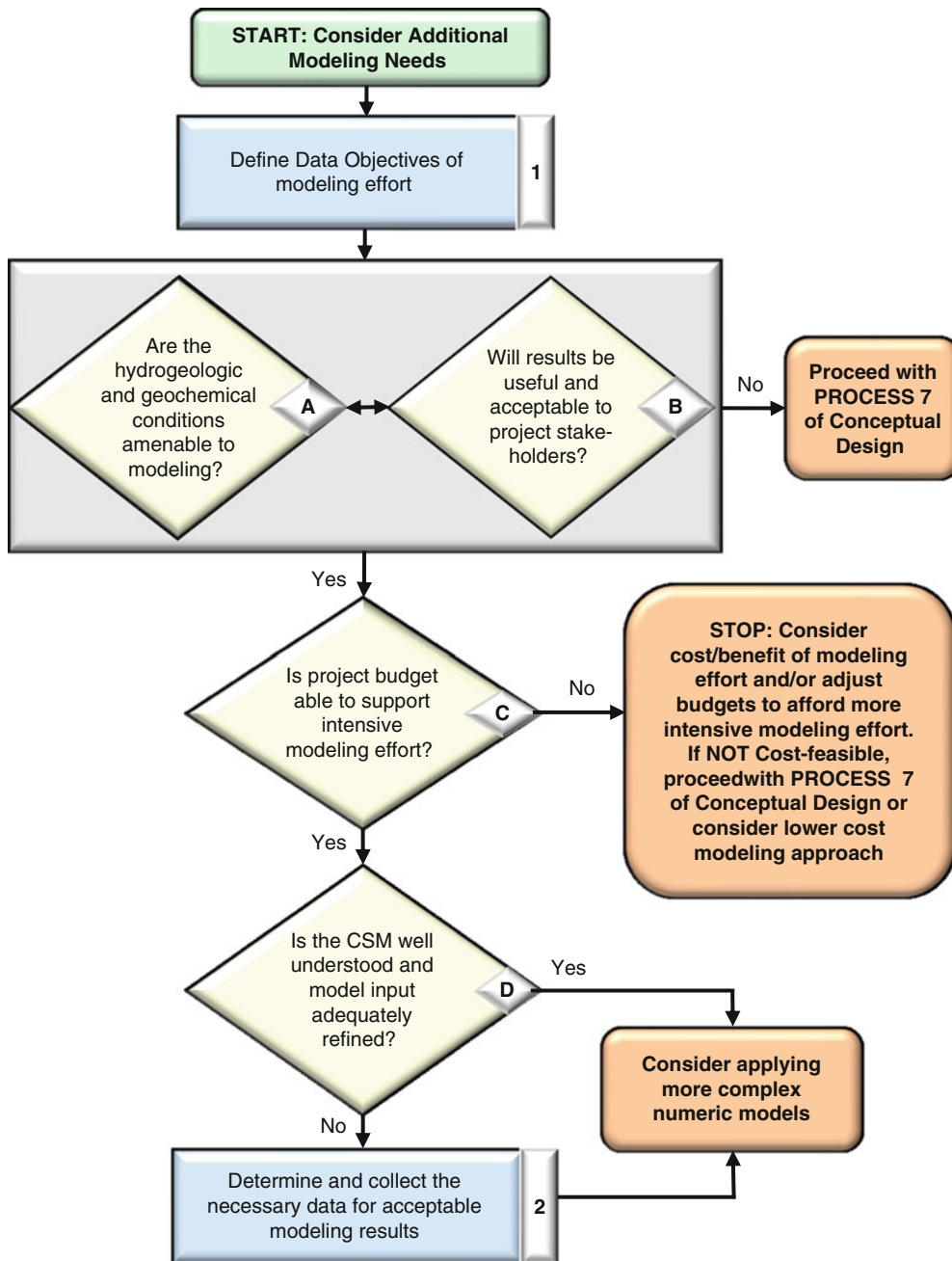


Figure 9.5. Additional modeling decision logic diagram for Tier 2 Conceptual Design.

The goal now is to finalize the Conceptual Design by iterative application of the design approach used in Tier 1 with any new information learned from additional data collection and modeling, if applicable. Looking ahead, after the cost estimating, this final stage of Conceptual Design will lead to a project-specific remediation alternatives analysis (such as in a FS).

9.3.6.5 Cost Estimation

Once the Conceptual Design has been finalized (either the original Tier 1 design or as modified through Tier 2 analyses), a full FS level cost estimation can be performed (Figure 9.3, Process 8). The cost of implementing an ISCO design is a key factor for determining its feasibility versus employing alternative remediation techniques. The cost estimation at this point in the ISCO Conceptual Design can be completed with a significantly greater level of certainty and detail than the process discussed in Section 9.3.3.2 above. Now capital, operation and maintenance, and life cycle costs for implementing a preferred ISCO approach can be evaluated. These ISCO-specific costs can then be output to a FS and compared to other remediation alternatives. The ISCO cost estimate should reflect screening-level engineering estimates for alternative comparison purposes only and should not be used for construction budgeting. The expected accuracy range for the Conceptual Design cost estimate process may be in the range of -30 to +50%. Therefore, factors such as unit costs and quantities, costs for professional and technical services, and contingency should be considered and evaluated carefully. Chapter 13 provides more details on cost estimating for ISCO projects.

9.4 DETAILED DESIGN AND PLANNING OF AN ISCO SYSTEM

9.4.1 Introduction

The primary purposes of the Detailed Design and Planning Process are (1) to complete an ISCO design, and (2) to prepare operation and contracting documents that can be used to implement the ISCO system. This process precedes the Implementation and Performance Monitoring Process (described in Section 9.5), which completes implementation of the ISCO remedy.

The following sections describe a process that can be followed to finalize an ISCO design and prepare the project work planning documents that will be later followed. The information below corresponds to the process steps and decision points depicted in Figure 9.6, The process is divided into three phases: (1) the preliminary design phase, (2) the final design phase, and (3) the planning phase.

While it is expected that most components of this process are prudent for most ISCO projects, some aspects of this process may or may not be applicable and depend significantly upon project-specific needs/goals and contracting approaches. The process can readily be tailored to meet stakeholder needs. For example, if a project requires design deliverables at the 30, 60, 90, and 100% complete stages, then the process presented herein must be adapted accordingly. The process outlined in this section prescribes a more streamlined approach to design, consisting of preliminary (approximately 30% design) and final (100%) designs only.

The process described herein focuses on best practices for technical design and documentation for ISCO implementation and does not specifically address regulatory documentation required for design approval. Since regulatory requirements vary significantly, no attempt has been made to tailor the process. However, in many cases, the Preliminary Basis of Design Report can be used to obtain regulatory approval for the remedial action. If regulators or other decision makers require additional detail, then approval may be obtained using the Final Design instead (see Detailed Design and Planning Process 3a or 3b in Figure 9.6).

9.4.2 Preliminary Design Phase

9.4.2.1 The Preliminary Basis of Design Report

A Preliminary Basis of Design Report is prepared as the initial step in the Detailed Design and Planning Process (Process 1, Figure 9.6). The purpose of the Preliminary Basis of Design Report is to formally establish and document design parameters that can be used for the Final Design phase. The Preliminary Basis of Design Report is typically reviewed and approved by all project stakeholders to ensure consensus on critical design parameters prior to proceeding with the Final Design phase of ISCO implementation.

This report incorporates all previous screening and Conceptual Design work completed. The Preliminary Basis of Design Report specifies details related to the following ISCO-related design parameters:

- Hydrogeochemical setting and contaminant geometry (e.g., a summary of the CSM)
- Location and dimensions of the TTZ
- Treatment objectives and goals
- Oxidant selection and ISCO treatment technology description
- Desired ISCO reaction chemistry
- Lithologic setting and oxidant delivery/contaminant contact design
- Oxidant dosage and injection volume
- Description of injection point/well construction methods
- Requirements for oxidant storage, transfer, mixing and delivery equipment (sizing, chemical compatibility, safety features, and user interfaces)
- Description of oxidant delivery process, including: injection probe/well layout; process flow diagram for oxidant mixing and transfer and monitoring; oxidant delivery concentration; target injection volumes, rate, pressure, and operating hours
- Preliminary delivery and treatment performance monitoring program (including monitoring locations, measurements, and frequency)
- Engineering controls required to maintain health and safety
- Permitting requirements
- Waste management requirements
- Implementation cost estimate

Basic design drawings are typically included with the Preliminary Basis of Design Report. At a minimum, the preliminary design drawing package includes the following:

- Process and Instrumentation Diagram
- ISCO treatment system layout
- Preliminary piping layout
- Well construction or probe injection details

Appendix D.5 shows an example of a Preliminary Basis of Design Report outline for an ISCO project employing direct-injection of permanganate. It should be noted that certain components of the Preliminary Basis of Design Report specified above may be omitted if a performance-based contracting approach will be adopted (see Decision B in Figure 9.6 described in Section 9.4.3.1 below). Examples of components that may be omitted include the oxidant volume/dosage, injection infrastructure, and injection well design.

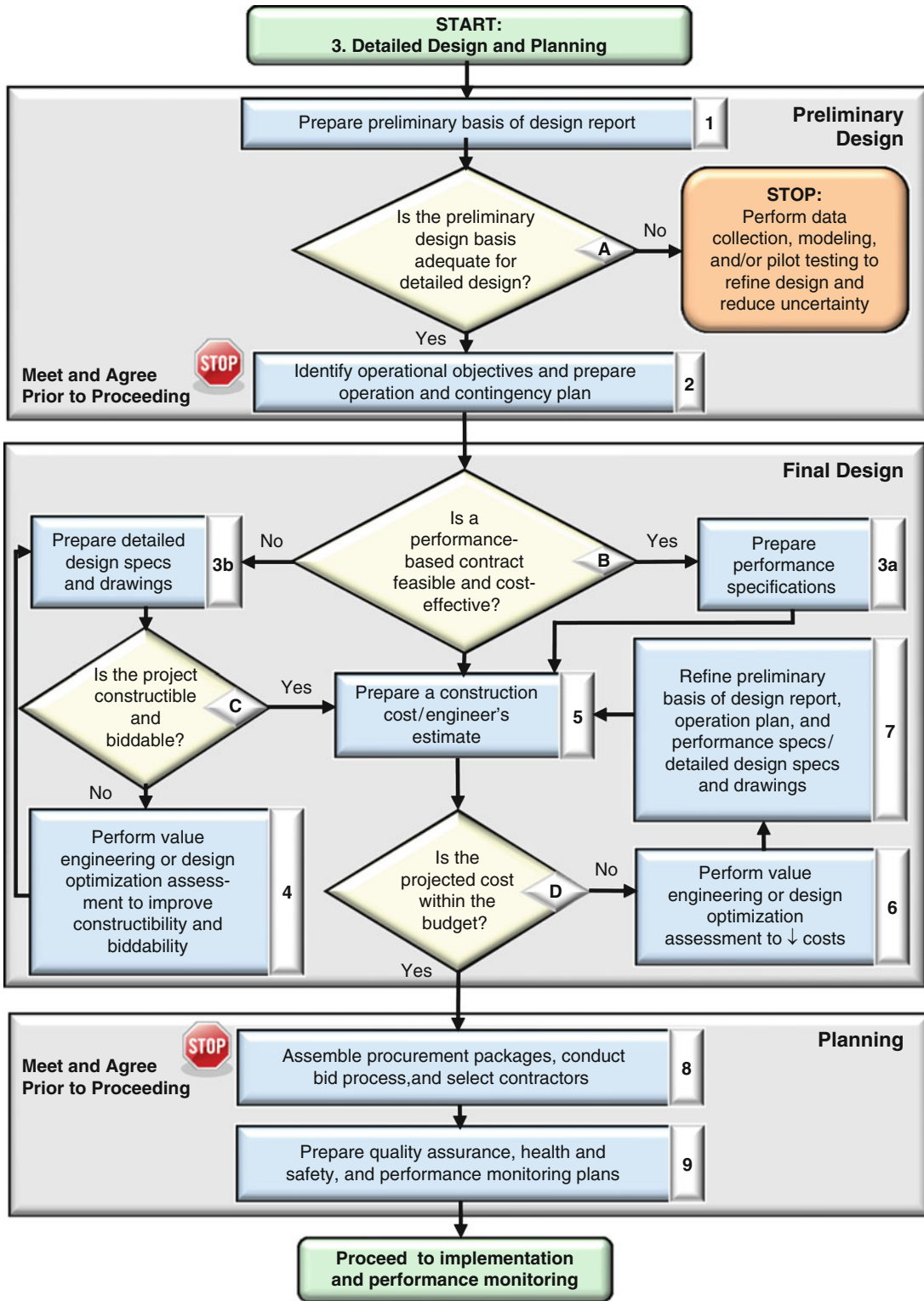


Figure 9.6. Decision logic diagram for the ISCO Detailed Design and Planning Process.

9.4.2.2 Data Adequacy for Design

Prior to the Final Design phase, the project stakeholders can review the Preliminary Basis of Design Report to evaluate the effectiveness of the proposed ISCO design and assess the adequacy of the data upon which the preliminary design is based (Decision A, Figure 9.6). This is an opportunity for a project team to reconsider the approach and identify additional data collection activities that may help reduce uncertainty in the design. This decision is centered on a thorough review of the preliminary design from the standpoint of (1) revisiting the confidence of CSM understanding, (2) evaluating if the design parameters are adequately quantified, and (3) assessing the probability of success and consequence of failure of the preliminary ISCO system design. These evaluations are further discussed below. The intent of this process is to maximize the chance for achieving ISCO treatment goals by decreasing uncertainty in the design basis.

9.4.2.3 The Operation and Contingency Plan

Upon project team agreement on the adequacy of the data used to support the ISCO system design and an endorsement of the Preliminary Basis of Design Report, an Operation and Contingency Plan is prepared (Process 2, Figure 9.6). The Operation and Contingency Plan is intended to formally document the following:

- Operational metrics and objectives
- ISCO treatment goals and milestones
- Contingency plans, including:
 - Operation decision logic
 - Optimization approach
 - Treatment cessation plan

It is important that these items are considered and agreed upon and then documented in the Operation and Contingency Plan prior to the Final Design phase so that (1) regulatory approval of the operation strategy and decision logic may be obtained up-front, and (2) planning can be initiated for appropriate labor and material provisions during the contracting stage. The specific components of a typical Operation Plan are illustrated in Appendix D.6. Contingency planning is described in detail in Chapter 11.

9.4.3 Final Design Phase

The final design phase described below is all-inclusive and most applicable to large-scale ISCO projects. All elements may not be applicable (warranted or affordable) to many of the typical smaller-scale ISCO projects. Elements can be implemented as appropriate on a site-by-site basis.

9.4.3.1 Contracting Approaches

The Final Design phase starts with determination of an implementation contracting approach and design type (Decision B, Figure 9.6). The contracting approach determines the level of detail that must be included within the design. The two basic options described in this section include (1) a performance-based contract, and (2) a traditional owner-engineer and owner-contractor execution with detailed design specifications and drawings (i.e., a prescriptive design).

The need or desire to use an Observational Method should be considered when selecting a contracting approach. As previously discussed, an Observational Method is based on the

assumption that field conditions will vary from the CSM and the implementation plans will be dynamic and require modification based on field experiences and monitoring data results. Most of the potential modifications can be predetermined during the contingency planning phase and included in the ISCO system design. Therefore, both performance-based and detailed prescriptive-based contracting approaches can be adapted to the Observational Method. Care must be taken when writing the details of either type of contract to allow fair adjustments to the contract amount if the contingencies are required.

Performance-based contracts are also known as design-build-operate contracts. This type of contract does not provide detailed information on what equipment is required or the means to achieve the project goals. Rather, it provides a set of minimum performance criteria (i.e., certain milestones, end points, and/or desired outcomes) that should be achieved with any methods and materials chosen. A combination of performance requirements may be included in a performance-based contract, along with other standard contract requirements/specifications, such as construction quality control (QC) and health and safety requirements.

Prescriptive-based contracts require that a set of specifications and drawings be prepared that detail the exact and complete scope of work required of the contractor (i.e., the company responsible for installation and operation of the ISCO system). There are typically no performance requirements for a traditional prescriptive design. The prescriptive-based specifications typically include the northing/easting location of wells, well completion and development details, oxidant and activation method selection, volume and mass of oxidant to be injected, oxidant mixing means and methods, and duration of injection and post-injection monitoring.

Very often a combination of performance and prescriptive elements are included in an ISCO implementation contract. For example, performance specifications can be embedded in an overall prescriptive contract. Certain activities, such as oxidant mixing and delivery, can be performance-based. However, overlapping performance and prescriptive elements on individual scope items should be avoided.

Contractors who have demonstrated specialized experience in ISCO technologies should be used for performance-based contracts. Some specialty contractors may charge a premium fee for a performance-based contract, depending on the performance specifications, contract structure, and the level of financial risk imposed on the contractor.

Trade-specific contractors such as drillers could be used if a prescriptive-based design is developed. This may allow a larger field of contractors to bid and may reduce the bid cost. However, a general contractor with limited experience is also likely to require more oversight and direction from the engineer (consultant responsible for ISCO system design).

For all types of contracting, close coordination with the potential contractors is suggested during the Preliminary Design phase so that the contract is written in a way that is consistent with the desired delivery and oxidant activation methods and also includes an appropriate amount of flexibility to allow the contractor to do his/her best.

Table 9.13 presents a comparison of the advantages and disadvantages of performance-based and prescriptive-based contracting approaches to aid in the selection of an implementation contract approach.

The step that follows selection of the contracting approach is to develop either (1) the minimum performance specifications the contractor is expected to achieve for a performance based contract (Process 3a, Figure 9.6), or (2) the detailed design specifications and drawings for a prescriptive-based contract (Process 3b, Figure 9.6). These processes are further described in Appendix D.7.

Table 9.13. Comparison of Performance-Based and Detailed/Prescriptive Contracting Approaches for ISCO

Selection criteria	Performance-based	Detailed/prescriptive
Level of effort for specification	Low	High
Contractor selection	Highly selective	Low to moderately selective
Level of CSM understanding	Moderate to high	Low to moderate
Amenable treatment goals	More amenable to numeric goals, such as achieve a 90% mass reduction	More amenable to non-numeric goals, such as achieve source mass reduction
Size of TTZ	Small to moderate	Moderate to large
Amenable delivery methods	Patented or proprietary systems	All non-proprietary systems
Overall implementation cost	Moderate to high	Low to high
Degree of financial risk	Variable depending upon the contractor knowledge and contract language	Variable depending upon the CSM understanding and design certainty
Potential for change orders	High if contract language is not tight	Low

9.4.3.2 Constructability Review

A constructability review can be conducted to evaluate if cost-effective and practicable approaches for field implementation have been included in a detailed prescriptive-based design (Decision C, Figure 9.6). If after review by the construction team, it is determined implementable and cost-effective, then it is deemed constructible and biddable. The scope of the constructability review will vary based on project requirements. At a minimum, it can involve a pre-bid site walk over with the site representative and prospective contractors to identify site conditions and logistical issues (e.g., vehicular and equipment access, terrain, existing site activities, working hours, etc.) that may complicate implementation of the ISCO system design. If a higher-level constructability review is performed, it should be conducted by a constructability review team (typically consisting of the design team and other affected project participants such as the client, technical consultants, and prospective ISCO contractors) and incorporate the following elements:

- **Review design concepts.** The team reviews the design objectives for the project, the probable sequence of field implementation, and other aspects of the project. The preferred method of accomplishing this exchange of information is through a team workshop session wherein the personnel responsible for the design can explain the design and address any specific design issues or elements that may affect field implementation.
- **Screen available lessons learned.** The team reviews any available lessons learned for the project type, and consults with appropriate participants of other similar projects to identify any special constructability considerations that may be applicable to the project.
- **Review performance/site conditions.** The team reviews site conditions, logistical constraints, and other potential contractual mandates to understand their implications on the field implementation. Schedules, restrictions on working hours, concurrent site operations, and availability of oxidants and materials all have an impact on the field implementation and can affect the sequence of field implementation.

A Constructability Implementation Guide prepared by the Construction Industry Institute (CII, <http://www.construction-institute.org>) provides detailed guidance on implementing constructability principles on a project, including updated case studies.

9.4.3.3 Value Engineering/Design Optimization Assessment

If the project constructability or biddability is determined to be low, value engineering (VE) can be applied to evaluate and select easily integrated design and field enhancements to simplify the design and operations, and/or improve system reliability. Guidance for executing VE is provided by the SAVE International (<http://www.value-eng.org/>). Examples of VE that could apply to an ISCO project include:

- Use of different oxidant handling options that may better suit site requirements such as: diluting oxidant in simple batch tanks on site, inline dosing of oxidant into an injection water line, or diluting oxidant off-site and delivering solution to site in a holding tank.
- Including automation, reliability, and maintainability in design features to minimize the need for field staff to be present on site, if site access or work hours are a factor.
- Use of modular designs with treatment capacity that can be easily downsized/increased without significant additional disruption of the site.

9.4.3.4 Construction Cost/Engineer's Estimate

Regardless of whether a performance-based or a prescriptive-based contracting approach is used, the next step following preparation of performance or detailed design specifications is a detailed refinement of the FS-level cost estimate prepared as part of the Conceptual Design process (Process 8, Figure 9.3, described above in Section 9.3.6.5). The level of detail and accuracy of the construction cost/engineer's estimate is expected to increase to -15 to $+20\%$, and be suitable for bid estimates, establishing contract value, and serving as a control baseline against which actual costs and resources will be monitored. This cost estimate is comparable to a Class 2 cost estimate as discussed in Chapter 13.

The level of effort and internal review required for preparing the construction cost/engineer's estimate depends on project-specific requirements. One option is to update the FS-level cost estimate (Process 8, Figure 9.3, described above in Section 9.3.6.5) with refined quantities and unit-prices, listed assumptions and clarifications, and updated equipment and contractor quotes. The ultimate method, however, is typically unique to a project team's experience and owner requirements.

9.4.3.5 Projected Cost Versus Budget

Following preparation of the cost estimate, the next step is to simply determine if the construction cost/engineer's estimate is within the budget allocated to the project (Decision D, Figure 9.6). At this stage of the ISCO design process, the level of accuracy of the cost estimate (-15 to $+20\%$) has already been refined by reducing uncertainty in design input parameters during the Conceptual Design process. If the answer to this decision point is "Yes," then the next step is to begin the process of assembling procurement packages, conducting the bid process, and selecting contractors. However, if the answer is "No," then further efforts should be taken to reduce projected costs or increase the project budget.

9.4.3.6 Cost Optimization

If the ISCO project cost is determined to be unacceptably high, then VE, as described above, can be applied to evaluate and select easily integrated design elements and field methodologies to reduce cost (Process 6, Figure 9.6). The VE process will vary based on project requirements. If a high-level V evaluation is performed, the same concepts for a formal VE team assessment presented above can be applied.

If beneficial design/operation changes were identified during the VE exercises conducted to improve constructability and/or reduce costs, the Operation and Contingency Plan and the Performance Specifications/Detailed Design Specifications and Drawings should be revised to reflect these changes (Process 7, Figure 9.6).

9.4.4 Planning Phase

The elements of the Planning phase include assembly of procurement packages, conducting the bid process, selecting contractors, preparing the quality assurance (QA) plan, preparing the health and safety plan, and finally preparing the performance monitoring plans. Many of the elements described below are not ISCO-specific and apply to most any *in situ* remediation project.

9.4.4.1 Procurement Packages, Bidding, and Contractor Selection

The services of contractors will typically be required for certain project activities such as: well installations, porous media and groundwater sample analyses, supplying oxidant, direct-push injection of oxidants, fabrication of injection equipment (depending on injection design), and mixing and injection of oxidants into injection wells (if injections will not be self-performed by the engineer). The procurement process is critical for identifying available contractors who have the qualifications to meet (at a minimum) the project's technical, health and safety, and schedule requirements. The following outlines the basic steps that should be followed during the procurement process:

- Prepare a contract/bid package and send to contractor(s) who have been pre-qualified based on relevant technical experience and acceptable health and safety records (as appropriate based on project requirements).
- Receive bids and conduct thorough review of price and technical approach; ensure contractor(s) can meet technical, schedule, and health and safety requirements.
- Negotiate and award contracts to winning contractor(s).

Payment requirements should be considered during the contracting process. Contracts can be written to be fixed-price (lump-sum) or time-and-materials. Under a strict, fixed-price, performance-based contract, the contractor is only paid if they achieve the performance specified. Under a time-and-materials contract, the contractor is paid for the hours that they work and for the materials they provide. A combination of fixed-price and time-and-materials can also be used. For example, unit pricing can be used for installation of injection into a single well, or injection of a unit quantity of oxidant. Incentives can also be written into a contract to reward the contractor for achieving certain performance. Unit price-based contracts with incentives may resolve the issue of motivating the contractor to achieve the desired outcome, while still providing flexibility. A payment schedule is usually provided in the contract. It defines the milestones and the percentage of the contract amount that will be paid when those milestones are achieved. The payment schedule should account for changes in project activities and schedule, as defined in the Operation and Contingency Plan. As such, unit price-based contracting may be the most appropriate contracting mechanism for a project that is heavily designed around an Observational Method strategy.

9.4.4.2 Quality Assurance, Health and Safety, and Performance Monitoring Plans

The last step in the ISCO Detailed Design and Planning Process is to prepare detailed quality assurance, health and safety, and performance monitoring plans. Each of these three

plans serves a key function during the ISCO Implementation and Performance Monitoring, described below in Section 9.5. The scope and level of detail included in these plans is highly dependent upon project-specific conditions and site regulator and owner requirements. Therefore, only general ISCO-specific content is included below.

Quality Assurance Project Plan

A project Quality Assurance Project Plan (QAPP) should provide a platform for presenting QA/QC procedures, policies, and requirements so data are scientifically valid and defensible. QAPPs should be prepared on a project-specific basis to meet the project's unique data quality objectives. As an example, the Department of Defense requires a QAPP for any projects with environmental sampling plans, under the Uniform Federal Policy (UFP-QAPP). Additional information on the UFP-QAPP can be found on the U.S. Environmental Protection Agency's website at <http://www.epa.gov/fedfac/documents/qualityassurance.htm>. A summary of typical QAPP contents per UFP-QAPP is presented in Appendix D.8.

The primary purpose of the QAPP is to specify the functional requirements necessary to ensure that data collected according to the Performance Monitoring Plan is analyzed and integrated into the decision logic specified in the Contingency Plan. The Performance Monitoring Plan states what data is to be collected, the QAPP prescribes the data analysis procedures, and the Contingency Plan uses the results of the data analysis to refine the course of ISCO operations. Data analysis methods are described further in the ISCO Implementation and Performance Monitoring section below (see Section 9.5).

ISCO-specific quality assurance procedures should include oversight and analysis of delivery and treatment processes to ensure that design parameters are met. From a QA perspective, often times multiple lines of evidence are necessary to ascertain effectiveness. For example, during delivery, hydraulic head, oxidant and activator concentration, and redox conditions are measured in monitoring wells within the expected zone of influence of the oxidant delivery approach. If all three lines of evidence indicate oxidant presence and COC contact, then the contractor is allowed to proceed to the next injection location, for example. QA for ISCO treatment effectiveness determinations also can involve using multiple lines of evidence. For example, the project must make sure that injection dilution effects have dissipated and hydraulic and contaminant partitioning re-equilibrium has been re-established prior to assessing contaminant treatment effectiveness. A discussion of treatment effectiveness monitoring is presented in Chapter 12.

Health and Safety Plan

A site-specific Health and Safety Plan should be prepared to comply with the Occupational Safety and Health Administration (OSHA) Hazardous Waste Operations and Emergency Response (HAZWOPER) Standard 29 Code of Federal Regulations (CFR) 1910.120 (Occupational Safety and Health Standards) and 29 CFR 1926.65 for Safety and Health Regulations for Construction. The Health and Safety Plan should be reviewed and endorsed by all members of the project team and by contractors working on-site. A copy of the Health and Safety Plan should be kept on-site, and amended as project activities or conditions change or when supplemental information becomes available.

Typical Health and Safety Plan components include (but are not necessarily limited to):

- Project information
- Site map and site plans
- Tasks to be performed during project
- Field team and health and safety communication plan
- Employee and contractor sign-off sheet

- Training requirements
- Required personal protective equipment (PPE)
- Hazard controls (project specific, general work environment, biological, chemicals of concern)
- Traffic control plan
- Air monitoring plan
- Decontamination procedures
- Site control plan
- Emergency response plan – emergency supplies and equipment, incident response and reporting, emergency facility contacts, directions to hospital
- Behavior-based prevention forms for: Job hazard analysis, pre-task safety planning, safe-work/loss prevention observations, loss/near-loss investigations

Many of the aforementioned Health and Safety Plan components are not unique to ISCO. A summary of ISCO-specific hazards is provided in ITRC (2005).

The primary hazards associated with oxidant use are inhalation and dermal exposure, gas and heat generation, high-pressure, and the potential for uncontrolled reaction through improper storage. Engineering controls and appropriate personal protective equipment must be employed in handling and mixing oxidants. The Health and Safety Plan should include safety precautions and appropriate training requirements for the specific oxidant(s) to be used on site, including oxidant activators such as acids or bases. Some important specific considerations include:

- Hazards of dusts of solid phase oxidants (e.g., potassium permanganate [KMnO₄] and sodium persulfate [Na₂S₂O₈]).
- Electrical hazards associated with oxidant generation on site (e.g., ozone).
- Oxidant surfacing or day-lighting when using pressurized probe injections, where oxidant may travel up the outside of the probe to the surface, or up through adjacent improperly abandoned investigation boreholes or wells – adding pressure relief valves along the injection pipe/hose, and pressure-tight capping nearby monitoring wells should help mitigate oxidant surfacing during pressurized injections.
- The need to monitor injection pressures real-time and incorporate automated system shutdowns if they exceed safe levels.
- Using pressure-tight caps with pressure gauges for all wells within the TTZ during injection, and the need to wait for the pressure to drop before opening the well.
- Provision of neutralizer for spill response and containment in case of day-lighting or short-circuiting.

Performance Monitoring Plan

The Performance Monitoring Plan should be designed to:

- Collect the necessary data to measure achievement of the operational objectives and treatment milestones.
- Monitor the ISCO system to continually confirm that its design is performing as designed and is being optimized if needed as prescribed by the Contingency Plan.
- Document whether the implementation was a success or failure with respect to the ISCO treatment goals (described further in Chapter 10).

This translates to an adequately designed delivery and treatment performance monitoring program that provides data that are consistent with operation and performance metrics endorsed by the project stakeholders during the Preliminary Design phase. The Performance Monitoring Plan should be reviewed and endorsed by all members of the project team. A copy of the Performance Monitoring Plan should be kept on-site and readily available to project team members, and amended as project activities or conditions change or when supplemental information becomes available that justifies plan modification.

The Performance Monitoring Plan should cover the three primary stages of ISCO implementation: baseline monitoring, delivery performance monitoring, and treatment performance monitoring. Typical Performance Monitoring Plan components include (but are not limited to):

- Clearly defined data needs and objectives (including measurements for contingency assessment)
- Number and location of monitoring points
- Frequency of monitoring
- Field and laboratory analytical methods
- Data quality objectives
- QA/QC sampling procedures
- General data analysis plan and reference to Contingency Plan for decision logic

Detailed ideas and recommendations for preparing the Performance Monitoring Plan are included in Chapter 12.

9.5 IMPLEMENTATION AND PERFORMANCE MONITORING

9.5.1 Introduction

The primary purposes of the ISCO Implementation and Performance Monitoring Process are (1) to construct and initiate implementation of the ISCO design, (2) implement the Performance Monitoring Plan to evaluate if the ISCO system is meeting delivery and treatment performance criteria, and (3) execute the Operation and Contingency Plan to adapt and optimize the ISCO system design or operation in response to new site data obtained and/or efficiently address performance deficiencies encountered during ISCO implementation. The objective of this process is to achieve the established ISCO treatment goals. This process is the last of the four major components of the systematic approach for engineering ISCO treatment systems described in this chapter, and completes implementation of the ISCO remedy.

The following sections describe a process that can be followed to implement and monitor an ISCO system. The subsequent information corresponds to the processes and decisions depicted in Figure 9.7, and, like the decision logic diagrams shown for the other three components of the systematic approach for engineering ISCO systems, the numbers in the figure refer to process steps, while the letters refer to decision points. The process is divided into three phases: (1) the implementation phase, (2) the delivery performance monitoring phase, and (3) the treatment performance monitoring phase.

Many components of the Implementation and Performance Monitoring Process included herein are remediation industry best practices and are not necessarily unique to an ISCO remedy. It is expected that most components of this process are necessary and prudent for most ISCO projects. However, some aspects of this process may or may not be applicable

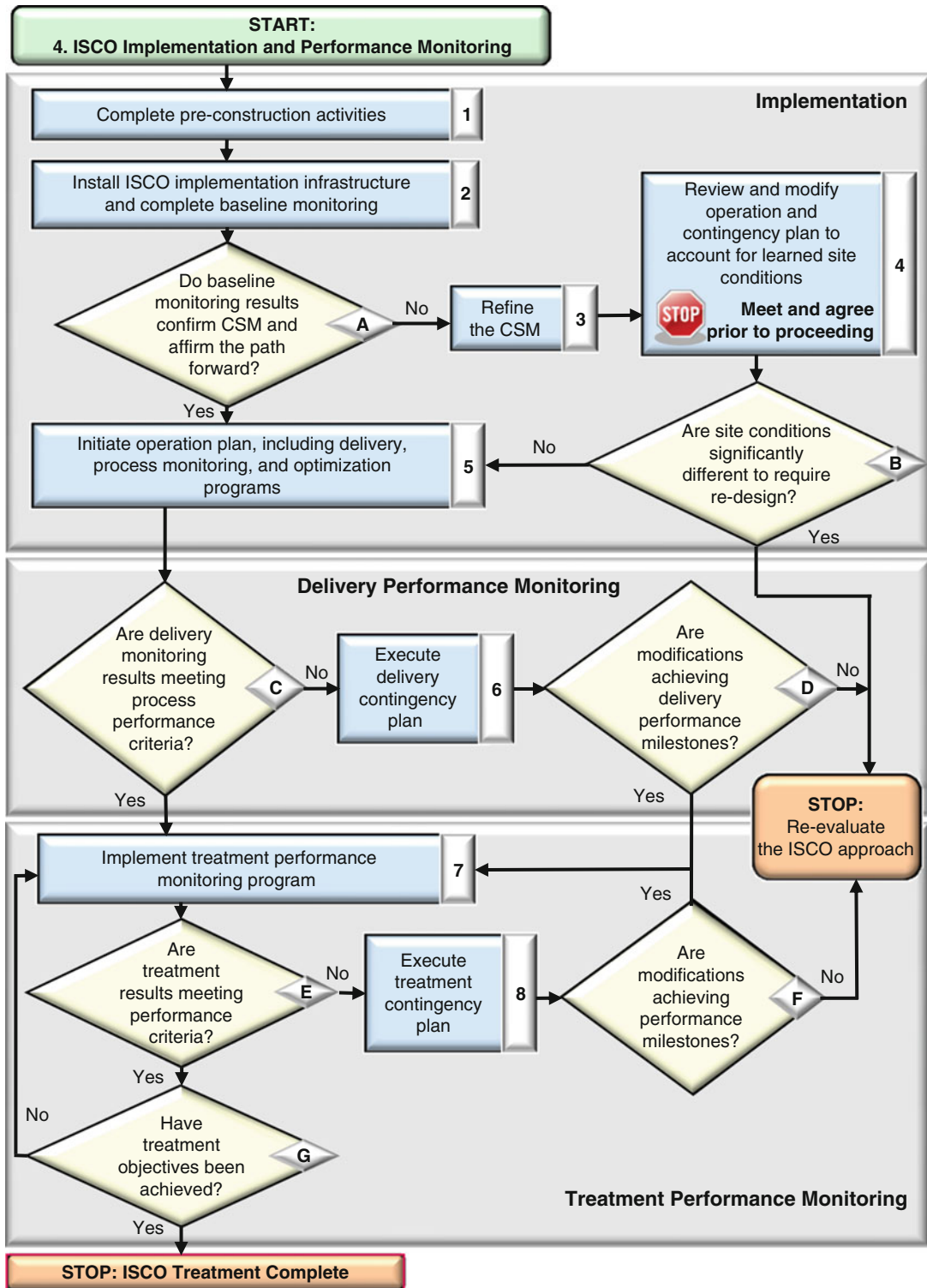


Figure 9.7. Decision logic diagram for ISCO Implementation and Performance Monitoring.

depending on project-specific needs/goals and contracting approaches. Implementation and Performance Monitoring can be tailored as necessary to meet stakeholder needs.

The process described herein focuses on best practices for the technical aspects of ISCO implementation and does not specifically address regulatory documentation required for implementation, optimization, and cessation. Since regulatory requirements vary significantly, no attempt has been made to tailor the process. However, in many cases, the data derived from this process can be used to obtain regulatory approval for the remedial action.

9.5.2 Implementation Phase

9.5.2.1 Pre-construction Activities

The purpose of this process (Process 1, Figure 9.7) is to ensure that: (1) ISCO is implemented in a manner that is compliant with local, state, and federal permitting codes, (2) the construction zone is cleared from above- and below-grade utilities and that the scope of engineering controls to avoid damage to existing utilities is understood, and (3) that all administrative and physical preparations have been made to prepare for the ISCO installation and operations. Pre-construction activities, described in more detail in Appendix D.9, include:

- Injection permitting
- Utility clearance
- Potential receptor survey
- Engineering controls
- Administrative
- Health and safety

9.5.2.2 ISCO Implementation Infrastructure

Process 2 shown in Figure 9.7 encompasses the fundamental activities that should be performed when installing ISCO injection infrastructure (e.g., injection wells, monitoring wells, manifold piping, injection equipment) and performing the baseline porous media and groundwater monitoring. More or fewer activities could be required depending on the actual injection design and methodologies employed, and site-specific requirements imposed by the site owner and/or regulatory oversight agencies. For example, if oxidant injection is to be via direct-push technology (DPT) only, then the ISCO infrastructure may be simpler than prescribed herein.

With all elements of this process, the Operation and Contingency Plan should be referred to for identifying all potential future project contingency requirements, so that all health and safety, subcontracting, site access, and material and equipment needs can be met, to the extent practical, without significant project delays.

Installation of ISCO infrastructure includes injection and monitoring wells, and setup of oxidant staging, mixing, and delivery equipment. Equipment may include the following: water supply, storage tanks, chemical hoppers and mixers, chemical feed systems, pumps, injection pipe/hose, injection well manifold assemblies, and instrumentation (pressure gauges, flow meters, etc.). The equipment used will vary depending on the method selected for handling and delivering the oxidant. Irrespective of the oxidant injected or delivery method selected, the following field practices should be employed during infrastructure installation activities:

- Proper oversight of contractors is necessary to ensure that ISCO infrastructure is installed as designed. QC staff familiar with the final design (ISCO Detailed Design

and Planning Process: Final Design Phase) and the project work planning documents (ISCO Detailed Design and Planning Process: Planning Phase) should be required to be on site during delivery and key treatment performance monitoring phases of field work.

- Frequent communication with the designated QC staff, contractor, engineer, and owner should be maintained so project decisions in response to changed field conditions and design basis can be made in an efficient manner.
- Thorough and detailed field documentation in a field book, field data sheets, and well construction logs should be maintained.

Appendix D.10 contains guidelines for construction and delivery QA/QC of the various oxidant delivery techniques. It lists the major delivery techniques, their primary construction elements, and the associated QA/QC inspections/tests that should be conducted to verify their integrity and effectiveness.

9.5.2.3 Baseline Monitoring

As per Decision A in Figure 9.7, baseline porous media and groundwater samples should be collected and analyzed in accordance with the Performance Monitoring Program (described in detail in Chapter 12). Porous media and groundwater baseline data should be used to verify that the current understanding of the CSM is correct and determine if and how the current ISCO design should be refined. The objective is to review all new information acquired, and to determine if any changes to the CSM will have significant impact on the effectiveness, implementability, or cost of the current ISCO design. If baseline monitoring results are significantly different than expected, then the CSM should be updated. During the Implementation and Performance Monitoring Process, a high overall degree of certainty should increase the chances of achieving ISCO treatment goals. If baseline monitoring results are not significantly different than expected, then the delivery operation may begin.

If changes in site conditions encountered during the installation of ISCO infrastructure or baseline monitoring are significantly different such that the current ISCO design is not expected to perform adequately, be implementable, be cost-effective, or be safe with only minor design refinements, a complete re-design may be required. The need for a complete re-design, and the degree to which the re-design is performed, will need to be evaluated and decided upon by the project team, taking into consideration the updated CSM data, regulatory drivers, schedule, and budget.

At this point, the Operation and Contingency Plan should be refined in order to optimize performance and cost of future ISCO efforts. At the implementation phase of an ISCO project, design optimization/refinements may include:

- Revising the TTZ lateral extent and depth and number of injection points.
- Refining oxidant dosage (total mass and injected concentration) based on porous media and groundwater analytical data for COCs, porous media and groundwater geochemistry (i.e., pH, alkalinity, metals, ORP, DO, and temperature), NOD, and/or additional laboratory oxidant persistence testing performed.
- Refining injection spacing or injection depth interval to optimize oxidant distribution/radius of influence, based on the porous media lithology and heterogeneities identified during drilling.
- Adding additional monitoring wells within and/or around the TTZ, if the TTZ was revised, to adequately monitor oxidant deliver and treatment performance.

- Refining the Performance Monitoring Plan and Operation and Contingency Plan based on ISCO design refinements, and also to address monitoring and management of previously unidentified redox-sensitive metals.

9.5.2.4 Initiating ISCO Operations

Process 5 in Figure 9.7 entails conducting initial ISCO system operations and process monitoring in accordance with the Operation and Contingency Plan and Performance Monitoring Plan (see Section 9.4.2.3). The ISCO work planning documents provide detailed guidance for performing the first oxidant injection event and specifying performance monitoring requirements needed to verify if the ISCO system meets basis of design and performance specifications. However, the design also should be optimized real-time by applying the Observational Method throughout the operation and monitoring programs. The goal of the Observational Method is to integrate performance monitoring results and decision logic real-time, allowing for design modification “as you go.” The Observational Method relies on understanding the uncertainties associated with the CSM, and on planning ahead for reasonable bounds of conditions that may occur at the site. The use of techniques such as DPTs and *in situ* sensors with data loggers have dramatically improved the ability to apply the Observational Method, and to improve outcomes associated with applying it. Chapter 11 provides additional information on the Observational Method.

As part of the Observational Method, monitoring field indicators during ISCO delivery is important to assess the distribution of oxidant and injection fluid, and the occurrence of desired oxidant reactions. Tracking field indicators (e.g., groundwater pH, ORP, color) will allow rapid assessment of the ISCO design delivery approach, and identify modifications to the delivery approach if needed (e.g., tighter injection spacing, changes to the injection volume/rate, and changes to the oxidant concentration dosage).

9.5.3 Delivery Performance Monitoring Phase

Oxidant delivery monitoring should be conducted in accordance with the Performance Monitoring Program (described in detail in Chapter 12). Oxidant monitoring results should be evaluated to determine if the specific oxidant delivery objectives (i.e., operational metrics) and milestones established in the ISCO Detailed Design and Planning Process (Section 9.4) are being met (Decision C in Figure 9.7). Each ISCO design will have its own project-specific objectives and milestones. However, the fundamental metric on which the delivery performance of a design should be evaluated is the extent and uniformity of oxidant distribution (at concentrations equal to or exceeding the target oxidant concentration) within the TTZ. If the delivery performance objectives are met, then the treatment performance monitoring program is implemented. If the delivery performance is deficient, then the delivery optimization components of the Contingency Plan should be executed (Process 6 in Figure 9.7).

Contingency response actions for deficient delivery performance were identified, evaluated, and defined as part of ISCO Detailed Design and Planning Process (Section 9.4). Based on the outcome of the initial phase of ISCO delivery progress monitoring, procedures pre-defined in the Operation and Contingency Plan should be followed to determine if any contingency response actions should be implemented to address deficiencies in delivery performance. Optimization approaches that address delivery deficiencies typically include additional injections, a different injection approach (e.g., bottom-up instead of top-down direct injection sequence), and installation of new injection wells.

The procedures performed for Decision C are repeated to assess the delivery performance of the optimized ISCO delivery design and to determine if the objectives and milestones for oxidant delivery are being met (Decision D in Figure 9.7). If the optimized ISCO delivery design is meeting delivery performance criteria, then the treatment performance monitoring program should commence (Process 7 in Figure 9.7). If delivery performance criteria are not being met, then the project team should stop and re-evaluate the selected ISCO delivery approach to determine what failure modes (i.e., field conditions, delivery techniques, oxidant dosage, etc.) are limiting delivery effectiveness, or if ISCO is not appropriate for the site.

9.5.4 Treatment Performance Monitoring Phase

ISCO system treatment performance monitoring should be conducted in accordance with the Performance Monitoring Program (described in detail in Chapter 12). Any modifications made to the Performance Monitoring Program during execution of the Operation and Contingency Plan during Process 6 (Figure 9.7) also should be carried out during this process.

Treatment performance monitoring results should be evaluated to determine if the specific ISCO treatment milestones established in the Operation and Contingency Plan (see Section 9.4.2.3) or modified during execution of the Operation and Contingency Plan during Process 6 (Figure 9.7) are being met (Decision E in Figure 9.7). As discussed in the ISCO Detailed Design and Planning Process, each ISCO design will have its own project-specific treatment milestones. If the ISCO system is meeting treatment performance criteria and making remediation progress, then operations continue and the next step is Decision G (Figure 9.7). If treatment performance criteria are not being met and milestones are not being met as expected, then the next step is execution of the treatment optimization components of the Contingency Plan (Process 8 and Decision F in Figure 9.7).

Associated with Process 8 (Figure 9.7), contingency response actions for treatment performance were identified, evaluated, and defined as part of ISCO Detailed Design and Planning Process (Section 9.4). Based on the results of the initial phase of ISCO treatment performance monitoring, procedures pre-defined in the Operation and Contingency Plan should be followed to determine if any contingency response actions should be implemented to address deficiencies in observed treatment performance. The prescribed decision logic should be followed to define the optimization approach to address the treatment deficiencies. Optimization approaches that address treatment deficiencies may include additional injections, modification of the activation approach, installation of new injection wells, refinement of the TTZ to be targeted for follow-on injections, and an extended ISCO operations period.

For Decision F (Figure 9.7), the procedures performed for Decision E are repeated to assess the treatment performance of the optimized ISCO treatment design and to determine if the milestones for treatment are being met. If the optimized ISCO treatment design is meeting treatment performance milestones, then treatment performance monitoring should continue. If treatment performance is deficient, then the ISCO treatment approach should be re-evaluated to determine what is limiting treatment effectiveness (i.e., field conditions, delivery techniques, oxidant dosage, etc.), or to conclude that ISCO is not appropriate for the site.

After most treatment milestones have been achieved, treatment performance monitoring data should be reviewed to determine if ISCO treatment goals have been achieved. As with most of the processes and decisions made during the ISCO Implementation and Performance Monitoring Process, determining if treatment goals have been achieved should be based on comparison to pre-established criteria and stakeholder consensus (see Chapter 10, Section 10.6). If, after careful analysis and scrutiny of the monitoring data and comparison to the treatment

goals and end points for ISCO operations, the project team consensus is that ISCO operations have been successful, then the ISCO remedy is complete. If not, then treatment continues and Process 7 (Figure 9.7) is revisited.

9.6 SUMMARY

A systematic approach to site-specific engineering of ISCO involves first screening the applicability of the technology to the site-specific conditions and treatment goals. The screening process includes choosing an appropriate oxidant and delivery approach for site-specific conditions, along with considering the coupling of ISCO with other treatment approaches for improved efficiency and cost-effectiveness. Next, using a comprehensive CSM, a Conceptual Design for one or more ISCO systems can be developed. This process involves determining appropriate oxidant dosing and delivery rate, delivery point spacing, number of delivery points, and number of delivery events (two or more events are common and expected). These system design attributes are site-specific. To improve design and cost certainty, additional data collection may be needed, including the determination of oxidant persistence (rate and extent of depletion in site media), generation of potential intermediates and/or byproducts, oxidant deliverability, or other characteristics affecting design and treatment. These data can be obtained through the use of laboratory tests, pilot tests, or modeling (simple analytical and/or numerical). The final design and implementation of the ISCO system will depend on the contracting approach, performance criteria, and lessons learned through real-time monitoring. Furthermore, real-time monitoring results allow for rapid and cost-effective decision making, which, in turn improves the probability of achieving ISCO treatment goals, and enabling the timely transition to post-ISCO MNA.

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CHAPTER 10

SITE CHARACTERIZATION AND ISCO TREATMENT GOALS

Robert L. Siegrist,¹ Tom Palaia,² Wilson Clayton³ and Richard W. Lewis⁴

¹Colorado School of Mines, Golden, CO 80401, USA; ²CH2M HILL, Englewood, CO 80112, USA; ³Aquifer Solutions, Inc., Evergreen, CO 80439, USA; ⁴Environmental Resources Management, Mansfield, MA 02048, USA

Scope

Site characterization methods to develop a conceptual site model (CSM) and enable screening and conceptual design of an *in situ* chemical oxidation (ISCO) technology to achieve ISCO treatment goals.

Key Concepts

- Development of a valid CSM is critical to enable effective screening and conceptual design of ISCO technologies.
- Expedited site characterization approaches such as the Triad Approach are well suited to development of a CSM for ISCO.
- Effective characterization for ISCO screening and conceptual design can be achieved by integrating technologies and methods spanning conventional to advanced diagnostics.
- Site characterization for ISCO requires the same general level of understanding that is necessary to select, design, and implement other *in situ* treatment technologies, but with additional focus on subsurface hydrogeologic and geochemical conditions, including:
 - Reactivity of an oxidant with subsurface media (can control oxidant depletion rate)
 - Oxidation-reduction potential (can provide insight into oxidant persistence)
 - pH and alkalinity (can influence oxidation chemistry and free radical scavenging)
 - Presence of redox- and pH-sensitive metals (can result in post-treatment toxicity)
- Treatment goals and operational endpoints need to be carefully established for an ISCO technology if it is to be successively deployed as a stand-alone remedy or as a component within a combined approach.

10.1 INTRODUCTION

Site characterization and monitoring activities are needed for many purposes during site remediation, including: (1) definition of the nature and extent of contamination, (2) establishment of remediation objectives and goals, (3) selection and conceptual design of a remediation

technology or approach, (4) detailed design of a remediation technology or approach, (5) monitoring and process control during application of a remedy, (6) verifying performance and achievement of remediation objectives and goals, and (7) enabling decisions regarding no further action and future land uses.

The first three purposes rely on characterization of initial site conditions and contamination characteristics and on the development of a valid conceptual site model (CSM). A valid CSM is needed to assess whether remediation is required and to what extent. A valid CSM also can help evaluate remediation technologies, such as *in situ* chemical oxidation (ISCO), and determine their viability for stand-alone use or as a component of a combined remedy.

This chapter describes site characterization approaches and activities needed to develop a CSM for a potential ISCO site and determine realistic treatment goals and operational endpoints. This chapter also discusses the types and levels of characterization required for proper screening of ISCO to assess its potential and enable initial conceptual design for one or more ISCO approaches. But this chapter does not cover activities that occur during a remediation project that can lead to an improved CSM and support detailed ISCO system design. These activities are often carried out during the ISCO design effort, pilot testing, or implementation of a full-scale remedy (refer to Chapter 9). Monitoring activities to define baseline conditions just prior to start up of ISCO operations and those that support ISCO process control and performance verification are covered in Chapter 12.

10.2 CONCEPTUAL SITE MODELS

10.2.1 General Description

A CSM is a comprehensive and integrated representation of multiple interrelated site attributes, which portray the current condition of, and current and potential risks posed by, environmental contamination at a site. The CSM should reflect how the contaminants of concern (COCs) were released into the subsurface, how they have migrated over time, where they reside, how they could migrate in the future, and how they have and may impact human health and the environment. A CSM also includes a representation of key site conditions including, but not limited to, geographic location, onsite and adjacent land uses, sensitive receptors (including those affected by vapor intrusion or surface water impacts), and physical site limitations due to above- and below-ground infrastructure. General guidance concerning the development of a CSM can be found in several publications (e.g., USEPA, 1996, 2006, 2008d; ITRC, 2003; USACOE, 2003; NAVFAC, 2008a). Once developed, a CSM may be documented in graphical, tabular, or narrative format, or through a combination of these formats.

In many cases, the CSM supports a generalized assessment of the potential performance of alternative remedial technologies and provides the basis for assessing potential strengths and weaknesses of the alternatives. For example, if the CSM indicates that a significant amount of residual contaminant is trapped in silty or fine-grained layers embedded within a permeable deposit, then technologies that enhance mass transfer (e.g., heating, fracturing) may be useful. Technologies that inject short lived treatment reagents (e.g. hydrogen peroxide) into the permeable strata may not be well matched to these conditions, but technologies that inject longer lived oxidant reagents (e.g., permanganate or persulfate) may be viable. To support screening of an *in situ* technology like ISCO, a CSM should address the major questions listed in Table 10.1.

Table 10.1. Considerations During Development of a Conceptual Site Model

Questions to be considered during development of a conceptual site model ^a
<p>1. Have above-grade and/or sub-grade contaminant release mechanism(s) been identified at the site?</p> <ul style="list-style-type: none"> • If the source of the original contaminant release is no longer in use, has it been properly decommissioned, abandoned, demolished, or removed? • If the facility is active, are routine tests performed with adequate detection limits to prove that spills and leakage are no longer occurring? • If the facility is active, are there periodic accidental spills that have a pathway to the subsurface?
<p>2. Are the COCs and co-contaminants identified?</p> <ul style="list-style-type: none"> • Are the contents of and/or releases from each source known? • Have full-suite analyses of all potential COCs been performed on an adequate number of samples from all potentially impacted media (porous media, groundwater, surface water, sediment) in the vicinity of the source? • Have co-contaminants been analyzed in the source and down gradient plumes? • Have analyses of other co-contaminants related to adjacent land use been performed? • Have an adequate number of representative samples been collected and analyses performed to reasonably define the nonaqueous phase liquid (NAPL) source?
<p>3. Is the subsurface porous media and geology/lithology of the site adequately characterized?</p> <ul style="list-style-type: none"> • Have proper subsurface sampling techniques with representative recovery been used to sample the site porous media? • Have analyses been completed to characterize key physical, chemical, and biological properties important to COC fate and transport as well as viability of potential remedies such as ISCO? • Has the heterogeneity of the subsurface at the site been assessed? • Is lithology consolidated or unconsolidated? Are lithologic lenses continuous? • If bedrock is present, what type of rock is it and what is the degree of fracturing or weathering? • If bedrock, does the rock have primary porosity and what is the permeability?
<p>4. Is the hydrogeology of the site characterized?</p> <ul style="list-style-type: none"> • Has the groundwater piezometric surface been measured at multiple times representative of seasonality and other variability of hydraulic gradients that may be present at the site? • Have confined and unconfined conditions been assessed for the aquifer(s) of concern? • Have horizontal and vertical gradients been measured across the site? • Has the saturated thickness been measured in the aquifer(s) of concern? • Have multiple tests been performed to assess variability of hydraulic conductivity? • Have groundwater-surface water hydraulic interactions been characterized? • Have tracer studies or pilot tests been conducted to help characterize the effective porosity at the site?
<p>5. Is the presence of mobile and/or residual NAPL in the subsurface suspected?</p> <ul style="list-style-type: none"> • Has NAPL accumulated in any monitoring well(s)? • Has NAPL physically been observed in a porous media or water sample? • How do dissolved phase concentrations compare to the solubility for NAPLs? • Have NAPL indication tools (laser-induced fluorescence (LIF), ribbon sampler, Sudan IV dye, etc.) been used?
<p>6. Has the size and shape of the NAPL source zone been assessed and delineated?</p> <ul style="list-style-type: none"> • Have the terms, "source material" and/or "source zone" been defined? • Has the lateral and vertical extent of source zone been defined to within an appropriate tolerance consistent with potential treatment approaches and to an acceptable level of certainty? • Is the NAPL in the vadose zone and/or the saturated zone? • Is NAPL accumulated at an identifiable lithological interface or the water table? • How much NAPL may have penetrated into low permeability and fined-grained layers?
<p>7. Is the size and shape of the groundwater contaminant plume characterized to an acceptable level of certainty?</p> <ul style="list-style-type: none"> • Has the lateral extent of the plume been defined in all principle directions? • Has the vertical extent of the plume been defined? • Is plume co-mingling, if any, well characterized?

(continued)

Table 10.1. (continued)

Questions to be considered during development of a conceptual site model ^a
<p>8. Have assessments been made to understand existing and potential future human and/or ecological impacts?</p> <ul style="list-style-type: none"> ● Is the source zone located such that there is high potential for human exposure (residential, worker, recreation via ingestion, dermal, inhalation)? ● Is the contamination within an aquifer that is used as a current or potential source for drinking water? ● Has the indoor air pathway been considered and assessed? Is the pathway complete? ● Has the plume migration rate/stability been assessed with respect to risk to potential receptors? ● Does the source zone appear to be contributing COCs to groundwater at a rate faster than natural attenuation (NA) can attenuate it (i.e., is the plume expanding with time)? ● Is there an effective connection between contaminated groundwater and surface water that may pose a risk to ecological resources? ● Is the contamination within the shallow subsurface (0–15 feet [ft] below ground surface [bgs]) and accessible by workers?
<p>9. Have the contaminant fate and transport mechanisms been characterized?</p> <ul style="list-style-type: none"> ● Have the contaminant migration pathways been defined from the source to the distal end of the plume? ● Have the mechanisms of NA been defined and assessed with respect to its ability to control the plume? ● Has site-specific fate and transport modeling been performed to predict long-term plume configuration? ● Has the variability of subsurface conditions been assessed with respect to its temporal impact to the contaminant plume?
<p>10. If remediation turns out to be required, what types of remedies might be feasible?</p> <ul style="list-style-type: none"> ● Are there remedies that are clearly applicable to the site conditions and suspected contamination? ● Could a treatment train and/or coupled approach to remediation be warranted and technically feasible? ● What characterization data might be readily collected that could aid early evaluation of likely remedies or coupled approaches (e.g., porous media total organic carbon [TOC] content, groundwater pH)?

^aThe questions listed in this table are intended to illustrate those that are important to consider and often address during development of a valid CSM. However, all contaminated sites have potentially unique attributes not listed here that should also be included during CSM development.

10.2.2 Developing a CSM for ISCO

At the beginning of a remediation project where an ISCO technology could be considered for remediation, site characterization activities should help build a valid CSM for decision-making. A valid CSM will capture key relevant features of a contaminated site such that potentially viable remediation technologies and approaches can be identified and properly considered. During development of the CSM, the potential viability of ISCO should be kept in mind so that the CSM has the right type and level of information to support an assessment of ISCO. Chemical oxidants that can be used for ISCO have the potential to transform a wide variety of common organic COCs and either mineralize them completely or transform them to intermediates that can be more readily biodegraded (see Chapters 2–5). Oxidant delivery methods for groundwater remediation often involve injection of aqueous solutions of oxidants (see Chapter 11). Based on the treatability of many organic COCs by one or more oxidants and the injection methods typically used for delivery of oxidants into the subsurface, ISCO should be considered as a potentially viable technology for many sites, particularly those with (1) source zones defined by the potential

presence of NAPL ganglia and (2) regions of groundwater with relatively high levels of organics in the dissolved and sorbed phase.

Development of a CSM for remediation of contaminated groundwater, including sites where ISCO may be a potentially viable technology, will typically be based on site characterization activities that address the following components:

- Site features and land use attributes
- Nature and extent of contamination
- Hydrogeologic conditions
- Geochemical conditions
- Fate and transport processes
- Analysis and visualization of site characterization data

The characterization methods and techniques associated with each of the above components are described in Section 10.4.

10.3 CHARACTERIZATION STRATEGIES AND APPROACHES

10.3.1 Introduction

Site characterization strategies and approaches have been described in a variety of publications, which formed the basis for the standard of practice at the time (e.g., Barcelona et al., 1985; USEPA, 1988, 1993; Aller et al., 1991; Nielson, 1991; Pohlmann and Alduino, 1992; Lapham et al., 1997; Yeskis and Zavala, 2002; UK EA, 2000; ITRC, 2006). For many years, site characterization efforts primarily focused on characterizing the nature and extent of contamination, with limited acquisition of information needed to evaluate the feasibility or support design of potential remediation technologies. Often sparse data sets were generated using conventional methods involving subsurface coring, sample collection and installation and sampling of groundwater monitoring wells. Samples collected were often analyzed in offsite laboratories using analytical methods that were standardized and prescribed for soil and water analyses. Analytical results were often not available until weeks after a field sampling effort was completed. When data surprises occurred or new data objectives emerged, remobilizations occurred at considerable additional expense.

Engineering under uncertainty associated with site characterization was recognized as a key technical factor involved in site remediation and this led to development of approaches for uncertainty management (Brown et al., 1990; USEPA, 1997). During the past decade, recognition has grown regarding the importance of expedited, accurate, and economical site characterization to help achieve cheaper, faster, more certain outcomes during site assessment and remediation. This recognition has evolved with time and experience as well as through technology developments. Site characterization can now include the use of systematic planning, dynamic work strategies, and real-time field measurements to reduce CSM uncertainty and expeditiously advance sites toward closure. This modern approach is termed the Accelerated Site Characterization process by the American Society for Testing and Materials (ASTM) and the Triad Approach by the U.S. Environmental Protection Agency (USEPA) (ITRC, 2003, 2007; ASTM, 2004; Crumbling et al., 2001, 2003; USEPA, 2008c). A unifying concept within site characterization approaches such as the Triad Approach is “managing uncertainty.” This can be accomplished by focusing on decision quality rather than just data quality as summarized in Table 10.2.

Table 10.2. Improving Site Characterization by Focusing on Decision Quality in Addition to Data Quality

Component	Key elements
Project decision quality	Identify decision goals with tolerable uncertainty
	Identify major uncertainties that can cause decision errors
	Identify strategy to manage each major uncertainty
Project data quality	Manage sampling uncertainties using field analytical methods and dynamic work plans
	Manage analytical uncertainties in data using quality assurance/quality control (QA/QC), method modification, etc.

10.3.2 Overview of the Triad Approach

The Triad Approach involves a series of interactive steps and phases such as depicted in Figure 10.1. This interactive, decision-oriented approach includes flexibility that facilitates modifications to field work as results are obtained. This approach is particularly useful to site characterization for ISCO applications because of its ability to generate high-resolution data regarding site conditions and contaminant characteristics. These data enable the development of a more accurate CSM, which is critical when considering the application of an ISCO technology to achieve a particular groundwater cleanup goal. Site characterization following a Triad Approach involves three key elements: (1) systematic planning, (2) dynamic work strategies, and (3) real-time measurements.

10.3.2.1 Systematic Planning

A sampling and analysis program must be devised to collect critical data to support the CSM and provide a basis for selection, design, and implementation of ISCO. Systematic planning is a process that may be used to define the data objectives and ensure project stakeholder consensus prior to development of the work plan. Depending upon the status of the ISCO project (e.g., ISCO screening, design, or implementation), varying degrees of CSM refinement and detail of data collection may be necessary.

For example, the ISCO screening process may require assessment of the general range of COC concentrations present and characteristics of the subsurface zone that might be targeted for treatment by ISCO, but may not require fine delineation of the target treatment zone (TTZ). Therefore, a data objective to define the nature of COC contamination may be included and contain sampling and analysis methods to delineate the contaminant source and plume using moderate data quality means (i.e., soil vapor sampling) and to conduct grab sampling of subsurface porous media and groundwater from only a few locations of high, moderate, and low concentration to verify the range of COC concentrations present. Data objectives to support ISCO feasibility evaluation and/or system design may not require as stringent a level of laboratory QA as traditional site characterization data.

However, to support the ISCO detailed design process, high data density and a combination of moderate and high quality sampling are required to delineate and characterize the TTZ and approximate the source mass and/or contaminant phase distribution. In order to accomplish this data objective, a method of high data density on tightly spaced probe points (e.g., cone penetrometer with membrane interface probe [MIP]) may be used along with confirmation

porous media and groundwater sampling from a moderate number of selected locations within the zone of characterization. Additional discussion of the methods for site characterization is provided in Section 10.4.

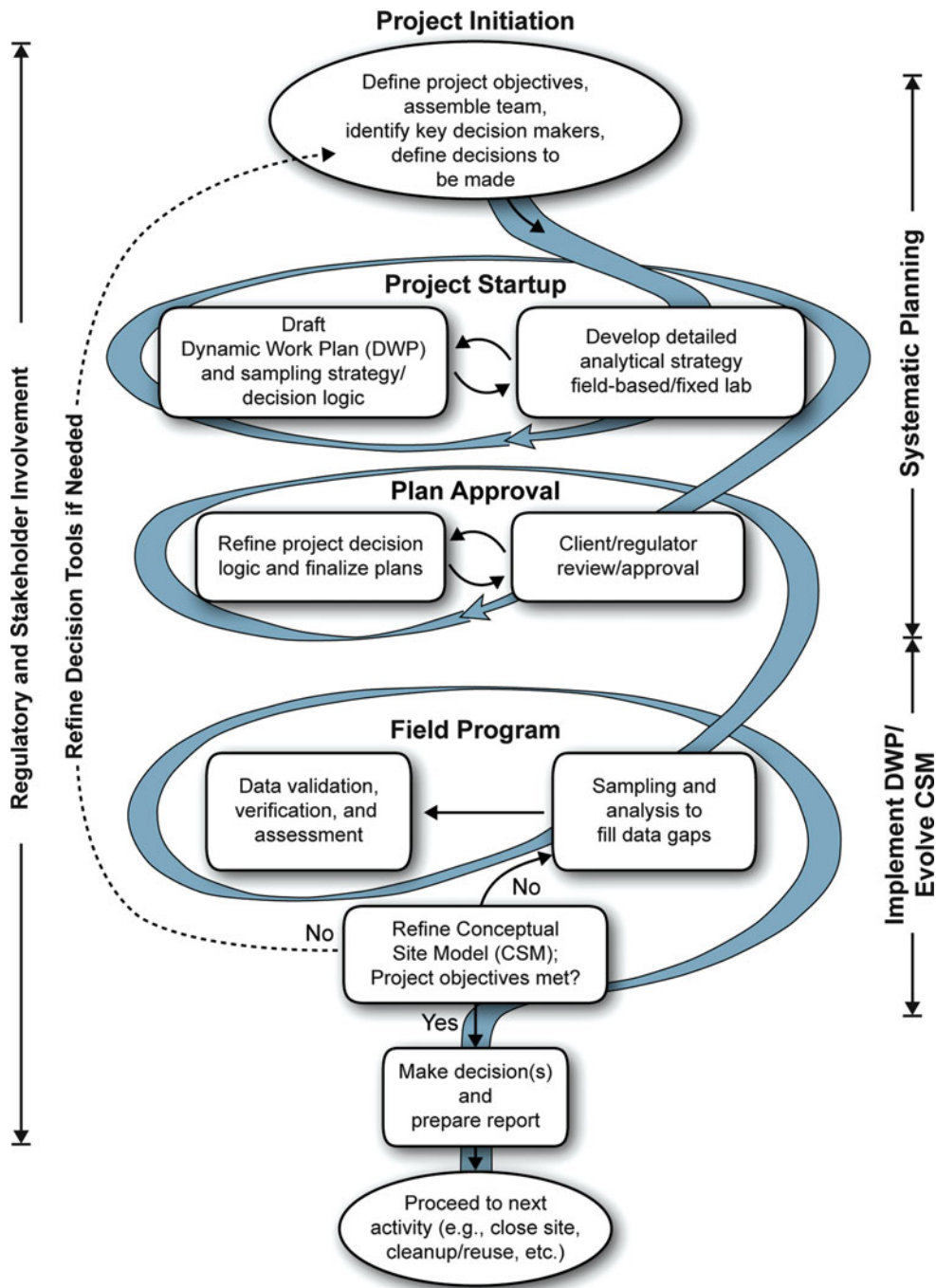


Figure 10.1. Illustration of the interactive phases and steps when following a Triad Approach to site characterization (adopted from USEPA, 2008c).

10.3.2.2 Dynamic Work Strategies

Dynamic work strategies are an integral component of a successful site characterization effort because they provide a means for a project to optimize its efforts during its implementation. In contrast to rigidly executed characterization work plans, dynamic work strategies consist of a contingency plan including trigger levels and decision logic that are designed to review data as they are collected and adapt data collection routines to ensure that investigation objectives are met. Because typical dynamic work strategies used for site remediation in general also are applicable to ISCO, they are not discussed in detail here. Additional general information on the use of dynamic work strategies for site characterization can be found elsewhere (USEPA, 2006, 2007; ITRC, 2007).

10.3.2.3 Real-Time Measurements

Rapid, and in some cases real-time, measurements can be made with sampling and field analytical methods to support CSM development, refinement for ISCO screening, as well as detailed design and implementation (e.g., NAVFAC, 2008b; USEPA, 2008a, b). These measurement techniques offer the benefit of providing characterization data while crews are in the field so that data objectives, such as COC delineation efforts, can be completed during a single mobilization. Real-time and rapid measurements also normally offer the added benefit of higher data density at lower cost per data point. Each data point is typically of lower data quality than that achieved through fixed-based laboratory analysis of samples collected using conventional or alternative means. However, higher density datasets even if comprised of somewhat lower quality data points can yield overall higher information quality for a given decision-making purpose (e.g., delineation of a TTZ for ISCO).

10.4 CHARACTERIZATION METHODS AND TECHNIQUES

This section describes the methods and techniques that are available and potentially applicable for characterization of a site to support development of a valid CSM and enable technology screening and early conceptual design. It is noted that all of the activities described below do not necessarily need to be carried out for every ISCO project. However, activities that are commonly employed for ISCO projects are noted. In Section 10.5 there is a summary of the relative importance of information in the key characterization areas described below and how the level of effort required for ISCO compares to that required of other *in situ* technologies.

10.4.1 Site Features and Land Use Attributes

The site features and land use attributes component of the CSM presents the physical conditions present at the site within which the ISCO technology would have to work. Therefore, it is important that a detailed site survey be conducted to identify key features such as property lines, landscape topography, water resources, bedrock outcroppings, building infrastructure, water and power utilities, underground utility corridors, abandoned utility lines, current and former underground tanks, old boreholes, inaccessible areas, and potential human and environmental receptors. It is particularly important to locate potential subsurface pathways and conduits for fugitive emissions that can result from some ISCO applications where exothermic reactions occur and gases are generated. A detailed site survey can be conducted using conventional survey equipment, a geographic positioning system, or aerial photogrammetric mapping. The site survey data can be represented in a site plan using manual or computer-aided methods (e.g., computer-aided design, geographic information system, or other 2-dimensional

(2-D) or 3-D geospatially ortho-rectified means). An example of a simplified site plan for an ISCO project along with a photograph of the site is shown in Figure 10.2.

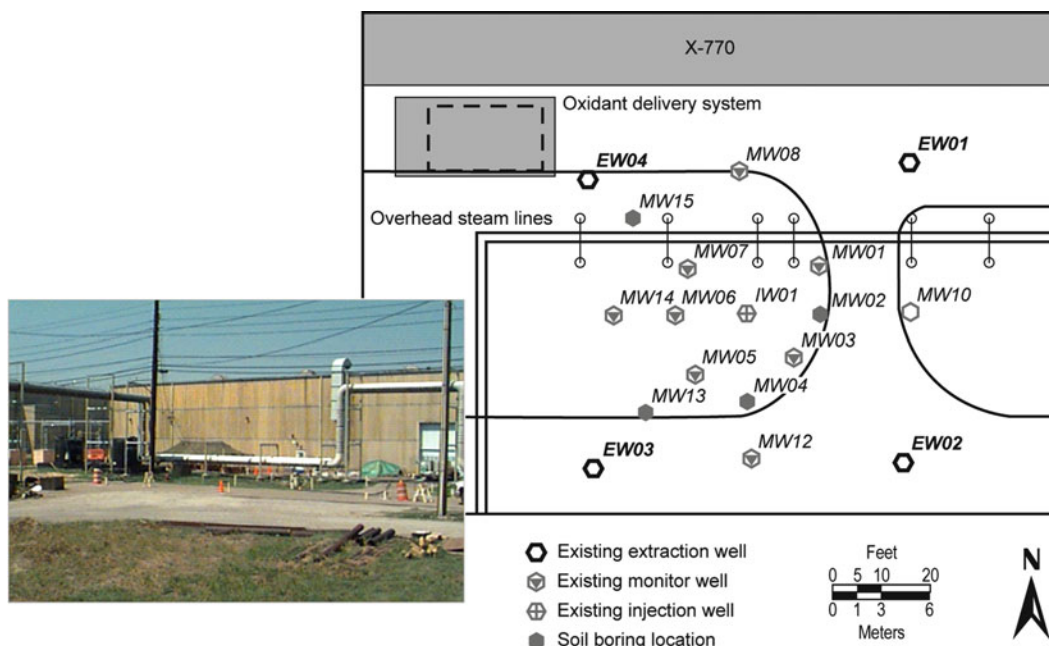


Figure 10.2. Site plan for an area suspected of being the source of a trichloroethene (TCE) groundwater plume (Siegrist et al., 2001; Lowe et al., 2002). ISCO was eventually deployed using vertical well recirculation of sodium permanganate (NaMnO_4).

10.4.2 Nature and Extent of Contamination

10.4.2.1 Characterizing the Contaminants of Concern

For proper consideration of ISCO for remediation of a contaminated site, characterization efforts need to accomplish the following three objectives related to the COCs at the site:

- Determine the COCs present and the range of concentrations in the subsurface to enable an assessment of their treatability by ISCO and selection of an effective oxidant and the appropriate reaction chemistry.
- Determine the distribution of COCs within the lithologic conditions present at the site so that appropriate ISCO delivery techniques can be designed and implemented.
- Delineate the lateral and vertical extent of the COCs so that the appropriate TTZ can be selected for ISCO treatment.

The COCs at a site must be identified so that their treatability by ISCO can be evaluated and the proper oxidant and reaction chemistry can be designed. Efforts should focus on identifying the parent chemicals and degradation products (biotic and abiotic). Organic chemicals are commonly among the COCs in contaminated groundwater (ATSDR, 2009). Characterization efforts should also delineate the levels of other organics that might be present as residuals of previous remedial activities and which can interfere with ISCO processes (e.g., surfactants/cosolvents, vegetable oils). Co-contaminants also should be identified even if they are currently not COCs, since some can be impacted by ISCO (e.g., redox-sensitive metals). In order to identify

chemicals, samples must be collected and analyzed by a suitable field-based or fixed-based laboratory following an approach and methodology consistent with data quality objectives (DQOs) for the effort. Guidance on assignment of DQOs and devising a sampling and analysis approach is available (USEPA, 2006). A summary of field sampling and analysis methods is shown in Table 10.3. The methods listed in Table 10.4 have particular relevance to NAPL source zones, but they also may be applicable to subsurface zones without NAPL present.

Table 10.3. Common Field Sampling and Analysis Methods Potentially Applicable for Characterization of a Site Where ISCO Could Be Deployed (adapted from FRTR, 2008)

Activity and method	Example technique/instrumentation
Subsurface access methods:	
Drilling methods for unconsolidated formations	Hollow stem auguring; sonic drilling
Drilling methods for consolidated formations	Cable tool; sonic drilling, rotary drilling
Drive methods	Cone penetrometer; direct push technology
Sampling installations for portable samplers	Single riser, limited interval wells; nested wells
Portable <i>in situ</i> groundwater samplers/sensors	Direct drive samplers; passive multilayer samplers
Fixed <i>in situ</i> samplers	Multilevel capsule samplers; multiport casings
Destructive sampling methods	Coring and extraction
Sample collection methods:	
Hand-held methods	Scoops, spoons, shovels; augers; tubes
Power-driven soil samplers	Split and solid barrel; thin-wall open tube
Groundwater sampling pumps	Low-flow bladder pump; peristaltic pump
Portable grab samplers	Bailer
Extractive collection methods	Diffusion bags; sorbent devices
Gas/air collection methods	Soil gas probes
Sample analysis methods (for organics):	
Sample extraction methods	Solvent extraction; purge and trap; headspace
<i>In situ</i> analysis methods	Solid/porous fiber optic, LIF, MIP
<i>Ex situ</i> analysis methods	Photo-ionization detector; flame-ionization detector; detector tubes; gas chromatography (GC) with detector or mass spectrometer; immunoassay colorimetry; bioassays

Of the various methods outlined in Tables 10.3 and 10.4, rapid field measurement techniques that are being used for ISCO screening, design, and implementation at sites containing volatile organic compounds (VOCs) and semivolatiles organic compounds (SVOCs), include the following:

- Depth-discrete sampling of groundwater (Waterloo Profiler™, Geoprobe® Screen Point, Hydropunch®, SimulProbe®, Iso-Flo®) with mobile laboratory analysis.
- Passive and active soil vapor sampling.
- Headspace monitoring of soil core samples.
- Cone penetrometer testing (CPT).
- Membrane interface probe (MIP).
- Laser-induced fluorescence (LIF).

- Electrical resistivity imaging (ERI).
- Electrical conductivity (EC) probing.

Use of these and similar technologies along with more conventional sampling and analyses methods can yield an optimum approach for delineating the nature and extent of contamination and minimizing decision uncertainty. Selection of the investigative approach should be based on the complexity of a particular site, recognizing that a variety of more conventional investigative approaches can provide adequate characterization data.

Table 10.4. Advantages and Limitations of Site Characterization Technologies Utilized for Contaminated Sites Including Those with NAPL Source Zones (USEPA, 2003)

Tool/method	Potential advantages	Potential limitations
Percussion probing (Geoprobe [®])	<ul style="list-style-type: none"> • Less expensive • More mobile and available • Well developed sampling tools • Availability of certain sensors 	<ul style="list-style-type: none"> • Difficult to penetrate hard dense soils • Depth limitation
CPT	<ul style="list-style-type: none"> • Greater depth penetration • Certain sensors better developed (LIF, tip resistance, sleeve friction, etc.) 	<ul style="list-style-type: none"> • More expensive • Less available • Less maneuverable
Organic vapor analysis screening of soil cores	<ul style="list-style-type: none"> • Rapid and inexpensive • High concentrations of VOCs associated with NAPL presence • Useful to focus sampling 	<ul style="list-style-type: none"> • Qualitative data • Readings sensitive to effective contaminant volatility, water content, sample temperature, and sample handling
Ultraviolet (UV) fluorescence detection methods	<ul style="list-style-type: none"> • Quick and inexpensive • Many NAPLs fluoresce • Can provide detailed information on relationship between stratigraphy and contaminant distribution • Can document using a digital camera 	<ul style="list-style-type: none"> • Requires fluorescent NAPL • Indiscriminant • Interfere from non-target fluorescent materials (such as shell fragments in coastal sediment) • Significant potential for false positives and false negatives
Hydrophobic dye shake test	<ul style="list-style-type: none"> • Simple, quick, and inexpensive field methods for qualitative assessment and visual confirmation • Does not require analytical equipment 	<ul style="list-style-type: none"> • Known background and NAPL-contaminated samples should be examined to check for interference and site-specific response • Can only detect NAPL if present in samples • Potential for false positives (reaction with other organic matter) and false negatives (not enough NAPL present) • Visual contrast can be difficult to discern in dark soil
Ribbon NAPL sampler (RNS) strips	<ul style="list-style-type: none"> • Relatively simple, direct and inexpensive • Can provide detailed information on relationship between stratigraphy and contaminant distribution 	<ul style="list-style-type: none"> • Minor discoloration of liner associated with handling and contact with plastic core sleeves • Relatively faint reaction to some NAPLs

(continued)

Table 10.4. (continued)

Tool/method	Potential advantages	Potential limitations
	<ul style="list-style-type: none"> • Amenable to rapid documentation via photography 	<ul style="list-style-type: none"> • Color fading and/or non detection due to evaporation • Potential for false positives and false negatives • Potential for cross contamination (open hole)
MIP	<ul style="list-style-type: none"> • Widely available • Simultaneous log of VOCs and soil conductivity • Operates in vadose zone and soil conductivity • Useful for delineating NAPL source zones • Rapid site screening (100 s of ft/day) • Cost savings 	<ul style="list-style-type: none"> • High detection limits, qualitative analytical data • Designed for volatile contaminants • Contaminant carryover can be high • Penetration resistance limitations • Shallow use
Downhole RNS (e.g., NAPL FLUTE™)	<ul style="list-style-type: none"> • Provides continuous record of NAPL distribution with depth at borehole location • Can be deployed in variety of hole types • Can provide cost savings 	<ul style="list-style-type: none"> • Heterogeneity may limit value of information • Relatively ambiguous reaction to some NAPLs may be difficult to interpret • Wicking may exaggerate NAPL presence • Potential for false positives and false negatives • Potential for cross contamination
CPT/LIF UV fluorescence probes	<ul style="list-style-type: none"> • Real-time delineation of stratigraphy and fluorescent contamination • Typical daily productivity of 300–400 ft at 10–15 locations • LIF waveforms offer product identification/verification and rejection of non-contaminant fluorescence • Reduced investigative derived waste and exposure to site COCs • Potential cost savings 	<ul style="list-style-type: none"> • Primarily applicable to polycyclic aromatic hydrocarbons • Subject to interferences • NAPL has to be adjacent to sapphire window • Limited availability • Cost
Direct push groundwater profiling	<ul style="list-style-type: none"> • No drill cuttings and little purge water • Can pump clean water out through screen during advancement to minimize clogging and drag down of contaminants • Can collect multiple samples (at any spacing) with depth using peristaltic or pneumatic low-flow pumping methods • Can perform saturated hydraulic conductivity (K_{sat}) tests • Can develop well screen • Holes can be grouted through rods 	<ul style="list-style-type: none"> • Limited by lithology (clogging, turbidity, and lack of yield problematic in fine-grained sediments) and depth (depending on drilling and sample collection methods) • Only provides a snapshot in time of water quality • Concentrations of metals and hydrophobic compounds likely to be biased due to sample turbidity • Vertical hydraulic gradients can impact backtracking interpretation

(continued)

Table 10.4. (continued)

Tool/method	Potential advantages	Potential limitations
	<ul style="list-style-type: none"> • Provides detailed concentration profiles that can be used for backtracking to NAPL source • Rapid and relatively cost effective 	<ul style="list-style-type: none"> • Due to heterogeneity and dilution effects can still be difficult to define morphology of dense nonaqueous phase (DNAPL) sources • Concentration > effective solubility indicates NAPL in sample, but concentration < effective solubility requires interpretation
Partitioning interwell tracer testing (PITT)	<ul style="list-style-type: none"> • Can estimate DNAPL saturation 	<ul style="list-style-type: none"> • Need to know DNAPL location • Need sufficient hydraulic conductivity for tracer test • Need small enough source to allow adequate well spacing to conduct tracer test in reasonable time frame • The presence of natural organic carbon may cause some difficulty with the interpretation of the results • For heterogeneous DNAPL distribution (especially pools), underestimates DNAPL volume • Expensive and regulatory concerns may require recovery of tracers

As discussed in Section 10.3, sampling uncertainty can be minimized through use of field measurements and, as needed, data analysis uncertainty can be addressed through appropriate laboratory analyses and QA/QC (Table 10.2). Selection of a characterization approach and the technologies employed should also include evaluation of what properties need to be measured and what detection limits need to be achieved. This is important to ensure that the measurements satisfy questions that are important to decision-making (e.g., concentrations of TCE in groundwater at $\leq 5 \mu\text{g/L}$, the maximum contaminant level [MCL]). For example, a MIP, which cannot detect low concentrations in a plume, can be used with cone penetrometer testing (CPT) to identify higher concentration zones and the short-range variability of organic COCs with depth in the subsurface. These data often reveal that the highest concentrations are present in lower permeability layers and this information can be important for tailoring the design of an ISCO delivery system. The complementary use of direct push technology and depth-discrete sampling with a mobile laboratory for sample analyses can enable quantification of the COC concentrations within the source zone and an associated groundwater plume.

At many sites contaminated with organic COCs, there can be concern over the presence of NAPL source zones. Site characterization activities that can help assess the presence of a DNAPL source zone and delineate its boundaries are summarized in Table 10.5. Characterization of DNAPL source zones can be critical to assessing the viability of ISCO to achieve a treatment goal as well as for selecting the best ISCO technology and its design attributes (e.g., oxidant concentration delivered and by what method). Due to the

complexity of this type of characterization challenge, multiple techniques such as those listed in Table 10.5 are often combined to yield multiple lines of evidence (Kueper and Davies, 2009).

Site characterization activities can provide the necessary parameter values (e.g., bulk density, porosity, fraction organic carbon, water-filled porosity), which when combined with chemical data, can be used to estimate the mass of contamination in the zone from which a sample is obtained. Equation 10.1 presents an equilibrium partitioning relationship, which accounts for the relationship of the organic COCs present in the sorbed, aqueous, and vapor phases within the subsurface. For application to a groundwater zone, Equation 10.1 can still be used if $\theta_a = 0$.

$$C_i^{Total} = \frac{C_i^w}{\rho_b} \left(K_{oc} f_{oc} \rho_b + \theta_w + H' \theta_a \right) \quad (\text{Eq. 10.1})$$

where C_i^{Total} = the total concentration of contaminant i in porous media including all phases (milligrams per kilogram [mg/kg]); C_i^w = groundwater concentration of contaminant i (mg/L); K_{oc} = organic carbon partition coefficient (milliliter per gram [mL/g]); f_{oc} = fraction of organic carbon (g/g), ρ_b = dry bulk density (g/mL), θ_w = water-filled porosity (L/L); H' = Henry's Law constant (unitless); θ_a = air-filled porosity (unitless). For example, based on monitoring data from a groundwater zone at a site, the aqueous phase concentrations of a contaminant (C_i^w) can be used in Equation 10.1 to calculate the total concentration of contaminant present (C_i^{Total}).

Along the lines of the calculation just presented, site characterization data can be used to determine the threshold concentration above which DNAPL presence would be suspected (Feenstra et al., 1991; USEPA, 1992; Kueper and Davies, 2009). This is done using Equation 10.1 by setting C_i^w = effective solubility of contaminant i in which case C_i^{Total} = the threshold total concentration above which a DNAPL phase would exist (mg/kg). As an illustration, for a groundwater zone located in a sandy formation ($f_{oc} = 0.00009$, $\rho_b = 1.58$ g/mL, $\theta_w = 0.39$ L/L), the DNAPL threshold, C_i^T was calculated to be 358 mg/kg for TCE ($C_i = 1,366$ mg/L, $K_{oc} = 166$ mL/g) or 39 mg/kg for perchloroethene (PCE) ($C_i = 150$ mg/L, $K_{oc} = 155$ mL/g) (Oesterreich and Siegrist, 2009).

If there is a known multi-component DNAPL situation, the effective solubility of each contaminant in the DNAPL can be estimated using Raoult's Law, which is shown in Equation 10.2:

$$C_i^w = m_i S_i \quad (\text{Eq. 10.2})$$

where C_i^w = effective solubility of component i in water (mg/L); m_i = mole fraction of component i in the DNAPL (unitless); S_i = single-component aqueous solubility of component i (mg/L). In this case, the effective solubility value for each component can be calculated using Equation 10.2 and these values (C_i) can be used in Equation 10.1 to calculate the threshold concentration for each of the contaminants present (threshold C_i^{Total}).

If samples from the groundwater zone (aquifer solids including pore water) revealed concentrations of a target COC that exceeded the calculated DNAPL threshold, the relative mass distribution in the DNAPL phase could also be estimated as that portion above the threshold concentration (C_i^{Total}). To aid calculations regarding the equilibrium phase distribution of COCs in a subsurface zone, analytical models can be used and implemented in computer-based spreadsheets such as SOILMOD (Dawson, 1997) or NAPLANL (<http://www.dnapl.com/publications/html>).

Table 10.5. Investigation Methods that Can be Combined for Assessment and Delineation of DNAPL Source Zones (Kueper and Davies, 2009)

Method	Comments
Site use/site history	<ul style="list-style-type: none"> • Certain industrial practices are associated with DNAPL presence in the subsurface (e.g., manufactured gas plants, wood preserving sites, dry cleaning operations, chemical production)
Visual observation	<ul style="list-style-type: none"> • While not common, DNAPL can be observed in a monitoring well, drill cuttings, or core samples obtained from the subsurface
Chemical concentrations in porous media above threshold DNAPL saturation	<ul style="list-style-type: none"> • Concentrations of DNAPL compounds in porous media that correspond to a threshold DNAPL saturation level (between 5 and 10% of pore space) provide evidence that DNAPL is present
Chemical concentrations in porous media above partitioning threshold	<ul style="list-style-type: none"> • Concentrations of DNAPL compounds in porous media that exceed the partitioning capacity in the dissolved and sorbed phases are indicative of DNAPL presence
Vapor concentrations	<ul style="list-style-type: none"> • Vapor phase plumes above a groundwater can be indicative of DNAPL compounds being present
Hydrophobic dye testing	<ul style="list-style-type: none"> • Hydrophobic dyes, such as Oil Red O, will partition into a DNAPL and impart a red color. Dye testing can be done above ground in a jar or using down-hole ribbon samplers
Magnitude of groundwater concentrations	<ul style="list-style-type: none"> • Groundwater concentrations that exceed 1% of the effective solubility indicate that groundwater may have come in contact with DNAPL
Persistent plume of contaminated groundwater	<ul style="list-style-type: none"> • Presence of a contiguous and persistent plume, long after the most likely release of contaminants into the groundwater
Presence of contamination in apparently anomalous locations	<ul style="list-style-type: none"> • Presence of contaminated groundwater in locations that are not downgradient of known or suspected contaminant releases can indicate DNAPL presence
Groundwater concentrations with depth trends	<ul style="list-style-type: none"> • Increasing concentrations of DNAPL compounds with depth in a groundwater zone can indicate DNAPL presence
Groundwater concentrations with time trends	<ul style="list-style-type: none"> • Concentrations of DNAPL compounds in a groundwater zone that decline to different degrees over time with distance in a plume can indicate a DNAPL source zone
Detection of high sorbing compounds in groundwater	<ul style="list-style-type: none"> • Detection of DNAPL compounds that have high sorption and low solubility may indicate a local DNAPL source
Other types of methods	<ul style="list-style-type: none"> • PITT methods; down-hole measurement probes with direct push platforms

Note: Kueper and Davies (2009) present example calculations related to several of the above methods.

Despite advancements and the array of methods and tools available today, the delineation of organic COCs, especially VOCs, in the subsurface at some sites remains very challenging and imprecise. Many of the potential problems and challenges are based on sampling and analysis of soil and groundwater zones due to (1) the potential for large measurement errors (up to 90% negative bias or more) with some organic compounds in some media (e.g., VOCs in soil and aquifer solids) (e.g., Hewitt, 1994; Siegrist et al., 2006; Oesterreich and Siegrist, 2009) and (2) the potential need for large numbers of samples to address site heterogeneities and temporal and spatial variability (West et al., 1995; Schumacher and Minnich, 2000; Parker et al., 2003). For source zones where DNAPLs are present, estimating the total mass of COCs present will likely be uncertain by a factor of 10 or more given the complexity of contaminant distributions in natural subsurface systems and the inability to collect enough samples to account for this complexity (SERDP and ESTCP, 2006).

10.4.2.2 Contaminant Mass Flux

Measurement of COC mass flux in groundwater is emerging as a potentially important metric for characterizing COC plumes and source-plume relationships (USEPA, 2003). However, there are still uncertainties and differing views about how to express the potential value without overstating its ease of implementation and usefulness to decision making. This section provides a summary of this metric and notes how it might be useful for considering ISCO as a potentially viable remedy.

COC mass flux (expressed as mass/time/area) and mass discharge integrated across a cross section of the COC plume perpendicular to flow (mass/time) represents both the COC concentration as well as groundwater flow (Figure 10.3). This information provides important data about the overall plume strength and dynamic response to treatment (Brooks et al., 2008; Guilbeault et al., 2005). Mass flux and mass discharge measurements can be used to more effectively develop treatment targets for COC plumes and/or COC source zones, and changes in COC mass flux or discharge in response to ISCO treatment may provide an important metric for understanding the overall treatment response. Tools for measuring mass flux are evolving and include passive techniques (Hatfield et al., 2004; ESTCP, 2007) and active techniques (Bockelmann et al., 2001). Goltz et al. (2007) present a review of different methods for measuring COC mass flux in groundwater.

Regulatory approaches to defining treatment goals for site remediation have not yet incorporated mass flux/mass discharge measurements, however these concepts are evolving within the regulatory framework. For instance, the preferred remedial option for one Superfund site includes a reduction of mass flux/discharge from the high concentration groundwater zone as one of the remedial action objectives (RAOs) (USEPA, 2009). For combined remedy approaches, the use of mass flux or mass discharge to develop treatment end points for a component technology such as ISCO may be very useful. For example, mass flux/discharge may provide a relevant basis to determine ISCO treatment end points at a site when bioremediation, monitored natural attenuation (MNA), or permeable reactive barriers are used to treat a down gradient plume. Effective use of mass flux/mass discharge can significantly reduce the uncertainty of site characterization in these applications. However, the degree of sampling necessary to achieve the desired level of uncertainty in a mass flux measurement can be complex and may be impractical in some situations. A cost benefit analysis will help ensure that the additional costs incurred result in a concomitant increase in characterization data usability and decision support.

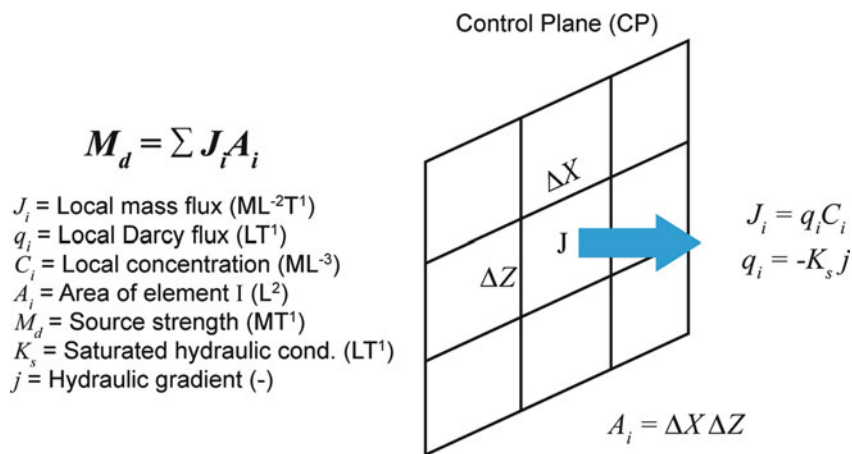


Figure 10.3. Schematic representation of a control plane, and a definition of the source strength (M_d) and local values for groundwater flux (q_i), and contaminant flux (J_i) (USEPA, 2003).

10.4.3 Hydrogeologic Conditions

It is important that the steady state and transient occurrence of groundwater in the subsurface be understood as part of the CSM. The hydrogeology at a site can have a large impact on the viability of different ISCO oxidants and delivery methods. Thus, it is important to understand the hydrogeologic conditions, including the following:

- Occurrence and characteristics of significant lithologic layers present within and immediately adjacent to the contaminated zone
- Identification of prominent confining or semi-confining layers that can govern groundwater flow
- If groundwater formation is unconsolidated:
 - Estimation of porous media permeability (primary/secondary)
 - Hydraulic conductivity as measured by field tests (if hydraulic conductivity is obviously high [e.g., coarse uniform sand] or obviously low [e.g., clay], measurement is not necessary for screening)
 - Characterization of heterogeneity (e.g., is formation primarily permeable or impermeable, assessment of likely variation in K between distinct strata, evaluation of interconnection of high K zones, evaluation of whether fractures or other preferential pathways exist)
- Estimation of groundwater elevations, hydraulic gradients (horizontal and vertical), flow direction
- If formation is consolidated, estimate of permeability (primary/secondary)

To characterize hydrogeologic conditions, site characterization data can be obtained by using an array of established techniques, including:

- Visual borehole logging
- Core sampling and physical properties analysis (intact or conventional split-spoon)
- Water levels in monitoring well or probe networks
- Hydraulic assessment of nested monitoring wells
- Hydraulic testing (pump testing or slug testing [conventional or pneumatic])
- Tracer testing
- Borehole flow meter (colloidal, thermal)
- Video microscope
- Geophysical techniques (magnetic, resistivity, conductivity, ground penetrating radar, borehole, seismic)

Due to the heterogeneous nature of subsurface settings, application of several of these techniques may be required within each of several unique layers within the contaminated region, or more of which could end up being within the ISCO TTZ. A range of values will be obtained for each of the parameters and these values will be useful for uncertainty or sensitivity analysis during ISCO screening and later during ISCO design. If unacceptable uncertainty exists, then additional characterization using additional methods and high-resolution application methods may be required.

10.4.4 Geochemical Conditions

Geochemical conditions in a subsurface zone considered for treatment by ISCO are very important as they can affect oxidation reaction chemistry and deliverability of chemical

oxidants throughout a TTZ. As a result, proper consideration of ISCO often requires more site characterization effort devoted to geochemical conditions than that required for other *in situ* technologies. Data particularly pertinent to ISCO include the parameters listed in Table 10.6.

Geochemistry plays a very important role in ISCO applications because the ISCO system must be designed to account for oxidant persistence in the subsurface including the effects of autodecomposition reactions and the natural oxidant demand (NOD) of the aquifer solids (ASTM, 2007; Appendix D). The oxidant and reaction chemistry must also account for potential activators (e.g., iron (Fe^{2+}), manganese (Mn^{2+})) and free radical scavengers (e.g., carbonate [CO_3^{-2}]). Understanding of the redox state of the subsurface, along with the presence of reduced metals and minerals and natural organic matter (NOM) rich deposits, can provide understanding of the potential NOD to be exerted. For example, groundwater zones with reducing conditions (low oxidation-reduction potential [ORP]) will normally be more challenging for ISCO than zones with oxidizing conditions present. The groundwater redox state under ambient conditions can also provide insight into the potential for mobilization of redox-sensitive metals like chromium (or immobilization for metals like arsenic).

As discussed in Chapters 9 and 12, geochemical data can be important during ISCO implementation and performance monitoring because while some effects can be reliably predicted, others like metal mobility, cannot be well predicted. Therefore, analysis of baseline and post-ISCO geochemistry can be important to monitor and demonstrate the effects (positive and negative) of ISCO.

Aqueous geochemical parameters are typically collected from conventional monitoring wells with moderate to relatively long screened intervals. Composite-type samples from these wells are adequate for the geochemical analysis since it is intended to characterize the local aquifer conditions. That said, it can be important to gain insight concerning the geochemical conditions within each unique stratum of the ISCO TTZ to quantify the range of conditions present at the site. Details regarding spatial variability can enable the tailoring of an ISCO approach for each stratigraphic layer, should any significant differences exist.

Table 10.6. Geochemical Data Obtained During Site Characterization Important to Determining if ISCO Is a Potentially Viable Remediation Technology

Media	Data	Importance to ISCO	General approach to measurement
Groundwater porous media solids	Color	Indicative of redox	Analyzed onsite using a Munsell color chart
	Organic matter content (TOC, f_{oc})	Used for partitioning calculations and is an indicator of NOD ^a	Analyzed in an offsite lab
	Mineralogy	Certain minerals can react with oxidants (NOD, catalysts)	Estimated from geologic maps and by geologic interpretation of core samples. Analyzed if needed in an offsite lab

(continued)

Table 10.6. (continued)

Media	Data	Importance to ISCO	General approach to measurement
Groundwater aqueous phase	Temperature	Can affect reaction rates	Meter used <i>in situ</i> or immediately onsite
	pH	Can affect reaction chemistry ^a	
	Dissolved oxygen (DO)	Indicative of redox ^a	
	ORP		
	Alkalinity	Can affect reaction chemistry ^a	Analytical measurement made in an onsite or offsite laboratory
	Anions (e.g., F ⁻ , Cl ⁻ , NO ₃ ⁻ , PO ₄ ⁻³ , SO ₄ ⁻²)	Potential radical scavengers	Analytical measurement normally made in an offsite laboratory
Cations (e.g., K ⁺ , Ca ⁺² , Na ⁺ , Al ⁺³ , Mg ⁺² , Fe ⁺² , Fe ⁺³ , Mn ⁺²)	Potential activators		
Groundwater solids and aqueous phase	NOD for permanganate or oxidant persistence for persulfate, peroxide, and ozone oxidants	Affects dose and deliverability of ISCO ^a	Bench-scale tests typically done in an offsite laboratory
	Redox sensitive metals (e.g., S ⁰ , Fe ⁰ , Fe ⁺² , Mn ⁺² , As ⁺³ , Cr ⁺³)	Oxidants can alter state and mobility ^a	Analytical measurement normally made in an offsite laboratory

Al - aluminum, As - arsenic, Ca - calcium, Cl - chloride, Cr - chromium, F - fluoride, Fe - iron, K - potassium, Mg - magnesium, Mn - manganese, Na - sodium, NO₃⁻ - nitrate, PO₄⁻³ - phosphate, S - sulfur, SO₄⁻² - sulfate.

Note: The data listed in this table are potentially important to screening and conceptual design of an ISCO technology, but only those data noted with an ^a are typically important at most sites and for most ISCO approaches.

10.4.5 Fate and Transport Processes

Site characterization data can improve the understanding of fate and transport processes that control the movement of COCs and oxidants at a site where ISCO may be implemented (see Chapter 6). This understanding is important to ensure that:

- The TTZ for ISCO is properly located
- Realistic treatment goals are established
- The optimal delivery of oxidant (and activators or stabilizers) is achieved without adverse effects on COC movement (e.g., displacement or mobilization of NAPL)
- There is understanding of the potential fate of oxidant chemicals during and after delivery into the subsurface (e.g., magnitude of drift)
- The potential for rebound after ISCO treatment is minimized (either by influx or matrix back-diffusion)
- ISCO can be properly designed to avoid (or at least minimize) any negative effects to a post-ISCO treatment technology

Understanding fate and transport processes such as NAPL mobility and dissolved phase advection, adsorption, diffusion, and dispersion and the effects these processes have had or may have on the contaminant distribution can help clarify the processes that will likely occur post-ISCO. For example, post-ISCO matrix back-diffusion from low permeability media and

desorption of sorbed contamination has occurred at some ISCO treatment sites (see Chapter 8). This can be due to the fact that the site characterization did not adequately identify the conditions that are amenable to back diffusion and desorption processes and the resulting ISCO system designs did not adequately address their potential occurrence. For example, the selection of the oxidant type and delivery method may not have been appropriately made to achieve penetration and longevity into low permeability zones and effectively treat the media and minimize back diffusion and COC rebound.

During site characterization efforts, data can be acquired regarding the occurrence and rate of natural attenuation processes in the TTZ and down gradient from it. Because bioremediation and/or MNA are often implemented at sites for post-ISCO polishing, it is often prudent during early site characterization efforts, to collect some biological and MNA parameters (e.g., biodegradation byproducts, nitrate, iron, sulfate/sulfide, methane, ethene, ethane, chloride, pH, temperature, etc.) along with microbiological data using molecular biology tools (e.g., molecular analysis, lipid analysis).

10.4.6 Analysis and Visualization of Characterization Data

Data analysis and visual representations of site characterization data are needed for many purposes. For example, geospatial analysis and visualizations of the nature and extent of contamination and hydrogeologic conditions are important to increased understanding as the CSM is developed and refined. These visualizations commonly illustrate such important CSM attributes as discontinuous, semi-confining lithologic layers, diving or separated contaminant plumes, and locations of multiple residual source zones. Visual depiction also aids understanding of the possible contaminant release migration routes and extent of source zones for ISCO treatment.

Mathematical analysis of characterization datasets can be accomplished using established environmental statistical methods (e.g., Gilbert, 1987; Keith, 1996; Gibbons et al., 2009), which can be implemented using commercially available software (e.g., Microsoft[®] Excel[®], SAS JMP[®]). Decision support software also includes statistical analysis routines including geospatial analysis (USEPA, 2005). Several examples of public-domain software packages are listed in Table 10.7.

Table 10.7. Examples of Decision Support Tools that Include Statistical Analysis and Geospatial Interpolation (after FRTR, 2009)

Program	Functions	Reference URL
Adaptive risk assessment modeling system (ARAMS)	CSM; statistical analysis; ecological risk assessment; human health risk assessment	http://el.erdc.usace.army.mil/arams/
GeoSEM	Visualization; geospatial interpolation; statistical analysis	http://esc.syrres.com/geosem/default.htm
Monitoring and remediation optimization system (MAROS)	Data management; monitoring network optimization; statistical analysis	http://www.gsi-net.com/en/software/free-software/maros.html
Spatial analysis and decision assistance (SADA)	Visualization; initial sampling; secondary sampling; geospatial interpolation; statistical analysis; human health risk assessment	http://www.tiem.utk.edu/~sada/index.shtml

Since most site characterization data consist of point source measurements, geospatial analysis of 2- or 3-D datasets involves mathematical interpolation (Isaaks and Srivastava, 1989; Cressie, 1991). There are various statistical packages that can be used for data analysis including 2- and 3-D geospatial analysis such as GeoSEM and SADA (Table 10.7). In addition, a public

domain software package known as R provides a wide variety of statistical methods (e.g., linear and nonlinear modeling, classical statistical tests, time-series analysis, classification, clustering) and graphical techniques (<http://www.R-project.org/>).

Site characterization data are visualized using various methods and techniques for reporting and communication purposes. A variety of 2-D maps, drawings and graphs are routinely used during ISCO screening and conceptual design, including:

- Site plan with COC plume overlay (e.g., see Figure 10.4)
- Geologic cross section with contaminant plume overlay
- Piezometric surface map (steady state and transient during precipitation event)
- Bedrock or confining layer isopleths map
- Isopleth maps of COC concentrations in groundwater (e.g., Figure 10.4)
- Isopleth maps of COC contaminant levels in groundwater (e.g., Figure 10.5)
- COC time series graphics for individual monitoring wells and an entire plume

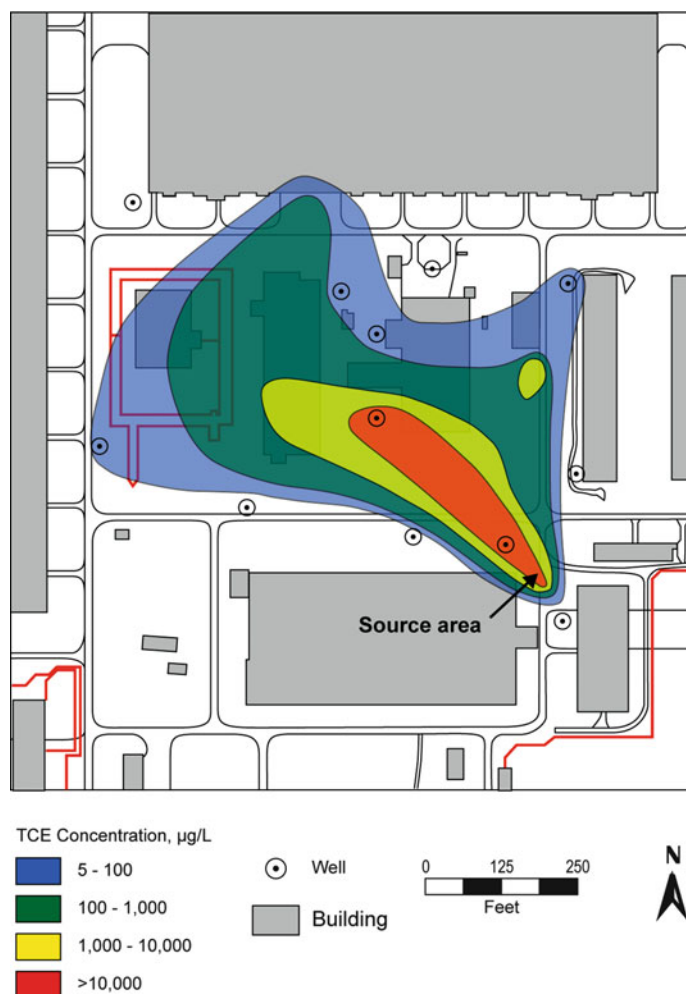


Figure 10.4. Example of a 2-D isopleth map showing TCE concentrations in groundwater at a U.S. Department of Energy (DOE) site in Ohio. The source area of this plume is shown in the site plan of Figure 10.2, which presents the footprint within the four corner extraction wells used for ISCO recirculation.

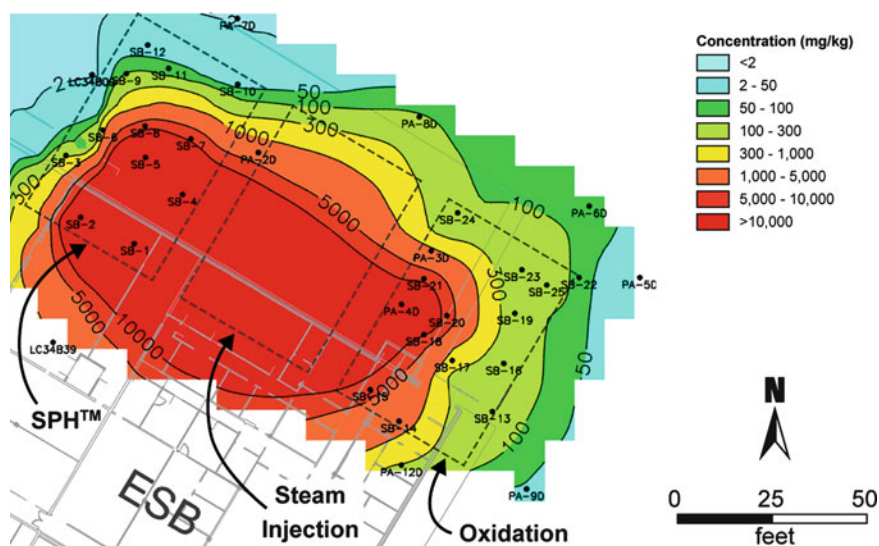


Figure 10.5. Example of a 2-D isopleth map of TCE concentrations in a groundwater zone at a U.S. National Aeronautics and Space Administration (NASA) site in Florida (Gavaskar, 2002). Analysis completed using geostatistical analysis of the results of depth-discrete CPT core sampling and field GC analyses. The contours represent the total concentration of TCE including that present in the dissolved, sorbed, and nonaqueous phases.

Visualizations can also take the form of 3-D realizations (e.g., concentration volumetric models such as shown in Figure 10.6) prepared using geostatistical software packages (e.g., see Table 10.7). While 2-D visualizations are convenient for project reporting purposes, color 3-D visualizations can offer a more complete picture of subsurface conditions. These visualizations can provide powerful output to help refine the CSM, to more clearly understand the spatial distribution of any source zones, and to optimize injection strategies, technologies and infrastructure for ISCO remediation.

Regardless of the 2- or 3-D presentation method chosen, the visualizations can give a false sense of the degree of understanding if they are based on limited datasets and weak interpolation parameters and boundaries. Actual data can be posted on an isopleth map so that the user understands the specific data that were used to generate the map.

10.5 SITE CHARACTERIZATION DATA NEEDED FOR ISCO

Throughout ISCO selection and design, and consistent with the Observational Method applied to site remediation, the CSM is periodically revisited to help make sure that a sufficient amount of data with appropriate quality has been collected and the CSM is adequately defined to support the decisions at hand (see Chapter 9). In general, data gaps in the CSM can introduce uncertainty in the selection or application of ISCO as a viable technology to help meet remediation objectives established for a site. The acceptable level of uncertainty will vary from site to site depending upon many factors including the stage of the ISCO project, the ISCO approach used, the COCs and site conditions, as well as the ISCO treatment goals established. For instance, less site characterization information is needed about a site at the ISCO screening stage than at the detailed design and planning stage. Also, a site with relatively homogeneous geology and without DNAPLs, for which an alternative cleanup level (ACL) objective has been established, will allow for greater uncertainty than a relatively heterogeneous site with a DNAPL source zone and MCLs as a clean-up objective.

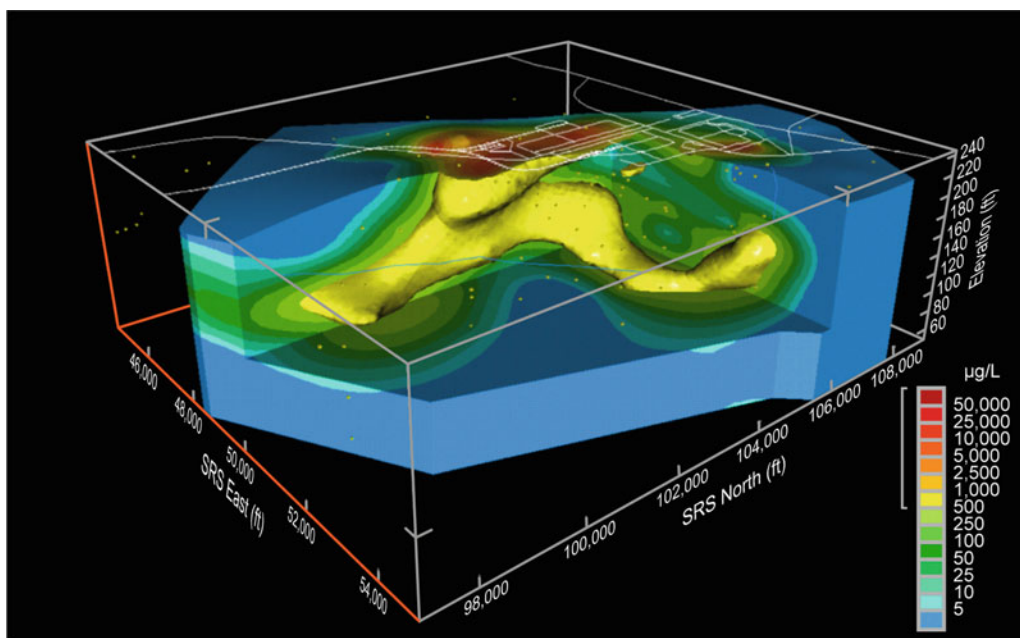


Figure 10.6. Example of a 3-D volumetric image revealing complex spatial distribution of TCE contamination in the subsurface at a DOE site in South Carolina (Jackson and Looney, 2001). The land surface dimensions are approximately 8,000 ft by 10,000 ft while the depth dimension is approximately 180 ft; TCE concentrations vary from near 5 $\mu\text{g/L}$ (light blue) to 50,000 $\mu\text{g/L}$ (dark red).

The question can arise as to how the site characterization needs for ISCO compare to those of other *in situ* technologies (e.g., those listed in Table 1.2). In general, if the question is constrained to the efforts needed to support the initial development of a valid CSM, which can enable proper screening of ISCO and conceptual design of an ISCO technology, then the data needs can be similar to those of most *in situ* technologies. Table 10.8 lists the key site characterization areas described in this chapter (Section 10.4) and the relative level of importance of the information gained in those areas for the purposes of selecting ISCO and enabling a conceptual design of one or more ISCO technologies (Tier 1 as presented in Chapter 9). Also shown in Table 10.8 is an assessment of the relative level of effort associated with site characterization for ISCO compared to some other *in situ* technologies, which are similar in that they involve delivery of a treatment fluid into a TTZ.

During an ISCO project, uncertainty in the CSM and in the application of ISCO can be reduced as the project proceeds. That is, additional data can be collected on an as-needed basis to fill important data gaps and address the related uncertainty. However, increasingly, practitioners are asked to minimize field investigation mobilizations and as a result they may collect site characterization data for development of a CSM that will also end up being used for technology selection and conceptual design. Thus, if ISCO is likely to be considered as a remediation technology, it may be prudent to conduct relatively inexpensive ISCO-specific analyses early on (e.g., pH, ORP, TOC, f_{oc} , grain size). These data often support the evaluation of other technologies as well. In addition, depending on relevant holding time issues, it can be prudent to collect excess porous media and groundwater for later tests that could be conducted if ISCO emerges as a viable remedy and the project proceeds to a conceptual design phase. This will save costs for future mobilizations for sample collection. For example, enough porous media and groundwater for NOD or

Table 10.8. Generalized Assessment of Additional Characterization Needs for Screening and Conceptual Design of an ISCO System

Characterization area	Level of importance ^a	Explanation	Is the characterization effort greater than for other <i>in situ</i> technologies? ^b
Site features and land use attributes	High	It is very important to define pathways and exposure scenarios for oxidants delivered into a TTZ if there is any potential for oxidant migration or fugitive emissions to occur	Yes, but increased effort required is not great
Nature and extent of contamination	High	Detailed delineation of COCs within a TTZ can be important at sites with a larger TTZ volume or increasing spatial variability. Detailed knowledge gained by high resolution, depth-discrete, direct-push sampling can enable targeted oxidant delivery	Potentially, depending on the other <i>in situ</i> technologies
Hydrogeologic conditions	High	Since ISCO involves delivery of a fluid (normally an aqueous solution) into a TTZ, a detailed understanding of hydrogeologic conditions is important to effective delivery	No
Geochemical conditions	High	Understanding of subsurface geochemical conditions is critical to provide insight into oxidant behavior and fate (e.g., activation, persistence, NOD) (see Table 10.6). However, simple and inexpensive data such as ORP, DO, pH, TOC, f_{oc} , and grain size analysis can be enormously useful and should not be overlooked	Yes, this is an area where ISCO characterization needs are greater, but the time and cost can be minimized
Fate and transport processes	Low to high	ISCO is often used in combination with another remediation technology (e.g., enhanced reductive dechlorination [ERD]) or approach (e.g., MNA) to achieve site-wide remedial action objectives. Depending on the type and nature of a planned combined remedy, understanding fate and transport processes can be important	Potentially, but not necessarily; depends on the specific comparison being made
Visualization of characterization data	Moderate	Visualization of characterization data can aid communication and decision making processes. This is true for all <i>in situ</i> remediation technologies and approaches	No

^aAdditional data needs are referenced to *in situ* technologies that involve delivery of fluids into a TTZ, such as ERD, *in situ* chemical reduction, or air sparging (see Chapter 1, Table 1.2).

^bLevel of importance (low, moderate, high) can vary from site to site based on contaminant characteristics, site conditions, and treatment goals as well as the stage of remediation (i.e., screening vs. conceptual design).

oxidant persistence tests could be collected and stored until it is clear that these data are needed for decision making. The number of samples to collect, along with collection procedure(s), handling, and storage should be guided by standard practices (e.g., USEPA, 1989, 1991; Keith, 1996; Popek, 2003).

10.6 ISCO TREATMENT OBJECTIVES AND GOALS

Remediation of a site is often carried out under the jurisdiction of a regulatory agency program and as a result, the remediation process can vary from one site to another and key terms and definitions can likewise vary. For the purposes of the discussion that follows concerning ISCO technology application and the desired outcome(s), several remediation terms are relevant and defined in Table 10.9.

Table 10.9. Definition of Terms Associated with ISCO Application and Outcomes

Term	Meaning and use with respect to ISCO
Remediation objectives	Remediation objectives can be established to state the purpose for which remediation is intended. They often tend to be high level outcomes that are desired but, in and of themselves, are often not directly measurable. For example, an objective might be stated as: remediation of a contaminated site to reduce the risk to human health for unrestricted current and future land use. RAOs under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) represent an example of an objective.
Remediation goals	Goals define what the remedial actions are intended to achieve or accomplish. Goals can be general for the overall remediation system (or treatment train), or they may be specific to one of the technologies in the treatment train (see Treatment Goals below). Under CERCLA goals are often numeric levels. For example, during the Feasibility Study process under CERCLA, preliminary remedial goals (PRGs) are the concentrations used to define the area to be remediated and to what level. PRGs become remedial goals (RGs) once a record of decision specifies the selected remedy and modifies the PRGs.
Cleanup levels	Cleanup levels are often used to describe the degree of remediation required with respect to achieving a certain concentration of COCs in soil, groundwater or other media at a given site or within a particular TTZ. Cleanup levels are commonly specified by regulatory authorities and programs and can include numeric values for specific media such as soils or groundwater (e.g., http://www.cleanuplevels.com/). Under some regulatory programs, cleanup levels may be used as remediation goals (e.g., PRGs developed under the USEPA CERCLA program).
Treatment goals	Treatment goals are specific criteria by which the successful completion of an activity can be determined. For example, an ISCO treatment goal might be established for a TTZ to which ISCO is to be applied.
Operational endpoints	Endpoints can also be established for application of a remediation technology such as ISCO. For example, an endpoint could be set as achieving a target concentration of oxidant throughout the TTZ for a specified period time after which active ISCO operations could be terminated. Operational endpoints can also be set such that they are equivalent to achievement of goals as defined above.

Note: The definitions and usage of the terms listed in this table are not universally consistent for all regulatory programs and jurisdictions that can govern assessment and remediation of contaminated sites.

In general practice, site characterization data support development of a valid CSM, which in turn enables assessment of whether remediation is warranted. If remediation is mandated by regulatory requirements or deemed warranted for other reasons (e.g., property transfer or change in land use), remediation objectives and goals (including RAOs and PRGs) can be established. Then ISCO may be considered as a viable stand-alone remedy or as one of several technologies and approaches within a combined approach. If ISCO is selected for implementation in a specific TTZ, ISCO-specific treatment goals need to be clearly defined and agreed upon. Operational endpoints also may be established for ISCO to enable a priori agreement on if, how, and when ISCO operations may be altered or terminated altogether and what next steps might be considered.

Consistent with site-wide remediation objectives and goals (e.g., RAOs, PRGs), the treatment goals for ISCO can be established in a relatively flexible manner and also recognize the fact that ISCO is often combined with other remediation technologies and approaches. Examples of optional statements for flexible ISCO treatment goals include the following:

- Reduce contaminant concentrations in a NAPL source zone, to the extent practicable
- Reduce contaminant mass flux to mitigate down gradient migration
- Reduce contaminant concentrations to expedite site closure
- Reduce contaminant mass flux to the extent necessary for bioremediation and/or MNA to achieve site closure within a reasonable timeframe

While these types of ISCO treatment goals are general statements of purpose, they can be helpful to communicate the basic expectations for groundwater remediation using an ISCO technology.

Development of quantitative ISCO treatment goals normally requires the establishment of a TTZ. Preliminary delineation of a TTZ within the CSM is important to bracket the physical limits of the region that ISCO might need to address and to enable establishment of the treatment goals that an ISCO technology must be able to meet (see Chapter 9 for more discussion of delineation of a TTZ). Delineation of a TTZ for an ISCO technology considers the CSM developed based on the components described in Section 10.2.2 as well as the remediation goals and cleanup levels established for the site. The TTZ includes clear boundaries for one or more subsurface zones to which oxidant chemicals will be delivered into and within which ISCO will need to achieve a specified treatment goal. Examples of the types of ISCO treatment goals that can be set for a particular TTZ include:

- Reduce contaminant concentrations to meet the respective MCLs in groundwater
- Reduce contaminant concentrations to meet ACLs in groundwater
- Reduce the concentration or mass of COCs by a predetermined percent or to a target final value
- Reduce the COC mass flux by a predetermined percent reduction from baseline or to a target flux value

For example, a TTZ could be set as the lower sand unit at the site depicted in Figure 10.6 with oxidant chemicals delivered throughout the zone delineated as having TCE concentrations about 10,000 $\mu\text{g}/\text{kg}$. Based on an ISCO treatment goal established for the TTZ (e.g., reducing the total mass of TCE in the TTZ by 90%) an ISCO technology could be designed and implemented (e.g., number and depth of injection points, oxidant concentrations and volumes delivered, etc.).

In development of ISCO treatment goals for a TTZ, it is important to recognize if ISCO will likely be combined with another technology or approach (see Chapter 7). If this is the case, the TTZ and the treatment goals for ISCO alone may not be able to achieve site-wide

remediation goals and cleanup levels. Rather, the combined technologies and approaches will be expected to eventually achieve the prescribed remediation goals and cleanup levels.

The benefit of assigning numeric treatment goals and operational endpoints for ISCO is that they can be clearly linked to site risk reduction and closure or transition to a post-ISCO remedial approach. Numeric endpoints provide a basis to which performance monitoring data can be compared using established statistical and geostatistical methods. A principal disadvantage of numeric endpoints is that it can be difficult to a priori predict the time and cost to reliably achieve them at the confidence required.

10.7 PERSPECTIVES ON CHARACTERIZATION AND ISCO

Site characterization data and the resulting CSM need to enable proper screening of ISCO for a particular site with a particular set of remediation goals and treatment objectives in mind. Depending on these considerations, ISCO may or may not be viable and if viable, one or another type of ISCO technology might be clearly preferred. Site characterization data need to be generated to sufficiently inform this type of decision making, while at the same time be affordable and achievable given funding and time constraints.

To illustrate how the extent of site characterization data and the ISCO treatment goals and objectives can interact during decision-making, Table 10.10 presents relevant remarks made during panel discussions at an ISCO Technology Practices Workshop (Siegrist et al., 2008). The participants, who included oxidant chemical manufacturers, ISCO practitioners, environmental consultants, site owners and managers, regulators, and researchers, discussed the importance of different types of site characterization data during different phases of an ISCO project.

At the same workshop, the participants were given six scenarios of contaminated sites. Given the characteristics of each scenario, the workshop participants shared their views about what additional data would be needed to properly screen ISCO as a viable remediation technology (Table 10.11). Table 10.12 presents a summary of the six scenarios while Figure 10.7 presents an example of one scenario to illustrate the level of detail provided to the participants for consideration of each scenario.

10.8 SUMMARY

Characterization of sites with contaminated groundwater where ISCO might be considered as a stand-alone technology or part of a combined remedy, involves approaches and technologies that are similar to those employed for other *in situ* remediation technologies. However, since ISCO can be strategically implemented to treat small or irregularly shaped TTZs, or portions thereof, ISCO screening and conceptual design can benefit from detailed spatial characterization of COCs in terms of geometry, concentration, and phase distributions. An additional quantity of data with lower analytical QA, such as obtained through field measurement methods, may be valuable to provide the needed spatial delineation at reasonable cost. Moreover, since ISCO involves delivery of reactive fluids into and throughout the subsurface, detailed understanding of geochemical conditions and injection hydraulics is essential. These data enable informed screening of potential ISCO feasibility and guide the conceptual design including the oxidant chemicals to be used and the implementation methods such as the injection method, number of applications, and so forth. Finally, based on the CSM that evolves through the site characterization efforts, a TTZ can be delineated and realistic treatment goals and endpoints can be established for an ISCO technology. In some cases, a more stringent ISCO treatment goal may dictate more detailed characterization work in order to reduce uncertainty and ultimately select and implement a successful ISCO technology, either as a stand-alone technology or part of a combined remedy. Under these circumstances, the requisite additional

Table 10.10. The Role and Value of Site Characterization Data to ISCO as Reflected by Panel Discussions at an ISCO Technology Practices Workshop (Siegrist et al., 2008)

Panel no. and topic	Summary of remarks relevant to site characterization for ISCO ^a
I: ISCO screening and selection	<ul style="list-style-type: none"> • 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 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 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
II: ISCO feasibility study; oxidant selection and delivery approaches; laboratory and field testing	<ul style="list-style-type: none"> • The first step in the oxidant selection process is to consider what oxidants are able to degrade the contaminants present at the site • The presence of relatively more insoluble organics (e.g., high octanol-water partition coefficient [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
III: ISCO system design and modeling tools	<ul style="list-style-type: none"> • 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)
IV: ISCO implementation and performance monitoring	<ul style="list-style-type: none"> • 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 TTZ, such as back diffusion from low permeability strata

^aThe consensus remarks given in this table are reproduced verbatim from the Workshop proceedings document (Siegrist et al., 2008) and only include those that are relevant to site characterization for ISCO.

Table 10.11. Additional Information Needed to Properly Evaluate ISCO as a Viable Remediation Technology for the Site Scenarios Presented in Table 10.12 (Siegrist et al., 2008)

Scenario	Views expressed by workshop participants concerning the need for additional data to properly consider ISCO during screening ^a
For all sites	<ul style="list-style-type: none"> ● NOD/oxidant persistence ● NAPL saturation ● Geologic cross sections with dissolved and sorbed COC levels ● Boring logs ● Good remedial investigation 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., adversarial vs. cooperative) ● Visit to site to determine access restrictions ● Timing and data quality (ISCO specific)
Scenario 1 – PCE in homogenous sand (DNAPLs)	<ul style="list-style-type: none"> ● Microbial molecular data
Scenario 2 – TCE in layered sand with silt (DNAPLs)	<ul style="list-style-type: none"> ● 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)	<ul style="list-style-type: none"> ● 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 ● Total petroleum hydrocarbon sampling ● Chemical oxygen demand testing
Scenario 4 – PCE in clay	<ul style="list-style-type: none"> ● None other than those listed under “For all sites”
Scenario 5 – TCE DNAPL in fractured granite	<ul style="list-style-type: none"> ● 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 (light nonaqueous phase liquid [LNAPL]) in fractured shale	<ul style="list-style-type: none"> ● 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 ● Groundwater flow measurements

1,1-DCA - 1,1-dichloroethane, 1,1,1-TCA - 1,1,1-trichloroethane, BTEX - benzene, toluene, ethylbenzene and total xylenes, MTBE - methyl tert-butyl ether.

^aSummary of views shared by Workshop participants during plenary discussion conducted during the ISCO Technology Practices Workshop (Siegrist et al., 2008).

Table 10.12. Site Characteristics for Six Site Scenarios Presented to Participants at an ISCO Technology Practices Workshop and Used to Elicit Views Regarding ISCO Screening, Design, and Performance Expectations (Siegrist et al., 2008)

Scenario parameter	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	Scenario 6
Site conceptual model						
Hydrogeology						
Morphology	Unconsolidated homogeneous	Unconsolidated heterogeneous	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)	Chloroethene (DNAPL)	Chloroethene (aqueous)	Chloroethene (DNAPL)	BTEX and MTBE (LNAPL)
Approximate age of spill (years)	2	15	20	15	20	5
Source zone area (m ²)	400	8,000	1,000	N/A	2,000	150
Plume area (m ²)	20,000	80,000	3,000	500	13,000	7,000
Depth of COCs (m bgs)	7	50	15	6	30	12

Eh = ORP - oxidation-reduction potential, m - meter, mV - millivolt.

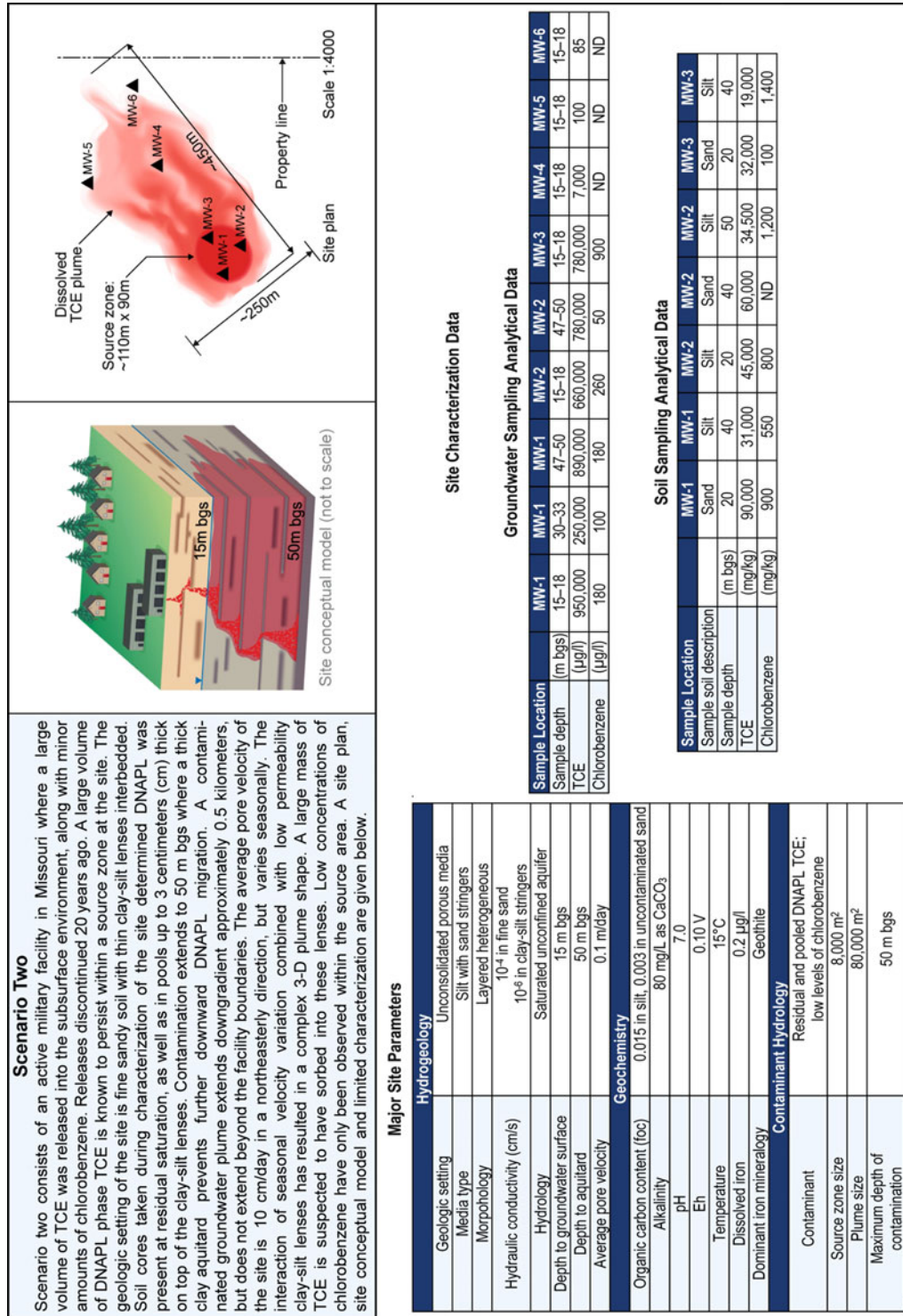


Figure 10.7. Site Scenario 2 detailed site characteristics provided to participants at an ISCO Technology Practices Workshop as a basis for assessing ISCO screening, design, and performance (Siegrist et al., 2008). Note: °C - degrees Celsius; CaCO₃ - calcium carbonate; V - volts.

site characterization data and CSM refinements will normally evolve as an ISCO project proceeds from conceptual design to detailed design and implementation.

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CHAPTER 11

OXIDANT DELIVERY APPROACHES AND CONTINGENCY PLANNING

Thomas J. Simpkin,¹ Tom Palaia,¹ Benjamin G. Petri², and Brant A. Smith³

¹CH2M HILL, Englewood, CO 80112, USA; ²Colorado School of Mines, Golden, CO 80401, USA; ³XDD, LLC, Stratham, NH 03885, USA

Scope

Approaches to deliver oxidants into the subsurface, as well as contingency planning to manage and adapt oxidant delivery systems.

Key Concepts

- There are a number of oxidant transport mechanisms that are important to understand and consider when selecting, designing, and implementing an *in situ* chemical oxidation project.
- A number of oxidant delivery approaches may be used, including injection wells, direct-push technology probes, sparge points, infiltration systems, recirculation systems, fracturing, mechanical mixing, and horizontal wells. Of these, injection wells and direct-push technology probes are most commonly used.
- Each delivery approach has characteristics that may make it most suitable for a particular oxidant and set of site conditions.
- The factors and challenges that should be considered when selecting and designing an oxidant delivery approach include aquifer heterogeneity, contaminant distribution, presence of underground utilities, contaminant displacement by the injection of oxidant, and mixing of activators with the oxidant (for those requiring activators).
- As a result of the many challenges and uncertainties with delivering oxidants into the subsurface, the Observational Method is often beneficial to achieve the desired performance.
- The Observational Method includes establishing appropriate contingency plans during the development of the project. The contingency plan(s) should include an inventory of possible outcomes, development of appropriate monitoring to detect deviations from the assumed conditions, and development of response actions if the deviations occur.

11.1 INTRODUCTION

A factor of primary importance in the success of *in situ* chemical oxidation (ISCO) is the effective delivery of the oxidant into the subsurface and achievement of oxidant-contaminant contact. As such, the oxidant delivery approach must be planned and designed carefully, taking into account surface and subsurface site conditions and contaminant distribution. In addition,

the optimum oxidant delivery approach depends on the oxidant that is used and its persistence in the subsurface. Consequently, oxidant selection and delivery must be considered in tandem.

Since oxidant delivery into the subsurface is difficult to predict with precision and results can often deviate from predictions, contingency planning must be included as an important aspect of the overall ISCO design approach. Contingency planning provides a means for project teams to anticipate, measure, and correct deficiencies as they arise. In so doing, known design uncertainty can be addressed during the implementation process.

This chapter first provides discussion of the fundamentals that impact delivery of oxidants (Section 11.2) and then the various approaches for delivering oxidants into the subsurface (Section 11.3). It also provides discussion of a number of the general considerations for oxidant delivery (Section 11.4). A section is provided on aboveground management of oxidants (Section 11.5), and a later section describes implementation approaches, such as the Observational Method, that can be used to monitor and adapt oxidant delivery systems in order to maximize the chance for achieving oxidant-contaminant contact (Section 11.6). Chapter 9 also provides guidance on oxidant delivery approaches for the different oxidants and site conditions, including tools for conceptual design.

Oxidants may be delivered to the subsurface in liquid, solid, or gaseous forms. Delivery as liquids (aqueous solutions of the oxidants) is the most common, and most of the discussion in this chapter focuses on those forms. Ozone is the only commonly used ISCO technology that is a gas, and some discussion is provided on delivering ozone gas. Very few of the oxidants can be effectively delivered as solids, so only limited discussion is provided on application of solid oxidants.

11.2 PRIMARY TRANSPORT MECHANISMS AFFECTING DISTRIBUTION OF LIQUID OXIDANTS

There are a limited number of mechanisms that control how an oxidant will be transported in the subsurface. These mechanisms need to be considered in the selection and design of the oxidant delivery systems. From a practical standpoint, the following are the general mechanisms by which oxidants get distributed in the subsurface. More detailed information on distribution mechanisms can be found in Chapter 6 of this volume, as well as in a number of other books (e.g., Siegrist et al., 2001; Huling and Pivetz, 2006; Payne et al., 2008; Kitanidis and McCarty, 2011).

11.2.1 Advection During Injection of Liquid Oxidants

During oxidant injection, the injection pressure causes injected fluid to displace pore water and to move out radially from the injection point. This movement of the injected fluid will stop once the injection is halted and any groundwater mound that was created dissipates (i.e., when the driving force stops). Figure 11.1 illustrates those processes. The shape and dimensions of the oxidant plume achieved will be a function of the volume and rate of the fluid injection, the spatial variability of hydraulic conductivity, and the rate at which the oxidant is consumed by reactions with activators, contaminants, and soil minerals or organic matter. It should be noted that pressures during injection can be as high as 20 pounds per square inch (psi) or more, which is equal to 46 ft of head and considerably greater than the natural gradients typically present in an aquifer. As a consequence, the groundwater velocities in a target treatment zone (TTZ) during the active injection period are likely to be much greater than velocities that occur naturally.

The extent of advective migration during injection will be similar to that of a conservative (inert) tracer except that the oxidant will be consumed by reactions in the subsurface. For permanganate, this consumption is governed by a finite total “demand” for the oxidant, which is rate-limited (natural oxidant demand [NOD], see Chapter 3 for additional discussion on the consumption of permanganate in the subsurface). Several models discussed in Chapters 3 and 6

have successfully simulated the movement and consumption of permanganate in the subsurface accounting for the effects of NOD.

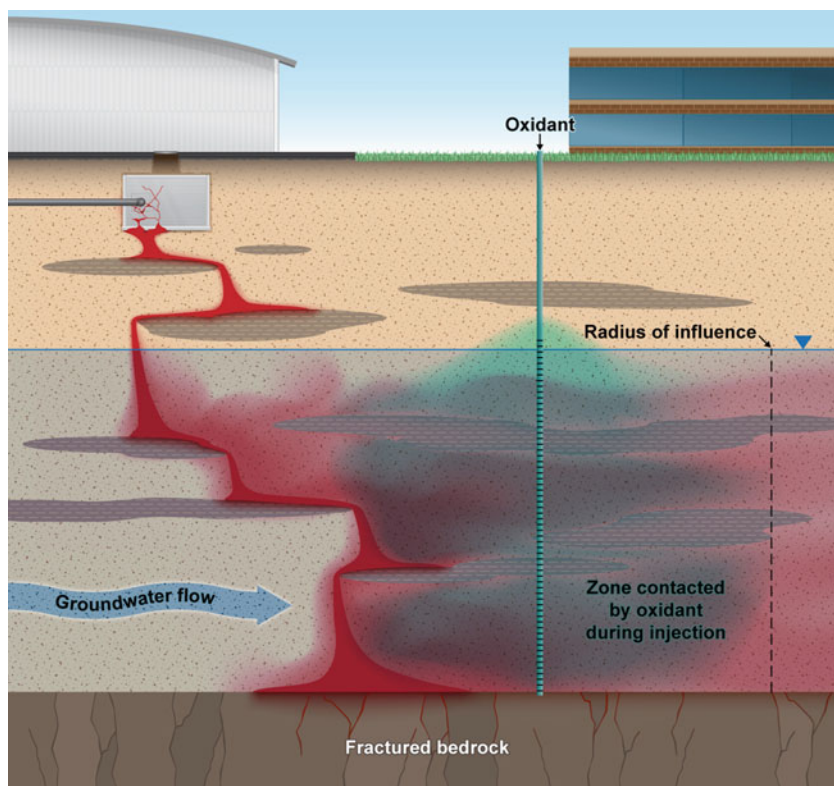


Figure 11.1. Oxidant movement during pressurized injection into a vertical well. Oxidant delivery and distribution is shown in teal blue and organic chemical contamination is shown in red.

For persulfate and catalyzed hydrogen peroxide (CHP), the consumption of these oxidants in the subsurface is typically more complex than with permanganate. These two oxidants are often delivered with activators or catalysts, which enable reactions with the oxidant to produce reactive species. Furthermore, each of the oxidants may also react with soil minerals or organic matter that likewise consume the oxidant. Thus, due to the complex properties of naturally occurring porous media, as well as delivering activators, stabilization aids, and the oxidant, the persistence of persulfate and CHP oxidants in the subsurface is typically much harder to predict compared to permanganate. As a result, no models are known to the authors that have successfully predicted the reactive transport of these oxidants. Instead, field experience, pilot tests, and the Observational Method are typically important components of design and implementation of ISCO using persulfate and CHP oxidants. With ozone, because the oxidant is a gas, the reactive transport mechanisms that affect its delivery and transport are even more complex due to the multiphase nature of this ISCO approach. However, because ozone is so unique among oxidants, the discussion of ozone transport phenomena is provided in Chapter 5 and the following discussion is limited to oxidants injected as aqueous solutions.

It should be noted that during advective transport processes, the oxidant will not displace all of the pore water. Dispersion will occur as the oxidant moves through the formation. Dispersion results from micro-scale velocity variations in the injected fluid during and after injection, resulting in mechanical mixing and spreading of oxidant. Dispersion will result in a decrease in oxidant concentration and also provides the opportunity for the oxidant to contact

dissolved contaminant. Dispersion may also vary by the oxidant used. For example, CHP has the tendency to evolve oxygen as a byproduct, and large volumes of oxygen gas can increase mechanical dispersion in the subsurface.

11.2.2 Advection After Injection

The oxidant, as long as it persists, will move with the ambient, natural groundwater flow once the injection is stopped and any water table mounding has diminished. This is sometimes called oxidant “drift”. Figure 11.2 illustrates this concept. Drift is a slower distribution process compared to the advective flow during oxidant injection; its maximum extent can be qualitatively evaluated by first computing the natural groundwater flow velocity and estimating the potential time of persistence of the oxidant. Sites with low effective hydraulic conductivities or low hydraulic gradients (thus low flow velocities) will have very limited oxidant drift.

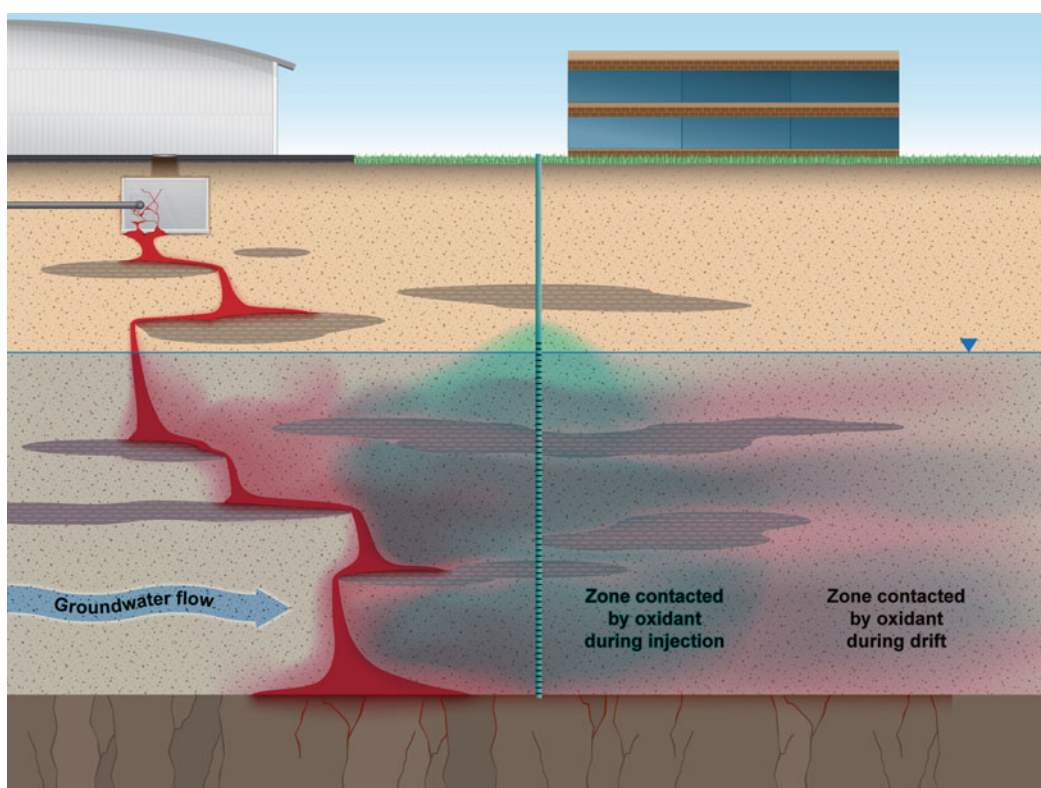


Figure 11.2. Oxidant movement during oxidant drift after active injection is terminated. Oxidant delivery and distribution is shown in teal blue and organic chemical contamination is shown in red.

The rate at which the oxidant reacts (is consumed) will also affect the extent of drift that occurs. As a consequence, the distance traveled during oxidant drift is likely to be significant only with longer-lived oxidants, such as permanganate and possibly persulfate. The extent of drift with permanganate will depend on the oxidant mass injected, the NOD, and the kinetics of the reactions between permanganate and NOD. In some cases, oxidant drift has been known to carry permanganate much further than predicted, and at times into areas where it was not

desired. Consequently, injection of excessive amounts of permanganate should be avoided, especially if the injections are upgradient of sensitive receptors.

11.2.3 Diffusion After Advective Delivery into the Subsurface

In addition to advective transport, oxidants may also diffuse from the zones where they were carried by advection into lower permeability zones that were not affected by active advection. Diffusion is driven by chemical gradients and random fluid movement (e.g., Brownian motion). Diffusion is a much slower process than advection and will depend on the concentration gradient, the thickness of the lower permeability layers, the porous media properties, and the intrinsic rate of diffusion of the compound. For example, while groundwater advection processes can move aqueous solutions at the rate of meters per day, Siegrist et al. (1999) observed that over a 10-mon period, permanganate was only able to diffuse only 40 cm from a permanganate solid emplaced by hydraulic fracturing into a low permeability clay. Diffusive transport distances into low permeability media may also be strongly impacted by oxidant persistence within the porous media to be treated. As another example, Seitz (2004) investigated the diffusion of permanganate into two media with nearly identical diffusive properties, but different NODs. In a low-NOD media, permanganate diffused 2.5 cm within 24 h, while a high NOD media required nearly 80 days for permanganate to diffuse the same distance. For short-lived oxidants delivered by advection of an oxidant solution, diffusive transport over significant distances (e.g., more than 10 cm) is unlikely to occur due to the time required to enable significant diffusive transport.

In addition to the diffusion of the oxidant into the lower permeability layers, contaminants will also diffuse out of these layers, and be treated in the layers with high residual oxidant concentrations (the higher permeability layers). This back diffusion of contaminants is also driven by the concentration gradient and since the concentration of the contaminants in the high permeability layers is likely to be low (because of the presence of the oxidant), the rates of back diffusion should be higher in the presence of the oxidant than under natural conditions. The rate of back diffusion will decline with time as the contaminant concentration in the lower permeability material at the interface of the two layers declines (i.e., reducing the driving force by decreasing the concentration gradient).

11.3 OXIDANT DELIVERY METHODS

Table 11.1 presents the common oxidant distribution methods and their prevalence of use, based on the case study database discussed in Chapter 8 and in Krembs (2008). Some key references, where more information on the delivery method can be found, are also presented in Table 11.1.

Based on the case study data described in Chapter 8 and Krembs (2008), subsurface oxidant delivery through direct push probes and conventional injection wells have been the most common approaches in the sites reviewed. These two delivery techniques generally offer: (1) the greatest flexibility in terms of scalability to different target treatment zone (TTZ) settings, treatment area sizes and geometries, (2) availability of experienced delivery contractors, (3) typically lower infrastructure costs, and (4) ability to combine with delivery enhancement techniques (e.g., recirculation and fracturing).

Krembs (2008) also provides a summary of the design parameters used in the projects for which data was available (Table 11.2). This information should be useful when considering the delivery approaches discussed below.

Table 11.1. Summary of Oxidant Delivery Methods

Description	Application depth	Comment	Frequency of use based on case studies ^a (%)	References
Injection wells				
Permanent or temporary wells used to inject oxidant	Virtually unlimited	Wells may be used for reinjection	47	Huling and Pivetz (2006), Los Angeles Regional Water Quality Control Board- <i>In Situ</i> Remediation Reagents Injection Working Group (2009), Siegrist et al. (2001), numerous others (see Krembs, 2008)
Direct push				
Direct push technology (DPT) used to inject oxidant	Limited to constraints of DPT equipment, typically about 100 ft	New points are required for re-injections	23	Huling and Pivetz (2006), Los Angeles Regional Water Quality Control Board- <i>In Situ</i> Remediation Reagents Injection Working Group (2009), Siegrist et al. (2001), numerous others (see Krembs, 2008)
Sparge points				
Sparging wells or points to inject ozone gas	Only limited by pressure required to deliver the ozone gas		14	Huling and Pivetz (2006), Siegrist et al. (2001), others (see Chapter 5)
Infiltration				
Trenches, galleries, vertical wellpoints installed in the vadose zone, or surface application so that the oxidant will migrate vertically through the treatment zone	Only limited by the depth of the vadose zone	High oxidant demand in the surface soil could limit penetration	10	Siegrist et al. (2001), Siegrist et al. (1998)
Recirculation				
Injection coupled with extraction with the recovered groundwater recirculated to the injection wells	Unlimited and may be the most cost effective approach for very deep aquifers where well drilling is expensive	Larger radius of influence (ROI) between wells is possible	7	Lowe et al. (2002), Palaia et al. (2004), West et al. (1998)

(continued)

Table 11.1. (continued)

Description	Application depth	Comment	Frequency of use based on case studies ^a (%)	References
Fracturing				
Hydraulic of pneumatic fracturing used to create flow paths through which the oxidant may be injected	Only limited by the high pressure required to create fractures at greater depths	Most applicable to low permeability formations. Oxidant must diffuse away from the fracture	6	Murdoch et al. (1997), Palaia and Sprinkle (2004), Siegrist et al. (1999)
Mechanical mixing				
Construction equipment or large augers are used to mix the oxidant with contaminated soil and groundwater	Limited by the depth the equipment can reach, which is about 60 ft below ground surface (bgs)	Can achieve high degree of mixing and contact between the contaminant and oxidant	2	Cline et al. (1997), Haselow et al. (2008)
Horizontal wells				
Horizontal directionally drilled wells used to inject oxidant. Most likely used with in a recirculation approach	Limited by the angle of penetration required to get to very deep depths, which is approximately 100 ft bgs	Can be used to work under buildings and other obstructions	1	West et al. (1998), Siegrist et al. (2001), Strong et al. (2006)

^aBased on the database of Krembs (2008) (see Chapter 8). Total number of sites = 181. Percentages sum to greater than 100% because multiple delivery techniques were used at some sites. "Infiltration" refers to trenches, galleries, or vertical wellpoints installed in the vadose zone so that the oxidant will migrate vertically through the treatment zone.

Table 11.2. Design Parameters for Vertical Injection Delivery, by Oxidant Used^a

	Permanganate	CHP	Persulfate	Ozone
Median design ROI (ft)	14 (n = 29)	15 (n = 30)	13 (n = 6)	25 (n = 5)
Median observed ROI (ft)	25 (n = 11)	15 (n = 6)	20 (n = 3)	No data
Median oxidant dose (g/kg)	0.4 (n = 36)	1.2 (n = 19)	5.1 (n = 6)	0.1 (n = 4)
Median number of pore volumes delivered	0.16 (n = 32)	0.073 (n = 26)	0.57 (n = 6)	No data
Median number of delivery events	2 (n = 65)	2 (n = 57)	1 (n = 10)	1 (n = 15)
Median duration of delivery events (days)	4 (n = 45)	6 (n = 42)	4 (n = 7)	210 (n = 15)

^aBased on the database of Krembs (2008) (see Chapter 8). n = number of sites.

11.3.1 Direct-Push Probes for Liquid Injection

Injections using direct-push technologies (DPTs) are conducted with equipment that drives small-diameter hollow rods into the ground. The rods are pushed to the same depth as, or slightly deeper than, the bottom of the TTZ; chemical injection is completed by forcing the oxidant solution through small perforations or slots at the end of the rods and into the formation. This “screened” portion at the end of the rod is typically between 1 and 5 ft long. After an injection is complete, the rod may be pulled up a few feet and another injection performed. This process is repeated until delivery into the TTZ depth interval is achieved. What is described here is a “bottoms up” approach (start injecting at the bottom and work up). A “top down” (start at the top of the target depth and work down) approach, may also be used. Proprietary tooling may be attached to the end of the rods to increase distribution uniformity or conduct high pressure injections resulting in formation fracturing or for other means of enhancing oxidant delivery in low permeability media. Direct push rigs can be used to deliver oxidants to the subsurface as liquid solutions, including permanganate, persulfate, and peroxide. Figure 11.3 is a schematic cross-section of direct push probe injection; Figure 11.4 is a photograph of a direct push rig and shows one type of injection tool.

The use of DPT during field implementation provides greater flexibility in locating injection points compared to installation of permanent injection wells. Once in the field, injection locations may be altered due to aquifer responses during injection. Subsequent injections may also be optimized to directly address hot spots. Specific depth intervals that may be known to contain more contamination may also be more easily targeted with DPT probes. The use of DPT fits in well with the Observational Method (see Section 11.6). DPT may also be preferred if it is not possible to leave a permanent well in place, if only a single injection event is planned, or when minimizing capital costs is a primary consideration. For shallow installations, the cost for DPT injections is relatively low, so a large number of injection locations can be used.

Because DPT points are not hydraulically developed like injection wells, the rate of injection or the total volume that is possible to inject at a single point may be limited. For example, typically only a few hundred gallons of oxidant solution are injected at one interval, depending on the screen length and the formation properties. As a consequence, the area around the injection point that is contacted by the oxidant (commonly called the ROI) is likely to be smaller than what could be achieved with a permanent well with the injection of a large volume of oxidant solution.

Table 11.3 provides some general guidelines on typical flow rates with DPT and other methods provided by the Los Angeles Regional Water Quality Control Board-*In Situ* Remediation Reagents Injection Working Group (Los Angeles Regional Water Quality Control Board-*In Situ* Remediation Reagents Injection Working Group, 2009). The Working Group (2009) also provides a number of other guidelines for safe injection of reagents into the subsurface. It should be noted that these suggested guidelines are focused primarily on DPT, and other practitioners have used larger volumes (percentage of pore volume and flow rate) using injection wells.

As a consequence of the smaller ROIs with DPT injections, DPT injections are typically done on a grid (rows of injection points spaced the same distance as the spacing of the points within the row). Figure 11.5 illustrates this approach. The DPT point spacing is based on the expected ROI, which is often based on experience, or on the design methods discussed in Chapter 9. An overlap factor should be provided to avoid dead zones between injection points.

The sequence of the injections will depend on the site objective but in general should start from the downgradient side and work upgradient; this should reduce the potential to push contamination further downgradient. An outside-in approach may also be used to push the contaminants towards the center. If more than one point is injected into at a time, it is typically best not to inject into adjacent points to avoid the potential for the injections to push against each other, thereby limiting the ROI of each.

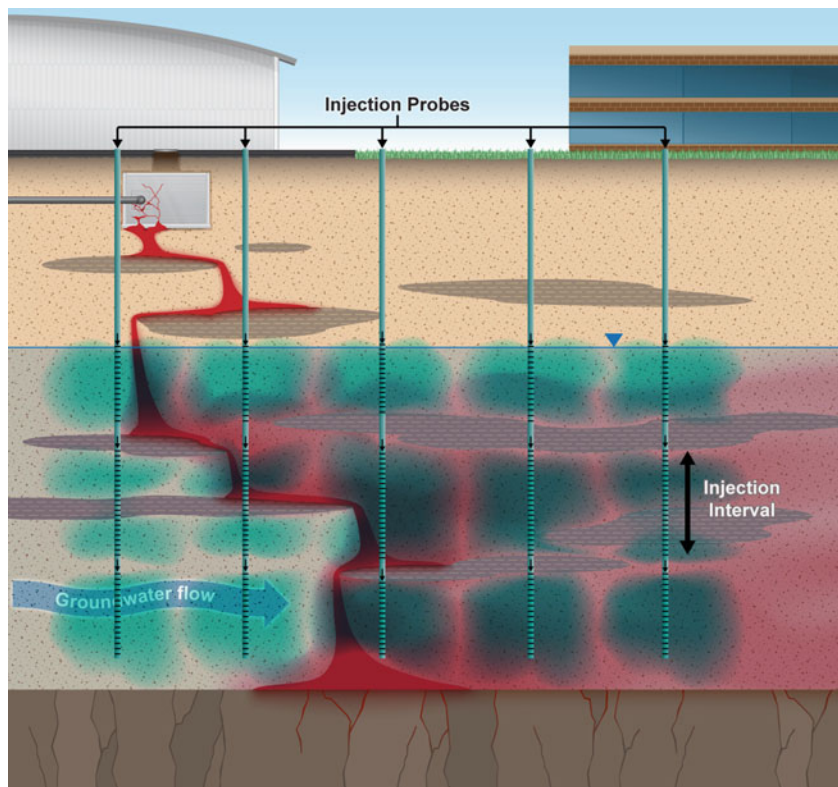


Figure 11.3. Schematic cross-section of direct-push injection probes. Oxidant delivery and distribution is shown in teal blue and organic chemical contamination is shown in red.



Figure 11.4. Photos of a direct-push technology rig and tooling.

Table 11.3. Guidelines for Chemical Injection into the Subsurface (Los Angeles Regional Water Quality Control Board-*In Situ* Remediation Reagents Injection Working Group, 2009)

Recommended chemical injection safety standards				
Parameter	Range	Reactive reagents	Non-reactive reagents	
			Liquid	Non-liquid
Injection				
Maximum % pore volume for site ^a	GP-SP	<33%	<33% ^b	<10%
	SP-SM	<10%	<33%	<10%
	ML-CL	<5%	<10%	<5%
ROI	GP-SP	<30 ft	<30 ft	<15 ft
	SP-SM	<15 ft	<15 ft	<5 ft
	ML-CL	<5 ft	<5 ft	<5 ft
Flow rate	GP-SP	1–5 ft bgs/<1 gpm (>5% peroxide solution not recommended)	1–5 ft bgs/gravity feed	1–5 ft bgs/<3 gpm
		5–10 ft bgs/<3 gpm	5–10 ft bgs/<5 gpm	5–10 ft bgs/<5 gpm
		10–30 ft bgs/<15 gpm	10–30 ft bgs/<15 gpm	10–25 ft bgs/<10 gpm
		>30 ft bgs/<25 gpm	>30 ft bgs/<25 gpm	>25 ft bgs/<15 gpm
	SP-SM	1–5 ft bgs/<1 gpm (>5% peroxide solution not recommended)	1–5 ft bgs/gravity feed	1–5 ft bgs/<3 gpm
		5–10 ft bgs/<3 gpm	5–10 ft bgs/<5 gpm	5–10 ft bgs/<3 gpm
		10–30 ft bgs/<15 gpm	10–30 ft bgs/<15 gpm	10–30 ft bgs/<10 gpm
		>30 ft bgs/<25 gpm	>30 ft bgs/<15 gpm	>30 ft bgs/<10 gpm
	ML-CL	1–5 ft bgs/(prohibited in SILT or CLAY soils)	1–5 ft bgs/gravity feed	1–5 ft bgs/<3 gpm
		5–10 ft bgs/<3 gpm	5–10 ft bgs/<5 gpm	5–10 ft bgs/<3 gpm
		10–30 ft bgs/<3 gpm	10–30 ft bgs/<15 gpm	10–30 ft bgs/<10 gpm
		>30 ft bgs/<3 gpm	>30 ft bgs/<15 gpm	>30 ft bgs/<10 gpm
Injection monitoring				
Pressure (psi)	Pressure should be maintained and monitored to limit fracturing unless required to obtain flow due to reagent physical characteristics or tight soil conditions. Where higher pressure is required to induce fracturing, a surfacing control mitigation plan shall be required			
Temperature	Temperature should be limited to minimize vapor generation unless a vapor control system is in place. Temperature should be limited to 150 °F (66 °C) so as to avoid undesirable side effects			
Flow rate (gpm)	Monitor to ensure compliance with recommended flow rates provided above			
Vapor concentrations (ppm)	When injection into high-contaminant volatile organic compound zones, vapor should be monitored at all potential pathways to the surface			

(continued)

Table 11.3. (continued)

Recommended chemical injection safety standards				
Parameter	Range	Reactive reagents	Non-reactive reagents	
			Liquid	Non-liquid
Other items				
Material compatibility	Injection of oxidants shall require compatible materials from tank storage to pumps to injection tooling or wells. Generally, stainless steel or polyvinyl chloride (PVC) is required for oxidants that are corrosive. Prior to injection of oxidants, applicators shall document compatibility of all equipment with the oxidant chosen			

Notes:

Range: **GP-SP** – Poorly graded gravels to poorly graded sand; **SP-SM** – Poorly graded sands to silty sands; **ML-CL** – Silt to clay.

Reactive reagents: Chemical oxidants that generate heat or oxygen/pressure (e.g., hydrogen peroxide, hydrogen peroxide activated with iron, sodium persulfate activated with hydrogen peroxide or iron or high pH).

Non-reactive reagents: Magnesium peroxide, calcium oxyhydroxide, calcium peroxide, glycerol tripolyacetate, lactic acid, glycerol, glycerol esters of polyacetate and fatty acids, zero-valent iron, sodium and potassium permanganate, calcium polysulfide, emulsified oils, other electron donors, bioaugmentation.

Maximum % pore volume for site: Percent volume of reagent injected of the effective porosity volume of the treatment zone.

ROI (radius of influence): The distance from the injection point where the reagents are expected to achieve their design contaminant destruction. Combination of reagent % pore volume injected and additional distribution that occurs through diffusion, dispersion, and advection.

°C - degrees Celsius; °F - degrees Fahrenheit; **gpm** - gallon(s) per minute; **ppm** - part(s) per million.

^aPer injection event.

^bIf application approach includes groundwater extraction then the maximum percent pore volume for the site can be equal to or less than 90%. All chemicals are reactive under certain conditions and should be handled under the guidelines provided on their material safety data sheets (MSDS).

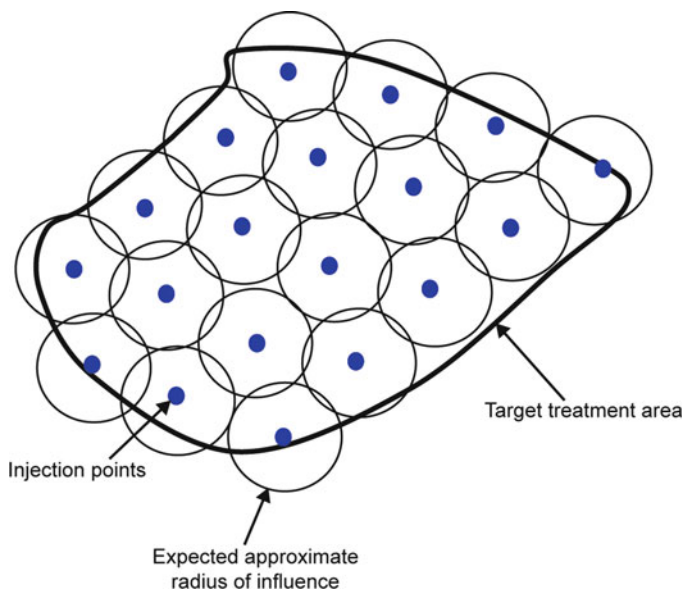


Figure 11.5. Illustration of a grid layout of injection points.

If multiple injections are required, the cost advantage of using direct push rigs may be negated compared to wells, which can be reused. DPT installations may not be effective in some formations. Injection depths may be limited to less than 100 ft, and the presence of rocks,

cobbles, or cemented layers may inhibit the application of DPT. However, new advances and larger rigs are being developed that may overcome some of these limitations.

11.3.2 Installed Wells for Liquid Injection

ISCO applications are frequently conducted using injection wells. Vertical injection wells can be installed using a number of different drill rigs and drilling methods. Some of these may affect the performance of the well (due to smearing of the well bore, etc.) so care is required in selecting and performing the drilling. The factors that affect the application and performance of ISCO injection wells are similar to those for groundwater production wells. For more detail on groundwater well design, drilling, construction, and development fundamentals, refer to Sterrett (2007). Figure 11.6 is a schematic cross-section that illustrates an injection well application.

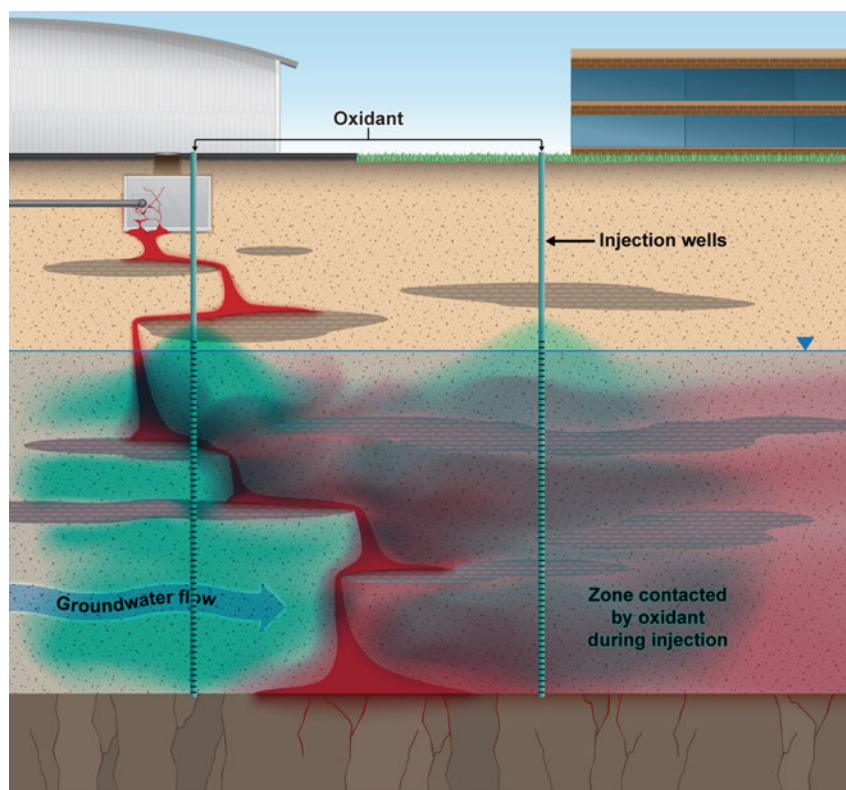


Figure 11.6. Schematic cross section of injection well applications. Oxidant delivery and distribution is shown in teal blue and organic chemical contamination is shown in red.

In general, injection wells should be designed as injection wells, not as monitoring wells. Efficient injection wells require a well design that is suitable for movement of a large amount of fluid, and provides a good hydraulic connection between the well and the groundwater zone to be treated. The most efficient injection wells use continuous slot (wire wrapped) well screens and relatively coarse sand pack or are designed specifically with the formation in mind. Continuous slot well screens have 50% greater open surface area than slotted pipe. The greater open area results in significantly greater injection rates and less well screen fouling.

Well screen length and diameter are also important considerations. Where feasible, the length of an injection well screen should be no more than 10–15 ft, particularly in heterogeneous formations or where treating highly concentrated source zones. In some cases, long-screen wells can be used and specific intervals packed off for injection. However, packers may not be effective if flow goes around them through the well's sand pack. If the formation is highly homogeneous (such as a thick sand unit), a longer screen may be acceptable. The problem with long injection well screens is that there is no way to control where the injectate leaves the well. It will simply follow the path of least resistance, which tends to be the more permeable portions of the formation across the well screen. The more permeable zone may or may not be where the greatest amount of contamination is located. A similar problem can occur with wells that are screened across the water table and in the vadose zone. There may be less resistance to flow in the vadose zone, so more of the flow may move through it than desired.

The diameter of the well and the boring theoretically have an impact on the flow rate that may be achieved in an injection well. However, it is likely that other factors will have a greater influence so most reasonable well sizes (2–6 in.) are likely to perform adequately.

Consideration should be given to gravity feed versus pressurized injection. If the depth to the injection interval is significant and a constant head can be maintained during injection, gravity feed may be suitable. However, a greater horizontal distribution may be attained during pressurized injection.

Pressures should never be so high that fracturing occurs, unless fracturing is the desired result. To avoid horizontal fractures from occurring, the injection pressure should be lower than overburden earth pressure above the injection point. High pressures may also result in cracks in the well seal and result in surfacing of the oxidant. Pressurized wells should be constructed of specific materials (high-pressure PVC or steel) that can sustain the higher-pressure forces.

The well casing needs to consist of a material that is compatible with the oxidants or activation aids to be injected into it (including any increase in temperature that may occur). PVC is one of the more versatile materials, but in some cases stainless steel or other materials are required (for example, when significant heat is used intentionally or is generated). Chemical compatibility databases should be consulted, and considered along with the concentration of the solution to be injected.

Injection wells may be laid out in a grid, similar to DPT points. At some sites, it may also be sensible to install injection wells in a series of rows perpendicular to the direction of groundwater flow. If the natural groundwater velocity is fast enough, and the oxidant persists, some drift of the oxidant may occur such that the rows may be spaced with a greater distance than the spacing of the wells within a row. This should result in fewer wells being required. Figure 11.7 illustrates one of the different approaches to laying out wells.

Installation of injection wells is advantageous when multiple injection events are planned, when injecting large quantities of fluid at each injection point, when the TTZ is beyond the depth that can be reached using DPT, or when injecting into bedrock. Also, horizontal wells may be used to achieve oxidant distribution under buildings or other infrastructure where vertical well installation or DPT is not feasible.

One drawback with permanent injection wells is that the subsequent injection events may not be as easily optimized in terms of locations (e.g., if tighter spacing is required or a new target area has been indentified). This is due primarily to the additional cost to go back in the field subsequent times with a drill rig. As discussed in Section 11.5, the installation of additional injection wells or filling in with DPT injection points, should be part of the contingency plan.

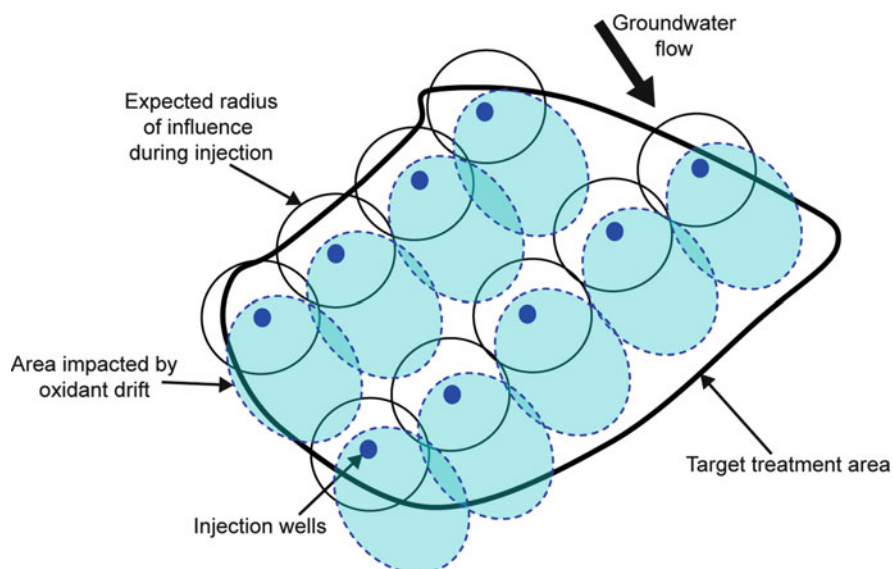


Figure 11.7. Injection well layout with some oxidant drift.

11.3.3 Installed Wells for Gaseous Sparging

Ozone is unique among the oxidants used for ISCO in that it is a gas. Chapter 5 provides detailed information on the fundamentals of ozone for ISCO. Since ozone is a gas, the methods for ozone distribution are limited to sparging into wells, either horizontal or vertical. In the case of ozone, horizontal wells offer an additional delivery benefit in that the primary transport of the oxidant is in the vertical dimension instead of the horizontal, and thus a sparging plume from a horizontal well can produce a vertical curtain of oxidant. The specifics of flow rate and well spacing for ozone sparging are based on experience with ozone sparging, but may follow the general trends in approaches used for air sparging (see Chapter 5 for more information). For example, the ROI of the sparging will be a function of the flow rate and the formation properties.

Gases move differently, and sometimes easier, through the subsurface than do liquids, in part due to their buoyancy. Consequently, it is theorized that ozone may be more efficient at contacting contaminants in the subsurface under some circumstances. However, under heterogeneous conditions, or low permeability conditions, the gas distribution in the subsurface can be widely variable as well, as some areas may be heavily contacted with oxidant and others bypassed entirely. The injection of a gas can also increase mechanical mixing of groundwater, and impact transport of volatile contaminants. All of these issues must be considered when implementing ozone through sparge wells.

11.3.4 Recirculation of Liquids

Recirculation systems are used to continuously treat a portion of an aquifer by drawing water into an extraction well and reintroducing the extracted groundwater, after amending it with oxidant, to the aquifer upgradient or crossgradient of the extraction well (Lowe et al., 2002). Figure 11.8 illustrates this concept. An aboveground treatment system may or may not be required, depending on injection regulations. Due to the cost and complexity, it is typically advantageous to not provide aboveground treatment if it is allowable to do so.

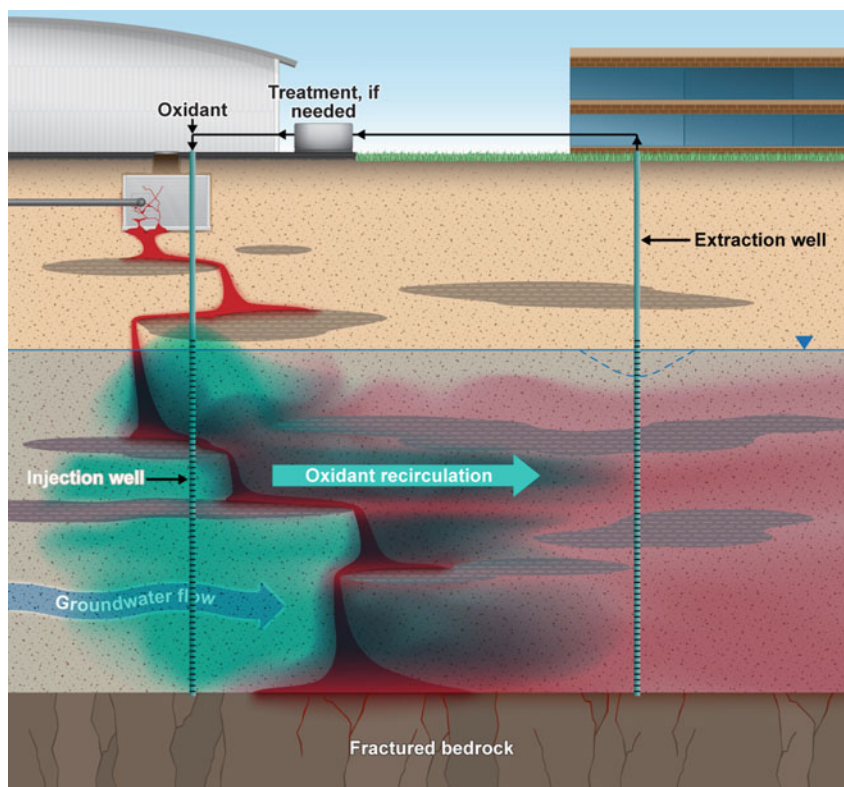


Figure 11.8. Schematic cross section of a recirculation approach for ISCO. Oxidant delivery and distribution is shown in teal blue and organic chemical contamination is shown in red.

Several circumstances are well suited to a recirculation approach:

- For attempting to transport oxidant into lower permeability layers
- For increasing the amount of time the TTZ is exposed to oxidant (which should allow for additional diffusion into lower permeability layers) by constantly replenishing the oxidant mass
- At sites with extremely high groundwater flow where the oxidant would otherwise be flushed from the TTZ before adequately contacting contamination in lower permeability zones
- At sites with large TTZs (e.g., large plumes), where an injection grid would not be practical and natural oxidant drift is not adequate to treat the plume
- As a means of hydraulic control, preventing the migration of oxidant beyond the TTZ or into other uncontrolled locations, such as surface water

The primary disadvantages of recirculation systems are their mechanical complexity and the increased equipment, pipeline, and operations and maintenance (O&M) costs, especially if aboveground treatment of contaminants is required. Recirculation systems can also commonly experience significant maintenance issues related to fouling or plugging (biologically and chemically). With permanganate, manganese oxide (MnO_2) solids are a significant plugging concern. As a consequence of these costs and complexities, recirculation systems are not commonly implemented. However, with additional research, methods to manage these disadvantages may be developed.

Temporary recirculation, or at least pumping, could also be used during a short-term injection to promote distribution of the oxidant. Pumping of an adjacent well could increase the amount of advective distribution of the oxidant. Once the oxidant reaches a certain point, such as the pumping well, the pumping could be stopped.

11.3.5 Trench or Curtain Emplacement of Oxidants

Trenches or curtains may be employed to create an oxidative zone that treats contaminants in groundwater as the groundwater passes through them. The trench or curtain is installed perpendicular to groundwater flow. In some cases, additional means of controlling groundwater flow, such as funnels and gates, may be required to ensure that contaminated water passes through the trench or curtain for treatment. Trenches or curtains are most applicable to ozone, which can be sparged into them. There have also been some applications of solid potassium permanganate in trenches (Siegrist et al., 2001).

Trenches are installed as a continuous excavation of aquifer material, and curtains are usually installed as a series of vertical injection wells. The trench may be backfilled with high-permeability material through which an oxidant solution or ozone gas is injected. It is typically desirable to design the injection systems to allow control over where the reagent goes (e.g., multiple injection points). Trenches are advantageous because there are minimal above-ground infrastructure and O&M requirements. Implementation of ISCO via a trench requires continued management of the trench.

11.3.6 Mechanical Mixing of Oxidants and Soil

In situ soil mixing is a means of introducing an oxidant into the subsurface through mechanical blending of the subsurface material and the oxidant. Soil mixing can be performed by using conventional construction equipment (such as a backhoe) or with specialty mixing equipment. Large mixing augers (5–10 ft diameter) or horizontally rotating heads are examples of the types of mixing equipment available. Figure 11.9 is a photograph of a large diameter auger equipment used for soil mixing. Soil mixing may be most applicable to remediation of low permeability material or very heterogeneous formations where subsurface injection of a fluid is not feasible. Soil mixing often produces immediate results because the physical structure of the subsurface is made more homogeneous, increasing the degree and rate of contaminant-oxidant contact. Soil mixing will also disrupt the preferential flow paths that exist naturally in the formation, which should reduce the migration of contaminated groundwater through the treatment zone. This can be enhanced further by the addition of bentonite clay during the mixing. Implementation of soil mixing is limited to the vertical extent the mixing equipment or augers are able to reach (currently 40–60 ft below grade). Furthermore, soil mixing is often more costly than common injection approaches, so its application may be limited to relatively small and well-defined source zones.

11.3.7 Fracturing for Oxidant Emplacement

Subsurface fracturing is a technique that has been used with ISCO to enhance permeability typically prior to oxidant injection. However, oxidants may also be delivered to the subsurface during the fracturing process. Fracturing is accomplished either hydraulically or pneumatically. Hydraulic fracturing is used to create sand-filled fractures in the subsurface by injecting a

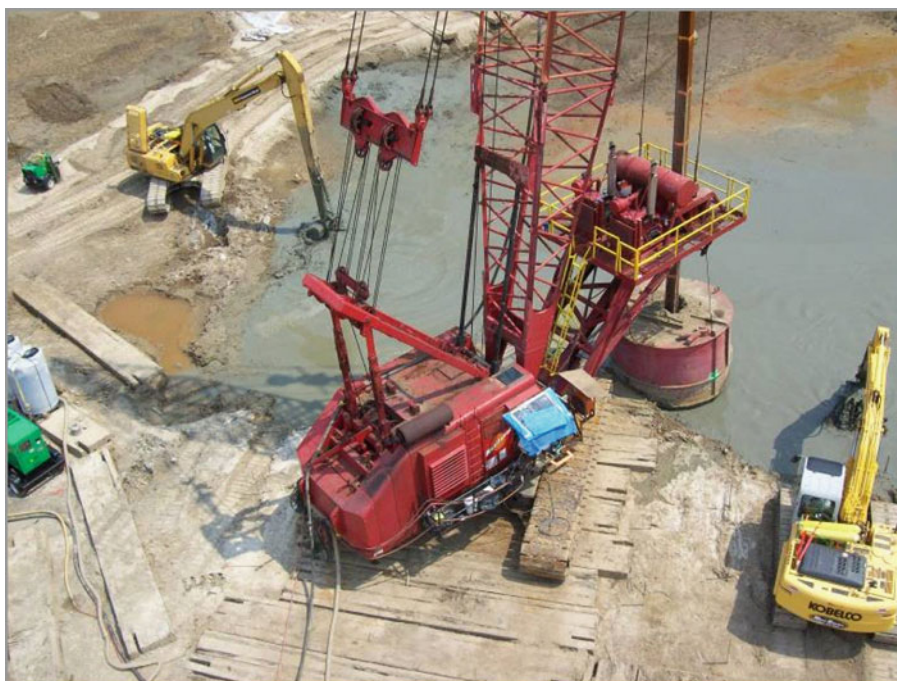


Figure 11.9. Large diameter auger equipment used for soil mixing.

slurry consisting of water, sand, and a guar gum gel at pressures exceeding the formation fracturing pressure. The sand acts as a proppant, holding open the fractures that subsequently act as high-permeability zones for oxidant injection. It is also possible to use a solid oxidant as the proppant and inject it during the initial fracturing (Siegrist et al., 1999). Hydraulic fracturing creates a single seam, and multiple fractures across a target treatment depth require multiple fracturing events. Figure 11.10 presents a schematic cross-section of hydraulic fracturing.

Pneumatic fracturing is done by injecting bursts of air or other gases under high pressures. No proppant is injected when conducting pneumatic fracturing and the fractures are generally smaller and more pervasive through the aquifer matrix (spider-web pattern) than the single seams created with hydraulic fracturing. After fracturing is complete, oxidant injections are then conducted in the same well where the fracturing was conducted. Nitrogen or air may also be injected with the oxidant to atomize the oxidant and to enhance its distribution. Figure 11.11 present a schematic cross-section of pneumatic fracturing and Figure 11.12 is a photo of pneumatic fracturing equipment used for potassium permanganate injection.

Soil fracturing helps increase the ROI and achievable injection rates in low permeability material. However, it is very difficult to predict and control the fracture pattern or radius of fracturing. Therefore, fracturing near structures and utilities can be dangerous. In addition, the entire vertical interval of the TTZ may not be fractured, potentially leaving portions of the TTZ unaffected by oxidant. Diffusion must be relied on to transport the oxidant from the fracture into the low permeability material (or to transport the contaminant out of the material into the fracture containing oxidant). Fracturing increases the cost of injections and there may be additional safety issues with fracturing, since high pressures are often used.

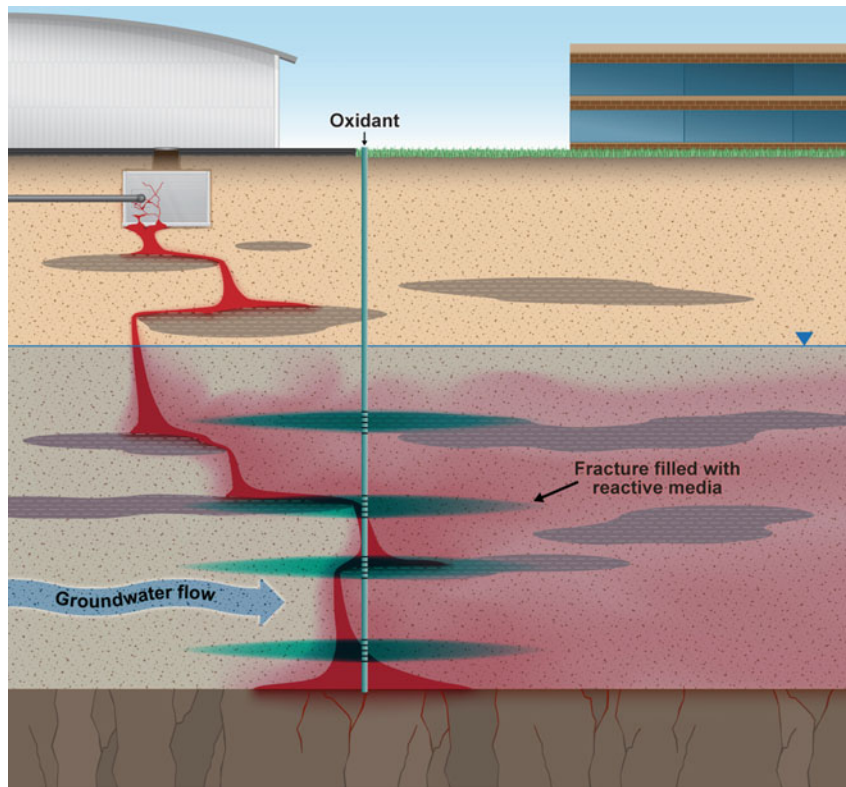


Figure 11.10. Schematic cross-section of hydraulic fracturing. Oxidant delivery and distribution is shown in teal blue and organic chemical contamination is shown in red.

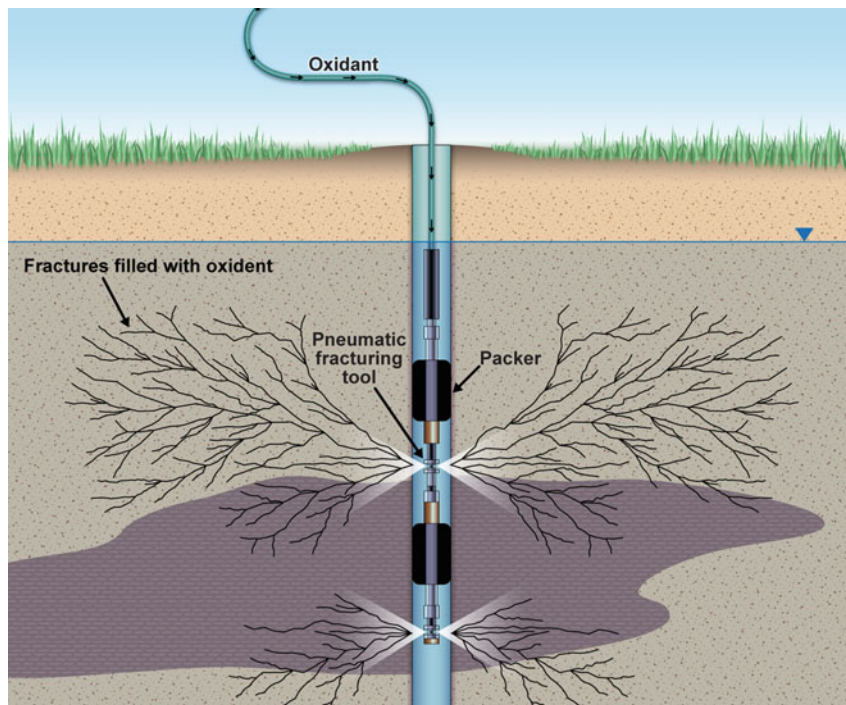


Figure 11.11. Schematic cross-section of pneumatic fracturing.



Figure 11.12. Potassium permanganate mixing and pneumatic injection (in the background).

11.3.8 Surface Application or Infiltration Gallery Methods

Surface application of oxidants is typically limited to spreading of an oxidant, as a solid, on the land surface and mixing the oxidant into the top 3–5 ft of soil. Oxidant then dissolves into shallow groundwater or with surface water percolating through the oxidant amended zone and into underlying groundwater. Generally, if the NOD in surface soil is high, most of the oxidant will be consumed before it can reach groundwater. However, an infiltration gallery may be used to gain more contact directly with groundwater.

An infiltration gallery application includes the installation of a high-permeability material, which extends into the subsurface. Oxidant, as a solution, is introduced to the gallery and then infiltrates into groundwater under gravity. Oxidants may also be emplaced as solids during construction of the infiltration gallery, after which they will dissolve into groundwater over time.

Installation of infiltration galleries is typically very economical. After installation is complete, infiltration galleries are a passive system and require minimal maintenance, other than ensuring oxidant loading as necessary. However, infiltration galleries also have very limited zones of influence. The infiltration gallery is most suitable for shallow aquifers with reasonable groundwater flow rates. The constant supply of oxidant in the gallery maintains the chemical concentration downgradient of the infiltration gallery, allowing time for oxidant to diffuse into lower permeability zones, if present. In addition, the constant oxidation mass available from the infiltration gallery maintains oxidant presence to address contaminants desorbing from the porous media matrix over time. Because the infiltration gallery is passive in nature, many years of operation may be required to achieve desired treatment results.

11.4 GENERAL CONSIDERATIONS FOR OXIDANT DELIVERY

Chemical oxidation has been used for decades for the treatment of water and wastewater. Compared to water/wastewater treatment, applying chemical oxidation *in situ* presents unique challenges related to delivery, including:

- Subsurface soil and rock formations are inherently heterogeneous and migration pathways are tortuous.
- The subsurface cannot be directly observed (or “seen”), and thus data on chemistry and hydrogeology must be obtained and interpolated from soil cores, groundwater samples, and probe, well, or boring logs.
- Complete and uniform mixing of oxidants with porous media cannot be achieved in the same manner as it is in aboveground water treatment reactors.

The following subsections discuss the characteristics of aquifers and contaminant source zones that pose challenges to successful implementation of ISCO and key considerations that must be accounted for during oxidant delivery design, implementation, and monitoring.

11.4.1 Aquifer Heterogeneity

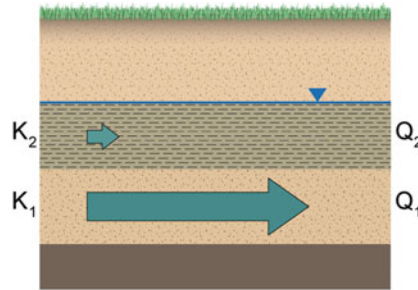
Aquifer systems all have a unique three-dimensional architecture resulting from the depositional processes that formed the aquifer units. These unique depositional processes result in a typically heterogeneous subsurface system with spatial variability in the size, shape, grain-size distribution, and permeability of each depositional unit (Payne et al., 2008; NRC, 2005). Subsequent natural processes can also cause fractures in both consolidated and unconsolidated units, creating preferential pathways in the aquifer system. A significant consequence of heterogeneity that must be taken into account when designing oxidant delivery systems is the fraction of the formation that will carry most of the flow of the oxidant. Even small variations in hydraulic conductivity may result in most of the injected flow going through discrete higher-permeability lenses, layers, or fractures. This factor can also be expressed in terms of the “mobile porosity” (Payne et al., 2008). The mobile porosity controls where the majority of fluid will flow during both oxidant injection and subsequent advection. Standard aquifer characteristic testing protocols will provide average aquifer properties across the entire well screen interval, which typically underestimates the actual flow velocity encountered during *in situ* remediation processes. Tracer tests or field pilot tests of oxidant delivery may be necessary to estimate the mobile porosity. Payne et al. (2008) suggests that mobile porosity from 0.02 to 0.10 is representative for many sites.

This concept of mobile porosity can also be described with the use of the dual domain concept (Suthersan et al., 2009). Figure 11.13 is a simple illustration of this concept. The proportion of the flow moving through the different domains will be dictated by the ratio of the hydraulic conductivity of the domains. It is common for hydraulic conductivities to vary more than an order-of-magnitude in most formations. Variations of an order-of-magnitude may even go undetected by visual observations of soil cores.

Again, the end result of the mobile porosity or dual domain flow will be that the majority of the oxidant will end up in only a fraction (the high permeability fraction) of the formation. As is discussed below, a significant amount of the contaminant mass may reside in the low permeability fraction. To contact this contamination, the oxidant must either diffuse into the low permeability fraction or be persistent long enough to allow the contaminant to diffuse out and be treated in the high permeability fraction.

Another possible approach to manage this dual domain issue is to flush a large amount of oxidant through the subsurface; this can often be accomplished in a more cost effective way with a recirculation system. If a large enough volume of oxidant solution is flushed through the total formation, some (as defined by the ratio of hydraulic conductivities (K)) solution will flow through the lower permeability layer. Figure 11.14 illustrates this concept. It may be necessary to flush as much as ten pore volumes through the high-permeability layer before even one pore volume is flushed through the low permeability layer (with a difference in hydraulic

conductivity of 10:1). However, this may be an acceptable approach, if a low cost re-circulation system can be established. Since recirculation systems recycle the oxidant, the additional oxidant requirements for this approach can be partially mitigated.



$$Q_t = Q_1 + Q_2 = K_1 * i * a_1 + K_2 * i * a_2$$

$K_1 = K_2 * 10$ is common (e.g., 1 ft/d vs. 10 ft/d), thus:

$$Q_1 = 10 * Q_2 \text{ with } a_1 = a_2$$

Figure 11.13. Simplistic dual domain model of hydraulic conditions in the subsurface. Note: Q_t - total groundwater flow; Q_1 and Q_2 - groundwater flow in layers 1 and 2, respectively; K_1 and K_2 - hydraulic conductivity of layers 1 and 2, respectively; i - hydraulic gradient of layers 1 and 2; a_1 and a_2 - cross-sectional area in layers 1 and 2, respectively.

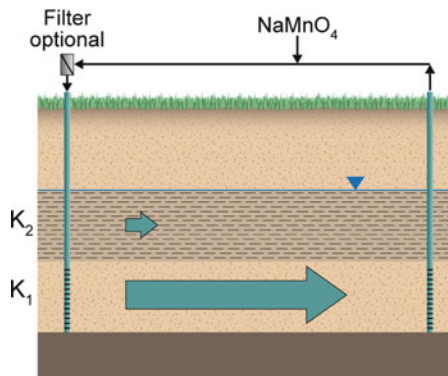


Figure 11.14. Oxidant delivery in the dual domain model under a recirculation system. Note: NaMnO_4 - sodium permanganate.

11.4.2 Contaminant Distribution

Another consequence of heterogeneity of the subsurface is that the contaminants are not likely to be uniformly distributed. The AFCEE Source Zone Initiative – Back Diffusion of Contaminants in Source Zones and Plumes (Sale et al., 2005) provides details on concepts related to contaminant distribution. Of most importance to this discussion is the fact that defining and delineating contaminant source zones and plumes is difficult and needs to take into consideration all of the subsurface media “compartments” where contaminant mass can be stored. These can include contaminants sorbed to porous media, dissolved contamination in groundwater (in both high- and low permeability zones), nonaqueous phase liquids (NAPLs), and vapor phase contamination. The highest percentage of contaminant mass may reside in low permeability media or as residual NAPL. Residual NAPL can exist as small blobs and

ganglia trapped in pore space, can be pooled above localized clay/silt lenses, or can reside in fractures in rock or desiccated clay. The mobile NAPL may be present in the more conductive zones, while residual NAPLs may hang up at the interface of two zones of different hydraulic conductivity. The areas where the highest percentage of contaminant mass resides may also be the most difficult to contact with an oxidant since they are often located away from the primary groundwater flow paths. For relatively old sites, the main flow channels may have already been depleted of contaminant mass due to natural groundwater flushing or diffusion into the lower permeability layers, but significant contamination may remain outside of the main flow channels. Additional discussion on contaminant distribution is provided in Chapter 6.

11.4.3 Underground Utilities and Other Preferential Pathways

In addition to natural heterogeneity and the associated preferential flow paths, manmade preferential pathways can also be present, and their impact must also be considered; this is especially important for shallow groundwater systems with shallow target injection intervals. The bedding material of utilities can be more permeable than the native formation and can act as a preferential flow conduit for injected oxidant, which can result in the oxidant migrating to unintended locations; with storm sewers, this can lead to releases of the oxidant in surface water bodies, and backfill areas around foundations can likewise collect oxidant.

Wells and improperly abandoned boreholes can also be an issue. If the seals on these wells or boreholes are not structurally sound they can act as preferential flow paths and surfacing of the oxidant can result during oxidant injection. Surfacing is a common issue, especially with injections into shallow formations (e.g. less than 10 ft of the ground surface). The injection pressure may need to be limited to minimize the risk of surfacing. The location of wells and borings in the TTZ should be identified, and their likelihood to act as a preferential pathway for surfacing should be considered.

11.4.4 Contaminant Displacement

During the design of an oxidant injection program, the potential for displacement of contaminant mass should be considered. The injection of a large volume of oxidant solution will “push” some of the dissolved contaminant away from the injection point. The magnitude of this displacement can be evaluated by determining the percent of a pore volume to be injected and the distance this might push the dissolved contaminant. As discussed in Chapter 8 and by Krembs (2008), the median pore volume of oxidant delivered to an ISCO site was 12% of the TTZ pore volume (PV), though the pore volumes applied may vary with site, delivery approach, and oxidant used. Since the size of a pore volume increases as the square of the distance as you move away from an injection point, the distance that fluid is pushed is not likely to be significantly larger than the ROI. For example, with an ROI of 20 ft, the original volume of fluid would only be pushed out to 28 ft (assuming complete plug flow and 12% PV).

However, this assumes a relatively homogeneous delivery of the injected fluid. If the actual flow path is very small (e.g., fractures in bedrock or thin sand lenses in a clay deposit), this may not be the case. The contaminant in these small flow paths may be effectively pushed a comparatively larger distance by the injected water. The movement of the contaminant can also be retarded, depending on subsurface conditions (e.g., the fraction of organic carbon).

Dispersion is likely to result in mixing of the oxidant with the dissolved contaminant plume, so the contaminant will not just be pushed in front of the oxidant in a perfect plug flow pattern. Pushing a large mass of contamination away may also be less of an issue if the majority of the mass is in low permeability zones, is sorbed to the soil, or exists as NAPL. It is not likely that

this material will be easily moved by the injected oxidant solution. With NAPLs, capillary forces tend to hold the contaminant in place and thus even in zones of high groundwater velocity, it will tend not to mobilize unless a surfactant is used.

Injection strategies, such as starting injection at the edge of the plume, can also be used to reduce the potential for pushing away dissolved contaminants if it is a major concern. For sites where large volumes of oxidant are necessary, recirculation systems may be used to limit the potential for contaminant displacement.

11.4.5 Need for Oxidant Activation

Oxidants that require activation (CHP and persulfate) have an extra degree of complexity to their delivery since the method of activation must be taken into account. For CHP applications, native mineral surfaces may be relied upon to catalyze the process in some cases; catalysis occurs as the oxidant contacts the subsurface media. However, if mineral catalysis is ineffective or too rapid, injection of other catalysts or stabilization aids may be needed. Because CHP catalysis reactions are rapid and transport distances of the various radicals are negligible due to their short-lived nature, activation must generally occur within the subsurface. This has been accomplished in two principal fashions:

- A catalyst solution is injected first, followed by the oxidant; catalysis occurs as the oxidant moves through the subsurface and contacts the catalyst through dispersion.
- Both the catalyst and oxidant solutions are injected simultaneously, with mixing at the injection point.

If mixing of the catalyst with oxidant is to occur at the injection point, then it is desirable to minimize the contact between the two prior to distribution into the subsurface since catalysis is rapid and oxidant decomposition prior to distribution represents a non-productive oxidant sink. However, the effectiveness of the different injection methods has not been extensively studied and reported in the literature, so it is difficult to determine which is more effective and under which circumstances. These approaches are also somewhat proprietary to the contractor/vendor doing the injection, so it is difficult to understand the details of the methods that have been used.

In activated persulfate systems, activation can be accomplished with a chemical amendment (such as bases (high pH), ferrous iron, chelated iron, or hydrogen peroxide) or with heat. Presently there is no standard way of adding chemical amendments. Persulfate itself is more stable than hydrogen peroxide and the free radicals formed from persulfate form more slowly than with CHP (see Chapter 4). For example, persulfate can persist for a few weeks, even after activation. Consequently, aboveground mixing can be applied with some of the chemical amendments; for example, aboveground mixing for alkaline activation is commonly practiced. However, for other chemical amendments, it is common to inject either the activation aid first and then the oxidant, or the oxidant first and then the activation aid. Presently, it is not clear whether one method is more effective than the other or how effective mixing of the activation aid and the oxidant is in the subsurface.

In the case of heat, the activation aid is a physical amendment that may be added through injection of steam or possibly by heating with electrodes. Possible injection methods include injection of persulfate after the subsurface has already been heated or, alternatively, the pre-placement of persulfate in the subsurface followed by heating to induce activation. In the case of the former, depending on the temperature as well as the media, oxidant decomposition may be rapid, limiting distribution. In the case of the latter, wider distribution may be possible because the kinetics of oxidant decomposition are likely to be slower at low temperature.

11.5 ABOVEGROUND OXIDANT HANDLING AND MIXING

Before an oxidant can be delivered to the subsurface, it must be handled and mixed using aboveground equipment. Having inappropriate aboveground equipment can affect the performance of the subsurface aspects of the project and can also create significant environmental and safety issues. Performance issues that can be tied to the handling equipment may include delivering concentrations of the oxidant either lower or higher than targeted; inadequate mixing resulting in injecting large amounts of solids that result in plugging of wells, direct push injection tooling, or the aquifer formation; and having extended down periods because of equipment failure resulting in oxidant losing its strength as it breaks down in storage. Environmental and safety issues can also result from malfunctions and failure of equipment.

Since many ISCO injections are performed for short durations, oxidant-handling equipment is typically not purchased by the site owner for one ISCO project. Rather, the equipment is supplied by the specialty contractor that performs the injections or it is rented from a number of sources, including oxidant chemical suppliers. Despite this, the consulting engineer or site owner should carefully review the proposed equipment layout and functionality to verify that the system is appropriately designed and will safely meet their oxidant mixing requirements.

The specifics of the oxidant mixing equipment that is used will depend on the oxidant and the form it is shipped and stored as. Table 11.4 summarizes the forms the most common oxidants are shipped and stored in, along with considerations for their handling. Oxidants that are shipped and stored as solids (e.g., potassium permanganate and sodium persulfate) must be safely and effectively transferred from the containers they are shipped in and mixed with water. If large volumes of the solid oxidant must be mixed, mechanical transfer equipment is recommended over manual-batch mixing. A filtration step is also recommended for potassium permanganate solutions so that undissolved solid material is not allowed to plug the injection wells or the formation. Table 11.5 provides a list of considerations for aboveground oxidant handling and mixing systems.

A number of oxidants are liquids (e.g., hydrogen peroxide and sodium permanganate) or can be delivered to a site as a solution so that the mixing step is not required. The concentrated oxidant can be diluted with water prior to injection using either inline mixers or in a batch mix tank. A batch mix tank provides greater control over the delivery concentration, but with the appropriate equipment, inline mixing can also be effective. For all applications, the appropriate pumps, flow meters, pressure gauges, and control valves must be used to provide the desired degree of accuracy and precision in the delivered flow, pressure, and concentration. Care must also be taken to make sure the materials of construction are appropriate with the chemicals being used. Figure 11.15 illustrates two mixing systems (one relatively simple and one more complex) while Figure 11.16 provides photos of a few systems.

If a recirculation system is used such that the source of water for the mixing system is groundwater, greater care must be taken when using permanganate. Manganese dioxide solids will be formed from the reaction of the permanganate with the contaminants or natural organics in the recycled water. The manganese dioxide solids may be difficult to remove with conventional solids removal technologies such as bag filters. Appropriately sized cartridge or multimedia filters may be required.

For oxidation systems that require activators, such as persulfate and peroxide, parallel handling and mixing systems will also be required for them. These might include handling acids or bases, peroxide, or iron salt solutions.

Ozone is typically generated on site with an ozone generator. These generators may be fed pure oxygen delivered to the site as a liquid or gas; for large systems, the oxygen may be generated on site. The very unique systems required to safely handle these gases are not discussed here. The ozone that is produced is typically diluted with pressurized air prior to injection.

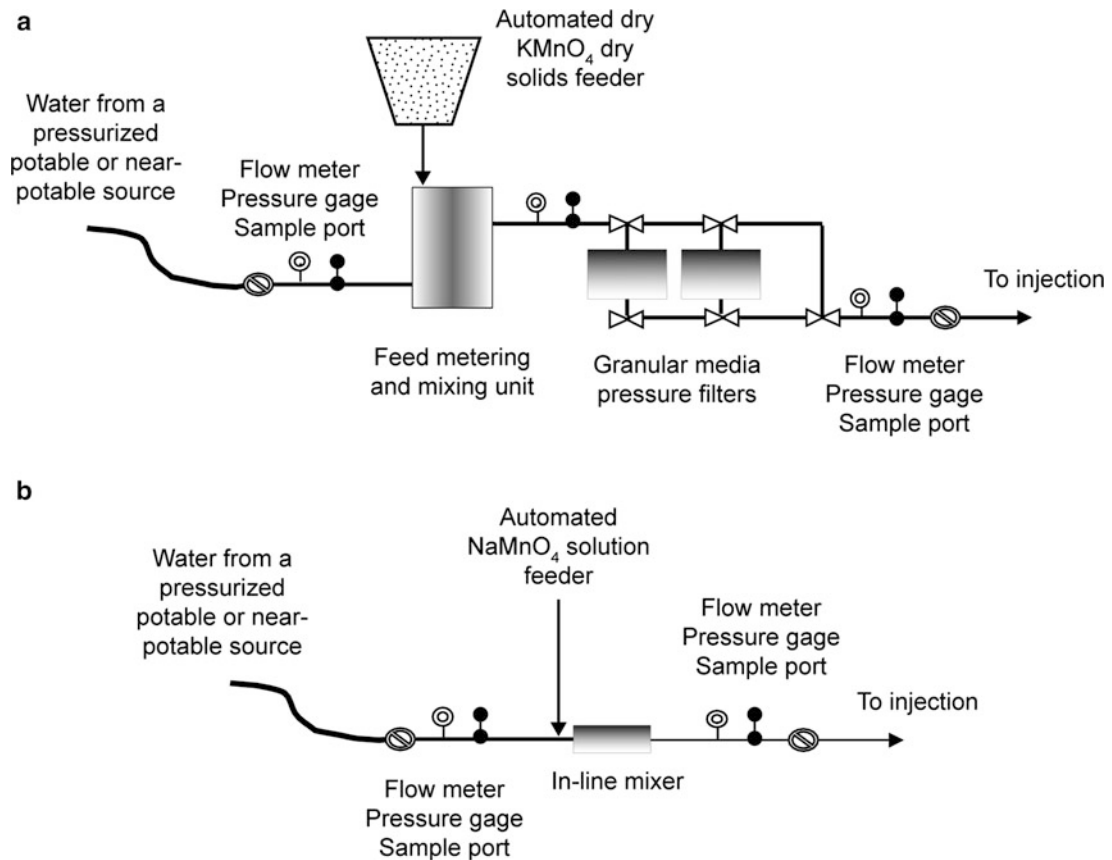
Table 11.4. Common Oxidant Handling Summary

Oxidant delivered to the site	Oxidant concentration delivered	Mixing systems required	Comments
Potassium permanganate solids	Typically 98% KMnO_4	Continuous solids feed or batch	Soluble at <2.5% but can be injected at higher concentrations as slurry, usually <6% unless fractured into formation
Potassium permanganate solution	<2.5%	Inline or batch	Soluble at <2.5% but can be injected at higher concentrations as slurry, usually <6% unless fractured into formation
Sodium permanganate solution	<40%	Inline or batch	Maximum concentration <20% due to safety considerations
Sodium persulfate solid	Typically 99+ % $\text{Na}_2\text{S}_2\text{O}_8$	Continuous solids feed or batch	Typical application is to add to tanks of water for injection or directly to soil for blending. Solids handling equipment should not allow for pinch points or excess heating of material from friction
Sodium persulfate solution	Not typically delivered as a solution. Maximum solubility is 43 weight percent (wt.%) at room temperature	Inline or batch	Persulfate solutions may generate low pH (~2) and cause acidic corrosion of soft metals. All tanks and piping should have adequate venting with no potential for dead-heading. All solutions should be utilized within 4 h
Hydrogen peroxide solution	Available in a range of concentrations; recommended <17.5% for injection. C-FATS regulations exist for concentration over 34%. The higher the concentration, the greater the potential for exothermic and gas-evolving reactions to take place	Inline or batch	Activator must be mixed in separate tank and typically injected sequentially rather than simultaneously
Ozone	Generated on site	Typically mixed with air	The power requirements for ozone generation may be significant (depend on the size of the generator). Specific safety precautions must also be used with the management of ozone generators

Appropriate instrumentation and controls should be used and will be specific to the oxidant handling and mixing system. The degree of complexity will depend on the amount of labor to be provided at the site. If unattended operations are to be used, the degree of automated process controls and secondary containment employed needs to be much greater to avoid spills or overflows.

Table 11.5. Considerations for Oxidant Handling and Mixing Equipment

Consideration	Description
Solids removal	Provide appropriate filtration of oxidant solution before injection
Flow measurement	Provide appropriate, compatible flow and pressure measurement devices for the range of flows expected and with the required accuracy. Note persulfate flows less than 1 gpm are difficult to measure due to compatibility issues with available flow meters
Flow control	Provide the appropriate and compatible type of flow control valves for the required accuracy. Note hydrogen peroxide ball valves need to be vented
Sampling ports	Provide sampling ports to easily collect samples in the locations needed to control the process
Spare parts	Provide spare parts (meters and valves) for all critical parts
Secondary containment	Provide secondary containment as appropriate and required by regulations or site owner requirements
Spill cleanup	Provide spill-cleanup systems and neutralizers appropriate for the chemicals on site. Disposal of recovered spills should not be mixed in feed tanks and should be managed separately since organic materials may result in vigorous reactions in tanks. All tanks should be properly vented

**Figure 11.15. Two examples of aboveground oxidant mixing systems.**

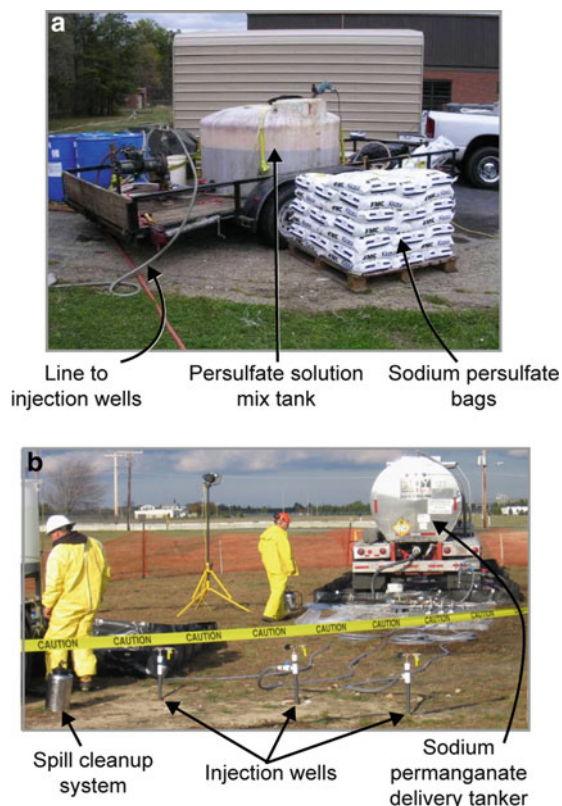


Figure 11.16. Photographs of mixing systems: (a) simple sodium persulfate mixing system using small mix tank (b) sodium permanganate liquid mix system with in-line dilution.

Oxidant handling and mixing systems should also be designed with the appropriate environmental and safety considerations. For example, secondary containment, tank overfill controls, and pressure relief valves can be required for most oxidants. Provisions for cleaning up spills and leaks should also be provided. This might include having clean water for flushing and neutralizing agents to neutralize the oxidant. The use of these should be clearly defined in the standard operating procedures or spill prevention and countermeasure plan for the project.

Given the properties of chemical oxidants, the use of ISCO requires diligent attention to safety and waste management issues. Worker and environmental safety have to be carefully considered and effectively managed. Potential worker safety risks include those associated with standard construction operations and work at a contaminated site. Additional worker risks specific to ISCO are primarily associated with the aboveground handling of the oxidants. The nature and seriousness of the risks will depend on the oxidant form, the concentrations used, and the methods of general handling and subsurface delivery. Product Material Safety Data Sheets (MSDSs) and other information from chemical suppliers should always be reviewed and a comprehensive safety plan should be set in place prior to application in the field. Material compatibility information should be obtained from the manufacturer to ensure safe and effective use of the oxidant. At all times, proper protective equipment should be worn.

11.6 OBSERVATIONAL METHOD AND CONTINGENCY PLANNING

As discussed above, there are several key factors (such as aquifer heterogeneity, contaminant distribution, preferential pathways, contaminant displacement, and oxidant activation) that are difficult to predict and important to consider and monitor during ISCO design and implementation. The Observational Method is one approach that can account for design and performance uncertainty, and be used to adapt ISCO delivery efforts as new data are collected. It is applied to maximize the chance for achieving oxidant-contaminant contact. Contingency planning is a part of the Observational Method and provides a means for project teams to anticipate, measure, and correct deficiencies as they arise.

11.6.1 Observational Method

The Observational Method is an adaptive design and implementation process that starts with a most probable design basis developed from the understanding of the available data, then provides contingency for conceivable deviations and uses performance monitoring results to adapt efforts in real time. It is particularly applicable for ISCO delivery as it was originally designed for subsurface engineering and explicitly acknowledges and incorporates conceptual site model (CSM) uncertainty into the process (USDOE, 1997). By using the Observational Method, the risk of failure during ISCO delivery can be reduced.

The Observational Method (Peck, 1969; Terzaghi et al., 1996) was originally developed for the geotechnical engineering profession to manage uncertainties in subsurface characteristics without excessively large amounts of sample collection. It has also been adapted for environmental remediation (Brown et al., 1989). The Triad Approach also uses many of the same principals as the Observational Method (Triad Resource Center, 2009). The Observational Method provides a flexible delivery program with data feedback used to adapt remediation efforts as they are being performed and helps to avoid fatal flaws and inefficient execution that can occur if linear approaches are used for *in situ* remediation.

11.6.2 Contingency Planning

The governing document that can be used to describe the Observational Method for a project is the Contingency Plan. The intent of contingency planning and the resultant Contingency Plan is to provide site-specific instructions to execute the Observational Method and prepare a real-time response action plan with decision logic to adapt the ISCO implementation based on the results of data collection.

Contingency planning is generally performed via the following steps:

- Sufficiently characterize the site to establish the general nature, pattern, and properties of the subsurface formation and contamination to a coarse level of detail. Prepare a CSM with the data collected.
- Establish an ISCO design based on a working hypothesis of the anticipated effectiveness of ISCO delivery and treatment performance under the most probable conditions.
- Evaluate the certainty in the CSM (see Chapters 9 and 10) to identify the most significant unfavorable and conceivable deviations.
- Select measurements to be taken during ISCO implementation and estimate their values on the basis of the working CSM hypothesis.

- Inventory potential treatment outcomes or deviations (what might go right and wrong). Perform a probability and cost-and-schedule-impact analysis for the deviations (provide a description of the condition and consequence of occurrence, probability of occurrence, potential cost of impact, potential schedule delay).
- Estimate measurement values under the most unfavorable conceivable deviations compatible with the available subsurface data (triggers at which response actions are required).
- Select and estimate the cost of contingency response actions for rectifying the possible deviations.
- Review the probability and magnitude (cost and schedule) of the response actions and assess whether additional refinement of the CSM or other mitigation measures are cost-effective to prevent it from occurring.

A number of useful outcomes should result from the contingency planning process:

- An assessment of the adequacy of the confidence in the CSM and conceptual design. If the range of cost and schedule impacts are too large or exceed some allowable budget or schedule constraint, the project team should consider additional data needs prior to proceeding with the project.
- Mitigation measures that may be taken now or during design to minimize the potential for occurrence.
- Performance measurements that should be taken and associated trigger levels to flag occurrence.
- Contingency response action plans (the primary outcome of the process).

Performance measurements for contingency assessment are designed to monitor the progress of ISCO treatment and compare actual performance against the design basis or predicted performance. These performance measurements are typically the same as those needed for delivery and treatment effectiveness monitoring. Delivery and treatment effectiveness monitoring is discussed in detail in Chapter 12. As it pertains to contingency assessment, the frequency of measurements may be increased to ensure that an “early warning” system is in place to avoid surprises and catch problems before they accrue wasted expense. Real-time measurements, such as those discussed in Section 12.4.2.3, are especially well suited for this purpose.

Estimating measurement values is an important process to establish milestones for tracking ISCO treatment progress. These estimates can be made using an analytical or numerical model. Results from treatability or pilot testing can also be used. In lieu of better resources, case-study literature can also be used to estimate measurement values. However, the uncertainty in these estimates should be clearly stated by assigning a range of measurement values rather than absolute values.

Uncertainties and unforeseen changes in field conditions can be managed by developing contingency response action plans for a range of conceivable deviations. Contingency response action plans are typically devised for high- to moderate-probability deviations that may result in moderate cost and schedule impacts. Deviations that could result in high cost and schedule impacts should be accounted for in the design as part of the data collection and design iteration process discussed above.

Table 11.6 lists example conceivable deviations, measurements, and their associated response actions in the event that measurements fall out of the desired range of values for a representative permanganate ISCO system.

Table 11.6 Example Deviations, Measurements, and Response Actions for Direct-Inject Permanganate ISCO Treatment Systems

Conceivable deviation	Measurement	Example values (anticipated/unfavorable)	Potential response action
Short circuiting to ground surface (day-lighting)	Visual inspection of ground surface	<i>Anticipated</i> – none <i>Unfavorable</i> – Presence of permanganate on ground surface	<i>Initial</i> – Offset injection location <i>Option 2</i> – Reduce injection pressure/flow <i>Option 3</i> – Modify delivery process
Non-uniform delivery in the vertical profile of the subsurface or laterally within the TTZ – oxidant follows preferential pathways of higher conductivity	Visual inspection of soil borings	<i>Anticipated</i> – full vertical penetration of purple color <i>Unfavorable</i> – Stratification without evidence of permanganate diffusion into lower permeability media (LPM)	<i>Initial</i> – Increase density of vertical injection intervals at existing injection locations <i>Option 2</i> – Increase the number of injection locations <i>Option 3</i> – Increase the permanganate injection concentration to increase chance for diffusion into low permeability material
	Multi-level, discrete-interval groundwater samplers (MLS)	<i>Anticipated</i> – permanganate in all MLS well screens <i>Unfavorable</i> – Absence in some well screens	
Rebound of contaminant concentrations to levels above baseline values	Contaminant concentrations in monitoring wells and/or MLS	<i>Anticipated</i> – numeric treatment goal <i>Unfavorable</i> – greater than numeric treatment goal	<i>Initial</i> – Review data and affirm performance of an additional injection <i>Option 2</i> – Consider use of another oxidant or treatment technology <i>Option 3</i> – Consider technical impracticability of ISCO

Contingency planning (or a first phase of it) is best performed during the ISCO conceptual design stage (see Chapter 9, Section 9.3). The results of the contingency evaluation can be used to assess whether to proceed with the existing conceptual design or if the data and design basis needs to be revisited. The results can also be used and updated later during the detailed design and planning process. The Contingency Plan should be developed with input from all project stakeholders, if possible. It provides a basis for their expectations and gets “buy-in” for the contingency response actions ahead of time, which should speed their implementation, if they are needed.

11.7 SUMMARY

The success of ISCO often can be driven by the effective delivery of the oxidant into the subsurface and achieving oxidant-contaminant contact. As a consequence care needs to be taken when selecting and designing oxidant delivery systems. In addition, the designer should have an appreciation of the oxidant transport mechanisms that will be involved since this can help to optimize delivery.

A number of oxidant delivery approaches may be used, including injections wells, direct-push technology probes, sparge points, infiltration systems, recirculation systems, fracturing, and mechanical mixing. Injection wells and direct-push technology probes are the most commonly used. Each delivery approach has characteristics that may make it most suitable for a particular oxidant and site setting.

The factors and challenges that should be considered when selecting and designing an oxidant delivery approach include aquifer heterogeneity, contaminant distribution, presence of underground utilities, contaminant displacement by the injection of oxidant, and mixing of activators with the oxidant (for those requiring activators).

Since oxidant delivery into the subsurface is difficult to predict with precision and results can often deviate from predictions, contingency planning must be included as an important aspect of the overall ISCO design approach. Contingency planning provides a means for project teams to anticipate, measure, and correct deficiencies as they arise. In so doing, known design uncertainty can be addressed during the implementation process.

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CHAPTER 12

ISCO PERFORMANCE MONITORING

Tom Palaia,¹ Brant Smith² and Richard W. Lewis³

¹CH2M HILL, Englewood, CO 80112, USA; ²XDD, LLC, Stratham, NH 03885, USA; ³ERM, Mansfield, MA 02048, USA

Scope

Considerations for, and approaches to, executing a performance monitoring program for *in situ* chemical oxidation (ISCO) including baseline, delivery, and treatment performance monitoring activities.

Key Concepts

- Specific monitoring objectives must be developed that are geared toward collecting the data necessary to evaluate the effectiveness of an ISCO project. The monitoring program must be succinctly linked to the ISCO treatment goals so that a focused and efficient data collection effort is maintained and adaptations can be made to achieve the best possible outcome.
- Baseline monitoring activities are focused on developing adequate documentation of the contaminants of concern (COCs) and subsurface conditions that are present at a site just prior to startup of ISCO operations and provide a reference for assessment of ISCO delivery and treatment performance.
- Delivery performance monitoring focuses on tracking oxidant delivery and distribution within a target treatment zone and providing a database upon which decisions can be made about the effectiveness of the ISCO implementation and if adaptation of ISCO operations is needed.
- Treatment performance monitoring focuses on tracking hydrogeologic and geochemical conditions and changes in the levels of the COCs and other constituents of potential concern such as redox-sensitive metals.
- There are many considerations, components, and options for monitoring programs and each project should formulate a performance monitoring program after carefully considering the ISCO technology within the site and project constraints.

12.1 INTRODUCTION

Monitoring programs to evaluate the performance of *in situ* chemical oxidation (ISCO) projects are typically designed to meet many objectives in the face of complex, uncertain, and difficult-to-predict conditions. Due to the fundamental limitations of *in situ* remediation, a level of interpretation, interpolation, and uncertainty is typical in a monitoring program. Yet, a well-designed, robust monitoring program can often result in a sound evaluation of the application of an *in situ* technology such as ISCO.

A properly designed performance monitoring program is essential to provide data that can be used to evaluate the achievement of operational and performance objectives and determine if ISCO met established treatment goals. A typical performance monitoring program includes, but is not limited to, three component parts and the elements highlighted in Table 12.1.

Table 12.1. Typical Performance Monitoring Program Components and Elements

Element	Performance monitoring component		
	Baseline monitoring	Delivery monitoring	Treatment monitoring
Clearly defined data needs and data quality objectives	X	X	X
Environmental media to be sampled	X	X	X
Number and location of monitoring points	X	X	X
Frequency of observations and sampling	X	X	X
Duration of the monitoring period	S	S	L
Field and laboratory analytical methods	F, La	F, La	F, La
Quality assurance/quality control procedures	X	X	X
General data analysis, evaluation, documentation	X	X	X

X - applicable, S - shorter, L - longer, F - field measurement, La - laboratory analysis.

This chapter describes key components of a performance monitoring program for ISCO, including establishment of operational objectives, monitoring baseline conditions, measuring oxidant delivery effectiveness, and evaluating contaminant treatment efficiency. This chapter is intended to complement Chapter 10, Site Characterization and ISCO Treatment Goals, by providing information on how to track performance, evaluate achievement of treatment goals, and meet end points. This chapter is also intended to complement Chapter 11, Oxidant Delivery and Contingency Planning, by explaining the importance of monitoring that yields the data necessary to evaluate the need for contingency response actions. An illustration of how performance monitoring can relate spatially to site characterization activities and oxidant delivery to a target treatment zone (TTZ) is shown in Figure 12.1.

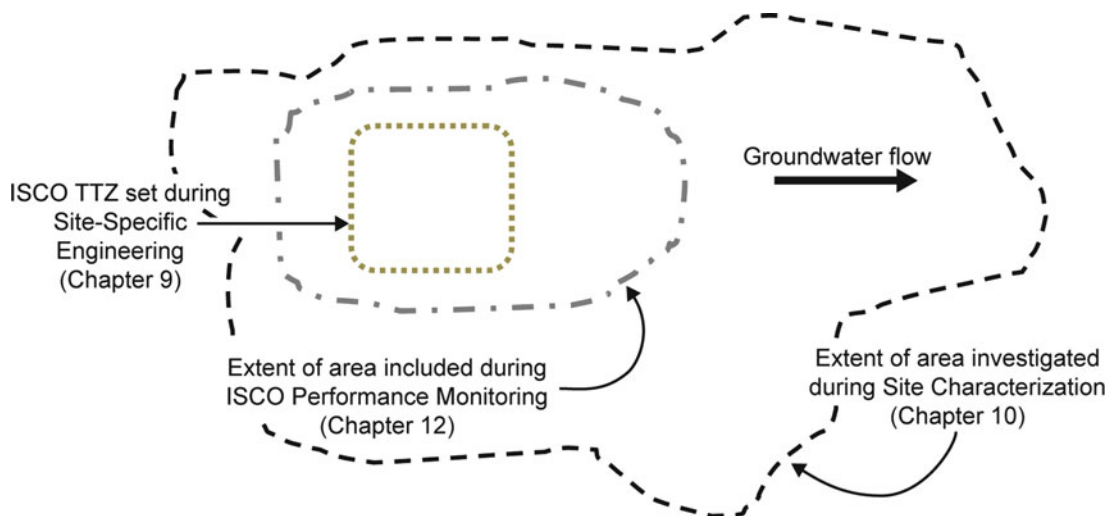


Figure 12.1. Illustration of how performance monitoring can relate spatially to site characterization and other ISCO project activities.

The remainder of this chapter describes each of the key components of a performance monitoring program and provides guidelines to help design and execute a successful program for ISCO. Examples of monitoring programs that illustrate application of select options are provided in the case studies presented in Appendix E.

12.2 GENERAL CONSIDERATIONS

12.2.1 Establishment of Operational Objectives

The details of a performance monitoring program are highly site-specific and will differ if the application is for a small pilot test, a single large full-scale application of ISCO alone, or if ISCO is part of a combined remedy. In general, the baseline, delivery, and treatment performance monitoring components of a performance monitoring program are conducted to achieve the following goals:

- Collect the necessary data to measure and document achievement of the ISCO operational objectives and treatment goals (Chapter 10 [Section 10.6]).
- Monitor the ISCO project to continually confirm that the design is performing as intended and, if applicable, is being optimized as prescribed by the Contingency Plan (Chapter 11 [Section 11.6]).
- Provide engineering performance parameters for subsequent applications and/or coupled post-ISCO technologies and approaches (Chapter 7).

A primary goal of a performance monitoring program for most if not all ISCO projects is to measure achievement of operational objectives and treatment goals. While ISCO treatment goals are typically established during the technology evaluation stage (e.g., feasibility study), operational objectives are generally established during the design process.

Operational objectives are defined as a set of specific delivery and treatment performance related objectives that, if met, should result in the achievement of the treatment goals for the ISCO remedy. Treatment goals are discussed in more detail in Chapter 10 (Section 10.6). Measurements associated with the operational objectives are assessed during the performance monitoring program to determine the effectiveness of the ISCO remedy. If established early in the ISCO design process, the operational objectives also can be used as a basis for performance specifications during the detailed design process (Chapter 9 [Section 9.4]).

In most cases, operational objectives are beneficial for use as a reference for performance related measurements and as a basis for follow-up optimization activities to improve ISCO treatment effectiveness. For example, an ISCO project employing oxidant recirculation may include a minimum runtime as an operational objective to ensure that the ISCO system is meeting oxidant delivery requirements. If the runtime does not meet the operational objectives, treatment goals will likely not be met and optimization activities are needed.

Typical operational objectives focus on ensuring that the oxidant makes contact with the contaminants within the TTZ for an adequate amount of time to achieve the desired reactions and contaminant destruction. For example, operational objectives that may be considered for an activated-persulfate ISCO application are listed in Table 12.2.

Care should be taken to ensure that the operational objectives are realistic and achievable and, if achieved, will help lead to a desired performance outcome for the ISCO project. It is often prudent to avoid absolute values, especially if they are unrealistic and unnecessary. For example, a target concentration of 500 milligrams per liter (mg/L) of permanganate may not be achievable everywhere within a TTZ, nor is it absolutely necessary to achieve this in order to meet a mass reduction treatment goal. An objective of at least 50 mg/L may be a more realistic and achievable operational objective. Operational objectives may be established based

on bench- or field-scale pilot testing, modeling, literature review, previous experience, or engineering judgment. Consultation with prospective or contracted ISCO technology vendors may be beneficial to help define operational objectives. Often, ISCO technology vendors have developed unique and proprietary knowledge of ISCO technologies and performance capabilities in different hydrogeochemical and contaminant settings.

Table 12.2. Example Operational Objectives for a Hypothetical ISCO Project Employing Activated Persulfate

Topical area	Example operational objective
Oxidant delivery concentrations	<ul style="list-style-type: none"> Co-deliver a minimum persulfate concentration of greater than "X" mg/L and activator concentration of greater than "Y" mg/L to the zones of highest groundwater contamination within the TTZ
Oxidant persistence in the TTZ	<ul style="list-style-type: none"> Maintain a minimum of "Z" days of persulfate residence time within the TTZ for the oxidation reaction to occur
Oxidant <i>in situ</i> control	<ul style="list-style-type: none"> Minimize loss of oxidant from the TTZ during the delivery process due to day-lighting or short-circuiting
Hydraulic control	<ul style="list-style-type: none"> Maintain hydraulic control and mitigate spread of contamination outside the TTZ
Process monitoring	<ul style="list-style-type: none"> Utilize a real-time measurement and data analysis routine to optimize/adapt the injection/monitoring program
Health and safety	<ul style="list-style-type: none"> Experience zero health and safety incidents

12.2.2 Accounting for ISCO Interactions in the Subsurface

The application of ISCO can result in a systemic change in subsurface conditions within the TTZ, and this can affect various characteristics of the subsurface. The nature and magnitude of the impacts are dependent on the characteristics of the subsurface prior to implementing an ISCO technology and the type of technology deployed at a site. The potential interactions of each oxidant within the subsurface are discussed in detail in Chapters 2–7. Table 12.3 summarizes key potential impacts associated with the introduction of an oxidant into the subsurface that warrant special consideration during design of a performance monitoring program for an ISCO technology. Some ISCO-induced changes can be monitored for and exploited as an indirect measure of oxidant delivery within a TTZ. For example, changes in dissolved oxygen (DO) can be indicative of the presence of hydrogen peroxide or ozone (past or present) and changes in specific conductance (Ec) can be indicative of permanganate or persulfate. With some oxidants a temporary increase in heavy metals might be anticipated in groundwater at a particular site and thus potential metals of concern should be included in the parameter list specified within the performance monitoring program.

Important to a performance monitoring program is the duration of any changes induced by ISCO and if and when the TTZ might reach a post-ISCO steady-state condition. Understanding the re-equilibration process at a particular site can be critical in determining the scope of monitoring needed and how long it should be carried out following termination of oxidant injection into the TTZ.

Experience shows that under conditions where a small oxidant dose was applied in comparison to the assimilative capacity of the subsurface, these changes may not be observed or will be minimal and temporary, with a return to baseline conditions after re-equilibration. In

this situation, re-equilibration occurs as intrinsic biotic and abiotic reactions occur and upgradient unaffected groundwater flows back into the ISCO TTZ and eventually re-establishes conditions similar to baseline. Likewise, ISCO-treated groundwater flows downgradient and eventually contacts sufficient unaffected media to return to a baseline state. The duration required for re-equilibration is highly site-specific and depends on many factors, such as the magnitude of any changes caused by ISCO, contaminant architecture, including type and phase of organic and inorganic compounds, the size of the ISCO TTZ, the degree of pre-ISCO microbial activity, the rate of groundwater flow and the composition and characteristics of the aquifer formation.

Table 12.3. Potential Impacts of the Introduction of an Oxidant into the Subsurface that Warrant Special Consideration During Design of a Performance Monitoring Program for ISCO

Characteristics of potential impact	Considerations potentially relevant to an ISCO performance monitoring program
Shift in geochemistry	<ul style="list-style-type: none"> ● Potential shift in pH, ORP, DO, ionic strength and composition (e.g., Fe^{+2}, Na^{+1}, K^{+1}, SO_4^{-2}), particulates (MnO_2), alkalinity (see Chapters 2–5 for information on oxidant interactions in the subsurface). ● Magnitude and nature of natural organic matter can change due to reactions with the injected oxidants and this can alter partitioning of organic contaminants between phases. ● Conditions such as temperature may increase if the exothermic energy associated with the ISCO application is strong and the specific heat capacity of the TTZ is not sufficient to attenuate it.
Perturbation in microbiology	<ul style="list-style-type: none"> ● ISCO can cause a drop in microbial abundance and diversity but these parameters generally return to pre-ISCO levels and may increase (Chapter 7).
Occurrence of metals and changes in mobility	<ul style="list-style-type: none"> ● Trace metals, present in some oxidant chemicals due to the mining and manufacturing processes, incidentally can be injected into the subsurface (see Chapters 2–5 for information on specific oxidants). ● Chemical manufacturers have increased purity to USP-grade or NSF60-certified levels. ● Due to ISCO induced changes in subsurface geochemistry (e.g., ORP, pH), the mobility of redox- or pH-sensitive metals – either naturally present or added with the oxidant injected – may become more or less mobile. ● Heavy metals of potential concern include: antimony, arsenic, barium, cadmium, hexavalent chromium, copper, iron, lead, mercury, nickel, and selenium. ● Site-specific consideration should be given to whether trace metals are a concern (e.g., review of pH-Eh phase diagrams) and if so, testing may help quantify the nature and magnitude of the risk (e.g., Appendix D.2). ● If an increase in the concentration of metals in groundwater does occur, it should be temporary and concentrations should return to pre-ISCO conditions after the aquifer has re-equilibrated (Chapter 8, Section 8.7).
Re-equilibration	<ul style="list-style-type: none"> ● ISCO-induced changes in subsurface conditions are usually temporary and after oxidant injection is terminated, the subsurface can re-equilibrate over time to conditions similar to those present before ISCO. One exception is with some permanganate ISCO projects where there can be a persistent accumulation of MnO_2 solids and associated constituents. ● The length of time it takes for re-equilibration depends on the ISCO design (e.g., size of the TTZ, oxidant used and concentration delivered) and the subsurface conditions (e.g., assimilative capacity, groundwater flow velocity).

Eh - electrode potential, Fe - iron, K - potassium, MnO_2 - manganese dioxide, Na - sodium, ORP - oxidation-reduction potential, SO_4^{-2} - sulfate, USP - United States Pharmacopeia, NSF60 - National Sanitation Foundation Standard 60.

12.2.3 Performance Monitoring for Site-Specific Conditions

After establishing ISCO treatment goals and specific operational objectives, a performance monitoring program can be developed to evaluate them. A properly designed monitoring program should be focused on the ISCO technology applied under the prevailing site-specific conditions. In general, a properly designed performance monitoring program considers and accounts for the factors listed in Tables 12.4 and 12.5. These factors can directly influence choices about the analyses made (e.g., discrete vs. composite, fixed-base laboratory vs. mobile field laboratory analyses), the phase monitored (e.g., vapor, sorbed, or groundwater), sampling methodologies (e.g., direct push probes vs. permanent wells), location of the monitoring points, measurement frequency and monitoring program duration.

Table 12.4. Site Conditions and Factors of Potential Importance to the Design of a Performance Monitoring Program for an ISCO Project

Conditions and factors	Comments
Contaminant properties	<ul style="list-style-type: none"> • Contaminant properties are important in selecting the media to be sampled (NAPL, soil, groundwater, and vapor) and locations of samples. • Density – affects movement in the subsurface and the possibility of nonaqueous phase liquids (LNAPL or DNAPL) being present and their location. • Solubility – affects capacity of the aqueous phase for COCs. For NAPL mixtures, Raoult's Law yields an effective solubility based on the mole fraction of contaminants in the mixture. • Vapor pressure – affects contaminant volatility; VOCs can be prone to measurement errors. • Henry's Law constant (K_H) – affects capacity of the vapor phase for COCs. • Organic carbon partitioning coefficient (K_{oc}) – affects capacity of aquifer solids to sorb COCs.
Contaminant concentration and phase distribution	<ul style="list-style-type: none"> • In concert with the contaminant properties and subsurface conditions, contaminant concentration will determine the phase distribution in the subsurface (up to a 3-phase system in groundwater: aqueous, sorbed, nonaqueous; up to a 4-phase system in the vadose zone: aqueous, sorbed, gaseous, nonaqueous). This will then determine the media (NAPL, soil, groundwater, and/or vapor) to be sampled.
Contaminant spatial distribution	<ul style="list-style-type: none"> • Contaminant distribution is a function of the type, size and age of the contaminant release, lithologic characteristics, subsurface heterogeneities, groundwater hydrology, and other factors. • Contaminant distribution in the subsurface is critical to delineation of a TTZ and to the ISCO technology implemented which in turn affect the sampling locations, methods, and duration.
Geologic conditions	<ul style="list-style-type: none"> • Geologic conditions of particular relevance include: potential for and character of preferential pathways (e.g., boreholes, tunnels, utility corridors), variable hydraulic conductivity and transport properties in lithologic sequences. As it pertains to monitoring, understanding of geologic conditions is critical to selection of sampling techniques and sample locations.
Groundwater conditions	<ul style="list-style-type: none"> • Groundwater conditions including delineation of high- and low-conductivity layers, flow directions and velocities, and quality characteristics are important in selecting monitoring point locations and depth intervals as well as developing a baseline for interpreting post-ISCO biogeochemical data.

COC - contaminant(s) of concern, DNAPL - dense nonaqueous phase liquid, LNAPL - light nonaqueous phase liquid, VOC - volatile organic compound.

Table 12.5. ISCO Technology Factors of Potential Importance to the Design of a Performance Monitoring Program for an ISCO Project

Factor	Comments
Oxidant properties	<ul style="list-style-type: none"> ● Each oxidant has specific characteristics that can impact the materials of construction of the monitoring apparatus and equipment selected for a performance monitoring program (e.g., Chapter 11). ● Based on its properties, each oxidant is amenable to detection during ISCO using one or more methods of analysis as noted in Appendix D.3 and highlighted below: <ul style="list-style-type: none"> – Hydrogen peroxide (H₂O₂) – Onsite measurement of H₂O₂ using a field-test method. – Sodium or potassium permanganate – Onsite measurement of permanganate (MnO₄⁻) presence by visual appearance (pink/purple coloration above 5 mg/L) or colorimetric tests (semi-quantitative across a wide range). Quantitative analyses of MnO₄⁻ ion by spectrophotometric methods. – Sodium persulfate – Measurement of specific reactive species is not readily done. Field test kits and titration methods are available for measurement of sodium persulfate. If used, chemical activators can be measured. – Ozone (O₃) – Onsite measurement of O₃ using a field test method. ● Each oxidant has the potential to alter subsurface conditions in different ways (Table 12.3) and monitoring can include field observations for such alterations: <ul style="list-style-type: none"> – Hydrogen peroxide – Increases in ORP, DO, and temperature (if used in high concentrations). – Sodium or potassium permanganate – Increases in ORP, slightly increased DO, substantially elevated specific conductance, a marked decrease in pH at some sites (e.g., a TTZ with DNAPLs and limited site assimilative capacity), and increases in sodium or potassium. – Sodium persulfate – Increases in ORP, decreases in pH (unless alkaline activation), slight increases in DO, substantially elevated specific conductance, and increases in sodium and sulfate. – Ozone – Increases in ORP and DO (especially if air containing oxygen is part of the sparge gas). ● The expected persistence of each oxidant in the subsurface varies and this can affect the frequency and duration of monitoring: <ul style="list-style-type: none"> – Hydrogen peroxide – Reacts very quickly, usually within minutes to hours, depending on the presence of native transition metals, which catalyze the H₂O₂ reactions, or scavengers, which can terminate the reactions (e.g., nitrate (NO₃⁻) and carbonate (CO₃²⁻)). Stabilizing chemicals can be injected with the H₂O₂ and extend the longevity, potentially up to weeks if conditions are optimum. – Sodium or potassium permanganate – Persistence can be on the order of days to months and depends on the level of reactants including the target COCs and the NOD. – Sodium persulfate – Persistence can be on the order of days to months and depends on the method of activation and the level of target COCs and other constituents involved in nonproductive reactions. – Ozone – Persistence can be minutes to hours depending on natural organic matter (NOM) present and reducing conditions present.
Site and project features	<ul style="list-style-type: none"> ● Effects on the development of a site-specific performance monitoring program for an ISCO project: <ul style="list-style-type: none"> – Access can be a constraint at facilities with operating infrastructure and personnel, especially if there are sensitive areas with security controls. – Physical constraints on where monitoring can take place are common and can be major limitations in monitoring ISCO. Examples include: buildings, traffic ways, above- and below-ground utilities, and landscaping.

(continued)

Table 12.5. (continued)

Factor	Comments
	<ul style="list-style-type: none"> – Technical constraints include equipment- or subsurface-related conditions such as inability to utilize local drilling or probing equipment or inability to quickly install monitoring points in bedrock layers. – Budgetary constraints are often present since costs associated with executing a performance monitoring program are covered by the same source of funds that are used to pay for the implementation of the ISCO technology. – Administrative constraints can include local, state, or federal regulations; private property access; public rights-of-way and traffic control requirements; and mission-critical access restriction or limited-time escort requirements at military facilities.
Regulatory oversight	<ul style="list-style-type: none"> • Certain regulations and requirements can stipulate that a specific approach or methodology must be used in a performance monitoring program. This often occurs in the form of a sampling and analysis plan, such as a UFP-QAPP.

Note: refer to Chapters 2–5 for details regarding the properties and chemistry of the oxidants.

NOD - natural oxidant demand, NOM - natural organic matter, UFP-QAPP - Uniform Federal Policy for Quality Assurance Project Plan (IDQTF, 2005), VOC - volatile organic compound(s).

12.3 MONITORING OF BASELINE CONDITIONS

12.3.1 Purpose and Scope

Baseline monitoring is a component of a performance monitoring program that is carried out to establish pre-existing conditions and provide a reference for comparison of data collected during and following the active oxidant delivery phases of an ISCO project. Characterization of baseline conditions can assist in identifying necessary refinements in the oxidant injection planned and the associated delivery monitoring program. Baseline monitoring is typically performed to achieve one or more of the following specific objectives:

- Determine pre-existing contaminant concentrations.
- Estimate pre-existing contaminant mass.
- Estimate pre-existing mass flux emanating from the contaminant source.
- If historical data is available or multiple rounds of baseline monitoring are possible, estimate ambient variability in water quality concentrations due to natural conditions such as precipitation infiltration, seasonal or tidal influence, and wet/drought cycles.
- Determine the concentrations of background metals if metals are of concern.
- Establish pre-ISCO geochemical conditions.
- Estimate pre-ISCO microbiological conditions.

Since baseline monitoring can be performed after ISCO infrastructure is installed, it is assumed that site characterization and design activities are complete. Therefore, baseline monitoring objectives typically focus primarily on a few key site conditions for the purpose of benchmarking pre-ISCO site conditions. Baseline monitoring often focuses on hydrogeologic parameters, water chemistry, and contaminant distribution.

Quantification of chemical concentrations is a relatively straightforward process and procedures are not ISCO-specific. However, quantification of contaminant mass and mass flux are particularly challenging because they involve integration of concentration data over control volumes and planar surfaces, respectively. In so doing, discrete sample data must be interpolated and extrapolated over control volumes or planes that are divided into uniquely

lithologic, hydrologic, or contaminated zones. The data can be input into simple spreadsheet tools or complex three-dimensional geospatial interpolation software.

It is important to bracket the uncertainty in the baseline monitoring data and estimates derived from it. Among other factors, uncertainty is introduced through ambient concentration variability and/or statistical confidence of geospatial interpolation. Quantification of the baseline uncertainty can support interpretation of the data generated during oxidant delivery and treatment performance monitoring. For example, if the baseline mass flux from a NAPL source zone was initially quantified as ranging from 0.05 to 0.5 kilograms (kg) per day with a median of 0.2 kg/day, one can be relatively confident that if the post-ISCO mass flux range is measured to be 0.01–0.05 kg/day, it is significantly lower than the baseline flux.

12.3.2 Approach and Methodologies

12.3.2.1 Baseline Monitoring Approach

Baseline monitoring is most commonly accomplished by supplementing an existing site characterization monitoring well network and a database of historic contaminant concentration data with new data collected from a few existing wells and new borings or wells within and around the TTZ. In this way, the ambient variability of contaminant concentrations can be assessed and a supplementary analysis of certain key analytes (e.g., some geochemistry parameters, metals, or microorganisms) can be used to meet the remaining baseline data objectives. For sites without a pre-existing monitoring network, baseline samples of porous media and groundwater can be collected using direct push technology (DPT) or through subsurface drilling and new permanent monitoring wells. While DPT sampling is preferred for some monitoring purposes, it is generally not preferred as the sole method for baseline monitoring to generate data for assessment of ISCO treatment performance. Properly screened monitoring wells can be very important to obtain representative and repeatable groundwater samples that enable time series data analysis. As discussed below, multiple rounds of baseline monitoring can help prevent inaccurate baseline assessment.

At sites where there is interest to expedite schedules by establishing ISCO infrastructure concurrently with baseline monitoring completed during the same mobilization, this approach should be carefully considered. Subsurface drilling, groundwater well installation and well development activities can cause significant disturbance to the groundwater system. Care must be taken to avoid sampling wells too soon after well development to ensure that baseline samples are representative of equilibrated conditions within the aquifer formation.

Mass flux measurement can be complex and generally requires a detailed understanding of a source zone and associated dissolved plume geometry within a particular hydrogeologic setting. Groundwater hydraulics can be measured using standard slug or pump testing techniques, tracer dilution testing, or passive flux meters (PFMs). Contaminant movement can be measured using a single or multiple set of transects of multi-level samplers (MLS), groundwater extraction/interceptor wells, or PFM.

12.3.2.2 Media and Locations to Be Monitored

Media to be sampled during baseline monitoring include those that may be affected by ISCO and are important for follow-on treatment performance monitoring or compliance purposes. For example, if source mass reduction is established as an ISCO treatment goal, then baseline monitoring of aquifer solids (including NAPL, if present) and groundwater is important for estimating mass. After evaluation of pre-existing mass fractions, it may be determined that future sampling of groundwater may not be necessary since only a small fraction of the total mass dissolves into the groundwater. If mass flux reduction is established as an ISCO treatment

goal, then baseline monitoring of groundwater via downgradient transect(s) perpendicular to groundwater flow emanating from the ISCO TTZ may be all that is required.

As discussed in Chapter 11, oxidant delivery can affect contaminant distribution by physical or chemical means. At sites using CHP or ozone, baseline monitoring of soil vapor may be needed if there is a concern for vapor migration and intrusion into buildings or other structures. Likewise, if a site contains potentially mobile NAPL, then its physical location should be ascertained as far as practicable prior to physical disturbance by oxidant injection methods. At some sites with NAPL consisting of a chemical mixture, like petroleum wastes, NAPL composition may or may not be of concern. If the ISCO treatment goal entails treatment of the NAPL mixture, then a baseline chemical analysis may be prudent as a benchmark for future risk reduction evaluation during the treatment performance monitoring phase.

Baseline groundwater monitoring should generally include: (1) locations upgradient of the contaminated zone of a site for establishing ambient influx conditions, (2) locations within the TTZ for establishing ambient baseline conditions, and (3) locations downgradient of the TTZ for treatment performance monitoring (e.g., if downgradient migration of oxidants is expected or if mass flux evaluations are conducted as a treatment cessation criterion). It is important to understand the water quality and contaminant properties of the groundwater influx in order to assess treatment limits and rebound/recontamination characteristics. ISCO TTZ are often placed within the core of a groundwater plume and the TTZ is thus subject to some degree of influx of upgradient groundwater, which can lead to recontamination in the TTZ after active oxidant injection is completed. Therefore, it is important to monitor this incoming water quality and use it as an upper bound estimate for contaminant reduction. Sampling within the TTZ is relatively straightforward as it is used for comparison to future delivery and treatment performance monitoring data. Downgradient monitoring is generally applicable to ISCO projects attempting mass flux reduction or to help assess water quality impacts to surrounding groundwater. Downgradient monitoring may be important for sites with low NOD, moderate to high groundwater advection, and potential downgradient receptors, such as a surface water body or groundwater extraction well. In this case, downgradient monitoring may serve the purpose of compliance monitoring to ensure protection of downgradient receptors. Understanding the baseline condition of the downgradient groundwater quality helps future evaluation of impacts due to the ISCO treatment and assignment of triggers for a response action, if needed.

Under certain circumstances, such as when the contamination has a low solubility in water or during aquifer solids sampling, it is prudent to sample at multiple locations within and immediately outside (for delineation purposes) the TTZ in order to understand sampling and analysis variability. Aquifer solids sampling outside of the TTZ for background purposes is generally not necessary for baseline monitoring since aquifer solids concentrations are generally static over the relatively short duration of ISCO treatment. In general, within and near the TTZ multiple samples should be collected from unique lithologic and contaminant settings. There is no generic number of aquifer solids samples that are required or appropriate for a particular ISCO project. The number should be determined based on the established data quality objectives for the baseline monitoring effort. For example, a larger number of aquifer solids samples are required for a project using a geostatistical tool to quantify the treatment performance in terms of source mass reduction versus a project concerned about a small hot-spot of contamination revealed by prior site characterization data. Aquifer solids sampling locations should be established such that follow-up performance sampling can be easily collocated with previous samples. Most often, a 1- to 2-foot (ft) (30- to 60-centimeter [cm]) borehole offset is sufficient. The intent of co-locating the samples is to match geospatial coverage rather than attempt side-by-side comparison of pre- and post-ISCO effects on porous media at a particular location.

If the ISCO technology planned for implementation is expected to affect soil vapor and if vapor intrusion is a concern, then baseline soil gas sampling may be warranted. Soil vapor is

generally subject to ebb and flow in response to barometric pressure changes (ITRC, 2007). As a result, it is subject to rebound/recontamination like groundwater, and baseline monitoring near/within the TTZ and surrounding areas is important.

12.3.2.3 Parameters and Analysis Methods

Selection of baseline analytical parameters depends on the oxidant used and the media to be sampled. Table 12.6 contains suggestions for baseline monitoring of sites planning to use hydrogen peroxide, potassium or sodium permanganate, activated persulfate, or ozone. Table 12.6 is focused on groundwater monitoring since it is typically the primary medium of concern. Porous media vapor parameters include carbon dioxide (CO₂), oxygen (O₂), and VOCs, and oxidant (if ozone is used). Aquifer solids parameters include COCs and non-target organics, total organic carbon and NOD. Other analyses can be performed on these media, such as metals in porous media, but are not usually necessary to meet typical data objectives. It is

Table 12.6. Parameters that are Commonly Included in a Baseline Monitoring Program

Parameter	Hydrogen peroxide	Potassium or sodium permanganate	Sodium persulfate	Ozone
Groundwater level or piezometric head	FI	FI	FI	FI
Color		V, DPT	V	V
Temperature	FI	FI	FI	FI
DO	FI, FK			FI, FK
ORP	FI	FI	FI	FI
pH	FI, FK		FI, FK	FI, FK
Specific conductance		DPT, FI	DPT, FI	
Alkalinity	L, FK		L, FK	L, FK
COCs (aquifer solids and groundwater)	DPT, L, FI, FK	DPT, L, FI, FK	DPT, L, FI, FK	DPT, L, FI, FK
Total organic carbon (aquifer solids and groundwater)	FK, L	FK, L	FK, L	FK, L
Chloride	L, FI, FK	L, FI, FK	L, FI, FK	L, FI, FK
Manganese		L, FK		
Potassium or sodium		L, FK	L, FK	
Iron	L, FK		L, FK	
Sulfate			L, FK	
Site-specific redox sensitive metals	L, FK	L, FK	L, FK	L, FK
Geochemical indicators for natural attenuation (NA) (e.g., nitrate, CO ₂) ^a	L, FK	L, FK	L, FK	L, FK
Microbiological parameters (e.g., biomass, DNA) ^a	L	L	L	L
Vadose zone gas (CO ₂ , O ₂ , VOC)	FI			FI

DNA - deoxyribonucleic acid, DPT - direct push technology (MIP for VOCs, conductivity probe for specific conductance), FI - field instrument (e.g., meter, gauge, thermometer, spectrophotometer), FK - field kit (e.g., colorimeter, color wheel, test strips), L - laboratory analysis, V - visual inspection.

^aAppropriate for systems utilizing a coupled approach with a biological component.

emphasized that Table 12.6 is provided for guidance purposes only, and site-specific conditions should be carefully considered prior to parameter selection, especially for ISCO projects employing physical or chemical activation methods.

The analysis methods for ISCO baseline monitoring are generally consistent with those used during site characterization activities (Chapter 10) and typical remediation practice so few specialized techniques are required. As shown in Table 12.6, there are a number of parameters that are determined by laboratory analyses and these can be carried out in a remote, fixed-base laboratory or using an on-site mobile laboratory (<http://www.nelac-institute.org/>). Laboratory data can be collected and analyzed in a rapid manner using an on-site laboratory (mobile or fixed-base) or by using overnight express courier and quick turnaround time (TAT) analysis at a remote laboratory. However, laboratory data are typically obtained with a 1- to 2-week TAT and data needs must be amenable to this lag.

12.3.2.4 Sampling Methods

Sampling methods employed during baseline monitoring are essentially the same as those employed during site characterization (Chapter 10 [Section 10.4] and Tables 10.3 and 10.4). Groundwater monitoring can be performed using discrete samples from DPT probes or temporary or dedicated monitoring wells. Screen lengths and depths are highly site-specific and should be selected carefully based on site hydrogeologic conditions and treatment goals. Low-flow sampling is generally used to collect representative groundwater samples. However, for parameters with semi-quantitative or low data-quality use, grab samples from a bailer or direct measurement down-well may be adequate. This direct measurement type approach can be much faster and more cost effective. Passive diffusion bag (PDB) samplers also can be used for monitoring some parameters, but several of the general water quality parameters such as DO, ORP, and dissolved metals cannot be determined with PDB samplers. In addition, the chemical compatibility of the PDB with the oxidant used must be evaluated prior to use. Regardless of the sampling technique, it is important that a common measurement technique (e.g., low-flow purging or PDB samplers) be selected and used throughout the performance monitoring program to ensure that data of comparable quality are collected. During longer duration monitoring programs, sites may change sampling approaches depending on testing requirements and use of the testing results, as well as for cost savings. Generally, however, before a change in method, comparisons are made to ensure that minimal deviations in concentrations are caused by a change.

Groundwater sampling and analysis for metals is typically undertaken during ISCO projects when metals sensitive to redox or pH are present or are incidentally introduced with the oxidant chemicals. Sampling for metals can require special procedures to avoid colloidal bias of analytical results. Manganese oxides, a colloidal particle generated during ISCO using permanganate, can be transported in groundwater and sorb some metals such as chromium. Therefore, submicron-filtration of the groundwater samples in the field prior to containerization is prudent in order to eliminate colloidal oxide-sorbed metals bias and obtain a groundwater analysis representative of the dissolved metals.

Typical sampling methods for aquifer solids include small discrete samples and long length intact cores collected with a Shelby tube or clear acetate sleeves. Aquifer solids samples can be collected using manually driven equipment, such as hand augers or drill rigs capable of DPT, hollow-stem, and sonic techniques. Care must be taken to collect a sample size that is representative using a method that results in the least amount of disturbance to the aquifer solids. Samples collected for VOC analysis require special methods to avoid contaminant loss during sampling, handling, shipping, and laboratory preparation. Examples of VOC sample

preservation to maintain the integrity of VOCs in the sample include the use of field solvent extraction, minimizing headspace, and storing the samples at a temperature of less than 4°C (Oesterreich and Siegrist, 2009).

Soil vapor sampling can be performed using multiple methods and can be a complex undertaking depending upon the intended use of the data. Data collection solely for documenting pre-existing conditions can use simpler methods than when risk assessment data quality are required. Considerable literature is available on this subject and the reader is advised to review it prior to implementing a baseline soil vapor survey (USEPA, 2008; ASTM, 2008; ITRC, 2007; DoD, 2008).

12.3.2.5 Frequency and Duration of Monitoring

Monitoring frequency generally refers to the number of times, and how frequently, a phase is monitored for a specific parameter. Monitoring duration refers to the overall period of time monitoring occurs. Sampling of aquifer solids and NAPL (if present) shortly before ISCO treatment is preferable to ensure conditions represent the baseline for comparison during oxidant delivery and for the assessment of treatment effectiveness. However, if prior characterization data reveals relatively constant subsurface conditions, then sampling once within a year of initiation of oxidant delivery may be adequate. Ideally, baseline groundwater and soil vapor monitoring, especially for the target COCs, should be conducted at least twice over a period of approximately a year immediately prior to implementing ISCO to gain an understanding of the ambient variability (including seasonality) inherent in many aquifer settings. These baseline monitoring data are particularly important as a reference for comparison with the post-ISCO treatment performance monitoring data. The magnitude of rebound can be more accurately estimated after accounting for any ambient variability in groundwater contaminant concentrations.

12.4 MONITORING DURING OXIDANT DELIVERY

12.4.1 Purpose and Scope

Monitoring of oxidant delivery is conducted to evaluate the nature and extent of oxidant distribution into the TTZ and any hydraulic effects associated with fluid injection such as water table mounding. Delivery monitoring includes physical measurements and sampling and analysis for parameters indicative of oxidant contact (past or current). Delivery monitoring does not typically include analysis of target COCs within the TTZ since this phase of monitoring is performed while oxidants may be present and the target contaminant(s) are still being actively degraded. Obtaining COC concentration data in the TTZ is the primary focus of the next phase of monitoring, ISCO treatment performance monitoring (Section 12.5).

Oxidant delivery monitoring is typically performed during and shortly after oxidant injection for one or more the following purposes:

- Develop a record of oxidant and activator injection flow rates and volumes.
- Develop a record of groundwater levels and hydraulic control methods.
- Monitor injection pressures to ensure aquifers are not plugging or excessive pressures are not applied that could cause well damage, formation deformation, or contaminant spreading outside the TTZ.
- Test observation wells for the appearance of the oxidant to determine if the planned distribution of an oxidant and activator (if used) is occurring throughout a TTZ.

- Monitor for changes in pH, DO, ORP, Ec and temperature, which can be used as indirect measures of oxidant distribution and chemical reactions.
- Monitor and manage aquifer conditions that affect oxidant chemistry such as pH.
- Monitor nearby utilities for potential breakout (i.e., sewer and storm drainage lines).
- Monitor migration/displacement of VOCs in vapor or groundwater during injection.
- Verify protection of sensitive receptors, human health, and the environment.

In general the delivery monitoring plan focuses on characterization of the nature and extent of oxidant delivery for the purposes of evaluating achievement of design conditions, deciding the scope of continued oxidant injection activities, and/or triggering contingency actions. As discussed in Chapter 11 (Section 11.6), the Observational Method is an adaptive approach that can be used during ISCO implementation. If the Observational Method is applied, then delivery monitoring data can be used to evaluate and optimize oxidant delivery operations. The delivery monitoring data are compared to trigger levels specified in an operational plan and the results are used to determine the next phase of work, whether it be for additional injections, lower pressure application, or delivery cessation because the delivery objectives have been achieved. Because delivery monitoring during ISCO is closely integrated with an operation plan, it is highly site-specific and the approach and methods outlined below are provided as suggestions only. It is most important that the scope of the delivery performance monitoring plan be consistent with the ISCO work planning documents, as discussed in Chapter 9 (Section 9.5).

Delivery performance monitoring includes physical and chemical measurements of equipment, injection fluids, and subsurface media. The goal of most delivery performance monitoring programs is to document delivery; if objectives are met, then the treatment performance monitoring phase of the ISCO project can proceed. If delivery goals are not met, then delivery efforts are adapted to achieve the goals or are optimized to come as close as possible. It is important that operational objectives (Section 12.2.1) be established that are consistent with the delivery design needs.

As discussed below, the approach and methods used during delivery performance monitoring depend on a variety of factors including the oxidant applied, the type of contamination being treated, and the oxidant's site-specific persistence in the formation. For some oxidants (e.g., CHP and ozone), delivery performance monitoring also includes the measurement of oxidant impact on groundwater temperature and off-gas generation in the vadose zone and well headspace. As such, delivery performance monitoring also can be an important component of a comprehensive ISCO health and safety program.

12.4.2 Approach and Methodologies

12.4.2.1 Delivery Performance Monitoring Approach

The equipment component of the delivery monitoring plan is dependent upon the oxidant delivery method used. Oxidant delivery methods can include:

- Direct-push probes
- Well injection (short- and long-term duration)
- Gaseous sparging
- Recirculation
- Trench or curtain
- Soil mixing (blending)

- Soil fracturing
- Surface application or infiltration gallery

Each of these delivery methods has unique infrastructure and equipment attributes (Chapter 11), which can dictate the approach needed to monitor delivery performance. In general, each of the above delivery methods should include the following monitoring devices:

- Pressure gauge (unless injection is under very low pressure)
- Flow rate meter and flow volume totalizer
- Fluid sampling port to measure injected oxidant (and activator if used) concentrations
- Flow control valve to allow optimization of delivery rates and volumes

Flow control is particularly important for manifolded delivery systems. Manifolded delivery systems are typically used to expedite oxidant delivery by concurrent injection into multiple wells or direct push points. Oxidant flow from a single injection header is typically split to multiple wells or points with similar or different subsurface screen intervals. As a result of the inconsistent screen depths and subsurface heterogeneity, variable injection pressure requirements exist for each well or point, which can cause non-uniform delivery. Therefore, it is important to measure the pressure requirement of each injection location and throttle pressure regulators and flow control valves to ensure adequate flow is provided. In some situations, it may be necessary to deliver oxidant into some lower permeability locations for a longer duration than others. Particular attention should be paid to flow totalizer data to ensure that design values are achieved.

The use of subsurface fracturing should be considered carefully as fracturing can lead to the production of preferential pathways. However, depending upon project oxidant delivery goals, lithologic fracturing may or may not be desired for an ISCO delivery. If oxidant delivery is desired without fracturing, then delivery monitoring must focus on remaining below a fracture threshold. Remaining below this pressure also minimizes the chances for failure of the annular seal of the injection well or point. The fracture threshold is primarily a summation of injection point headloss, formation pore entry pressure and internal friction angle, and overburden soil pressure (Payne et al., 2008). Payne et al. describe a method for estimating the allowable injection pressure.

For delivery methods using high pressures or pressures capable of entry into atmospheric locations, extreme caution should be taken to make regular visual observations of the surrounding area to minimize/avoid short-circuits, day-lighting, or surfacing of oxidation fluids into areas such as utilities, wetlands, surface water, or nearby extraction wells. As discussed below, these locations should be added to the delivery performance monitoring plan to ensure protection of human health and the environment.

A monitoring plan to assess oxidant distribution and effects in the TTZ and associated regions of the subsurface generally has similar elements to those outlined above for baseline monitoring (e.g., media to be sampled, locations to monitor, parameters to be analyzed, analytical frequency, and monitoring duration). Discussion of key elements is provided below. It should be noted that the suggestions provided below are for development of an initial delivery monitoring plan. As oxidant delivery proceeds and monitoring data are collected, an effort should be made to optimize the monitoring plan as necessary and appropriate based on interpretation of the new data. For example, there may be no need for additional oxidant measurements at locations where the presence of oxidant at targeted levels has already been observed.

Delivery performance monitoring for activated oxidants can be more complex because monitoring must also include the activator or conditioner. Sometimes this is as easy as monitoring pH to ensure proper acidic or alkaline conditions for the catalyzed hydrogen

peroxide or activated persulfate oxidation, respectively. For other sites, the monitoring may need to focus on additional chemical parameters such as iron, which is a catalyst for hydrogen peroxide and sodium persulfate reactions.

12.4.2.2 Media and Locations to Be Sampled

Media (e.g., groundwater and soil vapor) to be sampled during delivery performance monitoring include those that are identified within the operational objectives (Section 12.2). For example, groundwater monitoring is often required to verify the radius of influence (ROI) for oxidant distribution and to obtain information about oxidant persistence. Soil vapor may be sampled for ozone breakthrough and ROI information. Aquifer solids samples are not usually collected for the purposes of delivery evaluation and are not suggested for the typical ISCO project. However, if aquifer solids cores can be cost effectively collected, they can provide useful visual and analytical evidence for assessing delivery uniformity of a permanganate application. Discoloration in the subsurface due to staining by dark purple permanganate or dark brown manganese dioxides can provide direct evidence of oxidant delivery. Additionally, sub-samples can be extracted from a core for chemical analysis of pore water and solids. In some cases, as shown in Figure 12.2, the discoloration is not uniform which indicates preferential pathways within what appears to be a homogeneous sand formation. Aquifer solids cores can help evaluate delivery uniformity and whether additional injections or a different technique is needed to ensure a targeted uniformity of contact with the COCs.

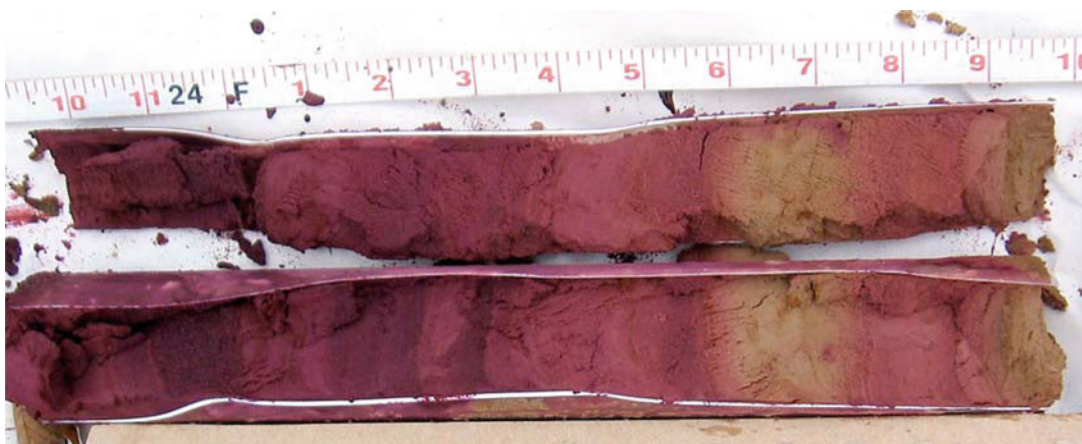


Figure 12.2. Aquifer solids core collected to verify permanganate distribution (from CH2M HILL project work at OU10, Hill Air Force Base, Utah).

Groundwater monitoring during oxidant delivery should generally encompass locations within the TTZ for establishing oxidant (and activator if used) delivery effectiveness and also locations immediately outside the TTZ for verification of extent of delivery. Some upgradient locations also may be included if natural fluctuations in ambient groundwater geochemistry are expected to vary sufficiently such that they would need to be monitored and screened out from the data collected within the TTZ; this could be caused by large precipitation events, for example. Understanding the water quality of the groundwater influx into a TTZ is important for assessing delivery effectiveness if surrogates such as Ec or ORP are used in lieu of direct oxidant measurements. For some sites, such as those with low NOD, high groundwater

advection, and potential downgradient receptors (e.g., surface water body or groundwater extraction well), downgradient monitoring may be implemented to ensure there are no unacceptable adverse effects.

Another consideration during delivery performance monitoring is that the injected oxidant solution's lateral and vertical distribution within groundwater in a TTZ is not typically uniform due to subsurface heterogeneities. Therefore, it is important to have an adequate, radial- and depth-variable monitoring network to capture the degree of non-uniformity of oxidant delivery. Vertically nested MLS wells also can be employed to provide a means of monitoring the vertical distribution of oxidant during injection, as well as MIP or DPT grab samples collected after the injection process.

As mentioned above, subsurface injection processes can be irregular and breach areas of least resistance. This can include obvious infrastructure like utility pipelines, trenches with high-permeability backfill or pipe bedding, and some not-so-obvious preferential pathways, such as overburden vadose zone desiccation cracks, open or naturally collapsed boreholes from previous investigations, or subgrade faults or cavities (e.g., limestone). As a result, project teams need to understand the subsurface at their sites and include monitoring of these potential pathways in their delivery monitoring programs.

12.4.2.3 Parameters and Analysis Methods

Table 12.7 contains suggestions for a delivery performance monitoring plan (parameter and frequency) for hydrogen peroxide, potassium or sodium permanganate, sodium persulfate, or ozone. Table 12.7 is focused on groundwater monitoring since that is typically the primary medium of concern and is provided for guidance purposes only. Site-specific conditions should be carefully considered prior to parameter selection, especially for ISCO projects employing oxidants with physical or chemical activation methods.

Field analytical methods are available for many of the parameters measured during oxidant delivery monitoring. Field methods generally have the advantage of rapid analyses yielding near real-time results and this can enable higher frequency monitoring. Selection of the proper field methods depends on project data needs and data quality objectives. Use of field analysis methods is particularly suited for projects with an aggressive schedule and the desire to achieve data objectives prior to demobilization.

Real-time measurements can be used to make delivery-related decisions, such as continuing or stopping oxidant injections to certain locations. If performed properly, use of field analyses can also be a cost-effective approach. For the purposes of delivery monitoring, unlike treatment performance monitoring for COCs (Section 12.5) when specific methods carried out by certified laboratories may be required, field analyses methods may provide data of sufficient quality. For example, field test kits for oxidant concentration are relatively accurate and may meet the data quality objectives to delineate oxidant distribution. Some field analysis methods are EPA-certified and may be able to meet more stringent data quality objectives if they are required for a project.

The number and diversity of field test methods continues to grow. One beneficial development in recent years has been in the area of continuous monitors with real-time, down-hole, and data-logging capabilities. Technology is available for monitoring simple parameters like E_c and temperature and some of the more complex parameters like VOCs and color. Data logging methods are attractive because they can reduce the labor required for delivery monitoring. Labor is typically a large component of monitoring cost; therefore, a relatively small to modest initial investment in a down-hole monitor can have a positive return on investment within the ISCO project period.

As shown on Table 12.7, there are some delivery-related parameters that must be measured in the laboratory. The analytical methods for ISCO projects are generally consistent with typical remediation practice, and few specialized techniques are required. The primary concern of using remote, fixed-based laboratory analysis during delivery performance monitoring is TAT; it is typically very important for results to be available quickly (near real-time) to optimize delivery while an injection contractor is mobilized. Laboratory analysis may be useful upon completion of the delivery activities to document the as-delivered subsurface conditions and to provide a confirmatory set of high quality data.

Table 12.7. Parameters Commonly Included During Oxidant Delivery Monitoring

Parameter	Hydrogen peroxide	Potassium or sodium permanganate	Sodium persulfate	Ozone	Example monitoring frequency ^a
Injection pressure	FI	FI	FI	FI	Constant
Injection flow rate	FI	FI	FI	FI	Constant
Injectate concentration	C, FK	C, FS, V, FK	C, FK	C, FI, FK	Daily during injection
Groundwater level or piezometric head	FI	FI	FI	FI	Daily during injection (or real-time monitoring with datalogger)
Temperature	FI		FI (heat activated)	FI	Daily during injection (or real-time monitoring with datalogger)
Color		V, DPT			Daily during injection
pH	FI, FK		FI, FK	FI, FK	Daily during injection (or real-time monitoring with datalogger)
DO	FI, FK			FI, FK	Daily during injection (or real-time monitoring with datalogger)
ORP	FI	FI	FI	FI	Daily during injection (or real-time monitoring with datalogger)
Specific conductance		DPT, FI	DPT, FI		Daily during injection (or real-time monitoring with datalogger), or once the day after injection
Alkalinity	L, FK			L, FK	Daily during injection
Oxidant	FK	FS, V, FK	FK	FI, FK	Daily during injection
Iron	L, FK		L, FK		Daily during injection
Sodium		L, FK	L, FK		Daily during injection

(continued)

Table 12.7. (continued)

Parameter	Hydrogen peroxide	Potassium or sodium permanganate	Sodium persulfate	Ozone	Example monitoring frequency ^a
Sulfate			L, FK		Daily during injection
Tracers	L, FI	L, FI	L, FI	L, FI	Daily during injection (or real-time monitoring with datalogger)
Vadose zone soil gas (CO ₂ , O ₂ , VOC, ozone)	FI			FI	Daily during injection

C - calculated, DPT - direct push technology (MIP for VOCs, conductivity probe for specific conductance), FI - field instrument (e.g., meter, gauge, thermometer), FK - field kit (e.g., colorimeter, color wheel, test strips), FS - field spectrophotometer, L - laboratory analysis.

^aActual monitoring frequency should be determined on a site- and an oxidant-specific basis, or negotiated as part of regulatory requirements. This may include extending the monitoring duration to accommodate longer-term re-equilibrium situations.

12.4.2.4 Sampling Methods

Sampling methods employed during oxidant delivery monitoring are essentially the same as those employed during site characterization (Chapter 10 [Section 10.4] and Tables 10.3 and 10.4) and baseline monitoring (Section 12.3.2.4). The reader is referred to these other sections for discussion of this topic.

12.4.2.5 Frequency and Duration of Monitoring

The frequency of data collection during delivery performance monitoring is highly dependent on the oxidant, injection design, and site-specific conditions. Monitoring during oxidant delivery is typically more frequent than during treatment performance monitoring (Section 12.5), and it may range from continuous monitoring with data logging to sampling and analysis carried out more than once a day to weekly for certain parameters. Delivery performance monitoring should generally be continued as long as the delivery system operates and oxidant persists in the subsurface. For example, for a longer-term ozonation project, primary monitoring may occur from a weekly to monthly basis. It is also important to understand the differences in oxidant distribution and injection fluid distribution when using indicators of oxidant distribution. Due to chemical reactions in the subsurface, the oxidant may not move as fast as the injected bulk solution or conservative (non-reactive) byproducts; this should be accounted for in the measurement frequency.

Measurement frequency and duration can be estimated from ISCO reagent delivery modeling or pilot testing. Estimates of measurement frequency are typically appropriate only for initial measurements. As data are collected, measurement frequency can be adjusted as long as data quality objectives are met (e.g., decrease frequency to avoid collecting unnecessary data or increase frequency to avoid missing key time points). The ability to adjust the sampling frequency should be incorporated into the initial sampling plan. As discussed previously, more frequent data collection during oxidant delivery is important to optimize delivery operations. Once delivery objectives are met, however, measurement frequency can be dramatically reduced or eliminated as the project progresses into the treatment performance monitoring

phase. Irrespective of site-specific choices, it is usually wise to collect a complete final round of measurements to formally document the final distribution of oxidant when the oxidant injection system is demobilized.

12.5 MONITORING OF TREATMENT PERFORMANCE

12.5.1 Purpose and Scope

ISCO is strongly influenced by the relatively slow pace of subsurface hydrogeologic and contaminant phase distribution equilibrium processes. As such, despite the rapid rates of ISCO contaminant destruction reactions, the re-equilibrated results of an ISCO application are typically not immediately observable. Therefore, treatment effectiveness monitoring within a performance monitoring program is typically initiated after oxidant delivery objectives are achieved and the goal is to determine whether the specific ISCO treatment goals established during the ISCO design phase have been met. Treatment performance monitoring is generally performed to achieve one or more of the following specific objectives:

- Measure progress toward and achievement of the ISCO treatment goals (e.g., the degree of source mass removal or source mass flux reduction).
- Evaluate nature and occurrence of recontamination and/or rebound within a TTZ.
- Evaluate changes in aquifer solids and water quality conditions due to ISCO operations.
- Monitor conditions to help determine the need for additional applications of ISCO or another technology using a treatment train approach.

Monitoring progress toward achieving an ISCO treatment goal is typically the primary objective of a treatment performance monitoring effort. Common ISCO treatment goals, discussed in detail in Chapter 9 (Section 9.3) and Chapter 10 (Section 10.6), typically include the following:

- Contaminant mass and/or mass flux reduction
- Numerical standard in a specific phase (soil gas, groundwater or aquifer solids)
- Removal of visible NAPL
- Achieving a risk-based concentration target

Treatment performance monitoring is often designed to include evaluation of the impact of ISCO on the mass of COCs in a TTZ, whether it is a specific ISCO treatment goal or not; this is because ISCO is most commonly used as a mass reduction technology and evaluation of the impacts to mass is typically indicative of the effectiveness of the ISCO treatment technology. At sites where mass flux reduction is an ISCO treatment goal, it may become important to understand the relationship between COC mass reduction in a TTZ and mass flux out of it. At many sites, the relationship is not linear and a large mass reduction may be needed to reduce the mass flux and meet an associated ISCO treatment goal. Refer to Chapter 10 (Section 10.4.2.2) for more information on this important issue.

Depending upon site-specific concerns of the stakeholders and others involved in the project, an objective of the treatment performance monitoring plan may also include monitoring the impact of ISCO on subsurface conditions. As discussed in [Section 12.2](#), ISCO has the potential to induce changes in geochemical conditions, microbial populations, and other site conditions.

Additionally, ISCO is often used as part of a combined remedy, and other remediation technologies, such as enhanced *in situ* bioremediation or monitored natural attenuation, may follow the application of ISCO (Chapter 7). In these situations, one of the objectives of the

treatment performance monitoring plan for ISCO can be to establish a baseline condition for a follow-up remedy. Therefore, parameters in addition to those specified, such as microbiological analysis, may be needed in the ISCO treatment performance monitoring plan.

12.5.2 Approach and Methodologies

12.5.2.1 Treatment Performance Monitoring Approach

A monitoring plan to enable evaluation of treatment performance should be developed to allow for modification based on initial observations and measurements. As the treatment monitoring proceeds, efforts should be made to optimize the monitoring plan as new data is collected and interpreted. For example, there may be no need for additional metals measurements if the initial measurements taken during the period of the oxidation reaction are negligible. As such, the treatment performance monitoring plan requires a dynamic component to allow real-time optimization by project stakeholders after review of performance monitoring results. It must allow for adjustments to monitoring parameters, locations, frequency, and durations as appropriate to obtain the necessary data to achieve the data objectives. Due to the short duration and rapid subsurface reactions typically associated with ISCO applications, a flexible performance monitoring plan is essential for efficiently and accurately assessing ISCO treatment performance and maximizing the value of investments in field and analytical resources.

12.5.2.2 Media and Locations to Be Sampled

Media to be sampled during treatment performance monitoring include those targeted for treatment and the focus of ISCO treatment goals. For example, if source zone mass reduction is established as a treatment goal, then sampling of aquifer solids (including NAPL, if present) and groundwater is important for mass estimation purposes. If COC mass flux is established as a treatment goal, then monitoring of groundwater along a downgradient transect(s) perpendicular to groundwater flow emanating from the ISCO TTZ may be all that is required.

As discussed in Chapter 11 (Section 11.4) and above, oxidant delivery and *in situ* chemical reactions can affect contaminant levels and spatial distribution. Therefore, it is important that all potentially affected media be monitored to enable comparison of post-ISCO conditions to baseline conditions. At sites using hydrogen peroxide or ozone, for example, soil vapor should be monitored to assess changes. This may be particularly important at sites with a concern for vapor migration and intrusion. NAPL, if present, may or may not be sampled during the treatment monitoring period depending upon the ISCO treatment goal (e.g., destruction of certain higher risk constituents in a NAPL vs. full treatment or biogeochemical stabilization). Likewise, if a site contains potentially mobile NAPL, then monitoring may be focused on verifying that the NAPL has not migrated.

Groundwater monitoring should generally encompass locations upgradient of the TTZ to determine the ambient influx of COCs, locations within the TTZ for evaluation of ISCO treatment effectiveness, and locations downgradient of the TTZ for treatment performance evaluation or water quality characterization (e.g., if downgradient migration of oxidants or byproducts is expected or if mass flux evaluations will be conducted as a treatment cessation criterion). Monitoring upgradient groundwater can be important for assessing treatment effectiveness while accounting for rebound/recontamination characteristics. If the baseline monitoring demonstrated significant variability in the influx of groundwater into the TTZ, then upgradient locations may be included to monitor influx water quality and use it as an upper bound expectation for contaminant reduction. Sampling within the TTZ is relatively straightforward for estimation of contaminant treatment efficiency. As discussed in

Section 12.4.2.2, downgradient monitoring is generally needed for projects designed for mass flux reduction or for assessing impacts to surrounding groundwater.

The appropriate number and spacing of monitoring points within a monitoring network depends on site-specific treatment goals and regulatory requirements. The monitoring network should be designed to achieve the data objectives for both operations monitoring (e.g., delivery effectiveness) and demonstration of treatment efficiency (e.g., treatment performance). For example, an adequate number of monitoring wells should be sited within and around the TTZ to demonstrate contaminant treatment efficiency both near the injection locations and at the farthest reaches of the predicted oxidant ROI. Where statistical methods may be used to estimate post-ISCO re-equilibrated conditions, an adequate number of sample locations will be needed to support a valid analysis.

Generally, injection points are not suited for monitoring of ISCO treatment performance. Concentrations of target COCs in injection wells should be lower than in the formation because of higher concentrations of oxidant; such measurements are not representative of post-ISCO conditions and can only be used for general progress monitoring purposes (i.e., oxidant persistence and some degradation rates). However, if sufficient time is allowed for hydro-geologic conditions to re-equilibrate after oxidant is consumed, monitoring at the injection points may be useful. Temporary DPT wells are an inexpensive way to augment an existing monitoring well network for post-ISCO treatment monitoring.

12.5.2.3 Parameters and Analysis Methods

Selection of treatment performance monitoring parameters depends on the oxidant to be used and the treatment goals established. Table 12.8 contains suggestions for treatment monitoring (parameter and frequency) for hydrogen peroxide, potassium or sodium permanganate, sodium persulfate, or ozone and is intended for general guidance only. Table 12.8 assumes that groundwater is the primary medium of concern. Specified frequencies are for example only. Site-specific considerations should be carefully evaluated prior to selecting monitoring parameters, especially for projects where specialized ISCO approaches are employed or where ISCO treatment goals are atypical or very stringent.

Table 12.8. Parameters Commonly Included During Monitoring of ISCO Treatment Effectiveness

Parameter	Hydrogen peroxide	Potassium or sodium permanganate	Sodium persulfate	Ozone	Example monitoring frequency ^a
Groundwater level or piezometric head	FI	FI	FI	FI	Periodically if deemed insightful
Temperature	FI	FI	FI	FI	Periodically if deemed insightful
Color	V	V, DPT			Periodically if deemed insightful
pH	FI, FK	FI, FK	FI, FK	FI, FK	Weekly to monthly
DO	FI, FK			FI, FK	Weekly to monthly
ORP	FI	FI	FI	FI	Weekly to monthly
Specific conductance		DPT, FI	DPT, FI		Weekly to monthly

(continued)

Table 12.8. (continued)

Parameter	Hydrogen peroxide	Potassium or sodium permanganate	Sodium persulfate	Ozone	Example monitoring frequency ^a
Alkalinity	L, FK			L, FK	Weekly to monthly
Oxidant	FK	FS, V, FK	FK	FI, FK	Weekly to monthly
Sulfate			L, FK		Weekly to monthly
Manganese		L, FK			Monthly for the first quarter
Chloride	L, FI, FK	L, FI, FK	L, FI, FK	L, FI, FK	Monthly and/or at end of treatment performance monitoring
COCs (groundwater)	DPT, L, FI, FK	DPT, L, FI, FK	DPT, L, FI, FK	DPT, L, FI, FK	Monthly to quarterly and/or at end of treatment performance monitoring
COCs (aquifer solids, also for vadose zone gases)	DPT, L, FI, FK	DPT, L, FI, FK	DPT, L, FI, FK	DPT, L, FI, FK	Post-ISCO, any time after the oxidant is consumed
Site-specific redox sensitive metals	L, FK	L, FK	L, FK	L, FK	At end of treatment performance monitoring
Geochemical indicators for NA (e.g., nitrate, CO ₂) ^b	L, FK	L, FK	L, FK	L, FK	At end of treatment performance monitoring
Microbiological parameters (e.g., biomass, DNA) ^b	L	L	L	L	At end of treatment performance monitoring

C - calculated, DNA - deoxyribonucleic acid, DPT - direct-push deployed sensor (for example, MIP for VOCs, conductivity probe for specific conductance), FI - field instrument (e.g., meter, gauge, thermometer), FK - field kit (e.g., colorimeter, color wheel, test strips), FS - field spectrophotometer, L - laboratory analysis, V - visual.

^aActual monitoring frequency should be determined on a site-specific and oxidant-specific basis, or negotiated as part of regulatory requirements. This may include extending the monitoring duration to accommodate longer term re-equilibrium situations.

^bAppropriate for systems utilizing a coupled approach with a biological component.

12.5.2.4 Sampling Methods

Sampling methods employed during oxidant delivery monitoring are essentially the same as those employed during site characterization (Chapter 10 [Section 10.4] and Tables 10.3 and 10.4) and for the other components of an ISCO performance monitoring program (i.e., baseline monitoring and oxidant delivery monitoring). However, data collection methods should be carefully considered with respect to data quality objectives and cost effectiveness. The method of data collection can range from simple sampling of dedicated wells, to DPT continuous core aquifer solids sampling or to real-time continuous data logging using down-hole sensors for VOC monitoring. The method chosen is typically based on site-specific conditions, so no additional method selection guidelines are provided here.

The use of real-time measurement techniques, such as DPT-employed technologies (e.g., MIP for evaluating the distribution of volatile contaminants) and down-well *in situ* sensors, have dramatically improved the ability to monitor ISCO treatment performance. Careful planning should be performed when employing DPT methods for monitoring, as the drilled probe holes, if not properly abandoned, can create preferential pathways for uncontrolled and undesirable oxidant migration during future oxidant injections.

12.5.2.5 Frequency and Duration of Monitoring

Treatment performance monitoring is typically conducted on a less frequent basis than delivery performance monitoring, but this varies depending on the longevity of the oxidant and time for re-equilibration, site-specific hydrogeology, and the regulatory monitoring requirements for ISCO by-products (e.g., redox-sensitive metals). In addition to the factors discussed in [Section 12.4.2.5](#), the data collection frequency and duration of a treatment performance monitoring effort are typically a function of the monitoring plan goals, oxidant persistence in the subsurface and the groundwater velocity through the TTZ.

Since ISCO is one of the more aggressive and rapid *in situ* remediation technologies, monitoring the impacts of ISCO often can be accomplished with a single sampling and analysis of the monitoring locations, as long as sufficient time has been allowed for re-equilibration of subsurface conditions within and near the TTZ. However, multiple monitoring events are useful if trying to evaluate trends or longterm effects such as re-contamination, contaminant rebound, persistence of metals, impacts to geochemical conditions, or post-ISCO biological activity.

It is ideal to start measuring field parameters (e.g., pH, Ec, DO, ORP and temperature) and oxidant concentrations soon after cessation of oxidant delivery to track migration and geochemical changes in the aquifer. In reality, this is simply a continuation of monitoring of a few relevant parameters used during the delivery performance monitoring phase. For contamination changes, however, it is generally best to monitor after the oxidant has been depleted in the subsurface and ample time has been allowed for re-equilibration of subsurface conditions. For ISCO projects employing relatively large doses of permanganate or persulfate at sites with low oxidant demand, it is common for the oxidant to persist for an extended period of time. Under these conditions, it may not be feasible to wait to start treatment performance monitoring. In fact, under these conditions, the presence of oxidant may be part of a longer term condition, and it may be necessary to begin monitoring while oxidation reactions are still occurring in and around the TTZ. In this case, alternative monitoring procedures may be required, such as the use of aquifer solids samples in lieu of groundwater samples. This may also be done if the contamination has a low solubility in water.

A practical approach to evaluating treatment performance monitoring duration is to perform monitoring until the parameters have stabilized to within the range of variability exhibited during baseline monitoring. [Figure 12.3](#) illustrates application of this approach for monitoring of trichloroethene (TCE) at a site. [Figure 12.3](#) shows a baseline TCE concentration ranging from 1,700 to 20,000 micrograms per liter ($\mu\text{g/L}$), slightly over one order of magnitude. After application of ISCO using permanganate, the TCE concentration was reduced to less than 10 $\mu\text{g/L}$ during active oxidation. When the permanganate oxidation reaction was complete (in July 2003), the TCE concentration rebounded to a range of 300–1,700 $\mu\text{g/L}$ for approximately 16 months. The variability exhibited during this period was similar to that observed during baseline and therefore, the 16-month duration of post-ISCO treatment monitoring was deemed sufficient to demonstrate re-equilibration and enable cessation of treatment performance monitoring.

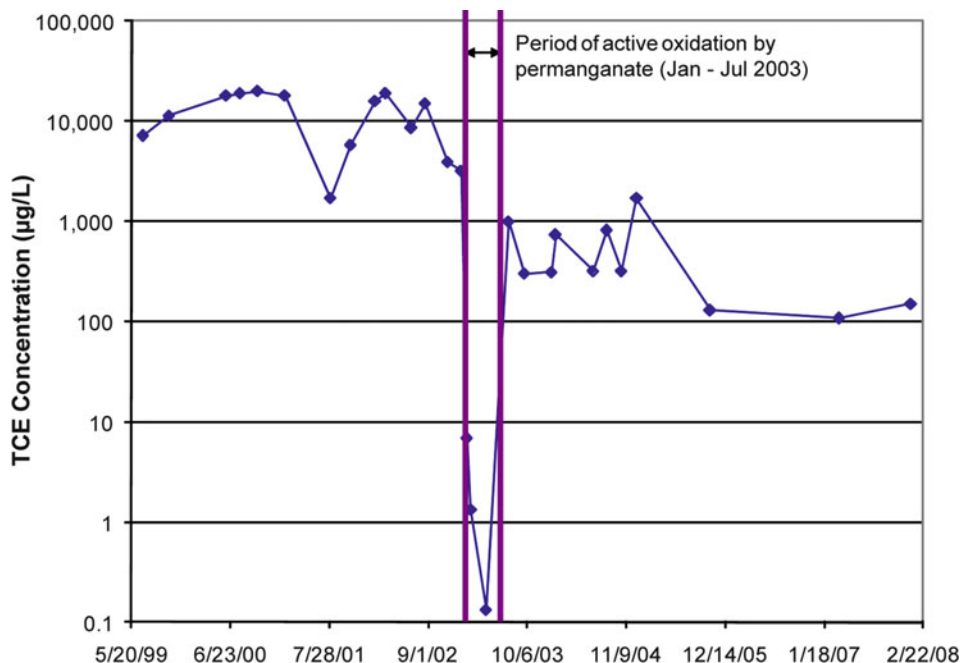


Figure 12.3. TCE concentration in groundwater before, during, and after permanganate oxidation.

The duration of monitoring for this approach (i.e., based on parameters stabilizing) is highly specific to each site and varies greatly from site to site. Project teams are advised to develop site-specific treatment performance monitoring guidelines that are based on site-specific data regarding likely re-equilibration processes. This data may be derived from pilot tests, previous subsurface treatment projects, or mathematical modeling.

For practical reasons, for some ISCO projects a fixed time period is established for post-ISCO monitoring. This is commonly done because of the unreasonably long period of time that may be required to achieve steady-state re-equilibrium conditions at some sites. Most state regulations specify a minimum amount of time for post-treatment monitoring prior to site closure, and this guidance can be used to help justify selection of post-ISCO monitoring duration. The Interstate Technology and Regulatory Council (ITRC) prescribes a minimum of 1 year following the completion of *in situ* treatment to ensure that no rebound occurs, to determine the effectiveness of treatment, and to evaluate whether the desired degree of oxidation and desorption was achieved in both saturated aquifer solids and the aqueous-phase (ITRC, 2005).

The design of an ISCO treatment performance monitoring plan should incorporate the potentially dynamic conditions that may exist or could be encountered in the field. The most common example is accounting for both average and preferential groundwater velocities. It is common for upgradient groundwater to migrate back into the TTZ immediately after hydraulic re-equilibration. If the upgradient groundwater is relatively uncontaminated then the performance assessment may not be affected since the measured concentrations within the TTZ will remain representative of the ISCO treatment performance. However, if the upgradient groundwater contains appreciable levels of COCs, there is a risk of recontamination of the aquifer solids and groundwater within the TTZ. In this situation, it is important to understand the rate of flow and quality of groundwater that migrates into the TTZ and to establish a time limit beyond which monitoring data collected in the TTZ may be tainted by contaminant influx. This tends to be a significant issue with pilot tests because they treat a subsection of a larger contaminated zone rather than treating the entire zone.

12.5.3 Data Evaluation

An ultimate objective of treatment performance monitoring is to collect data that determines progress towards or achievement of ISCO treatment goals. Interpreting monitoring data in support of evaluation of this objective should be subject to several important considerations as discussed below.

12.5.3.1 Aquifer Re-equilibration Evaluation

Most ISCO injection methods significantly disturb subsurface aquifer conditions via physical and chemical processes. Physical disturbance can be caused by drilling, groundwater extraction, displacement of groundwater by injected fluids and pressurized injection processes, and deposits left after oxidation (e.g., manganese oxides). Chemical disturbance can be caused by oxidation reactions, pH adjustments by oxidant activators, surfactant addition, and redox changes. At some sites, multiple pore volumes of low concentration oxidant fluids are delivered into a TTZ; in other cases, injected volumes of high oxidant concentration are only a small fraction of the pore volume of the TTZ. In either situation, it is important to account for these disruptions during data evaluation. Initial data evaluation should ensure that hydraulic re-equilibration (e.g., water table rebound) has occurred. After hydraulic re-equilibration, focus moves to chemical re-equilibration. Generally, chemical stabilization processes are slow due to groundwater flux and slow rates of chemical partitioning from aquifer solids of variable permeability (e.g., mobile and immobile subsurface domains). Chemical re-equilibration often requires a much longer period of time than hydraulic re-equilibration.

Monitoring of water levels and field water quality parameters (e.g., Ec, pH, DO, ORP and temperature) and tracer measurements can be used to understand the effects of displacement/dilution. Tracers contained in an oxidant solution, such as potassium/sodium or others added (such as bromide), can be used to assess dilution effects and re-equilibration. Baseline monitoring data should be compared to measurements taken within the TTZ over time to assess re-equilibration after the oxidation reactions are complete. When measurements within the TTZ fall within the range of ambient variation as determined during baseline monitoring, re-equilibration can be interpreted as complete. In most cases, the subsurface geochemistry within a TTZ eventually returns to near baseline conditions. ISCO effects at other sites may require a much longer duration to re-equilibrate. At these slower sites, effects from ISCO may appear quasi-permanent and require an alternative re-equilibration endpoint. This may involve discussions and negotiations with the interested parties after observation that certain conditions (e.g., pH, ORP or other parameters) have not returned to background. Chapter 10 provides discussion of alternative ISCO treatment endpoints.

12.5.3.2 Rebound and Recontamination

A concern inherent in remediation performance assessment is the potential for rebound of dissolved contaminant concentrations within the TTZ as a result of residual NAPL dissolution or back diffusion of dissolved COCs from low permeability layers that were not contacted or fully treated by oxidant during injections. Field experience (Chapter 8) indicates that rebound has occurred at ISCO sites, so the treatment performance monitoring plan should recognize the potential for some degree of contaminant rebound.

In general, ISCO should result in a significant reduction in contaminant mass within the TTZ over the course of the ISCO application. Since ISCO is generally viewed as a mass reduction technology, this abrupt change is typically best monitored in the phase(s) that contain a significant quantity of the contaminant mass (Section 12.5.2). The change in mass should be

permanent because these reactions are not reversible. However, long term monitoring of groundwater at certain sites has shown that aqueous concentrations decrease significantly soon after an ISCO application but gradually increase over time.

This phenomenon is collectively referred to as “rebound” even though it can be a combination of re-equilibration (technically termed rebound) and recontamination. Rebound occurs when contamination from within the TTZ re-partitions into groundwater from untreated aquifer solids or nonaqueous phases. Rebound is caused by the failure to contact a sufficient quantity of oxidant with the contaminant either because of oxidant distribution or insufficient oxidant application for the quantity of contamination mass present. Recontamination occurs when contamination from outside the TTZ migrates inward, re-contaminating the previously treated groundwater. While the result is the same, the cause of each of these phenomena is different. Recontamination occurs at sites that either intentionally locate the ISCO TTZ within a contaminant plume or at sites that failed to delineate the TTZ to include all of the significant contaminant mass.

Regardless, the rebound assessment procedure is important to demonstrate that an adequate amount of time is allowed post-ISCO reaction (i.e., after the oxidant is consumed) to allow for re-equilibration of the aquifer prior to final sampling and determination of treatment performance. Several methods can be used to determine the duration of post-ISCO monitoring. Regardless of the method selected, site-specific negotiations may likely be required based upon regulatory requirements and the objectives of site owners.

One method to evaluate rebound assessment procedures (e.g., monitoring frequency and duration) is to use mathematical modeling (Chapter 6). Mathematical modeling has been used for design and evaluation of ISCO technologies. In some cases, complex numerical models have been used to estimate the effects of rebound and back diffusion following application of source zone treatments such as ISCO and physical containment (Mundle et al., 2007; Chapman and Parker, 2005). However, these models are generally applied for research and educational purposes; they have not been widely used by ISCO practitioners. Therefore, the literature should be reviewed for general guidance and modeling should only be considered for complex DNAPL sites, for example, where the potential benefits outweigh the cost.

Because use of model simulations to estimate the re-equilibration timeframe is complex, uncertain, and expensive, many projects choose to collect multiple post-ISCO rounds of groundwater samples and use these results to judge aquifer stability and re-equilibrium. Taking a general rule of thumb from parameter stabilization criteria used during groundwater monitoring, a change of less than 10% in the field parameters and COC concentrations between three consecutive monitoring events can be used to demonstrate re-equilibration (USEPA, 1996). Alternatively, re-equilibration may be prescribed to have occurred when the geochemical parameter concentrations measured at certain monitoring locations are within the 95% confidence interval for the average baseline condition. Finally, as discussed earlier, a substantial length of time may be required for complete re-equilibration to occur depending upon the rates of advection versus COC desorption, back diffusion, and dissolution processes that occur in a particular lithologic and hydrogeochemical setting.

12.5.3.3 Consideration of Changes to Site Conditions

Data evaluation can be complicated by changes in subsurface conditions that occur during an ISCO project and treatment performance monitoring. Activities that can cause significant change in the TTZ conditions include heavy rainfall events, changes in nearby groundwater pumping operations, leaking utilities such as water mains or sewer lines, or facility construction/demolition. Even surface activities such as asphalt paving of a previously pervious surface

can have a dramatic effect on TTZ conditions. Ideally, ISCO treatments are conducted outside the times of these activities; however, some events are not preventable or foreseeable. Therefore, the value of baseline monitoring data should be carefully considered because it is dependent upon consistency in site conditions. If significant changes occur, then additional baseline data collection may be needed or re-evaluation of side-gradient data may be necessary as a point of comparison.

12.5.3.4 Statistical Methods

Multiple statistical methods are available for data evaluation (e.g., Gilbert, 1987; Helsel and Hirsch, 2002). While statistical methods may not be required, they may be useful for sites with the following data interpretation needs:

- Analyze large datasets that are generated for a large multi-layered, heterogeneous TTZ volume
- Generate spatially averaged chemical concentrations and upper confidence limits (UCLs)
- Test the statistical significance of a change in COC concentrations
- Perform a trend analysis of time-series concentration measurements for assessment of re-equilibration or treatment efficiency
- Estimate contaminant mass and mass flux reductions

Statistical methods have the unique capability to objectively analyze simple or complex data sets and, if applied appropriately, generate statistically valid and legally defensible results.

Geospatial techniques such as three-dimensional kriging can be a very useful tool to assist with the complex interpolation required to estimate pre- and post-treatment COC concentrations, mass levels and groundwater mass flux. Geospatial techniques are highly advanced and generally require a high-level of user training, as does most statistical analysis. The setup of geospatial “models” needs to be representative of the TTZ, and proper boundary conditions must be set to limit statistical analysis; this can be a complex undertaking for sites with complex hydrogeology. If necessary, multiple model domains must be established to stay true to site conditions. Simplifying assumptions should be carefully reviewed to ensure model applicability.

It should be noted that consensus among decision makers, including site regulatory officials, is prudent before statistical methods are chosen and applied. This is because the default for ISCO projects may be to meet treatment goals (i.e., target concentrations of COCs) at every point within the TTZ. In this case, simple comparison of the monitoring results to the treatment goals is all that may be needed for data interpretation. For other situations where it is recognized that *in situ* remediation often cannot achieve uniform treatment effectiveness throughout a TTZ, statistics may provide a means to make valid comparisons (e.g., comparing a 95% upper confidence limit on the average concentration of COCs after ISCO to a treatment goal).

The caveat is, however, that a statistically valid data set must be used for the analyses, which means that the monitoring plan must be designed with statistical data evaluation methods in mind. The appropriate number of samples must be collected from an adequate number of locations at enough points in time to generate meaningful statistical results; this is often challenging at environmental remediation sites with a limited budget. For example, because of the expense of collecting and analyzing aquifer solids samples, aquifer solids chemical data is rarely collected in adequate amounts to support statistical analysis, whereas groundwater data is often available and amenable to statistical analysis.

12.6 SUMMARY

A properly designed and executed performance monitoring program is essential to properly documenting ISCO implementation and to provide feedback on how to improve future applications. Examples of monitoring programs are provided in Appendix E. Baseline, delivery, and treatment performance monitoring data objectives are established to ensure that the operational objectives and treatment goals can be measured and evaluated. The performance monitoring program should help achieve and verify successful implementation of the ISCO system. As such, it must be designed to collect the necessary data and fit within project constraints such as schedule, site limitations, and budget. Performance monitoring data is also used to optimize the delivery process and to ensure that performance requirements are met in the face of uncertain subsurface response. The performance monitoring program must be flexible and adaptable and must pay close attention to a multitude of conditions that can confound data interpretation. ISCO project teams have access to a wide range of sample collection techniques, parameter measurement, and data analysis tools. The challenge is to select the most appropriate techniques to satisfy site-specific data objectives, to minimize redundancy, and remain within project budgetary and schedule constraints.

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CHAPTER 13

PROJECT COST AND SUSTAINABILITY CONSIDERATIONS

Thomas J. Simpkin,¹ Friedrich J. Krembs² and Michael C. Marley³

¹CH2M HILL, Englewood, CO 80112, USA; ²Aquifer Solutions, Inc., Evergreen, CO 80439, USA; ³XDD, Stratham, NH 03885, USA

Scope

Cost estimating approaches and key components that drive the cost of an *in situ* chemical oxidation (ISCO) system, including sustainability of applications.

Key Concepts

- Cost estimates can be prepared in a number of ways and levels of detail that influence accuracy. Understanding costing methods and associated uncertainty is necessary for effective ISCO implementation.
- The primary cost components of ISCO systems include professional services, capital costs, operations and maintenance (O&M) costs, and post-remediation closure. It is important to understand all of these components included in a cost estimate. The capital costs for ISCO systems may include the cost for wells and any infrastructure used. The cost for the oxidant may be included in the capital component, if the duration of the applications is short, or in the O&M component.
- Based on historical data (Chapter 8), the median cost of the ISCO projects in the database was \$220,000, while the median unit cost was \$94 per cubic yard (cy) treated. These costs should be used with caution because the cost components included in the data were not always consistent.
- For a hypothetical site (Section 13.4), the indirect capital costs, allowances, and markups were about 50% of the total capital costs. For this example, which used injection wells, drilling costs were 16% and injection costs were 62% of the total costs, respectively. These costs included both the labor and the chemicals. Monitoring, reporting, and site closure made up the rest of the costs.
- Making remediation projects more sustainable or greener is gaining in interest. A number of factors can be evaluated in a sustainability analysis of a project, including greenhouse gas emissions, energy consumption, reduction of risk to human health, returning an affected resource to beneficial use, and traffic fatalities and other injuries during implementation of the remedy.

13.1 INTRODUCTION

The cost of a remedial technology is a key factor in determining its viability. More specifically, a technology's cost versus the benefits it provides – compared to other alternatives – often will be the deciding factor in its selection and ultimate implementation. The costs and

benefits of a particular technology or approach must be assessed on a site-specific basis. This chapter provides a general discussion of cost estimating approaches, information on the primary components that drive the economics of *in situ* chemical oxidation (ISCO), and an example cost for a hypothetical site.

In addition to the traditional measures of a project’s effectiveness, implementability and cost, a relatively recent consideration for the selection of a remediation technology is its sustainability. Sustainable, or “green”, remediation can be defined in a number of ways, but the U.S. Environmental Protection Agency (USEPA) has defined it as “[t]he practice of considering all environmental effects of remedy implementation and incorporating options to maximize net environmental benefit of cleanup actions” (USEPA, 2008). Issues relating to the evaluation of the sustainability of ISCO remediation are also presented.

13.2 COST ESTIMATING APPROACHES

13.2.1 Classes of Estimates and Level of Details

Cost estimates can be prepared in a number of ways and with various levels of detail. This section provides an overview of the classification (the levels) of cost estimates and a discussion of possible methods to prepare them.

The American Association of the Advancement of Cost Engineering International (AACEI: previously the Association for the Advancement of Cost Engineering [AACE] International) has defined five classes of cost estimates (AACE International, 1997). The classes vary by the method and the procedures used to develop the estimates. Figure 13.1 illustrates the construction cost estimate classifications.

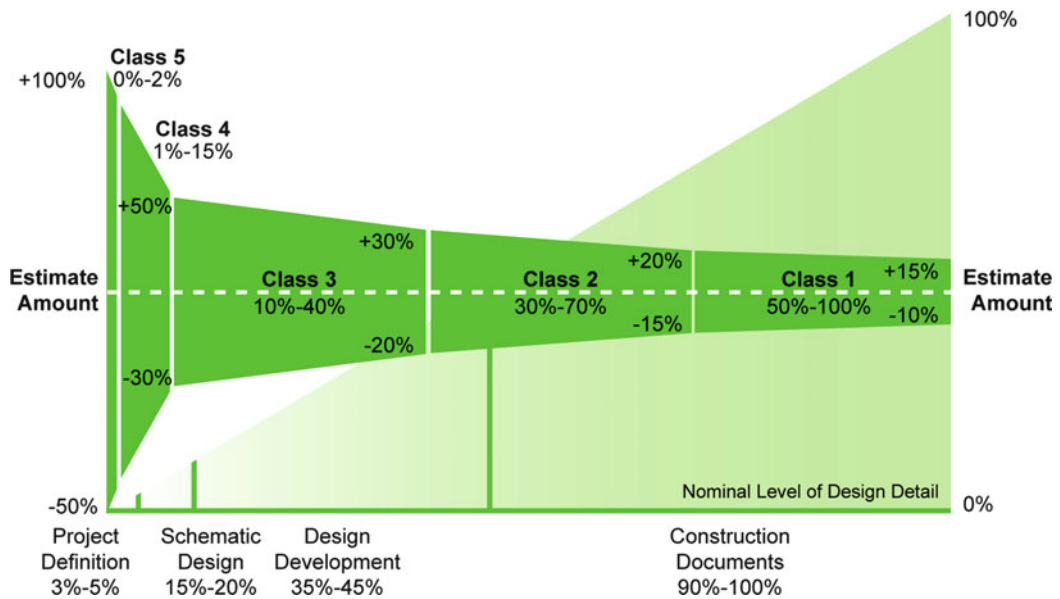


Figure 13.1. Construction cost estimating accuracy ranges (based on AACEI cost estimate classification system described in AACE International, 1997).

At the lower end of the spectrum are Class 5 estimates, which are generally concept, screening, or feasibility cost estimates. Class 5 estimates are generally used for comparison of remediation alternatives and are prepared based on limited information and possibly even

historical costs per area to be treated (although historical costs should be used with great caution). Class 5 estimates are generally accurate to +100 to –50%. On the other end of the spectrum, Class 1 estimates – which are “bid-tender” estimates – are based on detailed designs and bid documents. Class 1 estimates are based on detail takeoffs (e.g., measurements of pipe quantities from drawings) and unit price bids provided by equipment suppliers or vendors. Class 1 estimates are generally accurate to +15 to –10%.

Probably more common in remediation engineering efforts are Class 4 or 3 estimates. Class 4 estimates are feasibility study estimates based on pre- or conceptual designs, such as those prepared for feasibility studies. The level of accuracy for a Class 4 estimate is considered +50 and –30%. Class 3 estimates are budget-level estimates based on semi-detailed design information. Class 3 estimates are based on quotations (non-binding estimates) from equipment suppliers or vendors, but do not include detailed equipment takeoffs and are considered accurate to +30 and –20%. Class 2 or 3 estimate may be considered “engineers estimates” and are typically based on detailed designs prepared by engineers.

The procedure used to prepare a cost estimate will largely be a function of the class of cost estimate desired, the information available, and time and budget available. The USEPA Guide to Developing and Documenting Cost Estimates during the Feasibility Study (USEPA, 2000) is a good guidance document that should be consulted prior to implementing a cost estimate. Below is a brief discussion of the cost estimating methods that can be used.

13.2.2 Cost Estimating Methods

13.2.2.1 Historical and Parametric Cost Estimates

Historical and parametric estimates are based on historical costs (of previous projects) or “cost curves.” While cost curves are available for many water treatment technologies, they are not currently available for ISCO, so this not an option. Chapter 8 and Krembs (2008) present some information on historical costs. Historical, dollars per unit volume of treated soil costs could be used and assumed to be linear to estimate the costs for a given site. However, these per unit volume estimates could be inaccurate for the reasons discussed below. In addition, total costs are not likely to be linear with treated volume since some of the costs will be fixed (the same regardless of the volume treated), such as engineering and permitting.

The costs from a previous similar site could also be used and scaled up using the “power of 0.6 rule” which is as follows:

$$\frac{Cost_2}{Cost_1} = \left[\frac{Size_2}{Size_1} \right]^{0.6} \quad (\text{Eq. 13.1})$$

This scaling factor is commonly used for wastewater treatment facilities and other industrial systems (Remer and Chai, 1990). Size is typically the size or capacity of a treatment system. This equation may not be as applicable for *in situ* treatment technologies, which have less equipment than typical *ex situ* treatment systems.

13.2.2.2 Spreadsheet-Based Cost Estimates

Spreadsheets are often used to prepare Class 5, 4, or 3 estimates (and possibly Class 2 and 1). Section 13.4 provides an example of a spreadsheet for a Class 4 estimate. These spreadsheets may include various levels of detail depending on the desired class of estimate. For Class 3 or higher estimates, vendor or contractor quotes should be used. In this type of application, they can be considered detailed estimates. For Class 5 or 4, historical unit costs for items like well drilling may be used.

Spreadsheets do not need to be overly complex for Class 5 estimates and are preferred to using estimates based purely on historic costs. Spreadsheet-based estimates should be more site specific and accurate as long as the information feeding into them is accurate.

13.2.2.3 Remediation Cost-Estimating Software

Cost estimating software is available to assist with Class 5 or 4 estimates. Examples of software programs are Micro Computer Aided Cost Engineering System (MCACES), which is used by the Army Corps of Engineers, and Remedial Action Cost Engineering and Requirements (RACER). RACER is an environmental cost-estimating system originally produced by the U.S. Air Force (<http://www.fecpractice.com/?p=RACER>). It does not contain a module for estimating ISCO.

Most engineer consulting firms and construction contractors use cost-estimating software to develop Class 2 or 1 estimates. This software will estimate equipment and labor requirements for various civil works type of construction activities (e.g., excavation of soil). However, they are not likely to have the capability of estimating *in situ* remediation technologies, since they are not likely to have appropriate modules to estimate labor, chemicals, and equipment for drilling and injection. Consequently, hand input of cost data is often required. This data should include vendor and contractor quotes or bids for Class 2 and 1 estimates for specific activities and equipment (e.g., drilling and chemicals).

13.3 PRIMARY COST COMPONENTS

To understand the economics of ISCO, especially compared to other remedial technologies, it is important to understand the primary components that drive the total project costs. For this purpose, costs are categorized as: (1) professional services (including project management, design, laboratory testing, pilot testing, and construction management), (2) capital costs (generally including subcontractors and consumables), (3) operations and maintenance (O&M) (generally defined as post-injection activities), and (4) post-ISCO closure. The cost for the chemical oxidants, activators, and other required chemicals may be included in the capital costs or the operations costs. Other methods of classifying costs are often used. These are provided as a reference point. Table 13.1 provides information on the primary cost components.

Table 13.1. Primary Cost Components by Category

Subcategory	Description
Professional services	
Professional Services are costs associated with construction and O&M activities (e.g., capital, O&M, and post-closure) that are required to plan, design, procure, manage, oversee, and analyze the ISCO remedy. Professional/Technical Services cost elements can be broken down into sub-elements and include, but are not limited to, the following.	
Project management	Project management includes services that are not specific to remedial design, construction management, or technical support of O&M activities. Project management includes planning and reporting, community relations support during construction or O&M, and bid or contract administration.
Design characterization	As discussed in Chapter 9, additional design characterization beyond that required for traditional remediation investigations often will be necessary prior to the full-scale implementation of ISCO. This design characterization may include refining the vertical and horizontal delineation of the target contamination, obtaining natural oxidant demand (NOD) data, and defining other site hydrogeologic features.

(continued)

Table 13.1. (continued)

Subcategory	Description
Laboratory testing	Chapter 9 described the laboratory treatability testing that could be conducted to select, design, and evaluate an ISCO application.
Field pilot-scale testing	As discussed in Chapter 9, field pilot-scale tests may be desired in some situations. Such tests can be relatively simple and need not add substantially to the total cost. However, large and more complex pilot-scale tests maybe desired for some sites, which could increase the cost significantly. In such cases, it is usually beneficial to make the pilot tests large enough to achieve some significant remediation.
Mathematical analysis and modeling	As discussed in Chapter 6, modeling can be helpful in evaluating the potential removal capacity of a full-scale system, in designing a field demonstration, and in designing the full-scale system. The amount and cost of modeling desired as part of the design phase will depend on the hydrogeology, the chemical complexity of the site, and the degree of uncertainty that is acceptable.
Remedial design	As described in Chapter 9, various phases of design are required for typical ISCO system implementation. The cost for design should not necessarily be a significant component of the total cost, but these costs are likely to vary widely depending on the type of design chosen and the contract document requirements. For example, simple performance specifications imbedded in a Statement of Work may be sufficient for some projects, and the cost of such a design effort should be small. For typical civil construction projects (for example, road construction), the design may run 3–10% of the total construction cost. For remediation projects, the design costs for more complex designs are likely to be a higher percentage of the total because the design is less standard and the review process by the owner and regulators may be more rigorous and costly. For remediation projects, the design costs for complex designs may range from 6 to 20% of the total construction cost.
Construction management and service during construction	<p>Construction management and services during construction includes services to manage the following construction or installation of the remedial activities:</p> <ul style="list-style-type: none"> • Bidding and contract administration • Construction management and on-site observation • Change order negotiations • Submittal review and office services • Record drawings • Minor design modifications during construction • Preparations of O&M manual • Documentation of quality control/quality assurance <p>These are services typically provide by a consulting engineer or hydrogeologist and may often run between 5 and 10% of the total costs.</p>
Capital costs – direct	
<p>Numerous components make up a project’s construction or capital costs. The definition of capital costs for short-term injections, such as may be used with ISCO, is not hard and fast. If injection wells are used, their installation and any permanent equipment might be considered the capital costs and any injections considered operations cost. If all of the injections happened within a short time period (e.g., less than 2 years), it maybe easiest to consider them all capital costs. For ISCO projects, capital costs will generally include the items listed below:</p>	
Injection systems	<p>Injection wells or direct push points are the two most common approaches, as discussed in Chapter 11. The costs for wells or direct push points are typically a major component of the total ISCO project costs. The specific costs will depend on the hydrogeologic conditions and thus the number of wells or points needed. At some sites with very deep groundwater and difficult-to-drill conditions, individual wells can cost over \$300,000 each. In contrast, for sites with shallow groundwater and easy drilling or push conditions, total cost for the injection system may be as low as \$5,000 or less.</p>

(continued)

Table 13.1. (continued)

Subcategory	Description
Chemical mixing and delivery systems	Tanks, mixers, pumps, and piping are required to mix, dilute, and deliver the oxidant to the well or drive point. For the typical short-term ISCO project, many of these items will be rented or will be included in the injection contractor's total lump sum. A number of oxidant suppliers also rent the equipment for mixing their chemicals. For longer-term systems that use recirculation, the costs for this equipment can be significant.
Chemicals	The cost for the chemical oxidants, activators, and other required chemicals may be included in the capital costs or the operations costs.
General site preparation	Site preparation (e.g., grading and road development) may be required at a few sites with either difficult-to-reach well locations or where permanent recirculation systems are used.
Capital costs – indirect	
In addition to the major components identified above, other indirect capital costs or allowances and markups, are typically applied as a percentage of the total of the direct costs. Indirect capital costs may include the following:	
Mechanical/electrical installation	If permanent recirculation systems are installed and if uninstalled equipment costs are used, some allowance must be provided for installation of the equipment by a mechanical contractor and wiring of the equipment and its instrumentation by an electrical contractor. Factors for installation may range from 20 to 50%, depending on the requirement for mechanical or electrical work. If a detailed cost estimate is being prepared based on a detailed design, actual labor hours and rates can be estimated.
Contractor markups	Markups in the form of overhead, tax, bond and insurance, and profit (fee) are applied to arrive at the total bid price. Overhead includes two main types: (1) job or field-office overhead, also known as general conditions, and (2) home-office overhead, also known as general and administrative (G&A) costs. Markups are often applied to the estimate subtotal in a compounding manner to determine the total construction cost for the work.
Permitting and legal fees	These costs include permits and all legal fees associated with the project. A factor of 3–5% is typical for remediation projects. A larger percentage may be needed to cover permits or regulatory approvals required for the use of oxidants. Permitting can include Underground Injection Control (UIC) permits or Waste Discharge Requirements (WDRs) in California.
Contingency	A general contingency factor is typically included in cost estimates as a provision for unforeseen additional costs. Contingency costs have two components: bid contingency and scope contingency. Bid contingency covers the unknown costs associated with constructing a given project, such as adverse weather conditions, strikes by materials suppliers, geotechnical unknowns, existing utilities unknowns, and unfavorable construction market conditions. Scope contingency covers limited scope changes that invariably occur during remediation implementation. Contingency factors will vary depending on the level of cost estimating being prepared.
O&M	
O&M costs are post-construction costs necessary to maintain and monitor the continued effectiveness of the ISCO remedy. They may include the operations costs for long-term recirculation; they may also include additional injections of oxidants. Monitoring costs should also be included in this category of post-construction costs. Monitoring costs will include the labor for collection of samples, the analytical costs, and costs for preparing reports documenting the results of the project. A contingency also is typically applied to both the operations and the monitoring costs.	
Post-remediation closure	
At the completion of the remediation, the remediation wells, equipment, and piping will need to be dismantled, decontaminated, abandoned, or disposed. The cost of abandoning injection wells may be significant, if a large number of wells are installed. These costs are applied at the end of the project and often are not in the estimate or bid of the original ISCO contractor.	

Net present values (NPV) may be calculated for the longer-term costs if these costs are to be incurred out over a number of years. However, if the total number of years to be considered is relatively low (less than 5 years) and the discount rate to be used is low (as it is in 2010), the NPV may not be significantly different than the total costs. The USEPA Guide to Developing and Documenting Cost Estimates during the Feasibility Study (USEPA, 2000) or the Department of Defense (DoD) Instruction 7041.3: Economic Analysis and Program Evaluation for Resource Management (DoD, 1995) should be consulted for additional information on these components.

13.4 HISTORICAL AND ILLUSTRATIVE COST ESTIMATES

With the general understanding of the components of ISCO cost estimates from the above sections, actual costs for ISCO can now be considered. Section 13.4.1 discusses costs from case studies and Section 13.4.2 presents an illustrative example of the costs for a hypothetical example. Section 13.4.3 discuss issues to consider when comparing ISCO project costs.

13.4.1 ISCO Project Costs Based on Case Study Data

Chapter 8 and Krembs (2008) present information on historic costs for some ISCO projects included in a database of ISCO projects. The median cost of the ISCO projects in the database with data was \$220,000 ($n = 55$). Of those with enough information available to calculate a treatment zone volume ($n = 33$), the median unit cost was \$94 per cubic yard (cy) treated. However, these data should be used with caution for projecting costs for other projects because:

- The size of the target treatment zones (TTZs) at the sites used to calculate the unit costs from the database was relatively small (median of 6,300 cy). Hence, they may not be representative of larger projects without an adjustment factor.
- The information for each site that went into the database may not have been consistent with respect to what was included within the total project cost. For example, if only the costs from an ISCO vendor performing the injection are included, they may not include activities such as drilling, well abandonment, monitoring, and reporting.
- The ISCO application may not have been optimized (e.g., higher injection volumes might have increased the radius of influence and reduced the number of wells required).

However, the data do indicate a number of interesting trends. As discussed in Chapter 8, total costs were higher when dense nonaqueous phase liquids (DNAPL) was present, and the unit costs decrease as the volume of the TTZ increases. No correlation was found in regression analysis between the contaminant treated or the oxidant used (fuel-related sites had on average a lower cost, but this impact appeared to be due to the smaller treatment volume at these sites).

The Electric Power Research Institute (EPRI) has estimated costs for using ISCO for Manufactured Gas Plant (MGP) sites to range from \$100/cy to \$500/cy (EPRI, 2007). These costs may be higher than those from the database due in part to the high levels of contamination typically encountered at MGP sites (typically in the 1,000s of milligrams per kilogram) and the resulting robust and expensive designs.

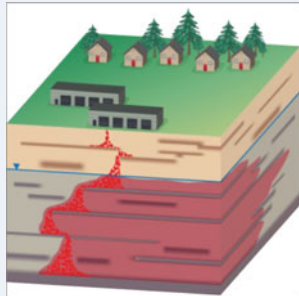
13.4.2 ISCO Project Costs Based on an Illustrative Example

To illustrate the cost of components for a typical ISCO application, the costs for an illustrative hypothetical example have been developed. Example 13.1 summarizes this site, which is the same as Example 9.1 discussed in Chapter 9. Table 13.2 provides a summary of

the conceptual design and assumptions for this site, while Tables 13.3–13.6 presents the detailed cost breakdown, and Table 13.7 provides a summary.

This illustrative example of a realistic ISCO project includes the use of sodium persulfate, injected into 25 injection wells, over the source area. It was assumed that one full injection would be performed the first year, and a second injection, with 75% of the full injection persulfate mass, would be performed the second year. The costs include 3 years of operations and monitoring, at which time the wells were abandoned.

For this example, the injections performed the first year were considered as part of the O&M costs. Only the well drilling is considered as part of the capital costs. The costs presented here are total costs and not net present worth costs. In this case, the project duration was so short, the difference between the present worth and total cost is relatively small.

Example 13.1. Cost estimate for a hypothetical site	
<p><i>Site X</i> contains chlorobenzenes where total chlorinated volatile organic compounds (CVOCs) in groundwater are present in concentrations up to 30,500 µg/L and are present in porous media in concentrations up to 40,000 µg/kg. DNAPL is suspected in some areas. Through site characterization activities, it has been determined that the greatest contaminant impact is between 10 and 30 ft below ground surface (bgs) over an area 100 ft by 100 ft. This site is permeable and heterogeneous glacial till with an average hydraulic conductivity of approximately 50 ft/day. The treatment goal at the site is simply to achieve some mass reduction.</p>	<p>Contaminants:</p> <ul style="list-style-type: none"> • Chlorobenzenes • Concentrations up to 30,500 µg/L total CVOCs in groundwater and 40,000 µg/kg in soil • DNAPL suspected in some areas • Greatest impact at 10–30 ft bgs <p>Geology/hydrology:</p> <ul style="list-style-type: none"> • Glacial till • Permeable and heterogeneous • Hydraulic conductivity (K) = 50 ft/day <p>Remedial action objectives:</p> <ul style="list-style-type: none"> • Reduce mass of CVOCs
	

Based on the information in Table 13.7, the indirect costs (basically everything besides the actual field work including allowances, and markups) can be a significant fraction of the cost. For this example, the indirect costs are about 50% of both the total capital cost and total O&M costs. This is very common with all remediation technologies and construction in general. However, care should be taken not to double count some of these markups when using quotes or bids from vendors or contractors. Vendor and contractor quotes should already include some of these markups, such as profits and fee.

The other major factors driving the total cost are revealed in the data. For example, the drilling costs for this example were about 16% of the total project cost. The injection costs (which were incurred over the first 2 years), were 62% of the total project cost. These injection costs include the associated markups tied to them, including contingency, as well as both the chemicals and the labor/equipment to perform the injections. The chemicals are about 60% of the injection cost in this example. As expected, the drilling and the injections were the majority of the total cost. Monitoring, reporting, and site closure make up the rest of the cost.

The cost for this example is \$154/cy, which is higher than the median cost of sites in the database discussed in Chapter 8. This cost example is potentially more inclusive (e.g., includes well abandonment) than costs reported in the database, which may be one reason it is higher. Another

possible reason is that the design is relatively conservative, and assumes a full pore volume will be injected with a radius of influence of 12.5 ft (well to well spacing of 25 ft). The costs could be brought down to \$105/cy if persulfate dose is reduced to 1 g/kg, and down to \$60/cy if the well to well spacing is increased to 40 ft (requiring seven wells), and only 50% of a pore volume is assumed to be injected. However, such an aggressive design might not have been effective for the site.

Table 13.2. Summary of the Conceptual Design and Assumptions

COST ESTIMATE ASSUMPTIONS – Direct injection into permanent wells				
Site: Site X		Prepared by: P. Eng		
Alternative: source remediation		Project number: 012345.67.89		
Description: activated persulfate injection – injection wells				
Note: some cells have user inputs and others are calculated				
	Value	Units	Value	Units
1. Site background data				
<i>Treatment zone</i>				
Length of target groundwater contamination zone	100	ft		
Width of target groundwater contamination zone	100	ft		
Area of contaminated groundwater target zone	10,000	sf		
Top of injection interval	10	ft bgs		
Bottom of injection interval	30	ft bgs		
Saturated thickness	20	ft		
Total porosity	0.4			
Volume of contaminated groundwater	598,440	gal		
Bulk density (dry weight basis)	110	lb/cu ft		
Volume of contaminated soil	7,407	cy		
Mass of contaminated soil	22,000,000	lb		
2. Oxidant delivery				
Preferred oxidant:	Persulfate			
Desired injected pore volumes for treatment	1			
Target injection volume	598,440	gal		
Target injection volume (from vendor or other design tool)	–	gal		
User-selected injection volume	598,440	gal		
Injection or rate per well	10	gpm		
Number of wells injected simultaneously	8			
Hours per day injected	8	hours		
Amount of active injection time	16	days		
Oxidant dose	4	g/kg soil		
Oxidant mass (total)	88,000	lb	17,632	mg/L

(continued)

Table 13.2. (continued)

COST ESTIMATE ASSUMPTIONS – Direct injection into permanent wells				
Site: Site X			Prepared by: P. Eng	
Alternative: source remediation			Project number: 012345.67.89	
Description: activated persulfate injection – injection wells				
Note: some cells have user inputs and others are calculated				
	Value	Units	Value	Units
Total mass of activator required (type and unit costs to be entered in cost details)	User entered	→	44,000	lb
Total mass of acid conditioner (type and unit costs to be entered in cost details)	N/A	→		lb
3. Injection system design				
<i>Injection well design</i>				
Well spacing	20			
Well placement in assumed grid pattern	5	by	5	
Number of wells	25			
Injection well depth	30			
Total linear feet of injection wells	750			
Wellhead completion method (select from pull-down menu)	Flush Mount			
Number of well head completions	25			
<i>Waste generation quantities</i>				
Drilling method (select from pull-down menu)	Hollow-Stem Auger			
Diameter of boreholes	8	in.		
Waste soil volume	9.69	cy		
Waste containerization requirements	36	55-gal drums		
<i>Field piping design (if applicable for manifold or recirculation design)</i>				
Length of trenching	0	lf		
Size of piping		in.		
Length of in piping		lf		
Quantity of pipe bedding		cy		
Quantity of backfill		cy		
Quantity of excavation waste		cy		
4. Monitoring system design				
Number of monitoring new wells	3			
New monitoring well depth (feet)	30			
Total linear feet of new monitoring well	90			
Wellhead completion method (select from pull-down menu)	Flush Mount			
Number of wellhead completions	3			
<i>Waste generation quantities</i>				
Drilling method (select from pull-down menu)	Hollow-Stem Auger			
Diameter of boreholes	8	in.		

(continued)

Table 13.2. (continued)

COST ESTIMATE ASSUMPTIONS – Direct injection into permanent wells				
Site: Site X			Prepared by: P. Eng	
Alternative: source remediation			Project number: 012345.67.89	
Description: activated persulfate injection – injection wells				
Note: some cells have user inputs and others are calculated				
	Value	Units	Value	Units
Waste soil volume	1.16	cy		
Waste containerization requirements	5	55-gal drums		
Total number of monitoring wells to be sampled	4			
Sampling rounds per year	4			
Total wells sampled per year	16			
Estimated total samples per well per round	1			
Estimated total samples per year	24			
5. Construction timeframe				
Total linear feet of drilling	840			
Drill rig production rate (including well completion)	100	ft/day		
Number of on-site days for drill rig	8	days		
Number of days for on-site equipment fabrication (if applicable)	0	days		
Total linear feet of trenching	0			
Trenching production rate (including pipe and backfill)	200	ft/day		
Number of days for trenching	0	days		
Number of days for equipment mobilization	2	days		
Total number of days for construction	10	days		
6. Injection time				
Total number of days for mobilization and site setup	2	days		
Amount of active injection time	16	days		
Amount of time for equipment setup and breakdown	50	hours (assumed: 1 h setup, 1 h breakdown per well)		
Total number of days for injection	18	days		
7. Post-remediation closure				
Wells to be abandoned	28	wells		
Total number of days for well abandonment	9	days		
Total number of days for equipment demobilization	1	day		
Total number of days for site restoration	10	days		

Note: bgs - below ground surface, cu ft - cubic feet, cy - cubic yard, ft - feet; g/kg - grams per kilogram, gal - gallon; gpm - gallons per minute; h - hour, in. - inch, lb - pound, lf - linear feet, mg/L - milligrams per liter, sf - square feet.

Table 13.3. Detailed Cost Breakdown – Capital Costs

COST ESTIMATE DETAILS					
Site: Site X			Prepared by: P. Eng		
Alternative: source remediation			Project number: 012345.67.89		
Description: activated persulfate injection – injection wells					
Note: some cells have user inputs and others are calculated					
Item/activity	Qty	Unit	Unit cost	Cost	Comments and references
CAPITAL COST					
Construction					
Pilot test					
Source area pilot test	0	ea	\$ 50,000.00	\$ 0	Field test at source to determine optimum oxidant/dose
Well installation and trenching subcontractors					
Well installation mobilization	1	ea	\$ 2,500.00	\$ 2,500	Hollow-Stem Auger
Injection well installation	750	lf	\$ 50.00	\$ 37,500	Sch40 PVC
Injection wellhead completions	25	ea	\$ 400.00	\$ 10,000	Flush Mount
Monitoring well installation	90	lf	\$ 40.00	\$ 3,600	Hollow-Stem Auger
Well development equipment rental	1	LS	\$ 2,000.00	\$ 2,000	Includes water quality meter, pumps, generator, tubing
Monitoring wellhead completions	3	ea	\$ 400.00	\$ 1,200	Flush Mount
Well permits	28	ea	\$ 30.00	\$ 840	Assume 1 permit for each well
IDW soil disposal	41	drum	\$ 350.00	\$ 14,350	Assume characterization, management, storage, transportation
Per diem for drilling subcontractors	10	days	\$ 624.00	\$ 6,240	Assume all travel expenditures (food, hotel, etc.)
Oversight					
Construction/well installation oversight	125	h	\$ 70.00	\$ 8,736	Assumes 12 h days
Well development labor – technician	56	h	\$ 70.00	\$ 3,920	Assumes 2 h development per well
System startup oversight	0	h	\$ 90.00	\$ 0	
Subtotal capital cost				\$ 90,886	
Site work allowance	0%	of	\$ 90,886.00	\$ 0	
Mechanical allowance	0%	of	\$ 90,886.00	\$ 0	
Instrumentation and controls allowance	0%	of	\$ 90,886.00	\$ 0	

(continued)

Table 13.3. (continued)

COST ESTIMATE DETAILS					
Site: Site X			Prepared by: P. Eng		
Alternative: source remediation			Project number: 012345.67.89		
Description: activated persulfate injection – injection wells					
Note: some cells have user inputs and others are calculated					
Item/activity	Qty	Unit	Unit cost	Cost	Comments and references
Electrical allowance	10%	of	\$ 90,886.00	\$ 9,089	
Miscellaneous equipment allowance	0%	of	\$ 90,886.00	\$ 0	
Subtotal capital cost				\$ 99,975	
Project management	8%	of	\$ 99,974.60	\$ 7,998	
Design	15%	of	\$ 99,974.60	\$ 14,996	
Construction management	5%	of	\$ 99,974.60	\$ 4,999	
Subtotal capital cost				\$ 127,967	
G&A	5%	of	\$ 127,967.49	\$ 6,398	
Field overhead	5%	of	\$ 127,967.49	\$ 6,398	
Tax				\$ 0	
Contingency	15%	of	\$ 127,967.49	\$ 19,195	
Subtotal capital cost				\$ 159,959	
Bonding and insurance	2%	of	\$ 159,959.36	\$ 3,199	
Fee	8%	of	\$ 159,959.36	\$ 12,797	
Total capital cost				\$ 175,955	

Note: ea - each, G&A - general and administrative, h - hour, IDW - investigative derived waste, lf - linear feet, LS - lump sum, Sch40 PVC - schedule 40 polyvinyl chloride.

Table 13.4. Detailed Cost Breakdown – First Year Implementation and Monitoring Costs

COST ESTIMATE DETAILS					
Site: Site X			Prepared by: P. Eng		
Alternative: source remediation			Project number: 012345.67.89		
Description: activated persulfate injection – injection wells					
Note: some cells have user inputs and others are calculated					
Item/activity	Qty	Unit	Unit cost	Cost	Comments
FIRST YEAR IMPLEMENTATION AND MONITORING					
Groundwater sampling					
Labor – technician	96	h	\$ 55.00	\$ 5,280	3 h/well, 2 people
Groundwater sample analysis	24	sample	\$ 450.00	\$ 10,800	VOC/MNA/metals analysis, incl. QA/QC samples and data validation
Sampling supplies	4	round	\$ 500.00	\$ 2,000	Includes consumables, shipping

(continued)

Table 13.4. (continued)

COST ESTIMATE DETAILS					
Site: Site X			Prepared by: P. Eng		
Alternative: source remediation			Project number: 012345.67.89		
Description: activated persulfate injection – injection wells					
Note: some cells have user inputs and others are calculated					
Item/activity	Qty	Unit	Unit cost	Cost	Comments
GW sampling equipment rental	4	round	\$ 1,300.00	\$ 5,200	Includes w/ meter, down hole water quality meter, pumps, generator
Total groundwater sampling				\$ 23,280	
Injection					
Subcontractor mobilization and per diem	2	days	\$ 900.00	\$ 1,800	Includes all support equipment, oxidator transport, and implementation
Oxidant supply	88,000	lb	\$ 1.75	\$ 154,000	Included shipping and handling
Activator supply	44,000	lb	\$ 0.39	\$ 17,160	25% NaOH solution
Acid conditioner supply	0	lb	\$ 1.30	\$ 0	
Injection and mixing equipment rental	16	days	\$ 100.00	\$ 1,600	
Injection subcontractor – labor	16	days	\$ 6,000.00	\$ 96,000	
Labor – engineer/hydrogeologist	160	h	\$ 90.00	\$ 14,400	
Total system startup (one injection event)				\$ 284,960	
Number of injection events (first year)	1	events			
Total injection				\$ 284,960	
Reporting					
Labor – engineer/hydrogeologist	160	h	\$ 90.00	\$ 14,400	
Labor – editor	20	h	\$ 65.00	\$ 1,300	
Labor – CAD technician	8	h	\$ 75.00	\$ 600	
Total reporting				\$ 16,300	
Subtotal injection implementation and monitoring				\$ 324,540	
Project management	8%	of	\$ 324,540.00	\$ 25,963	
Technical support	5%	of	\$ 324,540.00	\$ 16,227	
Construction management	0%	of	\$ 324,540.00	\$ 0	
Subtotal year 1 operations and monitoring				\$ 366,730	
G&A	5%	of	\$ 366,730.20	\$ 18,337	
Field overhead	5%	of	\$ 366,730.20	\$ 18,337	

(continued)

Table 13.4. (continued)

COST ESTIMATE DETAILS					
Site: Site X			Prepared by: P. Eng		
Alternative: source remediation			Project number: 012345.67.89		
Description: activated persulfate injection – injection wells					
Note: some cells have user inputs and others are calculated					
Item/activity	Qty	Unit	Unit cost	Cost	Comments
Tax				\$ 0	
Contingency	15%	of	\$ 366,730.20	\$ 55,010	
Subtotal year 1 operations and monitoring				\$ 458,413	
Bonding and insurance	0%	of	\$ 458,412.75	\$ 0	Bonding only applies to capital costs
Fee	8%	of	\$ 458,412.75	\$ 36,673	
Total first year implementation and monitoring cost				\$ 495,086	

Note: CAD - computer aided design, G&A - general and administrative, GW - groundwater, h - hour, lb - pound, MNA - monitored natural attenuation, NaOH - sodium hydroxide, QA/QC - quality assurance/quality control, VOC - volatile organic compound.

Table 13.5. Detailed Cost Breakdown – Second- and Third-Year Implementation and Monitoring Costs

COST ESTIMATE DETAILS					
Site: Site X			Prepared by: P. Eng		
Alternative: source remediation			Project number: 012345.67.89		
Description: activated persulfate injection – injection wells					
Note: some cells have user inputs and others are calculated					
Item/activity	Qty	Unit	Unit cost	Cost	Comments
SECOND YEAR IMPLEMENTATION AND MONITORING					
Groundwater sampling (% of first year cost)	50%	of	\$ 23,280.00	\$ 11,640	
Injection (% of first year cost)	75 %	of	\$ 284,960.00	\$ 213,720	
Reporting (% of first year cost)	50%	of	\$ 16,300.00	\$ 8,150	
Professional services (% of first year cost)	50%	of	\$ 42,190.20	\$ 21,095	
Subtotal year 2 O&M				\$ 254,605	
G&A	5%	of	\$ 254,605.10	\$ 12,730	
Field overhead	5%	of	\$ 254,605.10	\$ 12,730	
Tax				\$ 0	
Contingency	15%	of	\$ 254,605.10	\$ 38,191	
Subtotal year 2 O&M				\$ 318,256	
Bonding and insurance	0%	of	\$ 318,256.38	\$ 0	Bonding only applies to capital costs
Fee	8%	of	\$ 318,256.38	\$ 25,461	
Total second year implementation and monitoring cost				\$ 343,717	

(continued)

Table 13.5. (continued)

COST ESTIMATE DETAILS					
Site: Site X			Prepared by: P. Eng		
Alternative: source remediation			Project number: 012345.67.89		
Description: activated persulfate injection – injection wells					
Note: some cells have user inputs and others are calculated					
Item/activity	Qty	Unit	Unit cost	Cost	Comments
THIRD YEAR IMPLEMENTATION AND MONITORING					
Groundwater sampling (% of first year cost)	25%	of	\$ 23,280.00	\$ 5,820	
Injection (% of first year cost)	75%	of	\$ 284,960.00	\$ 0	
Reporting (% of first year cost)	25%	of	\$ 16,300.00	\$ 4,075	
Professional services (% of first year cost)	25%	of	\$ 42,190.20	\$ 10,548	
Subtotal year 3 operations and monitoring				\$ 20,443	
G&A	5%	of	\$ 20,442.55	\$ 1,022	
Field overhead	5%	of	\$ 20,442.55	\$ 1,022	
Tax				\$ 0	
Contingency	15%	of	\$ 20,442.55	\$ 3,066	
Subtotal year 3 operations and monitoring				\$ 25,553	
Bonding and insurance	0%	of	\$ 25,553.19	\$ 0	Bonding only applies to capital costs
Fee	8%	of	\$ 25,553.19	\$ 2,044	
Total third year implementation and monitoring cost				\$ 27,597	
Total implementation and monitoring cost (2nd and 3rd year)				\$ 371,314	

Table 13.6. Detailed Cost Breakdown – Post-closure Costs

Cost estimate details					
Site: Site X			Prepared by: P. Eng		
Alternative: source remediation			Project number: 012345.67.89		
Description: activated persulfate injection – injection wells					
Note: some cells have user inputs and others are calculated					
Item/activity	Qty	Unit	Unit cost	Cost	Comments
POST-CLOSURE COST					
Closure reporting					
Labor – engineer/hydrogeologist	80	h	\$ 90.00	\$ 7,200	
Labor – editor	16	h	\$ 65.00	\$ 1,040	
Labor – CAD technician	8	h	\$ 75.00	\$ 600	
Total closure reporting				\$ 8,840	

(continued)

Table 13.6. (continued)

Cost estimate details					
Site: Site X			Prepared by: P. Eng		
Alternative: source remediation			Project number: 012345.67.89		
Description: activated persulfate injection – injection wells					
Note: some cells have user inputs and others are calculated					
Item/activity	Qty	Unit	Unit cost	Cost	Comments
Well abandonment and equipment demobilization					
Well abandonment	28	well	\$ 300.00	\$ 8,400	Assumes abandonment of injections wells and new monitoring wells
Well abandonment permits	28	well	\$ 30.00	\$ 840	
Equipment demobilization	1	day	\$ 500.00	\$ 500	Assumes equipment reclamation and shipping returns
Equipment rental	1	week	\$ 200.00	\$ 200	PID
Subtotal well abandonment and equipment demobilization				\$ 9,940	
Site work allowance	10%	of	\$ 9,940.00	\$ 994	
Mechanical allowance	10%	of	\$ 9,940.00	\$ 994	
Instrumentation and controls allowance	0%	of	\$ 9,940.00	\$ 0	
Electrical allowance	0%	of	\$ 9,940.00	\$ 0	
Miscellaneous equipment allowance	0%	of	\$ 9,940.00	\$ 0	
Total well abandonment and equipment demobilization				\$ 11,928	
Subtotal post-closure cost				\$ 20,768	
Project management	8%	of	\$ 20,768.00	\$ 1,661	
Technical support	15%	of	\$ 20,768.00	\$ 3,115	
Construction management	15%	of	\$ 20,768.00	\$ 3,115	
Subtotal post-closure cost				\$ 28,660	
G&A	5%	of	\$ 28,659.84	\$ 1,433	
Field overhead	5%	of	\$ 28,659.84	\$ 1,433	
Tax				\$ 0	
Contingency	20%	of	\$ 28,659.84	\$ 5,732	
Subtotal post-closure cost				\$ 37,258	
Bonding and insurance	2%	of	\$ 37,257.79	\$ 745	
Fee	8%	of	\$ 37,257.79	\$ 2,981	
Total post-closure cost				\$ 40,984	

Note: CAD - computer aided design, h - hour, PID - photoionization detector.

Table 13.7. Cost Summary

COST ESTIMATE SUMMARY		
Site: Site X	Prepared by: P. Eng	
Alternative: source remediation	Project number: 012345.67.89	
Description: activated persulfate injection – injection wells		
Capital cost		% of total
Construction (well installation)	\$ 99,975	
Project management	\$ 7,998	
Design	\$ 14,996	
Construction management	\$ 4,999	
Overhead, tax, bonding, and insurance	\$ 15,996	
Fee	\$ 12,797	
Contingency	\$ 19,195	
Total capital cost	\$ 175,955	16%
Annual operations and monitoring		
Groundwater sampling	\$ 23,280	3%
Injection	\$ 284,960	36%
Reporting	\$ 16,300	2%
Professional services ^a	\$ 42,190	5%
Overhead, tax, bonding, and insurance	\$ 36,673	
Fee	\$ 36,673	
Contingency	\$ 55,010	
Total year 1 operations and monitoring	\$ 495,086	
Remaining annual operations and monitoring		
Year 2 injection monitoring and reporting	\$ 288,522	27%
Year 3 monitoring and reporting	\$ 55,195	5%
Year 3	\$ 27,597	3%
Total remaining annual operations and monitoring	\$ 371,314	
Post-closure cost		
Closure reporting	\$ 8,840	
Well abandonment and equipment demobilization	\$ 11,928	
Professional services ^a	\$ 7,892	
Overhead, tax, bonding, and insurance	\$ 3,611	
Fee	\$ 2,981	
Contingency	\$ 5,732	
Total post-closure cost	\$ 40,984	4%
Total cost	\$ 1,083,339	100%
	\$ 146	per cy
Total present worth	\$ 1,047,220	

Note: These cost estimates provided are to an accuracy of +50 to –30% and are prepared for the sole purpose of alternative comparison. The alternative cost estimates are based on conceptual design information available at the time of this study. The actual cost of the project would depend on the final scope and design of the selected remedial action, the schedule of implementation, competitive market conditions, and other variables.

^aProfessional Services include Project Management, Technical Support (i.e., data analysis), and Construction Management.

It should be noted that the cost estimates developed for this example are what would typically be considered an order-of-magnitude level, Class 4. Estimates of this type are generally accurate within “+50 or –30%.” The accuracy of these estimates is subject to substantial variation because the details of the specific designs will not be known until the projects are actually implemented. Factors that may affect the cost include site conditions, final project scope and schedule, design details, the bidding climate and other competitive market conditions, changes during construction and operations, productivity, interest rates, labor and equipment rates, tax effects, and other variables. As a result, actual costs will likely vary from these estimates.

13.4.3 Comparing ISCO Project Costs

The costs estimated for the illustrative example and the costs from past field sites discussed in Chapter 8 point out some of the factors that will affect the cost for an ISCO project. These factors, as well as others, are summarized in Table 13.8. The variability of these factors makes it difficult to compare the costs for different ISCO projects to each other. They also make it difficult to compare ISCO costs to those of other remediation technologies. Site-specific cost estimates for different technologies are likely required to make reasonably accurate comparisons of ISCO and other technologies.

Table 13.8. Factors That Can Affect the Cost for an ISCO Project

Factor impacting cost	Description
Volume and dimensions (especially depth) of the TTZ	Larger and deeper sites will be more expensive
Contaminant mass, especially if nonaqueous phase liquid (NAPL) is present	Higher contaminant mass will require more oxidant and possibly more injections
NOD and nonproductive oxidant depletion	Higher natural demands for the oxidant will require more oxidant and possibly more injections
Hydraulic conductivity	Low conductivity sites will require more wells/injection points
Level of formation heterogeneity	More heterogeneous sites may take more injections
ISCO treatment goals	For example, if maximum contaminant levels (MCLs) are the goal, then tighter well spacing, more oxidant, and more labor to perform more injections may be required
Overall remediation strategy	This is related to the treatment goals and could include the maximum number of injections planned before relying on MNA
Site-specific labor conditions and degree of automation on systems	Labor costs can be reduced if the injection systems are highly automated
Contracting mechanisms or type	Performance specification should reduce the design cost but may require more oversight in the field by an owner's representative. Fixed price contracts may also result in lower costs, but they may have higher performance risks and overall cost risks
Duration of monitoring to be included in the estimate	If the system transitions to MNA, which may carry on for a number of years, the monitoring cost can add up

13.5 SUSTAINABILITY CONSIDERATIONS

13.5.1 Sustainability Concepts and Definitions

Making remediation efforts more “sustainable” or “greener,” has recently become a topic of great interest. It has spawned new areas of consideration during technology selection and implementation at a contaminated site. While there are different perspectives on what is meant by sustainable remediation, USEPA has defined green remediation as (USEPA, 2008):

The practice of considering all environmental effects of remedy implementation and incorporating options to maximize net environmental benefit of cleanup actions.

USEPA’s Office of Solid Waste and Emergency Response (OSWER) provided additional clarification in 2009 in a document called Principles for Greener Cleanups (USEPA, 2009):

[W]e can optimize environmental performance and implement protective cleanups that are greener by increasing our understanding of the environmental footprint, and when appropriate, taking steps to minimize that footprint.

The Sustainable Remediation Forum (SURF) (an ad hoc group of remediation professionals that has banded together to look into sustainable remediation) has defined sustainable remediation broadly as follows (SURF, 2009):

[A] remedy or combination of remedies whose net impact on human health and the environment is minimized through the judicious use of limited resources. In order to minimize impacts we will embrace sustainable approaches to remediation that provide a net benefit to the environment. To the extent possible, these approaches will (1) minimize or eliminate energy consumption or the consumption of other natural resources, (2) reduce or eliminate releases to the environment, especially to the air, (3) harness or mimic a natural process, (4) result in the reuse or recycling of land or otherwise undesirable materials, and (5) encourage the use of remedial technologies that permanently destroy contaminants.

SURF, and many other organizations and companies, have adopted the tenants of the “triple bottom line” of sustainability: environmental, economic, and social benefits (Elkington, 1994). In terms of the triple bottom line, developing sustainable remediation systems seeks to maximize the net positive impact to all three categories.

The importance of considering green and sustainable remediation in the Department of Defense restoration program was spelled out in an August 10, 2009 policy statement (DoD, 2009). This policy was developed in part, in response to Executive Order 13423, *Strengthening Federal Environmental, Energy, and Transportation Management*. The Navy provides additional details on what sustainable remediation is and how it can be applied in *Sustainable Environmental Remediation Fact Sheet* (NAVFAC, 2009).

Part of the current effort with sustainable remediation is the development of calculation tools and methods to evaluate the net impacts of remediation efforts on the environment. These tools are designed to serve a number of purposes:

- Develop lists of impact areas (in terms of the triple bottom line) that are most significant for a particular project and will be evaluated. These impacts are also termed sustainability criteria – or green elements. They can include impacts such as air pollutants, greenhouse gas (GHG) emissions, and energy consumption.
- Quantify (to the extent possible) the net impacts of a remedy for each impact area defined as significant.

- Develop and implement a decision analysis approach to normalize and compare the results.
- Develop and implement an approach to incorporate the results in the decision-making process (e.g., the Comprehensive Environmental Response, Compensation, and Liability Act [CERCLA] Feasibility Study process).

Most tools incorporate the first two purposes listed above; more advanced tools address the latter two.

13.5.2 Making Technologies More Sustainable

The predominant focus of sustainable remediation has been on evaluation of already existing technologies; relatively little effort has been focused on developing new technologies that are more sustainable. However, an emerging focus of the remediation industry has been on developing new technologies and optimizing existing technologies to be more sustainable. These two areas are discussed below as they relate to ISCO.

13.5.2.1 Net Impacts of ISCO

The implementation of an ISCO remedy at a site could have the following positive effects on the triple bottom line, depending on site-specific conditions:

- A reduction of the mass of contaminants in the subsurface, which should reduce the risk to human health and the environment.
- Return of impaired resources to beneficial use. This could include restoring contaminated groundwater and restoring contaminated land (e.g., by allowing the property to be redeveloped, used for recreational purposes, or returned to an ecologically beneficial purpose).
- Creation of jobs during the remediation, as well as creation of future jobs through the beneficial future use of the property.

Implementation of ISCO, may also have negative effects to the triple bottom line of sustainability, as identified below:

- Emission of GHGs during production of oxidants, during drilling/injection, and during shipment of chemicals.
- Emission of other air pollutants during production and shipment of chemicals, and during drilling/injection.
- Consumption of non-renewable energy during production and shipment of chemicals, and during drilling/injection.
- Consumption of water resources during injection.
- Traffic fatalities during mobilization or demobilization, or shipment of materials and chemicals.

The potential positive and negative triple bottom line effects listed above could be realized with other remediation technologies as well as ISCO. The relative magnitude of these positive and negative net environmental effects of ISCO as compared to other technologies is highly site-specific. A few ISCO-specific details with which to calculate triple bottom line effects of an ISCO remediation are presented below. The reader is cautioned that a thorough sustainability evaluation will cover many more aspects of a project than discussed below. The reader is also cautioned to check available sources for the latest values of some of these factors.

The GHG emissions during production of the oxidants can vary widely for different oxidants and different manufacturing processes. For example, for the manufacture of potassium permanganate, the GHG emissions estimated from one source are 4 tons of carbon dioxide per ton of potassium permanganate.¹ The value might be more than ten times this if older roasting production methods are used. Additionally, the GHG emissions produced from a single process could be largely driven by the type of power used in the process (e.g., coal versus hydroelectric). The mass of carbon dioxide generated during the production of sodium persulfate and hydrogen peroxide is estimated to be 1.25 ton/ton and 1.2 ton/ton, respectively.² It should be noted that the basis of the value being used should be documented to clarify uncertainty, or attributes of the referenced value (e.g., does the value include infrastructure, mining, and other processes or does it simply quantify the manufacturing of the chemical). For example, the values cited above are only for the manufacture of the chemicals and not for the mining of the raw materials or shipping. These values also do not include the activators that are required for sodium persulfate or hydrogen peroxide. Comprehensive life cycle assessment (LCA) databases, such as the EcoInvent database (Hässig and Primas, 2007) can be consulted to better understand the basis of inventory factors used in GHG emission estimates.

For the illustrative example site discussed above that required 40 metric tons of sodium persulfate, approximately 50 metric tons of carbon dioxide would be emitted from the production of the persulfate (which is likely one of the largest single sources of emissions). This mass of GHGs is equivalent to 16 passenger cars for 1 year [assuming 6 metric tons of carbon dioxide is equivalent to 12,000 miles with a car that gets about 20 miles to the gallon (USEPA, 2005)].

As a rough comparison to other remediation technologies, the carbon dioxide produced during the manufacturing of a ton of commercial grade soybean oil (used for biological enhanced reductive dechlorination [ERD]) is estimated to be 0.43 tons/ton. The quantity of soybean oil that would be required to achieve equivalent treatment compared to any of the ISCO oxidants is impossible to estimate without doing site-specific conceptual designs. Most other aspects of ERD should be similar in GHG emissions to ISCO, such as well drilling. A detailed impact analysis (possibly using some of the new tools being developed in the industry) would need to be performed for a specific project to compare ISCO to ERD. For example, ISCO can typically be performed in a shorter time period, which might influence the outcome of such an analysis.

Since ISCO is an *in situ* technology, most applications do not require substantive infrastructure and operator attention compared with other technologies, such as pump-and-treat. Consequently, they may have a lower net impact over the lifetime of a remediation project compared to some other technologies.

13.5.2.2 Making ISCO More Sustainable

Making ISCO applications greener or more sustainable might be difficult since there are few opportunities to use greener twists to a standard ISCO approach. However, below are a few possible methods to make an ISCO application greener:

- Use less oxidant, and rely on other technologies, such as MNA or ERD to polish any remaining contaminants of concern (COCs).
- Develop oxidant chemistries that provide better longevity of the oxidant in the subsurface so it can be more effective.

¹ Personal communication with M. Dingens, Carus Chemical Company, Peru, IL, 2009.

² Personal communication with P. Block, FMC Corporation, Philadelphia, PA, 2009.

- Use oxidant in a more targeted (“surgical”) or optimized approach so that the oxidant is not consumed nonproductively or otherwise wasted. This could include doing more injections over smaller areas to target only the zones requiring treatment, and using MNA or ERD to polish zones with lower COC concentrations.
- Obtain the oxidant from sources that use less energy and produce less GHGs.
- Obtain oxidants and other resources from more local sources to reduce transportation.
- Use renewable energy to deliver oxidant (e.g., solar panels used to power injection systems) and for pumping.
- Consider passive monitoring techniques.

13.6 SUMMARY

The cost of a remedial technology is a key factor in determining its viability and will often be the deciding factor in its selection and ultimate implementation. Cost estimates can be prepared in a number of ways and to a number of levels of detail and thus accuracy. Understanding the method of preparation and the associated uncertainty is important for those who use the cost estimates. It is also important to understand the primary cost components of ISCO systems, especially when comparing one cost estimate to another. In general, the primary cost drivers for an ISCO project are often the cost of the oxidant and the drilling costs.

The historical costs from an ISCO database (Chapter 8) revealed a median project cost of \$220,000, while the median unit cost was \$94 per cy treated. These costs should be used with caution if applied to estimate the costs of other projects because the components that were included in the project costs for the sites in the database might not be consistent with those for the project for which an estimate is made.

Making remediation projects more sustainable or greener is gaining in interest. A number of factors can be evaluated in a sustainability analysis of a project, including GHG emissions, energy consumption, reduction of risk to human health, returning an affected resource to beneficial use, traffic fatalities, and other injuries during implementation of the remedy. It is impossible at this time to make general statements about the sustainability of ISCO within a triple-bottom line framework. Additional analysis will be required.

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CHAPTER 14

ISCO STATUS AND FUTURE DIRECTIONS

Robert L. Siegrist,¹ Michelle Crimi,² Thomas J. Simpkin,³ Richard A. Brown⁴ and Marvin Unger⁵

¹Colorado School of Mines, Golden, CO 80401, USA; ²Clarkson University, Potsdam, NY 13699, USA; ³CH2M HILL, Englewood, CO 80112, USA; ⁴Environmental Resources Management, Ewing, NJ 08618, USA; ⁵HydroGeoLogic, Inc., Phoenix, AZ 85004, USA

Scope

Optimal applications of *in situ* chemical oxidation (ISCO), emerging technologies and approaches, and research needed to enable increased applicability of ISCO and improved outcomes.

Key Concepts

- ISCO is a viable technology for remediation of contaminated soil and groundwater, but the likelihood of effective application depends on favorable site conditions and contaminant characteristics as well as realistic ISCO treatment goals.
- Among the numerous applications of ISCO to date, there are examples of what might be considered optimal applications as well as those deemed to be inappropriate or poorly implemented.
- Emerging technologies and approaches include: combining ISCO with other remedies, enhanced delivery methods, and improved monitoring and assessment methods.
- Specific research needs and areas for advancements are within ISCO process chemistry, reagent delivery, system design, and process control and assessment.

14.1 INTRODUCTION

In situ chemical oxidation (ISCO) has evolved over many years and its development and deployment are continuing. While in some respects, ISCO is a relatively mature technology for groundwater remediation, there are important areas for continued research and development as well as translation of advancements into widespread practice. This chapter summarizes the status of ISCO, highlights some emerging technologies and approaches, and outlines research and development that could enable breakthroughs and enhanced future applications.

The authors of this chapter gratefully acknowledge the insights and recommendations of the remediation researchers and practitioners who met during the Strategic Environmental Research and Development Program (SERDP)/Environmental Security Technology Certification Program (ESTCP) Partners in Environmental Technology Technical Symposium and Workshop in Washington, DC, in December 2009.¹ This chapter reflects the discussions the authors had with these experts.

¹ Bob Borden, North Carolina State University; Tissa Illangasekare, Colorado School of Mines; Rick Johnson, Oregon Health and Science University; Mike Kavanaugh, Malcolm Pirnie; Fritz Krembs,

14.2 STRIVING FOR OPTIMAL APPLICATIONS OF ISCO

As an *in situ* technology for remediation of contaminated groundwater, ISCO is well suited to certain site attributes but challenged by others. Consistent with other *in situ* technologies, these attributes include contaminant characteristics, treatment goals, and site conditions. Table 14.1 provides an example of a representative and potentially optimal application of ISCO that would be considered effective as well as one that might be viewed as inappropriate and poorly implemented and, as a result, ineffective.

Table 14.1. Illustration of a Potentially Optimal vs. a Poorly Implemented Application of ISCO for Remediation of Contaminated Groundwater

Potentially optimal application of ISCO	Potentially inappropriate application of ISCO
<p>A valid conceptual model has been developed of a well-characterized contaminated site, defining site conditions and contaminant characteristics. A target treatment zone (TTZ) has been established that encompasses an area of about 1 hectare (ha) (2.5 acres) and a depth interval of 3–10 meters (m) (9.8–32.8 feet [ft]) below ground surface (bgs). The contaminants of concern (COCs) are chlorinated alkenes (mostly perchloroethene [PCE] and trichloroethene [TCE]) and the ISCO treatment goal for the TTZ is to reduce the mass of sorbed and residual nonaqueous phase liquid (NAPL) (if present) in the TTZ by a substantial amount (e.g., 90%) though this is not explicitly stated or required. Using a network of direct-push injection probes at 3 m (9.8 ft) spacing, an oxidant solution (with or without activators or stabilizers) was delivered into the TTZ and monitoring included real-time measurements of groundwater chemistry, oxidant levels, COCs, and reaction products. After the first injection, rebound occurred in several locations and recognizing this possibility, time and budget had been allocated for a second injection event. The second injection was accomplished within 2 months of the initial injection event, after conditions in the TTZ had stabilized. Post-ISCO monitoring and data analysis revealed a 90% reduction in COC mass within the TTZ</p>	<p>An industrial site occupying a 5 ha (12.5 acre) parcel was found to have contaminated groundwater. This finding was based on only a limited number of samples collected from three groundwater monitoring wells. There are likely multiple sources of contamination. But due to time pressures related to moving forward with a property transaction, detailed site characterization prior to remedial action was not viewed as possible. ISCO was selected for implementation due to its rapid deployment and fast remediation timeframe. The COCs included a mix of fuel hydrocarbons and chlorinated aliphatic compounds within a region of the subsurface characterized by heterogeneous conditions with layers of clay interbedded within a sandy deposit. The subsurface was characterized by high levels of organic matter and reduced minerals. The ISCO treatment goal specified by the regulatory agency was to achieve maximum contaminant levels (MCLs) for COCs present in groundwater within the property boundary and in the depth interval of 10–30 m (32.8–98.4 ft) bgs. Budget was allocated for a single injection of oxidants using well-to-well flushing methods and delivery of 0.3 pore volumes (PV) of solution. Post-ISCO monitoring data revealed that COC concentrations in groundwater were reduced but then rebounded to levels approaching pre-ISCO conditions in some locations. No budget was allocated for further ISCO remediation and the property transfer did not occur as planned</p>

A general assessment of attributes that favor ISCO versus those that challenge effective applications of ISCO is summarized in Table 14.2. For the purpose of this assessment, *effective* is defined to mean achieving the prescribed ISCO treatment goal within the time and

Aquifer Solutions; Rick Lewis, ERM; Brian Looney, U.S. Department of Energy, Savannah River National Laboratory; John McCray, Colorado School of Mines; Ian Osgerby, U.S. Army Corps of Engineers; Ben Petri, Colorado School of Mines; Brant Smith, XDD, LLC; Neil Thomson, University of Waterloo; Paul Tratnyek, Oregon Health and Science University; Herb Ward, Rice University; Rick Watts, Washington State University (2009).

budget allocated and without any undesirable secondary effects. While Table 14.2 has been prepared specifically for ISCO, many of the conditions listed are also favorable or challenging to most, if not all, *in situ* remediation technologies.

14.3 EMERGING APPROACHES AND TECHNOLOGIES

As previously described, the number and diversity of applications of ISCO for groundwater remediation have grown rapidly during the past decade (e.g., see Chapter 1, Figure 1.9 and discussion in Chapter 8). Along with what might be considered *conventional applications* of ISCO (i.e., injection of a single oxidant into a network of direct-push probes to destroy organic COCs within a TTZ), important advancements in ISCO technology have been made. A summary of several emerging developments is provided in Table 14.3 and further discussion is given in the sections that follow. It is recognized that commercialization is very important to widespread application of new remediation technologies, including those that support ISCO. However, to avoid the impression of an endorsement or, conversely, a negative recommendation, this chapter does not include specific mention of proprietary technologies.

Table 14.2. Site Attributes that are Favorable or Challenging to Effective Application of ISCO for Groundwater Remediation

Attributes	Comments
Attributes that are favorable for ISCO	
<ul style="list-style-type: none"> • COCs are chlorinated alkenes (e.g., PCE, TCE) and other unsaturated aliphatic and aromatic compounds 	<ul style="list-style-type: none"> • Demonstrated to be rapidly oxidized by chemical oxidants used for ISCO
<ul style="list-style-type: none"> • COCs are present in dissolved and sorbed phases; there may be NAPL residual present as ganglia and blobs, but extensive pools of NAPLs are absent 	<ul style="list-style-type: none"> • Demonstrated ability to oxidize these phases with comparably low and readily deliverable oxidant loadings
<ul style="list-style-type: none"> • Co-contaminants are not pH- or redox-sensitive or otherwise adversely affected by oxidation chemistry 	<ul style="list-style-type: none"> • Mitigates concern over co-contaminant mobility due to ISCO
<ul style="list-style-type: none"> • ISCO treatment goal involves mass reduction (e.g., 90%) or achieving downgradient plume concentrations suitable for a combined remedy 	<ul style="list-style-type: none"> • Demonstrated ability to accomplish this type of goal
<ul style="list-style-type: none"> • The TTZ involves a relatively small region of the subsurface (e.g., <10,000 cy) and there are no obstructions to access (e.g., no buried utilities) 	<ul style="list-style-type: none"> • Ability to complete ISCO field activities quickly
<ul style="list-style-type: none"> • The TTZ is characterized by high permeability and low heterogeneity with no underground utilities or obstructions 	<ul style="list-style-type: none"> • Simplifies oxidant delivery and distribution and increases likelihood of effective contact between the oxidant and the COCs
<ul style="list-style-type: none"> • The geochemical conditions in the TTZ are characterized by circum neutral pH with limited levels of reduced constituents (e.g., groundwater DOC < 50 mg/L and f_{oc} < 0.005; limited reduced minerals) 	<ul style="list-style-type: none"> • Reduces natural oxidant demand and oxidant depletion enabling longer transport distances
<ul style="list-style-type: none"> • There are no nearby withdrawals of groundwater for potable uses 	<ul style="list-style-type: none"> • Mitigates public health concern over trace impurities and possible byproducts

(continued)

Table 14.2. (continued)

Attributes	Comments
Attributes that can challenge ISCO	
<ul style="list-style-type: none"> • COCs are chlorinated alkanes (e.g., CT, TCA) and other saturated aliphatic compounds 	<ul style="list-style-type: none"> • Demonstrated to be resistant to oxidation by one or more of the common oxidants
<ul style="list-style-type: none"> • COCs are present in pools of nonaqueous phases (i.e., as DNAPLs or LNAPLs) 	<ul style="list-style-type: none"> • High oxidant loadings are required and increased potential for secondary effects
<ul style="list-style-type: none"> • Co-contaminants are pH- or redox-sensitive or otherwise adversely affected by oxidation 	<ul style="list-style-type: none"> • Increased concern over co-contaminant mobility (e.g., chromium (Cr) (III) to Cr (VI))
<ul style="list-style-type: none"> • ISCO treatment goal involves achieving a stringent concentration based target in the TTZ (e.g., MCLs) 	<ul style="list-style-type: none"> • Ability to destroy high concentrations to sustained low concentration levels can be uncertain and difficult to predict a priori
<ul style="list-style-type: none"> • The TTZ involves a relatively large area or depth interval (e.g., >10,000 cy) 	<ul style="list-style-type: none"> • Equipment requirements can become complex and limited and implementation times can be long
<ul style="list-style-type: none"> • The TTZ contains layers or zones of low permeability into which COCs may have diffused over long-term exposure prior to treatment or has underground utilities or other obstructions 	<ul style="list-style-type: none"> • Complicates delivery and distribution of some short-lived oxidants and reduces the likelihood of effective contact between the oxidant and the COCs
<ul style="list-style-type: none"> • The geochemical conditions in the TTZ include high levels of reduced substances (e.g., groundwater DOC > 50 mg/L and $f_{oc} > 0.005$; high reduced mineral components) 	<ul style="list-style-type: none"> • Can lead to a high degree of unproductive oxidant consumption with non-target components and can limit transport distances and require closer delivery point spacing
<ul style="list-style-type: none"> • There are nearby withdrawals of groundwater for drinking water use 	<ul style="list-style-type: none"> • Increases concern over trace impurities and possible byproducts and adverse public health effects

CT - carbon tetrachloride, cy - cubic yards, DNAPL - dense nonaqueous phase liquid, DOC - dissolved organic carbon, f_{oc} - fractional organic carbon content, LNAPL - light nonaqueous phase liquid, mg/L - milligrams per liter, TCA - trichloroethane.

14.3.1 Combining ISCO with Other Technologies and Approaches

ISCO is often viewed and applied as a stand-alone technology. There is, however, increasing interest in using ISCO combined with other technologies (Section E1 of Table 14.3). Using ISCO as a component of a combined remedy can be accomplished simultaneously or through temporal or spatial implementation approaches. ISCO and other technologies can be applied sequentially to the same zone, such as ISCO followed by bioremediation or ISCO can be used to treat a portion of a site, with different technologies applied to other portions. For example, ISCO may be used to treat the source zone and *in situ* chemical reduction (ISCR) may then be used to treat the associated groundwater plume. As described in Chapter 7, there are a number of potential benefits to using ISCO as a component of a combined remedy. These include improved effectiveness, shorter treatment times, and less rebound.

14.3.2 Enhanced Delivery Methods for ISCO

ISCO normally involves injection and transport of an aqueous solution of oxidant (and possibly amendments) that can react with naturally occurring substances as well as target COCs. Oxidant delivery into a TTZ can be strongly affected by certain hydrogeologic and geochemical conditions (refer to Chapters 2–6 and 11). Oxidant delivery within a TTZ can be

enhanced by both (1) improved hydraulic delivery and distribution of the solution containing the oxidant and (2) improved oxidant stability and targeted reactivity toward the COCs (compared to natural substances). Improved hydraulic delivery can improve contact between the oxidant and COCs to increase treatment efficiency and effectiveness. Improved oxidant stability can lead to increased contact duration, which is important where reactions are limited because: (1) the COCs have slower reaction kinetics, (2) oxidation rates may be limited by desorption or dissolution (if COCs are present in sorbed or NAPL phases), or (3) COCs are entrapped in zones and layers of lower permeability media with limited physical contact (diffusive-transport limited). Oxidant stability can be improved by the addition of amendments to alter its chemical or physical properties, which can contribute to enhanced ISCO delivery. An array of methods that have been developed and are being demonstrated for enhanced delivery during ISCO (Table 14.3, Section E2).

14.3.3 Improved ISCO Monitoring and Assessment

The successful application of ISCO often requires field monitoring with adjustments to the oxidant application made either (1) real-time during the initial mobilization or (2) during a subsequent mobilization for additional rounds of oxidant injection (Chapters 9 and 12). The integrated use of field methods and real-time analyses in an expedited approach (e.g., Triad) can enhance ISCO system design and implementation. In addition, the development and deployment of *in situ* sensors and continuous data logging can aid in the understanding of how an ISCO application is progressing. Also, as described in Chapter 10, mass flux is an emerging technique for assessing the strength of a source zone and evaluating benefits to be gained by remediation of a TTZ. For use with ISCO, mass flux measurements include the COCs moving out of the TTZ as well as ISCO reaction products. These data can be integrated and interpreted to provide insight into the spatial distribution of oxidation reactions, the mass of COCs degraded, and the generation of beneficial byproducts (e.g., organic acids that can serve as substrates for monitored natural attenuation (MNA) in a downgradient groundwater plume). For example, mass flux/discharge may provide a relevant basis to determine ISCO treatment end points when bioremediation, MNA, or permeable reactive barriers are used to treat a downgradient plume.

Table 14.3. Examples of Emerging Approaches and Technologies for ISCO

Approach/technology	Description and examples
<i>E1. Combining ISCO with other technologies and approaches (refer to Chapter 7)</i>	
(a) ISCO via multiple oxidants	Use of more than one oxidant sequentially in one TTZ or delivery into different TTZs <ul style="list-style-type: none"> ● The sequential application of peroxide (e.g., catalyzed hydrogen peroxide [CHP]) and permanganate was used to treat a PCE plume (Bryant and Kellar, 2009)
(b) ISCO with enhanced <i>in situ</i> bioremediation (EISB)	Delivery of an oxidant into a TTZ to partially degrade recalcitrant COCs and stimulate biodegradation of daughter products <ul style="list-style-type: none"> ● At a manufactured gas plant (MGP) site, 1 month after persulfate injection, sulfate reduction occurred and both the sulfate and polycyclic aromatic hydrocarbons (PAH) levels dropped (Marley et al., 2003)

(continued)

Table 14.3. (continued)

Approach/technology	Description and examples
(c) ISCO with MNA	Use of ISCO in a TTZ to (1) reduce the COC mass flux in the downgradient plume and (2) enhance biodegradation by the generation of substrates and electron acceptors <ul style="list-style-type: none"> • Microcosm studies for an MGP site revealed that only the microcosms treated with an oxidant (peroxide or persulfate) showed an increase in DOC levels (Marley et al., 2003)
(d) ISCO with <i>in situ</i> chemical reduction	Combining oxidants with reductants in the same TTZ to achieve simultaneous oxidation and reduction <ul style="list-style-type: none"> • Persulfate and zero-valent iron (ZVI) mixtures appear capable of destroying chlorinated alkenes by oxidation and chlorinated alkanes (e.g., 1,1,1-TCA and CT) by reduction (Brown et al., 2004)
(e) ISCO with surfactants	Coinjection of an oxidant with a compatible surfactant/cosolvent solution to enhance degradation rate and extent for NAPLs <ul style="list-style-type: none"> • Surfactant enhanced ISCO has been successfully developed for permanganate (Dugan et al., 2008) and persulfate/peroxide (Hoag et al., 2007)
(f) ISCO with thermal	Delivery of oxidant into a TTZ followed by heating to activate the oxidant once dispersed. <ul style="list-style-type: none"> • Persulfate can be injected and then activated thermally (Waldemer et al., 2007)
E2. Enhanced ISCO delivery methods (refer to Chapters 2–5, 8, 9, 11)	
(a) Stabilized oxidants	Reliable stabilizers and formulations for field applications can help improve oxidant transport <ul style="list-style-type: none"> • Phytate, citrate, and malonate have been shown to increase the half life of hydrogen peroxide during CHP reactions (Watts et al., 2007)
(b) Encapsulated oxidants	Microcapsules containing oxidant can provide slow and long-term release of oxidant during use in permeable reactive barriers or in reactive zones established by soil mixing or fracturing methods <ul style="list-style-type: none"> • Potassium permanganate in solid microcapsules (Ross et al., 2005) or within a paraffin matrix (Dugan et al., 2009) to achieve controlled release into groundwater (Lee and Schwartz, 2007; Lee et al., 2009)
(c) Polymers and delivery aids	The chemical and physical characteristics of oxidant solutions can be altered to improve movement into low permeability zones and contact between oxidant and contaminant <ul style="list-style-type: none"> • Use of polymers like xanthan to overcome ISCO delivery problems caused by zones of low permeability, site heterogeneity, and excessive natural oxidant demand (Smith et al., 2008)
(d) Density driven delivery	Oxidant solutions can have a density sufficiently higher than water so that density driven flow can occur during oxidant delivery into a TTZ <ul style="list-style-type: none"> • Density driven flow was used to deliver permanganate to NAPL located in groundwater on top of an aquitard and a model (MIN3P-D) could simulate the observed behavior (Henderson et al., 2009)
(e) Mechanical mixing	Use of blending and mixing technologies to enhance oxidant contact with target COCs <ul style="list-style-type: none"> • Deep soil mixing for ISCO using potassium permanganate (KMnO₄) in low permeability silty deposits or ISCO using persulfate in shallow soils

(continued)

Table 14.3. (continued)

Approach/technology	Description and examples
E3. Improved ISCO monitoring and assessment (refer to Chapters 9, 10, 12):	
(a) Field methods	Integrated use of real-time monitoring methods for process control and monitoring of ISCO performance <ul style="list-style-type: none"> • Oxidation-reduction potential (ORP) and electrical conductivity (Ec) probes connected to data loggers in monitoring wells to provide real-time data for oxidant distribution
(b) Mass flux	Use of TTZ mass flux measurements to identify ISCO reaction zones and products and help target subsequent injections of oxidant <ul style="list-style-type: none"> • Mass flux/discharge may provide a basis to determine ISCO treatment end points when bioremediation, MNA, or permeable reactive barriers are used to treat a downgradient plume

Note: The approaches and technologies listed in this table are examples to illustrate the evolving trends in ISCO.

14.4 RESEARCH NEEDS AND BREAKTHROUGH AREAS

Despite the breadth and depth of ISCO science and technology for soil and groundwater remediation, there are knowledge gaps. Additional research is needed to more effectively and predictably apply ISCO to a broader range of sites and achieve equal or better outcomes with less time and expense.

Many of the emerging technologies and approaches described in Section 14.3 are the subjects of ongoing investigations supported by the DoD SERDP/ESTCP offices and other research sponsors. A summary of research needs and areas for potential ISCO technology enhancements are given in Table 14.4 and briefly discussed below.

Table 14.4. Summary of Research Areas and Needs to Enhance ISCO Development

	Area	Need
R1. ISCO process chemistry	(a) Reaction mechanisms and kinetics for complex COC conditions	Fundamental understanding of reaction mechanisms and kinetics for complex COC conditions (e.g., energetics, pesticides) or complicated mixtures (e.g., MGP residuals)
	(b) Oxidant chemistry within the subsurface	Understanding of oxidant behavior, with or without activation, to increase persistence of oxidants and decrease nonproductive consumption, and to improve ISCO technologies for treatment of larger groundwater plumes
	(c) Biogeochemical effects of ISCO	Improved understanding of how design and site-specific conditions impact porous media properties (amount and character of natural organic matter [NOM]), water quality, and the effects on post-ISCO natural attenuation
	(d) COC rebound and back diffusion following ISCO	Ability to predict the potential and timeframe for COC rebound including back diffusion from lower permeability zones, as well as methods to manage the rebound
R2. ISCO delivery	(a) Oxidant delivery into low permeability zones	Methods to cost effectively deliver oxidants (and activators or stabilizers, if required) into low permeability zone where a majority of the COCs may reside
	(b) Oxidant delivery into large groundwater plumes	Methods to cost effectively deliver and mix oxidants into TTZs composed of large plumes of contaminated groundwater with moderate concentrations of COCs

(continued)

Table 14.4. (continued)

Area		Need
R3. ISCO system design	(a) Analysis and modeling tools for ISCO used alone or in a combined remedy	ISCO simulators that accurately predict oxidant distribution and destruction efficiency for COCs within a TTZ. Analysis methods and models that predict the response of a downgradient plume to a given ISCO technology and that can guide the proper timing and means of transition from ISCO to another technology or approach
R4. ISCO process control and assessment	(a) Sensors, wireless sensor networks, intelligent control	Robust and reliable sensors that can be deployed <i>in situ</i> and transmit ISCO relevant data through wireless networks. Data can be interpreted and used with intelligent systems software to control ISCO operations
	(b) Integrated methods to assess ISCO treatment effectiveness	Real-time methods to assess ISCO treatment effectiveness and goal achievement (e.g., using a suite of monitored parameters and tracers) that can assess the effects of COC displacement, dilution, or rebound

Note: The research areas and needs shown in this table complement and supplement the areas of emerging technologies and approaches summarized in Table 14.3 above.

14.4.1 ISCO Process Chemistry

Reaction Mechanisms and Kinetics for Complex COC Conditions (R1a). A major research need is better understanding of the reaction chemistry and kinetics of the more complicated COCs (e.g., energetic compounds, pesticides) that are present as single components or as complex mixtures of COCs (e.g., MGP residues). Fundamental understanding of reaction mechanisms and COC destruction efficiency will help ensure that harmful daughter products do not result from ISCO application. Translation of kinetics information into useful rate expressions would be beneficial in optimizing oxidant delivery and COC destruction within a TTZ. The kinetics of COC degradation with oxidants is generally less of an issue since rates are generally very fast. Understanding the mechanisms and kinetics of nonproductive consumption of oxidants and activators (if used), also warrants further research.

Oxidant Chemistry within a Subsurface Environment (R1b). There is a need for greater understanding of the mechanisms and kinetics of reactions of oxidants (and activators where used) during movement through the subsurface. Greater knowledge in this area would help to decrease nonproductive interactions of oxidants with naturally occurring materials in the subsurface and possibly increase the effectiveness of controlled release oxidants. Attention to large, dilute contaminant plumes is increasing. For ISCO to become more viable (i.e., cost effective) for plume management, enhancements are needed to improve the efficiency of oxidant delivery. Mechanisms used could be physical or chemical in nature. Examples of currently investigated improvements are described in Section 14.3.2 above. Continued work in this area is needed.

Biogeochemical Effects of ISCO (R1c). Understanding of the near- and long-term impacts of ISCO on groundwater quality is limited, because there is limited field data available for many of the parameters of interest and because existing modeling tools have little focus on these effects. Biogeochemical effects of interest include: microbial community structure and function, metals mobilization, changes to natural organic carbon (and subsequent impacts on contaminant sorption), hazardous gases, and the geochemical parameters that impact natural attenuation. Greater understanding of biogeochemical effects of ISCO would improve

prediction of impacts allow for strategies to limit such impacts and help promote synergy between ISCO and post-ISCO natural attenuation.

COC Rebound and Back Diffusion Following ISCO (R1d). Storage of contaminants in less mobile, lower permeability media presents a complex challenge. There is a lack of understanding and tools available to predict the mass of contaminant stored or the rate and extent of contaminant release as a function of physical and chemical site characteristics. Likewise there is not sufficient understanding or tools available to predict these factors in response to ISCO treatment. Further research is needed to address these fundamental gaps in understanding and mathematical tools/models are needed to improve the predictability of impacts of contaminant storage, release, and treatment. This knowledge could help predict the occurrence and magnitude of COC rebound and enable methods to manage the rebound anticipated.

14.4.2 ISCO Delivery

Delivery of oxidants and amendments into a TTZ with controlled reactivity toward the contaminants of concern represents a key area for further research and development. Of all areas noted herein, this is perhaps the most critical to further development and enhancement of ISCO applications.

Oxidant Delivery into Low Permeability Zones (R2a). Delivery of oxidants (and amendments) into low permeability zones requires oxidant mass transport through means other than simple advection of an oxidant solution. Diffusive transport from an oxidant solution delivered via mobile groundwater represents one option, but without some enhancement, transport can be slow and the depth of penetration achieved in low permeability media can be limited. Emerging technologies such as oxidant-compatible polymers and delivery aids, as well as pulsed pressure technologies are being developed and tested to determine if they can facilitate oxidant movement through existing pore channels within low permeability media. Mechanical mixing and blending technologies also have been developed and applied to achieve more uniform oxidant distribution in such media through physical homogenization. Continued research and development in these areas could yield breakthroughs and increased cost effectiveness of ISCO at sites with low permeability zones and which unavoidably have concerns over COC rebound and back diffusion.

Oxidant Delivery into Large Groundwater Plumes (R2b). In Table 14.3 there are several examples of emerging technologies and approaches for enhanced delivery of oxidants into large groundwater plumes (e.g., stabilized oxidants and encapsulated controlled release oxidants). While controlling oxidant release and reactivity is important, there is also a need to develop new techniques for oxidant mixing and distribution to treat moderate concentrations of COCs within large plumes.

14.4.3 ISCO System Design

Design approaches and tools for site-specific engineering of ISCO have improved over the past few years, but additional understanding and new analysis and modeling tools are needed to help improve the efficacy of ISCO and the cost effectiveness of field applications.

Improved design tools are needed that take improved oxidant decay kinetics (previously mentioned) and incorporate them into simple, but effective models of oxidant distribution during and after injection. CDISCO (discussed in Chapter 6) is a start, but this type of tool could be modified to make it applicable for other oxidants. In addition “medium range”

modeling tools that could model subsurface complexities more rigorously than CDISCO, but are easier and cheaper to apply than complex models, such as CORT3D, would be beneficial.

Also needed are improved analysis and modeling tools to predict subsurface responses to ISCO applications. For example, since rebound is a significant challenge with ISCO, tools are needed to help understand and predict processes occurring with oxidants and contaminants at the pore and macro scale to better predict and manage rebound. This could require modeling of desorption, back diffusion, and other processes.

Tools are also needed to assess and demonstrate the benefits and limitations of combining ISCO with other technologies and when it would be most cost effective to transition from ISCO to EISB or MNA.

14.4.4 ISCO Process Control and Assessment

Sensors and Wireless Sensor Networks (R4a). The development of sensors that are robust and reliable for measuring subsurface conditions relevant to ISCO are needed. Sensors could be deployed and interfaced with a data acquisition system to interpret conditions near real-time for process control of an ISCO system, especially if oxidant delivery systems can be improved.

Integrated Methods to Assess ISCO Treatment Effectiveness (R4b). Real-time methods to obtain field data and assess ISCO treatment effectiveness and goal achievement are needed. Approaches and techniques involving a suite of monitored parameters and tracers are needed to identify and account for any effects of COC displacement, dilution, or rebound. Tools also are needed to accurately and cost effectively help understand how and why rebound occurs, when it might occur, and how to avoid it. Also, a primary question is what treatment end point is adequate to allow natural attenuation to achieve remedial objectives in a reasonable time period. Improved diagnostic and monitoring tools to help assess attenuation mechanisms and capacity of an aquifer would be beneficial. This could include tools for improved and more cost effective mass flux measurements. The biological and abiotic mechanisms that occur naturally in the subsurface may be modified by ISCO and tools to help measure these effects would be valuable. Tools to help measure the other attenuation mechanisms (e.g., dispersion) would help predict how a plume that remains after ISCO might impact a receptor.

14.5 SUMMARY

ISCO has evolved over the past decade or more and today represents an *in situ* remediation technology that can be successfully deployed to achieve realistic treatment goals at sites contaminated with an array of problem COCs. However, like all *in situ* technologies, ISCO is not sufficiently robust and reliable that it can be blindly applied to any particular site. While current applications strive for optimal strategies with high probability of success, emerging technologies and approaches are gaining increased attention. Most notable in this regard may be the combination of ISCO with other technologies and approaches, particularly ISCO with bioremediation and MNA. Consistent with that of other *in situ* technologies, areas for research and development encompass fundamental processes, oxidant delivery, predictive modeling, and diagnostic tools. Current knowledge will support continued growth in the application of ISCO, but new research is needed to improve the efficacy of ISCO for recalcitrant COCs and complex hydrogeologies and expand the market for ISCO applications.

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APPENDIX A

LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS

°C	Degrees Celsius	AFB	Air Force Base
°F	Degrees Fahrenheit	AFCEE	Air Force Center for Engineering and the Environment (previously the Air Force Center for Environmental Excellence)
°K	Degrees Kelvin		
(aq)	Aqueous phase	ANT	Anthracene
(g)	Gas phase	AOP	Advanced oxidation process
(s)	Solid phase	ARAMS	Adaptive Risk Management Modeling System
µg	Microgram(s)	ARAR	Applicable or relevant and appropriate requirements
µg/kg	Microgram(s) per kilogram		
µg/L	Microgram(s) per liter	AS	Air sparging
µm	Micrometer	ASCE	American Society for Civil Engineering
µM	Micromolar	ASTM	American Society for Testing and Materials
1,1-DCA	1,1-Dichloroethane	atm	Atmosphere
1,1-DCE	1,1-Dichloroethene	ATSDR	Agency for Toxic Substances and Disease Registry
1,2-DCA	1,2-Dichloroethane	BaA	Benz(a)anthracene
1,1,1-TCA	1,1,1-Trichloroethane	BaP	Benzo(a)pyrene
1,1,2-TCA	1,1,2-Trichloroethane	BbF	Benzo(b)fluoranthene
1,1,1,2-TeCA	1,1,1,2-Tetrachloroethane	bgs	Below ground surface
1,1,2,2-TeCA	1,1,2,2-Tetrachloroethane	BkF	Benzo(k)fluoranthene
1,2,4-TMB	1,2,4-Trimethylbenzene	BPLM	By-product like material
1,3,5-TMB	1,3,5-Trimethylbenzene	BTEX	Benzene, toluene, ethylbenzene, and total xylenes
1-D	One dimensional	BTOC	Below top of casing
2,4-D	2,4-Dichlorophenoxyacetic acid	CAD	Computer aided design
2,4,5-T	2,4,5-Trichlorophenoxyacetic acid	CB	Chlorobenzene
2-CP	2-Chlorophenol	CCMS	Committee on Challenges for Modern Society
2-D	Two dimensional	CDISCO	Conceptual Design for ISCO
3-D	Three dimensional	CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
AACE	Association for the Advancement of Cost Engineering		
AACEI	American Association of the Advancement of Cost Engineering International		
ACC	American Chemistry Council		
ACE	Acenaphthene		
ACL	Alternative (risk-based) cleanup level		

CFR	Code of Federal Regulations	EDTA	Ethylenediaminetetraacetic acid
CFU	Colony forming units	EFR	Enhanced fluid recovery
CHP	Catalyzed hydrogen peroxide	Eh	Redox potential
CHR	Chrysene	EISB	Enhanced <i>in situ</i> bioremediation
cis-DCE	<i>cis</i> -1,2-dichloroethene	EPCRA	Emergency Planning and Community Right to Know Act
cm	Centimeter	EPRI	Electrical Power Research Institute
cm/s	Centimeter(s) per second	ERD	Enhanced reductive dechlorination
CMC	Critical micelle concentration	ERI	Electrical resistivity imaging
CMT	Continuous multichannel tubing	ESTCP	Environmental Security Technology Certification Program
COC	Contaminant of concern	FA	Fulvic acid
COD	Chemical oxygen demand	FID	Flame ionization detector
CORT3D	Chemical oxidation reactive transport in three-dimensions	FLA	Fluoranthene
CP	Cone penetrometer	FLU	Fluorine
CPT	Cone penetrometer testing	<i>f_{oc}</i>	Fractional organic carbon content
CSI	Construction Specification Institute	FRTR	Federal Remediation Technology Roundtable
CSIA	Compound specific isotopic analysis	FS	Feasibility Study
CSM	Conceptual site model	ft	Feet
CSTR	Continuously stirred tank reactor	ft/d	Feet per day
CT	Carbon tetrachloride	g	Gram
CTL	Cleanup target level	G&A	General and administrative
cu ft	Cubic feet	g/cm³	Gram(s) per cubic centimeter
CVOC	Chlorinated volatile organic compound	g/kg	Gram(s) per kilogram
cy	Cubic yard	g/L	Gram(s) per liter
d	Day	g/mol	Gram(s) per mole
DCDD	2,7-Dichlorodibenzo- <i>p</i> -dioxin	gal	Gallon(s)
DCE	Dichloroethene	GAO	U.S. Government Accountability Office
DI	Deionized	GC	Gas chromatography/ chromatograph
DNA	Deoxyribonucleic acid	GHG	Greenhouse gas
DNAPL	Dense nonaqueous phase liquid	gpm	Gallon(s) per minute
DNT	Dinitrotoluene	GW	Groundwater
DO	Dissolved oxygen	HA	Humic acid
DOC	Dissolved organic carbon	ha	Hectare
DoD	Department of Defense	HAZWOPER	Hazardous Waste Operations and Emergency Response
DOE	U.S. Department of Energy	HBCD	Hydroxypropyl- β -cyclodextrin
DPE	Dual phase extraction	HCA	Hexachloroethane
DPT	Direct push technology	HCBD	Hexachlorobutadiene
DQO	Data quality objective	HEDPA	1-Hydroxyethane-1,1-diphosphonic acid
DRO	Diesel-range organics	HMP	Hexametaphosphate
DWP	Dynamic work plan	HMX	Tetrahexamine tetranitramine
E^o	Standard reduction potential		
E_a	Activation energy		
ea	Each		
Ec	Specific conductance		
EC	Electrical conductivity		
ECD	Electron capture detector		

h	Hour	min	Minute
HSM model	Hoigné, Staehelin and Bader model	MIP	Membrane interface probe
IDQTF	Intergovernmental Data Quality Task Force	mL	Milliliter
IDW	Investigative derived waste	MLS	Multi level sampler
in.	Inch	mm	Millimeter
ISCO	<i>In situ</i> chemical oxidation	mM	Millimolar
ISCR	<i>In situ</i> chemical reduction	mmol	Millimole
ISS	<i>In situ</i> stabilization	MNA	Monitored natural attenuation
ITRC	Interstate Technology & Regulatory Council	mol	Mole
J	Joules	MSDS	Material Safety Data Sheet
K	Saturated hydraulic conductivity	MTBE	Methyl tert-butyl ether
K_d	Distribution coefficient	mV	Millivolt
kg	Kilogram	MW	Monitoring well
kJ	Kilojoules	NA	Natural attenuation
K_{oc}	Organic carbon partition coefficient	NAP	Naphthalene
K_{ow}	Octanol-water partition coefficient	NAPL	Nonaqueous phase liquid
L	Liter	NAS	Naval Air Station
lb	Pound	NASA	U.S. National Aeronautics and Space Administration
lbm	Pound-mass	NATO	North Atlantic Treaty Organization
LCA	Life cycle assessment	NAVFAC	Naval Facilities Engineering Command
LEA	Local equilibrium assumption	nCi	Nanocuries
lf	Linear foot (feet)	NDMA	N-nitrosodimethylamine
LIF	Laser-induced fluorescence	NHE	Normal hydrogen electrode
LNAPL	Light nonaqueous phase liquid	nm	Nanometers
LPM	Low permeability media	NOD	Natural oxidant demand
LS	Lump sum	NOM	Natural organic matter
LTHA	Low temperature heat activation	NPL	National priorities list
LTM	Long term monitoring	NPV	Net present value
LUST	Leaking underground storage tank	NRC	National Research Council
m	Meter	NSB	Naval submarine base
M	Mass, molar	NSF60	National Sanitation Foundation International Standard 60
MAROS	Monitoring and Remediation Optimization System	NTA	Nitilotriacetic acid
MBT	Molecular biological tools	NTC	Naval Training Center
MCACES	Micro Computer Aided Cost Engineering System	O&G	Oil and grease
MCB	Monochlorobenzene	O&M	Operation and maintenance
MCL	Maximum contaminant level	OAM	Oxidizable aquifer material
meq/L	Milliequivalent(s) per liter	OCDD	Octachlorodibenzo- <i>p</i> -dioxin
mg	Milligram	ORP	Oxidation-reduction potential
mg/kg	Milligram(s) per kilogram	OSHA	Occupational Safety Health Administration
mg/L	Milligram(s) per liter	OSWER	Office of Solid Waste and Emergency Response
MGP	Manufactured gas plant	OU	Operable unit
		P&ID	Process and Instrumentation Diagram
		P&T	Pump-and-treat

PAH	Polycyclic aromatic hydrocarbons	rRNA	Ribosomal ribonucleic acid
PBB	Polybrominated biphenyls	RT3D	Reactive transport in three dimensions
PCB	Polychlorinated biphenyl	s	Second(s)
PCE	Perchloroethene (also termed perchloroethylene or tetrachloroethylene)	SADA	Spatial analysis and decision assistance
PCP	Pentachlorophenol	SDS	Sodium dodecyl sulfate
PCR	Polymerase chain reaction	SDWA	Safe Drinking Water Act
PDB	Passive diffusion bag	SEAR	Surfactant enhanced aquifer remediation
Pe	Péclet number	SEM	Scanning electron microscope (or microscopy)
PFM	Passive flux meter	SER	Steam enhanced remediation
PHE	Phenanthrene	SERDP	Strategic Environmental Research and Development Program
PLFA	Phospholipid-derived fatty acids	sf	Square foot (feet)
PID	Photo ionization detector	SOD	Soil oxidant demand
PITT	Partitioning interwell tracer test	SOM	Soil organic matter
pKa	Acid dissociation constant	SRB	Sulfate-reducing bacteria
PLC	Process logic controller	St	Stanton number
PLFA	Phospholipid fatty acids	STP	Standard temperature (20°C) and pressure (1 atm)
PNNL	Pacific Northwest National Laboratory	STPP	Sodium triphosphate
ppb	Part(s) per billion	SURF	Sustainable Remediation Forum
PPE	Personal protective equipment	SVE	Soil vapor extraction
ppm	Part(s) per million	SVOC	Semivolatile organic compound
PRB	Permeable reactive barrier	T-RFLP	Terminal restriction fragment length polymorphism
PRG	Preliminary remedial goal(s)	TAME	Tert-amyl methyl ether
psi	Pounds per square inch	TAT	Turnaround time
PV	Pore volume	TBA	Tert-butyl alcohol
PVC	Polyvinyl chloride	TBF	Tert-butyl formate
PYR	Pyrene	TCA	Trichloroethane
QA	Quality assurance	TCDD	2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin
QAPP	Quality Assurance Project Plan	TCE	Trichloroethene
QC	Quality control	TDS	Total dissolved solids
qPCR	Quantitative polymerase chain reaction	TEA	Terminal electron acceptor
R&D	Research and development	TMB	Trimethylbenzene
RACER	Remedial action cost engineering and requirements	TNT	2,4,6-Trinitrotoluene
RAO	Remedial action objective	TOC	Total organic carbon
RCRA	Resource Conservation and Recovery Act	TOD	Total oxidant demand
RCRA-CA	RCRA Corrective Action	TPH	Total petroleum hydrocarbons
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine <i>or</i> Royal Demolition eXplosive	<i>trans</i>-DCE	<i>trans</i> -1,2-Dichloroethene
RG	Remedial goal(s)	TSA	Tryptic soy agar
RI	Remedial investigation	TTZ	Target treatment zone
RIP	Remedy in place	UCL	Upper confidence limit
RNS	Ribbon NAPL sampler	UFP-QAPP	Uniform Federal Policy for Quality Assurance Project Plan
ROD	Record of decision		
ROI	Radius of influence		

UIC	Underground injection control
USEPA	U.S. Environmental Protection Agency
USP	United States Pharmacopeia
UST	Underground storage tank
UV	Ultraviolet
V	Volt
v/v	Volume to volume ratio
VC	Vinyl chloride
VE	Value Engineering
VOC	Volatile organic compound
WDR	Waste discharge requirements
wk	Week
wt.	Weight
wt. %	Weight percentage
ZVI	Zero-valent iron

CHEMICAL FORMULAS

Ag	Silver	Fe(OH)₃	Ferric hydroxide
Al	Aluminum	α-FeOOH	Goethite
As	Arsenic	FeSO₄·7H₂O	Ferrous sulfate heptahydrate
Br	Bromide	H⁺	Hydrogen ion
-COOH	Carboxyl functional group	H[•]	Solvated hydrogen atom
C-OH	Hydroxyl functional group	HCl	Hydrogen chloride
C=O	Carbonyl functional group	HCO₃⁻	Bicarbonate
Ca	Calcium	HCO₃[•]	Bicarbonate radical
CaCO₃	Calcium carbonate	HMnO₄	Protonated form of permanganate
CaO₂	Calcium peroxide	HO₂[•]	Perhydroxyl radical
Cd	Cadmium	HO₂⁻	Hydroperoxide anion
CH₄	Methane	HO₃[•]	Hydrogen trioxide
CHCl₃	Chloroform	HO₄[•]	Hydrogen tetraoxide
Cl⁻	Chloride ion	H₂O₂	Hydrogen peroxide
Cl₂	Chlorine gas	H₂O₃	Trioxidane
Cl₂^{•-}	Dichloride radical anion	HS⁻	Bisulfide
ClHCD[•]	Chloro-hydroxy-cyclohexadienyl radical	I	Iodide
Co	Cobalt	K	Potassium
CO₂	Carbon dioxide	KMnO₄	Potassium permanganate
CO₃²⁻	Carbonate	KOH	Potassium hydroxide
CO₃^{•-}	Carbonate radical	Mg	Magnesium
COCl₂	Phosgene gas	Mn	Manganese
Cr	Chromium	Mn²⁺	Manganese ion
Cu	Copper	Mn(VII)	Heptavalent manganese
F	Fluoride	MnCO₃	Rhodochrosite
Fe	Iron	MnO₂	Manganese dioxide
Fe(II)	Ferrous iron	MnO₂²⁻	Manganate ion
Fe(III)	Ferric iron	α-MnO₂	Hollandite
Fe(IV)	Ferryl iron or FeO ²⁺	β-MnO₂	Pyrolusite
FeCl₃	Ferric chloride	δ-MnO₂	Birnessite
Fe(ClO₄)₃·6H₂O	Ferric perchlorate	γ-MnO₂	Nsutite
FeCO₃	Siderite	MnO₄⁻	Permanganate anion
Fe₂O₃	Hematite	MnO₄²⁻	Green manganate ion
Fe₃O₄	Magnetite	Mn₂O₃	Manganate
Fe₂O₃·0.5H₂O	Ferrihydrite		

Mn₃O₄	Hausmannite
Mn(OH)₂	Pyrochroite
MnOOH	Manganite
MnSO₄	Manganese(II) sulfate
Mo	Molybdenum
Na	Sodium
-NH₂	Amino functional group
NH₃⁺	Ammonia
-NO₂	Nitro functional group
NO₃⁻	Nitrate
N₂	Nitrogen gas
N₂O	Nitrous oxide
NaCl	Sodium chloride
NaMnO₄	Sodium permanganate
NaOH	Sodium hydroxide
Na₂CO₃·1.5H₂O₂	Sodium percarbonate
Na₂S₂O₈	Sodium persulfate
Ni	Nickel
O^{•-}	Oxide radical
O₂	Oxygen
¹O₂	Singlet oxygen
O₂^{•-}	Superoxide radical
O₃	Ozone
O₃⁻	Ozonide
OH[•]	Hydroxyl radical
OH⁻	Hydroxide anion
-OH	Hydroxyl functional group
Pb	Lead
PO₄³⁻	Phosphate
S	Sulfur
-SO₃H	Sulfonate functional group
SO₄²⁻	Sulfate
SO₄^{•-}	Sulfate radical
SO₄²⁻	Persulfate anion
SO₅^{•-}	Peroxymonosulfate radical
SO₅²⁻	Peroxymonosulfate
S₂O₈²⁻	Persulfate ion
Ti	Titanium
U	uranium
Zn	Zinc

MATHEMATICAL SYMBOLS (FROM CHAPTERS 2–6)

Chapter 2

A	Arrhenius frequency factor
C_1, C_2, C_3	Concentrations of scavengers and/or target reactants
$C_{reactant1}$	The concentration of the reactant of interest
$C_{reactant2}$	The concentration of the other reactant
E_a	Activation energy of the reaction
k	Specific reaction rate constant
k_2	Second-order rate constant
k_{p1}	Pseudo first-order rate constant

Chapter 3

α	Reaction order with respect to the organic [A]
β	Reaction order with respect to the oxidant [B]
θ	Porosity
ρ_B	Soil bulk density
A_f	Arrhenius frequency factor
C_e	Effective aqueous solubility limit of a contaminant
C_S	Saturation concentration of the DNAPL
C_s	Solubility limit of the contaminant in pure solution
E_a	Activation energy of the reaction
f_{oc}	Fraction of organic carbon
k	Specific reaction rate constant
k'	Pseudo-first-order rate constant
k_2	Second-order reaction rate constant
K_d	Distribution coefficient for contaminant between aqueous and organic matter phases

k_{La}	Bulk mass transfer rate coefficient
K_{oc}	Contaminant organic carbon partition coefficient
n	Porosity
R	Gas constant (8.314 joules [J] $K^{-1} mol^{-1}$)
t	Time
T	Temperature (Kelvin [K])
V	Total volume
X_n	Mole fraction of the contaminant in the NAPL mixture

Chapter 4

A	Arrhenius frequency factor
E_a	Activation energy of the reaction
f_{oc}	Fraction of organic carbon (unitless)
k	Kinetic reaction rate constant
K_d	Distribution coefficient representing the distribution of sorbed versus aqueous contaminant mass
K_{oc}	Contaminant-organic carbon partitioning coefficient (L/kg)
pKa	Dissociation constant
R	Ideal gas constant
T	Absolute temperature

Chapter 5

k_2	Second-order rate constant
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Chapter 6

$\Delta h/\Delta x$	Hydraulic gradient
ϕ or n	Porous media porosity
ϕ_{eff}	Effective porous media porosity
λ_{cont}	Linear sorption coefficient ($L^3 M^{-1}$)

μ_w	Aqueous phase dynamic viscosity ($\text{ML}^{-1} \text{T}^{-1}$)		of oxidant with the <i>ith</i> NOD component depleting oxidant
θ_n	Volumetric NAPL content	k_{La}	NAPL dissolution rate or lumped mass transfer coefficient (T^{-1})
θ_w	Water content (equal to ϕ_{eff} for the fully water saturated case)	k_{NOD_i}	First-order oxidation rate for NOD component <i>i</i> (T^{-1})
ρ_B	Porous media bulk density	k_{NOD_f}	First-order oxidation rate for fast NOD sites (T^{-1})
ρ_w	Aqueous phase density (ML^3)	$k_{r,w}$	Relative water permeability
$\sum R_n$	Reaction term ($\text{ML}^{-3} \text{T}^{-1}$)	k_s	Second-order slow NOD consumption rate
v	Advective flow velocity (LT^{-1}) for saturated subsurface materials	K_s	Saturated hydraulic conductivity (LT^{-1})
ζ	Rate-limited sorption mass transfer coefficient (T^{-1})	K_{xx}, K_{yy}, K_{zz}	Hydraulic conductivity along the x, y, and z coordinate axes corresponding to the x, y, and z axes of hydraulic conductivity (LT^{-1})
b	Empirical exponent related to the type of porous media		
c^*	Aqueous solubility limit of the soluble component (ML^{-3})		
c_∞	Aqueous solute concentration (ML^{-3}) of the bulk solution	L	Characteristic or dissolution length in the flow direction (L)
$C_{oxidant}$	Concentration of oxidant (ML^{-3})	q_s	Volumetric flow rate per unit volume of aquifer representing fluid sources (positive) and sinks (negative) (T^{-1})
C_s^k	Concentration of the source or sink flux of species <i>k</i> (ML^{-3})		
d_{50}	Representative (median) grain size (L)	R	Retardation factor (dimensionless)
$Da(l)$	Damkohler number (dimensionless)	Re	Reynolds number (dimensionless)
dc_∞/dt	Rate of change of aqueous concentration per time ($\text{ML}^{-3} \text{T}^{-1}$)	Sc	Schmidt number (dimensionless)
D_e	Effective diffusion coefficients ($\text{L}^2 \text{T}^{-1}$)	Sh	Sherwood number (dimensionless)
$D_{i,j}$	Hydrodynamic dispersion coefficient tensor ($\text{L}^2 \text{T}^{-1}$)	S_n	Saturation of immobile component in the pore space
d_M	Diameter of a “medium” sand grain	$S_{r,w}$	Residual water saturation for the porous media
D_m	Molecular diffusion coefficient ($\text{L}^2 \text{T}^{-1}$)	S_s	Specific storage of the porous medium (L^{-1})
dX_i/dt	Rate of change in mass fraction for component <i>i</i> with time	t	Time (T)
dX_{NOD_i}/dt	Rate of change in mass of NOD component <i>i</i> with time	\bar{v}	Average linear groundwater velocity (LT^{-1})
h	Hydraulic head (L)	W	Volumetric flux per unit volume representing sources and sinks of fluid (T^{-1})
K	Subsurface hydraulic conductivity (LT^{-1})	x	Distance into the residual NAPL source in the direction of flow (L)
k_i	First-order oxidant depletion rate for the reaction of oxidant with the <i>ith</i> NOD component depleting oxidant	X_i	Mass fraction of the <i>ith</i> NOD component depleting oxidant
$k_{2_NOD_i}$	Second-order oxidation rate for NOD component <i>i</i> ($\text{L}^3 \text{M}^{-1} \text{T}^{-1}$)	X_{NOD_i}	Mass fraction of NOD component <i>i</i> (MM^{-1})
k_{2i}	Appropriate second-order oxidant depletion rate for the reaction	X_{NOD_f}	Mass fraction of NOD sites with a faster oxidation rate (MM^{-1})

X_{NOD_s}	Mass fraction of NOD sites with a slower oxidation rate (MM^{-1})
X_{sorb}	Mass fraction of sorbed contaminant in the porous media (MM^{-1})
X_{soil}	Mass fraction of sorbed contaminant in the soil (MM^{-1})
Y_{ij}	Stoichiometric molar mass ratio of component i to component j

APPENDIX B

UNIT CONVERSION TABLE

Multiply	By	To Obtain
Acres	0.405	Hectares
Acres	1.56 E-3	Square miles (statute)
Centimeters	0.394	Inches
Cubic feet	0.028	Cubic meters
Cubic feet	7.48	Gallons (U.S. liquid)
Cubic feet	28.3	Liters
Cubic meters	35.3	Cubic feet
Cubic yards	0.76	Cubic meters
Feet	0.305	Meters
Feet per year	9.66 E-7	Centimeters per second
Gallons (U.S. liquid)	3.79	Liters
Hectares	2.47	Acres
Inches	2.54	Centimeters
Kilograms	2.20	Pounds (avoir)
Kilograms	35.3	Ounces (avoir)
Kilometers	0.62	Miles (statue)
Liters	0.035	Cubic feet
Liters	0.26	Gallons (U.S. liquid)
Meters	3.28	Feet
Miles (statue)	1.61	Kilometers
Ounces (avoir)	0.028	Kilograms
Ounces (fluid)	29.6	Milliliters
Pounds (avoir)	0.45	Kilograms
Square feet	0.093	Square meters
Square miles	640	Acres

APPENDIX C

GLOSSARY¹

Abiotic - Occurring without the direct involvement of organisms.

Absorption - The uptake of water, other fluids, or dissolved chemicals by a porous material, a cell or an organism.

Activated carbon - A highly adsorbent form of carbon used to remove odors and/or toxic substances from liquid or gaseous emissions.

Activation - Chemical reaction where an agent reacts with an oxidant parent chemical (e.g., hydrogen peroxide [H₂O₂]) to yield a reactive species (e.g., hydroxyl free radical, OH[•]).

Adsorption - A process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms (the adsorbate).

Advection - Transport of a substance by a fluid (e.g., groundwater) due to the fluid's bulk motion in a particular direction.

Aerobic - Environmental conditions where oxygen is present. Aerobic respiration by living organisms requires oxygen to generate energy.

Air sparging - Technology in which air or oxygen is injected into an aquifer to volatilize or biodegrade contaminants.

Aldehyde - A broad class of organic compounds having the generic formula R-CHO and characterized by an unsaturated carbonyl group (C=O). They are formed from alcohols by either dehydrogenation or oxidation and thus occupy an intermediate position between primary alcohols and the acids obtained from them by further oxidation.

Aliphatic compounds - Any chemical compound belonging to the organic class in which the atoms are not linked together to form a ring.

¹This glossary is a compilation of definitions of terms synthesized by the volume editors and chapter authors from a variety of published and unpublished sources, including previous volumes in the SERDP/ESTCP Remediation Technology Monograph Series.

Alkane - Non-aromatic saturated hydrocarbons with one or more carbon-carbon single bonds and having the general formula $C_nH_{(2n+2)}$.

Alkalinity - A measure of the ability of a solution to neutralize acids, equal to the stoichiometric sum of the bases in the solution. An expression of the buffering capacity of the solution.

Alkene - Unsaturated, open chain hydrocarbons with one or more carbon-carbon double bonds, having the general formula $C_nH_{(2n)}$.

Alluvial - Relating to or involving sand deposited by flowing water.

Alternative cleanup level (ACL) - A numerical concentration goal for a contaminant that is different than the more stringent maximum contaminant level (MCL) and, generally developed by site-specific risk assessment or formal regulatory framework for low yield or low risk aquifers.

Ammonium persulfate - A white crystal obtained from the electrolysis of concentrated solution of ammonium sulfate and recovered by crystallization.

Anaerobic - Environmental conditions where oxygen is absent. In groundwater, a dissolved oxygen concentration below 1.0 milligrams per liter (mg/L) is generally considered anaerobic. Anaerobic respiration is a means for a living organism to generate energy in the absence of oxygen.

Analytical model - A mathematical model that has a closed form solution (the solution to the equations used to describe changes in a system can be expressed as a mathematical analytic function). Analytical solutions can be more exact and aesthetically pleasing than numerical models, but analytical solutions to equations describing complex systems can often become very difficult.

Anion - A negatively charged ion.

Anisotropy - In hydrology, the conditions under which one or more hydraulic properties of an aquifer vary with respect to direction.

Anoxic - "Without oxygen." Anoxic refers specifically to conditions of no dissolved oxygen but with nitrate.

Aquifer - An underground geological formation that stores groundwater. A confined aquifer lies beneath a confining unit of lower hydraulic conductivity. An unconfined aquifer does not have a confining unit and is defined by the water table.

Aquitard - An underground geological formation of low permeability that does not readily transmit groundwater.

Assimilative capacity - The capacity of a natural body of water to receive and degrade wastewaters or toxic materials.

Attenuation - Reduction of contaminant concentrations over space or time. Includes both destructive (e.g., biodegradation, hydrolysis) and non-destructive (e.g., volatilization, sorption) removal processes.

Attenuation rate - The rate of contaminant concentration reduction over time. Example units are milligrams per liter per year (mg/L/year).

Autotrophic - Self-sustaining or self-nourishing. Organisms that must synthesize their own food from inorganic materials, such as carbon dioxide and ammonium.

Bacterium - A single-celled organism of microscopic size (generally 0.3–2.0 micrometers [μm] in diameter). As opposed to fungi and higher plants and animals (*eukaryotes*), bacteria are *prokaryotes* (characterized by the absence of a distinct, membrane-bound nucleus or membrane-bound organelles and by deoxyribonucleic acid (DNA) that is not organized into chromosomes).

Baseline - A set of data representing ambient conditions that are collected before remediation is implemented. Compared with post-treatment data to evaluate the effectiveness of remediation.

Bedrock - The solid or fractured rock underlying surface solids and other unconsolidated material or overburden.

Bench-test - See “treatability test.”

Bentonite - An expandible clay mineral, subject to swelling during wetting and shrinking during drying. Can be formed by chemical alteration of volcanic ash.

Bioaugmentation - Addition of microbes to the subsurface to improve the biodegradation of target contaminants. Microbes may be “seeded” from populations already present at a site or from specially cultivated strains of bacteria.

Bioavailability - The degree or ability to be absorbed and ready to interact in an organism.

Biobarrier - A remediation technology designed to intercept and biologically treat a contaminant plume as it passes through a permeable subsurface barrier. Biobarriers are created by installing wells or trenches across the width of a plume to deliver substrate to the microorganisms in the aquifer as groundwater flows through the barrier.

Biochemical - Produced by or involving chemical reactions of living organisms.

Biodegradation - Biologically mediated conversion of one compound to another.

Biofouling - Impairment of the functioning of wells or other equipment as a result of the growth or activity of microorganisms.

Biomarker - A biochemical within an organism that has a particular molecular feature that makes it useful for identifying a specific biological activity.

Biomass - Total mass of microorganisms present in a given amount of water or solid material.

Bioremediation - Use of microorganisms to control and destroy contaminants.

Biotransformation - Biologically catalyzed transformation of a chemical to some other product.

Biowall - A form of passive *in situ* bioremediation, in which the contaminant plume is intercepted and treated as it passes through an emplaced porous barrier (e.g., trenches filled with sand-mulch mixtures). Microorganisms growing on the wall materials remove contaminants through biodegradation processes as groundwater passes through the barrier.

Buffering capacity - A measure of a solution's ability to resist changes in pH upon addition of acid or base.

Capture zone - The three-dimensional region that contributes the groundwater extracted by one or more wells or drains.

Carboxylic acid - An organic acid characterized by one or more carboxyl groups ($-\text{COOH}$).

Catalyst - A substance that promotes a chemical reaction but does not itself enter into the reaction.

Catalyzed hydrogen peroxide (CHP) - An oxidant formulation consisting of hydrogen peroxide and a catalyst, generally ferrous iron. Also called Catalyzed Hydrogen Peroxide Propagations. Generally used interchangeably with Fenton's Reagent and Modified Fenton's reagent.

Cation - A positively charged ion.

Chelating agent - A compound, typically organic, that is capable of causing chelation.

Chelation - The formation or presence of two or more separate modes of binding between a ligand and a single central atom. The ligands are normally organic compounds such as ethylenediaminetetraacetic acid (EDTA) and can be called chelants, chelators, chelating agents, or sequestering agents.

Chlorinated solvent - A hydrocarbon in which chlorine atoms substitute for one or more hydrogen atoms in the compound's structure. Chlorinated solvents commonly are used for grease removal in manufacturing, dry cleaning, and other operations. Examples include trichloroethene (TCE), perchloroethene (PCE), and trichloroethane (TCA).

Chloroethane - (also ethyl chloride) A colorless, flammable gas, $\text{C}_2\text{H}_5\text{Cl}$, belonging to the family of organohalogen compounds. Used as a refrigerant, solvent, and anesthetic. At one time, used as a high-volume industrial chemical in the preparation of the gasoline additive tetraethyl lead.

Cleanup level - Used to describe the degree of remediation required with respect to achieving a certain concentration of contaminants of concern (COCs) in soil, groundwater or other media at a given site or within a particular target treatment zone (TTZ). Cleanup levels are commonly specified by regulatory authorities and programs and can include numeric values for specific media. Under some regulatory programs, cleanup levels may be used as remediation goals.

Co-contaminant - A contaminant that is present, but is not considered the a COC as a primary driver of remediation, due to relatively lower concentration or level of risk. May or may not be targeted by ISCO (or other technologies) when treating the primary COC.

Cometabolism - The simultaneous metabolism of two compounds, in which the degradation of the second compound (the secondary substrate) depends on the presence of the first compound (the primary substrate). For example, in the process of degrading methane, some bacteria can degrade chlorinated solvents that they would otherwise be unable to attack.

Compound specific isotope analysis (CSIA) - An analytical technique that compares ratios of stable isotopes in a particular compound (e.g., ^{13}C to ^{12}C in TCE). It is used to distinguish degradation processes (chemical oxidation, biodegradation), which change the ratio of these isotopes, from physical processes (dilution), which do not affect stable isotope ratio.

Conceptual site model (CSM) - A hypothesis about how contaminant releases occurred at a site, the current state of the contaminant source, site conditions and transport/fate pathways to receptors, and the current plume characteristics (plume stability).

Contaminant of concern (COC) - One or more contaminants present at a site that contribute to the risk and impact the nature and extent of remediation. They may be selected as the targets to be destroyed by ISCO or otherwise removed during remediation.

Contaminant rebound - An initial decrease in aqueous contaminant concentration immediately after site remediation followed by an increase in concentration over the course of the post-treatment monitoring period.

Contingency planning - The intent of contingency planning and the resultant Contingency Plan is to provide site-specific instructions to execute the Observational Method and prepare a real-time response action plan with decision logic to adapt a remedy (e.g., ISCO) implementation to the results of data collection.

Coupling - A term used to describe the proactive combination of two or more remediation approaches or technologies. Also known as combined remedies.

Data quality objective (DQO) - Qualitative and quantitative statements of the overall level of uncertainty that a decision-maker will accept in results or decisions based on environmental data. They provide the statistical framework for planning and managing environmental data operations consistent with user's needs.

Dechlorination - A type of dehalogenation reaction involving replacement of one or more chlorine atoms with hydrogen.

Degradation - The transformation of a compound through biological or abiotic reactions.

Dehalogenation - Replacement of one or more halogens (e.g., chlorine, fluorine, or bromine) with hydrogen atoms.

Dehalorespiration - Energy-yielding respiratory metabolism that encompasses the reductive metabolism of halogenated compounds, such as chlorinated and brominated ethenes.

Delivery performance monitoring - Period of ISCO remedy during which oxidant injection occurs and measurements are made to evaluate the effects of the delivery process on the target treatment zone and its surroundings

Dense nonaqueous phase liquid (DNAPL) - A liquid that is denser than water and does not dissolve or mix easily in water (it is immiscible). In the presence of water, it forms a separate phase from the water. Many chlorinated solvents, such as TCE, are DNAPLs.

Desorption - Opposite of sorption; the release of chemicals from solid surfaces.

Dichloroethene (DCE) - Chlorinated ethene used as a degreaser; a dechlorination breakdown product of PCE and TCE.

Diffusion - Dispersive process resulting from the movement of molecules along a concentration gradient. Molecules move from areas of high concentration to areas of low concentration.

Dilution - The combined processes of advection and dispersion resulting in a net dilution of a substance in a fluid (e.g., groundwater).

Direct push - A method of drilling in which a rod is advanced with percussive techniques. Colloquially referred to as geoprobe. For ISCO applications, this method consists of advancing a temporary well screen to the desired depth(s) and injecting oxidants.

Dispersion - The spreading of a substance (e.g., solutes) along and away from the expected groundwater flow path during advection as a result of mixing of groundwater in individual pores and channels.

Effectiveness - The COC destruction rate and % destroyed represent the effectiveness of an ISCO system, where higher values represent a more effective system.

Efficiency - Media demand, oxidant demand, and oxidant depletion rate are measures of ISCO system efficiency, and reflect how much and how fast oxidant is utilized to treat a given mass of contaminated media, or a given amount of contaminant. A lower value represents a more efficient system.

Electron - A negatively charged subatomic particle that may be transferred between chemical species in chemical reactions. Every chemical contains electrons and protons (positively charged particles).

Electron acceptor - Substance that receives electrons (and therefore is reduced) in the oxidation-reduction reactions that are essential for the growth of microorganisms and for bioremediation. Common electron acceptors in the subsurface are oxygen, nitrate, sulfate, iron, and carbon dioxide. Chlorinated solvents (e.g., TCE) can serve as electron acceptors under anaerobic conditions.

Electron donor - Substance that donates electrons (and therefore is oxidized) in the oxidation-reduction reactions that are essential for the growth of microorganisms and

bioremediation. Organic compounds (e.g., lactate) generally serve as an electron donor during anaerobic bioremediation. Less chlorinated solvents (e.g., vinyl chloride) and hydrogen generated in fermentation reactions can also serve as electron donors.

Emulsified edible oil - A formulation in which an edible oil (such as soybean oil) is dispersed into water (e.g., through stirring or use of homogenizers) to form a mixture of oil droplets in water. Emulsifying the oil greatly improves the distribution of the oil in the subsurface.

Emulsion - A suspension of small globules of one liquid in a second liquid with which the first will not mix (e.g. oil and water).

Endpoints - Operational criteria, which can be established for application of a remediation technology such as ISCO. For example, an endpoint could be set as achieving a target concentration of oxidant throughout the TTZ for a specified period time after which active ISCO operations could be terminated. Operational endpoints can also be set such that they are equivalent to achievement of goals.

Enhanced *in situ* bioremediation (EISB) - See “*In situ* bioremediation.”

Enzyme - A protein created by living organisms to use in transforming a specific compound. The protein serves as a catalyst in the compound's biochemical transformation.

Ex situ - Latin term referring to the removal of a substance from its natural or original position, such as the treatment of contaminated groundwater aboveground.

Fenton's reagent - A solution consisting of hydrogen peroxide and an iron catalyst used to oxidize contaminants. The reagent was discovered by H.J.H. Fenton in the 1890s.

Fermentation - Oxidation of organic compounds occurring in the absence of any external electron acceptor.

Ferrous salt - Soluble iron salt.

First-order reaction - Chemical reaction in which the rate is dependent on the concentration of only one of the reactants.

Fluvial - Of, relating to, or happening in a river.

Free radical - See “Radicals.”

Full scale - Implementation of a remediation technology at a scale that is intended to represent what would be deployed to treat the entirety of a target treatment zone.

Geochemical - Produced by or involving non-biochemical reactions of the subsurface.

Growth substrate - An organic compound upon which bacteria can grow, usually as a sole carbon and energy source.

Half-life - Time required to reduce the concentration of a constituent to half of its initial value.

Hydraulic conductivity - A measure of the ability of a porous medium to transmit water when subjected to a hydraulic gradient.

Hydraulic fracturing - Method used to create fractures that extend from a borehole into the surrounding subsurface formations. Fractures are typically maintained by a proppant, a material such as grains of sand or other material that prevent the fractures from closing. Used to increase or restore the ability of the subsurface to transmit fluids.

Hydraulic gradient - Change in head (water pressure) per unit distance in a given direction, typically in the principal flow direction.

Hydraulic head - Elevation of a water body above a particular datum level. Specifically, the energy possessed by a unit weight of water at any particular point; measured by the level of water in a manometer at the laboratory scale or by water level in a well, borehole, or piezometer in the field. Water invariably flows from points of larger hydraulic head to points of lower head.

Hydraulic residence time - The average time water spends within a specified region of space, such as a reactor or a treatment zone within the subsurface.

Hydrocarbons - Chemical compounds that consist entirely of carbon and hydrogen.

Hydrogen bonding - Attractive force between the hydrogen attached to an electronegative atom of one molecule and an electronegative atom of a different molecule. Usually the electronegative atom is oxygen, nitrogen, or fluorine, which have partial negative charges, and the hydrogen then has a partial positive charge.

Hydrogen peroxide (H₂O₂) - An unstable compound used especially as an oxidizing and bleaching agent, antiseptic, and as a propellant.

Hydrolysis - The decomposition of organic compounds by interaction with water.

Hydrophilic - Having a strong affinity for water. Hydrophilic compounds tend to be found in the aqueous phase.

Hydrophobic - "Water-fearing." Hydrophobic compounds, such as oils and chlorinated solvents, have low solubilities in water and tend to form a separate nonaqueous phase.

Hydroxyl (-OH) - The chemical group or ion that consists of one atom of hydrogen and one of oxygen and is neutral or negatively charged.

Hydroxyl radical (HO[•]) - The neutral form of the hydroxide ion (OH⁻). Hydroxyl radicals are highly reactive and consequently short-lived. Hydroxyl radicals are produced from natural processes and engineered reactions.

Hypochlorous acid - An oxyacid of chlorine containing monovalent chlorine that acts as an oxidizing or reducing agent.

Hypoxic - A condition of "low" or "deficient" oxygen content.

Hysteresis - A retardation of an effect when the forces acting upon a body are changed. For example, the relationship between moisture content and water potential generally differs depending on whether a porous media is being wetted or dried. Similarly, sorption and desorption of a compound may occur at different rates.

Immiscibility - The inability of two or more substances or liquids to readily dissolve into one another, such as oil and water.

Impermeable - Not easily penetrated. The property of a porous media or soil that does not allow, or allows only with great difficulty, the movement or passage of water.

Infiltration gallery - A reagent delivery method in which horizontal wells or trenches are installed in the unsaturated zone, and fluids are injected into them so that fluids percolate downward into a treatment zone.

In situ - Latin term meaning “in place” – in the natural or original position, such as the treatment of groundwater in the subsurface.

In situ air stripping - Treatment system that removes or “strips” volatile organic compounds from contaminated groundwater or surface water by forcing an air stream through the water, causing the compounds to volatilize.

In situ bioremediation - The use of microorganisms to degrade contaminants in place with the goal of producing harmless chemicals as end products. Generally, *in situ* bioremediation is applied to the degradation of contaminants in saturated soils and groundwater, although bioremediation in the unsaturated zone can occur.

In situ chemical oxidation (ISCO) - Technology that oxidizes contaminants in place by adding strong oxidants, such as potassium permanganate or hydrogen peroxide, resulting in detoxification or immobilization of the contaminants.

In situ chemical reduction (ISCR) - Technology that reduces contaminants in place by addition of chemical reductants, such as zero-valent iron, resulting in detoxification or immobilization of the contaminants.

In situ thermal treatment - Treatment system that generates high temperatures to remove and destroy contaminants in place. In practice, three types of technologies have been used – steam injection, electrical resistance heating (generating heat by applying an electrical current) and thermal conductive heating (using electrical subsurface heaters to radiate heat outwards through the solid matrix).

Influent - Water, wastewater, or other liquid flowing into a reservoir, basin, or *in situ* target treatment zone.

Initiation - A chemical reaction that yields a net increase in the number of free radicals in the system.

Injection well - A well installed for the purpose of injecting remediation agents into the aquifer. Generally not acceptable as a performance monitoring location because they may not be representative of the conditions in the treatment zone as a whole.

Inorganic compound - A chemical that is not based on covalent carbon bonds. Perchlorate is an inorganic compound, as are metals, nutrients (such as nitrogen and phosphorus), minerals, and carbon dioxide.

Interfacial tension - The force at the interface between two immiscible liquids (such as a DNAPL and water) that results from the attractive forces between the molecules in the different fluids. Generally, the interfacial tension of a given liquid surface is measured by finding the force across any line on the surface divided by the length of the line segment (so that interfacial tension is expressed as force per unit length, equivalent to energy per unit surface area).

Intrinsic bioremediation - A type of *in situ* bioremediation that uses the innate capabilities of naturally occurring microbes to degrade contaminants without requiring engineering steps to enhance the process.

Intrinsic remediation - *In situ* remediation that uses naturally occurring processes to degrade or remove contaminants without using engineering steps to enhance the process. Also known as natural attenuation and if process monitoring is carried out, monitored natural attenuation.

Investigation-derived waste (IDW) - Waste generated in the process of investigating or examining an actual or potentially contaminated site; includes solid and hazardous waste, media (including groundwater, surface water, soils, and sediments), and debris.

Ionization - The physical process of converting an atom or molecule into an ion by adding or removing charged particles, such as electrons or other ions.

Ionization potential - Work required to remove (to infinity) the topmost electron in an atom or molecule when the gas atom or molecule is isolated in free space and is in its ground electronic state.

Isoconcentration - More than one sample point exhibiting the same concentration.

Isotope - Any of two or more species of an element in the periodic table with the same number of protons. Isotopes have nearly identical chemical properties but different atomic masses and physical properties. For example, the isotopes chlorine 37 (^{37}Cl) and chlorine 35 (^{35}Cl) both have 17 protons, but ^{37}Cl has two extra neutrons and thus a greater mass.

Isotope fractionation - Selective degradation of one isotopic form of a compound over another isotopic form. For example, microorganisms degrade the ^{35}Cl isotopes of perchlorate more rapidly than the ^{37}Cl isotopes. ISCO reactions also can degrade lighter isotopes preferentially, resulting in changes in fractionation as oxidation proceeds.

Karst - Geologic formation of irregular limestone deposits with sinks, underground streams, and caverns.

Ketone - Chemical compound with a carbonyl group (with a carbon-to-oxygen double bond); can be formed by the oxidation of organic matter or alcohols.

Kinetics - The rate at which a reaction occurs determined by an applicable reaction rate law and rate constant.

Lactate - A salt or ester of lactic acid.

Leachate - Solution formed when a fluid (e.g., water) percolates through a permeable medium. When passing through contaminated media, the leachate may contain contaminants in solution or in suspension.

Leaking underground storage tank (LUST) - The U.S. Congress created the leaking underground storage tank (LUST) Trust Fund in 1986 by amending Subtitle I of the Resource Conservation and Recovery Act (RCRA). The LUST Trust Fund has two purposes. First, it provides money for overseeing and enforcing corrective action taken by a responsible party, who is the owner or operator of the LUST. Second, the Trust Fund provides money for cleanups at LUST sites where the owner or operator is unknown, unwilling, or unable to respond, or which require emergency action.

Life cycle cost - The overall estimated cost for a particular remedial alternative over the time period corresponding to the life of the project including direct and indirect initial costs plus any periodic or continuing costs of operation and maintenance.

Light nonaqueous phase liquid (LNAPL) - A nonaqueous phase liquid with a specific gravity less than 1.0. Because the specific gravity of water is 1.0, most LNAPLs float on top of the groundwater table. Most common petroleum hydrocarbon fuels and lubricating oils are LNAPLs.

Lipid - Amphiphilic molecule, possessing the ability to separate two different phases or layers (such as separating water and oil). Often refers to a cell's outer membrane. An amphiphile possesses both a polar-charged region, which attracts water molecules, and a non-charged and non-polar area, which attracts non-polar oils and fats.

Liquid chromatography - A chemical separation technique in which the mobile phase (a liquid) passes over or through a stationary phase.

Local equilibrium assumption (LEA) - An assumption that reactions of interest (such as NAPL dissolution or sorption) are "sufficiently fast" so that local equilibrium can be assumed. In the case of dissolution, it could be that the dissolution occurs rapidly compared to flow through the porous media so that the dissolved concentration immediately adjacent to the NAPL is equal to the NAPL's solubility. For sorption, it means that sorption and desorption occur rapidly relative to flow through the porous media so that any change in concentration is immediately accompanied by a corresponding change in sorbed mass.

Log K_{ow} - Logarithmic expression of the octanol-water partition coefficient (K_{ow}), a measure of the equilibrium concentration of a compound between octanol and water.

London-van der Waals forces - Weak, transient electrical forces (attractive or repulsive) between two molecules that arise from the movement of their intermolecular electrons.

Long-term monitoring (LTM) - Monitoring conducted after a remedial measure achieves its objectives, to ensure continued protection and performance.

Low permeability media (LPM) - A region of low permeability within the subsurface. Can act as a localized barrier to groundwater flow or NAPL migration. Can initially act as a sink

for dissolved and sorbed contaminant mass, and later as a secondary source via back-diffusion.

Macroscopic - Large enough to be seen by the unaided eye.

Magnetite - Common mineral of black iron oxide strongly attracted to magnetic fields. Important iron ore. Capable of reducing chlorinated solvents in groundwater.

Mass balance - An accounting of the total inputs and outputs to a system. For dissolved plumes, it refers to a quantitative estimation of the mass loading to a dissolved plume and the mass attenuation capacity within the affected subsurface environment.

Mass discharge - The rate of mass flow across an entire plume at a given location. Also referred to as “total mass flux” or “integrated mass flux.” Expressed in units of mass per time (e.g., grams per day [g/day]), mass discharge essentially integrates several individual mass flux measurements (expressed as mass/area/time, such as grams per square meter per day [g/m²/day]).

Mass flux - The rate of mass flow across a unit area (typically measured in g/m²/day). Typically calculated by integrating measured groundwater contaminant concentrations across a transect. Often incorrectly used interchangeably with mass discharge or mass loading (expressed in g/day) to describe the mass emanating from a source zone or the mass passing a given transect across the plume.

Mass spectrometer - Instrument used to identify the chemical structure of a compound. Usually, the chemicals in the compound are separated beforehand by chromatography.

Mass transfer - The general term for the physical processes involving molecular and convective transport of atoms and molecules within physical systems. In this context, the term refers to the transport of solute mass from the nonaqueous phase (e.g., NAPL) into the aqueous phase, between the aqueous phase and the gas phase, and between the sorbed phase and the aqueous phase. The rate of mass transfer is controlled by the differences in concentrations between the phases, as well as the interfacial tension at the NAPL:water interface.

Matrix diffusion - Diffusion of substances in groundwater into, and back out from, the surrounding solid materials in the subsurface. Important in matrices such as low permeability clays and rock matrices in which diffusion is the rate-controlling process for contaminant movement. Can result in initial attenuation of plumes and eventual long-term releases of contaminants back into the groundwater.

Matrix storage - Storage of substances in the surrounding solid materials in the subsurface. Significant fractions of the total contaminant mass may be stored in the low permeability or inaccessible areas, greatly complicating subsurface remediation.

Maximum contaminant level (MCL) - Standards set by the U.S. Environmental Protection Agency (USEPA) or state equivalent for drinking water quality that provide for a legal threshold limit on the amount of a hazardous substance that is allowed in drinking water under the Safe Drinking Water Act. The limit is usually expressed as a concentration in milligrams or micrograms per liter of water.

Media - Groundwater, porous media, soil, air, surface water, or other parts of an environmental system that can contain contaminants and be the subject of regulatory concern and remediation activities.

Membrane interface probes (MIPs) - Probe with a permeable membrane on its side that is inserted into the subsurface and heated to volatilize nearby organic compounds. The volatile organic compounds (VOCs) permeate the membrane and are delivered to the surface for analysis using one or more detectors, such as a photo ionization detector (PID), flame ionization detector (FID) or an electron capture detector (ECD). Useful as semi-quantitative tool to locate VOC contamination by monitoring continuously as the MIP is pushed into the subsurface or placed at desired depth intervals.

Metabolism - The chemical reactions in living cells that convert food sources to energy and new cell mass.

Metabolite - The intermediates and products of metabolism.

Metal chelators - Chemicals that form multiple bonds with a single metal ion to produce soluble, complexed metal-chelant molecules. Used to enhance solubility and uptake of metals or to inhibit production of precipitates or scale.

Methanogen (methanogenic archaea) - A microorganism that exists in anaerobic environments and produces methane as the end product of its metabolism. Methanogens use carbon dioxide or simple carbon compounds such as methanol as an electron acceptor.

Methanogenesis - Process of producing methane gas during biological metabolism.

Methanotroph (methanotrophic bacteria) - A microorganism able to metabolize methane as its only source of carbon and energy. Methanotrophs can grow aerobically or anaerobically and require single-carbon compounds.

Micelle - An aggregate of surfactant molecules dispersed in a liquid colloid. A typical micelle in aqueous solution forms an aggregate with the hydrophilic "head" regions in contact with surrounding solvent, sequestering the hydrophobic single-tail regions in the micelle center.

Microcosm - A laboratory vessel established to resemble the conditions of a natural environment.

Microemulsion - Clear, stable, isotropic liquid mixtures of oil, water and surfactant, frequently in combination with a cosurfactant. The aqueous phase may contain salt(s) or other ingredients; the "oil" may actually be a complex mixture of different hydrocarbons and olefins. Microemulsions form upon simple mixing of the components and do not require the high shear conditions generally used in the formation of ordinary emulsions. The two basic types of microemulsions are direct (oil dispersed in water) and reversed (water dispersed in oil).

Microorganism (microbe) - An organism of microscopic or submicroscopic size. Bacteria are microorganisms.

Mineral - A naturally occurring solid formed through geological processes that has a characteristic chemical composition, a highly ordered atomic structure, and specific physical properties. A rock, by comparison, is an aggregate of minerals and/or mineraloids and need not have a specific chemical composition.

Mineralization - The complete degradation of an organic chemical to carbon dioxide, water, and possibly other inorganic compounds or elements.

Miscible - Two or more liquids that can be mixed and will remain mixed under normal conditions.

Mitigation - Measures taken to reduce adverse impacts on the environment.

Modified Fenton's reagent - Hydrogen peroxide activated by addition of ferrous (II) or ferric (III) iron to dramatically increase its oxidative strength. This increase is attributed to the production of hydroxyl radicals (OH^\bullet) and initiation of a chain reaction, involving formation of new radicals. The reaction of iron catalyzed peroxide oxidation at pH 3–5 is called a "Fenton's Chemistry" after its discoverer H.J.H. Fenton. Classical Fenton's chemistry has been "Modified" by use of higher oxidant concentrations and additional chelants and stabilizers so that it can be effective under environmental conditions at a higher pH range.

Moiety - One of the portions or subdivisions into which something is divided.

Mole fraction - The number of moles of a component of a solution divided by the total number of moles of all components.

Molecular biological tool (MBT) - Laboratory tests based on biological molecules such as DNA that can measure the presence and activity of microbes at a site. They can be used to assess the potential for and performance of monitored natural attenuation and bioremediation strategies for remediation of environmental contaminants.

Molecular diffusion - Also known as "simple diffusion," it is the inactive, spontaneous transport of a substance from a region of high concentration to a region of low concentration by means of random molecular motion.

Monitored natural attenuation (MNA) - Refers to the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives.

Monitoring well - A well installed for the purpose of monitoring groundwater quality in an aquifer, and not used to facilitate the injection of remediation agents.

Monod kinetics - Equation based on the Michaelis-Menten equation for enzyme kinetics that relates a microbial culture's specific growth rate (μ) to the substrate concentration (s). Requires empirically derived parameters for the maximum growth rate (μ_{max}) with excess substrate available, and the half-maximal saturation constant (K_s) – the substrate concentration at which the growth rate is half of μ_{max} . The fundamental equation is $\mu = \mu_{\text{max}} (s / [K_s + s])$.

Monte Carlo simulation - A problem-solving technique used to approximate the probability of certain outcomes by running multiple trial runs, called simulations, using random variables. Monte Carlo methods allow evaluation of complex situations involving random behavior, such as games of chance, and can help reduce uncertainty in estimating future outcomes in areas such as risk assessment or actuarial analyses.

Mudstones - A fine-grained sedimentary rock whose original constituents were clays or muds – hardened mud; a mix of silt and clay-sized particles.

Nanoscale - Generally deals with structures of the size 100 nanometers (nm) or smaller. For example, reactive iron produced in this size range is referred to as nanoscale iron.

Natural attenuation - Reduction in the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater caused by natural processes that act without human intervention. These *in situ* processes include biodegradation, dispersion, dilution, sorption, volatilization, radioactive decay, and chemical or biological stabilization, transformation, or destruction of contaminants.

Natural organic matter (NOM) - A form of naturally occurring organic matter that has been broken down to some base-level compounds (such as cellulose, chitin, protein, lipids, etc.). NOM provides nutrients to insects, bacteria, fungi, fish, and other organisms at the base of the food chain.

Natural oxidant demand (NOD) - Refers to one or more chemical reactions that can occur between an oxidant (typically permanganate) and naturally occurring substances in the subsurface (e.g., NOM, reduced metals, minerals). The oxidant consumed during these reactions is unavailable for reaction with the target COCs.

Nonaqueous phase liquid (NAPL) - An organic liquid that maintains itself as a separate phase from water.

Nonproductive - Term used to describe the consumption of oxidant during ISCO due to chemical reactions that occur and lead to depletion of the oxidant without degradation of a target COC. See NOD and Persistence.

Non-wetting DNAPL - Wettability is a measure of a liquid's relative affinity for a solid. Where two liquid phases are present, the "wetting" fluid will preferentially spread over the solid surface at the expense of the "non-wetting" fluid. Wettability is depicted by the concept of a Contact Angle. Since wettability conventionally refers to the nonaqueous phase, the angle is measured through the aqueous phase. A majority of DNAPL contaminants are non-wetting (water occupies the smaller pore spaces and preferentially spreads across solid surfaces while the DNAPLs are restricted to the larger openings).

Numerical model - A mathematical model that uses a numerical time-stepping procedure to estimate behavior of a system over time (as opposed to an analytical model). The mathematical solution is represented by a generated table and/or graph. Numerical models require greater computing power, but they can allow more realistic simulations of complex systems.

Observational Method - An approach to site remediation that explicitly takes into account uncertainty in site characterization understanding and attempts to reduce costs while

enabling timely and effective remediation. The Observational Method has key elements applicable to site remediation including: characterization to define the general nature of site conditions to be encountered; remedial design based on most probable site conditions; identification of reasonable deviations from those most probable conditions; identification of key parameters to observe to detect deviations during remediation; and preparation of contingency plans for potential deviations.

Octanol-water partition coefficient (K_{ow}) - Ratio of the concentration of a chemical in octanol and in water at equilibrium and at a specified temperature. Octanol is an organic solvent used as a surrogate for NOM. This parameter is used in many environmental studies to help determine the fate of chemicals in the environment. Inversely related to aqueous solubility (a high K_{ow} indicates a compound will preferentially partition into an organic phase rather than into water).

Operations and maintenance (O&M) - Activities conducted at a site after a remediation activity has been implemented to ensure the technology or approach implemented is effective and operating properly. The term O&M covers a wide range of activities, from overseeing the proper functioning of a remediation system to conducting environmental monitoring to evaluate the effectiveness of a remedial action.

Organic - Referring to or derived from living organisms. In chemistry, any compound containing carbon.

Oxic - Containing oxygen or oxygenated. Often used to describe an environment, a condition, or a habitat in which oxygen is present.

Oxidant - A chemical compound that gains electrons in a chemical reaction. An oxidant can also be referred to as an oxidizing agent. As a result of the reaction, the oxidizing agent becomes reduced.

Oxidant concentration - The concentration (mass/volume) of an oxidant in a liquid oxidant solution.

Oxidant dose - See "Oxidant loading rate". Often incorrectly used as a synonym for oxidant concentration.

Oxidant loading rate - A design parameter that is the ratio of the mass of oxidant applied to the mass of subsurface solids in the target treatment zone, usually expressed in units of g/kg or mg/kg.

Oxidant persistence - Refers to the ability of an oxidant (usually applied to CHP, persulfate and ozone) to remain present and reactive over time in the subsurface after its initial delivery via an injection well, probe, or other method.

Oxidation - Transfer (loss) of electrons from a substance, such as an organic contaminant. The oxidation can supply energy that microorganisms use for growth and reproduction. Often but not always, oxidation results in the addition of an oxygen atom and/or the loss of a hydrogen atom.

Oxidation-reduction potential (ORP) - The tendency of a solution to either gain or lose electrons when it is subject to change by introduction of a new species. A solution with a

higher (more positive) reduction potential than the new species will have a tendency to gain electrons from the new species (to be reduced by oxidizing the new species); a solution with a lower (more negative) reduction potential will have a tendency to lose electrons to the new species (to be oxidized by reducing the new species). A positive ORP indicates the solution is oxidizing, while a negative ORP indicates reducing conditions are dominant.

Ozone (O₃) - A simple triatomic molecule, consisting of three oxygen atoms. An allotrope of oxygen that is much less stable than the diatomic oxygen (O₂). A powerful oxidizing agent. Unstable at high concentrations, decaying to ordinary diatomic oxygen.

Ozonide - Compound formed by the addition of ozone to an organic compound.

Partition coefficient (K_d) - Ratio of the concentrations in a liquid phase in contact with a solid phase. Measure of the sorption potential, whereby a contaminant is divided between the solid and water phase.

Partitioning interwell tracer testing (PITT) - Method to quantify the volume of NAPL in a contaminated aquifer by injecting and recovering a tracer that will partition into the NAPL phase. Provides information about the NAPL volume distribution in a relatively large-scale area.

Passivation - Process of making a material “passive” in relation to another material. Often used to refer to the formation of a hard non-reactive surface film on many reactive or corrosive materials (such as aluminum, iron, zinc, magnesium, copper, stainless steel, titanium, and silicon) that inhibits further reactivity.

Passive injection (passive treatment) - Remediation approach involving additions of amendments to the subsurface on a one-time or very infrequent basis.

Passive treatment - *In situ* bioremediation approach in which amendments are added to the subsurface on a one-time or infrequent basis. Passive treatment relies on the use of slow-release electron donors, which can be injected into the subsurface or placed in trenches or wells.

Pathogen - Microorganisms (e.g., bacteria, viruses, or parasites) that can cause disease in humans, animals, and plants.

Percarbonate - Any of a family of perhydrates of carbonate compounds, such as sodium percarbonate (2Na₂CO₃·3H₂O). Percarbonate compounds can undergo chemical reactions under certain environmental conditions to yield free radicals.

Perchlorate - An anion consisting of one chlorine atom and four oxygen atoms, with the chlorine atom present at an oxidation state of +7. Occurs naturally; because it is a potent oxidizer, it also has been manufactured and used for solid rocket propellants and explosives.

Perchloroethene (PCE, perchloroethylene, tetrachloroethene, tetrachloroethylene) - A colorless, nonflammable organic solvent, Cl₂C:CCl₂, used in dry-cleaning solutions and as an industrial solvent.

Percolation - Movement of water downward and radially through subsurface soil layers, usually continuing downward to groundwater; can also involve upward movement of water. Slow seepage of water through a filter.

Permanganate - General name for a chemical compound containing the manganate (VII) ion, (MnO_4^-). Because manganese is in the +7 oxidation state, the manganate (VII) ion is a strong oxidizing agent.

Permeability - A measure of the ability of a material, such as soil or aquifer porous media, to transmit fluids such as water. Units of measure are L^2 .

Permeable reactive barrier (PRB) - A permeable wall or vertical zone containing reactive media or creating a set of reaction conditions and oriented to intercepting and remediating a contaminant plume as groundwater migrates through the wall or zone.

Peroxone - A combination of ozone and hydrogen peroxide yielding a product not requiring a catalyst and used to treat contaminated soil and water.

Persistence - See "Oxidant persistence".

Persulfate - Ions or compounds with more oxygen than normal sulfates, such as sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$). Persulfate compounds can be activated by transition metals, heat, or elevated pH to yield sulfate free radicals.

pH - An expression of the intensity of the basic or acid condition of a liquid; may range from 0 to 14, where 0 is the most acid and 7 is neutral. Natural waters usually have a pH between 6.5 and 8.5.

Phospholipid fatty acid analysis (PLFA) - Analysis of the phospholipids, which are major components of all cell membranes. PLFA can provide a broad description of the entire microbial community with information obtained about viable biomass concentrations, community composition, and metabolic status.

Photolysis - The splitting of molecules by means of light energy.

Phytoremediation - The use of plants and in some cases the associated rhizosphere (root zone) microorganisms for *in situ* remediation of contaminants.

Piezometer - A non-pumping well, generally of small diameter, for measuring the pressure head at a given depth and location in a groundwater zone.

Pilot scale - A scale of demonstration, testing or evaluation under laboratory or field conditions that can incorporate certain features and processes that are representative of a full scale system. A pilot-scale study is often used to investigate the design and performance of a full-scale system. See "Full scale" and "Pilot test".

Pilot test - A trial run of a remediation technology implemented at the field scale. Performed to assess the feasibility of the remediation technology and/or to collect field-scale data on which to base full scale design. Generally conducted at smaller scale than full-scale treatment.

Plume - A zone of environmental media containing contaminants. As applied to groundwater, it usually originates from a contaminant source zone and extends for some distance in the direction of groundwater flow.

Pneumatic fracturing - Injection of gas into the subsurface at pressures exceeding the natural *in situ* pressures and at flow volumes exceeding the natural permeability of the subsurface. Creates a network of artificial fractures in a geologic formation that can facilitate removal of contaminants out of the geologic formation; may be used to introduce remedial agents.

Polychlorinated biphenyls (PCBs) - A group of toxic, persistent chemicals used in electrical transformers and capacitors for insulating purposes and in gas pipeline systems as lubricant. The sale and new use of these chemicals, also known as PCBs, were banned by U.S. law in 1979.

Polycyclic aromatic hydrocarbon (PAH) - Chemical compound that consists of fused aromatic rings and does not contain heteroatoms or carry substituents. PAHs occur in oil, coal, and tar deposits, and are produced as byproducts of fuel burning (whether fossil fuel or biomass). As a pollutant, they are of concern because some compounds have been identified as carcinogenic, mutagenic, and teratogenic.

Polymerase chain reaction (PCR) - Technique to amplify a single or few copies of a specific DNA sequence by several orders of magnitude. Allows detection of a target gene or parts of a gene, even when present at low concentrations in soil or groundwater, for example. PCR relies on thermal cycling, consisting of cycles of repeated heating and cooling of the reaction for DNA melting and enzymatic replication.

Polyvinyl chloride (PVC) - A tough, environmentally indestructible plastic that releases hydrochloric acid when burned.

Pore volume (PV) - The volume of void space within a porous medium (e.g., soil). A design metric that is the ratio of the volume of injected reagents to the volume of pore space in the target treatment zone. Also termed the number of pore volumes.

Porosity - The fraction of the subsurface volume filled with pores or cavities through which water or air can move.

Potassium permanganate (KMnO₄) - A chemical oxidant commonly used for ISCO; characterized by its purple to pink color in solution.

Potassium persulfate (K₂S₂O₈) - A chemical oxidant commonly used for ISCO.

Potentiometric surface map - A contour map that represents the top of the groundwater surface in an aquifer.

Precipitate - A substance separated from a solution or suspension by chemical or physical change.

Pressure transducer - A sensor device that converts pressure into an analog electrical signal, allowing measurement.

Primary substrates - The electron donor and electron acceptor that are essential to ensure the growth of microorganisms. These compounds can be viewed as analogous to the food and oxygen that are required for human growth and reproduction.

Propagation reaction - Chemical reactions involving free radicals in which the total number of free radicals remains constant.

Pseudo first-order reaction - A second-order reaction in which one of the reactants is present in such great amounts that its effect is not seen and the reaction thus behaves as first-order.

Pump-and-treat (P&T) - A remediation approach in which groundwater is extracted from the subsurface using a network of pumping wells and treated *ex situ* to remove COCs. P&T also can be applied as a containment strategy.

Pyrite - An iron sulfide mineral with the formula FeS_2 . The most common of the sulfide minerals. Also called fool's gold.

Radicals - Atoms, molecules, or ions with unpaired electrons, which are highly reactive. Chemical oxidants like H_2O_2 can be activated during use in ISCO and yield one or more types of radicals (often call free radicals), which serve as the primary oxidizing agents.

Radius of influence (ROI) - The radial distance from the center of an injection point or well to the point where there is no significant impact from the injected material.

Raoult's Law - Relates the vapor pressure of components to the composition of the solution. If the components are sufficiently similar, the vapor pressure of the solution will depend on the vapor pressure of each chemical component and the mole fraction of the component present in the solution. Used to predict the soluble concentrations of each compound in a mixture of similar compounds (e.g., benzene, toluene, ethyl benzene and xylenes [BTEX] in gasoline) that is in equilibrium with the aqueous phase, based on the mole fraction of each compound in the mixture.

Rebound - see "Contaminant rebound".

Recharge - Process by which water is added to a zone of saturation, usually by percolation from the ground surface (e.g., the recharge of an aquifer via precipitation and infiltration).

Recirculation wells - A groundwater well that is specially designed so groundwater enters and exits the well and causes a spherical recirculation pattern in the groundwater formation. While groundwater is within the well, treatment can be achieved (e.g., by air stripping or sorption processes) and *in situ* treatment in the groundwater formation can also be enabled if amendments are added and carried out as groundwater exits the well (e.g., bionutrients, oxidants).

Record of decision (ROD) - A public document that explains which cleanup alternative(s) will be used at National Priorities List sites where, under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Trust Funds pay for the cleanup.

Redox reactions - Reduction/oxidation reactions are those in which atoms have their oxidation number changed. For example, carbon may be oxidized by oxygen to yield carbon dioxide or reduced by hydrogen to yield methane. The redox potential (ORP) reflects the tendency of a chemical species to acquire electrons and thereby be reduced. In a redox reaction, one chemical species – the reductant or reducing agent—loses electrons and is oxidized, and the other – the oxidant or oxidizing agent – gains electrons and is reduced.

Reducing - Environmental conditions that favor a decrease in the oxidation state of reactive chemical species (e.g., reduction of sulfates to sulfides).

Reduction - Transfer of electrons to a substance such as oxygen; occurs when another substance is oxidized.

Reductive dechlorination (hydrogenolysis) - Reaction involving removal of one or more chlorine atoms from an organic compound and their replacement with hydrogen atoms. A subset of reductive dehalogenation. Key reaction for anaerobic degradation of chlorinated solvents.

Reductive dehalogenation - The process by which a halogen atom (e.g., chlorine or bromine) is replaced on an organic compound with a hydrogen atom.

Remedial action - The actual construction or implementation phase of a contaminated site cleanup following remedial design.

Remedial action objectives (RAOs) - Specific goals for protecting human health and the environment that address the overall cleanup process.

Remediation - Cleanup technology or approach used to remove or contain contamination.

Remediation goal - Goals define what the remedial actions are intended to achieve or accomplish. Goals can be general for the overall remediation system (or treatment train), or they may be specific to one of the technologies in the treatment train (see “Treatment Goals” below). Under CERCLA goals are often numeric levels. For example, during the Feasibility Study process under CERCLA, preliminary remedial goals (PRGs) are the concentrations used to define the area to be remediated and to what level. PRGs become remedial goals (RGs) once a ROD specifies the selected remedy and modifies the PRGs.

Remediation objective - Remediation objectives can be established to state the purpose for which remediation is intended. They often tend to be high-level outcomes that are desired but, in and of themselves, are often not directly measurable. For example, an objective might be stated as: remediation of a contaminated site to reduce the risk to human health for unrestricted current and future land use. RAOs under the CERCLA represent an example of an objective.

Residual NAPL - Saturation level below which NAPL will no longer freely drain.

Residual saturation - Saturation level below which water will no longer freely drain.

Retardation - Slowing of the movement of substances in an aquifer relative to the groundwater velocity. For example, a contaminant plume exhibiting a retardation factor of 5 expands one-fifth as fast as the water itself or a non-reactive tracer such as chloride, which has a retardation factor near 1.0.

Reverse osmosis - A treatment process used in water systems by adding pressure to force water through a semi-permeable membrane. Removes most drinking water contaminants. Also used in wastewater treatment.

Salinity - Percentage of salt in water.

Saturated zone - Part of the subsurface that is beneath the water table and in which the pores are filled with water.

Saturation - Refers to the fraction of porous media pore space that contains fluid (for example, water or NAPL). If no fluid is specified, it is generally taken to refer to water saturation.

Scavenger - Refers to a substance that can react with a free radical to inhibit the free radical from participating in oxidation reactions with COCs. Scavengers include organic compounds like formate and ethanol and inorganic compounds like bicarbonate and carbonate.

Second-order reaction - A chemical reaction with a rate proportional to the concentration of the square of a single reactant or the product of the concentration of two reactants: rate = $k[A][B]$ or $k[A]^2$

Secondary groundwater parameters - As used in this volume, a set of aquifer parameters other than concentrations of target COCs that may change as a result of ISCO implementation (e.g., pH, microbial communities, metals concentrations).

Sediments - Soil, sand, and minerals carried from land into water bodies.

Seepage velocity - The average pore water velocity. Since groundwater flow actually occurs only through interconnected pores and not through the entire subsurface volume – as assumed in calculating the Darcy velocity (V) – the seepage velocity (V_s) is equal to the Darcy velocity divided by the porosity (n), or $V_s = V/n$.

Semi-passive treatment - *In situ* remediation approach in which amendments are added to the subsurface intermittently (at intervals of a few weeks to a few months).

Site characterization - The collection of environmental data that are used to describe the conditions at a property and delineate the nature and extent of a site's contamination.

Slug test - A particular type of aquifer test where water is quickly added to or removed from a groundwater well, and the change in hydraulic head is monitored through time, to determine the near-well aquifer characteristics. It is a method used by hydrogeologists and civil engineers to determine the transmissivity and storativity of the subsurface material surrounding the well.

Sodium permanganate (NaMnO₄) - A chemical oxidant used for ISCO; more concentrated than potassium permanganate and available in liquid form.

Sodium persulfate (Na₂S₂O₈) - A chemical oxidant commonly used for ISCO.

Soil mixing - An approach used to deliver and distribute chemical oxidants (or other remedial amendments) into the subsurface.

Soil organic matter (SOM) - Organic constituents in the soil, including undecayed plant and animal tissues, their partial decomposition products, and the soil biomass. SOM includes high-molecular-weight organic materials (such as polysaccharides and proteins), simpler substances (such as sugars, amino acids, and other small molecules), and humic substances.

Soil oxidant demand (SOD) - Refers to one or more chemical reactions that can occur between an oxidant and the soil or porous media in the subsurface. The oxidant consumed during these reactions is unavailable for reaction with the target COCs. NOD is the preferred terminology for the same set of nonproductive reactions and NOD is used in this volume (see NOD).

Soil vapor extraction (SVE, soil venting) - An established technology for the *in situ* remediation of VOCs in the vadose (unsaturated) zone. The process removes soil vapor contaminated with VOCs and enhances the mass transfer of VOCs from the soil pores to the vapor phase by applying a vacuum to extract soil contaminants and gases.

Solubility - Ability of a substance to dissolve (or solubilize). The solubility of a specific solute is its maximum concentration in a given solvent at a reference temperature.

Solute - A substance (usually in lesser amount) dissolved in another substance. A relevant example of a solution is oxidant dissolved in groundwater: oxidant is the solute and groundwater is the solvent.

Solvent - A substance, usually a liquid, capable of dissolving another substance.

Sorb - To take up and hold by either adsorption or absorption.

Sorption - Collection of a substance on a solid by physical or chemical attraction. Can refer to either absorption (in which one substance permeates another) or adsorption (surface retention of solid, liquid, or gas molecules, atoms, or ions).

Sorption isotherm - Describes the sorption of a material at a surface at constant temperature. Determined by comparing the sorbed concentration of a compound to its concentration in solution. Describes the ability of a dissolved contaminant to adsorb or absorb onto the solid particles (soil or particulates).

Source strength - The mass discharge from a source zone. Represents the mass loading to the plume per unit time (e.g., grams TCE released per day).

Source zone - A subsurface zone that serves as a reservoir of contaminants that sustain a plume of dissolved contaminants in groundwater. Includes the subsurface material that is or has been in contact with the contaminants originally released into the subsurface

(e.g., DNAPLs for chlorinated solvents); the source zone mass includes the sorbed and aqueous phase contaminants, as well as any residual NAPL.

Sparge - Injection of gases into water. As used for *in situ* remediation, air (or another gas) is sparged to strip dissolved VOCs and/or oxygenate groundwater to facilitate aerobic biodegradation of organic compounds. Ozone in air is sparged to oxidize organic compounds.

Specific conductance (electrical conductivity) - Rapid method of estimating the dissolved solid content (total dissolved solids) of a water by testing its capacity to carry an electrical current.

Stabilization/solidification - Remediation technique in which contaminants are physically bound or enclosed within a stabilized mass (solidification) or their mobility is reduced due to chemical reactions induced between a stabilizing agent and the contaminants (stabilization).

Stabilizer - Term used to describe a substance that can reduce the rate of reaction of a chemical oxidant during transport in the subsurface.

Stakeholder - A person (other than regulators, owners, or technical personnel) who has a legitimate interest in a contaminated site.

Steady-state - A condition of a physical system or device that does not change over time or in which any one change is continually balanced by another, such as the stable condition of a system in equilibrium.

Steam enhanced remediation (SER) - An *in situ* thermal treatment technology involving steam injection and aggressive vapor and liquid extraction to mobilize and remove organic contaminants from a source zone.

Steric effects - The influence of the structural configuration of reacting substances upon the rate, nature, and extent of reaction.

Sterilization - The removal or destruction of all microorganisms, including pathogenic and other bacteria, vegetative forms, and spores.

Stoichiometry - The calculation of quantitative (measurable) relationships of the reactants and products in a balanced chemical equation.

Storativity - The volume of water an aquifer releases from or takes into storage per unit surface area of the aquifer per unit change in head. It is equal to the product of specific storage and aquifer thickness. In an unconfined aquifer, the storativity is equivalent to the specific yield. Also called storage coefficient.

Stratum (strata) - A layer of subsurface media with internally consistent characteristics that distinguishes it from contiguous layers. Each layer is generally one of a number of parallel layers that lie one upon another, laid down by natural forces. Typically seen as bands of different colored or differently structured material exposed in cliffs, road cuts, quarries, and river banks.

Substrate - A compound that microorganisms can use in the chemical reactions catalyzed by their enzymes.

Sulfate radical - A radical which can be produced during ISCO by activation of sodium persulfate.

Sulfate-reducing bacteria (SRB, sulfate reducer) - Bacteria that convert sulfate to hydrogen sulfide. Often play important roles in the oxygen-limited subsurface.

Superoxide radical anion - An anion with the chemical formula O_2^- . It is important as the product of the one-electron reduction of dioxygen O_2 , which occurs widely in nature. With one unpaired electron, the superoxide ion is a free radical and, like dioxygen, is paramagnetic. Superoxide is biologically quite toxic and is deployed by the immune system to kill invading microorganisms. Because superoxide is toxic, nearly all organisms living in the presence of oxygen contain isoforms of the superoxide scavenging enzyme, superoxide dismutase, which is an extremely efficient enzyme; it catalyzes the neutralization of superoxide nearly as fast as the two can diffuse together spontaneously in solution.

Surfactant - A material that can greatly reduce the surface tension of water when used in very low concentrations. Primary ingredient of many soaps and detergents.

Surfactant flushing (Surfactant enhanced aquifer remediation [SEAR]) - Remediation technology involving injection of a solution of surfactants into a subsurface containing NAPLs. Surfactants increase the effective aqueous solubility of the NAPL constituents, greatly enhancing NAPL removal during flushing.

Sustainable - Sustainable, or “green”, remediation can be defined in a number of ways, but the U.S. Environmental Protection Agency has defined it as “[t]he practice of considering all environmental effects of remedy implementation and incorporating options to maximize net environmental benefit of cleanup actions”.

Target Treatment Zone (TTZ) - The portion of the subsurface that the remediation technology or approach is intended to treat.

Termination reaction - Chemical reactions involving free radicals resulting in a net decrease in the number of free radicals. Typically, two free radicals combine to form a more stable species.

Thermodynamic - The study of the conversion of energy into work and heat and its relation to macroscopic variables, such as temperature and pressure.

Tortuosity - The actual length of a fluid flow path in porous media, which is sinuous in form, divided by the straight-line distance between the ends of the flow path.

Total dissolved solids (TDS) - Combined content of all inorganic and organic substances in a liquid that are present in a molecular, ionized, or micro-granular (colloidal sol) suspended form.

Total organic carbon (TOC) - A measure of the mass of carbon bound in organic compounds in a substance (e.g., soils, sediments, and water). Often used as a nonspecific indicator of water quality.

Toxicity - The degree to which a substance or mixture of substances can cause harm to organisms. Acute toxicity involves harmful effects in an organism through a single or short-term exposure. Chronic toxicity is the ability of a substance or mixture of substances to cause harmful effects over an extended period.

Tracer test - Used to “trace” the path of a migrating fluid. For groundwater applications, tracer tests are commonly conducted by dissolving a tracer chemical into groundwater at concentrations that do not significantly change the aqueous density. Tracer chemicals must behave conservatively, meaning that no mass is lost through reaction or partitioning into differing phases. Bromide ion is often employed as a solute tracer (added to groundwater as potassium or sodium bromide salt).

Transmissivity - Rate at which water of a prevailing density and viscosity is transmitted through a unit width of an aquifer or confining bed under a unit hydraulic gradient (units of area/time, e.g., ft²/day). A function of properties of the liquid, the porous media, and the thickness of the porous media. Equal to hydraulic conductivity (K) times aquifer thickness.

Transverse dispersivity - An empirical factor that quantifies how much contaminants stray away from the path of the groundwater carrying them. Some contaminants will be “behind” or “ahead of” the mean groundwater path, giving rise to a longitudinal dispersivity; some will be “to the sides of” the pure advective groundwater flow, leading to a transverse dispersivity.

Treatability test - A means of evaluating the suitability of treatment technologies or processes prior to their implementation. Treatability tests are commonly carried out under laboratory conditions.

Treatment goal - Treatment goals are specific criteria by which the successful completion of an activity can be determined. For example, an ISCO treatment goal might be established for a TTZ that ISCO is to be applied to.

Treatment performance monitoring - Monitoring to obtain data concerning the effectiveness of a technology or approach and achievement of treatment goals.

Trichloroethane (TCA) - An industrial solvent (CH₃CCl₃). Other names for it include methyl chloroform and chloroethene. Occurs in two isomers: 1,1,1-TCA and 1,1,2-TCA.

Trichloroethene (TCE, trichloroethylene) - A stable, low boiling point colorless liquid (CH₃Cl:CHCl₂). Used as a solvent or metal-degreasing agent and in other industrial applications. Toxic if inhaled, and a suspected carcinogen.

Unsaturated zone - The region of the subsurface above the groundwater table where media pores are not fully saturated, although some water may be present. Also called the vadose zone.

Vadose zone - The region of the subsurface above the groundwater table where pores are partially or largely filled with air. Also called the unsaturated zone.

Vapor intrusion - Migration of volatile chemicals from the subsurface into overlying buildings.

Vapor pressure - A measure of a substance's propensity to evaporate. The force per unit area exerted by vapor in an equilibrium state with surroundings at a given pressure. Increases exponentially with an increase in temperature. A relative measure of chemical volatility, vapor pressure is used to calculate water partition coefficients and volatilization rate constants.

Vaporization - Conversion of a substance from the liquid or solid phase to the gaseous (vapor) phase. There are two types of vaporization: evaporation and boiling.

Vinyl chloride (VC) - A chemical compound ($\text{CH}_2\text{:CHCl}$) that is highly toxic and believed to be carcinogenic. A colorless compound and an important industrial chemical chiefly used to produce the polymer PVC.

Viscosity - The molecular friction within a fluid that produces flow resistance.

Volatile - Evaporates readily at normal temperatures and pressures.

Volatile organic compound (VOC) - Any organic compound that has a high enough vapor pressure under normal conditions to significantly vaporize and transfer from a liquid to a gas phase.

Volatilization - Transfer of a chemical from the liquid to the gas phase (as in evaporation).

Water solubility - The maximum possible concentration of a chemical compound dissolved in water.

Water table - The top of an unconfined aquifer. Indicates the level below which subsurface porous media are saturated with water.

Wellhead - The assembly of fittings, valves, and controls located at the land surface and connected to the flow lines, tubing, and casing of the well so as to control the flow from a groundwater zone.

Wettability - The relative degree to which a fluid will spread into or coat a solid land surface in the presence of other immiscible fluids.

Zero-order reaction - Chemical reaction in which the rate is independent of the concentrations of the reactants.

APPENDIX D

SUPPORTING INFORMATION FOR SITE-SPECIFIC ENGINEERING OF ISCO

D.1 TEST PROCEDURES FOR MEASUREMENT OF NATURAL OXIDANT DEMAND AND OXIDANT PERSISTENCE

D.1.1 Introduction

When oxidizing agents are delivered into the subsurface (e.g., by probe injection or well delivery), they can react nonproductively through interactions with porous media and groundwater constituents. The reactions that occur and their rates are site specific, depending on the type and concentration of oxidizing agent employed and the media characteristics (e.g., presence of reactive minerals, organic carbon, etc.). Because oxidizing agents are consumed during contaminant degradation and nonproductive reactions, their transport typically will be retarded compared to the transport of the injected solution during injection and transport. For example, Figure D.1 presents a highly simplified comparison of the radius of influence (ROI) of the total volume of injection solution delivered compared to that of the oxidizing agent itself for an example scenario where oxidant depletion during subsurface transport may be relatively rapid.

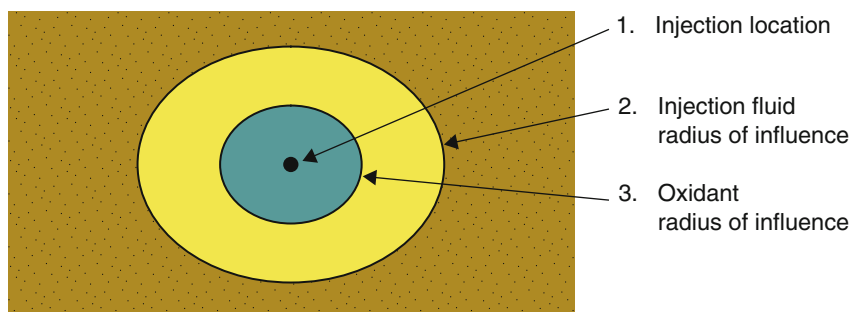


Figure D.1. Hypothetical radius of influence (ROI) of an injected solution versus the oxidant (e.g., permanganate) during subsurface injection (plan view). The ratio of the oxidant ROI to fluid ROI is primarily a function of the rate of injection and rate of reaction of an oxidant during interactions with target contaminants of concern (COCs) and constituents that are naturally present in the subsurface.

The extent of transport of the oxidant solution injected is dependent on injection rate and hydrogeologic conditions in the zone to which delivery is occurring (e.g., thickness of mobile zone). The transport of the oxidizing agent away from the injection location is a function of the delivery rate compared to the oxidant depletion rate. A higher transport distance can be

anticipated under rapid oxidant delivery conditions and slow rate of nonproductive oxidant depletion conditions (e.g., very persistent oxidant). An exception is the potential for enhanced delivery of hydrogen peroxide that can result due to gas generation, which can facilitate movement beyond the estimated ROI of the injection solution. While the rate of oxidizing agent delivery is controlled by system design, the rate of oxidant depletion is site-specific and it can be evaluated and quantified to improve certainty associated with the design ROI.

The following procedures have been developed to assist *in situ* chemical oxidation (ISCO) remediation practitioners with the collection of data for site-specific media to determine the rate and extent of oxidant depletion. These procedures are intended to capture what is commonly referred to as “natural oxidant demand” (NOD) for permanganate, or oxidant persistence for free radical-based oxidants such as catalyzed hydrogen peroxide (CHP) and activated persulfate. These data can be used to estimate the oxidant ROI for use during modeling with design tools such as CDISCO, described in Chapter 6. It is important to note that these procedures are offered as guidance and there may be a variety of means to meet the objectives of obtaining these data. The procedures outlined in this document are based on a simplified “1 pore volume (PV)” plug-flow approach and are provided herein for illustration purposes, assuming the target oxidant delivery volume is equal to 1 PV of the target treatment zone (TTZ). The test procedures can be modified as necessary for more or less than 1 PV.

D.1.2 Sample Collection, Preservation, and Storage

The number of samples of porous media to be collected for a given site is a function of the size and extent of heterogeneity of the site, particularly with respect to the design TTZ. At least one sample of field porous media is necessary from each distinct lithologic zone to be contacted with oxidant, and at least three samples from each zone are recommended. Even within a given lithologic zone, there can be high variability in oxidant persistence measurements for a particular media. The number of samples collected should be a function of the degree of certainty in the oxidant persistence measurement necessary to have sufficient certainty in cost and delivery effectiveness. The number of samples to collect, along with their collection procedure(s), handling, and storage should be guided by standard practices (e.g., see USEPA, 1989, 1991 and references therein).

In general, uncontaminated, background samples of the site porous media and groundwater are preferred, assuming they are representative of the TTZ. The procedure can be conducted with contaminated media, however extrapolating results across the TTZ where contaminated water and porous media concentrations may vary by several orders of magnitude needs to be done carefully. If evaluations are conducted with media containing a high contaminant mass (e.g., dense nonaqueous phase liquid [DNAPL] residual), the oxidant persistence measured in the tests may underestimate the persistence in zones with lower contamination levels. The mass of media and volume of sample to collect should be decided based on the outcome of calculations made in the procedures below, and allowing for appropriate sample replication. Media should be collected in a manner that maintains *in situ* field conditions (e.g., field moist intact porous media cores), with minimum handling until ready for test preparations.

D.1.3 Test Procedure for Measuring Oxidant Persistence

Test Procedure Steps

1. Determine the maximum achievable fluid radius of influence (R_{\max}) for the intended system design. This value is assumed to be the MAXIMUM possible oxidant ROI (R_{ox}). If the R_{\max} is unknown or uncertain, based on field experiences, a reasonable

default value may be 15 feet (ft) (4.6 meters [m]) for probe injection and 30 ft (9.2 m) for well injection (the two most commonly used delivery approaches).

- Calculate the total bulk treatment volume (V_b).

$$\text{Area} = \pi(R_{\text{max}})^2 \quad (\text{Eq. D.1})$$

$$V_b = \text{Area} \times \text{Thickness} \quad (\text{Eq. D.2})$$

Thickness = thickness of subsurface zone to be treated.

Note that the volume that will be contacted at the site is less than this maximum value because heterogeneities will cause preferential flow through more mobile zones. If the mobile porosity can be accounted for based on tracer tests or other site characterization information, then a correction can be applied here (i.e., use mobile zone volume instead of total volume).

- Calculate the mass of porous media (M_{media}) associated with this volume using the media dry bulk density, typically in the range of 1.6–2.0 grams per milliliter (g/mL) (99.9–124.9 pounds per cubic foot [lb/ft³]).
- Calculate the volume of oxidant solution to be delivered (1 PV) that is associated with the ROI (V_{fl}). If an approach using less than 1 PV is desirable, modify V_{fl} accordingly.

$$V_{\text{fl}} = \text{Porosity of site media} \times V_b \quad (\text{Eq. D.3})$$

- Select the maximum desirable oxidant concentration (C_{max}) that may be chosen for use at the site. (Note that oxidant concentrations are conventionally expressed as milligrams [mg]- MnO_4^- /liter [L], mg- H_2O_2 /L, or mg- $\text{S}_2\text{O}_8^{2-}$ /L for permanganate, catalyzed hydrogen peroxide, and persulfate, respectively.) This concentration chosen may be based on a variety of factors including:

- Oxidant solubility
- Site contaminants – type, concentration, mass, mass distribution
- Potential for anticipated undesirable byproducts (e.g., gas, oxidant impurities, solids, pH)
- Outcome/output of Tier 1 Conceptual Design (see Chapter 9)
- Hazards associated with the oxidant
- Practitioner experience

Alternatively, C_{max} may be determined using more complex analytical or numerical modeling of the ISCO system applied at the site (see Chapter 6).

- Calculate the maximum oxidant dose anticipated (mg-oxidant/kilogram [kg]-media (dry wt.) initial condition (D_o)) (Equation D.4):

$$D_o = (C_{\text{max}})(V_{\text{fl}})/M_{\text{media}} \quad (\text{Eq. D.4})$$

Units: $D_o = \text{mg-oxidant/kg-media (dry wt.)}$

$C_{\text{max}} = \text{mg-oxidant/L-solution}$

$V_{\text{fl}} = \text{L-solution}$

$M_{\text{media}} = \text{kg-media (dry wt.)}$

- Select two fractions of D_o that span the range of desirable conditions to evaluate (e.g., $0.5D_o$, $0.1D_o$), designated D_1 and D_2 .
- For a reaction vessel size of at least 40 mL, calculate the mass of media (M_{rx}) (Equation D.5) and volume (V_{rx}) (Equation D.6) of solution to use to achieve a

1:1 (v/v) solids to solution ratio with minimal resulting headspace. These are the values that will be employed in the tests for EACH oxidant dose and EACH replicate (20% replication of all test conditions is a standard approach). An example calculation is provided below assuming use of a 40 mL reaction vessel and a media particle density of 2.65 g/mL (NOTE: a larger volume reaction vessel may be needed to handle a representative sample volume obtained at sites with heterogeneous subsurface conditions (e.g., samples of very low bulk density or fractured bedrock).

$$M_{rx} = (40 \text{ mL})(0.5)(2.65 \text{ g/mL}) = 53 \text{ g of porous media (dry wt.)} \quad (\text{Eq. D.5})$$

$$V_{rx} = (40 \text{ mL})(0.5) = 20 \text{ mL of solution} \quad (\text{Eq. D.6})$$

NOTE: where field moist solids are employed, M_{rx} and V_{rx} must be corrected for water content, where V_{rx} is decreased by the water content associated with the solids and M_{rx} is increased by this value (applying water density of 1.0 g/mL). For example, if field moist porous media solids having a water content of 0.25 v/v are used, then V_{rx} must be decreased by 5 mL ($5 \text{ mL} = 0.25 \times 20 \text{ mL}$), which accounts for the volume the water in the field moist solids will occupy; and M_{rx} must be increased by 13.25 g ($13.25 \text{ g} = 0.25 \times 20 \text{ mL} \times 2.65 \text{ g/mL}$) to obtain a new M_{rx} , which accounts for the weight of water in the field moist sample.

- Calculate the concentration of oxidant (C_o) (Equation D.7) that will result in the D_o dose value. (Note: while D_o was based on an initial high concentration value that may be desirable for the site (C_{max}), it is the resulting dose (mg-oxidant/kg-media [dry wt.]) from the application of this concentration to the target media (M_{media}) that must be evaluated in these studies. This may result in using a different concentration in the lab tests than C_{max} because of the predetermined mass of media (M_{rx}) used in the tests.) Perform the same calculation to achieve C_1 and C_2 values. An example calculation for C_o is provided below. C_1 and C_2 will be the same resulting fractions of C_o as the D_1 and D_2 values selected in Step 5.

$$C_o = (M_{rx})(D_o)/V_{rx} \quad (\text{Eq. D.7})$$

Units: $C_o = \text{mg-oxidant/L-solution}$

$M_{rx} = \text{kg-media (dry wt.)}$

$D_o = \text{mg-oxidant/kg-media (dry wt.)}$

V_{rx} total = Volume solution added plus water content in field moist solids if used (L)

- Choose a reaction vessel compatible with the oxidant of interest and contaminants of concern for the site. Amber or colored glass vials are recommended due to the photo-sensitivity of some oxidants. NOTE: for gas producing oxidant, it may be necessary to choose a vessel that will allow for gas release (i.e., venting with or without capture and analysis) during reaction.
- Weigh the appropriate mass of media into the replicate reaction vessels. Field moist porous media is recommended to mitigate potential changes to porous media characteristics that can result with air or oven drying. It is best to use field moist porous media that has been properly preserved to avoid oxidation by atmospheric oxygen while drying. However if field moist media is used, the M_{rx} and V_{rx} calculations must be adjusted for water content as described in Step 8.
- Add the appropriate concentrations of oxidant as per Step 9 calculations. NOTE: if volumes lower than V_{rx} of stock oxidant are used, the additional make-up solution to achieve V_{rx} may be provided as site groundwater or deionized water. Use of site

groundwater is recommended for those sites anticipated to have a high concentration of reduced constituents or oxidant scavengers in groundwater. In this case, it is recommended that at least 75% of V_{rx} total be composed of groundwater and 25% or less of oxidant solution. Typically the reaction of oxidant with groundwater constituents at most sites is a small fraction of the loss of oxidant from reaction with the porous media. An exception may be sites with high total dissolved solids (TDS) concentrations, the constituents of which may have significant oxidant scavenging capacity.

13. Completely mix the reaction vessels throughout the reaction period. NOTE: it may be necessary to release gas from reaction vessels for gas producing oxidants. If contaminated porous media is used and VOCs are present, they may be released. If this is the case, the vented gas needs to be captured and properly handled for safety reasons. If contaminant degradation is being measured the VOCs in the vented gas need to be quantified (e.g., by using a solvent trap and with appropriate analytical methods).
14. Sample each reaction vessel and measure oxidant concentration at multiple time points (at least 4) within the initial 48 h of reaction and daily thereafter (at least 3 additional days) until there is minimal change (e.g., <5–10% decline) in oxidant concentration over three consecutive sampling events. For rapidly reacting oxidants, such as peroxygen oxidants, a more condensed sampling timeframe is recommended, with multiple sample time points within the first several hours and additional samples every several hours thereafter. It is recommended to take the minimum volume of sample needed for analysis given the oxidant's analytical detection limit if dilution is necessary. This is to avoid significant loss of volume from the reaction vessel, development of headspace, and/or leakage from septa if applicable. For example, it is often reasonable to remove 0.1 mL of sample per measured time point, then to dilute the sample to the volume necessary for oxidant measurement procedures. If it is necessary or desirable to use a larger sample volume for analysis, then it may be prudent to use a reaction vessel larger than 40 mL or use a separate 40-mL reaction vessel for each time point measurement.
15. Characterize reaction rates for each oxidant dose (D_o , $0.5D_o$, $0.1D_o$) evaluated. For hydrogen peroxide and persulfate, it is appropriate to determine a pseudo first-order rate for oxidant decomposition for the duration of the test. For permanganate, a range of values for NOD can be collected as defined below and illustrated in Figure D.2:

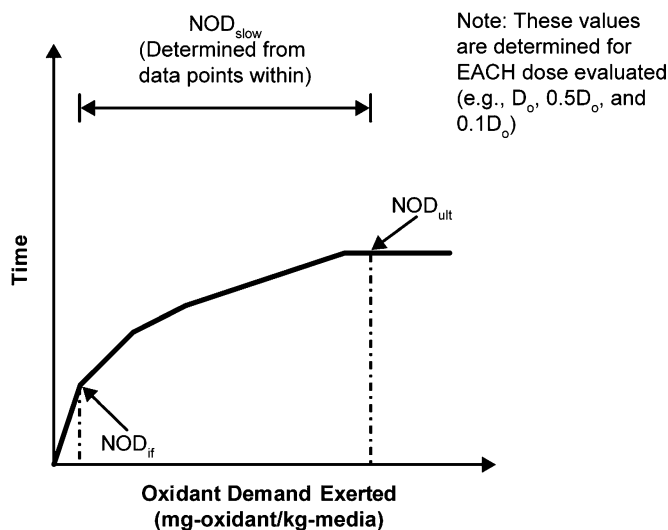


Figure D.2. Illustration of NOD terms for permanganate laboratory tests.

- Ultimate NOD (NOD_{ult}) is the total demand exerted over the entire test duration in (mg-oxidant/kg-media (dry wt.)).
 - Instantaneous fraction of NOD (NOD_{if}) is the initial fast reaction of permanganate with naturally occurring media constituents. This is the fraction of the NOD_{ult} that is exerted typically within the first 8–12 h of the test. NOD_{if} is unitless and <1.0 .
 - The pseudo-first-order or the second-order, slower rate of NOD expression (NOD_{slow}) is the rate at which the remainder of the oxidant reacts with the media ($NOD_{ult} - NOD_{if} \times NOD_{ult}$). NOD_{slow} is determined using at least four data points if any pseudo first-order or second-order reaction rate is determined.
16. Plot initial oxidant dose vs. depletion rate (or all three terms for permanganate) to generate a curve (i.e., model) of dose versus rate of oxidant depletion (Figure D.3). From this curve, an estimate of oxidant depletion rate can be made for a range of oxidant doses falling within the three test values (D_o , $0.5D_o$, and $0.1D_o$).
 17. Manage materials and wastes appropriately upon test completion.

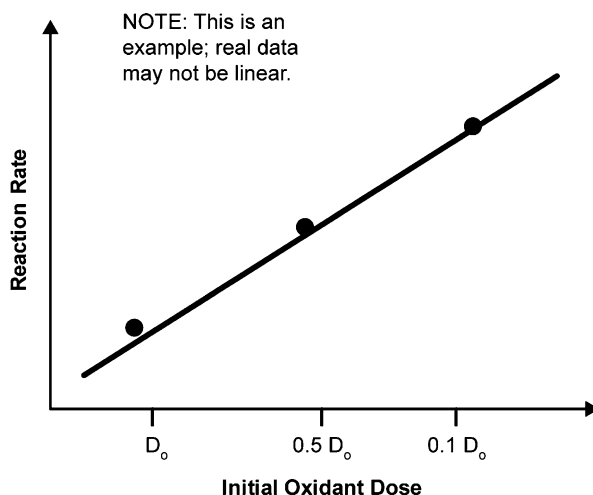


Figure D.3. Illustration of oxidant dose vs. rate of oxidant depletion assessment.

D.1.4 Example of Test Procedure and Data Analysis

Example D.1 below demonstrates the procedure in its entirety. The use of these data is discussed in Chapter 9, Section 9.3 with respect to both Tier 1 and Tier 2 Conceptual Design. The uses of the rate data are also discussed as a model (analytical or numerical) input variable in Chapter 6. Examples of the relationship of laboratory studies to field-scale design are included in Appendix D.4 focused on design of pilot-scale evaluations.

Example D.1

An ISCO system employing permanganate was designed (conceptual) for a site with an anticipated injection solution radius of influence (R_{max}) of 12 ft (3.7 m). The contamination at the site is between 10 and 30 ft (3 and 9.1 m) below ground surface (bgs) (20 ft total (6.1 m)), but only approximately 15 ft (4.6 m) of this is accessible to a delivered solution (mobile zone) due to

heterogeneities as determined through inspection of boring logs for the site. Based on the Tier 1 Conceptual Design, the oxidant concentration to be delivered is 5,000 mg-MnO₄⁻/L.

Laboratory tests were conducted to determine rates of oxidant depletion to be used in the Conceptual Design process to help verify the anticipated oxidant ROI. This was needed to determine the number and spacing of injection points. Amber volatile organic analysis (VOA) vials (40-mL) with Teflon-lined septa caps were used. A stock solution of 10,000 mg-MnO₄⁻/L (C_{stock}) was prepared and used. There was sufficient site porous media and groundwater available for tests with media collected from multiple locations at the site in duplicate. Table D.1 shows the results of calculations performed to set up the tests (Steps 1–7 of the simplified procedure outlined above).

Table D.1. Laboratory Test Conditions and Setup Calculations

Parameter	Equation/value	Unit	Notes
R_{max}	12.0	ft	As per conceptual design
	3.7	m	
V_{fi}			
Area	452.2	ft ²	Equation D.1
	43.0	m ²	
Depth	20.0	ft	Site condition
	6.1	m	
V_b	Area × Depth		Equation D.2
	9,043.2	ft ³	
	256.2	m ³	
V_{fi}	Porosity × V_b		Equation D.3, Assumed porosity = 0.3
	2,713.0	ft ³	
	76.9	m ³	Equivalent to 76,900 L (for D_o calc)
M_{media}	903,415.7	lb	Assumed 1.6 g/mL (99.9 lb/ft ³)
	410,196.6	kg	
M_{media} Mobile zone	677,561.8	lb	15 of 20 ft depth
	301,440.0	kg	4.6 of 6.1 m depth
C_{max} (MnO ₄ ⁻)	5,000.0	mg/L	As per conceptual design
D_o	$C_{max} \times V_{fi}/M_{media}$		Equation D.4
D_o	1,275.5	mg/kg	
0.5 D_o	637.8	mg/kg	
0.1 D_o	127.6	mg/kg	
M_{rx}	53.0	g	Equation D.5
	0.053	kg	
V_{rx}	20.0	mL	Equation D.6
	0.020	L	
C_o	$M_{rx} \times D_o/V_{rx}$		Equation D.7
C_o	3,380	mg/L	
C_1	1,690	mg/L	
C_2	338	mg/L	

Aliquots of the porous media were weighed (M_{rx}) and added to the VOA vials and then appropriate volumes of groundwater (V_{gw}) and oxidant (V_{ox}) were added as per the calculations shown in Table D.2. The VOA vials were placed in an end-over-end mixer maintained at 20°C to complete procedural Steps 8–11. At reaction times of 1, 4, 8, 24 h, and daily thereafter for 1 week, a 0.1 mL subsample was removed by syringe through the septa of the reaction vials (procedural Step 12). Permanganate concentrations were measured spectrophotometrically (5 point-calibration) at 525 nanometers (nm). Example data for one replicate of one media sample are presented in Table D.3 and Figure D.4. These were converted to a permanganate

Table D.2. Calculations for Groundwater and Stock Oxidant Solution Additions

Parameter	Equation/value	Unit	Notes
C_{stock}	10,000	mg/L	Stock solution
V_{rx}	0.02	L	
Oxidant mass for:	$(C \times V_{rx})$		
C_0	67.6	mg	$3,380 \text{ mg/L} \times 0.02 \text{ L}$
C_1	33.8	mg	$0.5 C_0$
C_2	6.76	mg	$0.1 C_0$
Volume of stock for:	$(1,000 \times (C/C_{stock}))$		
$V_{ox} - C_0$	6.8	mL	
$V_{ox} - C_1$	3.4	mL	
$V_{ox} - C_2$	0.7	mL	
Volume of groundwater for:	$(20 \text{ mL} - V_{ox})$		
$V_{gw} - C_0$	13.2	mL	
$V_{gw} - C_1$	16.6	mL	
$V_{gw} - C_2$	19.3	mL	

Table D.3. Example Data for One Replicate of One Media Sample

Time (h)	Permanganate concentration (mg-MnO ₄ ⁻ /L)			Permanganate mass consumed (mg-MnO ₄ ⁻)			Oxidant demand (mg-MnO ₄ ⁻ /kg-solids)		
	D _o	0.5 D _o	0.1 D _o	D _o	0.5 D _o	0.1 D _o	D _o	0.5 D _o	0.1 D _o
0	1,275	638	128	0.00	0.00	0.00	0.0	0.0	0.0
1	1,004	526	111	5.42	2.23	0.33	102.2	42.1	6.3
4	884	461	96	7.83	3.53	0.64	147.7	66.6	12.1
8	805	430	86	9.40	4.14	0.83	177.3	78.2	15.7
24	666	402	86	12.19	4.72	0.83	230.0	89.0	15.7
48	595	379	83	13.61	5.18	0.89	256.7	97.7	16.7
72	540	363	78	14.72	5.48	0.98	277.7	103.5	18.6
96	499	346	75	15.52	5.83	1.06	292.8	110.0	20.0
120	476	335	73	15.98	6.06	1.10	301.5	114.3	20.7
144	455	325	72	16.40	6.25	1.12	309.4	117.9	21.1
168	440	321	71	16.71	6.32	1.14	315.2	119.3	21.4

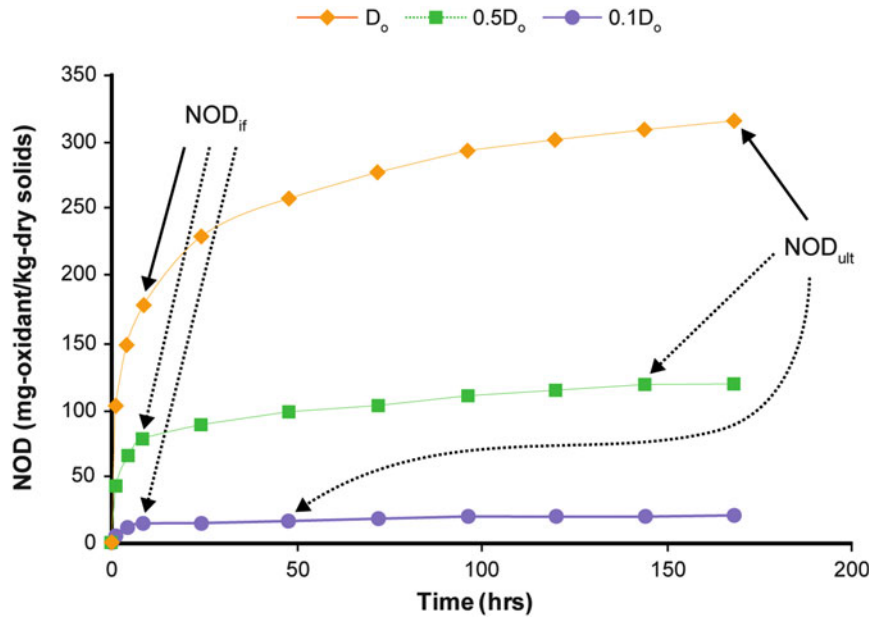


Figure D.4. Oxidant demand results for one replicate of one media sample at doses D_o , $0.5 D_o$, and $0.1 D_o$.

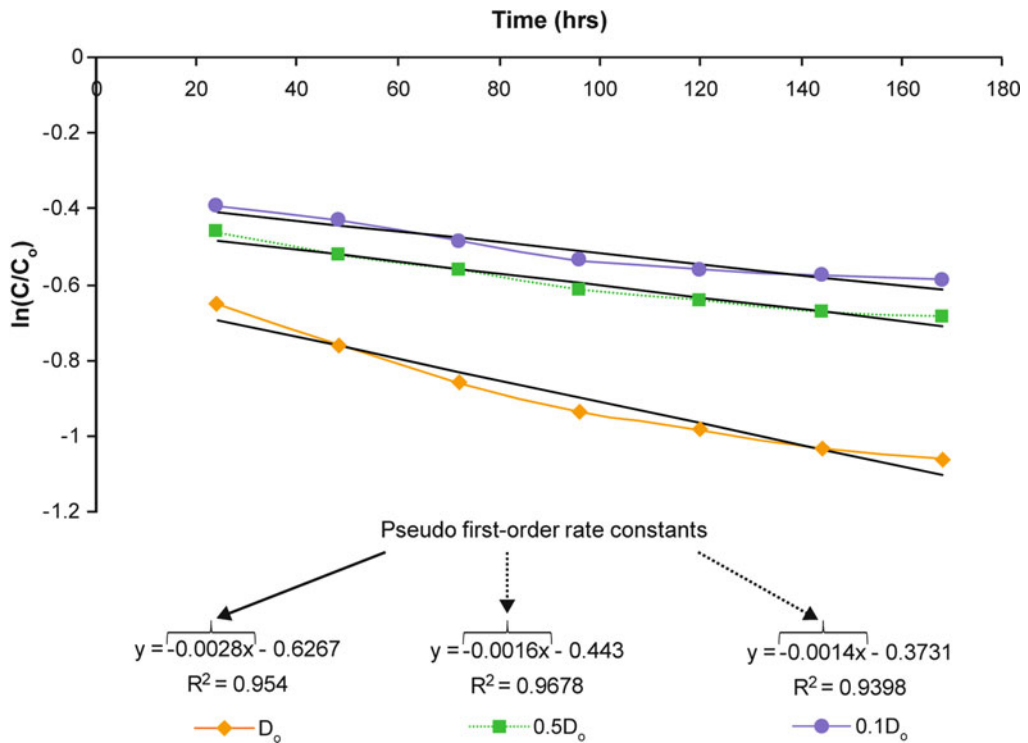


Figure D.5. Linearization of time points from 24 hours (h) to 1 week to determine NOD_{slow} via pseudo first-order rate assessment.

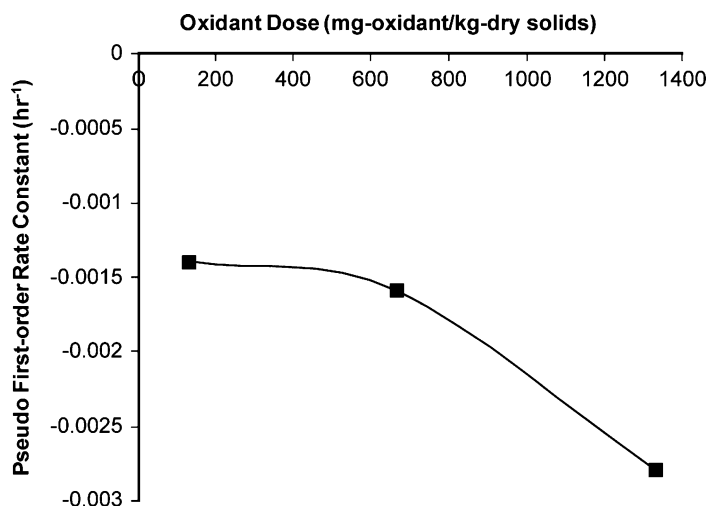


Figure D.6. Oxidant dose vs. rate of oxidant depletion.

mass consumed (concentration measured times 20 mL liquid volume) then to permanganate oxidant demand (mass consumed/mass of porous media). The data beginning at the 8 h time point through the duration of the experiment were linearized (log normal transformation) to determine NOD_{slow} . These results are shown in Figures D.5 and D.6 shows the resulting plot of oxidant dose vs. reaction rate from which reaction rates could be estimated for alternative doses, if needed.

D.1.5 References

- USEPA (U.S. Environmental Protection Agency). 1989. Soil Sampling Quality Assurance User's Guide, 2nd ed. EPA 600/8-89/046. USEPA Environmental Monitoring Systems Laboratory, Las Vegas, NV, USA. March. 279 p.
- USEPA. 1991. Site Characterization for Subsurface Remediation; Seminar Publication. EPA 625/4-91/026. USEPA Office of Research and Development, Washington, DC, USA. November. 268 p.

D.2 TEST PROCEDURES FOR EVALUATING CONTAMINANT TREATABILITY AND REACTION PRODUCTS

D.2.1 Introduction

ISCO system effectiveness at destroying contaminants of concern (COCs) can be affected by site-specific conditions. Thus, it may be necessary to compare or optimize ISCO approaches using laboratory tests with groundwater and porous media from a site to improve design and help assure treatment effectiveness.

Additionally, while simplified design approaches can capture primary reaction and transport processes related to ISCO effectiveness for destruction of dissolved contaminants, there are additional reaction processes to consider for sites with extensive nonaqueous phase liquid

(NAPL) or sorbed phase contaminant, co-contaminants, or potential for reaction byproducts or intermediates that may be of concern. These processes can affect contaminant destruction efficiency and effectiveness, and include:

- Oxidant activation (critical to catalyzed hydrogen peroxide (CHP) and activated persulfate oxidants)
- NAPL dissolution
- Contaminant desorption
- Impact of co-contaminants on contaminant dissolution, desorption, and destruction and the associated rates thereof
- Metals solubilization/mobilization

The following simplified procedures have been developed to: (1) guide the selection of an optimum activation approach, which is necessary for CHP and persulfate oxidants; (2) provide refined input to the ISCO Conceptual Design process; (3) provide insight into the ability to meet treatment goals (e.g., extent of contaminant mass destruction with NAPL or highly sorbed contaminant); and (4) guide monitoring approaches during and after active ISCO operations (e.g., based on byproducts or metals “red flags” that may be outcomes of the procedures outlined herein). It is important to note that these procedures are offered as guidance and there may be a variety of means of accomplishing the objectives noted above.

D.2.2 Test Procedures to Optimize Oxidation Chemistry

The goal of this procedure is to generate data to help determine the most efficient and effective approach for ISCO with respect to: (1) oxidant activation and (2) the ratio of oxidant to target contaminant (often evaluated only for sites with high contaminant mass density). NOTE: These evaluations are deemed critical for CHP and persulfate oxidants, and the Test Procedures for Measurement of Natural Oxidant Demand and Oxidant Persistence (Appendix D.1) can be conducted concurrently with this procedure (i.e., it is not necessary to conduct the two procedures separately).

Based on the results of the ISCO Screening Process (see Chapter 9), there may be more than one oxidant and more than one activation approach (as appropriate per oxidant) deemed viable for general site conditions. In support of the Tier 1 Conceptual Design process, kinetic parameters that affect oxidant distribution are assumed and contaminant destruction rates based on the literature are applied. These values are used in the design process to assess the most promising injection configuration(s) and oxidant delivery concentrations to achieve the most extensive and cost effective oxidant distribution and thus contaminant destruction. The procedures outlined in this section are intended to refine the estimates and literature values employed in the Tier 1 Conceptual Design process to optimize the ISCO system chemistry to achieve oxidant distribution and contaminant treatment. The procedure to evaluate/optimize oxidation chemistry is outlined in the steps below:

1. Select one or more oxidants and the range of oxidant doses (milligram (mg)-oxidant/kilogram (kg)-media [dry wt.]) to test. It is recommended to evaluate at least three oxidant doses for each oxidant to be evaluated. The following are recommendations for the initial oxidant doses to consider for these tests. These recommended values are based on available literature findings (Chapters 2–5) and case study review (Chapter 8) and correspond to typical field oxidant doses that have yielded oxidant effectiveness, as well as addressed practical considerations such as oxidant handling and safety, injection permitting, etc. NOTE: The recommended doses are the target *in situ* doses at

the oxidant's maximum radius of influence (ROI) distance from injection. Injection concentrations will be later scaled accordingly.

Permanganate: Recommended test doses include 10, 100, and 1,000 times the amount (mole [mol]) of dissolved contaminant to be treated in the target treatment zone (TTZ) (kg-media (dry wt.)). These values reflect those typically targeted for full-scale application, and are typically sufficient to satisfy the nonproductive media demand for the oxidant, as well as sorbed or NAPL contaminant under a majority of oxidant delivery conditions. If NAPL or sorbed mass is deemed exceptionally high, it may be appropriate to extend the range of doses to evaluate up to an order of magnitude or greater than these recommended values. An example for determining target doses is included below:

Maximum site dissolved trichloroethene (TCE) concentration = 10 mg/liter (L)

TTZ includes 10,000 kg-media (dry wt.)

Site dry wt. bulk density = 1.6; porosity (n) = 0.3

$$\begin{aligned} \text{TTZ pore volume} &= (\text{kg-media})(n)/1.6 \text{ kg/L} = (10,000 \text{ kg})(0.3)/1.6 \text{ kg/L} \\ &= 1,875 \text{ L} \end{aligned}$$

$$\begin{aligned} \text{TCE} &= (10 \text{ mg/L})(1,875 \text{ L})/(131.4 \text{ g/mol})(1,000 \text{ mg/g}) = 0.14 \text{ mol} \\ &0.14 \text{ mol-TCE}/10,000 \text{ kg-media} = 1.4\text{E-}05 \text{ mol/kg} \end{aligned}$$

$$\begin{aligned} \text{Oxidant dose} &= (10)(1.4\text{E-}05 \text{ mol/kg}) = 1.4\text{E-}04 \text{ mol/kg} \\ &= (100)(1.4\text{E-}05 \text{ mol/kg}) = 1.4\text{E-}03 \text{ mol/kg} \\ &= (1,000)(1.4\text{E-}05 \text{ mol/kg}) = 1.4\text{E-}02 \text{ mol/kg} \end{aligned}$$

$$1.4\text{E-}04 \text{ mol/kg} = \text{approx. } 16.6 \text{ mg-MnO}_4^-/\text{kg-media}$$

$$1.4\text{E-}03 \text{ mol/kg} = \text{approx. } 166.5 \text{ mg-MnO}_4^-/\text{kg-media}$$

$$1.4\text{E-}02 \text{ mol/kg} = \text{approx. } 1,665 \text{ mg-MnO}_4^-/\text{kg-media}$$

Hydrogen Peroxide: Recommended test oxidant doses include 1,875 mg-oxidant/kg-media (dry wt.), 5,625 mg/kg, and 18,750 mg/kg. These values translate to concentrations of 1 weight percent (wt.%), 3 wt.%, and 10 wt.% hydrogen peroxide solutions under the example field conditions presented above for permanganate. These values provide molar ratios of oxidant to contaminant for the 10 mg/L TCE example presented above of approximately 4,000, 12,000, and 40,000 (mol-oxidant/mol-TCE), respectively, which are significantly higher than typical permanganate doses because of the autocatalytic nature of hydrogen peroxide decomposition. Concentrations above these wt.% values have increasingly serious safety risks that must be addressed if used (e.g., heat and gas evolution can rupture vials).

Persulfate: Recommended test oxidant doses include 937.5 mg-persulfate/kg-media (dry wt.), 2,810 mg/kg, and 5,625 mg/kg. These values translate to concentrations of 5, 15, and 30 g/L of sodium persulfate solution under the example field conditions presented above for permanganate. These values provide molar ratios of oxidant to contaminant for the 10 mg/L TCE example presented above of approximately 281, 843, and 1,689 (mol-oxidant/mol-TCE), respectively.

2. Select range of conditions for oxidant activation, as necessary. This step may be omitted where permanganate is the test oxidant since permanganate does not require activation.

Hydrogen Peroxide: General test conditions should be based on the outcome of the ISCO Screening process (Chapter 9), and may include:

- No activation (relying on catalysis by metals and minerals naturally present in porous media at the site)
- Dissolved iron addition (typically ferrous or ferric)
- Dissolved iron plus acid addition
- Chelated iron addition (typically ferrous sulfate [FeSO₄] plus ethylenediaminetetraacetic acid [EDTA] or citrate)

For low pH activation, a pH of 2–3 is the optimum value. However, acid addition requirements may be great, and metals may be mobilized by this low of a pH, and thus many practitioners employing pH adjustments may not try to depress pH to this low of a value. The amount of acid to add to achieve the desired pH must be determined on a case-by-case basis for the site media prior to beginning testing. It is important to note that pH may drift during experimentation, so when determining the target acid volume to add, it is critical to monitor pH of the system over at least 24 h to ensure the low pH condition is maintained.

Ranges of iron to evaluate typically span ~0.001–0.1 times the molar concentration of hydrogen peroxide (for CHP) to be tested. In determining the specific concentration of iron to add, it is important to evaluate dissolved iron concentrations naturally present at the site. If it is anticipated that the natural site media (porous media and groundwater) contain high iron(II) concentrations (e.g., ~>100 mg/L), then it is likely that very little to no additional iron will be necessary to catalyze hydrogen peroxide decomposition to generate oxidative free radicals.

Ranges of chelating agent to evaluate typically span 0.1–10 times the molar concentration of iron to be tested (naturally present or added iron).

Persulfate: General test conditions should be based on the outcome of the ISCO Screening Process (Chapter 9), and may include:

- No activation (relying on catalysis by metals naturally present in porous media at the site)
- Chelated iron addition (typically FeSO₄ plus EDTA or citrate)
- Base addition for elevated pH activation
- Heat activation
- Addition of hydrogen peroxide

Ranges of iron to evaluate typically span 0.1–1.0 times the molar concentration of persulfate to be tested. In determining the specific concentration of iron to add, it is important to evaluate dissolved iron concentrations naturally present at the site. If it is anticipated that the natural site media (porous media and groundwater) contain high iron concentrations, then it is likely that very little to no additional iron will be necessary to catalyze oxidant decomposition to generate free radicals. Ranges of chelating agent to evaluate typically span 0.1–10 times the molar concentration of iron to be tested (naturally present or added iron).

For high pH activation, a pH of 10 or greater is typically the target. The amount of base to add to achieve this pH must be determined on a case-by-case basis for the site media prior to beginning testing. It is important to note that pH may drift during experimentation, so in determining the target acid volume to add, it is critical to monitor pH of the system over at least 24 h to ensure the high pH condition is maintained.

The appropriate temperature for heat activation is contaminant-specific, although ranges typically span 20 degrees Celsius (°C) (68 degrees Fahrenheit [°F]) to 50°C (122°F). It is important to note that typical groundwater temperatures can be well below the typical 20°C “room temperature”. Variations in experimental temperatures can be achieved via use of temperature-control ovens or water baths.

The dual oxidation approach of persulfate plus hydrogen peroxide should be tested at varied molar ratios of the two oxidants, ranging from 10:1 to 1:10 hydrogen peroxide to persulfate. The higher the initial hydrogen peroxide concentration, the faster the contaminant destruction and oxidant depletion (both oxidants) will be.

3. According to the target oxidant and activator conditions selected in Steps 1 and 2 above, samples are prepared according to the general procedure outlined in the Test Procedures for Measurement of Natural Oxidant Demand and Oxidant Persistence (Appendix D.1), beginning at Step 6 of that procedure, with the following modifications:
 - The contaminant of concern at the site MUST be included in the systems at a mass or concentration representative of site conditions. This may be achieved using a contaminant spike prepared from purchased chemical, however it is recommended to use contaminated site groundwater and porous media, particularly if there are co-contaminants present at the site.
 - Oxidant is added LAST to all systems (i.e., oxidant activators other than heat are added before the oxidant is added).
 - It may be necessary to prepare a separate reaction vessel for each time point to be assessed depending on the volume of sample necessary to perform oxidant and contaminant concentration analyses over time.
 - Analyses are to be made for both oxidant and contaminant concentrations over time using standard methods, and rates of depletion/destruction of each are quantified.
 - It is necessary to perform a final, full-vessel extraction for contaminant, without quenching the oxidant (which may modify system chemistry), to determine if any sorbed or NAPL contaminant remains in the system. Extractants (laboratory-grade) to employ are oxidant- and contaminant-specific. Examples of typical extractants include methanol and hexane.
4. Compare results to select optimal reaction chemistry. The optimal system will result in the most extensive contaminant destruction under the conditions that yield the most persistent oxidant behavior. Ideal systems will demonstrate:
 - Maximum contaminant destruction
 - The slowest oxidant depletion rate(s)
 - The fastest contaminant destruction rate(s)
 - Minimum or controlled evolution of off-gas

D.2.3 Test Procedures to Explore Additional System Chemistry Considerations

The goal of this procedure is to generate data that can help determine the impact of the presence of NAPL or sorbed contaminant on overall contaminant destruction or the potential

generation of reaction intermediates/byproducts. Note that the results of these procedures will likely provide an overestimate of contaminant destruction due to the completely mixed, ideal conditions of the reaction system. The procedure is outlined below

1. Follow the general sample preparation procedures described in the Test Procedures for Measurement of Natural Oxidant Demand and Oxidant Persistence (Appendix D.1), beginning at Step 6 of that procedure, with the following modifications:
 - Use optimized reaction chemistry determined in the Chemistry Optimization procedure (Appendix D.2.2)
 - Adapt preparation according to data objectives. Adaptations for example data objectives are included in Table D.4.

Table D.4. Adaptations of Laboratory Test Procedures for Specific Data Objectives

Data objective	Method adaptation
NAPL dissolution	Add the appropriate mass/volume of site NAPL to the reaction vessel to achieve a representative saturation; allow for 24 h equilibration period prior to oxidant addition
Contaminant desorption	Add the appropriate mass/volume of contaminated field porous media to system with site groundwater (using contaminated media from the field is critical as system aging will impact rate and extent of contaminant desorption); allow for 24 h equilibration period prior to oxidant addition
Co-contaminant treatment/effects	Use contaminated site groundwater having representative mixture constituents and concentrations; scale oxidant concentration to the total molar concentration of all constituents totaled
Byproducts/intermediates assessment	Conduct a thorough review of the literature to understand possible byproducts and intermediates that may be generated; modify analyses accordingly; employ multiple reactors to assess byproducts/intermediates over time (keeping in mind that metals increases noted in the field are typically transient even when laboratory tests show persistent increases in metals concentrations)
Metals solubilization/mobilization	Ensure reactors include specific site media of concern (natural or co-contaminant metal sources); conduct a thorough site characterization and review of the literature to understand potential for and implications of metals solubilization/mobilization
Kinetic assessments	It may be necessary to prepare a separate reaction vessel for each time point to be assessed depending on the volumes of sample necessary to perform analyses for the analyte of interest over time as per standard methods

2. Adapt measurements and analytical approaches according to data needs. Adaptations for example data objectives are presented in Table D.5.
3. Consider the implications of the results with respect to affirming or modifying the current ISCO system design. Example approaches for doing so include:
 - For sites with significant NAPL and sorbed contaminant mass:
 - Use multiple delivery events. This calls for revisiting the Conceptual Site Model between each delivery event and allowing time between events for significant contaminant desorption/dissolution.
 - Maximize oxidant persistence by modifying system chemistry, employing a combination of Contaminant Treatability and Byproducts Procedures 1 and 2 above to evaluate impacts on oxidant depletion and contaminant destruction.

Table D.5. Adaptations of Measurements/Analytical Approaches for Specific Data Objectives

Data objective	Method adaptation
NAPL dissolution	Perform a full extraction for contaminant(s) with solvent compatible with contaminant characteristics; include sacrificial vials for each time point to be measured
Contaminant desorption	
Co-contaminant treatment/effects	Assess total contaminant destruction in addition to primary COC destruction
Byproducts/intermediates assessment	Conduct analyses for potential intermediates/byproducts over time employing standard methods for each analyte of interest and including sacrificial vials for each time point to be measured
Metals solubilization/mobilization	In considering analytical results, consider changes as a function of oxidation-reduction potential (ORP), pH, and ionic strength – longer-term impacts may be estimated as a function of the return of post-ISCO conditions to pre-ISCO conditions. For example, while high manganese (Mn^{2+}) concentrations may be anticipated during ISCO and immediately post-treatment due to high pH and ORP, if initial site conditions include moderate pH and ORP, long-term elevated Mn^{2+} will not likely be a concern (i.e., treatment effects may be short-lived; changes during and post-ISCO may be predictable based on results of lab tests)

- Modify the planned delivery approach as appropriate to consider a recirculation delivery scheme to provide a continuous supply of oxidant via multiple pore volumes of oxidant delivery. Viability will depend significantly on site hydrogeological conditions as described in the ISCO Screening Process (see Chapter 9).
- For sites where byproducts/intermediates, including metals, may be a concern:
 - Consider duration required to return to pre-ISCO site conditions (e.g., ORP and pH) to determine if the issue may be short-lived.
 - Evaluate the risk implications of the presence of the byproduct/intermediate or metal(s). Weigh the overall risk reduction benefit of implementing ISCO.
 - Consider modifications to system chemistry to avoid undesirable byproducts/intermediates of metals. For example, increasing oxidant concentrations may facilitate complete transformation of harmful intermediates to harmless byproducts. Also, decreasing oxidant concentrations may decrease concentrations or the accumulation of byproducts or metals of concern.
 - Consider coupled ISCO processes for managing byproducts/intermediates and/or metals.

D.2.4 General Guidance

The procedural guidance offered above provides a general framework for conducting laboratory tests and acknowledges that a range of approaches may be used to meet the goals of these procedures. Associated with the test procedures outlined above, range-finding tests can be helpful to limit the number of conditions and levels to be evaluated. Initial range-finding experiments over a shorter-duration may be appropriate with respect to optimizing oxidation chemistry prior to conducting kinetic evaluations of oxidant depletion and contaminant destruction rates. To do so, samples are prepared as described above, however measurements are made at only one time period (e.g., 8, 24, or 48 h) to provide data to compare activation

approaches or ratios of oxidant to activator and/or contaminant. Following this approach, at the time point of interest, a measurement is made of an aliquot of the aqueous phase of the sample for oxidant concentration, then a full extraction of the reaction vessel is performed to measure contaminant concentration(s) at this time point. The “best” ISCO approach will provide the greatest extent of contaminant destruction with the least amount of oxidant depleted. The more expensive and extensive kinetic evaluations may then be focused on the approach that offers the most favorable results. Selection of the time period of interest must be based on general oxidant characteristics. For example, CHP is a faster reacting oxidant and would call for a shorter reaction period than the more persistent persulfate and permanganate oxidants.

Quenching the oxidant to halt the oxidation reaction for later measurement of contaminant concentrations at a given reaction period is not recommended. Quenching can alter system chemistry in a way that impacts other measurements that may be of interest (e.g., pH, ORP, metals concentrations, byproducts/intermediates, etc.). Impacts of quenching are not well understood, therefore it is best avoided. A better approach is to extract the COCs from the dissolved phase sample (where oxidant is maintained) into an extractant that effectively halts the chemical oxidation reactions. It is important to use an extractant that: (1) will not react, or only react minimally, with the oxidant; (2) is compatible with the planned analytical approach (e.g., gas chromatography and detector); and (3) will fully extract the contaminant(s) of interest.

D.2.5 Precautions with Interpretation and Application of Results

Results of both Contaminant Treatability and Byproducts Procedures 1 and 2 must be considered as the “best case” or “worst case” scenarios, as appropriate, when extrapolating to anticipated effects at the full scale under field conditions. For example, when considering the extent of contaminant treated in laboratory studies, results must be considered “best case” due to the complete contact, complete mixing, and idealized opportunity for contaminant mass transfer. The extent of treatment observed at the field-scale is often less than predicted in the laboratory. Results of oxidant depletion must be considered “worst case” also due to complete contact, complete mixing, and idealized opportunity for mass transfer. Rates of oxidant depletion in the field are often slower than predicted based on measurements made in the laboratory. Also, when examining intermediates/byproducts and/or metals mobilization, results must be considered “worst case”, primarily due to the lack of important processes that occur in the field that can minimize these processes, including dilution, return to pre-ISCO equilibrium conditions (via reaction completion or flow from upgradient zones), or other natural attenuation processes. These tests and the results derived from them are intended to guide monitoring approaches and are not to be considered pro forma indicators that ISCO is not appropriate for a site.

D.3 ANALYTICAL METHODS FOR OXIDANT CONCENTRATIONS

D.3.1 Readily Available Methods

Table D.6 summarizes analytical methods for analysis of oxidants commonly used for ISCO. These generally represent methods that involve simple equipment and less intensive sample preparation and preservation because often they may be used to monitor ISCO in the field or for use in treatability studies. There may be other useful analytical methods that are not included in Table D.6 that may either reduce the interferences or provide more certainty in

Table D.6. Summary of Analytical Methods for Commonly Used ISCO Oxidants

Citation	Necessary equipment	Available as test kit?	Reagents	Synopsis	Interferences	Estimated time per sample ^c
Hydrogen peroxide						
Kolthoff and Sandell, 1969	Glassware only	Yes	Potassium iodide; Sodium thiosulfate; Ammonium molybdate; Sulfuric acid; Starch (indicator)	Iodometric titration with back titration to the starch endpoint	Other oxidants	~5 min prep
						5 min rxn
Permanganate						
Standard Method ^a 4,500-KMnO ₄	Spectrophotometer, filtration apparatus (e.g., 0.2 micron), glassware	No	None	Direct measurement of permanganate at 525 nm	Manganese dioxide. Any turbidity or color that absorbs at 525 nm	~2 min prep
Persulfate						
Kolthoff and Carr, 1953	Glassware only	No	Potassium iodide; Sodium bicarbonate; Sodium thiosulfate; Starch (indicator)	Iodometric titration with back-titration to the starch endpoint	Other oxidants	~5 min prep
						15 min rxn
Liang et al., 2008	Spectrophotometer, glassware	No	Potassium iodide; sodium bicarbonate; sodium thiosulfate	Iodometric titration with absorbance read at 352 nm	Other oxidants	~5 min prep 15 min rxn
Huang et al., 2002	Spectrophotometer, glassware	No	Sulfuric acid; Ferrous ammonium sulfate; Ammonium thiocyanate	Persulfate is reacted with ferrous iron in acidic solution, thiocyanate added and read at 450 nm	Other oxidants, possibly organics, ^b background absorbance at 450 nm	~5 min prep
						40 min rxn
Ozone						
Standard Method ^a 4,500-O ₃	Spectrophotometer or filter colorimeter, glassware	Yes	Phosphoric acid; Monobasic sodium phosphate; Indigo (potassium indigo trisulfonate)	Indigo colorimetric method. Ozone rapidly decolorizes indigo in acidic solution and is read at 600 nm or compared to a color wheel	Manganese and other oxidants. H ₂ O ₂ is okay if samples are read promptly	~5 min prep

NOTE: min - minute; nm - nanometer rxn - reaction.

^aSee Eaton et al., 2005.

^bKolthoff and Carr (1953) reported that organics interfered with the iron(III) reaction yield due to propagation reactions involved with persulfate free radical chemistry. This interference may be overcome by the addition of a significant scavenger, such as potassium bromide.

^c“prep” indicates the estimated preparation time per sample, “rxn” indicates the estimated reaction time (if any) per sample.

results, but they are also more likely to be equipment and preparation intensive. However, an exception to this may include ozone where many real-time ozone monitors for both gas and aqueous phase concentrations are available, but are not included here.

It is worth pointing out that the most common analytical methods for persulfate and hydrogen peroxide are virtually identical, with the exception of the catalyst (ammonium molybdate). Furthermore, although the indigo method is more common for ozone, iodometric titration will also quantify ozone (Eaton et al., 2005). If only one of these oxidants is present, then good agreement between this titration and the actual oxidant concentration can be expected. This allows for the establishment of a calibration curve to determine oxidant concentration.

However, some ISCO approaches involve the injection of multiple oxidants into the subsurface, such as hydrogen peroxide and persulfate, or hydrogen peroxide and ozone. In these instances, the iodometric method is incapable of distinguishing between the oxidants. Hence this method is not an oxidant specific test but rather measures the bulk oxidizing potential of a sample. The indigo method with ozone is more oxidant specific, as ozone rapidly decolorizes indigo, whereas hydrogen peroxide, the most likely oxidant to be coupled with ozone, decolorizes indigo much slower. Thus prompt measurement may minimize this interference. One general interference that can impact any of the methods results from any natural color, turbidity or absorbance in the sample background that may interfere with the spectrophotometer reading, or the ability of the analyst to view colorimetric endpoints.

It is also worth noting that most of these methods, especially those with colorimetric or spectrophotometric readings, perform optimally (e.g., linear calibration) when low oxidant concentrations are measured (e.g., 1–100 mg/L). As this concentration range is generally far below the range of concentrations applied in the field during ISCO, samples must often be diluted by a factor of 100 or more to bring them down to the optimal range, and a source of nonreactive dilution water will be required.

Virtually all of these methods involve some degree of wet chemistry to determine the oxidant concentration. Some methods, including those for hydrogen peroxide and ozone, have commercially available test kits that spare the user the work of having to prepare and measure reagents. However, others may not be available and may require the user to prepare their own reagents. Technology vendors will often be able to provide additional expertise for oxidant analysis.

D.3.2 References

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D.4 CONSIDERATIONS FOR ISCO PILOT-SCALE TESTING UNDER FIELD CONDITIONS

The following are some of the key considerations related to performing a field pilot test of ISCO.

D.4.1 Pilot Test Objective

Realistic pilot test objectives should be developed based on the time and budget available, coupled with site-specific conditions and the desire to reduce uncertainty. Possible objectives of a pilot test include one or more of the following:

- Evaluation of possible treatment effectiveness (i.e., mass removal or achievable concentration reductions) to reduce the uncertainty in the full-scale performance
- Evaluation of reagent distribution and the radius of influence
- Refinement of input parameters for a design tool (i.e., design parameters) to help reduce the uncertainty in the ISCO system design and associated costs
- Identification/troubleshooting of challenges on a smaller scale at lower cost
- Evaluation of the potential for fatal flaws that would make ISCO impractical for full-scale
- Achievement of some COC mass removal

The approach for pilot testing should take into account the fact that the Observational Method may be employed for full-scale application of ISCO. In other words, multiple injections may be required, with the subsequent injections based on the performance of the earlier injections. Despite this, pilot testing may still be desired to reduce the uncertainty in the design, and thus the cost, and also to evaluate for fatal flaws.

Evaluating treatment effectiveness may be challenging to achieve with pilot tests. The factors that complicate achieving this objective include:

- The potential for contaminants to flow into the pilot test treatment zone from untreated upgradient locations. This may be significant in highly permeable sites with higher hydraulic gradients and where there is significant contamination upgradient. This may be managed by appropriate upgradient monitoring and modeling or by hydraulic control methods.
- The potential for the oxidant to persist in the formation beyond the time available for the pilot test, so that true endpoint concentrations cannot be obtained. The true endpoint concentrations should be obtained after time is allowed for the oxidant to dissipate, the subsurface to re-equilibrate and return to ambient geochemical conditions, and for rebound (if any) to occur.
- The potential for the water added as part of the oxidant injected to displace or dilute the *in situ* contaminant concentrations temporarily. This is especially challenging when the majority of the contaminant mass is in a dissolved phase. At sites with significant sorbed or residual NAPL this should be less of a concern since the contaminant mass that is in a sorbed phase or residual NAPL phase is typically much higher and overwhelms that in the dissolved phase. The contaminants will be treated in the dissolved phase as long as the oxidant persists, but dissolved phase concentrations will likely increase after the oxidant is exhausted (rebound) if sorbed or residual NAPL remains.
- Some oxidants cause significant desorption and dissolution of sorbed or residual NAPL. This may cause a temporary increase in the aqueous phase concentration observed in groundwater samples and may mask mass removal that is actually occurring (if the mass in the dissolved, sorbed, and NAPL phases is considered).

If assessment of the ability of the ISCO system design to meet the ISCO treatment goals is one of the required pilot test objectives, significant thought should be put into the design of the pilot test to avoid the above issues (i.e., use large pilot area, allow sufficient time for re-equilibration of contaminants in the subsurface, and use an adequate number of monitoring points). The pilot test should represent the key attributes anticipated in the full-scale design.

The other pilot test objectives are focused more on obtaining information on the distribution of the oxidant in the subsurface during an injection event. Design parameters that can be refined through pilot testing include:

- Contaminant mass and concentration in the target treatment zone. The additional wells installed while preparing for the pilot test will provide additional information on the characteristics of the site.
- Dimensions of the target treatment zone (area and depth).
- Thickness of mobile zone (through which the reagent will flow).
- Magnitude of the rate and extent of oxidant depletion due to reactions with the contaminant and natural media.

Achieving some initial mass removal is not always explicitly stated as an objective of a pilot test, but it may still exist. It may drive the pilot test to be larger than it would otherwise need to be.

D.4.2 Injection Probe or Well Spacing and Volume/Mass of Oxidant

The number of injection probes or wells (hereafter referred to as just wells) used for the pilot test should be based on the test objectives and the budget. Significant information can be obtained (thus uncertainty reduced) with just one injection well. This is especially true with respect to the distribution of the oxidant. However, to evaluate the performance of an ISCO approach in terms of contaminant reduction, multiple injection locations (at least four) are desirable. The monitoring wells used to evaluate performance should be placed between the injection locations to avoid transport of contaminants into the treatment zone monitored.

If funds are limited, it may be beneficial to put more money into more monitoring locations rather than injection locations. As a rule of thumb, the minimum number of monitoring wells is 3. These wells should be spaced at different distances from the injection well to evaluate the distribution of the oxidant during the injection period (and thus obtain information on the well space required). Using monitoring wells with short screen lengths (e.g., 2 feet [ft]), located at different depths is also desirable to obtain information on the vertical distribution of the oxidant during injections. Because distribution of injected chemicals will not be perfectly circular around an injection point, it is desirable to have monitoring wells located in different directions.

The proposed full-scale injection pattern should also be considered when developing the design of a pilot test. If an “inject and drift” approach is proposed for a persistent oxidant, monitoring wells placed downgradient of the injection point should be used to evaluate the drift achievable (and thus the spacing between rows of injection wells). But, monitoring wells relatively close to the injection points should also be installed to evaluate the oxidant distribution during the injection period (used to space wells in the injection row). If a grid pattern is proposed for full-scale, then understanding oxidant drift is not as critical. The design of injection wells and monitoring wells used for a pilot test should be the same as, or very similar to, those used for full-scale.

As with full-scale systems, care should be taken to avoid utilities during well installation. In addition, utilities and other possible preferential flow paths should be considered in laying out the wells to avoid sending oxidant down the utility bedding.

It should be noted that tracer tests may be a very useful component of a pilot test. Injection of a conservative tracer alone can be used to evaluate the “injectability” of fluids (i.e., detect a

fatal flaw) and the potential distribution of an oxidant (thus the mobile zone). For example, bromide is a commonly used tracer that can be injected prior to or during the injection of the oxidant. Caution should be exercised when combining bromide with some oxidants, as bromoform can be created under certain conditions (high oxidant concentrations and high organic matter concentrations).

The mass and volume of oxidant injected should be estimated as per the ISCO Conceptual Design process described in Chapter 9, Section 9.3. Specific suggestions for mass and volume include:

- Avoid under-estimating the volume of oxidant solution to be injected. It may be better to inject at a lower oxidant concentration with a higher volume for a pilot test to evaluate the distribution of the oxidant.
- Specific to permanganate: At sites with low natural demand for oxidant, avoid overdosing with too much permanganate. The oxidant may travel further and last longer in the subsurface than desired.

D.4.3 Equipment

The equipment used to perform the pilot tests (i.e., the oxidant mixing, delivery system, and monitoring devices) may be similar to that used for the full-scale ISCO system. However, since the duration of injections will be much shorter and mass/volume injected much smaller, different equipment may be used. For example, a simple liquid sodium permanganate dilution system could be used for a pilot test rather than a potassium permanganate system that requires mixing dry chemicals. However, practitioners are encouraged to weigh the cost savings realized by substituting different equipment than that to be used in the full-scale application against the lessened ability to identify and troubleshoot potential operational issues with that full-scale equipment (e.g., pump bladders being corroded by oxidant, filtration systems not performing as designed).

D.4.4 Monitoring

The monitoring program for a pilot test could be similar to that used for a full-scale system application. More information on monitoring for full-scale systems is provided in Chapter 12. A few precautionary notes for monitoring are provided here:

- Provide sufficient baseline monitoring to understand the natural variability in groundwater concentrations. This is especially true of contaminant concentrations, which may vary over space by an order of magnitude or more and over time under ambient conditions by as much as $\pm 50\%$.
- Sample frequently enough after the oxidant injections to be able to observe the distribution of the oxidants and reaction products (or conservative tracers). This is especially true with the short-lived oxidants, but may also be true with permanganate if the natural demand for oxidant (NOD) is high.
- Consider using real-time monitoring with data loggers to help collect continuous information on the distribution of the oxidants. This may alleviate some of the need for very frequent sampling, and may be used to guide sample collection.

D.4.5 Examples

Examples of well-conducted pilot studies, including observations and lessons learned, are presented in Appendix E.

D.5 EXAMPLE PRELIMINARY BASIS OF DESIGN REPORT OUTLINE FOR *IN SITU* CHEMICAL OXIDATION BY PERMANGANATE DIRECT INJECTION

1. Project Introduction
 - 1.1. Site Background and Remediation Status
 - 1.2. Summary of Previous *In Situ* Chemical Oxidation (ISCO) Test Results
 - 1.3. Remediation Drivers
2. Brief Summary of Conceptual Site Model
 - 2.1. Source Description
 - 2.2. Lithology
 - 2.3. Hydrogeology
 - 2.4. Geochemical Setting
 - 2.5. Contaminant Geometry
 - 2.5.1. Nature and Phases
 - 2.5.2. Extent and Location
3. ISCO Treatment Goals and Milestones
 - 3.1. Overall Site Remediation Action Objectives (RAOs) and Remediation Goals (RGs)
 - 3.2. Treatment Train Description
 - 3.3. ISCO Treatment Goals
4. Target Treatment Zone Delineation
 - 4.1. Lateral Extent
 - 4.2. Depth Interval(s)
 - 4.3. Lithologic Setting and Complexity
5. Treatment Technology Description
 - 5.1. Oxidant Selection and Desired Reaction Chemistry
 - 5.2. Oxidant Delivery Design
6. Contracting, Design, and Implementation Approach
 - 6.1. Contracting Method
 - 6.2. Level of Design Detail
 - 6.3. Implementation Approach
7. ISCO Design Details
 - 7.1. Oxidant Dosage and Injection Volume
 - 7.1.1. Calculations and Results
 - 7.2. Contaminant Contact and Reaction Time Design
 - 7.3. Injection Point Design and Installation Method
 - 7.4. Oxidant Storage, Transfer, Mixing, and Delivery Methods
 - 7.4.1. Injection Point Layout
 - 7.4.2. Process Flow Diagram
 - 7.4.3. Injection Mixing and Transfer Process

- 7.4.4. Injection Process and Depth Intervals
- 7.4.5. Target Injection Volume, Rate, and Pressure
- 8. Contingency Evaluation
 - 8.1. Technical Risk Analysis Results
 - 8.2. Management Risk Analysis Results
 - 8.3. Probability and Schedule/Cost Impact Results
- 9. Delivery and Treatment Performance Monitoring Program
 - 9.1. Delivery Monitoring Program
 - 9.1.1. Monitoring Locations
 - 9.1.2. Parameters and Monitoring Frequency
 - 9.2. Treatment Monitoring Program
 - 9.2.1. Monitoring Locations
 - 9.2.2. Parameters and Monitoring Frequency
 - 9.3. Contingency Assessment Monitoring
 - 9.4. Treatment Cessation Monitoring
- 10. Schedule
 - 10.1. Injection Schedule and Number of Events
 - 10.2. Delivery Monitoring Schedule
 - 10.3. Treatment Monitoring Schedule
 - 10.4. Potential Impacts of Contingency on Schedule
- 11. General Requirements
 - 11.1. Health and Safety
 - 11.2. Engineering Controls
 - 11.3. Permitting Requirements
 - 11.4. Waste Management
- 12. Implementation Cost Estimate
 - 12.1. Construction and Injection Cost
 - 12.2. Delivery Performance Monitoring Cost
 - 12.3. Treatment Performance and Cessation Monitoring Cost
 - 12.4. Potential Impacts of Contingency on Cost
- Appendix A. Preliminary Design Drawings
 - Basic design drawings are typically included with the Preliminary Basis of Design Report. At a minimum, the preliminary design drawing package includes the following:
 - Process and Instrumentation Diagram (P&ID)
 - ISCO Treatment System Layout
 - Preliminary Piping Layout
 - Well Construction Details

Note: It should be noted that certain components of the Preliminary Basis of Design Report specified above may be omitted if a performance-based contracting approach will be adopted. Examples of omitted design components include the oxidant volume/dosage, injection infrastructure, and injection well design.

D.6 TYPICAL COMPONENTS OF AN OPERATION PLAN FOR ISCO IMPLEMENTATION

D.6.1 Operational Metrics

Operational metrics are defined as a set of specific operation-related objectives, which if achieved, will result in the achievement of the ISCO treatment goals. These operational metrics will be measured and assessed during the performance monitoring program to determine ISCO performance effectiveness and success. These metrics can be used as a basis for performance specifications. For example, operational metrics and objectives, which may be considered for an ISCO application are:

1. Delivery of a minimum permanganate concentration of X mg/L throughout the TTZ
2. Maintenance of a minimum of X days of permanganate residence time within the TTZ for the oxidation reaction to occur
3. Minimize loss of oxidant from the TTZ during the delivery process due to day-lighting or short-circuiting
4. Utilize a real-time measurement and data analysis routine to optimize/adapt the injection/monitoring program and ensure cost-effective treatment
5. Zero health and safety incidents

Establishing operational metrics and objectives involves project-specific decisions. In most cases, they can be used as a metric for performance measurement and as a basis for follow-up optimization activities to improve ISCO treatment efficiency. For example, an oxidant recirculation project may want to include a minimum X-percent runtime operational objective. If runtime does not meet the objectives, then optimization activities are needed to improve its operation.

Care should be taken to ensure that the operational objectives are realistic and achievable and, if achieved, will lead to successful ISCO treatment. Consultation with prospective ISCO technology vendors may be beneficial at this preliminary design phase. Often times, vendors have developed unique knowledge of ISCO application under certain hydrogeochemical and contaminant settings. If appropriate vendors have been identified as valuable to a project, then they should be consulted during the operational objective setting process. This will help ensure that the objectives are practical and realistically achievable. In so doing, the vendor becomes vested in the process and, if contracted appropriately, jointly or wholly responsible for achieving the objectives.

D.6.2 ISCO Treatment Milestones

ISCO treatment milestones are temporal goals that are geared toward sustaining ISCO operations and making progress toward ISCO treatment goals. Milestones are highly site-specific and dependent upon site owner needs and contractual/regulatory requirements. ISCO-related milestones are typically integrated with the type of treatment goal. For example, if 90% mass flux reduction is the treatment goal, then the milestones may include a 50% intermediate milestone in addition to the use of 90% as the final ultimate milestone. Use of intermediate milestones helps project teams measure progress and make midway adjustments, if needed, to improve treatment efficiency.

Other ISCO milestones may include:

- Remedy-in-Place (RIP) (Department of Defense [DoD]-specific goal) upon initiation of ISCO treatment
- Oxidant delivery complete (e.g., achieved operational objective 1 above)
- Oxidant reaction complete (e.g., achieved operational objective 2 above)
- Rebound period complete (e.g., oxidant reacted and aquifer redox state returned to baseline conditions)
- 50% of treatment goal achieved (dissolved concentration, contaminant mass, mass flux, etc.)
- 100
- % of treatment goal achieved and ISCO treatment complete (can't be achieved without achieving Rebound Period Complete milestone)

D.7 DEVELOPMENT OF ISCO PERFORMANCE SPECIFICATIONS AND/OR DETAILED DESIGN SPECIFICATIONS AND DRAWINGS

For the purposes of the discussion in this appendix, the following terminology is used:

- Owner – Site owner responsible for site remediation and regulatory compliance
- Engineer – Consultant responsible for design of the *in situ* chemical oxidation (ISCO) treatment system
- Contractor – ISCO contractor responsible for physical implementation of the ISCO system

D.7.1 Performance Specifications

If a performance-based contract will be implemented, contractor performance specifications will be prepared to document the set of minimum performance criteria (i.e., project milestones, endpoints, and/or desired outcomes) that the contractor is expected to achieve. The objectives of the performance specifications can include the following:

- Define the roles and responsibilities of site Owner, Engineer, Contractor(s)
- Prescribe ISCO treatment goals
- Ensure that pertinent details are included such that the Contractor has detailed knowledge of the site conditions to maximize chances of achieving ISCO treatment goals
- Maximize Contractor flexibility
- Hold the Contractor accountable for their treatment effectiveness claims
- Ensure that proper data is collected to document treatment effectiveness
- Prescribe a payment milestone process consistent with anticipated treatment milestones
- Require compliance with the Operation and Contingency Plan including post-ISCO re-equilibration monitoring and treatment effectiveness determination procedures

In general, the performance requirements should be written to be consistent with the ISCO operational objectives and treatment goals. They could include:

- Deliver a target mass of oxidant to the target treatment zone
- Achieve a target radius of influence around the injection points

- Achieve a target concentration of oxidant in the subsurface in certain monitoring wells
- Avoid/minimize groundwater and/or oxidant surfacing/daylighting
- Achieve a target contaminant concentration, mass reduction, or mass flux reduction over a certain area

The performance specifications should be prepared as part of a Scope of Work and Bid Sheet to send to prospective contractors. Separate scopes of work and bid sheets should be prepared if the ISCO implementation work is to be performed by more than one specialty contractor (e.g., driller, controls and mechanical equipment, oxidant injection), each with its own task-specific health and safety requirements.

Care should be taken to avoid writing conflicting performance-based specifications that, for example, specify a certain performance in terms of contaminant reduction and at the same time specify the number of wells and mass of oxidant to be used which may not be adequate to meet the performance objectives. In general, selection of materials, means, and methods should be left up to the contractor. In some cases, minimal materials and methods specification is acceptable to meet site-specific requirements. For example, bench testing may have been performed and dictated that alkaline-activated persulfate be used to oxidize the mixture of contaminants. Another site may have low permeability media and field testing may dictate that pneumatic fracturing be required to deliver the oxidants.

Achieving a certain concentration or contaminant mass reduction is extremely difficult to predict. Likewise, it is difficult to predict the radius of influence that can be achieved, unless pilot tests or previous injections have been performed. Consequently, most contractors will charge a premium if a performance contract is written with either of these conditions specified. The prospective ISCO contractors should be consulted during this stage to ensure that performance criteria are realistic and achievable and that a cost effective performance-based contract is prepared that is agreeable to both the owner and contractor.

D.7.2 Detailed Design Specifications and Drawings

A detailed set of design specifications and drawings will be required if a prescriptive contract is to be used. The level of detail and format is typically as prescribed by the Construction Specification Institute (CSI: <http://www.csinet.org/>). The level of detail of the design specifications and drawings will vary depending on the contract structure and the level of expertise possessed by the contractor. For example, a prescriptive contract for a simple direct-push ISCO design that will be implemented by an experienced contractor may include minimal design specifications such as the northing/easting location of wells, well completion and development details, oxidant and activation method selection, volume and mass of oxidant to be injected, oxidant mixing means and methods, and duration of injection and post-injection monitoring.

For a more complicated ISCO design that will be constructed/operated by one or more trade-specific contractors, a complete set of detailed design specifications and drawings is required. Example design specifications and drawings for direct injection (Table D.7) and more complex automated recirculation delivery ISCO treatment (Table D.8) systems are shown below.

Regardless of the complexity of the ISCO design or the level of detail included in the design document, the specifications and drawings should include all necessary information under a single document. In addition, design requirements for specific components should be specified in detail for the project, rather than deferring to general vendor specifications or cut sheets.

Table D.7. Detailed Design Specifications and Drawings for an ISCO System Using Direct Probe Injection

Category	Example design specifications/drawings
General	<ul style="list-style-type: none"> • Cover sheet • Drawing list
Civil	<ul style="list-style-type: none"> • Layout plan (site boundary, access routes, locations of wells, equipment, storage areas, construction lay-down areas) • Well construction diagrams • Miscellaneous civil details (well vaults, trenches, concrete pads, fencing, bollards)
Process and Instrumentation	<ul style="list-style-type: none"> • Process flow diagram (oxidant and activator mixing, conveyance, and delivery equipment) • Piping and instrumentation diagram (oxidant and activator mixing, conveyance, and delivery equipment)
Mechanical	<ul style="list-style-type: none"> • General arrangement plans (control building; mixing, conveyance, and delivery equipment) • Well vault layouts and sections • Storage tank details • Miscellaneous mechanical details (pipes, supports, spill containment)
Electrical	<ul style="list-style-type: none"> • Single line diagram • Power plan and schedules

Table D.8. Detailed Design Specifications and Drawings for an ISCO System Using Well-to-Well Recirculation

Category	Example design specifications/drawings
General	<ul style="list-style-type: none"> • Cover sheet • Drawing list
Civil	<ul style="list-style-type: none"> • Layout plan (site boundary, access routes, locations of wells, piping, equipment, storage areas, construction lay-down areas) • Well construction diagrams • Miscellaneous civil details (well vaults, trenches, concrete pads, fencing, bollards)
Architectural	<ul style="list-style-type: none"> • Plans and elevations (control building)
Structural	<ul style="list-style-type: none"> • Foundation plans (control building, storage tanks, unloading stations)
Process and instrumentation	<ul style="list-style-type: none"> • Process flow diagram (oxidant and activator mixing, conveyance, and delivery equipment) • Piping and instrumentation diagram (oxidant and activator mixing, conveyance, and delivery equipment)
Mechanical	<ul style="list-style-type: none"> • General arrangement plans (control building; mixing, conveyance, and delivery equipment) • Well vault layouts and sections • Storage tank details • Isometric piping detail • Miscellaneous mechanical details (pipes, supports, spill containment)
Electrical	<ul style="list-style-type: none"> • Buried conduit network • Single line diagram • Building power plan and schedules • Building lighting plan • Process logic controller (PLC) interconnect diagrams

D.8 QUALITY ASSURANCE PROJECT PLAN (QAPP) CONTENT

Project Management and Objectives

- Project Organization
 - Project Organizational Chart
 - Communication Pathways
 - Personnel Responsibilities and Qualifications
 - Special Training Requirements and Certification
- Project Planning/Problem Definition
 - Project Planning (Scoping)
 - Problem Definition, Site History, and Background
- Project Quality Objectives and Measurement Performance Criteria
 - Development of Project Quality Objectives Using Systematic Planning Process
 - Measurement Performance Criteria
- Secondary Data Evaluation
- Project Overview and Scheduling

Measurement/Data Acquisitions

- Sampling Tasks
 - Sampling Process Design and Rationale
 - Sampling Procedures and Requirements
 - (a) Sample Containers, Volume, and Preservation
 - (b) Equipment/Sample Containers Cleaning and Decontamination Procedures
 - (c) Field Equipment Calibration, Maintenance, Testing, and Inspection Procedures
 - (d) Supply Inspection and Acceptance Procedures
 - (e) Field Documentation Procedures
- Analytical Tasks
 - Analytical Standard Operating Procedures (SOPs)
 - Analytical Instrument Calibration Procedures
 - Analytical Instrument and Equipment
 - Maintenance, Testing, and Inspection Procedures
 - Analytical Supply Inspection and Acceptance Procedures
- Sample Collection Documentation, Handling, Tracking, and Custody Procedures
 - Sample Collection Documentation
 - Sample Handling and Tracking System
 - Sample Custody
- Quality Control Samples
 - Sampling Quality Control Samples
 - Analytical Quality Control Samples
- Data Management Tasks
 - Project Documentation and Records
 - Data Package Deliverables

- Data Reporting Formats
- Data Handling and Management
- Data Tracking and Control

Assessment/Oversight

- Assessments and Response Actions
 - Planned Assessments
 - Assessment Findings and Corrective Action Responses
- Quality Assurance (QA) Management Reports
- Final Project Report

Data Review

- Data Review Steps
 - Step I: Verification
 - Step II: Validation
 - Step III: Usability Assessment
 - Data Limitations and Actions from Usability Assessment Activities
- Streamlining Data Review
 - Data Review Steps To Be Streamlined
 - Criteria for Streamlining Data Review
 - Amounts and Types of Data Appropriate for Streamlining

D.9 DESCRIPTION OF POTENTIAL PRE-CONSTRUCTION ACTIVITIES FOR AN ISCO PROJECT

D.9.1 Injection Permitting

Permitting requirements can be determined during evaluation of applicable or relevant and appropriate requirements (ARARs) during the feasibility study (FS) stage and formally applied to an ISCO remedy by the Record of Decision (ROD). If necessary, implementation of the ISCO remedy must incorporate the appropriate engineering, monitoring, and contingency controls to ensure compliance with ARARs.

Permitting requirements and processes vary significantly from state-to-state and it is advised to supplement this guidance with a review of site-specific permitting and utility clearance requirements. The Interstate Technology & Regulatory Council (ITRC, 2005) provides detailed information regarding typical regulatory concerns/barriers, along with examples highlighting the permitting process. The ITRC also compiled regulatory permitting requirements for oxidant injection and organized them by state.

A few common permitting concerns that regulators may want addressed include:

- Chemical storage and spill containment and control procedures
- Injection of chemical reagents into potable water classified groundwater zones
- Injection of manufacturing derived impurities such as trace metals
- Oxidant migration into adjacent water supply or irrigation wells with or without hydraulic controls
- Permanent impacts to primary or secondary water quality characteristics such as taste, color, and odor. These parameters could be impacted by oxidation by-products such as

sulfate from activated persulfate, manganese from permanganate, and iron from catalyzed hydrogen peroxide (CHP) or activated persulfate.

- Potential for surface water effects and associated ecological impacts
- Temporal change in redox state and associated potential impacts on naturally-occurring metal adsorption/dissolution

The injection of oxidants and reagents is regulated primarily through the Underground Injection Control (UIC) program of the Safe Drinking Water Act (SDWA), the Resource Conservation and Recovery Act (RCRA) for *ex-situ* systems, the Comprehensive Emergency Response, Compensation, and Liability Act (CERCLA), and the Emergency Planning and Community Right to Know Act (EPCRA). In addition to approvals obtained through these environmental programs, an injection permit may also be required from local and state environmental agencies. Some states have issued variances, waivers, and permit exceptions that may affect ISCO activities. For example, a waiver was issued for a short-term, closed-loop (i.e., equal extraction and injection flow rates), permanganate recirculation system in a shallow aquifer on an industrial/commercial-zoned property. Regulatory examples of six states (NJ, CA, FL, KS, MO, TX) are provided in the ITRC document in which chemical oxidation can be used for porous media and groundwater remediation (ITRC, 2005). Individual states may have more restrictive regulations than the Federal programs listed above. Regulatory constraints on each ISCO project should be assessed on a case-by-case basis.

Care should be taken during the permitting process to clarify that monitoring will be used to demonstrate that some geochemical changes, such as increases in the concentrations of dissolved metals, are temporary and little, if any, permanent change to the aquifer is expected (Crimi and Siegrist, 2003; Moore, 2008). This is a typical phenomenon at many sites with a natural capacity (i.e., natural organic matter or reduced metals) to re-equilibrate to pre-existing conditions. For sites with a low natural capacity to re-equilibrate after a large ISCO injection program, a contingency plan may be prescribed which will quench detrimental oxidation byproducts using direction injection of oxidant neutralizing or consuming agents such as sodium thiosulfate, sugar water, or lactate. Quenching agents may also be used to stimulate post-ISCO coupled treatment approaches such as enhanced reductive dechlorination. More discussion on the geochemical effects of the various oxidants is provided in Chapters 2–5.

D.9.2 Utility Clearance

All drilling and underground work will also require utility clearance, at a minimum, by marking out the work area and calling the local underground service alert network (e.g., Call before you dig, Digger's Hotline, One-call, and Miss Utility). Utility clearance via the local underground service alert is required by law, and notifies all utility companies owning underground lines (water, wastewater, storm, natural gas, electrical, telephone, cable, and fiber optic) in the proposed work area. Once notified, the utility owners will then denote the line locations with color-coded markings. It is also recommended that a private utility locator be subcontracted to provide a more thorough utility survey of the site, especially on privately owned property where some public utilities will not be marked through the underground service alert network, or where the location and alignments of utilities and other underground structures are not well documented.

In all cases, when utilities are located within or immediately adjacent to the target treatment zone (TTZ), the chemical compatibility of underground utilities with the oxidant to be used should be evaluated. Engineering controls will be needed if the material is chemically incompatible. Engineering controls are discussed further below.

The location of utilities is important not only for health and safety reasons, but for understanding potential effects on delivery uniformity as well. Utility bedding/trenches often represent a potential short circuit at shallow ISCO injection sites since they can be more permeable than the native formation. If injection locations are cited too close to a utility corridor, then oxidant may be lost or wasted. Worst case, the oxidant may react with the incompatible material of construction of the utility and cause damage. Best case, oxidant is lost and new injection locations will be needed to distribute oxidant into the adjacent targeted native formation. It should be noted that in some cases, ISCO treatment of utility corridors is acceptable for treatment of contaminants that may have migrated into them. Extreme care should be taken to ensure that the oxidant will not harm the utility (e.g., concrete storm sewer line with no immediate discharge point) and that the oxidant will indeed follow a similar flow path as the contaminant. If this approach is taken, extreme care should be taken to monitor all potential exposure pathways including vapors in manholes/vaults.

D.9.3 Potential Receptor Survey

Another important pre-construction activity is a site walk over and survey of the TTZ and surrounding area (above- and below-grade) for potential exposure pathways that may lead to human health and environment risk during the ISCO operations. The pathways and potential receptors are site-specific. For example, a high pressure direct injection approach may lead to a higher risk for breach of utility manholes than a hydraulically-controlled oxidant recirculation system. Potential receptors include human and ecological flora and fauna. Example exposure pathways include:

- Utility vault or manhole
- Wetlands
- Ground surface ponding via short circuiting from lithologic fractures or old boreholes
- Surface water (e.g., stream or pond)
- Drainage swale/ditch or culvert
- Indoor air

The site should be carefully surveyed and ISCO injection scenarios reviewed to assess potential for exposure. Each of these potential exposures should then be considered for necessary and appropriate engineering controls and/or contingency response actions. The mitigation measures should be included in the Operation and Contingency Plan prepared as part of ISCO Detailed Design and Planning Process, Chapter 9 Section 9.4.

D.9.4 Engineering Controls for ISCO Implementation

In some extreme cases where ISCO treatment adjacent to sensitive utilities or receptors like wetlands is necessary, engineering controls can be used to protect them from oxidant contact. For example:

- Temporary sheet piling can be driven to protect fiber optic cables
- Manhole/vaults can be vented (passive or mechanical) to prevent the build-up of vapors
- Hydraulic controls (i.e., groundwater circulation) can be used to control extent of oxidation
- Sentinel monitoring program to ensure that ISCO injection is controlled and results in no exposures

The nature and extent of engineering controls should be carefully evaluated, and if needed they should be designed, installed, and monitored by experienced project team personnel.

D.9.5 Administrative Activities

Administrative activities that are conducted after contract procurement and prior to mobilization should include the following activities:

- Obtain site access and personnel clearance (as appropriate) for all site workers.
- Perform a pre-construction meeting with field contractor(s) to identify underground and overhead utilities, review general work plan, review general health and safety hazards, and other existing site activities that could interfere with the ISCO implementation over the duration of the project.
- Ensure contractor(s) will have the specified equipment and materials and additional equipment identified during the pre-construction meeting, and ensure chemical compatibility of all equipment to be used.
- Verify availability of, and access to, a water source and electrical supply.
- Confirm field schedule and identify/resolve any technical issues prior to mobilization.

D.9.6 Health and Safety Preparations

It is critical to ensure that the site will be equipped with all appropriate health and safety facilities and equipment as documented in the Health and Safety Plan. Some examples include:

- Personal protective equipment
- Chemical storage and handling facilities
- Oxidant neutralization and spill containment and control kit
- Eye wash and shower stations
- Fire extinguishers

Detailed safety checklists, as typically specified in the Health and Safety Plan, should be completed and reviewed by the entire project field team. The contractor should complete these checklists and include information on specific methods of the operation and measures that should be employed to correct deficiencies. Safety checklists should be developed based on project-specific health and safety requirements, and the field team should verify that all high risk site activities are addressed during pre-construction. High-risk project activities may include (but not be limited to) the following:

- Drilling
- Electrical
- Forklifts
- Hand and power tools
- Hazardous materials
- Respiratory exposures
- Traffic control
- Waste characterization, sampling, and analysis

D.9.7 References

- Crimi ML, Siegrist RL. 2003. Geochemical effects on metals following permanganate oxidation of DNAPLs. *Groundwater* 41:458–469.
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D.10 CONSTRUCTION AND DELIVERY EFFECTIVENESS QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC) GUIDELINES

Table D.9 provides QA/QC guidelines for construction and delivery effectiveness for various ISCO delivery approaches.

Table D.9. QA/QC Guidelines for Construction and Delivery Effectiveness for Various ISCO Delivery Approaches

Applicable oxidant(s)	Element	Data objective	QA/QC procedure	Troubleshooting measure
Direct-push probe				
Permanganate, catalyzed hydrogen peroxide (CHP), activated persulfate	Drilling	<ul style="list-style-type: none"> Injection point coordinate accuracy Depth accuracy Lithologic verification at injection depth 	<ul style="list-style-type: none"> Surveying Probe rod or auger flight accounting Blow counting 	<ul style="list-style-type: none"> Cone penetrometer technology (CPT) survey to verify lithologic interfaces Continuous soil sampling and logging
	Discrete depth injection	<ul style="list-style-type: none"> Injection effectiveness Hydraulic radius of influence (ROI) Oxidant/activator delivery ROI 	<ul style="list-style-type: none"> Injection pressure and flow rate Injectate oxidant/activator concentration Surrounding monitoring point pressure Monitoring well water level Monitoring well oxidation-reduction potential (ORP) 	<ul style="list-style-type: none"> Adjust delivery sequence (e.g., top-down or bottom-up) Continuous soil sampling and logging Electrical resistivity tomography (ERT) survey Tracer injection and perimeter monitoring Use continuous down-well ORP dataloggers and/or specific conductivity
	Borehole abandonment	<ul style="list-style-type: none"> Borehole plug effectiveness 	<ul style="list-style-type: none"> Grout from bottom-up and account grout quantity 	<ul style="list-style-type: none"> Over drill and re-abandon borehole Offset injection location if old borehole is causing injectate short-circuiting

(continued)

Table D.9. (continued)

Applicable oxidant(s)	Element	Data objective	QA/QC procedure	Troubleshooting measure
Well				
Permanganate, CHP, ozone, activated persulfate	Drilling	See Objectives and Procedures for "Direct-push probe" Delivery Technique		
	Injection well installation and completion	<ul style="list-style-type: none"> • Bentonite seal integrity • Proper well development 	<ul style="list-style-type: none"> • Filter and bentonite seal material accounting • Purge water quantity and quality monitoring 	<ul style="list-style-type: none"> • Pressure test • Re-evaluate screen slot and filter pack design • Over drill and reinstall well
	Injection	<ul style="list-style-type: none"> • Injection effectiveness • Hydraulic ROI • Oxidant/activator delivery ROI 	<ul style="list-style-type: none"> • Injection well efficiency • Injection pressure and flow rate • Injectate oxidant/activator concentration • Surrounding monitoring point pressure • Monitoring well water level • Monitoring well ORP 	<ul style="list-style-type: none"> • Tag injection well total depth to assess sedimentation • Adjust delivery sequence (e.g., top-down or bottom-up) • Continuous soil sampling and logging • ERT survey • Tracer injection and perimeter monitoring • Use continuous down-well ORP dataloggers and/or specific conductivity
Recirculation				
Permanganate	Drilling	See Objectives and Procedures for "Direct-push probe" Delivery Technique		
	Injection/extraction well installation and completion	See Objectives and Procedure specified above for "Well" Delivery Technique		
	Process equipment construction	<ul style="list-style-type: none"> • Process piping integrity • Equipment performance verification 	<ul style="list-style-type: none"> • Hydraulic pressure testing • Functionality testing (process, instrumentation, and controls) 	<ul style="list-style-type: none"> • Mechanical and control logic repair
	Groundwater extraction	<ul style="list-style-type: none"> • Extraction effectiveness • Hydraulic ROI – capture zone • Influent water quality 	<ul style="list-style-type: none"> • Extraction pressure and groundwater flow rate • Monitoring well water level • Extraction water quality sampling (field parameters and COCs) 	<ul style="list-style-type: none"> • Re-evaluate screen slot and filter pack design

(continued)

Table D.9. (continued)

Applicable oxidant(s)	Element	Data objective	QA/QC procedure	Troubleshooting measure
Recirculation				
Permanganate (continued)	Oxidant dosing	<ul style="list-style-type: none"> • Oxidant usage rate 	<ul style="list-style-type: none"> • Oxidant consumption monitoring 	<ul style="list-style-type: none"> • Re-evaluate oxidant measurement technique • Assess dosing system stability (hydraulic and concentration)
	Oxidant injection	<ul style="list-style-type: none"> • Injectate oxidant concentration • Hydraulic injection ROI • Oxidant delivery ROI 	<ul style="list-style-type: none"> • Oxidant concentration • Injection pressure and flow rate • Surrounding monitoring point pressure • Monitoring well water level • Monitoring well ORP 	<ul style="list-style-type: none"> • Adjust delivery pressure • Evaluate injection well efficiency • Continuous soil sampling and logging • ERT survey • Tracer injection and perimeter monitoring • Use continuous down-well ORP dataloggers and/or specific conductivity
Trench and curtain				
Ozone	Drilling	See Objectives and Procedures for "Direct-push probe" Delivery Technique		
	Injection well installation and completion	See Objectives and Procedures specified above for "Well" Delivery Technique		
	Process equipment construction	See Objectives and Procedures specified above for "Recirculation" Delivery Technique		
	Oxidant dosing	See Objectives and Procedures specified above for "Recirculation" Delivery Technique		
	Oxidant injection	See Objectives and Procedures specified above for "Recirculation" Delivery Technique		
Soil mixing				
Permanganate, CHP, activated persulfate	Process equipment construction	See Objectives and Procedures specified above for "Recirculation" Delivery Technique		
	Soil mixing	<ul style="list-style-type: none"> • Mixing effectiveness 	<ul style="list-style-type: none"> • Post-mixing porous media sampling and analysis for [COC] and oxidant/activator • Visual inspection or grab sampling during mixing 	<ul style="list-style-type: none"> • Evaluate mixing tool device consistency with site-specific media type • Premix porous media with an excavator to loosen it prior to oxidant/activator mixing
	Oxidant/ activator dosing	See Objectives and Procedures specified above for "Recirculation" Delivery Technique		

(continued)

Table D.9. (continued)

Applicable oxidant(s)	Element	Data objective	QA/QC procedure	Troubleshooting measure
Fracture-emplaced				
Permanganate, Activated Persulfate	Drilling	See Objectives and Procedures for "Direct-push probe" Delivery Technique		
	Fracturing	<ul style="list-style-type: none"> • Fracture break • Fracture propagation • Fracture ROI 	<ul style="list-style-type: none"> • Continuous fracture borehole pressure monitoring • Continuous fracture borehole gas flow rate monitoring • Monitoring wellhead pressure (maximum drag-arm gauges or data logging) • Surface heave surveying • Visual inspection 	<ul style="list-style-type: none"> • CPT survey to verify lithologic interfaces • Continuous soil sampling and logging • Ascertain packer integrity, use double packer assembly • Use steel casing to maintain borehole integrity • Perform fracturing in offset borehole(s)
	Discrete depth oxidant/ activator injection	See Objectives and Procedures specified above for "Direct-push probe" Delivery Technique		
	Borehole abandonment	See Objectives and Procedures specified above for "Direct-push probe" Delivery Technique		
Surface application and infiltration gallery				
Permanganate, activated persulfate	Process equipment construction	See Objectives and Procedures specified above for "Recirculation" Delivery Technique		
	Groundwater extraction	See Objectives and Procedures specified above for "Recirculation" Delivery Technique		
	Oxidant/activator dosing	See Objectives and Procedures specified above for "Recirculation" Delivery Technique		
	Oxidant/activator injection	See Objectives and Procedures specified above for "Recirculation" Delivery Technique		

APPENDIX E

CASE STUDIES AND ILLUSTRATIVE APPLICATIONS

E.1 CASE STUDY: OZONE PILOT TEST

E.1.1 Abstract

The Cooper Drum Superfund Site is a drum refurbishing facility in California that has operated since the 1940s and was added to the National Priorities List (NPL) in 2001. The site is underlain by stratified deposits of sand and silt with clay lenses and groundwater is located at a depth of 45 feet (ft) below ground surface (bgs). Groundwater has been impacted by chloroethenes and 1,4-dioxane. A previous pilot test found that enhanced biological attenuation was not successful in degrading 1,4-dioxane. An *in situ* chemical oxidation (ISCO) treatability study found that ozone was capable of degrading 1,4-dioxane, both with and without hydrogen peroxide as an activator. The similarity of the results of the two systems was contrary to the literature, which indicates that ozone and hydrogen peroxide (peroxone) should react more quickly than ozone alone. Naturally-occurring iron and alkalinity are possible reasons why the ozone system degraded 1,4-dioxane as quickly as it did. The ISCO pilot test was conducted for nearly 1 year beginning in July 2005. Concentrations of contaminants of concern (COCs), including 1,4-dioxane, were reduced by approximately 60–70%. Monitoring results showed no secondary groundwater impacts. Based on the results, the engineer recommended full-scale use of ISCO with peroxone at this site.

E.1.2 Summary of Site Characteristics

COCs in Pilot Test Area

- Maximum concentrations in groundwater:
 - Trichloroethene (TCE): 940 micrograms per liter ($\mu\text{g/L}$)
 - 1,4-Dioxane: 750 $\mu\text{g/L}$
- Dense nonaqueous phase liquid (DNAPL) not directly observed

Geology, Hydrology and Baseline Geochemistry of Pilot Test Area

- Interbedded deposits of sand and silt with clay lenses
- Saturated hydraulic conductivity: 61 ft/day
- Depth to water: 45 ft bgs
- Groundwater pore seepage velocity: 0.3 ft/day (porosity = 0.4, gradient = 0.002)
- pH: 7.2
- Oxidation-reduction potential (ORP): –51 millivolts (mV)

- Total organic carbon (TOC): 19.5 milligrams per liter (mg/L)
- Alkalinity: 17 milliequivalents per liter (meq/L)
- Iron: 2.8 mg/L

Site Characterization Methods

- Site characterization began in 1996, and included soil, groundwater, and soil gas sampling for volatile organic compounds (VOCs). Cone penetrometer technology (CPT) was also used to assess the site geology and collect depth-discreet groundwater samples.

E.1.3 Summary of Pilot Test Features and Results

Pilot Test Objectives

- The goal of the pilot test was to assess the ability of ozone and peroxone to degrade the COCs present at the site, with particular interest in 1,4-dioxane, which at the time of the pilot test, had not been treated using ISCO according to case study source documents. A second goal of the pilot test was to assess the soil oxidant demand (natural oxidant demand or NOD) *in situ*. The success of the pilot test was gauged by significant reduction of COCs; a lack of permanent increases in secondary by-products (e.g., hexavalent chromium); and minimal rebound of COCs.

Pre-Pilot Treatability Testing

- Batch testing used pilot test site groundwater and porous media. Tests evaluated the destruction efficiency of the COCs using both ozone and peroxone. COC destruction was confirmed by comparing to similar aquifer materials sparged with inert nitrogen gas. COCs were measured in the aqueous phase, sparging off-gas, and solid phase (when present). Batch testing used 100 g of aquifer solids and 1,000 milliliters (mL) of groundwater. Ozone concentrations were 26–31 mg/L in air, sparged at a rate of 200 mL per minute (mL/min) for 3 h.
- Due to the unexpectedly high destruction efficiency observed in the ozone tests, additional tests were run to analyze what groundwater constituents might be acting as ozone enhancers. Ferrous iron, chelated iron, TCE, and bicarbonate (to provide alkalinity) were evaluated using deionized water spiked with 1,4-dioxane.
- Batch tests also evaluated impacts of ozone and peroxone sparging on metals and bromate.

Pilot Test Design

- Target treatment zone (TTZ): 270,000 cubic feet
- Oxidant: Ozone alone at 0.55–1.9 pounds per day (lb/day) for first 5 months, followed by ozone with hydrogen peroxide delivered in 2:1 molar ratio of peroxide to ozone (2.5–5 gallons of 16% hydrogen peroxide per day) for the next 5 months
- Activation method: Hydrogen peroxide during second half of pilot test
- Number of delivery events: 1
- Duration of delivery event: 321 days with 91% runtime
- Delivery method: Three sparge wells constructed with two sparge points each (70 and 90 ft bgs), spaced 30–50 ft apart, pulsed with a 1 h frequency. The radius of influence (ROI) was assumed between 15 and 20 ft.

Pilot Test Monitoring

- In addition to monitoring for achievement of the pilot test objectives and success factors specified above, monitoring was also performed to evaluate the actual ROI and optimize system operation. By monitoring dissolved oxygen (DO) and ORP and modifying oxidant injection rates, the optimal system operating parameters were eventually achieved.
- Monitoring during this pilot test focused solely on groundwater.
- Five monitoring wells were monitored at distances between 10 and 30 ft of the sparge wells. Two were screened within 50–70 ft bgs, two were screened within 70–90 ft bgs, and the last was screened between 50 and 90 ft bgs.
- Wells were sampled once at baseline prior to injection, every 3 weeks for 9 weeks after system startup, followed by every 4–6 weeks for 36 weeks. A rebound monitoring event was performed 3 months after cessation of the pilot test. A total of 14 groundwater sampling events were performed. Sampling was conducted using low-flow sampling techniques with a flow-through cell configuration.
- Monitoring wells were sampled for the following analytes: COCs, ozone, hydrogen peroxide, pH, DO, and ORP. The frequency of these analyses varied depending on the analyte.
- Down-hole data loggers were used to monitor DO and ORP. Real-time monitoring data were critical to optimizing the ozone and hydrogen peroxide dosing strategy.
- Vertical profiling of DO and ORP in existing extraction wells with long screens was used to evaluate the variation of ozone impacts with depth.
- Figure E.1 presents the system layout and results of the TCE concentrations from baseline monitoring event.
- Figure E.2 overlays the monitoring well network on a geologic cross section to show the locations of the monitoring wells (some nested) in relation to the more permeable sand lithology. It also presents in-well baseline and final (immediately following cessation of injection) TCE and 1,4-dioxane concentrations to demonstrate post-treatment conditions. The data, however, may not be used for treatment performance assessment because no documentation was provided to demonstrate that sampling was performed after aquifer re-equilibration.
- Figure E.3 shows the results of the real-time ORP data logging that was used to understand the impacts of ozonation on water quality within a monitoring well that is located approximately 20 ft from an ozonation point. Because the well was screened within a permeable sand lithology, an immediate response to oxidant injection was observed. It also suggests that the initial ozone dose was adequate to achieve and sustain an elevated ORP.

ISCO Effectiveness

- Goal: Significant reduction of COCs with minimal rebound and optimization of ISCO system design parameters.
- Goals achieved: Yes
- Post-ISCO maximum concentrations of COCs in groundwater (immediately after cessation of injection)
 - TCE: 180 µg/L (versus initial of 940 µg/L)
 - 1,4-Dioxane: 99 µg/L (versus initial of 750 µg/L)

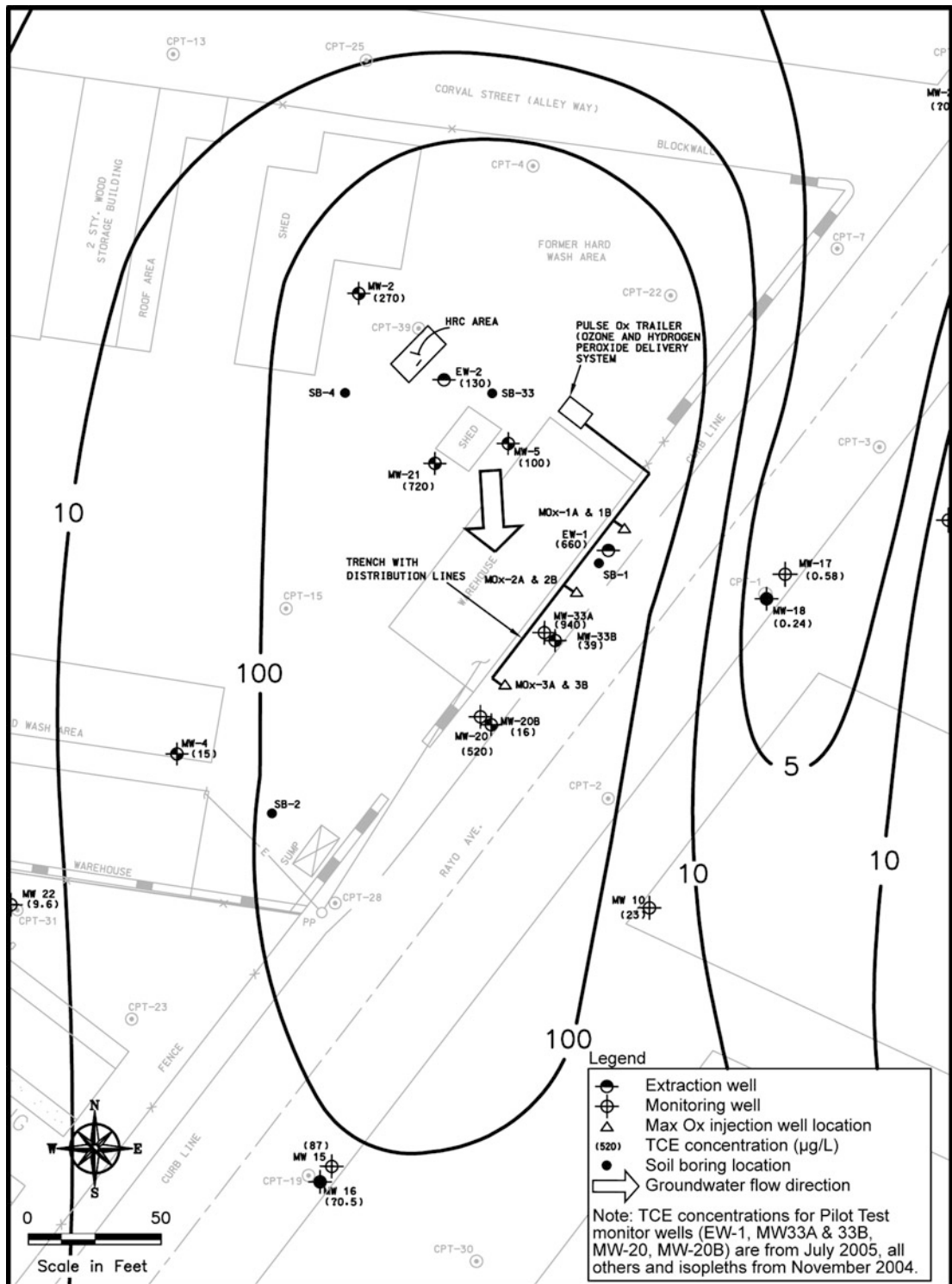


Figure E.1. Pilot test layout with baseline TCE concentrations (μg/L) shown in parentheses beneath well labels, Cooper Drum Superfund Site, South Gate, CA (from URS Group, 2006).

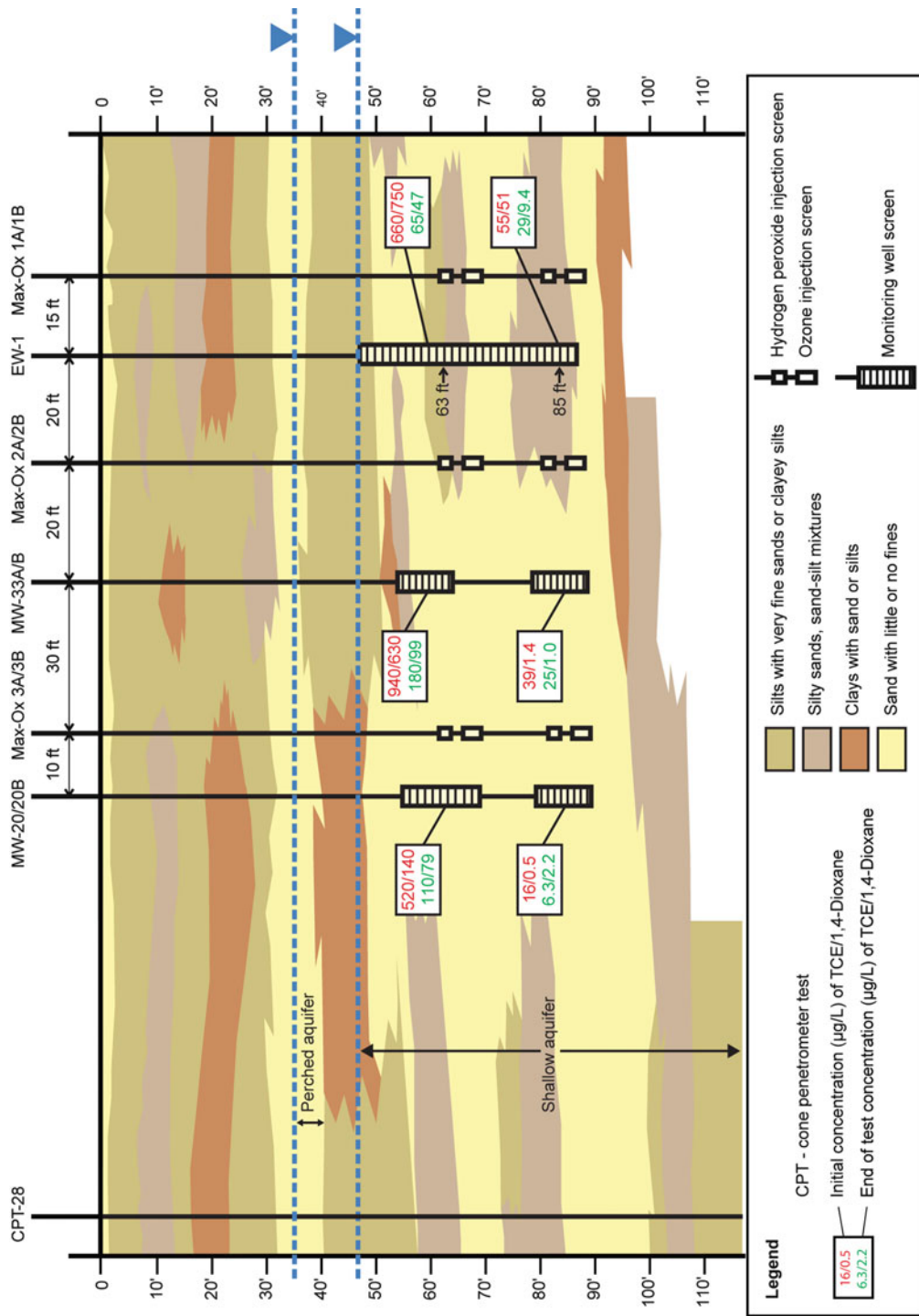


Figure E.2. Geologic cross section of the pilot test layout, Cooper Drum Superfund Site, South Gate, CA (from URS Group, 2006).

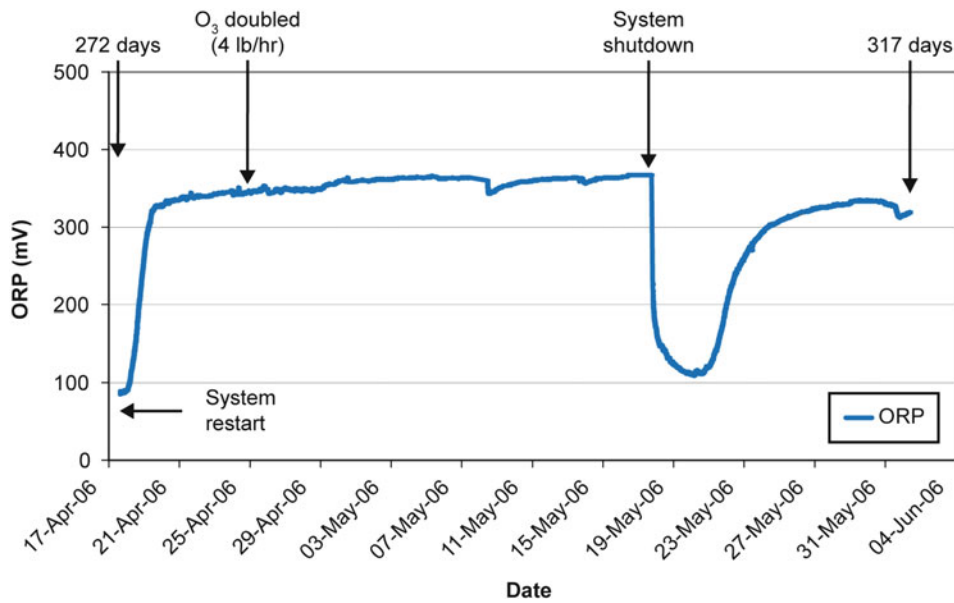


Figure E.3. Real-time down-hole ORP data logger summary from MW-33A, Cooper Drum Superfund Site, South Gate, CA (from URS Group, 2006).

- Rebound: There was zero to modest rebound of COC concentrations in the pilot study monitor wells 3 months after cessation of the pilot study. Some rebound was expected because contaminated plumes originating 30 ft or further upgradient were expected to reach the pilot study area during this time. Modest rebound was observed where the largest reductions in concentrations were obtained during the pilot study. Other areas showed some rebound and conversely some continued to decline during the 3 months.
- Byproducts formation: Hexavalent chromium and bromate were not detected
- Reduction in microbial activity: Not analyzed
- Case status: Open
- Future work: The project engineer designed a full-scale peroxone system for the source zone.

Other Observations and Lessons Learned

- The average observed ROI was approximately 30 ft, which was the largest distance between an injection well and a monitoring well. A larger ROI (50–80 ft) was seen in the shallow zone and may be related to the presence of a less permeable overburden.
- An ozone injection rate of 1 lb/day per injection interval achieved optimal results.
- The effect of hydrogen peroxide on contaminant destruction was not clear.
- The rate of air injection was not found to be an important factor though injection at rates above 1 cubic foot per minute should be avoided to minimize agitating fine sediments in the formation.
- Real time data loggers measuring DO and ORP were valuable in optimizing system design.

- Modifications to the ozone loading rate were made and subsequent changes in COC reductions were measured to assess the impact of this design criterion.
- One well became plugged during the pilot test, presumably from scaling or biofouling. This well was successfully rehabilitated with dilute acid.

E.1.4 References

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E.2 CASE STUDY: PERSULFATE PILOT TEST

E.2.1 Abstract

Naval Air Station North Island is an operational military base located adjacent to the city of Coronado in San Diego County, California. The Operable Unit (OU) 20 groundwater plume is approximately 0.5 miles long, up to 80 feet (ft) below ground surface (bgs), and contains trichloroethene (TCE) and associated degradation products resulting from aircraft maintenance and other base operations conducted in this area since 1945. *In situ* remediation was deemed necessary due to the potential for TCE to impact San Diego Bay, which abuts the site to the northeast. The *in situ* chemical oxidation (ISCO) pilot test targeted a portion of the plume containing TCE at an average concentration of approximately 4,000 micrograms per liter ($\mu\text{g}/\text{L}$), and was selected based on contaminant concentrations, accessibility, and infrastructure considerations. Prior to implementation of the pilot test, elevated chromium concentrations were detected in groundwater, which dictated relocation of the pilot test area.

E.2.2 Summary of Site Characteristics

COCs in Pilot Test Area

- Maximum concentrations
 - TCE: 16,500 $\mu\text{g}/\text{L}$ in groundwater, 0.22 milligrams per kilogram (mg/kg) in soil
 - *cis*-1,2-Dichloroethene (*cis*-DCE): 1,100 $\mu\text{g}/\text{L}$ in groundwater, 0.11 mg/kg in soil
- Dense nonaqueous phase liquid (DNAPL) not directly observed.

Geology, Hydrology and Average Baseline Geochemistry of Pilot Test Area

- Fine to very fine sand and silty sand
- Saturated hydraulic conductivity: 22–30 ft/day
- Depth to groundwater: 20 ft
- Groundwater pore seepage velocity: 0.04–0.05 ft/day (porosity = 0.3, gradient = 0.0005)
- pH: 7.5
- Oxidation-reduction potential (ORP): +112 millivolts (mV)
- Temperature: 22 degrees Celsius (°C)
- Dissolved oxygen: 0.4 mg/L

Site Characterization Methods

- Large-scale delineation of OU-20 plume in 2002. Concentrations of contaminants of concern (COC) in pilot test area confirmed with membrane interface probe (MIP) testing at seven locations and direct push groundwater sampling for volatile organic compounds (VOCs) and chromium in an area of approximately 6,400 square feet.
- The MIP effort defined the target treatment interval of 44–54 ft bgs as containing the highest detected zone of contamination.

E.2.3 Summary of Pilot Test Features and Results

Pilot Test Objectives

- The goal of the pilot test was to assess the ability of activated sodium persulfate to reduce TCE and *cis*-DCE concentrations in groundwater by at least 90% using ambient groundwater temperatures as the activation method.
- This plan included a contingency for steam activation if 90% reductions were not achieved.
- The pilot test also assessed the distance of influence, the impact on metals and on parameters regulated by secondary groundwater standards, and changes in formation permeability as a result of ISCO treatment.

Pre-Pilot Treatability Testing

- Batch testing used an aquifer solids-water slurry comprised of contaminated materials collected from the pilot test site. The purpose of the batch tests was to evaluate natural oxidant demand (NOD) and degradation effectiveness of various activators, including heat, iron-ethylenediaminetetraacetic acid (Fe-EDTA), alkaline conditions, and ambient groundwater temperature of 22°C. Pilot testing also evaluated gypsum solids precipitation ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The slurries consisted of a 1.5:1 ratio of site groundwater to aquifer solids, and were spiked with TCE to ensure aqueous phase TCE concentrations were similar to those recorded in the field. Slurries were mixed during testing and sampled for oxidant and TCE concentrations at 0, 1, 3, and 7 days.
- The treatability test results showed that Fe-EDTA activation resulted in reaction inhibition and poor COC degradation. Heat activation at 60 and 40°C were most successful (>99% groundwater concentration reduction), but closely followed by alkaline 93–97%) and ambient groundwater temperatures (96% reduction at 22°C),

- Treatability test results indicated that the ambient groundwater temperature activated persulfate NOD was 2.3 grams (g) of persulfate consumed per kg of wet aquifer solids at a persulfate concentration of 30 g/L after 7 days.
- Gypsum precipitation (<1% of the aquifer solids mass) occurred, but did not impact the aquifer matrix grain size distribution. After batch testing, the grain size distribution was nearly identical to an untreated sample.

Pilot Test Design

- Target treatment zone: 17,000 cubic feet
- Oxidant: Sodium persulfate at 45 g/L
- Activation method: Ambient heat of 22°C, with a contingency to introduce steam should the ambient temperature not result in the desired contaminant degradation
- Pore volumes delivered: 1.7, 60,000 gallons of groundwater were recirculated
- Oxidant dose (g oxidant/kg media): 7 (23,000 pounds of sodium persulfate)
- Number of delivery events: 1
- Delivery method: Continuous recirculation for 5 days with central injection well and four extraction wells located at distances of 20 or 30 ft from the injection well, all stainless steel (due to potential use of steam activation later) and screened from 44 to 54 ft bgs. Groundwater was filtered (10 µm bag filters) after extraction and after oxidant dosing prior to reinjection. The injection rate was 10 gallons per minute (gpm) at the start of the pilot test and was reduced to 6 gpm during the second half of the test due to the increased hydraulic head caused by the cone of injection.
- Figure E.4 shows a plan view of the system layout including injection, extraction, and monitoring wells and the vapor monitoring point.
- Figure E.5 presents a piping and instrumentation diagram for the groundwater extraction, filtration, oxidant dosing, and injection components of the recirculation treatment system.

Pilot Test Monitoring

- In addition to monitoring for achievement of the pilot test objectives and success factors specified above, monitoring was also performed to evaluate potential migration of aqueous and gaseous contaminants outside the zone of oxidant recirculation.
- Monitoring during this pilot test focused on groundwater and soil vapor.
- Four monitoring wells were installed inside the treatment cell between the single central injection and four perimeter extraction wells. A fifth monitoring well located outside and downgradient of the treatment cell.
- A single vapor probe was installed above the treatment zone.
- Monitoring wells, extraction wells, and injection well were sampled for the following analytes: VOCs, persulfate, pH, DO, ORP, salinity, chloride, sulfate, total dissolved solids (TDS), and metals including hexavalent chromium. The frequency of these analyses varied depending on the analyte.
- Wells were sampled once at baseline prior to injection and at 7, 19, 30, 60, and 90-days following cessation of oxidant injection. Sampling was conducted using a micro-purge sampling technique using a non-dedicated low-flow bladder pump that was located at the midpoint (approximately 49 ft bgs) of each well screen. Each monitoring well was purged until extracted groundwater field parameters had stabilized for three

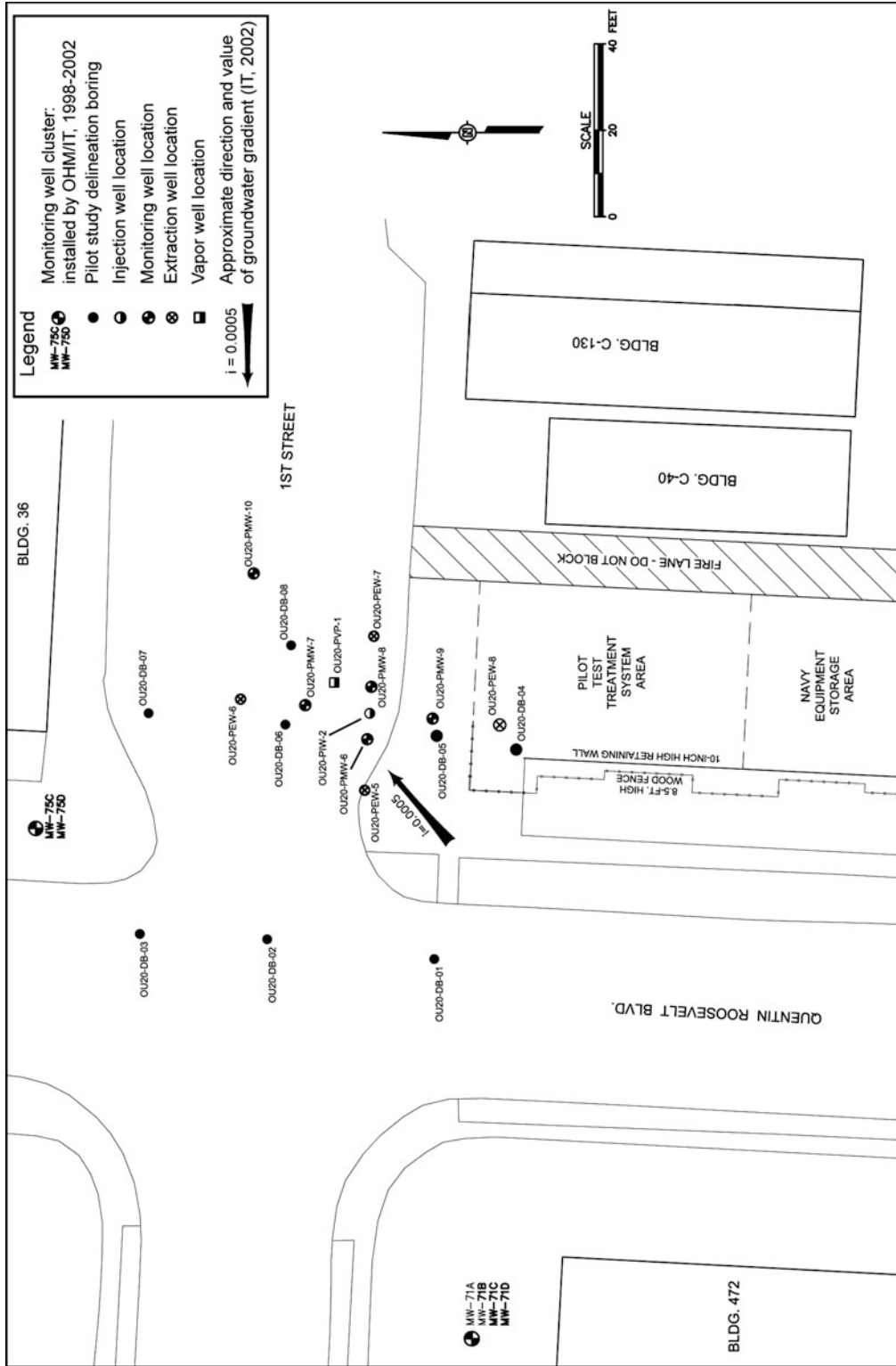


Figure E.4. Site map and pilot study layout, Building C-40, OU20, Naval Air Station, North Island, San Diego, CA (from Shaw, 2007).

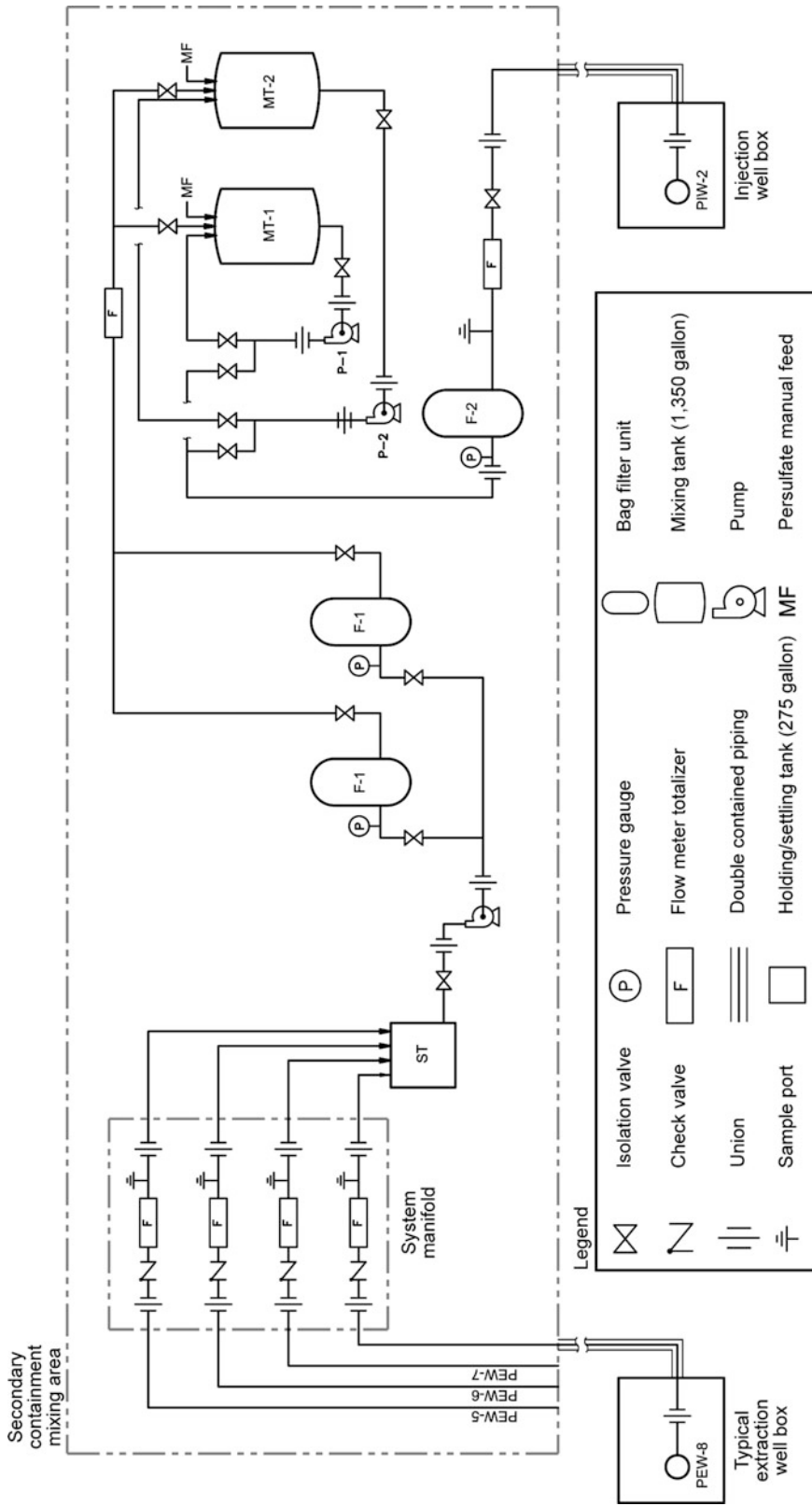


Figure E.5. Persulfate recirculation system piping and instrumentation diagram, Building C-40, OU20, Naval Air Station, North Island, San Diego, CA (from Shaw, 2007).

consecutive readings. Monitoring of field parameters was performed using a YSI-556 water quality meter and associated flow cell. Geochemical field parameters that were tracked to assess groundwater stabilization included temperature, conductivity, salinity, DO, pH, and ORP.

- During recirculation, persulfate analyses were conducted at the extraction wells using starch iodide test kits.
- Figure E.6 presents the results of the baseline monitoring event in aqueous concentrations and mass fraction of total VOCs. It shows that TCE comprised 80 to 90% of the total VOCs detected at baseline.
- Figure E.7 illustrates the results of water level monitoring at the five monitoring wells during the ISCO system operation. Groundwater levels at all monitoring wells displayed an initial increase (0.2–0.4 ft) and then fluctuated for the duration during the pilot test. The downgradient well located approximately 30-ft down- and side-gradient from the nearest extraction wells recorded at 0.1-ft increase during the same period.

ISCO Effectiveness

- Goal: 90% reduction of TCE and *cis*-DCE concentrations in groundwater
- Goal Achieved: Yes. At 19 days post-ISCO, average concentrations among the ISCO performance monitoring wells had been reduced by 90%, indicating that steam activation would not be used per the project's scope of work.
- Post-ISCO monitoring well maximum TCE concentrations (these results were all detected within the same upgradient monitoring well, and were likely due to an influx of untreated groundwater from upgradient)
 - 3,900 µg/L at 19 days (versus initial maximum of 16,500 µg/L)
 - 12,500 µg/L at 30 days
 - 3,500 µg/L at 60 days
 - 4,200 µg/L at 90 days
- Post-ISCO monitoring well mean TCE concentrations
 - 1,300 µg/L at 60 days (86% reduction)
 - 2,000 µg/L at 90 days (78% reduction)
- Metals mobilization: No
- Permeability reduction: No (verified by slug testing)
- Reduction in microbial activity: Not tested
- Current Plans for Future Work: Project team is evaluating implementation of persulfate at full scale.
- Vapor monitoring of the worker breathing zones and in the vadose zone during the pilot tests demonstrated that VOCs were not released into worker breathing zones or the vadose zone. PID readings collected from those areas during the pilot test never reached or exceeded 1 ppm_v.
- Figure E.8 summarizes the results of the TCE and *cis*-DCE groundwater treatment performance monitoring. The first data point shown is baseline and the next is approximately 7 days after cessation of circulation.

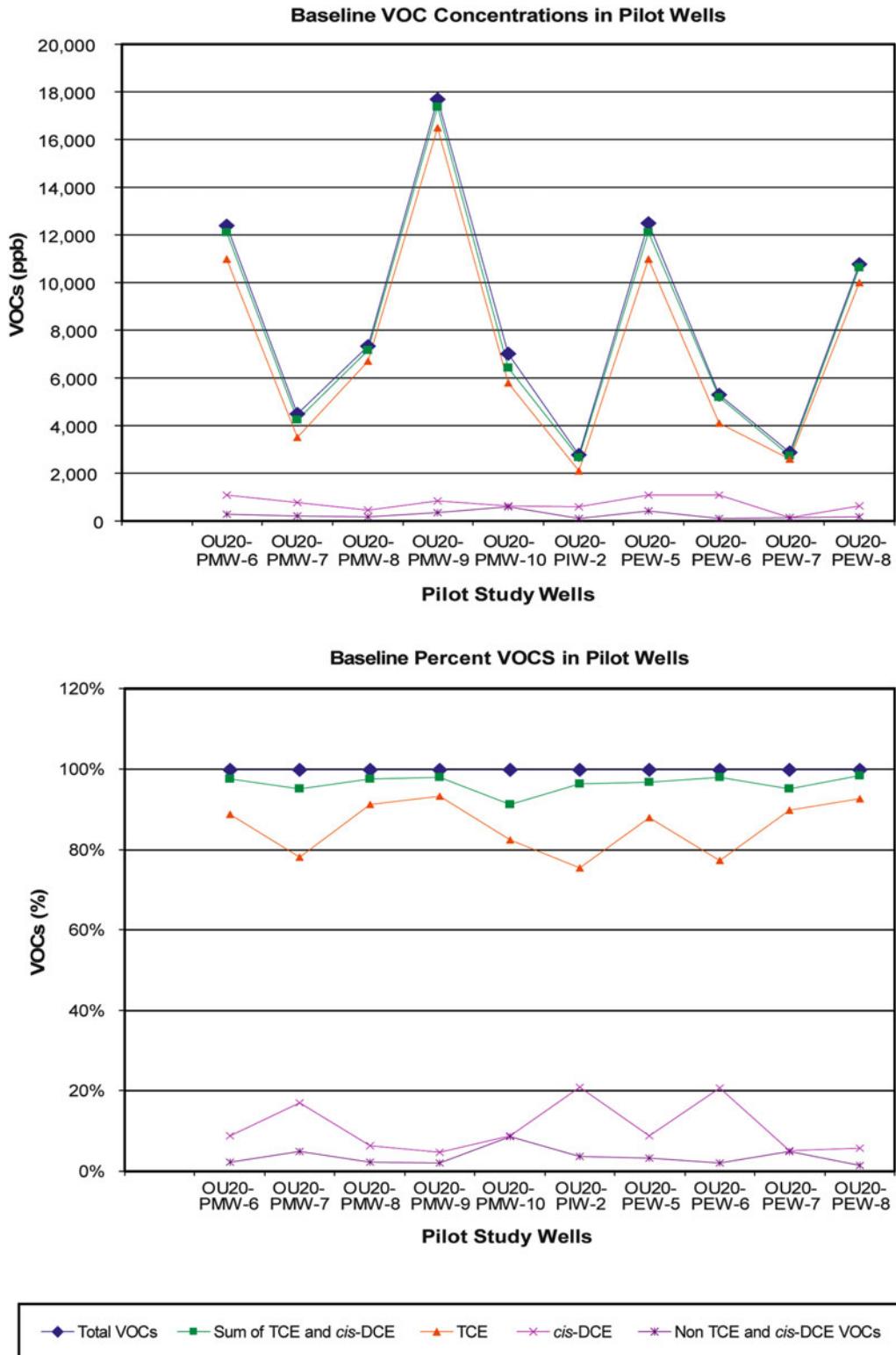


Figure E.6. Baseline monitoring results, Building C-40, OU20, Naval Air Station, North Island, San Diego, CA (from Shaw, 2007).

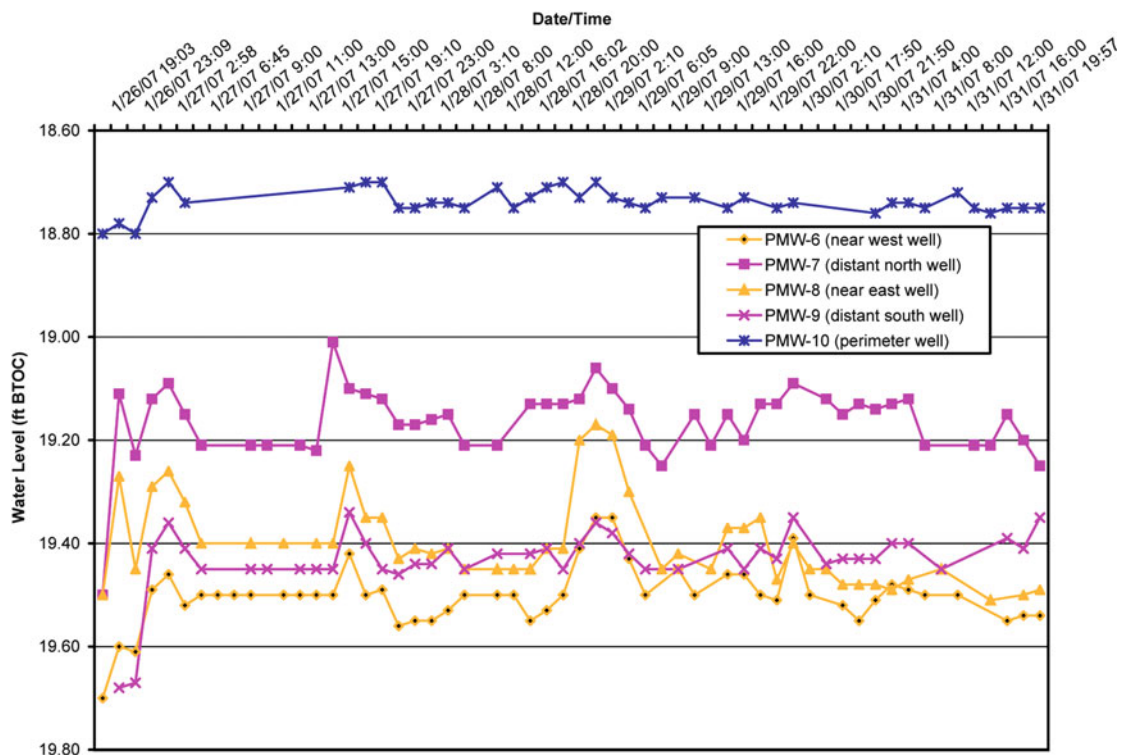


Figure E.7. Groundwater level monitoring during ISCO treatment, Building C-40, OU20, Naval Air Station, North Island, San Diego, CA (from Shaw, 2007). (Note: BTOC – below top of casing measuring point).

Other Observations and Lessons Learned

- Goals were achieved without the need to introduce steam and elevate the thermal activation temperature. It should be noted that the low temperature heat activation (LTHA) is the “perceived” method of activation that resulted in significant contaminant reduction at the site. But, specific testing was not performed to verify LTHA as the main activator. Therefore, LTHA may not work at other sites that do not have similar groundwater and porous media (geochemical) characteristics to those at this site.
- Increases in TCE concentrations in groundwater at some monitoring locations were attributed to inflow of contaminated groundwater from upgradient areas that were outside the TTZ.
- Project team used low-flow sampling techniques during post-ISCO monitoring. It was hypothesized that anomalous high concentrations of TCE observed in monitoring wells during the 7-day post-treatment sampling event were the result of untreated, stagnant groundwater remaining in those monitoring well after ISCO. For this reason the project team purged three well volumes from site monitoring wells and then resampled those wells for VOCs (19 day post-treatment sampling).
- Persulfate was observed to persist for up to 19 days in treatment area.
- Corrosive nature of persulfate required maintenance of certain equipment, such as pump bladders.
- During injection it was observed that the injection well seal was forced open by the pressure of injections. This caused the injected solution to flow through the buried

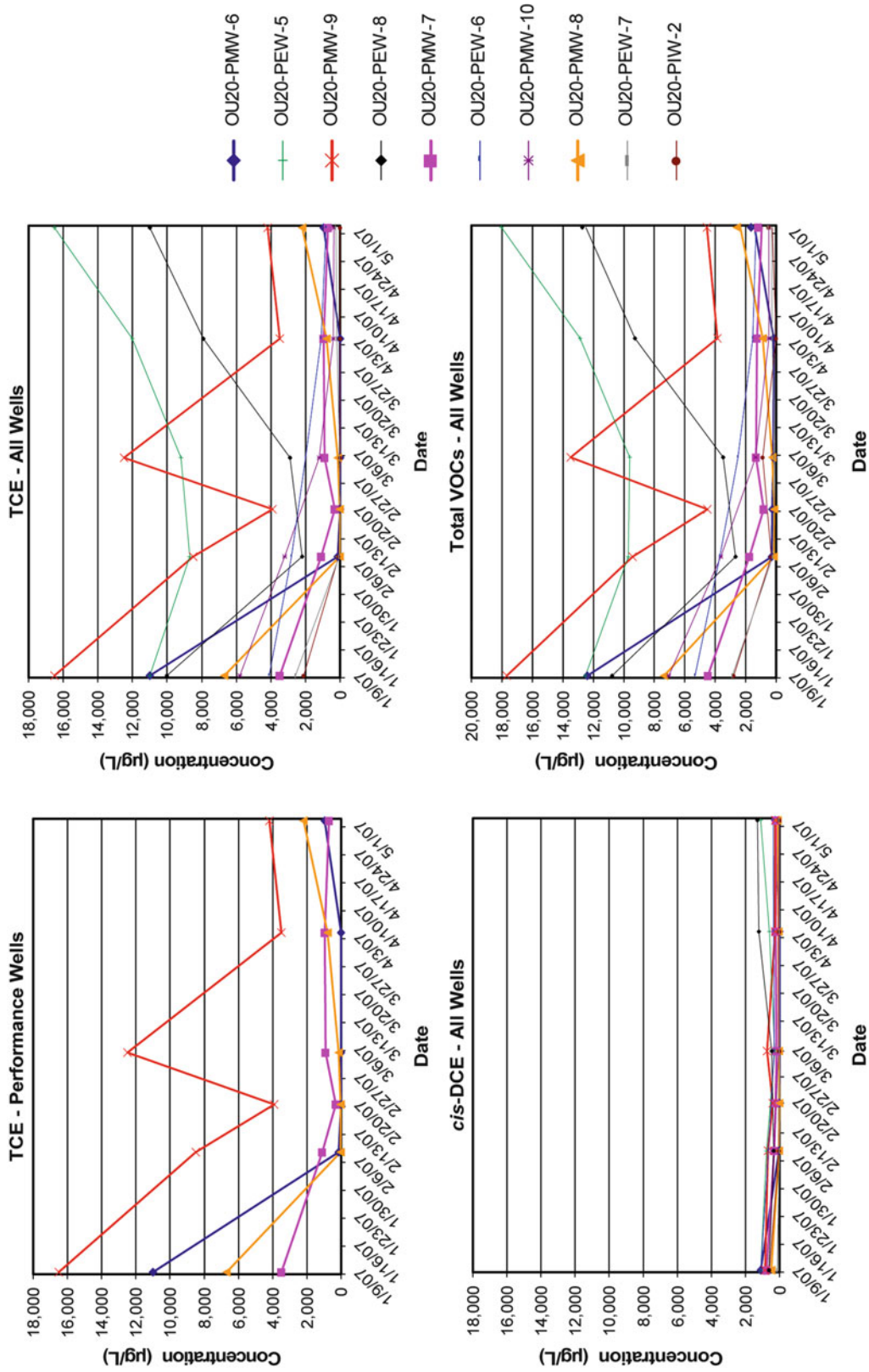


Figure E.8. Treatment performance monitoring results, Building C-40, OU20, Naval Air Station, North Island, San Diego, CA (from Shaw, 2007).

pipng trench and into an extraction well, causing short circuiting of the system. The well was resealed and additional persulfate was added to the system to make up for the short circuiting.

- Bench-scale testing verified that activation of the persulfate radical occurred under ambient conditions and produced significant VOC contaminant reduction without the application of an activator (elevated heat, pH adjustment, etc.). Because elevated groundwater temperature (approximately 20–24°C) is the primary difference between OU-20 and other sites, generation of the persulfate radical is attributed to low temperature heat activation.

E.2.4 References

Shaw. 2007. Persulfate Pilot Test Summary Report, Naval Air Station North Island Operable Unit 20, San Diego, CA. Prepared for Navy Facilities Engineering Command Southwest, San Diego, CA by Shaw Infrastructure, Inc., San Diego, CA. November.

E.3 CASE STUDY: HYDROGEN PEROXIDE PILOT TEST

E.3.1 Abstract

The Letterkenny Army Depot in Pennsylvania is a former disposal area with impacted groundwater. A pilot test was performed to test the effectiveness of catalyzed hydrogen peroxide (CHP) injections into a karst aquifer to treat chloroethene contaminants including DNAPL. Injections proceeded continuously over a period of 4 days. Extensive monitoring showed that hydrogen peroxide and the ferrous sulfate activator were distributed across the treatment area. Performance results showed significant decreases in contaminant concentrations among wells in the treatment area that had detectable levels of hydrogen peroxide. Rebound was noted after treatment, however. Significant rainfall occurred during the post-treatment monitoring period, causing groundwater levels to rise several feet higher than during treatment and baseline sampling.

E.3.2 Summary of Site Characteristics

COCs in Pilot Test Area

- Maximum concentrations in groundwater prior to ISCO treatment:
 - Perchloroethene (PCE): 1,500 micrograms per liter (µg/L)
 - Trichloroethene (TCE): 6,000 µg/L
 - *cis*-Dichloroethene (*cis*-DCE): 5,600 µg/L
 - Vinyl chloride (VC): 560 µg/L
- DNAPL observed to be present in monitoring well PW-6 within the treatment zone. Product was observed to be a combination of DNAPLs and light non-aqueous phase liquids (LNAPLs).

Geology, Hydrology and Baseline Geochemistry of Pilot Test Area

- Karst limestone bedrock
- Saturated hydraulic conductivity: 27–80 feet per day (ft/day)
- Rock matrix hydraulic conductivity: <1 ft/day

- Depth to groundwater: 6–30 ft
- Groundwater pore seepage velocity: 8–2,500 ft/day
- Average hydraulic gradient: 0.0054 ft/ft
- Bedrock effective porosity: 0.003–0.13 (average 0.063)
- pH: 6.6
- Temperature: 16 degrees Celsius (°C)
- Alkalinity: 7 milliequivalents per liter (meq/L)
- Iron: 37 milligrams per liter (mg/L)
- Calcium: 115 mg/L

Site Characterization Methods

- Dye tracer tests
- Packer testing (COCs, specific capacity, and hydraulic communication)
- Borehole geophysics (temperature, caliper, fluid resistivity, optical, and acoustic televiewer logging)

E.3.3 Summary of Pilot Test Features and Results

Pilot Test Objectives

- The goal of the pilot test was to assess the ability of CHP to effectively degrade the chloroethene contaminants in this karst system. Specifically, the impacts of the formation's high conductivity and heterogeneity, the ability to lower pH to the optimal range for Fenton's chemistry, the necessity and effectiveness of continuous injection of reagents, and the effectiveness of the monitoring program were evaluated.
- Should the pilot program be deemed effective upon its completion, another goal of this study was to collect data for full-scale system design.

Pre-Pilot Treatability Testing

Bench scale testing was performed to meet the following objectives, utilizing site groundwater and rock cores:

- Evaluate the ability of CHP to oxidize contaminants in groundwater. Total VOC concentrations were reduced from a pre-test value of 73.1 mg/L down to a range of 0.65 mg/L to non-detect. A chloride concentration increase of up to 8% was observed after reactions were complete.
- Evaluate the impact of the limestone bedrock on the pH of the activator solution. The results indicated that a proper catalyst mixture would be capable of maintaining the pH required for the chemical oxidation reaction to occur.
- Evaluate the potential for the acidic activator to dissolve the limestone bedrock. Only a very slight reaction was observed between the activator (pH of approximately 3) and the native formation carbonate minerals.
- Evaluate the clogging potential of the ferric iron precipitate that could result from the addition of the ferrous iron activator.
- Evaluate the potential of the limestone bedrock and mineral precipitates coating fracture surfaces to activate (or decompose) hydrogen peroxide. Only a very slight reaction was observed between hydrogen peroxide solutions and the native formation

carbonates. The strongest reaction was observed with a fracture coated with a tar-like organic material. Once this material was scrubbed off, the hydrogen peroxide reaction was reduced considerably.

- Optimize the concentrations of activator and hydrogen peroxide. In order to minimize any potential reaction of the pH-adjusted catalyst with the limestone bedrock formation, the recommended target pH for the pilot study was 5.0. Oxidation efficiency was only mildly influenced by hydrogen peroxide concentration.

Pilot Test Design

- Target treatment zone (TTZ): 4,800,000 cubic ft
- Oxidant: 12,700 gallons (gal) hydrogen peroxide at 596 grams per liter (g/L) (50% by weight)
- Activation method: 36,000 gal of ferrous sulfate and phosphoric acid solution (concentration unreported)
- Pore volumes delivered: 0.0055 (based upon hydrogen peroxide volume)
- Oxidant dose: 0.052 g oxidant/kilogram (kg) media
- Number of delivery events: 1
- Delivery method: Continuous injection of reagents over a period of 3.5 days (24 hr/day) into five injection boreholes. Injection began using the activator solution only to obtain the optimal pH (determined to be 5 during bench scale testing). Once the aquifer was conditioned, hydrogen peroxide was added and supplemented with additional activator as necessary. Reagents were delivered through proprietary equipment designed to mix the hydrogen peroxide and activator solutions at the injector head located within the wells.
- The objective for locating the injectors was to establish an injection system on the upgradient edge of the source area that delivered chemical oxidation fluids into the bedrock both along strike and along the groundwater flow pathway. In this way, the injection program would utilize the anisotropic characteristics of the bedrock aquifer to deliver oxidation fluids to target areas, while also preventing recontamination of injectors from upgradient areas.
- Dual-purpose injectors/monitoring points were open boreholes. The open boreholes were geophysically logged and several were pumped, sampled, and analyzed for degree of hydraulic influence and communication with the other wells and VOC concentrations at multiple flow zones using isolation packers. These data were used to support placement of the injectors.
- Figure E.9 shows a plan view of the system layout including injection and monitoring wells. The primary injection wells were IP02, IP05, and IP06.
- Figure E.10 illustrates a generalized geologic cross section showing the approximate nature of the bedrock beneath the landfill cap, the 25-ft zone of water table fluctuation, and an injector screen interval.

Pilot Test Monitoring

- During injection, the groundwater conditions were monitored to determine the distribution of injection fluids and physical evidence of reaction.
- After injection, the groundwater conditions were monitored to estimate the mass of chlorinated VOC destroyed and to document any changes to the limestone bedrock.

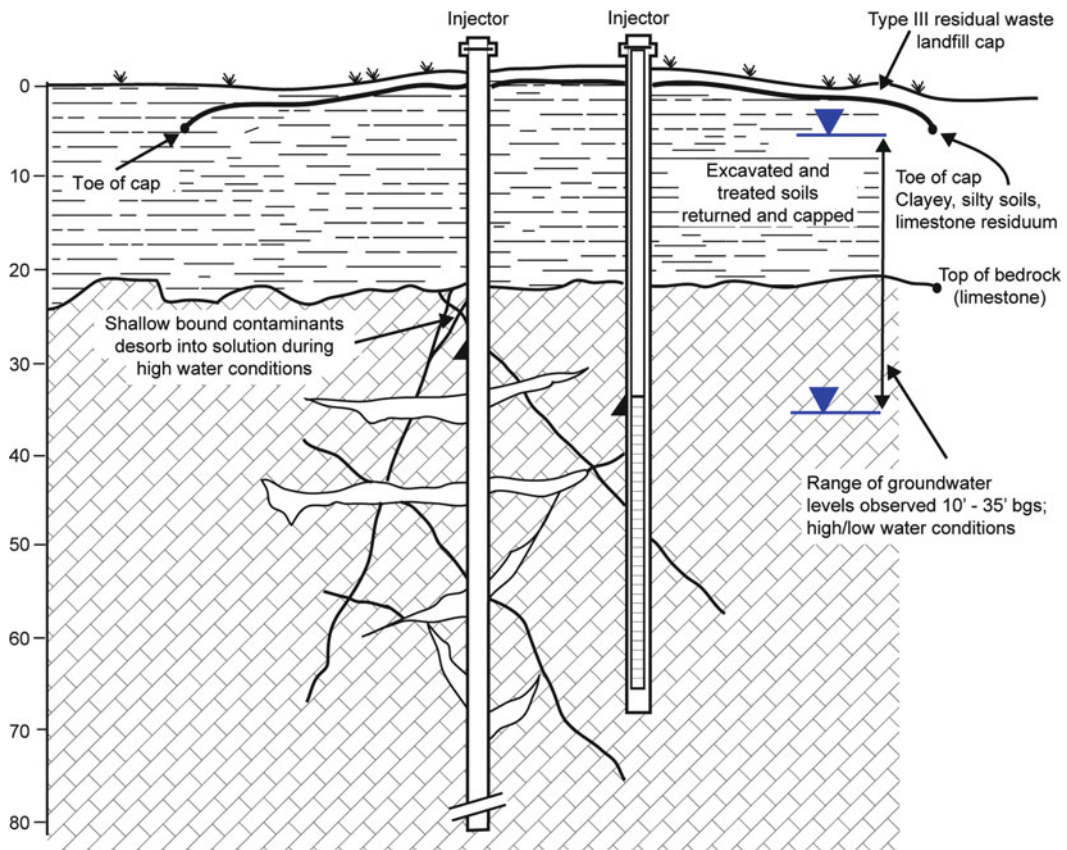


Figure E.10. Generalized injector schematic, K-1 Area, Letterkenny Army Depot, Chambersburg, PA (from Weston, 2000).

- Tables E.1 and E.2 summarize the pilot study monitoring program. They prescribe the monitoring point depth intervals and schedule of parameters.
- Monitoring during this pilot test focused solely on groundwater.
- The following parameters were monitored during the injections, measured with field instruments unless otherwise noted. Hydrogen peroxide interfered with some of the test methods, and therefore some tests could not be performed when hydrogen peroxide was detected above 3 mg/L.
 - Iron (with test kit)
 - pH
 - Specific conductivity
 - Temperature
 - Carbon dioxide
 - Dissolved oxygen
 - Hydrogen peroxide (with test kit)
 - Chloride (with test kit)
 - Hardness (with test kit: measured to assess degradation of limestone bedrock, if any)
 - Groundwater elevations

Table E.1. Discrete Zones Selected for Field Monitoring during the DA Pilot Study, Letterkenny Army Depot, Chambersburg, PA

Field monitoring location	Total depth (ft bgs)	Depth to zones selected for field monitoring (ft bgs)
Upgradient/crossgradient		
96-DA-17	241	63–64; 87; 181–183
PW-2	127	68
OW-6-1	170	31–35; 45–48; 69–73
PW-5	47	37
96-DA-16	220	37–39; 48–50; 70
Source area		
IP01	100	47, 54, 79
IP03	100	54
IP04	100	48, 61, 68
PW-6	80	76
Downgradient		
95-DA-1	222	29–32 (void); 70; 174; 188
96-DA-12	87	36–39; 65–68; 145
95-DA-8	220	58–60; 95; 141
96-DA-13	223	33, 43, 75.6, 182
82-1	35	34

- VOCs were monitored in groundwater 10 days prior to injection, and 5 days, 20 days, 3 months, and 9 months after injections. Sampling was conducted by first purging the wells using a submersible pump and a flow-through cell for monitoring. Purging was completed when field parameters stabilized or three well casing volumes were removed, whichever came first. Samples were collected using a disposable Teflon bailer after the purge pump was removed. Geochemical field parameters that were tracked to assess groundwater stabilization included temperature, specific conductivity, and pH.
- Figure E.11 shows a typical Waterra sampling system setup. The Waterra pump was moved up and down in the water column, slowly bringing water from the depth of the check valve to the surface. To minimize clogging of the Waterra pumps/check valves, the system was placed inside a 2-in. diameter drop pipe that was inserted at each monitoring location. This drop pipe prevented the check valve from scraping the borehole sidewall when it was moved up and down in the water column. The drop pipe was slotted at the zones targeted for monitoring.
- Figure E.12 delineates the extent of hydrogen peroxide distribution as measured using the field test kits on the last day of injection after 66–72 hr of injection. The distribution of hydrogen peroxide at greater than 100 mg/L extended 225 ft, which was the farthest continuous distribution noted during the pilot test. These data show that the oxidant delivery was primarily in the direction of the bedrock strike.
- Figure E.13 depicts groundwater temperature contours on the last day of injection (same monitoring event as shown on Figure E.12). A maximum groundwater temperature of 60°C was detected in IP03, which was not being used as an injection point at the

Table E.2. Summary of Field Monitoring and Injection Activity, DA Pilot Study, Letterkenny Army Depot, Chambersburg, PA

Monitor point	Zone	Depth (ft)	Field monitoring date			
			6/21/1999	6/22/1999	6/23/1999	6/24/1999
Upgradient/Crossgradient						
96-DA-17	1	63	Monitored	H ₂ O ₂	H ₂ O ₂	H ₂ O ₂
96-DA-17	2	87	Monitored	H ₂ O ₂	H ₂ O ₂	H ₂ O ₂
PW-2	1	68	Monitored	H ₂ O ₂ at 20:05	H ₂ O ₂	H ₂ O ₂
OW-6-1	1	33	Monitored	H ₂ O ₂ at 2:05	H ₂ O ₂	H ₂ O ₂
OW-6-1	2	46	N/A	H ₂ O ₂ at 16:29	H ₂ O ₂	H ₂ O ₂
OW-6-1	3	70	Monitored	H ₂ O ₂ at 2:05	H ₂ O ₂	H ₂ O ₂
PW-5	1	37	N/A	Monitored	Monitored	Monitored
96-DA-16	1	38	Monitored	Monitored	Monitored	Monitored
96-DA-16	2	49	Monitored	Monitored	Monitored	Monitored
96-DA-16	3	70	Monitored	Monitored	Monitored	Monitored
Source area						
PW-6	1	76	Monitored	Product	H ₂ O ₂ at 9:50	H ₂ O ₂
IP01	1	47	H ₂ O ₂	Injector	Injector	H ₂ O ₂
IP01	2	54	H ₂ O ₂	Injector	Injector	H ₂ O ₂
IP01	3	79	H ₂ O ₂	Injector	Injector	Clogged
IP02	1	50	Injector	Injector	Catalyst?	Catalyst?
IP03	1	54	H ₂ O ₂	H ₂ O ₂	H ₂ O ₂	H ₂ O ₂
IP04	1	48	Monitored	Injector	Injector	Injector
IP04	2	61	Monitored	Injector	Injector	Injector
IP04	3	68	Monitored	Injector	Injector	Injector
IP05	1	40	Injector	Injector	Catalyst?	H ₂ O ₂
IP06	1	40	Injector	Injector	Injector	Injector
Downgradient						
95-DA-1	1	30	H ₂ O ₂	H ₂ O ₂	H ₂ O ₂	H ₂ O ₂
95-DA-1	2	70	H ₂ O ₂	H ₂ O ₂	H ₂ O ₂	H ₂ O ₂
95-DA-1	3	174	Monitored	H ₂ O ₂	H ₂ O ₂	H ₂ O ₂
96-DA-12	1	37	Monitored	Monitored	H ₂ O ₂ at 20:55	H ₂ O ₂
96-DA-12	2	67	Monitored	Monitored	H ₂ O ₂ at 20:55	H ₂ O ₂
95-DA-8	1	59	Monitored	Monitored	Monitored	Monitored
95-DA-8	2	95	Monitored	Monitored	Monitored	Monitored
95-DA-8	3	141	Monitored	Monitored	Monitored	Clogged
96-DA-13	1	33	Monitored	Monitored	H ₂ O ₂ at 11:52	H ₂ O ₂
96-DA-13	2	43	Monitored	Monitored	H ₂ O ₂ at 11:52	H ₂ O ₂
96-DA-13	3	75.6	Monitored	Monitored	H ₂ O ₂ at 11:52	H ₂ O ₂
96-DA-13	4	182	Monitored	Monitored	H ₂ O ₂ at 11:52	H ₂ O ₂
82-1	1	34	N/A	N/A	Monitored	Monitored
Rowe Spring	N/A	N/A	N/A	N/A	Monitored	Monitored

Catalyst? = Monitor point used to inject catalyst.

Clogged = Monitor zone had become clogged with sediments.

H₂O₂ = Hydrogen peroxide.

H₂O₂ at 11:52 = Military time of first H₂O₂ detection; modified field parameters.

Monitored = All field parameters monitored.

Injector = Monitor point used as an injector.

N/A = Location not monitored.

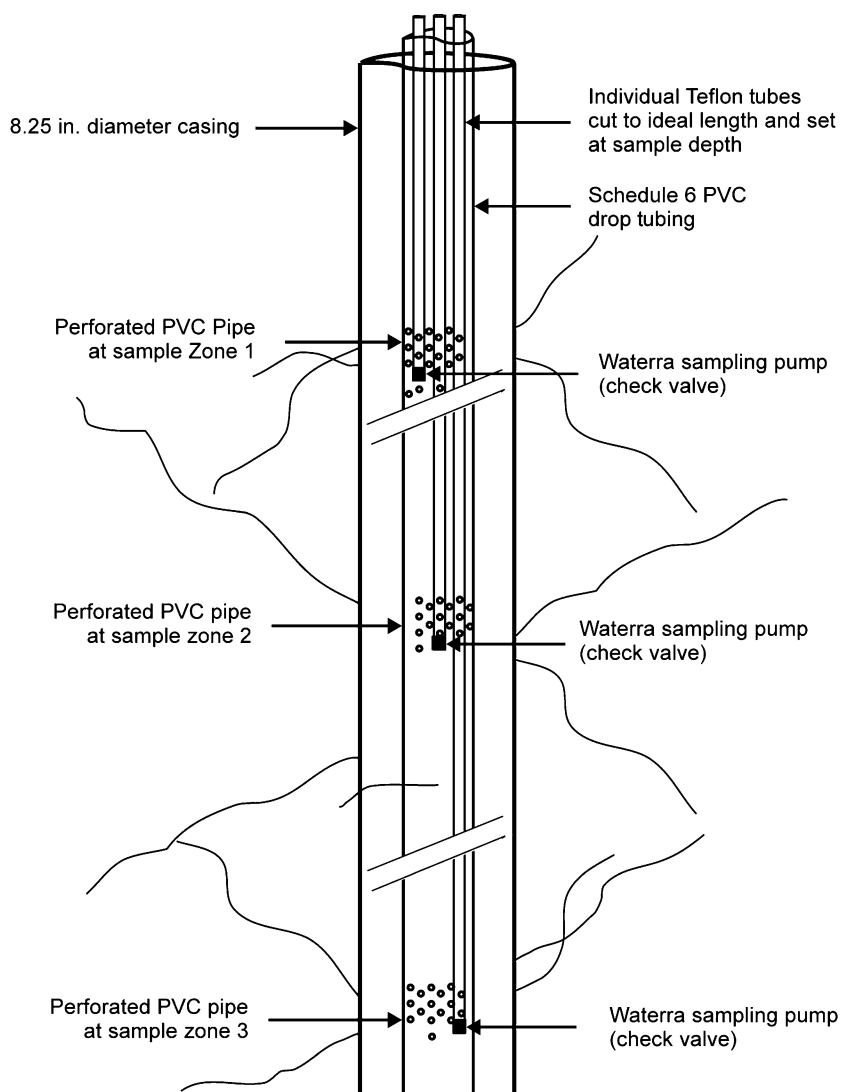


Figure E.11. Typical Waterra multi-level sampling well schematic, K-1 Area, Letterkenny Army Depot, Chambersburg, PA (from Weston, 2000).

time. Groundwater temperatures above ambient conditions were detected at each injector and extended farther to the north (along the direction of bedrock strike) where elevated concentrations of hydrogen peroxide were noted to be present.

- Figure E.14 presents the results of the baseline monitoring event for total chlorinated VOCs. It shows concentrations of greater than 1 mg/L at all injector locations and greater than 10 mg/L at two locations.

ISCO Effectiveness

- Goal: Evaluate ability of CHP to remediate chloroethene contamination in karst aquifer
- Goal Achieved: Yes. CHP proved to be effective in some locations, though less so in others. Concentrations were observed to rebound during the post-ISCO monitoring period presumably due to dissolution of untreated contaminants in the shallow

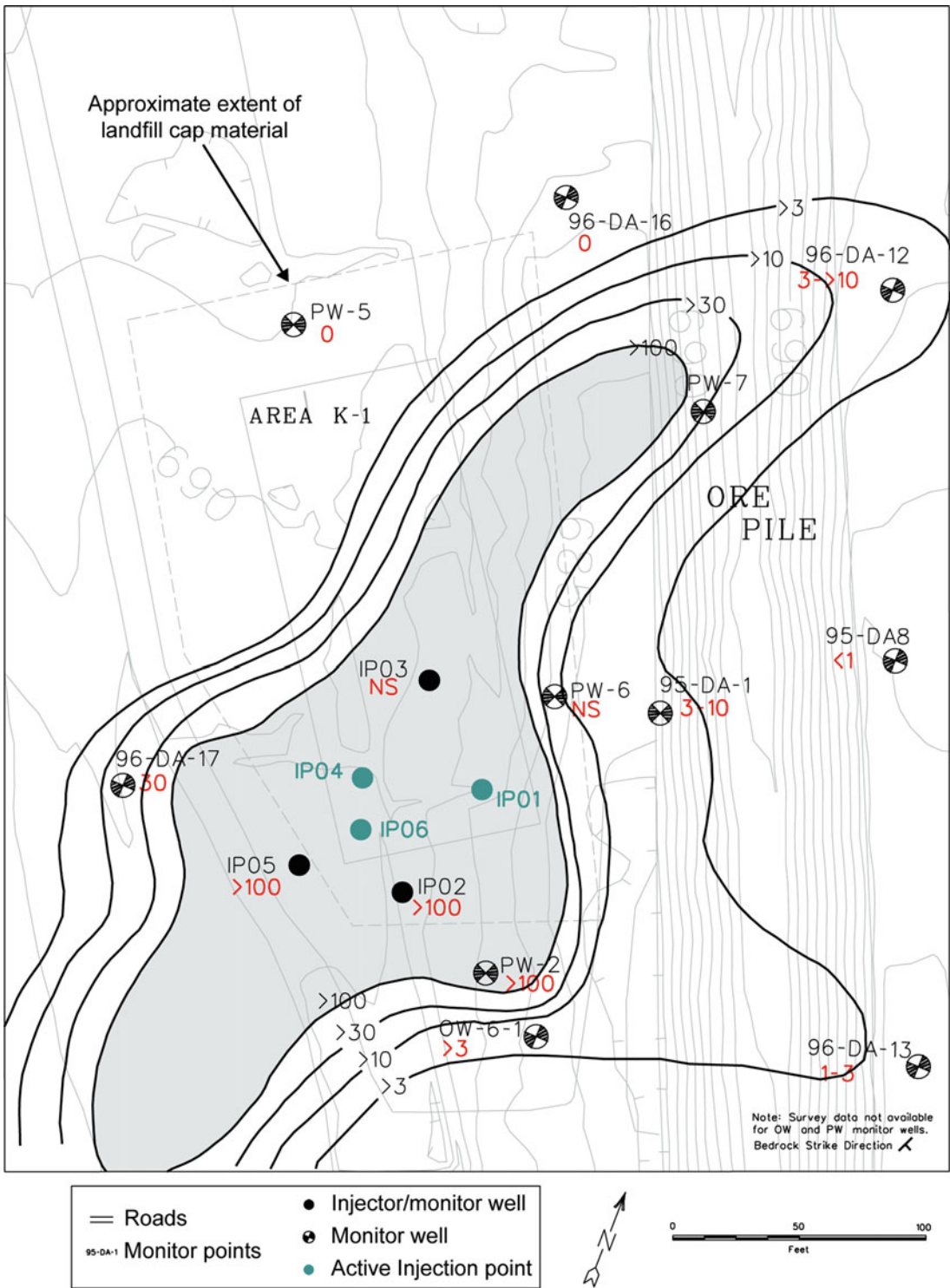


Figure E.12. Hydrogen peroxide (mg/L H₂O₂) distribution in groundwater, 24 June 1999, Area K-1, Letterkenny Army Depot, Chambersburg, PA (from Weston, 2000).

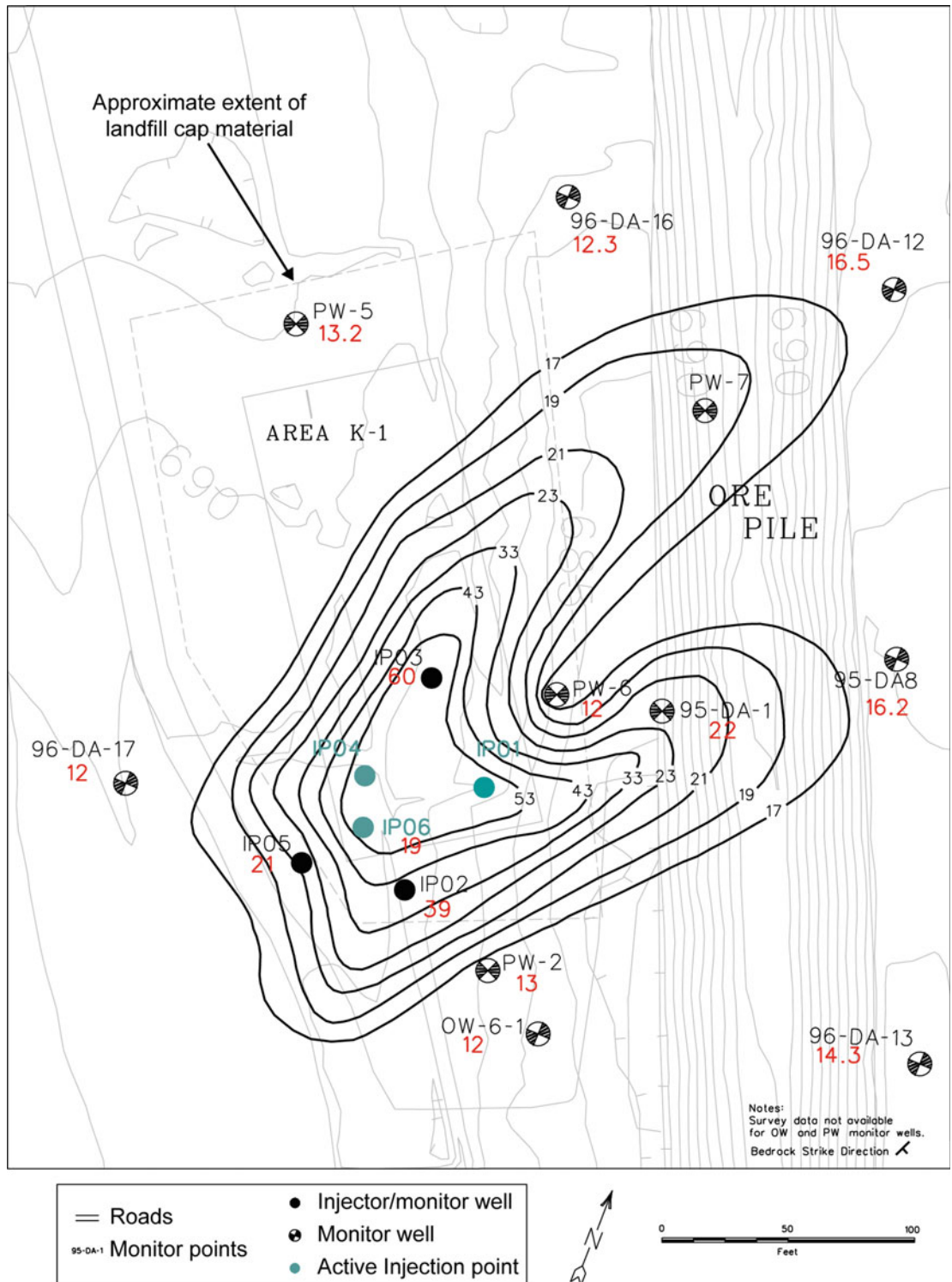


Figure E.13. Temperature (°C) distribution in groundwater, 24 June 1999, Area K-1, Letterkenny Army Depot, Chambersburg, PA (from Weston, 2000).

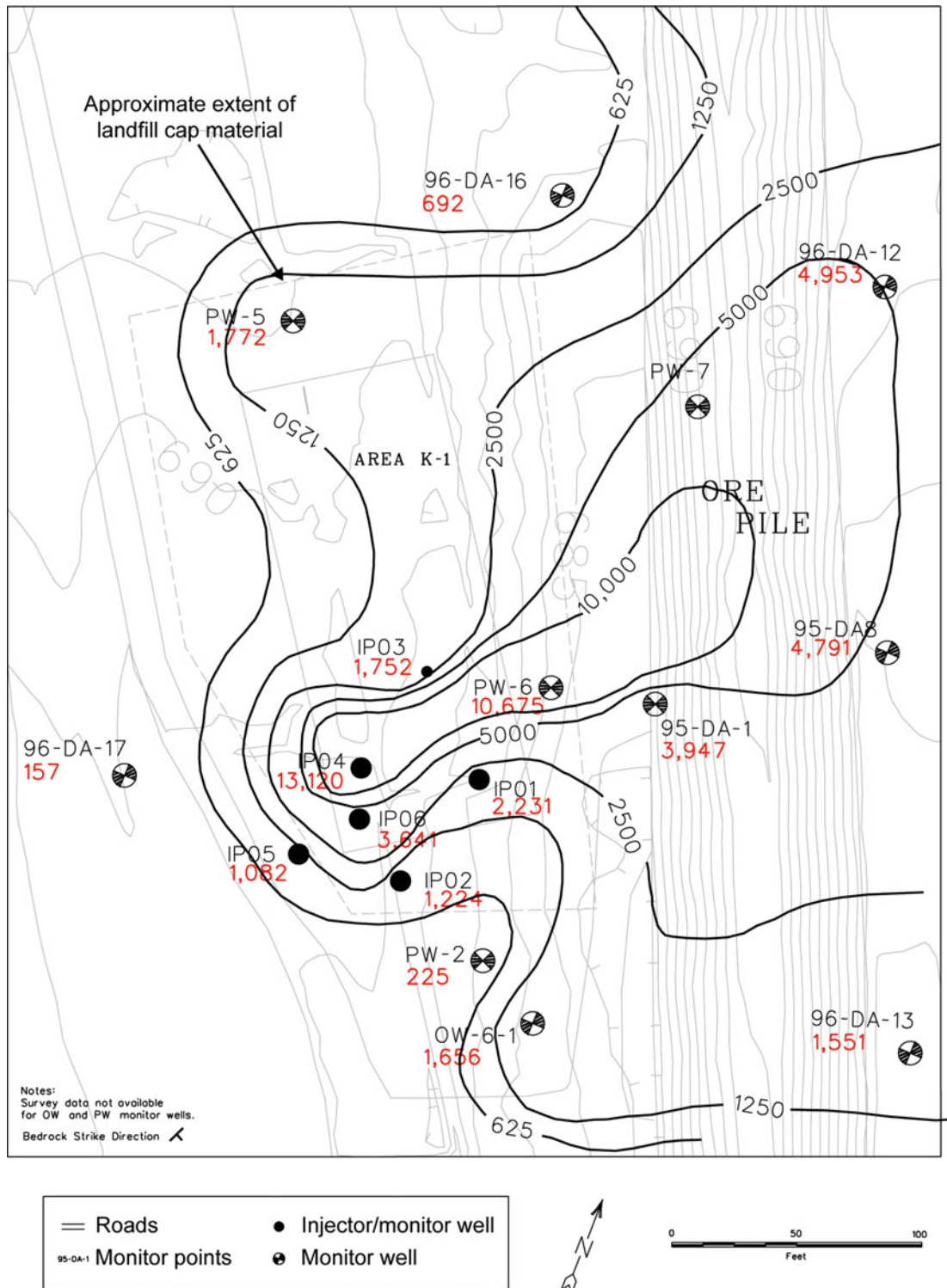


Figure E.14. Baseline total chlorinated VOC monitoring results ($\mu\text{g/L}$), 10 June 1999, Area K-1, Letterkenny Army Depot, Chambersburg, PA (from Weston, 2000).

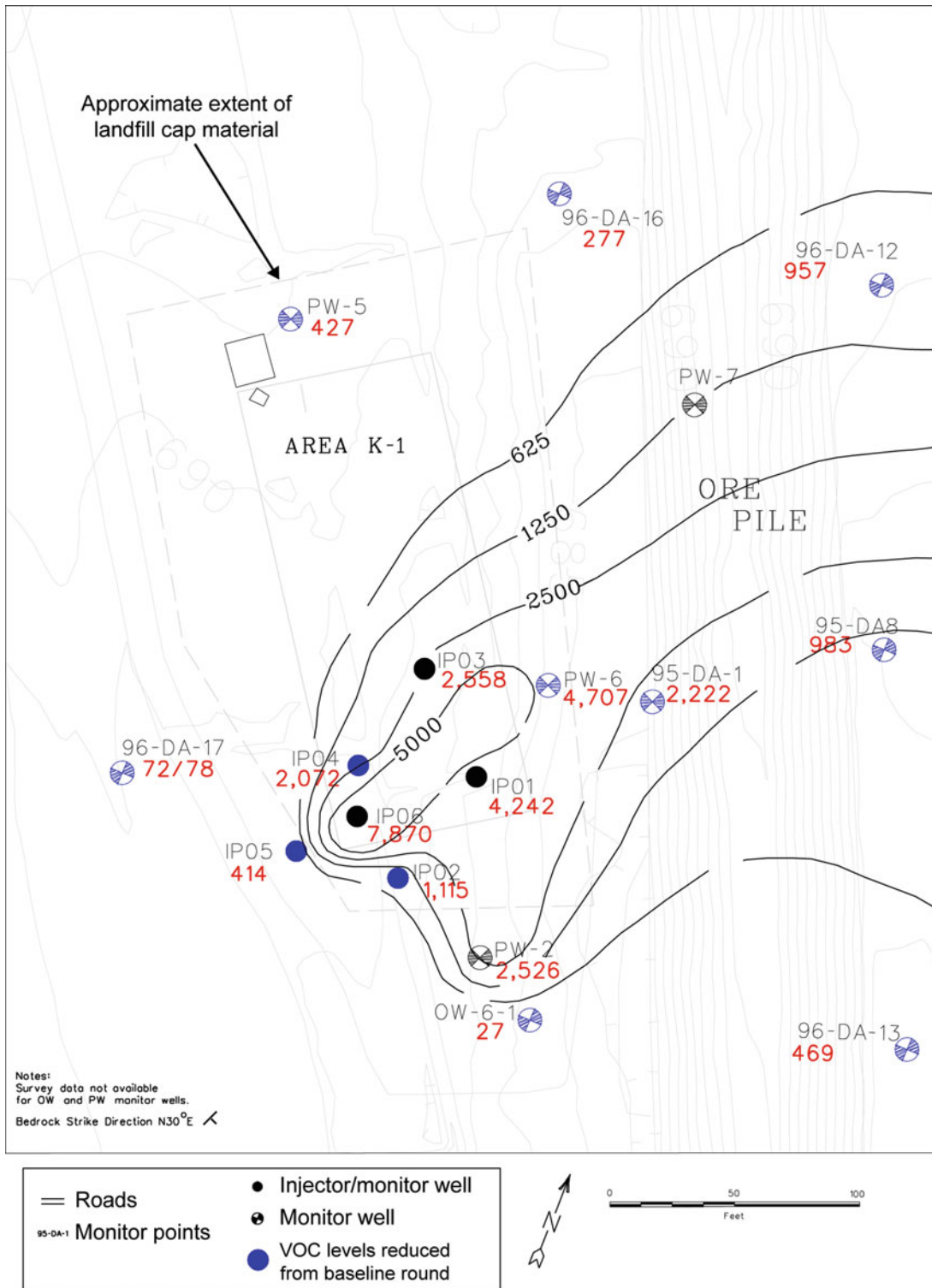


Figure E.15. Total chlorinated VOC (µg/L) treatment performance monitoring results, 17–21 April 2000, Area K-1, Letterkenny Army Depot, Chambersburg, PA (from Weston, 2000).

bedrock/overburden transition zone where ISCO injections were not performed. The mass of chlorinated VOCs destroyed, 1,900 pounds, was estimated by use of groundwater chloride concentrations.

- Metals mobilization: None reported
- Permeability reduction: None Reported
- Reduction in microbial activity: Not Tested
- Current plans for future work: The project team gave several-full scale design recommendations in the pilot test report. Future plans for the site are currently unknown.
- Figure E.15 summarizes the results of the groundwater treatment performance monitoring for total VOCs approximately 9 months after injection was completed. It shows eradication of total VOC concentrations greater than 10 mg/L and a reduction in the 5 mg/L isoconcentration contour. Total VOC concentrations in the well that initially contained DNAPL were reduced from 10.8 to 4.7 mg/L.

Other Observations and Lessons Learned

- Significant rainfall events occurred during the post-ISCO monitoring period, causing groundwater elevations to rise several feet above historic levels and those that existed during this pilot test. This confounds the interpretation of contaminant rebound.
- Interference between oxidants and sampling methods (e.g., field test kits and instruments) are important to be aware of during ISCO monitoring.
- To avoid unnecessary, nonproductive consumption of the oxidant during injection, the project team recommended monitoring the hydrogen peroxide concentration at the perimeter of the target treatment zone, and reducing the hydrogen peroxide injection rate once concentrations at the perimeter reached 100 mg/L.
- Injecting activator solution only around the perimeter of the planned injection zone was suggested as a means of providing an “oxidative barrier” to prevent VOCs from migrating outside the TTZ.
- No effects to the limestone bedrock were measured.
- Modify the injection approach from continuous to reduced rates and ramping down to collect chloride readings for evaluating the degree of chloride production (e.g., destruction of chlorinated VOCs). This approach will likely reduce/eliminate unnecessary loss of hydrogen peroxide to nontarget areas, prevent the excess injection of hydrogen peroxide, reduce the mobilization of VOCs, and allow for a more comprehensive evaluation of the chloride production to determine the degree of chlorinated VOC destruction.

E.3.4 References

Weston. 2000. Summary Report for the In Situ Chemical Oxidation Pilot Study of the Bedrock Aquifer at the Southeastern (SE) Disposal Area (DA), Letterkenny Army Depot. Prepared by Roy F. Weston, West Chester, PA for the U.S. Army Corps of Engineers, Baltimore, MD. October.

E.4 ILLUSTRATIVE APPLICATIONS: COMBINED APPROACHES

E.4.1 Impacts of Potassium Permanganate on Anaerobic Microbial Communities for Remediation of Chlorinated Solvents

The Savage Municipal Water Supply Well Site, Operable Unit 1, in Milford, New Hampshire has a small perchloroethene (PCE) DNAPL source area that created a larger dissolved PCE plume in groundwater. The source area had been contained by a slurry wall, but *in situ* chemical oxidation (ISCO) was selected several years later to provide mass destruction in the vicinity of the DNAPL. It was recognized, however, that polishing following ISCO would be required, and enhanced *in situ* bioremediation (EISB), via reductive dechlorination, was thought likely to be the most appropriate technology for this application. As such, an effort was undertaken to thoroughly characterize the microbial community structure prior to performing ISCO, 1 year after initial ISCO injections, and then 1 year after a larger, second round of ISCO injections (Macbeth et al., 2005; Macbeth, 2006; Weidhaas and Macbeth, 2006). In addition, specific sampling for *Dehalococcoides* spp. organisms was performed to determine whether bioaugmentation might be required as part of an EISB polishing strategy.

Baseline groundwater samples were collected at the site in 2003 from both the area to be treated and areas outside the treatment zone. Immediately thereafter, 8,500 pounds (lb) of potassium permanganate was injected in the treatment zone via two injection wells. Samples to evaluate the response of the microbial community were collected again in 2004, 1 year after the permanganate injections. A second round of permanganate treatment comprising 24,000 lbs of potassium permanganate injected via eight wells followed. Finally, groundwater samples were collected in late 2005, 1 year after the second round of treatment.

Groundwater samples were analyzed for ORP, TOC, DOC, permanganate, and chlorinated volatile organic compounds (CVOCs). The microbial community was evaluated using a variety of non-culture based deoxyribonucleic acid (DNA) analysis techniques. Specifically, terminal restriction fragment length polymorphism (T-RFLP) was used to “fingerprint” the community at different points in time, to estimate the number and the relative abundance of species. Clone library analysis was used to sequence some of the more common genes encountered as a basis for tentative identification and evaluating relatedness and diversity. Finally, quantitative polymerase chain reaction (qPCR) was used to detect and quantify the presence of *Dehalococcoides* spp. bacteria in space and over time. In all cases, the 16S ribosomal ribonucleic acid (rRNA) gene was targeted for analysis.

From the baseline samples in 2003 to the 2005 samples, PCE concentrations decreased between slightly less than 90% to over two orders of magnitude in the treatment area monitoring wells, with final concentrations ranging from 17 to 190 micrograms per liter ($\mu\text{g/L}$). ORP increased steadily in all of these wells from 2003 to 2005, ranging from 889 to 925 millivolts (mV) in 2005. DOC was fairly low throughout, but increased slightly from 2003 to 2005. No impact of ISCO was observed for these parameters in downgradient monitoring locations from 2003 to 2004. In 2005, however, the two downgradient wells nearest the treatment area showed a significant increase in ORP and DOC as well as decreases in PCE concentrations (though not as significant as in the treatment zone).

In the baseline T-RFLP samples, microbial diversity (as measured by species “richness,” or number of species, and related indices) was fairly high in all of the wells, though it was somewhat lower in the treatment zone wells, presumably due to the higher PCE concentrations. The species richness dropped dramatically in the treatment area wells in 2004, and remained at similar levels in 2005. Species richness was fairly constant in all wells outside the treatment area

in all three sampling events. Another measure of microbial community structure and diversity is “evenness,” which is related to the extent to which the relative abundance of species is “even” (i.e., similar abundance for various species or predominance of a few species). While evenness was similar between treatment area and downgradient wells in 2003, it dropped substantially in treatment area wells in 2004 as the community became dominated by a very small number of species that could tolerate the high permanganate concentrations. The evenness did recover somewhat in treatment area wells in 2005, and was unchanged in downgradient wells throughout. Clone library analysis provided similar insights in that sequences from downgradient wells represented a wide range of bacteria with only distant relationships, while sequences from the treatment area in 2004 were mostly very closely related fermentative bacteria (*Desulfosporosinus*). In 2005, the number and range of genera increased in the treatment area, though most were still closely related to *Clostridia*.

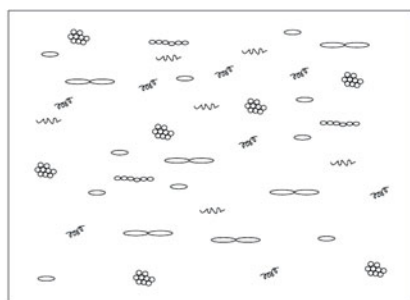
Based on these results relating permanganate concentration, DOC, microbial richness, and evenness, a conceptual model for the microbial community dynamics before, during and after treatment was developed (Macbeth et al., 2005; Macbeth, 2006). This conceptual model must be considered merely a hypothesis at this point because detailed data are not available from many sites, but it might be useful as a starting point for anticipating the likely impact of ISCO on *in situ* microbial communities in general. The model is summarized as a sequence of six scenarios that are a function of permanganate concentration as follows (shown schematically in Figure E.16):

- Scenario 1: Pre-ISCO conditions in which diversity is quite high though biomass is low (this assumes organic carbon is low, which is generally true in aquifers not contaminated with petroleum hydrocarbons)
- Scenario 2: Permanganate is present at very high concentrations following an ISCO flood; both diversity and biomass are at their lowest levels
- Scenario 3: Permanganate concentrations are still somewhat high, but have dropped enough to allow certain bacteria to thrive in the presence of the elevated DOC; diversity is still low, but biomass is actually higher than baseline
- Scenario 4: Permanganate is still present, but concentrations are decreasing; biomass is reaching a maximum because of the elevated DOC as diversity is continuing to recover
- Scenario 5: With permanganate now gone and DOC levels dropping, biomass is beginning to decline, but diversity continues to rise
- Scenario 6: Sufficient time has passed to allow the community to return to something like the original equilibrium structure as permanganate is long gone and DOC levels have returned to background for some period of time.

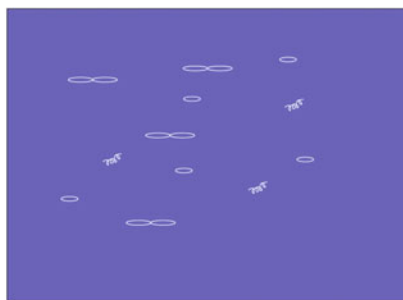
While this hypothesized conceptual model was based on the field data from this case study, it appears to be consistent with most of the laboratory work presented in Chapter 7, Section 7.2. It should be noted, however, that the timeframe for sampling in the case study was not sufficiently long to achieve the return to the baseline equilibrium hypothesized in Scenario 6.

The final component of microbial community analysis in the case study was the detection and monitoring of *Dehalococcoides* spp. During the baseline sampling in 2003, *Dehalococcoides* spp. bacteria were detected in low concentrations at two wells in the treatment area. In 2004, 1 year after the first permanganate injection, *Dehalococcoides* spp. were detected in one well within the treatment area, and in one well outside the area. One year after the second permanganate injection, no *Dehalococcoides* spp. were detected in any of the wells. While multiple permanganate injections likely significantly impacted the population in the treatment area, it is not known whether *Dehalococcoides* spp. would have recovered naturally in the source area given more time. Certainly it appeared that bioaugmentation might be required in

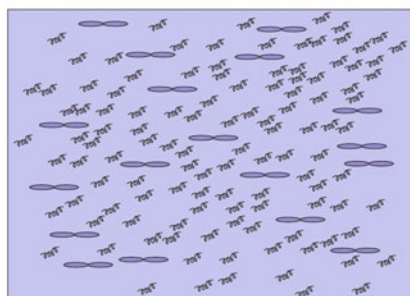
the source area to achieve complete dechlorination of the remaining PCE to ethene if polishing via EISB was applied within a year or so of the final permanganate injection.



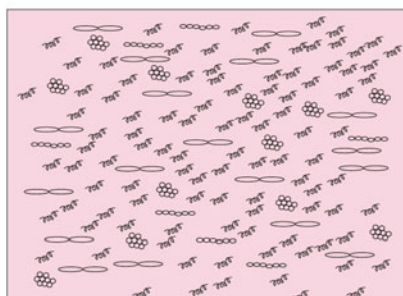
Scenario 1: Microorganisms at equilibrium under ambient environmental conditions.
Highest Diversity - 10 on a relative scale
Low Biomass - 3 on a relative scale



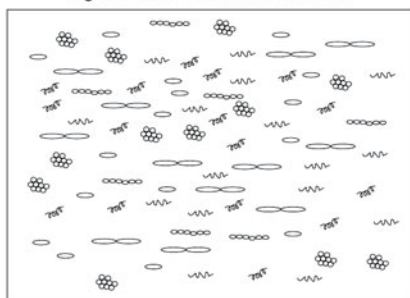
Scenario 2: High concentration permanganate flood.
Lowest Diversity - 1 on a relative scale
Lowest Biomass - 1 on a relative scale



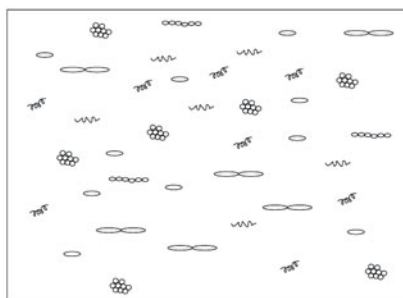
Scenario 3: Permanganate concentration declines sufficiently to allow for growth of permanganate-resistant bacteria, stimulated by increased carbon availability.
Low Diversity - 3 on a relative scale
High Biomass - 5 on a relative scale



Scenario 4: Concentration of permanganate low, which allows for additional growth of microorganisms stimulated by increased carbon availability.
High Diversity - 5 on a relative scale
Highest Biomass - 10 on a relative scale



Scenario 5: Permanganate gone, but microorganisms stimulated by increased carbon availability.
Higher Diversity - 7 on a relative scale
Higher Biomass - 7 on a relative scale



Scenario 6: Permanganate gone and carbon is back to near or below pre-ISCO concentrations.
Highest Diversity - 10 on a relative scale
Low Biomass - 3 on a relative scale

Figure E.16. Hypothesized conceptual model for microbial community dynamics at a chlorinated solvent site following permanganate ISCO based on detailed molecular analysis at the Savage Municipal Water Supply Well Site (Macbeth, 2006).

E.4.2 Catalyzed Hydrogen Peroxide and Associated Exothermicity for PAH Recovery and Remediation at a Former Manufactured Gas Plant Site

Approximately 2.2 ha at a former manufactured gas plant (MGP) site in Augusta, Georgia were impacted with byproduct-like material (BPLM) (Bryant and Haghebaert, 2008). The site is

located in an urban area with numerous historic structures. Much of the site was remediated with *in situ* stabilization (ISS), but BPLM required remediation under several offsite buildings including a gasoline station, an historic church, and private homes. CHP was selected to address remaining BPLM. The remedial strategy exploited multiple mechanisms of Fenton's chemistry to achieve remedial objectives: (1) exothermicity to facilitate product recovery, and (2) oxidative mechanisms for contaminant destruction.

Coal tar was trapped in a highly permeable sand seam, overlain by impermeable clay and underlain by dense saprolite. The lithology inhibited release of carbon dioxide and oxygen produced by CHP and helped to protect the structures from buildup of off-gases and potential instability that could be caused by the injection. Characterization of coal tar NAPL mass in poorly accessible areas was incomplete, and in accessible areas was likely to be optimistically low. Recovery efforts served to reduce the impact of these uncertainties on the stoichiometric requirements for treatment.

A pilot test included installation of 45 injection wells in a 1,308 m² area, with injection of 104,476 liters of CHP solution (10.9% H₂O₂), equivalent to a mass ratio of 5 kilograms (kg) H₂O₂ per kg of BPLM. Injection wells were designed to accommodate elevated temperatures and pressures during injection as well as NAPL extraction points. During the pilot test, enhanced mobilization of the BPLM was observed due to the increased groundwater temperature and circulation. The viscosity of the BPLM was reduced and allowed active collection to improve treatment efficiency. The results indicated approximately 81% reduction in BPLM mass in the pilot test area.

Based on the results of the field pilot, full-scale treatment was implemented. A total of 686 additional injectors were installed, based on presence of BPLM. If BPLM was observed at a boring location, an injector was installed and a new boring was advanced further down-gradient. A total of 118 borings were analyzed for VOCs and polycyclic aromatic hydrocarbons (PAHs) to establish BPLM mass. The full-scale injection began in November 2004 and was completed in September 2005. A total of 1,201,259 kg of H₂O₂ was injected at an average peroxide concentration of 14%. Treatment was continued until no separate-phase BPLM was observed, VOC readings were below 50 parts per million at every location, and peroxide persisted in groundwater for at least 21 days. Long-term groundwater monitoring at the site documented 88–97.5% reduction in VOC and PAH concentrations.

Injection of CHP resulted in elevated groundwater temperatures and circulation, which initially decreased the viscosity of the residual BPLM. The off-gasses produced by the CHP, coupled with the effective pressure cap provided by the silty clay overburden, resulted in pressurization of the sand and gravel zones impacted with BPLM. The BPLM was forced out of the adjacent injectors and into a collection pipe system, which discharged into several collection sumps.

As the treatment progressed, the physical characteristics of the residual BPLM were modified by partial oxidation. After the initial decrease in BPLM viscosity due to the increased groundwater temperature, the BPLM became progressively more viscous. This was likely due to preferential destruction of the monoaromatic and lower molecular weight PAH compounds, which generally react more quickly with CHP than higher molecular weight compounds. The residual, higher molecular weight fraction exhibited much higher viscosity, which reduced extraction and collection efficiency.

As demonstrated in this case, active product recovery prior to or concurrent with ISCO can reduce treatment time and cost. Furthermore, the reduced contaminant mass allowed more efficient chemical injection and distribution. The lithology at the site created conditions particularly conducive to exploiting the exothermicity of the CHP process.

E.4.3 Excavation Combined with Catalyzed Hydrogen Peroxide and Sodium Permanganate ISCO to Achieve Maximum Contaminant Levels at a PCE Site

In 2007, the city of Orlando, Florida identified a groundwater PCE plume with a source area located beneath the proposed footprint for a new sports arena (Bryant and Kellar, 2009). The contamination threatened to delay a tight construction schedule. To prevent such disruption, a combination of hot spot excavation and CHP and sodium permanganate ISCO was selected to achieve stringent cleanup goals.

The aquifer was primarily sand, with some finer-grained (silty sand) zones to a depth of approximately 40 ft below grade, underlain by a dense clay aquitard in the treatment area. The maximum PCE concentration found in the source area groundwater was 14,600 micrograms per liter ($\mu\text{g/L}$), which exceeded the Florida groundwater Cleanup Target Level (CTL) of 3 $\mu\text{g/L}$. Maximum concentrations of 57 $\mu\text{g/L}$ TCE and 98 $\mu\text{g/L}$ *cis*-1,2-dichloroethene (*cis*-DCE) were detected, exceeding their CTLs of 3 and 70 $\mu\text{g/L}$, respectively. Shallow soil (2–4 ft below grade) was also impacted in two discrete areas. The maximum soil PCE concentration was approximately 0.49 milligrams per kilogram (mg/kg), which exceeded the Florida soil CTL for leachability of 0.03 mg/kg.

In addition to stringent cleanup goals, the remedial timeframe was driven by arena construction schedules. Remediation was conducted in three phases. The first phase consisted of ISCO with CHP to target the concentrated source area. The second phase consisted of additional ISCO using sodium permanganate to target potential residual contaminants remaining after the catalyzed peroxide application. The third phase consisted of removal with offsite disposal of impacted shallow soil.

The sequential application of CHP and permanganate at this site exploited particular advantages of each oxidant. CHP rapidly destroys contaminants and is capable of significant mass destruction within a period of weeks for a site of this size. However, the short lifetime of CHP in the subsurface limits its effectiveness in treating contaminants slowly diffusing out of fine-grained (silt or clay) aquifer matrices, and the oxidant itself does not survive long enough to diffuse into those matrices. Long-term diffusion of contaminants from fine-grained aquifer matrices may pose a rebound problem, and prevent achievement or maintenance of the CTLs. Permanganate, by comparison, is generally a less aggressive oxidant than CHP. Permanganate therefore tends to persist much longer in the subsurface than CHP. Residual permanganate may last for months to address contaminants slowly diffusing from fine-grained matrices and may also diffuse into finer-grained aquifer matrices to directly attack those contaminants.

Seventy-two injection wells were installed across three depth intervals between approximately 10–40 ft below grade, in an 80-ft by 130-ft area. The first phase of remediation consisted of injecting 85,000 gal of CHP solution over approximately 3 weeks. VOC readings in the headspace over groundwater samples from four monitoring wells showed an initial spike related to desorption of VOCs from the aquifer matrix, followed by non-detectable levels during treatment. These data were used to determine when to cease CHP injection to complete the first treatment phase.

One week was allowed for residual peroxide to degrade before beginning permanganate injection for the second phase. The same network of injection wells installed for the CHP injection was utilized for the permanganate. This second phase of remediation consisted of injecting 21,000 gal of 4% sodium permanganate solution for 1 week. Field monitoring for sodium permanganate consisted of collecting groundwater samples for visual analysis, which

showed that permanganate was distributed throughout the treatment area following the injection.

The third phase of remediation consisted of soil removal during a 3-day period, 15 days after permanganate injection ended, from two areas impacted with PCE. A total of 94 tons of soil was removed. During the removal, a polyvinyl chloride (PVC) pipe and apparent floor drain system were discovered. The pipe was found to contain residual sludge and exhibited elevated VOC readings. Located directly over the groundwater source area, this was presumed to be the discharge source. The piping and associated bedding were also removed.

Post-ISCO performance was monitored via three intermediate groundwater sampling events and a final sampling event 177 days after injection ended. During the intermediate sampling events, the VOC concentrations in all five of the performance monitoring wells were reduced to below the CTLs, with one exception. In one sample collected 164 days after injection ceased, PCE was detected at 11 $\mu\text{g/L}$, as confirmed by a second analysis. This sample came from a shallow well adjacent to the soil removal area, thus the PCE may have been associated with the soil removal. Additional permanganate treatment was applied in the area of this well, and all VOCs were subsequently below CTLs. The injection and monitoring wells were then abandoned in accordance with Florida regulations.

This case suggests that injection of sodium permanganate following an initial campaign of CHP can be a particularly effective and cost-effective remedial strategy for chlorinated solvent contamination where rebound prevention and time to closure are important considerations. It also illustrates how important it is to know the presence of primary sources of contamination, and that excavation may be most effective means of removing these sources. Such a strategy takes advantage of the reactivity of CHP along with the persistence and ability to penetrate low permeability strata offered by sodium permanganate.

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