

**GUIDANCE DOCUMENT: ASSESSING THE
POTENTIAL FOR METALS MOBILIZATION
DURING THE APPLICATION OF IN SITU
CHEMICAL OXIDATION TECHNOLOGIES**

Prepared For:

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1.0 SUMMARY

This report provides an assessment of the potential for metal mobilization during the application of In Situ Chemical Oxidation (ISCO) technologies. It begins with a review of historical evidence of metals mobilization due to ISCO both in the laboratory and the field; the environmental issues associated with metals release and the regulatory framework governing metals contamination in the United States. A review of the fundamental science for sub-surficial fate and transport of metals in groundwater and the major oxidation chemicals currently used in ISCO technologies is then discussed. Finally, guidance is provided for evaluating site-specific metal mobilization potential and how to design for the minimization, monitoring and response to metals mobilization in a field event.

Background

In situ chemical oxidation (ISCO) has been applied at numerous sites, including Department of Defense (DoD) facilities, to treat organic contaminants in the subsurface, and has evolved into a standard approach for cost-effective remediation of contaminated soil and groundwater (Siegrist et al., 2011). While simple in concept, ISCO relies on a complex myriad of geochemical interactions and transport mechanisms that need to be well understood to ensure a high certainty of meeting treatment objectives. One of these interactions is the variation of naturally occurring geochemical conditions (e.g., pH, Eh) of the treatment area in the subsurface which creates a variety of oxidation products that have the potential to interact with naturally occurring metals in both soils and groundwater.

Objectives

The objective of this guidance document is to provide site owners, engineers, scientists and practitioners with the following:

- Fundamental background of the chemistry behind the ISCO technologies and factors affecting metals mobilization.
- Methods for identifying if metals mobilization may be a concern at a specific site.
- Guidance in determining bench-scale testing that may benefit site evaluation for metals mobilization.
- Approach for monitoring for the potential of metals mobilization during a field event.
- Methods for mitigating metals mobilization.
- Methods to address metals if they are mobilized.

Approach

This guidance document is organized into three basic sections to aid the user. These sections include:

- Fundamental Science of Metals Mobilization.
- Evaluating Site-Specific Metals Mobilization Potential.
- Design, Monitoring and Actions for Metals Mobilization in an ISCO Field Event

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LIST OF ACRONYMS/ABBREVIATIONS

%	percent
°C	degrees Centigrade
AAP	alkaline activated persulfate
Ag	silver
Al	aluminum
As	arsenic
BTEX	Benzene, toluene, ethylbenzene and xylenes
Cd	cadmium
CEC	cation exchange capacity
CERCLA	Comprehensive Emergency Response, Compensation and Liability Act
COCs	contaminants of concern
CHP	Catalyzed Hydrogen Peroxide
Cr	Chromium
CT	carbon tetrachloride
Cu	copper
DOC	dissolved organic carbon
DoD	Department of Defense
EDTA	ethylenediaminetetraacetic acid
E _H	activity of electrons
EPA	United States Environmental Protection Agency
EPCRA	Emergency Planning and Community Right to Know Act
Fe	iron
g	gram
g/Kg	grams per kilogram
g/L	grams per liter
Hg	mercury
ISCO	In Situ Chemical Oxidation
ITTs	innovative treatment technologies
kg	kilogram
L	liter
lbs	pounds
MCL	maximum contaminant level
Mg	magnesium
mg/L	milligrams per liter
mL	milliliter
mM	milliMolar
Mn	Manganese
MSDS	Material Safety Data Sheet
MTBE	methyl tert-butyl ether
mV	millivolt
Ni	nickel
NOM	natural organic matter
ORP	oxidation reduction potential

PAHs.....	polyaromatic hydrocarbons
Pb.....	lead
PCE.....	tetrachloroethene
PFOA.....	perfluorooctanoic acid
pH.....	activity of hydrogen
PRB.....	Permeable Reactive Barrier
RCRA.....	Resource Conservation and Recovery Act
RDX.....	hexahydro-1,3,5-trinitro-1,3,5-triazine
RPM.....	Remedial Project Manager
Se.....	selenium
SDWA.....	Safe Drinking Water Act
SOP.....	standard operating procedure
SPLP.....	Synthetic Precipitation Leaching Procedure
TCA.....	1,1,1-trichloroethane
TCE.....	trichloroethene
TCLP.....	Toxicity Characteristic Leaching Procedure
TNT.....	trinitrotoluene
TOC.....	total organic carbon
UIC.....	Underground Injection Control
µg/L.....	micrograms per liter
V.....	volts
Zn.....	Zinc

2.0 INTRODUCTION

In situ chemical oxidation (ISCO) has been applied at numerous sites, including Department of Defense (DoD) facilities, to treat organic contaminants in the subsurface, and has evolved into a standard approach for cost-effective remediation of contaminated soil and groundwater (Siegrist et al., 2011). While considered a relatively mature technology, ISCO has benefited greatly from research and development efforts that have been conducted since its first application. Similarly, ongoing research efforts continue to refine, develop and pave the way for future applications of this technology.

While ISCO is proven effective for treating organic contaminants, similar to other in-situ remedial approaches, the technology application can alter the subsurface geochemistry. These altered subsurface conditions can result in a change of state of metals and metalloids naturally found in site soils. The addition of oxidants can cause changes in subsurface pH (activity of hydrogen), Eh (activity of electrons), ionic strength and composition which can all affect metal speciation and mobility (Bennedsen, L.R., Kruschker, A. et al., 2012). Knowledge and understanding of how the geochemical properties of the subsurface are impacted by the addition of oxidants is imperative for designing ISCO applications to minimize metal mobilization.

The research funded by SERDP grant ER-2132 (ER2132), evaluates the long term effect of ISCO on the mobilization of subsurface metals. The research found that changes in the geochemical conditions (in particular pH, and Eh), changes to organic material and anions into the subsurface during the application of ISCO could result in a *generally transient* mobilization of metals and metalloids at some sites. This Guidance Document has been generated as part of ER2132.

2.1 BACKGROUND

ISCO involves the addition of reagents into the subsurface that chemically react with, and transform, the site contaminants of concern (COCs) into acceptable compounds such as carbon dioxide and chloride. ISCO has many forms and has gained widespread acceptance as a remediation technology due to its ability to successfully treat most common COCs at various concentrations in a relatively short period of time.

Compounds that ISCO technologies are known to treat include:

- Chlorinated solvents (e.g. tetrachloroethene [PCE], trichloroethene [TCE], carbon tetrachloride [CT], 1,1,1-trichloroethane [TCA], etc.).

- Petroleum hydrocarbons (e.g. polyaromatic hydrocarbons [PAHs], benzene, toluene, ethylbenzene, and xylenes, [BTEX], etc.).
- Energetics (e.g. trinitrotoluene [TNT], hexahydro-1,3,5-trinitro-1,3,5-triazine [RDX], etc.).
- Additives (e.g. 1,4-dioxane, methyl tert-butyl ether [MTBE], etc.).
- Pesticides.
- Perfluorinated compounds (e.g. Freon, perfluorooctanoic acid [PFOA], etc.).

The most common ISCO technologies are based upon the permanganate anion, hydrogen peroxide, the persulfate anion, and ozone. Oxidant solutions are typically injected through a network of injection and/or recirculation wells designed to disperse the solution across the target treatment area through natural or induced advective gradients. While simple in concept, ISCO relies on a complex myriad of geochemical interactions and transport mechanisms that need to be well understood to ensure a high certainty of meeting treatment objectives. Scientists, engineers and practitioners have introduced several modifications or enhancements to each ISCO technology to meet site-specific requirements, which has created unique chemistries for each ISCO technology (Section 3).

There are still aspects of ISCO which require further understanding to fully characterize the impacts of these treatments. The primary focus of this guidance document, is the potential for mobilization of metals naturally present in the subsurface due to the application of oxidants. ISCO alters the geochemical conditions (e.g., pH, Eh) of the treatment area in the subsurface and creates a variety of oxidation products that have the potential to interact with naturally occurring metals in both soils and groundwater. The rate and extent of geochemical changes is dependent upon a number of factors including the lifetime of the oxidant, total quantity and concentration of oxidant and other reagents delivered, the buffering capacity of the subsurface, and local hydrodynamics. Primary goals of ER2132 included identifying and addressing the major factors contributing to metals mobilization and design of a modified ISCO approach to mitigate the potential for mobilization of the metals.

2.2 HISTORY / EVIDENCE OF METALS MOBILIZATION

As stated above, the application of ISCO can alter metals mobility through several processes; these processes have undergone numerous evaluations in both the laboratory and for a limited number of field studies (Siegrist et al., 2011). The specific interactions depend on a wide range of variables including the oxidant and activation aids used to deliver the oxidant, natural geochemical conditions within the aquifer and the different geochemical speciation behavior of various metals.

2.2.1 EMPIRICAL FIELD EVIDENCE

Field studies that have monitored dissolved metals concentration fluctuations are limited, both in scope and in quantity. The majority of studies were conducted on permanganate and peroxide ISCO sites. Researchers typically found a temporary increase in select metals mobility; however, in these studies, generally all dissolved metals concentrations returned to background levels over time and space after the injection of oxidant was terminated.

Krembs (2008) evaluated 242 sites where ISCO had been applied and found that metals were monitored in 23 of the sites. Of these 23 sites, 57 percent indicated an increase in dissolved metals concentrations. Krembs noted that the duration and severity of the increases was highly site-specific, and was generally limited to the area where ISCO was directly applied (treatment area). Krembs noted that in only 2 of the 23 sites increased concentrations of chromium were measured down gradient of the ISCO treatment area. Both of the sites where applications of ozone/peroxone and chromium concentrations abated within 1 month of system shutdown.

As part of ER2132, a survey was performed to collect data on additional ISCO sites. A total of 89 case studies were identified and were used to populate a database. Case studies that were bench-scale studies were not included in the database as ER2132 was focused on field implementation. In addition, case studies with inadequate site or performance data were also excluded from the database. The most commonly applied oxidant from the database was permanganate (56 sites) followed by hydrogen peroxide (55 sites), sodium persulfate (19 sites), and ozone (15 sites). In some of the sites, treatment involved the use of multiple oxidant types. Among the sites, only one site used calcium peroxide.

From the database, the most common oxidant delivery method was through direct injection using temporary or permanent wells (85 sites). Direct push (12 sites) and recirculation (11 sites) were methods employed less frequently. Several sites used multiple injection strategies to maximize the subsurface distribution of the oxidant (e.g., a combination of recirculation and permanent wells or a combination of direct push technology and direct injection using temporary wells).

Metals were monitored at a total of 19 sites (21%) within the database. An increase in metals concentration was measured in 12 out of these 19 sites (63%). There was not enough data at the 12 sites to determine whether the mobilized metals concentrations eventually abated. Chromium (Cr [total and hexavalent]), iron (Fe), manganese (Mn) and arsenic (As) were the four most frequently measured mobilized metals in these 12 sites. Amongst the Resource Conservation and Recovery Act (RCRA) and Priority Pollutant Metals, chromium (maximum contaminant level [MCL] = 0.1 mg/L) and arsenic (MCL = 0.01 mg/L) were measured most frequently. A total of 10 out of the 12 sites had metals that exceeded their MCLs. Overall, based on sites with sufficient data (i.e. sites with more than three monitoring events), mobilized metals concentrations indicate a decreasing trend post-ISCO injection. The duration and degree of the dissolved metals concentrations increases were highly site-specific.

2.2.2 LABORATORY SCALE

In general, laboratory studies have demonstrated that the use of oxidants can, at least temporarily, promote the release of various metal ions. The degree of release, as well as the mechanism, depends greatly on situational factors as listed in Table 2.1.

TABLE 2.1 – Factors Affecting Metals Release Mechanisms

ISCO Factor	Relevant Oxidants	Impact on Metals Release	Relevant Literature
Destruction of natural organic matter (NOM)	CHP Permanganate Persulfate	Release of NOM associated metals	Brennan, 1991
Oxidation of mineral substrate	CHP Permanganate Persulfate	Changes in mobility and toxicity	Siegrist et al., 2001 Rock et al, 2001
Decrease in pH (associated with oxidant or due to activation aids)	CHP Permanganate Persulfate	Increased mineral solubility	Chaun et al., 1996 Huling and Pivetz, 2006
		Sorption capacity of substrate reduced	Seigrist et al., 2001
Addition of chelates	CHP Permanganate Persulfate	Increased mobility	Monahan et al., 2005
Generation of precipitates from oxidation reactions	Permanganate	Absorption of mobile metals	Siegrist et al., 2001 Al et al., 2006
Introduction of metal impurities associated with oxidant	Permanganate	Introduction of metals into the groundwater system	Siegrist et al., 2001

(CHP = Catalyzed hydrogen peroxide)

Rock et al. (2001) assessed chromium mobilization during hydrogen peroxide oxidation in four diverse soils. Monahan et al. (2005) found that zinc (Zn), cadmium (Cd), copper (Cu) and lead (Pb) were desorbed from soils with the addition of hydrogen peroxide in laboratory studies. ISCO using permanganate has shown elevated levels of nickel (Ni), Mn, and Cr (Seigrist et al., 2011). Other authors have noted changes in metals speciation and mobility during oxidation with ozone (Kim and Nriagu 2000, Lestan et al. 2005).

Another concern with regard to increasing concentrations of metals during injection of oxidants is the presence of elevated levels of heavy metals in the oxidant provided by the manufacturer.

Permanganate has been known to contain metal impurities such as chromium and arsenic. As a result, some of the early applications using technical grades of permanganate exceeded the MCLs for these metals. Another study found elevated levels of chromium in groundwater at a site treated with permanganate and attributed this with to the combination of traces of chromium in the permanganate, as well as oxidation of chromium in the subsurface (Seigrist et al, 2011). Manufacturers have more recently developed special grades of permanganate specifically for ISCO that have lower concentrations of these metals.

2.3 ENVIRONMENTAL ISSUES ASSOCIATED WITH METALS

The most common regulated metals at Superfund sites, and primary metals addressed in this guidance manual, include arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium (Se), silver (Ag) and zinc. Various environmental institutions and regulatory agencies may include other naturally occurring electropositive elements as metals including aluminum (Al), iron, magnesium (Mg) etc. Similarly, in pure chemical terminology, arsenic and selenium are metalloids, not metals. Because of these categorical inconsistencies, the term “metals” include all elements under discussion within this guidance document. ISCO treatments are not generally applicable to remediate metals (inorganic) contaminated sites; however, the reagents used in ISCO applications can have wide ranging effects on the metals naturally occurring in the environment. Therefore, a comprehensive understanding of metals and their geochemistry is important in evaluating overall potential impacts of remediation at a site using ISCO technologies. This section provides a brief overview of the chemistry that can control these processes. In addition, Sections 3.1 and 3.2 provide a summary of the fundamental science associated with the fate and transport of metals. A more detailed account of the science of metals is discussed in the publications provided in Table 2.2.

TABLE 2.2 – Selected Publications on Metals Behavior

Agency	Manual Title	Citation
United States Environment Protection Agency (EPA)	Behavior of Metals in Soils	McLean and Bledsoe, 1992
EPA	Framework for Metals Risk Assessment	EPA, 2007

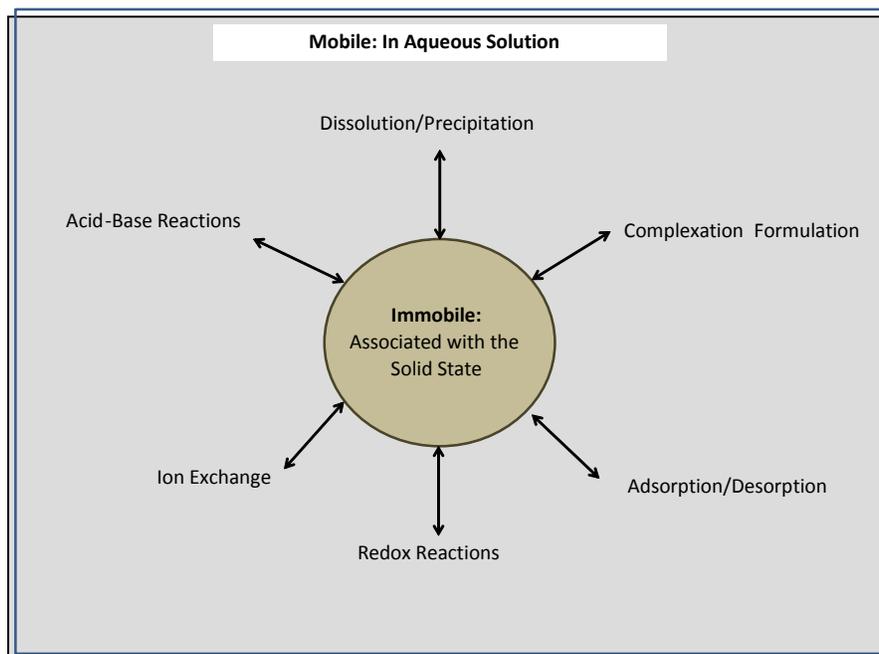
Metals are ubiquitous in the natural environment and can range widely in concentrations depending upon the local geology of a specific area. Metals exist in several locations within the soil and/or groundwater, collectively referred to as the soil solution. These locations include within primary or secondary mineral structures, as precipitates, occupying an exchange site on a soil constituent, adsorbed to a soil constituent or in aqueous solution. Additionally, these metals may exist in several free or complexed species (chemical forms). Complexed species are molecular units in

which a central metal ion is bonded with a secondary or multiple additional atoms called ligands (Table 2.3). Ligands can be organic or inorganic with various bond strengths and formations that form positive, negative or balanced charged species. Alternatively, free species are uncomplexed metal ions which are not associated with a ligand (Cd^{+2} , Pb^{+2} , Zn^{+2}). The speciation of a metal affects not only its toxicity but also other important physical properties such as volatilization characteristics, photolysis, sorption, atmospheric deposition, acid/base equilibria, polymerization, complexation, electron-transfer reactions, solubility and precipitation equilibria, microbial transformations and diffusivity (Bodek et. al., 1988).

TABLE 2.3 – Common Metal Ions and Ligands

Metal Ions		Common Ligands
Ag^{+1} , Al^{+3} , Ba^{+2} , Be^{+2} , Cd^{+2} , Cr^{+1} , Cu^{+2} , Fe^{+3} , Hg^{+2} , Mn^{+2} , Ni^{+2} , Pb^{+2} , Zn^{+2}	Inorganic	Cl^{-1} , OH^{-1} , HS^{-1} , CO_3^{-2} , PO_4^{-3} , SO_4^{-2} , NO_3^{-1} , NH_3 , $\text{H}_n\text{AsO}_4^{n-3}$
	Organic	$\text{CH}_3\text{COO}^{-1}$, ROH^{-1} , RNH_2 , Amino Acids, Fulvic Acids

Mobilization occurs when metals associated with the solid phase (in the mineral phase, adsorbed, precipitated or occupying an ion exchange site) are released into aqueous solution. Chemically, this transfer can be induced for several natural or anthropogenic reasons including changes in acid-base equilibria, complex formation, redox reactions, ion-exchange, adsorption and the precipitation/dissolution of solids (Figure 2.1). Once in aqueous solution, metal species are subject to the movement of groundwater and/or rainwater infiltration traveling through the vadose zone. A large shift in the equilibrium of any of these processes can result in the mobilization of metals, and if not mitigated naturally or by design, can have significant environmental impacts on receiving surface water bodies and other more ecologically active areas.

FIGURE 2.1 – Chemical Reactions Affecting the Mobilization of Metals

2.4 REGULATORY FRAMEWORK

EPA has been providing several initiatives to help develop the regulatory framework for the use of ISCO technology by granting states the authority to implement the Treatability Exclusion Rule; the Research, Development, and Demonstration Permit Program; and the Subpart X Permit Program. This simplifies the approval process for technologies and allows flexibility in testing and demonstrating innovative treatment technologies (ITTs) (EPA Clu-in website). States have also modified permitting and variance requirements to become more supportive of the use of technologies like ISCO (ITRC, 2005).

The injection of oxidant and reagents is regulated primarily through the Underground Injection Control (UIC) program of the Safe Drinking Water Act (SDWA). Other regulations are 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 these, an injection permit may be required from local and state environmental agencies.

2.4.1 SAFE DRINKING WATER ACT/UNDERGROUND INJECTION CONTROL

Injection of oxidants and reagents are regulated by the UIC program under the SDWA. EPA's UIC Program is responsible for regulating the construction, operation, permitting, and closure of injection wells that place fluids underground for storage or disposal. Injection of any fluid into a well is prohibited except as authorized by permit or rule under the UIC program. The purpose of the UIC program is to protect underground sources of drinking water (USDW) by prohibiting injections that may affect water quality. The UIC website offers guidance to inform state regulators

and owners and operators of injection wells on how to operate injection wells safely to prevent contamination of underground drinking water resources.

State UIC programs may be delegated complete or partial enforcement responsibility (or primacy) by EPA. Table 2.4 illustrates the specific state requirements. Injection wells incidental to aquifer remediation and experimental technologies are designated as Class V under the UIC program. They are distinguished from hazardous waste injection wells. Class V wells covered by the federal UIC program are authorized by rule and do not require a separate UIC permit. However, a Class V well regulated by a state UIC program may require a permit.

TABLE 2.4 - Regulatory Permitting Requirements by State

State	ISCO	Agency
Alabama	UIC permit	ADEM Water and Land Division
Alaska	No permit required, must inventory	EPA Region 10
Arizona	No permit required, must inventory	EPA Region 9
Arkansas	No permit required, must inventory	Dept. of Environmental Quality
California	No permit required, must inventory	EPA Region 9
Colorado	No permit required, must inventory	EPA Region 8
Connecticut	UIC permit	Dept. of Environmental Protection
Delaware	UIC Authorization	Dept. of Natural Resources and Env Control
District of Columbia	No permit required, must inventory	EPA Region 3
Florida	UIC permit	FLDEP Division of water resource management
Georgia	UIC permit	GEPD Geologic Survey
Hawaii	No permit required, must inventory	EPA Region 9
Idaho	No permit required, need approval	Dept. of Water resources
Illinois	No permit required, must inventory	Env Protection Agency Bureau of Land
Indiana	No permit required, must inventory	EPA Region 5
Iowa	No permit required, must inventory	EPA Region 7
Kansas	UIC permit	KDHE Bureau of Water Env Geology Unit
Kentucky	No permit required, must inventory	EPA Region 4

State	ISCO	Agency
Louisiana	UIC permit	LDNR Office of Conservation
Maine	License by rule, must inventory	Dept. of Env protection
Maryland	UIC permit	Dept. of environment
Massachusetts	No permit required, need approval	MADEP regional offices
Michigan	No permit required, must inventory	EPA Region 5
Minnesota	No permit required, must inventory	EPA region 5
Mississippi	No permit required, must inventory	Dept. of Environmental quality
Missouri	UIC permit	MDNR Water pollution control program
Montana	No permit required, must inventory	EPA Region 8
Nebraska	UIC permit	Dept. of Environmental Quality
Nevada	UIC permit	Dept. of Environmental Protection
New Hampshire	UIC registration	Dept. of Environmental Services
New Jersey	UIC permit	NJDEP Site Remediation Program
New Mexico	UIC permit	Environment Dept.
New York	No permit required, must inventory	EPA Region 2
North Carolina	UIC permit	Dept. of Env and Nat. resources
North Dakota	No permit required, must inventory	Dept. of Health
Ohio	No permit required, need exemption	Ohio EPA
Oklahoma	UIC approval	Dept. of Env Quality
Oregon	UIC permit	Dept. of Env Quality
Pennsylvania	No permit required, must inventory	EPA Region 3
Rhode Island	UIC permit	Dept. of Env Management
South Carolina	UIC permit	Dept. of Health and Env Control
Tennessee	No permit required, must inventory	EPA Region 4
Texas	No permit required, need approval	TCEQ groundwater protection division
Utah	No permit required, must inventory	Dept. of Env Quality
Vermont	No permit required, need approval	Dept. of Env Conservation
Virginia	No permit required, must inventory	EPA Region 3

State	ISCO	Agency
Washington	No permit required, need approval	Dept. of Ecology
West Virginia	UIC permit	Division of Environmental Protection
Wisconsin	No permit required, need approval	Dept. of Natural Resources
Wyoming	UIC permit	Dept. of Environmental Quality

(Adapted from ITRC, 2005)

2.4.2 RESOURCE CONSERVATION AND RECOVERY ACT

A typical ISCO application takes place using injection wells. In some case, it may be implemented using soil mixing. In cases of ex-situ soil mixing, there is a need for a permit for treatment, storage, and disposal due to the potential hazardous waste generated. The permit requirements for these remediation practices can be time-consuming and expensive. EPA has encouraged streamlining RCRA permits to help expedite the process. They have also encouraged the state adoption of streamlined EPA authorization.

2.4.3 COMPREHENSIVE ENVIRONMENTAL RESPONSE, COMPENSATION AND LIABILITY ACT

Releases of certain quantities of hazardous chemicals are required to be reported to the National Response Center under CERCLA. ISCO treatment would be considered a “process” rather than a “release” and therefore exempt from CERCLA reporting.

2.4.4 EMERGENCY PLANNING AND COMMUNITY RIGHT-TO-KNOW ACT

EPCRA created a national program for emergency planning, notification, and reporting for releases of extremely hazardous or toxic chemicals. The three sections (302, 311 and 312) that apply to ISCO treatment are listed in Table 2.5 below.

TABLE 2.5 - EPCRA Section 302, 311 and 312

Section	Description
Section 302	This requires facilities to prepare a comprehensive emergency response plan if an extremely hazardous substance will be stored or handled in quantities greater than established limits. For example, if 1,000 pounds (lbs.) or greater of H ₂ SO ₄ is stored at a facility for a CHP ISCO project, a comprehensive emergency response plan must be prepared.
Section 311	This requires the submission of Materials Safety Data Sheets (MSDS) to state and local planning commissions and to fire departments if extremely hazardous substances and/or CERCLA hazardous substances are stored in quantities greater than the established limits.
Section 312	This requires an emergency and hazardous chemical inventory form to be submitted to state and local planning commissions and to the local fire department for hazardous substances and/or CERCLA hazardous substances stored in quantities greater than the established limits. It may not be applicable for most ISCO projects if chemical storage no longer occurs once chemical injection into the subsurface takes place.

It is usually strongly recommended that the appropriate regulatory agency be contacted prior to the commencement of an ISCO project to make certain that all reporting requirements are satisfied.

2.5 OBJECTIVES OF GUIDANCE DOCUMENT

The objectives of this guidance document are to provide site owners, engineers, scientists and practitioners with the following:

1. Fundamental background of the chemistry behind the ISCO technologies and factors affecting metals mobilization.
2. Methods for identifying if metals mobilization may be a concern at a specific site.
3. Guidance in determining bench-scale testing that may benefit site evaluation for metals mobilization.
4. Approach for monitoring for the potential of metals mobilization during a field event.
5. Methods for mitigating metals mobilization.
6. Methods to address metals if they are mobilized.

2.6 DOCUMENT ORGANIZATION

This guidance document is organized into three basic sections to aid the user. These sections include:

- Fundamental Science of Metals Mobilization.
- Evaluating Site-Specific Metals Mobilization Potential.
- Design, Monitoring and Actions for Metals Mobilization in an ISCO Field Event.

3.0 FUNDAMENTAL SCIENCE OF METALS MOBILIZATION

In general, subsurface contamination at most sites has been present for a sufficient period of time that the localized metals concentrations in site groundwater are in equilibrium with various minerals associated with the soils. Often the metals equilibrium concentrations in groundwater in the area affected by the contamination is different from unaffected areas. For example, in an oxidative or mildly reducing aquifer, the area impacted with petroleum hydrocarbons will typically have more reducing conditions than the overall aquifer. This could result in different concentrations of dissolved metals within the contaminated areas, compared to the portions of the aquifer outside the area of contamination. The implementation of ISCO and several other common in situ remedial technologies have the potential to disrupt the metals equilibrium between soils and groundwater by affecting the groundwater geochemistry, causing changes to the concentrations of dissolved metals.

This section will outline the fundamental science behind the potential for metals mobilization and the fundamental chemistries associated with the primary ISCO technologies.

3.1 METALS EQUILIBRIUM

All soils contain trace levels of naturally occurring metals that primarily originate from the geologic formation that is the source of the soil material (McLean and Bledsoe, 1992). These metals are either present in the aqueous or the solid phase. Metals are present in the soil solution either as free ions, as soluble complexes that form with organic and inorganic ligands, or they are associated with colloidal material (i.e., iron and manganese oxides, organic matter, and clay minerals). Metals in the solid phase are either attached to the inorganic surface of soil particles through adsorption or precipitation reactions (e.g., adsorbed on iron and manganese oxides and clay minerals, which have high surface areas for absorption), are associated with the soil organic matter, or they are part of the mineral structure.

The behavior of metals in soils has typically been examined under equilibrium conditions (McLean and Bledsoe, 1992). A particular equilibrium state is associated with reactions that are more likely to occur under the specified conditions, but information on the kinetics involved is not provided. There are several interrelated processes that determine the concentration of metals in the soil solution at equilibrium, the most important of which are adsorption/desorption, precipitation/dissolution, oxidation-reduction, and inorganic and organic complex formation. The metal of concern, the presence and concentration of inorganic and organic ligands, the pH, and the oxidation-reduction potential (ORP) define a specific thermodynamic equilibrium condition that in turn determines the solution composition under those circumstances. Thermodynamic equilibrium models constructed from the data that define this equilibrium state provide the opportunity to test the way changes in soil solution properties will affect dissolved metal concentrations and speciation, and ultimately influence the fate and transport of these elements.

3.2 METALS FATE AND TRANSPORT / MOBILIZATION

Metals that are dissolved or otherwise associated with the aqueous phase of soils have the potential to be transported with groundwater. The dissolved metals are also in the most bioavailable form and can be taken up by plants and other ecological and human receptors. Therefore, understanding the solid-solution partitioning of metals in a given system is critical in terms of risk avoidance and

management. The same chemical processes that determine the equilibrium of metals also regulate their fate. Processes that might govern the fate of metals in soils include adsorption/desorption, precipitation/dissolution, complexation, oxidation-reduction, and acid-base reactions. These processes are interrelated and together they characterize subsurface systems that tend to be complex in nature.

In depth knowledge of the above chemical processes can reveal important information regarding the potential of metals mobilization. For example, at low concentrations, metals tend to form inner-sphere complexes via specific adsorption, forming strong connections with the soil surface (McLean and Bledsoe, 1992). This process will typically prevent metals from entering groundwater and therefore being transported. However, when sites available for specific adsorption are filled, outer-sphere complexes are formed on so called exchange sites. Connections formed on exchange sites are typically weaker and metals can potentially become more mobile. Competition with major ions also becomes important at exchange sites. Factors affecting adsorption and precipitation reactions include cation competition, complexation, pH, and oxidation-reduction conditions.

In the following subsections, the role of pH, ORP, and ion competition are the focus, as these factors typically regulate the fate of metals in most soil environments and they are also important determinants of ISCO systems.

3.2.1 pH

pH is a measure of the hydrogen ion concentration in an aqueous solution, which is generally reported on a scale between 1 and 14 representing the inverse log of hydrogen concentration. Solutions with low pH values, representing high H^+ concentrations, are referred to as acidic while high pH values are referred to as basic. It is also worthwhile to note that due to the log scale pH is reported in, a change of 1 pH unit represents an order of magnitude change in H^+ concentration. In water chemistry, pH is considered a master variable due to the large impact it has on the solubility and chemical speciation of inorganic compounds.

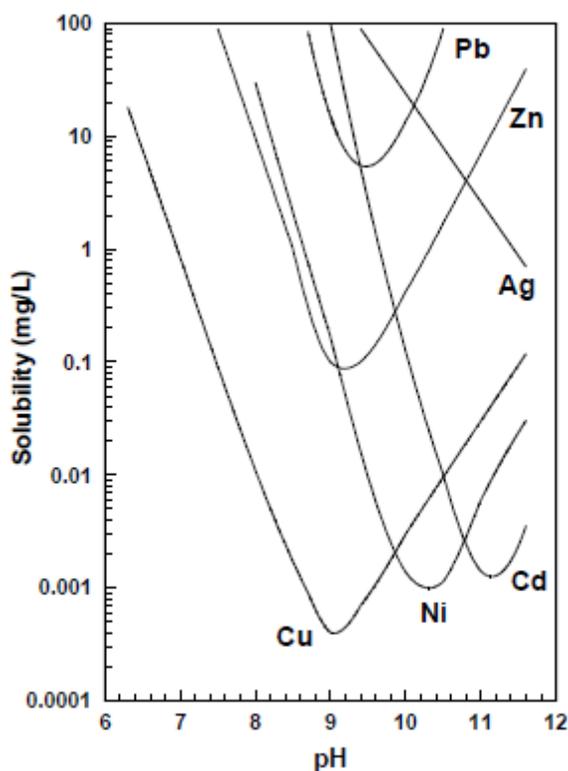
The pH of the subsurface is an important factor that controls metals release as it directly or indirectly affects several metal retention mechanisms (McLean and Bledsoe, 1992). In addition, the solubility of metals is also pH-dependent (Langmuir et al., 2004); the greatest metal solubility is usually measured at acidic pH values. Chemical processes that are directly impacted by pH include sorption/desorption, precipitation/dissolution, complex formation, and oxidation-reduction reactions (McLean and Bledsoe, 1992). For example, pH-dependent adsorption sites are common on iron and manganese oxides, organic matter, carbonates, and edges of clay minerals. As the pH decreases, the number of negative sites for cation adsorption also decreases, therefore the adsorption of cations typically increases with rising pH. The opposite is true for anionic metals (i.e. oxyanions) that tend to be adsorbed more favorably as the pH decreases.

Precipitation/dissolution reactions are also impacted by pH. Metal precipitates tend to form under alkaline conditions and dissolution is also strongly pH-dependent (McLean and Bledsoe, 1992). For example, hydrous ferric oxides that have a high affinity for metal adsorption dissolve below pH 6 resulting in the release of previously adsorbed metals. Similarly, reduced adsorption and

therefore increased mobility of metals complexed with dissolved organic carbon (DOC), an organic ligand, is especially prominent at higher pH values.

Figure 3.1 provides a solubility diagram for several metal hydroxides which are exemplary of other common metal ligands found in groundwater systems. The solubility for most metals decreases as pH increases from acidic to neutral conditions. As pH continues to increase from neutral to basic conditions the solubility increases again for metal hydroxides as with several other, but not all, metal ligands.

FIGURE 3.1 - Solubility of Metal Hydroxides as a function of pH



(EPA, 1983)

In natural groundwater systems, pH is controlled by the dissolution of impurities as it travels through the hydrological cycle. Notable impurities impacting the pH include carbon dioxide, sulfur and nitrous oxides in the atmosphere which acidify the water as it precipitates through the atmosphere; in addition, acid neutralizing components dissolve as the natural waters travel along the earth's surface and infiltrate into the ground. The dissolution of these gasses and minerals leads to an equilibrium which has a large effect on the fate and transport of metals within the subsurface. Although factors such as acid rain and global warming continue to slowly erode the current equilibrium, the introduction or formation of acid or base solutions associated with ISCO treatments can have a large localized impact on pH equilibrium in the treatment area.

In the groundwater systems, changes in pH affect the mobility of metals through two primary mechanisms: the dissolution/precipitation of metal complexes and the desorption/sorption of metals from pH dependent charged surfaces. Through either mechanism, reduced pH conditions

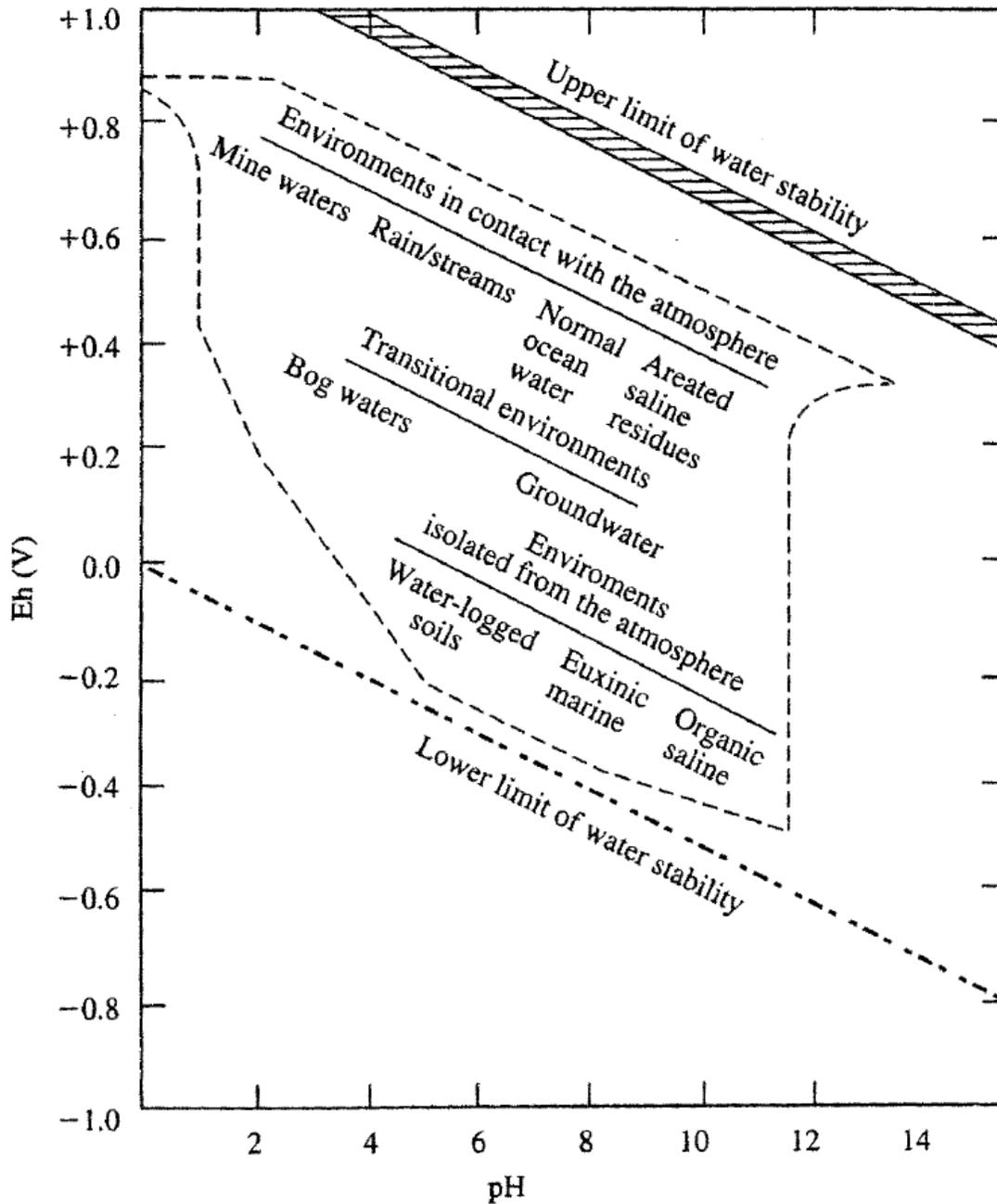
result in increased mobilization of cationic metals (e.g., Cd, Pb and Zn). Dissolution of solid phase complexes may directly or indirectly mobilize metals. Direct mobilization occurs when a metal ligand dissolves from a precipitate (solid state) to the aqueous phase as demonstrated for various metal hydroxides in Figure 3.1. Indirect mobilization is due to the dissolution of more common metal hydroxides, such as $\text{Fe}(\text{OH})_2$ and $\text{Mn}(\text{OH})_2$, that have trace metals adsorbed onto them. As these compounds become soluble, any adsorbed ions will also mobilize into the aqueous phase. Due to the higher prevalence of certain metals, such as iron and manganese, in groundwater systems, the indirect release of adsorbed metals may be a more dominant mechanism for metal mobility in groundwater (Lindsay, 1979).

pH can also affect the surface charge of oxides, hydroxides, carbonates precipitated on clay minerals, as well as the surface charge of some types of organic matter. As pH increases, the dissociation of H^+ ions on the surface of the functional group results in a net negative charge. This net charge attracts and can form a number of adsorptive bonds with positively charged cations in solution. Conversely, as pH decreases, the association of H^+ ions along the surface of the functional group increases, creating a net positive charge, which will attract and adsorb oxyanions. Because of this sorptive capacity, Jenne (1968) concluded that iron and manganese oxides are the principle soil surface that controls the mobility of metals in natural waters and soils.

3.2.2 ORP

ORP, or redox potential, is a measurement of the amount of electrons available within in an aqueous system. In natural water systems, ORP is typically measured in volts (V) as E_H or described as the unitless value pe ; which is the inverse log of the electron activity (as pH is the inverse log of H^+ activity). Both units are acceptable and easily converted between one another, this section will use the E_H convention moving forward. As the E_H increases within a free ion or complex due to the acceptance of an electron, the ion or complex is described as being oxidized; conversely, as the voltage is lowered by the loss of an electron, the ion or complex is reduced. In closed systems, the transfer on an election will lead to the simultaneous oxidation of one compound while the second is reduced, resulting in an electrochemically balanced reaction. However, in larger systems the availability, or activity, of elections maybe stratified due to physical, biological or chemical factors resulting in various ORP conditions. In groundwater systems, ORP is generally controlled by the presence of oxygen, in which there are four general conditions at neutral pH described by Patrick and Mahapatra (1968) as oxidized ($> +400$ millivolt [mV]), moderately reduced (+400 to +100 mV), reduced (100 to -100 mV) and highly reduced (-100 to -300 mV). Figure 3.2 shows the electrochemical potential limits for natural water systems.

FIGURE 3.2 – E_H vs. pH Conditions for Natural Water Systems.



(EPA, 1983)

The ORP of a soil system determines if the environment is oxidizing (aerobic) or reducing (anaerobic), and has a major influence on the fate and transport of metals (McLean and Bledsoe, 1992). Many metals that are typically of concern in the environment can be present in more than one oxidation state depending on the oxidation-reduction conditions in the soil systems. Contrary to organic compounds, metals cannot be degraded, but they can be transformed from one oxidation state to another to form compounds that might be less mobile or toxic. For example, hexavalent chromium, i.e. Cr(VI), is very toxic and relatively mobile, while trivalent Cr(III) is less toxic and

tends to sorb strongly to soil surfaces. Similarly, arsenite, i.e. As(III), is more soluble and toxic than arsenate, i.e. As(V).

As another example, Fe(III) will readily precipitate at a neutral pH, where Fe(II) will dissolve into the aqueous phase. As discussed previously, the dissolution of abundant elements, such as iron and manganese, have a large impact on the mobility of other trace cationic elements which are adsorbed to them. Therefore, a shift in ORP, leading to this dissolution or precipitation will have a large effect on metals mobility. In general, oxidized conditions within groundwater systems will limit the mobility of metals while reduced conditions will contribute to accelerated migration (McLean and Bledsoe, 1992).

3.2.3 CONDUCTIVITY OR ION COMPETITION

The number of free ions in solution, commonly measured as conductivity, can affect the mobility of trace metals in groundwater. Metals can adsorb onto the soil surface in a number of different formations. These different formations have various bond strengths associated with them which can be described through surface complexation models (Sposito, 1989). Site-specific adsorption (inner sphere complexation) forms ionic or covalent type bonds with the soil surface. Adsorbed metals are relatively immobile due to this strong bonding and will not generally be released due to the exposure of a higher concentration of major cations. Conversely, hydrated metals in solution can form diffuse ion or outer sphere complexes, where the metal ion does not directly bond to the soil surface but is held due to weaker electrostatic forces. These bonds still form a significant adsorptive force but are classified as exchange reactions because the exposure of elevated concentrations of major cations can replace and mobilize the trace metals originally adsorbed to the soil surface. Latterell et. al. (1978) proposes that exchange sites may represent the most significant reserve of potentially mobile metals in soil, and therefore maybe a critical mechanism in the mobilization of metals that may occur with ISCO treatments.

3.3 IN SITU CHEMICAL OXIDATION

The chemistry and destruction of organic compounds by the addition of chemical oxidants has been investigated for over a century (Fenton, H.J.H., 1894). ISCO is a descendant of technology first utilized in 1930, where strong oxidants were introduced for drinking water and waste water treatment. This technology was used as a disinfectant and for removal of organic contaminants from municipal and industrial waters (Bjerg, P.L. 2008). The same treatments were later adopted for remediation of groundwater in “pump and treat” (ex-situ) applications. In 1984, chemical oxidation processes were first applied in-situ to remediate groundwater contaminated with formaldehyde (Brown et al., 1986). Since that time, research has continued to further the scientific understanding and application of the technology. Numerous studies have been conducted to identify and evaluate new and more effective oxidant solutions, understand oxidant interactions with the natural soils, advance oxidant transport and delivery mechanisms, and evaluate DNAPL interactions as well as the combination of ISCO with other remediation processes (treatment trains). The accumulation of this prior work and the state of current ISCO practice is discussed at length in several publications including those provided in Table 3.1.

TABLE 3.1 – Select ISCO Guidance Publications That Include Metals Mobilization

Agency	Manual Title	Citation
SERDP-ESTCP	In Situ Chemical Oxidation for Groundwater Remediation	Siegrist et.al., 2011
ITRC	Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater	ITRC, 2005
EPA	In-Situ Chemical Oxidation	Huling and Pivetz, 2006

The most common ISCO technologies in use today are based upon the following oxidants:

- Persulfate anion.
- Permanganate anion.
- Hydrogen peroxide.
- Ozone.

Each of the oxidant technologies has their own unique chemistry, and in some instances, several unique variations of the chemistry. The following subsections will highlight several of the more common variations of each chemistry.

3.3.1 PERSULFATE ANION

3.3.1.1 *Background*

The persulfate anion is a powerful oxidant, with a standard reduction potential to sulfate of 2.01 V. The anion has a molecular formula of $S_2O_8^{2-}$. The compound is often referred to in literature as peroxydisulfate, which describes its chemical structure, as persulfate appears as two sulfate molecules joined by an oxygen-oxygen, or peroxygen, bond. Persulfate is thought to react directly with several compounds or it can be “activated” to form a variety of radicals. Depending upon the activation method, the persulfate anion can result in the formation of different radicals including oxidants such as the sulfate radical (2.4 V) and hydroxyl radical (2.6 V) and a reductant such as superoxide radical (-0.33 V). Common methods of persulfate activation include:

- **Electron Transfer Activation Methods:** If the persulfate anion reacts with a single electron it destabilizes and forms a sulfate and sulfate radical. As the sulfate radical is the species formed, the following activation methods are oxidative:
 - *Iron activation.* The electron is donated by Iron (II) going to Iron (III).
 - *Iron chelate activation.* The same as iron activation with the presence of a chelate to help keep the iron in solution, as Iron (III) has a low solubility at neutral pH.
 - *Hydrogen peroxide activation.* The electron is donated by hydrogen peroxide as it is oxidized to oxygen.

- *Activation with Organic Material.* A direct reaction with organic material can result in the organic material donating an electron to persulfate resulting in the formation of the sulfate radical and additional reactions.
- *Natural Activation.* Reduced metals and organic material present in the subsurface can also donate an electron to the persulfate molecule resulting in the formation of the sulfate radical. In this instance, the persulfate may be injected into the subsurface without any additional activator. However, not all aquifers will have sufficient natural activators.
- **Alkaline Activation.** Alkaline activation is achieved at $\text{pH} > 10.5$. Under alkaline activation the persulfate anion disassociates to form the sulfate radical and reacts with water to form hydroperoxide (the conjugate base of hydrogen peroxide), the hydroxyl radical, and superoxide. As these compounds include oxidants, a nucleophile, and a reductant, alkaline activated persulfate (AAP) is able to react with a wider assortment of compounds, such as carbon tetrachloride and 1,1,1-trichloroethane, compared to the electron transfer methods of activation.
- **Heat Activation.** Persulfate can decompose at elevated temperature disassociating into two sulfate radicals. Higher temperatures increase the rate of disassociating of the persulfate and the resulting reaction with the contaminants generally following the Arrhenius equation.

Sodium persulfate is typically available as a dry crystal with the approximate consistency of table salt. The solubility of sodium persulfate varies with temperature but can be greater than 500 grams per liter (g/L) at temperatures greater than 20 degrees centigrade ($^{\circ}\text{C}$).

3.3.1.2 Potential for Metals Mobilization

The persulfate anion, has the potential to mobilize metals as temporary localized changes in site conditions can occur which, as described previously, can affect the metals equilibrium concentrations in groundwater. In addition to the increased oxidative potential that will be common with all ISCO technologies, potential changes in groundwater conditions specifically regarding common methods of applying persulfate include:

- Changes in pH.
- Addition of organic material.
- Addition of cations and anions.

The decomposition of persulfate results in the generation of two moles of acid for every mole of persulfate. Often the buffering capacity of the soil material is sufficient to neutralize this acid generation, but if the buffering capacity is exceeded, the pH of the aquifer in impacted areas could decrease. In addition, the chelates used in iron chelate activated persulfate can be acids, which could impact the aquifer pH. Alkaline activation intentionally creates alkaline conditions in the impacted aquifer. However, in a properly designed alkaline activated persulfate application, the alkaline conditions should be temporary as the acid generated from the decomposition of persulfate returns the system to near pH neutral conditions.

Organic material can be added as the chelate in iron chelate activation or in organic material activation systems. In addition, organic material that can affect mobilization can be naturally present at the site. The interaction of metals with organic material varies both with the metal and the type of organic material. Even organic materials that are considered chelates can preferentially bind with certain metals. However, when anticipating the potential for metals mobilization, organic material within an ISCO system should be considered dynamic as most organic material has the potential to react with the ISCO technologies.

Significant cations, most notably, sodium, and anions, most notably persulfate and sulfate, are introduced into the subsurface during an application of persulfate. Both the anions and cations have the potential to displace metals from the surface of soils. Most metals are present as cations, including cadmium, chromium, nickel, zinc, etc. However, it should be noted that several metals are commonly found in the environment as oxyanions, ions comprised of metals and oxygen, such as arsenic which is commonly found as arsenite (AsO_3^{3-}) or arsenate (AsO_4^{3-}) in the environment.

3.3.2 PERMANGANATE ANION

3.3.2.1 Background

The permanganate anion, MnO_4^- , is a selective oxidant that is characterized by a deep purple color at concentrations greater than approximately 1 g/L and an increasingly pink color at lower concentrations. The anion is typically available as either sodium permanganate or potassium permanganate. Permanganate oxidizes compounds as it transitions from Mn (VII) to either Mn (II) at $\text{pH} < 3.5$ (5 electron transfer), Mn (IV) at $3.5 < \text{pH} < 12$ (3 electron transfer), or to Mn (VI) at $\text{pH} > 12$ (1 electron transfer). In most aquifers, the permanganate reaction occurs between $3.5 < \text{pH} < 12$ resulting in the formation of manganese dioxide (MnO_2) a brown to black solid phase precipitate. The neutral pH reaction has a standard reduction potential of 1.7 V.

The solubility of sodium and potassium permanganate varies with temperature. Sodium permanganate is miscible in water but is typically available in concentrations up to 40 percent by weight with water. Potassium permanganate is typically available as a purple, sometimes bronze-like, crystal and has a theoretical solubility of approximately 28 g/L at 0°C and 65 g/L at 20°C.

3.3.2.2 Potential for Metals Mobilization

As previously discussed, permanganate has been known to contain metal impurities such as chromium and arsenic. As a result, some of the early applications using technical grades of permanganate exceeded the MCLs for these metals in groundwater. Manufacturers have more recently developed special grades of permanganate specifically for ISCO that have lower concentrations of these metals. Therefore, the primary mechanism for mobilizing metals as a result of a permanganate application is the typical increase in subsurface ORP. This can promote the mobilization of metals that are more soluble in higher oxidation states (e.g. Cr (VI) tends to be more mobile than Cr (III)). The elevated oxidative state will diminish as the permanganate anion completely reacts. The oxidative state may stay elevated above background as the residual manganese dioxide is also an oxidant, albeit weaker than permanganate (1.2 V).

Other metals mobilization mechanisms, changes in pH, addition of cations/anions and/or organic material, appear to have a lesser impact with permanganate applications. The application of permanganate tends to have a minimal impact on pH because it doesn't require activation or stabilization. The addition of the permanganate anion is negated as it diminishes after the oxidative reaction and the manganese precipitates out of solution as manganese dioxide. However, the cation, either sodium or potassium, remains in solution and can affect the natural metals equilibrium through ion exchange on the soils surfaces.

3.3.3 HYDROGEN PEROXIDE

3.3.3.1 *Background*

The application of hydrogen peroxide has been performed under a variety of names, including Fenton's reagent, catalyzed hydrogen peroxide, catalyzed H₂O₂ propagations, stabilized hydrogen peroxide. Though there are different trade names and procedures for the various application approaches, they are all based on the injection of hydrogen peroxide into the subsurface. For example, Fenton's reagent tends to refer to a reaction between hydrogen peroxide and iron; catalyzed hydrogen peroxide and catalyzed H₂O₂ propagations tend to refer to any subsurface application of hydrogen peroxide; and stabilized hydrogen peroxide tends to refer to the application of hydrogen peroxide with the addition of a compound, often a chelate, intended to slow the reaction.

Hydrogen peroxide is unique among the common oxidants in that it can both be oxidized to oxygen and reduced to form water. Functionally, hydrogen peroxide reacts with a transition metal either injected with the hydrogen peroxide or present in the subsurface to form the hydroxyl radical (OH•; an oxidant; 1.8 V). Because hydrogen peroxide can be both oxidized and reduced, the hydroxyl radical can then initiate a series of reactions where both superoxide (O₂⁻•; a reductant; -0.33 V) and hydroperoxide (HO₂⁻; a nucleophile) are produced. The hydroxyl radical can react with other compounds available in the subsurface to form additional radicals, such as with sulfate to form the sulfate radical (SO₄⁻•).

3.3.3.2 *Potential for Metals Mobilization*

The application of hydrogen peroxide will increase the oxidative potential of the groundwater; however, as hydrogen peroxide quickly decomposes to oxygen and water long term geochemical impacts to the subsurface are minimal. However, as a part of the injection procedure, several other compounds are often added with hydrogen peroxide. These additional compounds can have effects on the subsurface geochemistry, including temporary impacts to pH and the addition of organic material, cations or anions into the subsurface.

The degree to which each of the above potential changes in groundwater chemistry will occur will be a function of the application design. There are many methods for applying hydrogen peroxide in practice, including:

- Pre-acidification of the aquifer.
- Addition of chelated iron.

- Addition of organic chelates to stabilize the hydrogen peroxide.
- Addition of inorganic chelates to stabilize the hydrogen peroxide.

Several of these variations have the potential to modify the subsurface pH. A pre-acidification step often targets a range of pH of between 2 and 6. Chelates can increase, decrease, or buffer the pH, depending upon the chelate used. For example, citric acid will decrease the pH and buffer the pH from increasing, whereas another source of the citrate anion, trisodium citrate, should result in near neutral pH and buffer against decreases in pH. Other common chelates, such as phosphate and ethylenediaminetetraacetic acid (EDTA), also have the potential to change and buffer pH depending upon the type of each compound that is applied. Generally, the more salt (sodium or potassium) in the compound formula the more alkaline it will be in solution and, conversely, the more hydrogen atoms (H^+) that can disassociate the more acidic the solution.

As previously discussed, the organic or inorganic chelates that are added with some oxidants including hydrogen peroxide have the potential to mobilize metals. Organic material can be added as the chelate in iron chelated activation (e.g., iron and citric acid) or in organic material activation (e.g., phytic acid) systems. In addition, organic material can be naturally present at the site. The interaction of metals with organic material varies both with the metal and the organic material. Even organic materials that are considered chelates can preferentially bind with certain metals. However, when anticipating the potential for metals mobilization, organic material within an ISCO system should be considered dynamic as most organic material has the potential to react with the ISCO technologies.

As previously discussed, significant cations and anions can be introduced into the subsurface during an application of some oxidants including hydrogen peroxide. These compounds are typically either associated with pre-acidification of the aquifer, an activator solution or a stabilizer solution. Both the anions and cations have the potential to displace metals from the surface of soils.

3.3.4 OZONE

3.3.4.1 Background

Ozone (O_3) is an oxidative gas (2.08 V) that can dissolve into the aqueous phase. Direct oxidative reactions can occur in either the gas or aqueous phases. In aqueous systems, direct oxidation pathways, especially in the absence of catalysts, tend to dominate under acidic conditions. Under alkaline conditions, ozone can react to form a variety of transient oxygen species including the hydroxyl radical, superoxide, hydroperoxide, and others.

Ozone is typically generated onsite because of its instability, requiring a source of on-site electricity. Ozone generators tend to produce 1 to 2 percent ozone by volume with an air feed and up to 8 to 10 percent ozone by volume if using a pure oxygen feed. The solubility of ozone in groundwater primarily varies depending upon temperature and concentration of ozone. In general, the solubility of ozone in groundwater is less than 50 milligrams per liter (mg/L), and its solubility increases with increasing gas phase ozone concentration and decreases with increasing groundwater temperature.

3.3.4.2 *Potential for Metals Mobilization*

Similar to the other ISCO technologies, ozone has the potential to mobilize metals whose oxidized state is more soluble than their reduced state, such as chromium. Also, the oxidation of natural organic matter could make it more likely to behave as a chelate, which could increase metals mobilization. Unless it is applied with additional amendments, other metals mobilization mechanisms typically do not apply to an ozone application.

3.4 OTHER REMEDIAL TECHNOLOGIES

While the potential mobilization of metals through ISCO is the primary focus of this Guidance Document, the reader should be aware that several of the common, available remedial technologies can also impact the equilibrium concentrations of metals in groundwater. The potential for fouling of zero valent iron permeable reactive barriers by chemical precipitates is an example of altered geochemical conditions resulting in a change in the equilibrium between metals concentrations in groundwater and in the solid phase. In that instance, the highly reducing conditions created by the zero valent iron causes metals to precipitate out of solution, potentially fouling the barrier system. Any remedial application that alters the subsurface conditions has the potential to impact the equilibrium concentrations of metals in the subsurface. This includes the following commonly applied remedial technologies and common associated subsurface condition modifications (in parentheses):

- Aerobic bioremediation (increased oxidative potential, amendments with anion nutrients).
- Anaerobic bioremediation (increased reductive potential, addition of anion nutrients and organic substrate).
- Zero valent iron (increased reductive potential, addition of iron).
- Soil vapor extraction (potential for increased oxidative potential by influx of oxygen).
- Air sparging (increased oxidative potential by influx of oxygen).

4.0 EVALUATING SITE-SPECIFIC METALS MOBILIZATION POTENTIAL

From the above discussions on the fundamental science of metals and ISCO technologies, it can be seen that there are multiple potential changes that can occur to subsurface conditions as a result of an ISCO application. These changes may affect the metals equilibrium and therefore the dissolved metals concentrations in groundwater, at least transiently. Therefore, the potential for the mobilization of metals, fate of the metals (if mobilized), and the impact of the metals (if mobilized) are going to vary depending upon site-specific factors and the selected ISCO technology design. The potential for metals mobilization and impacts from metals mobilized during an ISCO application are best evaluated prior to a field event, during the site assessment and through bench-scale testing.

4.1 SITE ASSESSMENT

At a typical ISCO site geology, groundwater hydraulics, many geochemical parameters (e.g., pH, conductivity, alkalinity, and ORP) as well as dissolved phase COCs are extensively characterized (both spatially and temporally) in the typical site characterization phases. In these typical site

characterization efforts, metals are typically associated with the solid phase and are not detected in groundwater analyses. Furthermore, in many situations, metals may not be among the dissolved phase analytical parameters evaluated. In either scenario, site characterization efforts preceding ISCO application are not sufficient to either detect metals present at the site or reveal the mechanism by which these metals are associated with the solid phase, thus there is limited predictive capability to anticipate mobilization of metals due to an ISCO application.

As discussed in Section 3, the aqueous concentration of metals is a function of several subsurface conditions. Often, contamination is present in both sufficient quantities and periods of time to have created subsurface conditions (pH, organic content, ORP, etc.) different from the surrounding non-contaminated aquifer. Thus, in performing a site assessment on the potential for mobilization of metals it is important to consider the following areas on site:

1. The area impacted with contamination.
2. The area impacted with contamination to be treated with ISCO.
3. The area not impacted with contamination.

While the significance of each condition can vary site to site, the following data, that may not be available from prior site assessment efforts, should be collected from each of the on-site areas to aid in evaluating the potential for metals mobilization and impacts from metals, if mobilized:

- Metals concentrations on soil and in groundwater.
- Total Organic Carbon (TOC) on both soils and in groundwater and DOC.
- Concentrations of major cations and anions.
- Proximity to receptors.
- Soils cation exchange capacity.

4.1.1 METALS CONCENTRATIONS ON SOIL AND IN GROUNDWATER

Groundwater is both the medium through which mobilized metals could impact potential receptors and, via analyses, an indicator of which metals may be present at the site. Soil is the reservoir from which metals are mobilized. Depending upon the site-specific geochemical conditions, groundwater may not always accurately show all metals that could be mobilized during an ISCO application, which is why it is important to determine the metals on soils.

Groundwater metals concentrations can be readily determined using EPA Method 6010C. Common metals evaluated include the RCRA 8 metals and /or the Priority Pollutant metals (Table 4.1). However, if there is historical evidence, due to past practices or previous site activities, to suggest the presence other metals that could be present at a particular site at levels exceeding regional screening levels, these metals should be included among the list of analytical parameters.

Metals on soils can be evaluated using several methods. The two primary methods used are leaching procedures; the Toxicity Characteristic Leaching Procedure (TCLP; EPA SW-846 Method 1311) or the Synthetic Precipitation Leaching Procedure (SPLP; EPA SW-846 Method 1312). These two methods were developed to simulate the slightly acidic conditions potentially found in landfill groundwater or caused by slightly acidic rain, respectively. The primary issue with both tests is that while each of these conditions may indicate leachable metals present in the

soil, they may not emulate the conditions to which the soils will be exposed during an ISCO application. For example, neither test emulates the alkaline conditions associated with alkaline activated persulfate, the chelates associated with a stabilized hydrogen peroxide application, or the oxidative conditions associated with permanganate applications. Other methods exist to evaluate metals on soils including x-ray diffraction.

TABLE 4.1 – RCRA 8 and Priority Pollutant Metals

Contaminant	RCRA Metals	Priority Pollutant Metals	Maximum Contaminant Level (mg/L)
Arsenic	X	X	0.01
Barium	X		2.0
Cadmium	X	X	0.005
Chromium (total)	X	X	0.1
Lead	X	X	0.015
Mercury (inorganic)	X	X	0.002
Selenium	X	X	0.05
Silver ^(a)	X	X	0.1
Antimony		X	0.006
Beryllium		X	0.004
Copper		X	1.3
Thallium		X	0.002
Nickel ^(b)		X	None
Zinc ^(a)		X	5.0

(a) Secondary Maximum Contaminant Level

(b) There is no current MCL for Nickel, it has been remanded back to EPA for further regulation. Previously, the MCL was 0.1 mg/L

As will be discussed in more detail in Section 4.2 below, perhaps the best method to identify the potential metals to be mobilized from a site-specific soil is to perform a bench test exposing the soil to the ISCO conditions that are planned to be applied in the field. The bench test, in essence, is a modified leaching procedure test.

4.1.2 TOTAL ORGANIC CARBON AND DISSOLVED ORGANIC CARBON

Quantifying the amount of organic carbon present on soils and in groundwater can help both understand the potential for metals mobilization and the fate of metals if mobilized. Methods for measuring dissolved organic carbon content include SM5310C. Dissolved organic carbon can bind with or chelate metals once mobilized to help keep the metals in solution. Also, the organics may be transformed during the ISCO application releasing metals sorbed on the organic matter. Regarding the eventual fate of metals, if mobilized, the presence of organics down gradient of the treated area and the influx of organic material in groundwater moving into the ISCO treatment

area can aid in returning the aquifer to background conditions. It is common that when the aquifer returns to background conditions the metals equilibrium conditions would also revert to background concentrations. It should be noted that areas impacted with contamination may have significantly higher organic carbon content compared to the background conditions thus the impacts of organic carbon on metals mobility may vary spatially dependent on post-ISCO organic carbon distribution.

4.1.3 CONCENTRATIONS OF MAJOR CATIONS AND ANIONS

Equilibrium chemistries tend to dominate subsurface geochemistry. Anions and cations are major components of that geochemistry acting as pH buffers, and speciating with metals or oxyanions. Common anions include chloride, carbonate, bicarbonate, sulfate, sulfide, nitrate, nitrite, and phosphate. Common cations, in addition to the RCRA 8 or Priority Pollutant metals, include sodium, potassium, iron, calcium, and magnesium.

Methods for measuring major cations and anions include EPA6010C and EPA300.0, respectively.

4.1.4 PROXIMITY TO RECEPTORS

A site assessment should also consider the location of potential receptors with respect to the dissolved metals. The pathway for mobilized metals will be through contact with groundwater. Thus, the common potential receptors to be impacted by mobilized metals would be groundwater extraction wells. The proximity to receptors would need to be considered in conjunction with the groundwater velocity and the expected time for the geochemical conditions to revert to background conditions in evaluating potential metals impacts to the receptors.

4.1.5 SOIL CATION EXCHANGE CAPACITY

Soils are both a potential source of metals to be mobilized during an ISCO application and also a sink for metals in groundwater that migrates down gradient of the treatment area. In addition to the mineral constituents that are present in soils, different soil types have varying cation and anion exchange capacities that will affect the metal mobility. Table 4.2 (website: soils.tfrec.wsu.edu) provides an example of cation exchange capacity (CEC) for various soil types.

TABLE 4.2 - Cation Exchange Capacity of Soils

Soil texture	CEC (milliequivalents/100g soil)
Sands (light-colored)	3-5
Sands (dark-colored)	10-20
Loams	10-15
Silt loams	15-25
Clay and clay loams	20-50
Organic soils	50-100

4.2 BENCH-SCALE TESTING

4.2.1 ISCO FEASIBILITY EVALUATION

As discussed in Section 3, each ISCO technology has unique characteristics / chemistries that can make different ISCO technologies better suited for site-specific conditions. More specifically, some ISCO technologies are capable of treating certain COCs while others either have a very slow rate of reaction or do not react with the specific COC. For example, alkaline activated persulfate and hydrogen peroxide based technologies are better suited for treating carbon tetrachloride or 1,1,1-trichloroethane while all of the technologies are capable of treating trichloroethene or tetrachloroethene. Other specific oxidant characteristics can be factors in the oxidant selection process (e.g., the heat and gas evolution that can occur with the application of hydrogen peroxide). For a more detailed discussion on ISCO technology selection the reader is referred to Chapter 9 in the SERDP - ESTCP Remediation Technology Monograph Series, 2014, "Chlorinated Solvent Source Zone Remediation" (SERDP-ESTCP 2014) and Siegrist et.al. 2011.

Based on the limitations of the different ISCO technologies, bench-scale tests are typically performed to select the optimum ISCO technology for a site and to develop design parameters for the ISCO application. With respect to the potential for metals mobilization, bench-scale testing allows for evaluating the site-specific soils and the potentially applicable ISCO technologies to determine whether metals mobilization could be a concern at the site (discussed in this section) and, if required, how best to mitigate metals mobilization (discussed in Sections 5.2 and 5.3). As the potential metals mobilization varies for each ISCO technology and soil type, it is important to test the ISCO technology and reagent mixture that is proposed to be used in the field application.

The scope of bench-scale testing can vary in complexity dependent on the site-specific objectives of the ISCO application. Typical bench test objectives, with respect to metals mobilization, include:

- Confirmation that metals of concern will be mobilized in the treatment area.
- Evaluate the change in dissolved metals concentrations over time (metals release can be time dependent).
- Evaluate the potential fate and transport of any mobilized metals of concern.

As has been discussed previously, it has been demonstrated that the release of metals during ISCO applications is typically transient in nature, is highly site-specific, and that metals mobilization depends on both soil characteristics and oxidant / reagent chemistries (Gardner, 2012; Hadnagy et al., in review; Gardner et al., 2014). Therefore, it is recommended that site remedial project managers (RPMs) and designers consider incorporating the bench testing protocols, as outlined in this Guidance Document, into their site assessment and treatability study investigations.

Bench-scale testing can be run using either batch reactors or columns. The batch reactor testing is typically lower cost and can provide good insight into the mobilization potential of the metals for site-specific soils. The column testing is typically of longer duration and higher costs but can also provide additional data on the expected fate and transport of the mobilized metals. The following subsections provide information on batch reactor and column bench testing; for additional details the reader is referred to Gardner et al., 2014.

4.2.2 BATCH BENCH-SCALE TESTS

Table 4.3 presents recommendations on potential batch bench-scale testing that can be performed to develop expectations on metals mobility for site-specific soils and ISCO chemistries.

TABLE 4.3 - Recommended Testing Protocols to Determine Potential Metals Mobilization Issues and Evaluate Mitigation Measures at an ISCO Site.

Name	Test Type	Description/Purpose
Metals release screening tests.	Bench-scale, batch.	Identify metals release issues, i.e. the amount and types of metals mobilized from a given soil when treated with a particular ISCO chemistry.
pH-dependent metals mobilization.	Bench-scale, batch.	A detailed evaluation of metals release for the chosen ISCO technology to elucidate the impact of pH.

4.2.2.1 *Screening level determination of potential metals release*

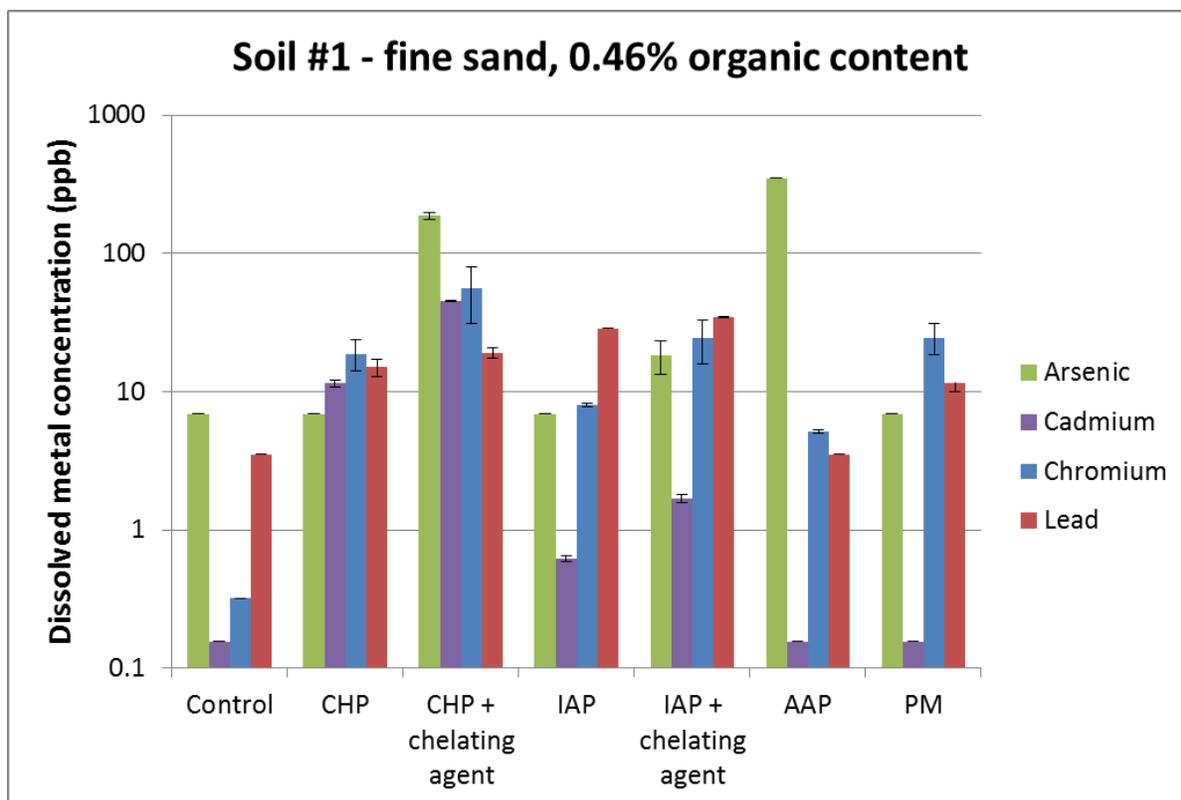
Bench-scale tests have been developed to assess potential metals release from contaminated site soils due to ISCO applications. These laboratory batch experiments allow for a simultaneous and rapid evaluation of multiple samples to assess potential metals release, i.e. the types and amount of metals mobilized, from contaminated soils treated with various oxidant chemistries and loadings. This screening test can be run in conjunction with testing to determine the effectiveness of the oxidant chemistry of interest on the degradation of the COCs for the site, if bench-scale evaluation is the preferred option, and thus time and resources could be saved by simultaneously obtaining COCs treatability and metals mobilization measurements for the ISCO technologies that are being considered for a site.

A detailed, step-by-step procedure of the screening test is provided in Appendix A, which is a modification of an EPA SW-846 batch method to evaluate liquid to solid portioning (USEPA, 2012). The general procedure is as follows: first, a portion of a homogenized site soil sample is mixed with laboratory grade water at a 10: 1 liquid to solid ratio. Then, the various chemical reagents (i.e. oxidant, chelating agent, catalyst) are injected in the desired quantity and the treated slurry is agitated for 48 hours. If desired, a whole suite of oxidant doses can be tested simultaneously to determine the relationship between reagent dose and metals mobilization. Control batches are prepared in the same fashion, but without the addition of chemical reagents. It is recommended that tests are conducted in duplicate or triplicate runs. The pH of the solution is not adjusted, instead it is determined by the oxidant chemistry applied. After 48-hours of exposure, the pH and the ORP of the solution is recorded. Then, the solid and liquid phases are separated by centrifugation and the decanted liquid is filtered through a 0.45 micron filter to obtain a solution containing only dissolved phase metals. Finally, a sample aliquot is taken for dissolved metals analysis and the sample is preserved using high purity, concentrated nitric acid.

Figure 4.1 shows an example of the results of metals mobility testing obtained using the recommended screening test procedures. The figure shows how the application of various ISCO

chemistries impact the release of arsenic, cadmium, chromium, and lead from a sandy soil with 0.46 percent (%) organic content. Oxidant loadings and concentrations used are shown in Table 4.4. Control samples were run without the addition of ISCO reagents and therefore served as the baseline for metals mobilization. The results show an increase in arsenic release in the alkaline- and the iron-activated persulfate and the iron-activated hydrogen peroxide chemistries when the chelating agent was present (in this example, citric acid was used as the chelating agent). On the other hand, the leaching of cadmium increased in the iron-activated persulfate and hydrogen peroxide systems both in the presence and absence of the chelating agent, even though the amount released was higher when citric acid was present. Chromium release increased in all ISCO applications. Similarly, lead mobilization increased in the presence of all oxidant chemistries, except for alkaline-activated persulfate.

FIGURE 4.1 - Arsenic, Cadmium, Chromium, and Lead concentrations detected in the dissolved phase in Soil #1



(CHP = iron-activated hydrogen peroxide, IAP and AAP = iron- and alkaline-activated persulfate, respectively, and PM = permanganate. Citric acid was used as the chelating agent. Reagent doses used are shown in Table 4.4. Numbered soils description is provided in Appendix B).

TABLE 4.4 - Oxidant Concentrations used in the Metals Release example shown in Figure 4.1

Oxidant Name	Oxidant Dose	Oxid. Aqueous Conc. ^(a)			Catalyst ^(b)	Chelating Agent	Molar Ratio of Oxidant : Fe(II) : Citric Acid
	g/Kg	g/L	mM	%			
Control	0	0	0	0	na	na	na
Potassium Permanganate	6.8	0.68	4.3	na	na	na	na
Catalyzed Sodium Persulfate	60.2	6.02	25.3	na	Fe(II)	na	100 : 1
					Fe(II)	Citric Acid	100 : 1 : 2
					NaOH	na	pH > 11 ^(c)
Catalyzed Hydrogen Peroxide	300	30	882	3	Fe(II)	na	100 : 1
					Fe(II)	Citric Acid	100 : 1 : 2

^a For a batch solution with a 10 : 1 = liquid to solid ratio (w/w)

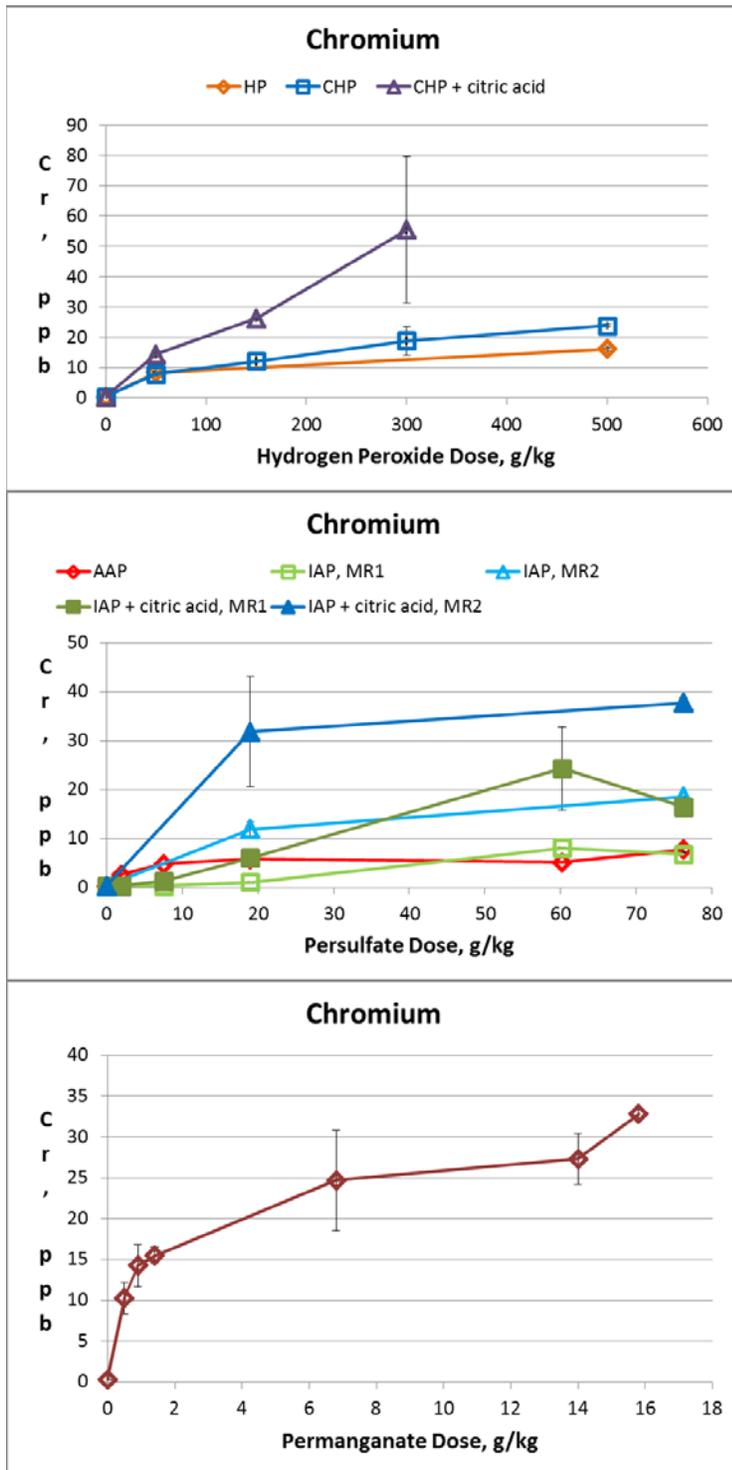
^b Fe(II) was added in the form of FeSO₄·7H₂O [iron(II) sulfate heptahydrate]

^c Base neutralizing capacity of the soil + 2:1 = NaOH:Na₂S₂O₈ molar ratio

na = not applicable; g/Kg = grams per kilogram; mM = millimolar; NaOH = sodium hydroxide

Another important type of information that can be obtained in the screening tests is the oxidant loading or dose dependent metals mobilization. Figure 4.2 shows the amount of chromium mobilized due to the application of various loadings of different ISCO chemistries. In most instances, the amount of chromium mobilized increased as the oxidant dose increased.

FIGURE 4.2 - Chromium Mobilization as a function of Oxidant Dose in Soil #1



(HP = hydrogen peroxide; CHP = iron-catalyzed hydrogen peroxide), AAP = alkaline-activated persulfate; IAP = iron-catalyzed persulfate; MR = molar ratio of oxidant: Fe(II) : citric acid; MR1 = 100:1:2 and MR2 = 12.5:5:1; numbered soils description provided in Appendix B)

A more detailed bench-scale case study on metals mobilization including a description of the numbered soils used throughout this Guidance Document is provided in Appendix B.

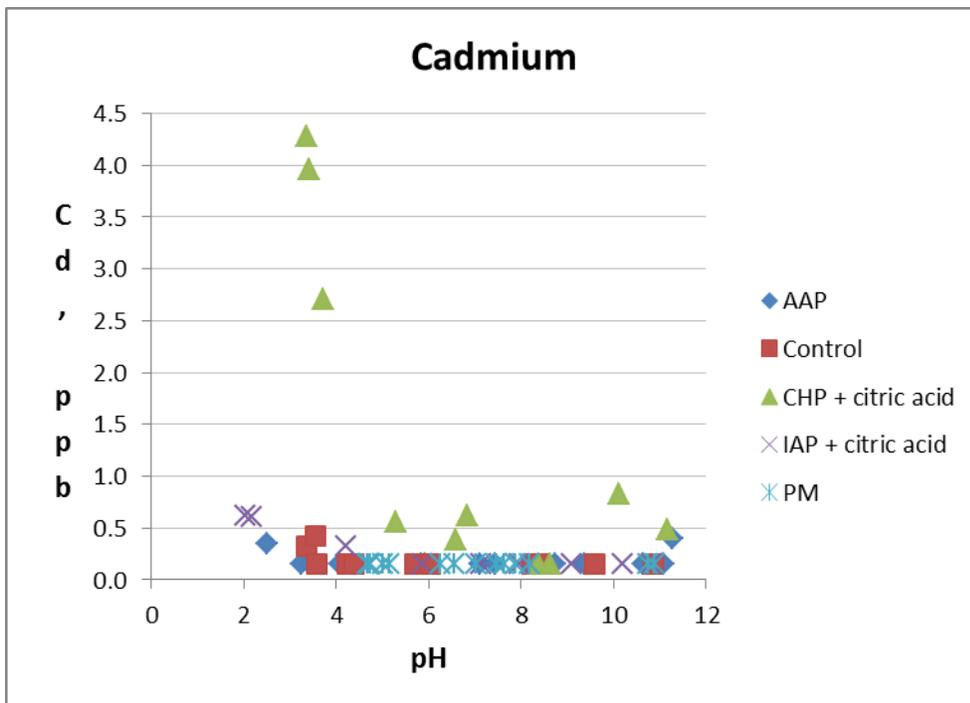
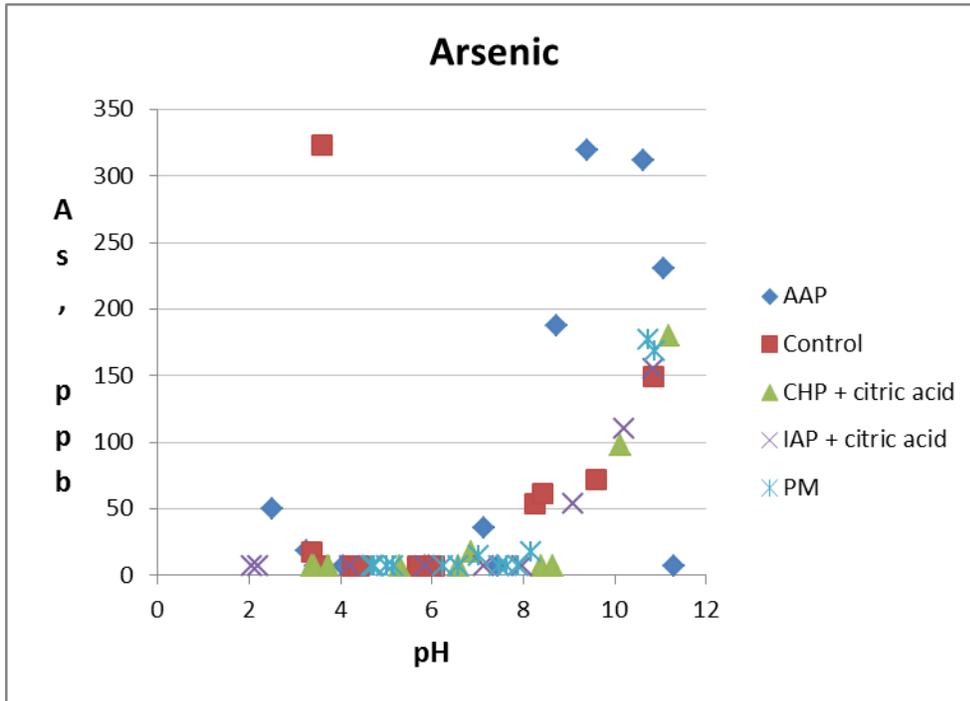
4.2.2.2 The pH-dependent leaching of metals

Laboratory batch tests have also been developed to evaluate the pH-dependent leaching behavior of metals from soils treated with different ISCO chemistries. This test is meant to be a follow-up to the screening tests to gain more detailed information on metals release for select treatments. The results of these tests are pH-dependent leaching curves for the treated and untreated / control soils that show the relationship between dissolved metal concentrations and the pH. These curves help elucidate if pH is a controlling factor in the release of specific metals from site-specific soils treated with different ISCO chemistries and whether there are other mechanisms resulting in the release observed in the screening tests. The results of the pH-dependent leaching tests can also be used as input parameters in geochemical speciation modeling, if needed.

Figure 4.3 shows the pH-dependent mobilization of arsenic and cadmium in Soil #1 due to the application of various ISCO chemistries. Oxidant doses used in these tests are shown in Table 4.4. The results show that arsenic mobilization increased in the presence of alkaline-activated persulfate above pH 8. Similarly, cadmium mobilization increased due to the application of chelated iron-activated hydrogen peroxide (in this example, citric acid was used as a chelating agent), but in a lower pH range, i.e. below pH 5. The pH was the controlling factor for other ISCO chemistries tested (i.e., there was no difference in metals release from untreated and treated soils).

Detailed procedures of the pH-dependent leaching test are provided in Appendix A. Similarly to the screening evaluation, the soil is mixed with laboratory grade water and the chemical reagents. The difference in the pH-dependent tests is that the soil is first exposed to the ISCO chemistry for 48 hours, without adjusting the pH, and after that the solution pH is adjusted and the slurry is mixed using an end-over-end tumbling device for an additional 48 hours. The first 48 hours of this test is essentially the same as the screening tests and the second part is based on standard leaching protocols that are routinely performed to evaluate metals mobilization from waste materials (USEPA, 2012; Kosson et al., 2002). The chosen liquid to solid ratio and reaction time are consistent with values recommended in these standard leaching tests. After 96 hours, the pH and the ORP of the solution are recorded, the solid and liquid phases are separated by centrifugation, and the solution is filtered through a 0.45 micron filter. Finally, samples are taken for dissolved metal, DOC, and major ions analysis (such as sulfate, nitrate, phosphate, bromide, chloride).

FIGURE 4.3 - The pH-dependent release of Arsenic and Cadmium in Soil #1



(AAP = alkaline-activated persulfate; CHP and IAP = iron-activated hydrogen peroxide and sodium persulfate, respectively; PM = permanganate; numbered soils description provided in Appendix B)

4.2.3 COLUMN BENCH-SCALE TESTS

The ISCO treatment area will contain the highest concentration of the ISCO reagents, and will therefore coincide with the largest shifts in pH and ORP; the two master variables that influence metals mobilization and attenuation. Therefore, metals mobilized due to ISCO application are most likely to occur from within the ISCO treatment area. As part of the scope of work of ER2132 an evaluation of the fate and transport of metals in soils using bench-scale column studies was performed.

In the column studies evaluation, three different soils were contacted with four different ISCO chemistries – alkaline activated persulfate; chelated iron activated persulfate, hydrogen peroxide, and potassium permanganate. Soils were equilibrated with solutions containing the ISCO reagents, packed into column, and eluted with groundwater (uncontaminated). Dissolved metals were analyzed in the initial extraction and from three vertically-spaced side-ports on each column in order to estimate the aqueous phase concentrations of metals during transport along the soil column.

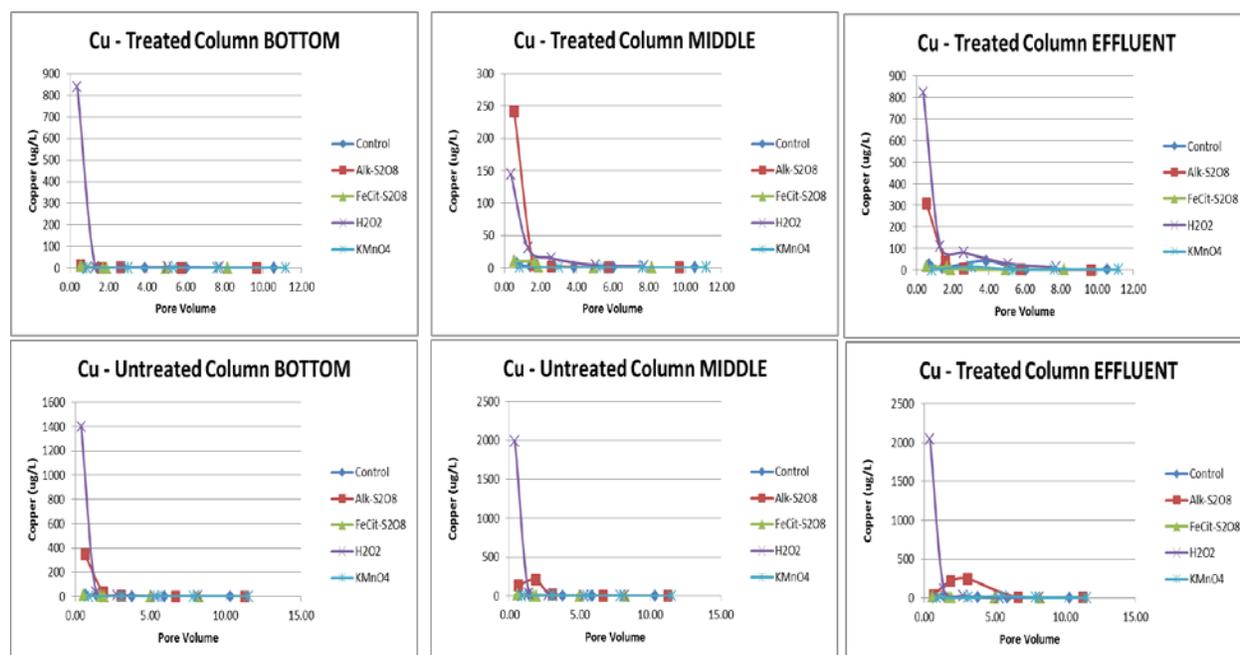
The columns were operated in an up-flow manner, such that the bottom port captures the influent solution and the effluent sample port is on the top of the column. Two columns, connected in series, were used for this study, where the first column was loaded initially with soils equilibrated with the ISCO reagents, and the second column (down gradient from the first) was loaded with soils equilibrated with groundwater only. Columns were eluted with groundwater such that the groundwater passed through the first column (from bottom to top), flushing the ISCO reagents into the second column (also up-flow direction), allowing the reagents to decompose and neutralize along the flow path. This is presumably due to the combination of flushing with clean groundwater and decomposition of the reagents due to reaction with the native materials within the second column.

For the study, the metals analyses focused upon metals common to many remediation sites: arsenic, chromium, copper, nickel, lead and zinc. This suite of metals was also chosen in order to capture metals that would be expected to behave differently, such as oxyanions (As, Cr) and divalent cations (Cu, Ni, Pb, and Zn). The column test results demonstrated that metals release due to contact with an ISCO chemistry is site-specific. This observation reinforces the recommendation that all sites should be initially screened for the potential for metals mobilization, especially if there is knowledge of historical uses and/or suspected prior metals releases.

Aside from the site-specific nature of the study results, there are two additional valuable observations that were made. First, even though all ISCO chemistries can dramatically raise the ORP, not all ISCO reagents mobilize metals to the same extent. Secondly, in those cases where two or more reagents were found to mobilize the same metal from the same soils, not all reagents maintain metals in solution for equal time. Essentially, once the ISCO reagents are effectively neutralized by the soils and/or influent groundwater, most metals revert back to their original attenuated (non-aqueous, non-mobile) condition; as was determined from the review of field studies by Krembs, 2008. These two observations are elaborated in the study results discussed below.

In the graphical series shown in Figure 4.4, copper leaching from Soil #2 is used to illustrate the effect of ISCO reagents on metals mobilization. As can be seen, only two of the four ISCO chemistries mobilized copper from these soils – alkaline activated persulfate and hydrogen peroxide. Even though alkaline activated persulfate and peroxide both generated concentrations of soluble copper as high as 0.3 mg/L for persulfate and 2 mg/L for peroxide, the other two ISCO chemistries (iron-activated persulfate and permanganate) did not release copper to any extent greater than the control. Therefore, it is conceivable to select an ISCO technology that will effectively treat the target COCs without affecting the mobilization of metals.

FIGURE 4.4 - Copper Transport During ISCO Treatment with Soil #2



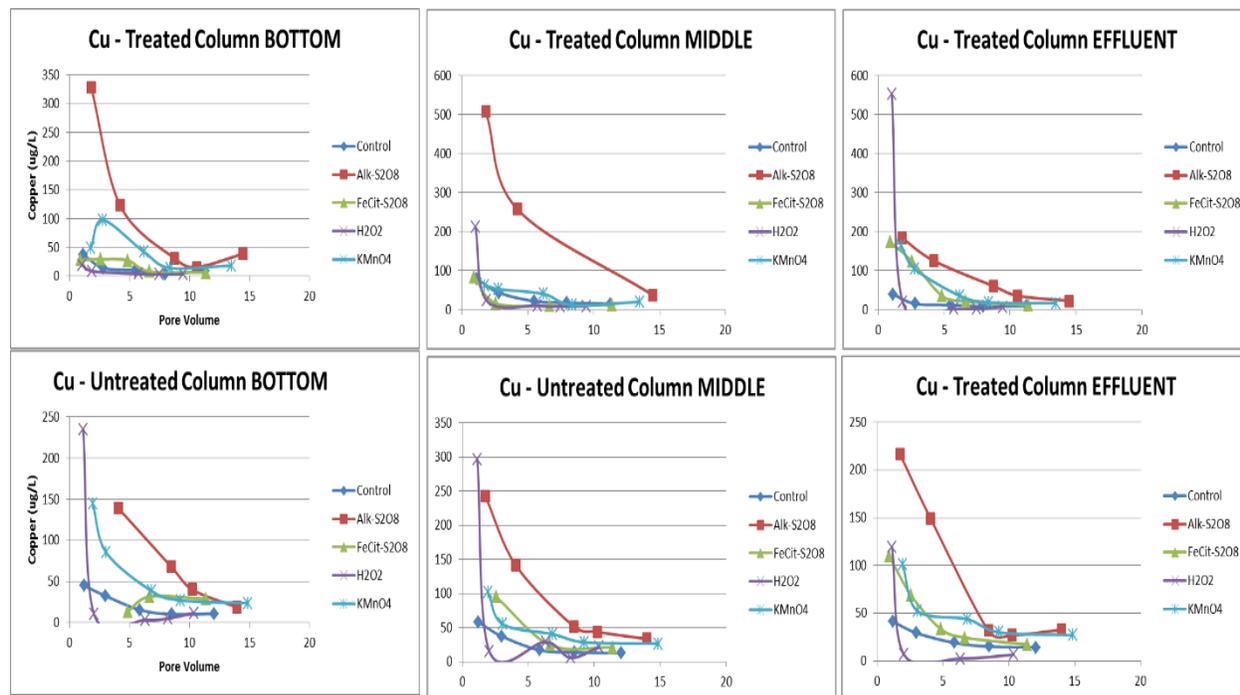
(Upper three plots represent data from the bottom, middle and effluent sample ports from the column containing soils treated with ISCO chemistries (up gradient column). The lower three plots represent data from the bottom, middle and effluent sample ports from the column containing aquifer materials and only groundwater (down gradient from the first column). For reference, the drinking water screening level is 62 micrograms per liter [$\mu\text{g/L}$].)

Secondly, the plots in Figure 4.4 illustrate that copper released from Soil #2 due to peroxide treatment is initially highly mobile, with the entire volume of mobilized copper moving through both columns with nearly conservative transport (i.e. in approximately 1 pore volume flush), whereas the copper mobilized from the alkaline persulfate treatment requires an approximately 5 pore volume flush to migrate through the two columns. Thus, not all chemistries mobilize metals with equal propensity to migrate at the same velocities as site groundwater.

This effect is more dramatic when considering the results from Soil #4 (Figure 4.5) and the contrasting effect of alkaline persulfate treatment on the mobilization of copper. In the more organic-rich and finer textured aquifer material represented by Soil #4, elevated levels of dissolved copper are maintained for many more pore volumes relative to Soil #2 (more sandy, less organic).

Whereas the dissolved copper concentrations return to pre-ISCO (alkaline persulfate) / baseline conditions after < 5 pore volumes for Soil #2, the dissolved levels of copper in the experiment with Soil #4 require > 5 pore volumes to return to baseline conditions. Thus, different ISCO chemistries not only determine the extent to which metals are released, but also have an important influence on the length of time they will remain mobilized.

FIGURE 4.5 - Copper Transport during ISCO Treatment with Soil #4.



(Upper three plots represent data from the bottom, middle and effluent sample ports from the column containing soils treated with ISCO chemistries (up gradient column). The lower three plots represent data from the bottom, middle and effluent sample ports from the column containing soils and only groundwater (down gradient from the first column). For reference, the drinking water screening level is 62 µg/L.)

Table 4.5 shows the propensity of the different ISCO chemistries to mobilize metals from the different soils tested. As can be seen from Table 4.5, each soil responded differently to the different ISCO chemistries. However, for the study a few trends can be observed that could be used in the selection of the ISCO chemistry for the soils, based upon considerations of metals mobilization. First alkaline activated persulfate mobilized arsenic, where the other treatments did not. This trend is consistent across other studies performed under ER2132 where consistently elevated concentrations of arsenic were measured after contact with alkaline activated persulfate. Permanganate was found to mobilize chromium in Soils #1 and #2 to much higher levels than the other chemistries. For the divalent metals Cu, Ni and Pb, hydrogen peroxide was found to mobilize metals for all three soils. As such, for these soils and perhaps other soils this table may be used as a general guide for ISCO chemistry selection; however, bench-scale testing with site-specific soils is still highly recommended.

TABLE 4.5 - Metals Mobilized from 3 Soils using 4 ISCO Chemistries.

<i>Metal</i>	Soil #1		Soil #2		Soil #4	
	<i>Mobile</i>	<i>Not Mobile</i>	<i>Mobile</i>	<i>Not Mobile</i>	<i>Mobile</i>	<i>Not Mobile</i>
Arsenic	AAP	IAP CHP PM	AAP	IAP CHP PM	None	None
Chromium	AAP PM	IAP CHP	AAP CHP PM	IAP	AAP CHP	PM
Copper	IAP CHP	AAP PM	AAP CHP	IAP PM	AAP CHP	None
Nickel	IAP CHP	AAP PM	CHP	IAP PM	AAP CHP	PM
Lead	AAP CHP PM	IAP	Mobilized by all	None	AAP CHP	PM
Zinc	AAP IAP CHP	PM	AAP IAP CHP	PM	AAP IAP CHP PM	None

(AAP = alkaline-activated persulfate; CHP and IAP = iron-activated hydrogen peroxide and sodium persulfate, respectively; PM = permanganate)

5.0 DESIGN, MONITORING, AND ACTIONS FOR METALS MOBILIZATION IN AN ISCO FIELD EVENT

This section of the Guidance Document will not focus on every aspect of the development of an ISCO design and monitoring program. The intent of this section is to provide guidance as to how the potential for metals mobilization could be incorporated into an ISCO design and monitoring program, if it is deemed necessary, following the steps outlined above in Section 4. In addition, this section will discuss steps to consider to mitigate metals mobilization. For additional information on general approaches to ISCO design the reader is referred to Siegrist et al., 2011 or ITRC, 2005.

The design of an ISCO field application is typically based upon site characterization data, the results of a bench-scale test, and, if available, the results of a field pilot test. This creates the following typical sequence leading to the ISCO full-scale design and implementation:

1. Site investigation and characterization.
2. Feasibility study to confirm ISCO as a viable technology.
3. Design of the field application:
 - a. ISCO bench-scale testing.
 - b. Collection of additional site data, if needed.
4. Field applications.

- a. Field pilot test.
- b. Full-scale application.

, If based on site-specific concerns, metals mobilization is determined to be a potential issue during the feasibility evaluation or bench-scale testing, as discussed in Section 4, and the application of ISCO is planned, it is recommended that the potential for metals mobilization be considered and incorporated into the following design components:

- Field Application Monitoring Program.
- Field Application Design.
- Metals Mobilization Contingency Plan.

Each of these design components should be considered whether the field event planned is a pilot test or full-scale application.

5.1 FIELD APPLICATION MONITORING PROGRAM

5.1.1 MONITORING PROGRAM OBJECTIVES

The objectives of a general ISCO monitoring program are designed to match the remedial objectives for the site and the ISCO application. For example, the objectives of a pilot test may be to ascertain field design parameters such as reagents distribution, radius of influence, injection rates and pressures, in addition to the effectiveness of treatment of the CVOCs on soil or in groundwater. For a detailed discussion of primary objectives for general ISCO monitoring programs, the reader is referred to Siegrist, 2011.

The objectives of an ISCO monitoring program specific to metals mobilization should include:

- Determine the background / baseline equilibrium metals concentrations in each of the potential monitoring areas.
- Evaluate the changes to the dissolved metals concentrations in the ISCO treatment area over time.
- Evaluate the potential migration of mobilized metals to areas down gradient of the ISCO treatment area.
- Determine if changes in dissolved metals concentrations are a result of ISCO chemistry changes or treatment of the COCs and the return of the aquifer to background / baseline conditions.
- Identify potential risk of dissolved metals migration to down gradient receptors.

5.1.2 MONITORING AREAS

The areas impacted by COCs may have different equilibrium concentrations of dissolved metals compared to background / non-impacted areas. In such sites, treatment of the COCs may be sufficient to revert the equilibrium dissolved metals concentrations back to baseline / background conditions when / if the geochemical conditions revert back to background conditions.

To best understand the behavior of metals resulting from an ISCO application it is important to characterize the concentration of metals and the factors influencing metals mobilization in the following areas:

1. Background area.
2. The area impacted by COCs.
3. The ISCO treatment area.
4. The area down gradient of the ISCO treatment area.

A background area would be an area that is not impacted with COCs but is in the same general geologic setting as the COCs impacted areas. It could be directly up gradient or side gradient of the impacted area and should share several common features as the impacted area. These common features should include geologic setting, soil type, and source of groundwater.

The area impacted by COCs will likely include several subareas, depending upon site-specific characteristics such as the age and evolution of the COCs plume. These subareas could include a source area, and down gradient areas impacted by the COCs including the COCs plume or areas where the factors influencing metals equilibrium concentrations have been impacted by the COCs.

The ISCO treatment area is the area in which ISCO reagents are applied while the area down gradient of the ISCO target area is the areas that it is reasonable to expect that the ISCO reagents could migrate. This will largely be a function of groundwater velocity which can vary from feet per year to feet per day, depending upon site-specific conditions.

Sufficient monitoring wells should be located in each of these areas to adequately characterize each area to meet the objectives of the monitoring program.

5.2 DESIGN OF A FIELD APPLICATION

There are several references outlining steps that go into the design of an ISCO application (e.g., Siegrist, 2011 and SERDP-ESTCP, 2014). This Guidance Document will focus on considerations for the typical ISCO design that incorporate the potential for metals mobilization.

5.2.1 TECHNOLOGY SELECTION

Many factors should be considered in selecting which ISCO technology / chemistry is optimal for application at any specific site. Often these factors include theoretical reactivity of the oxidant with COCs; the results of bench-scale testing on the reactivity of the oxidants with the site-specific soils, non-target COCs oxidant demand and oxidant loading to achieve the site-specific ISCO remedial goals; cost; and previous experience. If deemed necessary and as discussed in Section 4, the potential for metals mobilization may be included as an ISCO technology selection factor and could be included in the bench-scale testing objectives.

While each ISCO technology has the potential to mobilize metals, the data presented in Table 4.5 and Table 5.1 (from Gardner et al., 2014) indicate that specific metals are more likely to be mobilized when using certain ISCO technologies. Therefore, if the likely transient mobilization of metals at a site is a critical design parameter, the ISCO technology that minimizes the metals mobilization may be the deciding factor in the technology selection. Ideally, it may be possible to select an ISCO technology that is equally effective in treating the site COCs and that would not

mobilize the metals present at the site. Due to the variability in the potential mobility of metals at different sites with the different ISCO chemistries, site-specific bench-scale testing is highly recommended when metals mobility is a concern.

TABLE 5.1- Database Summary of Dissolved Metals Concentrations as Function of ISCO Technology

Dissolved Metal (ug/L):	Ag	As	Ba	Be	Cd	Cr	Cu	Pb	Sb	Se	Zn
MCL (ug/L): ^(a)	100	10	2000	4	5	100	1300	15	6	50	5000
Background											
Site Max > MCL (sites/total sites)	0/10	1/10	0/10	0/10	0/10	0/10	0/10	2/10	0/10	0/10	0/10
Site Max > MCL (% of total sites)	0	10	0	0	0	0	0	20	0	0	0
Alkaline-Activated Persulfate											
Site Max > MCL (sites/total sites)	0/9	9/9	0/9	0/9	0/9	0/9	0/9	1/9	0/9	0/9	0/9
Site Max > MCL (% of total sites)	0	100	0	0	0	0	0	11	0	0	0
Site Max > Background (sites/total sites)	2/9	9/9	2/9	2/9	1/9	9/9	8/9	1/9	0/9	0/9	3/9
Site Max > Background (% of total sites)	22	100	22	22	11	100	88	11	0	0	33
Catalyzed Hydrogen Peroxide											
Site Max > MCL (sites/total sites)	0/9	1/9	0/9	4/9	6/9	0/9	0/9	5/9	1/9	0/9	0/9
Site Max > MCL (% of total sites)	0	11	0	44	66	0	0	55	11	0	0
Site Max > Background (sites/total sites)	5/9	1/9	7/9	7/9	8/9	9/9	9/9	6/9	1/9	0/9	8/9
Site Max > Background (% of total sites)	55	11	77	77	88	100	100	66	11	0	88
Catalyzed Hydrogen Peroxide with Citric Acid											
Site Max > MCL (sites/total sites)	0/10	8/10	0/10	6/10	9/10	3/10	0/10	6/10	9/10	0/10	0/10
Site Max > MCL (% of total sites)	0	80	0	60	90	30	0	60	90	0	0
Site Max > Background (sites/total sites)	8/10	8/10	9/10	10/10	10/10	10/10	10/10	6/10	9/10	1/10	10/10
Site Max > Background (% of total sites)	80	80	90	100	100	100	100	60	90	10	100
Iron-Activated Persulfate											
Site Max > MCL (sites/total sites)	0/9	0/9	0/9	2/9	0/9	0/9	0/9	4/9	0/9	0/9	0/9
Site Max > MCL (% of total sites)	0	0	0	22	0	0	0	44	0	0	0
Site Max > Background (sites/total sites)	3/9	0/9	8/9	5/9	4/9	7/9	5/9	4/9	0/9	0/9	5/9
Site Max > Background (% of total sites)	33	0	88	55	44	77	55	44	0	0	55
Iron-Activated Persulfate with Citric Acid											
Site Max > MCL (sites/total sites)	0/10	2/10	0/10	4/10	1/10	0/10	0/10	5/10	0/10	0/10	0/10
Site Max > MCL (% of total sites)	0	20	0	40	10	0	0	50	0	0	0
Site Max > Background (sites/total sites)	3/10	2/10	9/10	7/10	8/10	8/10	8/10	6/10	0/10	0/10	7/10
Site Max > Background (% of total sites)	30	20	90	70	80	80	80	60	0	0	70
Permanganate											
Site Max > MCL (sites/total sites)	0/10	0/10	0/10	0/10	0/10	1/10	0/10	0/10	0/10	0/10	0/10
Site Max > MCL (% of total sites)	0	0	0	0	0	10	0	0	0	0	0
Site Max > Background (sites/total sites)	2/10	0/10	4/10	2/10	0/10	10/10	3/10	0/10	0/10	2/10	0/10
Site Max > Background (% of total sites)	20	0	40	20	0	100	30	0	0	20	0

^(a) Secondary Maximum Contaminant Level for Ag and Zn

Color scheme: green = less than 1/3 of sites; yellow = between 1/3-2/3 of sites; red = over 2/3 of sites

Table 5.2 presents the results of bench-scale testing for metals mobility from Soil #6, preformed as part of the ER2132.

TABLE 5.2 – Bench-Scale Test Results on Soil # 6

Soil 6					
Selected Metals	Metals Concentrations (µg/L)				
	Control	CHP	KMn	IAP	AAP
Arsenic	14	14	14	14	3,230
Cadmium	0.31	9.4	0.31	5.6	0.31
Chromium	0.88	49	123	11	27
Copper	2.6	1,123	1.5	1,488	497
Lead	7.1	7.1	34	35	7.1
Nickel	1.5	131	1.5	478	2.0
Zinc	14	199	2.3	518	3.9

(AAP = alkaline-activated persulfate; CHP and IAP = iron-activated hydrogen peroxide and sodium persulfate, respectively; KMn = permanganate)

As shown in Table 5.2, the metals mobilized from Soil #6 varied with the unique chemistry of each ISCO technology. RPMs, designers, and practitioners can use this site-specific bench-scale test data to evaluate metals that may be a concern at a site with the ISCO technology least likely to mobilize that metal. For example, if chromium is abundant at a site with soil similar to Soil #6, permanganate was found to have the greatest risk of mobilizing chromium, with chelated iron activated persulfate and alkaline activated persulfate mobilizing close to an order of magnitude less. If arsenic is the present in the formation at the site, the designer may choose to apply hydrogen peroxide, permanganate, or chelated iron activated persulfate rather than alkaline activated persulfate.

5.2.2 POTENTIAL MODIFICATIONS TO AN ISCO TECHNOLOGY TO MITIGATE METALS MOBILIZATION

The scope of work of ER2132 included evaluating the addition of reagents to mitigate the mobilization of metals for four common ISCO technologies:

- Hydrogen peroxide (catalyzed with chelated iron).
- Potassium permanganate.
- Alkaline activated persulfate.
- Iron chelate activated persulfate.

The reagents evaluated and discussed within this subsection should be considered to be currently at the research stage of development and would require bench and pilot testing prior to full-scale implementation.

This part of the study focused on reagents for metals mobility mitigation that may be applied in one or more of three general stages of the ISCO technology implementation:

- Pretreatment. Soils would be treated with a reagent prior to the application of ISCO.
- During Treatment. The reagent would be added directly with the ISCO technology reagents.
- Post Treatment. The reagent would be added a period of time following the ISCO application.

If reagents were to be added either in the pre- or post-treatment stages of ISCO implementation a second mobilization to the site would be required to inject the new reagents.

The results of the ER2132 evaluation of reagents addition to mitigate metals mobilization are provided in detail in Gardner et al., 2014. Table 5.3 provides an example of the quantitative results from the bench-scale testing on Soil #6 for chromium mobility using permanganate as the ISCO technology. Tables 5.4 through 5.7 present the qualitative results of all the bench-scale testing performed on select metals for the four ISCO technologies studied. A brief discussion on the qualitative results of reagent addition on metals mobility mitigation, for the four ISCO technologies tested, is provided in the following subsections.

TABLE 5.3 – Quantitative Results of Reagent Addition to Soil #6 on Chromium Mobility

Treatment Phase (reagent)	Day	Soil #6		
		Control	Permanganate Only	Permanganate + Reagent
		µg/L		
Pretreatment (Ferric Sulfate)	2	0.9	122.5	87
	28	7.7	377.2	99
	56	0.6	409.0	60
	90	0.6	235.1	50
With Treatment (Sodium Lactate)	2	0.9	122.5	10
	28	7.7	381.7	35
	56	0.6	390.5	94
	90	0.6	535.4	11
Post Treatment (Sodium Sulfide)	30	7.7	377.2	1
	56	0.6	409.0	2
	84	0.7	518.4	4
	118	0.6	678.3	45

5.2.2.1 *Hydrogen Peroxide*

This study focused on hydrogen peroxide reacted with iron chelated with citric acid. The results of the study show that cadmium, chromium, copper, nickel and zinc mobilized above the control levels after contact with the hydrogen peroxide solution only. Table 5.4 presents the qualitative results of the addition of reagents intended to help mitigate the mobilization of each metal.

TABLE 5.4 Qualitative Results of Promising Reagents for Metals Mitigation with CHP Technology

Selected Metals	CHP		
	4.1: Pretreatment	4.2: With Treatment	4.3: Post Treatment
Arsenic			
Cadmium	Sodium Sulfide	Acetate, Citrate, Phosphate, and Phosphate Buffer	pH Neutralization
Chromium		Acetate, Citrate, and Sodium Sulfide	
Copper	Sodium Sulfide	Acetate, Citrate, and Phosphate Buffer	
Lead			
Nickel		Acetate, Citrate	
Zinc	Sodium Sulfide	Acetate, Citrate, and Phosphate Buffer	pH Neutralization

(CHP = catalyzed hydrogen peroxide)

5.2.2.2 Potassium Permanganate

Potassium permanganate was evaluated in the study and it was found that only chromium and lead increased above control levels. Table 5.5 presents the qualitative results of the addition of reagents intended to help mitigate the mobilization of each metal.

TABLE 5.5 Qualitative Results of Promising Reagents for Metals Mitigation with KMnO₄ Technology

Selected Metals	KMn		
	4.1: Pretreatment	4.2: With Treatment	4.3: Post Treatment
Arsenic			
Cadmium			
Chromium	Ferric Sulfate	Lactate	Sodium Sulfide
Copper			
Lead	Ferric Sulfate		Sodium Sulfide
Nickel			
Zinc			

(KMn = potassium permanganate)

5.2.2.3 Iron Chelate Activated Persulfate

Sodium persulfate activated by iron chelated with citric acid was studied. Cadmium, chromium, copper, lead, nickel, and zinc were all mobilized at levels above the control levels in this study. While the list of metals mobilized in the chelated iron system is the longest, the mitigation of the mobilized metals had the longest list of effective treatment reagents. Table 5.6 presents the qualitative results of the addition of reagents intended to help mitigate the mobilization of each metal.

TABLE 5.6 Qualitative Results of Promising Reagents for Metals Mitigation with IAP Technology

Selected Metals	IAP		
	4.1: Pretreatment	4.2: With Treatment	4.3: Post Treatment
Arsenic			
Cadmium	Sodium Sulfide, and Sodium Phosphate	Acetate, Sodium Phosphate, Sodium Bicarbonate, and Sodium Bicarbonate Buffer	pH Neutralization, and Sodium Sulfide
Chromium	Sodium Sulfide, and Sodium Phosphate	Sodium Phosphate, Sodium Bicarbonate, and Sodium Bicarbonate Buffer	pH Neutralization, and Sodium Sulfide
Copper	Sodium Sulfide, and Sodium Phosphate	Sodium Phosphate, Sodium Phosphate Buffer, Sodium Bicarbonate, and Sodium Bicarbonate Buffer	pH Neutralization, and Sodium Sulfide
Lead			pH Neutralization, and Sodium Sulfide
Nickel	Sodium Sulfide, and Sodium Phosphate	Sodium Phosphate, Sodium Phosphate Buffer, Sodium Bicarbonate, and Sodium Bicarbonate Buffer	pH Neutralization, and Sodium Sulfide
Zinc	Sodium Sulfide, and Sodium Phosphate	Sodium Phosphate, Sodium Phosphate Buffer, Sodium Bicarbonate, and Sodium Bicarbonate Buffer	pH Neutralization, and Sodium Sulfide

(IAP = iron activated persulfate)

5.2.2.4 *Alkaline Activated Persulfate*

The study also evaluated alkaline activated persulfate. Three metals were mobilized above the control levels in this study: arsenic, chromium, and copper. Table 5.7 presents the qualitative results of the addition of reagents intended to help mitigate the mobilization of each metal.

TABLE 5.7 Qualitative Results of Promising Reagents for Metals Mitigation with AAP Technology

Selected Metals	AAP		
	4.1: Pretreatment	4.2: With Treatment	4.3: Post Treatment
Arsenic	<i>Sodium Sulfide and Ferric Sulfate</i>		pH Neutralization, and Sodium Sulfide
Cadmium			
Chromium	<i>Sodium Sulfide, and Ferric Sulfate</i>		pH Neutralization, and Sodium Sulfide
Copper	<i>Sodium Sulfide, Sodium Phosphate, and Ferric Sulfate</i>		pH Neutralization, and Sodium Sulfide
Lead			pH Neutralization, and Sodium Sulfide
Nickel			
Zinc			

(AAP = alkaline activated persulfate)

5.2.3 FIELD PILOT TEST

Field pilot tests are typically used to confirm and / or evaluate full-scale design parameters and treatment effectiveness in a limited field application at the selected site. The scope of the pilot test can range from tests using single to multiple injection points. If mobilization of metals has been identified as a potential issue, a field pilot test can also provide an opportunity to both confirm metals mobilization, evaluate the fate and transport of the mobilized metals, and demonstrate metals mobility mitigation.

With respect to metals mobilization, a further benefit of the field pilot test is that it would be performed in a limited portion of the site, minimizing any potential risk posed by mobilized metals. The changes to a typical ISCO field-scale pilot test to include evaluation of the metals mobility should include:

- Sufficient monitoring points to characterize the various areas on-site (as discussed in Section 5.1.2, most critically, the ISCO treatment area and area directly down gradient of the treatment area).
- A sufficient monitoring period to adequately evaluate the fate of any mobilized metals, including the results of any reagents added to mitigate the metals mobility.
- Associated laboratory analyses for any dissolved metals of concern.

These changes would likely include minimal additional effort over the typical ISCO field-scale pilot test.

The density of the monitoring wells to be installed in each of the areas discussed in Section 5.1.2, and number and frequency of the sampling events needed to meet the pilot test objectives would be part of the monitoring program development discussed in Section 5.1. Typically, field pilot tests have a more elaborate monitoring program and denser monitoring well network than a full-scale application as the field pilot objectives typically are associated with confirmation / development of the design for the full-scale application; whereas the objectives of a full-scale application tend to be to measure and confirm the application results.

5.2.4 FULL-SCALE APPLICATION

Full-scale applications of a remedy such as ISCO are typically the end product of significant efforts to study, plan, test, and design the remedy. The full-scale implementation of an ISCO remedy typically has a goal such as a specific reduction in groundwater COCs concentrations, mass flux reduction, or reduction in COCs mass. The potential for mobilization of metals at a site as a result of a full-scale ISCO remedy implementation should be thoroughly evaluated prior to the ISCO implementation, as discussed and recommended in this Guidance Document. There are several considerations in a full-scale ISCO remedy design to accommodate the evaluation of metals mobilization, if deemed a concern. These include:

- Down gradient monitoring wells to assess the fate and transport of potentially mobilized metals or to serve as sentry wells between an ISCO treatment area and potential down gradient receptors.
- Monitoring wells in the background (non-contaminant impacted) areas.
- Monitoring wells within the ISCO treatment areas.

The positioning and intent of the down gradient monitoring wells should be to observe the potential migration of any mobilized metals and help protect potential receptors. These monitoring wells would help identify if any unplanned metals migration occurred and, if so, could trigger implementation of a Contingency Plan, as outlined in Section 5.4. The monitoring wells provide data to compare dissolved metals concentrations in the ISCO treatment area and the background area to assess any differences in the equilibrium concentrations. As previously discussed, the presence of contaminants can create conditions that will alter the equilibrium dissolved metals concentrations compared to background areas. As a site is remediated and the levels of the contaminants are reduced it is important to not only compare the post-ISCO equilibrium dissolved metals concentration with the baseline levels in the formerly contaminated areas, but also to the levels in the background monitoring wells.

5.2.5 ASSESSMENT OF POTENTIAL FOR OFF-SITE MIGRATION AND METALS ATTENUATION

In some cases, metals may become mobilized despite efforts to better characterize the site and institute pre-emptive measures to mitigate the potential for mobilization of metals during an ISCO application. In cases where metals of concern were not detected in pre-ISCO groundwater characterization, these metals are likely to be attenuated and immobile under the natural groundwater conditions. Consequently there are site-specific factors that must be evaluated and considered before deciding upon any potential mitigation plan to address metals impacts. For example, no mitigation may be necessary if the target area is a large distance from the nearest receptor (or property boundary), and the rates of attenuation exceed the potential for metals to reach a potential receptor (or property boundary). However, should the target area be in close

proximity to a surface water or drinking water receptor, and/or threaten to move across a down gradient property boundary, active mitigation of mobilized metals may be warranted.

In the instance where metals have been mobilized due to an ISCO application, a site-wide approach should be created to strategically develop a robust conceptual model of metals fate and transport in order to evaluate the need for mitigation. The site-wide characterization strategy can be approached in a similar framework for most ISCO sites where the aim is to understand the physical setting and the dominant processes controlling metal transport behavior. The general approach for site characterization for an ISCO site where metals have been mobilized has the following elements:

- Site layout, including target area and historical inventory of chemicals released.
- Hydrogeologic environment and transport potential.
- Background geochemical conditions of groundwater aquifer.
- Spatial distribution of dissolved metals.
- Contaminant flux and rate for ISCO reagent degradation and reversion to pre-ISCO conditions.
- Metal stability under post-ISCO conditions.

Much of this information will be available from the characterizations performed up to and post implementation of the full-scale ISCO application.

5.2.5.1 Site layout and history

If an ISCO remedy has already been implemented, it is likely that there is already significant information regarding the site layout. The contaminant plume and the ISCO target area have probably been delineated. However, it is important to understand the source of the metals that have been mobilized. For example, for metals that are geogenic in origin, it is likely that they will be attenuated under post-ISCO conditions. If metals were a component of the release or waste stream, their individual chemistry under post-ISCO conditions need to be considered when evaluating down gradient attenuation processes. This is because metals that were released as part of a release or waste stream may behave differently under background geochemical conditions compared to within a contaminant plume. Furthermore, the concentration of the metals in source areas is important to estimate in order to generate mass flux estimates in the context of attenuation capacity of the aquifer outside the target zone.

5.2.5.2 Hydrogeological conditions and background geochemical conditions of groundwater aquifer

Hydrogeological characterization begins with understanding groundwater flow direction and velocity. If ISCO has already been implemented, it is likely that the flow direction and groundwater velocities in and around the target area have already been established. Additionally, the geochemistry of groundwater under pre-ISCO conditions should be established in order to interpret mixing rates with groundwater from the target zone. Together, an understanding of groundwater hydrology and groundwater geochemical conditions from pre- and post-ISCO conditions can be used to estimate the time required to re-establish background conditions.

5.2.5.3 Spatial distribution of dissolved metals

For a site where metals have been mobilized, it is critical to delineate the vertical and lateral extent of metals mobilization. This information can typically be obtained from the current network of wells in the area, as well as down gradient monitoring wells to the extent necessary. The spatial distribution of metals should also be considered in the context of the background geochemical conditions and ISCO conditions. If it is apparent that the metal may be influenced by changes in ORP (e.g., chromium (III) oxidation to hexavalent chromium), additional redox speciation of the dissolved metals may be merited. This information is critical to understanding the extent of the impacts and understanding if an active remedy is required for the site.

5.2.5.4 Contaminant flux and rate for ISCO reagent degradation

Continued monitoring over the first two weeks after ISCO implementation is critical to rapid understanding of the potential problem prior to metals reaching down gradient receptors. In order to estimate the potential for down gradient impacts it is necessary to monitor the degradation of the ISCO reagents and re-establishment of background conditions. Particularly for those metals released through changes in pH and ORP, changes of both of these parameters to neutral and background conditions may promote attenuation, although this needs to be considered for individual metals as their chemistries can be very different.

5.2.5.5 Metal stability under post-ISCO conditions

Upon completion of ISCO implementation, re-establishment of pre-ISCO groundwater conditions, and decreased metals groundwater concentrations, it is likely that the metal of interest has partitioned to the solid phase and not been degraded or removed. The stability of the new solid phase metal species under background groundwater conditions is important to establish. Understanding the nature of the solid phase metal chemistry can be used to evaluate the potential for future release depending on the evolution of the local groundwater chemistry.

5.2.5.6 Groundwater Flux

The rate at which groundwater flows into and out of the ISCO treatment area is important in understanding the fate and transport of metals, if mobilized. Following an ISCO application the ISCO reagent solution will migrate out of the ISCO treatment area due to both the natural groundwater flow and, dependent on the oxidant and the oxidant concentration, density-driven gradients (i.e. certain ISCO reagents solutions are denser than groundwater which may induce a vertical component to the reagents migration). In addition certain oxidants can cause the precipitation of solids (e.g. manganese dioxide) which may impact the hydraulic conductivity of the subsurface and therefore the migration rate of the groundwater. But, generally, the ISCO reagent solution should be expected to migrate with the groundwater. The rate at which the reagents migrate from the target area will be determined by the groundwater velocity. Certain preferential pathways may have a much higher velocity than the average velocity across a specified geologic interval.

The rate at which the groundwater fluxes from the treatment area and the groundwater velocity within preferential flow paths will determine the distance the reagent impacted groundwater travels before contacting sufficient soils outside of the treatment area to return the groundwater to the baseline geochemical conditions. Under the baseline geochemical conditions the metals concentrations are expected to return to close to baseline concentrations. The up gradient groundwater quality / constituents and the rate at which groundwater flows into the ISCO treatment area will help determine the period of time that is required for the treatment area to return to baseline geochemical conditions.

5.3 METALS MOBILIZATION CONTINGENCY PLAN

RPMs, designers, and practitioners should consider including a Metals Mobilization Contingency Plan as a component of the ISCO design. The scope of the contingency plan will depend upon the potential impacts to receptors of mobilized metals. The potential and degree of metals mobility should have been determined during the site investigation, bench and pilot testing phases of the project, prior to a full-scale ISCO application. The prior testing should have indicated:

- If metals were likely to be mobilized with the selected ISCO technology.
- Which metals were likely to be mobilized and to what levels.
- Are proven reagents to mitigate the metals migration incorporated into the ISCO remedy.
- Proximity of treatment area to potential receptors.
- Type of potential receptors.
- Groundwater velocity.
- Anticipated fate and transport of the metals with and without proven reagents to mitigate the metals migration incorporated into the ISCO remedy.

The contingency plan, if deemed necessary, could consist a variety of detail, for example, the plan could include:

- Background.
- Objectives.
- Corrective remedies to be implemented in the event metals migration occurs outside of the expectations developed from prior evaluations.

The exact content of a Metals Mobilization Contingency Plan is expected to vary based on site-specific needs and requirements. The plan components provided in the following subsections is intended as a potential plan template.

5.3.1 CONTINGENCY PLAN: BACKGROUND

The background section could include:

- A summation of critical site investigation data including:
 - Identification of background, COCs impacted, ISCO treatment and down gradient areas.
 - Groundwater contour plot and flow direction.
 - Groundwater velocity.
 - Potential receptors.

- Soil type and geologic cross-sections.
- Description of metals likely to be mobilized
 - Summary of site investigation, bench and pilot test results regarding metals mobilization and potential mitigation reagents (if tested).
 - Description of risks and concerns regarding each metal that is expected to be mobilized.

5.3.2 CONTINGENCY PLANS: OBJECTIVES

The objectives of the contingency plan will likely be very site-specific. The overall concept would be to have an understanding of the potential risk and actions to be taken if the metals mobilized during the ISCO application did not attenuate as expected due to down gradient conditions or due to added reagents to mitigate the metals migration.

Typical objectives could include:

- Identification of thresholds that would trigger actions within the contingency plan.
- Identification of the technologies that would be used to remedy the unexpected metals migration.
- Add sufficient level of design for the preferred contingent remedy to allow timely response to action.

5.3.3 POTENTIAL CORRECTIVE ACTIONS

This contingency plan section would provide the details required to meet the plan objectives. Threshold conditions would be developed to trigger implementation of the contingency plan. The triggers could include:

- Measuring metals above set concentrations at down gradient sentinel wells.
- Geochemistry changes in down gradient wells indicative of migration of metals.

If metals are mobilized and the expected attenuation of the mobilized metals does not occur such as to trigger implementation of the contingency plan; the plan should include a discussion regarding the corrective actions to be taken. Depending upon site-specific conditions, such as risk to potential receptors or the environment, the corrective actions could range from additional monitoring to contingent remedy implementation.

Corrective remedies could include:

- In situ metals stabilization.
- Removal of the impacted groundwater for above ground treatment or disposal.
- Permeable reactive barriers.

The specific remedy recommended will likely be site and metal specific. In situ stabilization technologies tend to function by creating geochemical conditions that are more favorable to precipitation of the metal. How this is accomplished is specific to the metal and the site geochemical conditions; but would likely involve the injection of chemicals that would either

return the aquifer pH to near neutral, create reducing conditions in the groundwater, create an elevated pH, or include the addition of a sulfide compound to precipitate the metals as a low solubility compound.

The removal of the impacted groundwater for above ground treatment or disposal would essentially be a temporary pump and treat system. Depending upon the groundwater velocity and time elapsed since the injection, the impacted groundwater could be extracted from the treatment area, down gradient plume, or both locations. This groundwater could be treated above ground and reinjected, discharged to an acceptable source such as a sewer, or not treated and disposed of or discharged to an acceptable source such as a wastewater treatment system.

A permeable reactive barrier (PRB) is a viable remedy to treat mobilized metals. The use of a PRB would likely utilize similar technologies as in situ metals stabilization. The primary difference is that the reagents for the in situ stabilization technologies would be injected throughout the groundwater plume of mobilized metals whereas the PRB would be installed down gradient of the mobilized metals plume, typically between the plume and potential receptors. As most of the in situ technologies for metals mitigation are based upon precipitating the metals, designers would need to consider the impacts to soil and PRB permeability's when assessing the potential implementation of a PRB.

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Appendix A

Recommended Bench Test Protocols

Screening Evaluation of Metals Mobilization Potential from Soils Treated using In Situ Chemical Oxidation

1. PURPOSE AND DESCRIPTION:

These laboratory batch tests are designed to evaluate metals mobilization potential from soils treated with In Situ Chemical Oxidation (ISCO) without an intervention to adjust the pH; the pH of the system is determined by the native pH of the soil material and by the ISCO chemistry applied. Results of these tests show the types of metals mobilized and the amount released from a specific site soil using a particular ISCO chemistry. Using multiple oxidant doses, a dose-response curve can be developed showing the relationship between oxidant dose and metals release. This standard operating procedure (SOP) is based on SW-846 Method 1313 (USEPA, 2012) and methods developed by Kosson et al. (2002) for the pH-dependent leaching evaluation of metals from waste materials. This SOP contains modifications to the cited standard protocols in order to incorporate ISCO exposure of soil materials into the process. In addition, the pH of the batch solutions is not adjusted in the current tests. Please refer to the SOP on the “pH-dependent leaching of metals from soils treated with ISCO” below for protocols that elucidate the impact of pH on metals release. Both SOPs should be used as a general guideline; for further details on the cited methods, please refer to SW-846 Method 1313 (USEPA, 2012) and to Procedure A.2. SR002.1 in the leaching evaluation framework developed by Kosson et al. (2002).

2. GENERAL PROCEDURE:

Expose contaminated site soil(s) to various ISCO chemistries and measure metals release.

3. REAGENTS AND MATERIALS:

- Reagent grade water
- ISCO reagent solutions
- Quenching agents – chemicals used to quench the ISCO reaction, e.g. ascorbic acid for permanganate (see Johnson et al, 2012)

4. APPARATUS:

- Wide-mouth high-density polyethylene (HDPE) bottle with cap – batch reactor
- Rotary platform shaker or equivalent – for sample agitation during ISCO exposure
- Vacuum filtration apparatus (recommended for batch volumes greater than 50 mL)
- Syringe filters (recommended for batch volumes less than 50 mL)
- Filtration membranes – 0.45 µm mixed cellulose ester (MCE) membrane filters

- pH and ORP meter and electrodes
- Adjustable pipettes with disposable tips
- Centrifuge – to aid the separation of the solid and liquid phases prior to filtration
- Volumetric flasks – for chemical stock solution preparation
- Sample bottles

5. PREPARATORY PROCEDURES:

5.1 Experimental design:

- 5.1.1. Choose the ISCO chemistries to be tested – i.e., oxidant type and dose and if applicable, the activation method, activator dose, chelating agent type and dose, and the molar ratio of the reagents used.
- 5.1.2. Identify analytes of interest – dissolved metals, and potentially dissolved organic carbon and major ion (such as sulfate, phosphate, nitrate, chloride) content.
- 5.1.3. Determine batch volume based on sample volumes needed for analysis.
- 5.1.4. Determine the amount of soil to be added to make up a slurry with a liquid to solid (LS) ratio of 10 : 1 (based on dry soil weight).

5.2 Soil preparation:

Soil samples should be thoroughly homogenized prior to use. The moisture content of the soils should be determined prior to the test, e.g. by measuring the original wet weight and the dry weight obtained by drying a representative soil sample at 105 C for 24 hours.

5.3 Acid washing:

All laboratory equipment, glassware and containers that come into contact with the leachate should be acid washed using nitric acid.

6. DETAILED PROCEDURES:

6.1 Soil exposure to ISCO condition – duration: 48 hours

- 6.1.1. Prepare batch solutions in wide mouth HDPE bottles based on the experimental design outlined in 5.1. First, add the soil followed by lab grade water to make a soil slurry. Next, inject the ISCO reagents, cap the bottles, shake well, and record the start time of the reaction. Control/background batches should be prepared for each soil without the addition of the oxidant. Each unique experimental batch should be prepared in at least duplicates or triplicates. (Note: when using oxidants that generate a significant amount of gas, such as hydrogen peroxide, it is necessary to vent the bottles until gas generation subsides to prevent the explosion of closed reactors.)

6.1.2. Place the capped bottles on a rotary shaker, or equivalent, at 125 rpm to keep the bottles agitated for 48 hours. After 48 hours, commence Step 6.2 right away.

6.2 Data collection and sampling for analysis:

6.2.1. Calibrate pH meter and measure the pH and ORP of the soil slurry right after taking the batch reactor off the end-over-end tumbler; make sure the slurry is well mixed.

6.2.2. Centrifuge the batch reactor for at least 20 min and at least 3,000 rpm.

6.2.3. Filter the soil slurry using a vacuum filter apparatus (or syringe filters) and 0.45 μm MCE filter paper. Filter the solution gradually and in small volumes at a time; be careful not to disturb the solids that settled out during centrifugation. If the filter clogs, change the filter paper.

6.2.4. Sampling for dissolved metals analysis: Pour the required volume of the filtered solution into sample containers reserved for dissolved metals analysis samples. Add sufficient amount of high purity concentrated nitric acid to each container to reduce the pH to below 2. Keep the samples at 4 C until analysis.

6.2.5. Sampling for major ion and DOC analyses: Pour the required volume of the filtered solution into sample containers reserved for major ion and DOC analyses samples. Follow the procedures for sample preservation and storage for the particular methods that will be used for analysis.

6.2.6. Oxidant quenching: If desired, add reaction quenching reagents into the sample solutions to ensure the passivation of residual oxidants. For example, ascorbic acid can be used to eliminate permanganate reactivity (Johnson et al., 2012).

References

Johnson, KT, M Wickham-St. Germain, S Ko, SG Huling, 2012. Binary Mixtures of Permanganate and Chlorinated Volatile Organic Compounds in Groundwater Samples: Sample Preservation and Analysis. *Groundwater Monitoring & Remediation*, 32(3): 84-92

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pH-Dependent Leaching of Metals from Soils Treated with In Situ Chemical Oxidation

1. PURPOSE AND DESCRIPTION:

These laboratory batch tests are designed to evaluate the pH-dependent leaching behavior of metals from soils treated with In Situ Chemical Oxidation (ISCO). The outputs of these tests are pH-dependent leaching curves that show the relationship between metal concentrations in the dissolved phase and the pH. These curves help elucidate if pH, or some other factor, is controlling the release of specific metals from site soils treated with particular ISCO chemistries. This standard operating procedure (SOP) is based on SW-846 Method 1313 (USEPA, 2012) and methods developed by Kosson et al. (2002) for the pH-dependent leaching evaluation of metals from waste materials. This SOP contains some modifications to the cited standard protocols in order to incorporate ISCO exposure of soil materials into the process. This SOP should be used as a general guideline; for further details on the cited methods, please refer to SW-846 Method 1313 (USEPA, 2012) and to Procedure A.2. SR002.1 in the leaching evaluation framework developed by Kosson et al. (2002).

2. GENERAL PROCEDURE:

- A. Expose contaminated site soil(s) to various ISCO chemistries
- B. Characterize the ISCO exposed soils using pH-dependent leaching

3. REAGENTS AND MATERIALS:

- Reagent grade water
- ISCO reagent solutions
- Acid and base solutions – nitric acid and sodium hydroxide used for pH-adjustment
- Quenching agents – chemicals used to quench the ISCO reaction, e.g. ascorbic acid for permanganate (see Johnson et al, 2012)

4. APPARATUS:

- Wide-mouth high-density polyethylene (HDPE) bottle with cap – batch reactor
- Rotary platform shaker or equivalent – for sample agitation during ISCO exposure
- End-over-end tumbler – for sample mixing during pH-dependent leaching procedure
- Vacuum filtration apparatus (recommended for batch volumes greater than 50 mL)
- Syringe filters (recommended for batch volumes less than 50 mL)

- Filtration membranes – 0.45 µm mixed cellulose ester (MCE) membrane filters
- pH and ORP meter and electrodes
- Adjustable pipetters with disposable tips
- Centrifuge – to aid the separation of the solid and liquid phases prior to filtration
- Volumetric flasks – for chemical stock solution preparation
- Sample bottles

5. PREPARATORY PROCEDURES:

5.1 Experimental design:

- 5.1.1. Choose the ISCO chemistries to be tested – i.e., oxidant type and dose and if applicable, the activation method, activator dose, chelating agent type and dose, and the molar ratio of the reagents used.
- 5.1.5. Identify analytes of interest – dissolved metals, and potentially dissolved organic carbon and major ion (such as sulfate, phosphate, nitrate, chloride) content.
- 5.1.6. Determine batch volume based on sample volumes needed for analysis.
- 5.1.7. Determine the amount of soil to be added to make up a slurry with a liquid to solid (LS) ratio of 10 : 1 (based on dry soil weight).
- 5.1.8. Identify the target pH range; e.g. for the pH range of 3 to 11 plan to run batch tests at pH 3, 5, 7, 9, and 11.

5.2 Soil preparation:

Soil samples should be thoroughly homogenized prior to use. The moisture content of the soils should be determined prior to the test, e.g. by measuring the original wet weight and the dry weight obtained by drying a representative soil sample at 105 C for 24 hours.

5.3 Soil titration curves:

- 5.3.1. Prepare a titration curve for each soil to be tested following Procedure A.6. pH001.0 in Kosson et al. (2002). Soil slurry batches used for titration should be prepared at the LS ratio of 10 : 1 to be consistent with subsequent batch tests. A titration curve should be developed for the whole pH range of interest in the pH-dependent leaching tests (see 5.1.5.).
- 5.3.2. Develop titration curves for each ISCO chemistry tested (i.e. titrate soil slurries that contain the ISCO reagents) following the procedure outlined in 5.3.1.

5.4 Acid washing:

All laboratory equipment, glassware and containers that come into contact with the leachate should be acid washed using nitric acid.

6. DETAILED PROCEDURES:**6.3 Soil exposure to ISCO condition** – duration: 48 hours

- 6.1.1. Prepare batch solutions in wide mouth HDPE bottles based on the experimental design outlined in 5.1. First, add the soil followed by lab grade water to make a soil slurry. Next, inject the ISCO reagents, cap the bottles, shake well, and record the start time of the reaction. Control/background batches should be prepared for each soil without the addition of the oxidant. A sufficient number of batch reactors should be prepared to allow for pH adjustment to the desired target pH levels identified in 5.1. Each unique experimental batch should be prepared in at least duplicates or triplicates. (Note: when using oxidants that generate a significant amount of gas, such as hydrogen peroxide, it is necessary to vent the bottles until gas generation subsides to prevent the explosion of closed reactors.)
- 6.1.2. Place the capped bottles on a rotary shaker, or equivalent, at 125 rpm to keep the bottles agitated for 48 hours. After 48 hours, commence Step 6.2 right away.

6.4 pH-dependent leaching of soils exposed to ISCO – duration: 48 hours

- 6.2.1. Calibrate pH meter and measure the pH of each batch solution; make sure the slurry is well mixed.
- 6.2.2. Calculate the volume and strength of titrant needed to adjust the pH to the desired level (based on the appropriate soil titration curve determined in 5.3).
- 6.2.3. Measure the ORP of each batch; make sure the slurry is well mixed.
- 6.2.4. Adjust the pH to the desired level. (Note: the total batch volume and therefore the LS ratio will slightly vary from batch to batch.)
- 6.2.5. Cap the bottles and place them on the end-over-end tumbler for continuous mixing of the batch solutions for 48 hours. At the end of 48 hours, do Step 6.3 right away.

6.3 Data collection and sampling for analysis:

- 6.3.1. Calibrate pH meter and measure the pH and ORP of the soil slurry right after taking the batch reactor off the end-over-end tumbler; make sure the slurry is well mixed.
- 6.3.2. Centrifuge the batch reactor for at least 20 min and at least 3,000 rpm.
- 6.3.3. Filter the soil slurry using a vacuum filter apparatus (or syringe filters) and 0.45 μm MCE filter paper. Filter the solution gradually and in small volumes at a time; be careful not to

disturb the solids that settled out during centrifugation. If the filter clogs, change the filter paper.

- 6.3.4. Sampling for dissolved metals analysis: Pour the required volume of the filtered solution into sample containers reserved for dissolved metals analysis samples. Add sufficient amount of high purity concentrated nitric acid to each container to reduce the pH to below 2. Keep the samples at 4 C until analysis.
- 6.3.5. Sampling for major ion and DOC analyses: Pour the required volume of the filtered solution into sample containers reserved for major ion and DOC analyses samples. Follow the procedures for sample preservation and storage for the particular methods that will be used for analysis.
- 6.3.6. Oxidant quenching: If desired, add reaction quenching reagents into the sample solutions to ensure the passivation of residual oxidants. For example, ascorbic acid can be used to eliminate permanganate reactivity (Johnson et al., 2012).

6.4 Interpretation

The outputs of the above tests are pH-dependent leaching curves that show the relationship between metal concentrations in the dissolved phase and the pH. By comparing pH-dependent leaching curves developed for the control (i.e. no ISCO reagents added) and treated soils, it can be determined if the pH, or some other factor, is controlling the release of specific metals from site soils treated with particular ISCO chemistries.

References

- Johnson, KT, M Wickham-St. Germain, S Ko, SG Huling, 2012. Binary Mixtures of Permanganate and Chlorinated Volatile Organic Compounds in Groundwater Samples: Sample Preservation and Analysis. *Groundwater Monitoring & Remediation*, 32(3): 84-92
- Kosson, DS, HA van der Sloot, F Sanchez, AC Garrabrants, 2002. An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials. *Environmental Engineering Science*, 19(3): 159-204
- USEPA, 2012. SW-846 Method 1313, "Liquid-Solid Partitioning of Extract pH Using Parallel Batch Extraction Procedure", in SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods"

Appendix B

Case Study

Impacts on Groundwater Quality Following the Application of ISCO: Understanding the Cause of and Designing Mitigation for Metals Mobilization

SERDP Project ER-2132

CASE STUDY

A comprehensive evaluation of metals release issues and potential mitigation measures have been undertaken in ER2132. In this project, ten contaminated site soils (see Table B.1) have been subjected to select ISCO chemistries and metals mobilization potential, return to baseline conditions, and the effectiveness of various metals release mitigation measures have been investigated. Detailed results of this investigation are presented elsewhere (Gardner et al. 2014). This case study shows highlighted results from this work to demonstrate the utility of testing protocols developed for the evaluation of metals mobilization issues at ISCO sites.

Soil # ^(a)	Site Description	Site Owner	Soil Type	Total Organic Carbon (%)	Historic Metals Mobilization	Contaminated With
1	NE DOD Coastal Facility	DOD	Fine Sand	0.46	Yes: As	Petroleum; COCs: Benzene, Naphthalene
2	Navy Facility in California	Navy	Sand	0.59	unknown	Anticipated COCs: Cr(VI) and TCE
3	Navy Facility in California	Navy	Medium to Fine Sand	1.27	Yes: Cr, Cd	unknown
4	US Army Core Site in Mid Atlantic	USACE	Soil with Gravel	5.64	unknown	Anticipated COCs: Pb and Cr(VI)
5	Industrial Facility in NE	Confidential	Sand	0.65	unknown	TCE
6	Gasoline Station in NE	Confidential	Sand	0.67	unknown	Petroleum

Soil # ^(a)	Site Description	Site Owner	Soil Type	Total Organic Carbon (%)	Historic Metals Mobilization	Contaminated With
7	Gasoline Station in NE	Confidential	Silts	0.53	unknown	Petroleum
9	Navy Facility in the SE	DOD	Silty Sand	3.75	unknown	cVOCs
10	EPA Site in the S	EPA	Silty Clay	2.16	unknown	Heavy Petroleum/Creosote; NAPL
11	Former Industrial Facility in SW	Confidential	Sand	1.14	unknown	unknown

^(a) A total of 10 soils were tested, as soil #8 was not included in the analysis.

Metals Mobilization Potential at ISCO Sites: Screening Evaluation

Laboratory batch tests were conducted to evaluate the metals mobilization potential in ten contaminated site soils subjected to six ISCO chemistries (i.e., permanganate, chelated and unchelated iron-activated hydrogen peroxide and sodium persulfate, and alkaline-activated persulfate; citric acid was used as chelating agent). The site soils originated from various geographic locations in the US and they varied in soil type, the soil organic carbon content, the types of organic contaminants present, and historically observed metals mobilization (Table B.1). Soils were exposed to the ISCO chemistries in a slurry form (using a liquid to solid ratio of 10 to 1) for the duration of 48 hours. Batch reactors were constantly agitated on a rotary shaker at 125 rpm for the length of the test. The pH of the batch solutions was not adjusted, and therefore was determined by the oxidant chemistry and the native pH and buffering capacity of the soils. At the end of the tests, the pH and the ORP of the soil slurries were measured, and after solid-liquid separation samples were taken for dissolved metals analysis.

Figure B.1 shows the release of arsenic, cadmium, and chromium from the ten soils subjected to the six ISCO chemistries listed above. Oxidant doses used in these tests are summarized in Table B.2. The leaching of these three metals was the function of the metal in question, the oxidant chemistry (i.e., oxidant type, activation method, presence or absence of chelating agent), and the soil characteristics. For example, arsenic mobilization was most significant in the presence of alkaline-activated persulfate, and chelated iron-activated hydrogen peroxide.

TABLE B.2 - Oxidant Concentrations used in the Metals Release Study

Oxidant Name	Oxidant Dose	Oxid. Aqueous Conc. ^(a)			Catalyst ^(b)	Chelating Agent	Molar Ratio of Oxidant : Fe(II) : Citric Acid
	g/kg	g/L	mM	%			
Control	0	0	0	0	na	na	na
Potassium Permanganate	6.8	0.68	4.3	na	na	na	na
Catalyzed Sodium Persulfate	60.2	6.02	25.3	na	Fe(II)	na	100 : 1
					Fe(II)	Citric Acid	100 : 1 : 2
					NaOH	na	pH > 11 ^(c)
Catalyzed Hydrogen Peroxide	300	30	882	3	Fe(II)	na	100 : 1
					Fe(II)	Citric Acid	100 : 1 : 2

^a For a batch solution with a 10 : 1 = liquid to solid ratio (w/w)

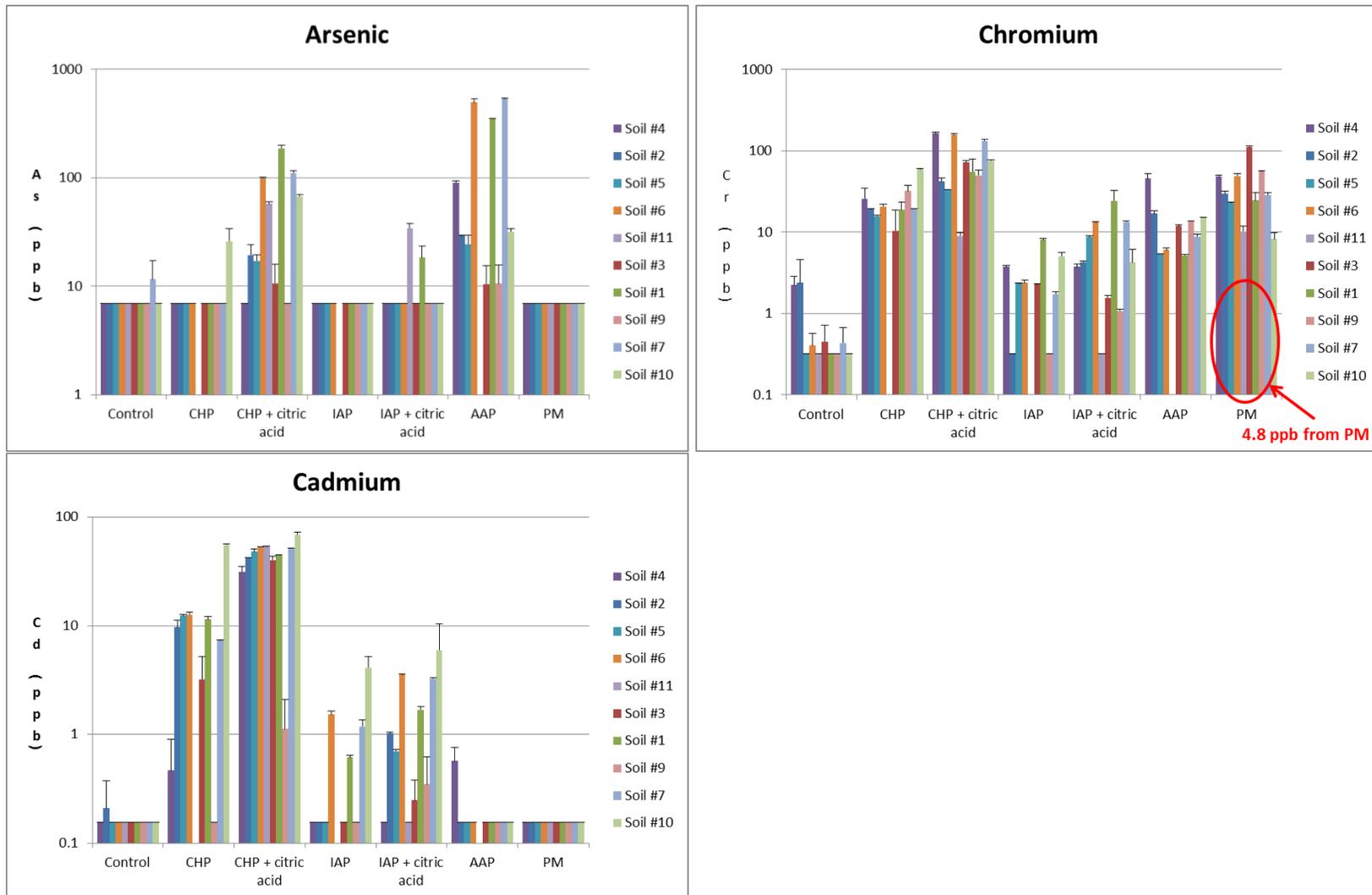
^b Fe(II) was added in the form of FeSO₄·7H₂O [iron(II) sulfate heptahydrate]

^c Base neutralizing capacity of the soil + 2:1 = NaOH:Na₂S₂O₈ molar ratio

na = not applicable

On the other hand, cadmium release was most pronounced in the two catalyzed hydrogen peroxide applications, i.e. both the unchelated and chelated conditions. In general, most metals release has been observed in the hydrogen peroxide and persulfate applications (i.e., at the two pH extremes) and less in the presence of permanganate. For the latter oxidant, most metals observed originated from the reagent; manganese dioxide formation was also believed to have a significant mitigation effect for certain metals. Some ISCO chemistries did not mobilize certain metals, for example there was no significant arsenic and cadmium release in the presence of permanganate, or arsenic mobilization in the unchelated iron-activated persulfate application in any of the ten soils tested. For metals that were impacted by all oxidant chemistries, such as the release of chromium, the amount mobilized varied, which could make it possible to select a chemistry that is expected to result in the least release. Finally, while soil characteristics have been shown to impact release, no trends have been observed between metals mobilization and grain size distribution or total organic carbon content.

Figure B.1 The leaching of Arsenic, Cadmium, and Chromium from site soils exposed to various ISCO chemistries



(CHP = iron-activated hydrogen peroxide; IAP and AAP = iron- and alkaline-activated persulfate; PM = permanganate). Soils are shown in the order of coarsest (Soil #4) to finest in grain size (Soil #10).

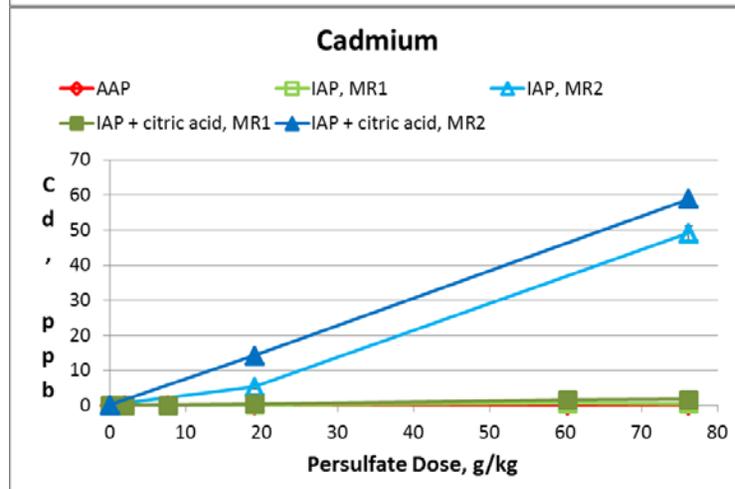
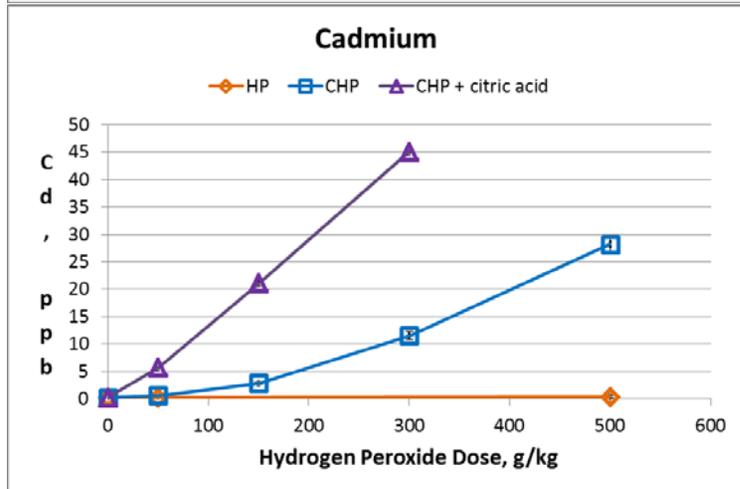
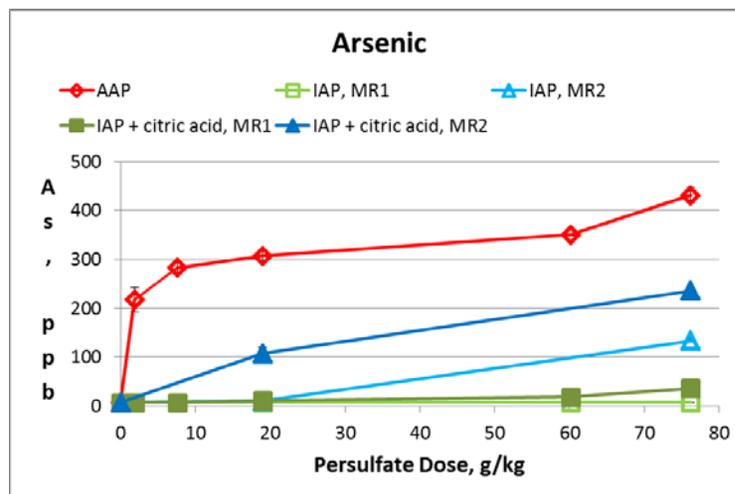
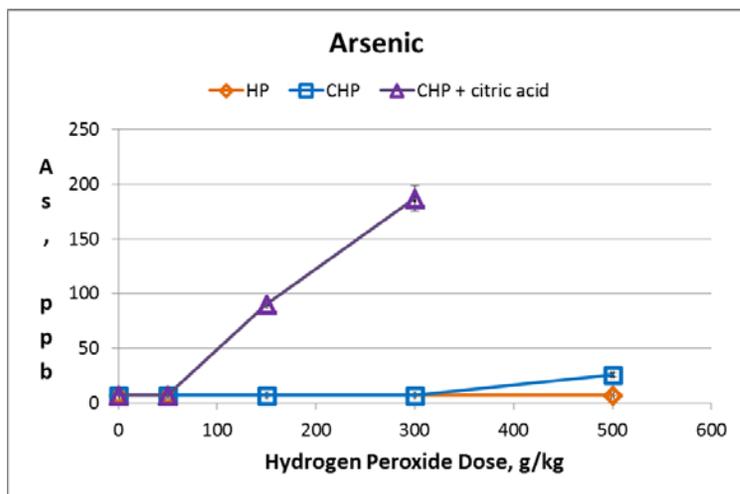
The oxidant dose dependent leaching of metals was also tested. Figure B.2 shows the mobilization of arsenic and cadmium, and Figure B.3 the release of lead and chromium. Both arsenic and cadmium mobilization increased with rising oxidant dose (Figure B.2), but while a significant arsenic leaching occurred at both low and high pH, cadmium release was only observed at low pH. Both these metals were released in higher amounts in the presence of the citric acid chelating agent. On the other hand, lead mobilization increased with rising oxidant dose only for select ISCO chemistries (Figure B.3). In addition, the relative impact of ISCO chemistries on lead release was oxidant dose-dependent. Chromium was the only metal that was impacted by all ISCO chemistries tested, including permanganate. In general, the release of most metals increased in the presence of the citric acid chelating agent in the iron-catalyzed persulfate and hydrogen peroxide applications. For persulfate, iron-activation resulted in more release for most metals than alkaline-activation (some exceptions included arsenic and vanadium).

Metals Mobilization Potential at ISCO Sites: pH-dependent Leaching Evaluation

Laboratory batch tests were also performed to evaluate the pH-dependent release of metals from select soils, i.e., Soils #1, 2, and 4 (see Table B.1). The same test conditions were used as in the metals mobilization screening evaluation (e.g., liquid to solid ratio of 10 to 1, see the above section for a description of the test conditions), but in this test the pH of the batch solutions was adjusted after the soils have been exposed to the oxidants for 48 hours. The target pH range was 3 to 11. The pH-dependent leaching was conducted for an additional 48 hours, after which the pH, ORP, and dissolved metals were measured.

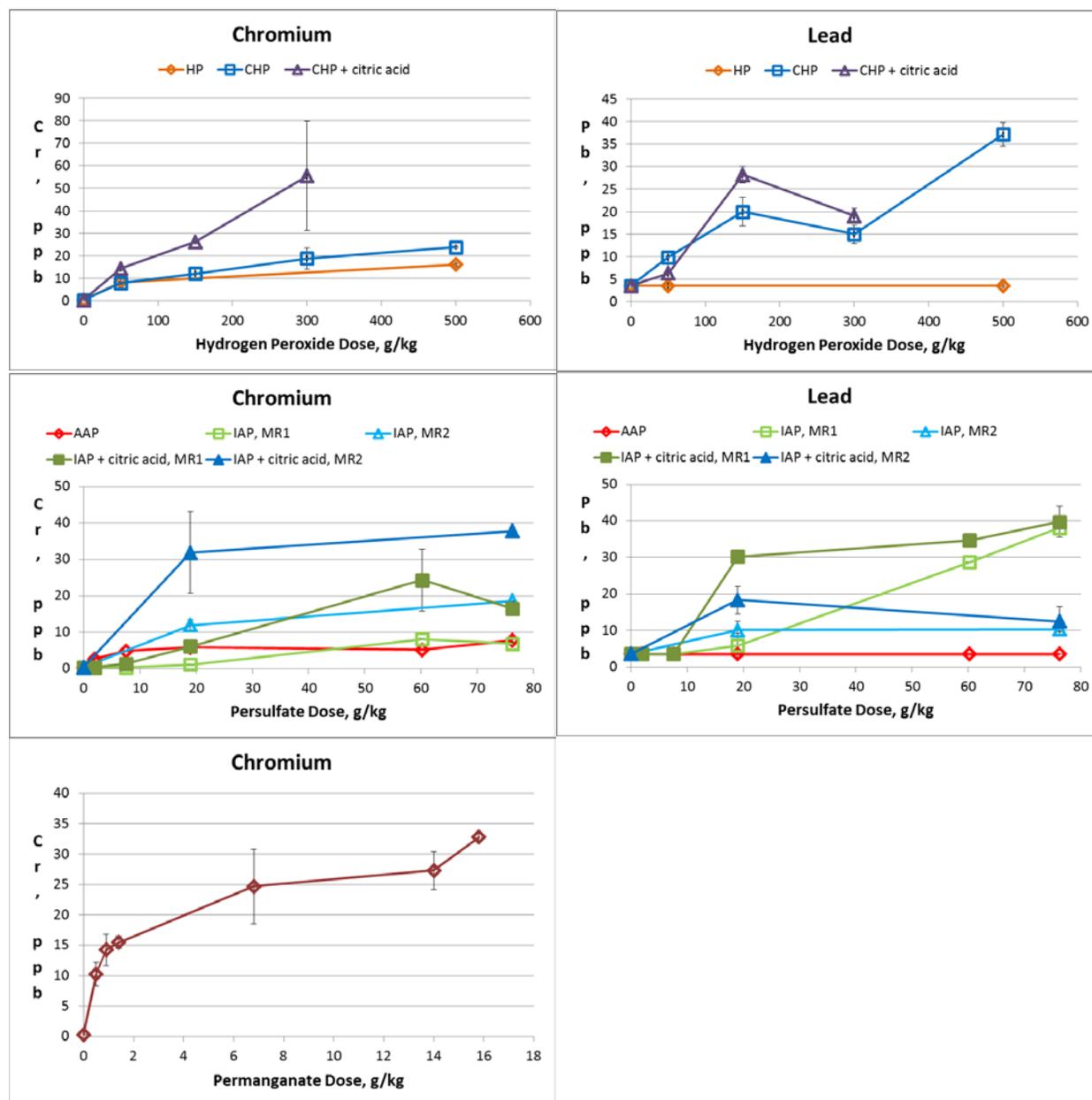
Figures B.4, B.5, and B.6 show the pH-dependent leaching of arsenic and chromium, cadmium and lead, and barium and cobalt, respectively. Arsenic and chromium mobilization increased in the presence of alkaline-activated persulfate above pH 8 in both Soils #1 and #4 (Figure B.4), as did lead release in Soil #1 (Figure B.5). Chromium release also increased in the presence of chelated iron-activated hydrogen peroxide and permanganate, the latter reagent contained 4.8 ppb of the metal, in both Soils #1 and #4 (Figure B.4). The leaching of cadmium and cobalt increased in the presence of catalyzed hydrogen peroxide in Soils #1 and #2, respectively, but only below pH 5 (Figure B.5) and 7 (Figure B.6), respectively. Lead release increased in the presence of chelated iron-activated persulfate in Soil #1 (Figure B.5); in the permanganate application lead originated from the reagent. On the other hand, barium mobilization decreased in the presence of catalyzed hydrogen peroxide and iron-activated persulfate below pH 6 in Soil #1 (Figure B.6), and in the alkaline- and iron-catalyzed persulfate applications in Soil #4, also below pH 6. Cobalt leaching also decreased in the presence of alkaline-activated persulfate, as well as permanganate below pH 4.5 in Soil #2. The pH was the controlling factor for other ISCO chemistries tested for these metals.

Figure B.2 The oxidant dose dependent leaching of Arsenic and Cadmium from Soil #1 exposed to various ISCO chemistries



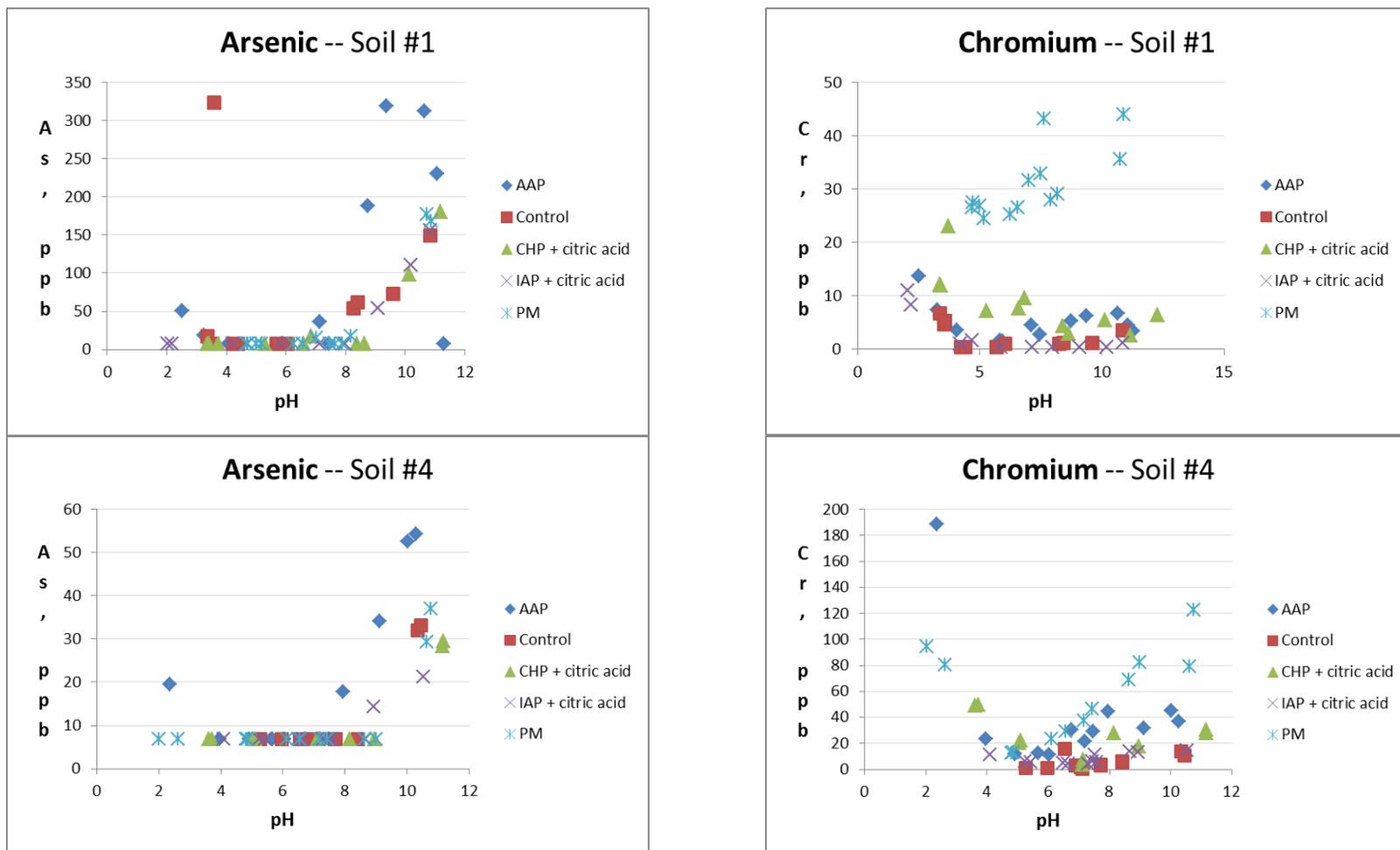
(HP = hydrogen peroxide, CHP = iron-activated hydrogen peroxide; IAP and AAP = iron- and alkaline-activated persulfate; MR = molar ratio of oxidant : Fe(II) : citric acid; MR1 = 100:1:2 and MR2 = 12.5:5:1).

Figure B.3 The oxidant dose dependent leaching of Chromium and Lead from Soil #1 exposed to various ISCO chemistries



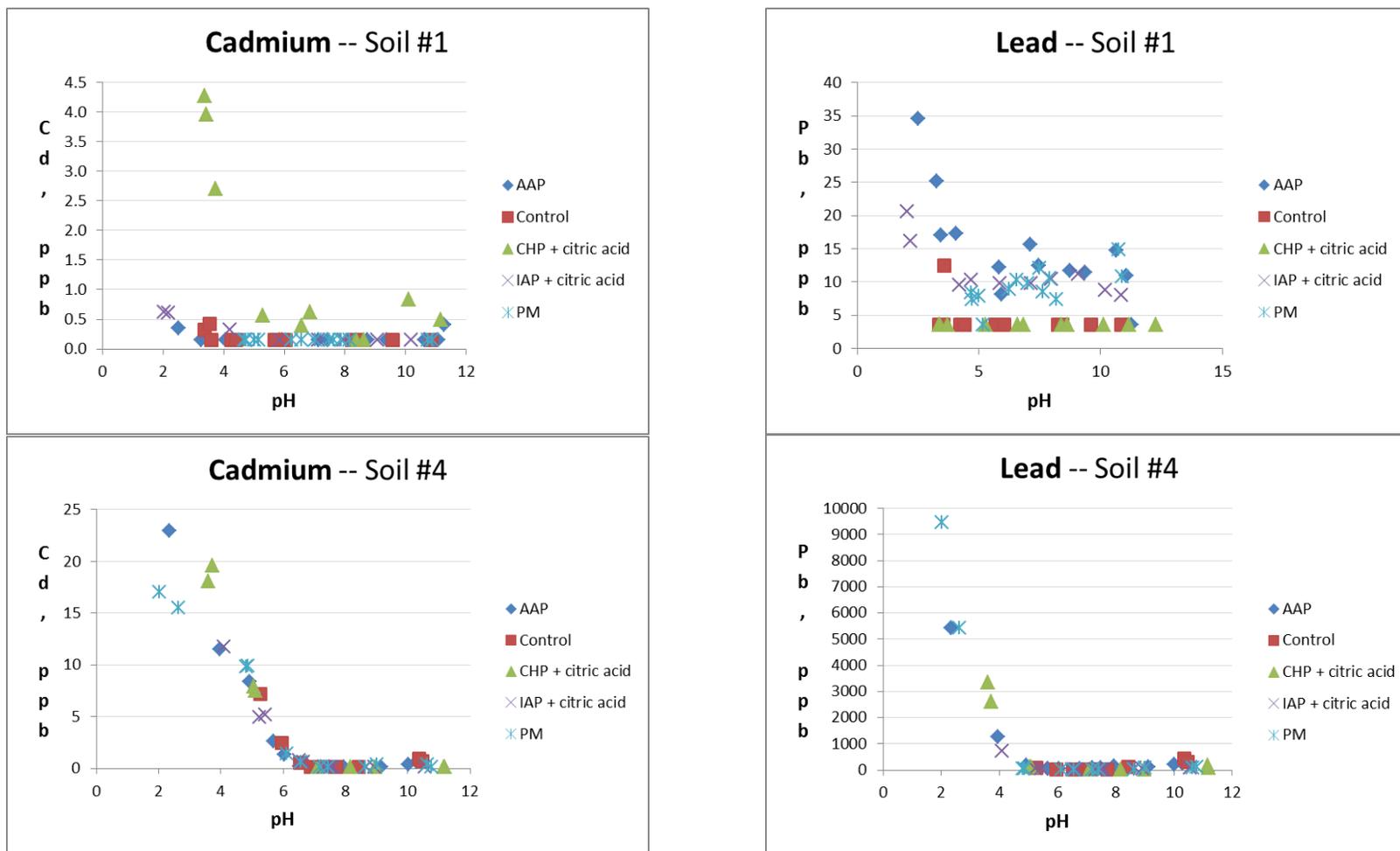
(HP = hydrogen peroxide, CHP = iron-activated hydrogen peroxide; IAP and AAP = iron- and alkaline-activated persulfate; MR = molar ratio of oxidant : Fe(II) : citric acid; MR1 = 100:1:2 and MR2 = 12.5:5:1; PM = permanganate).

Figure B.4 The pH-dependent release of Arsenic and Chromium in Soil #1 and #4 due to the application of various ISCO chemistries



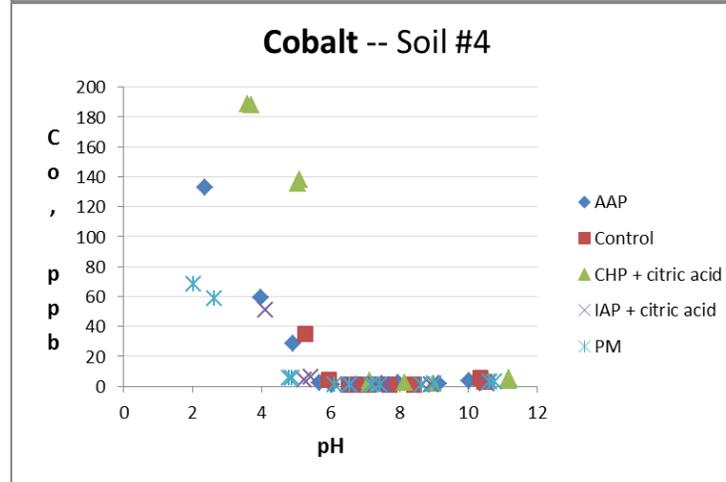
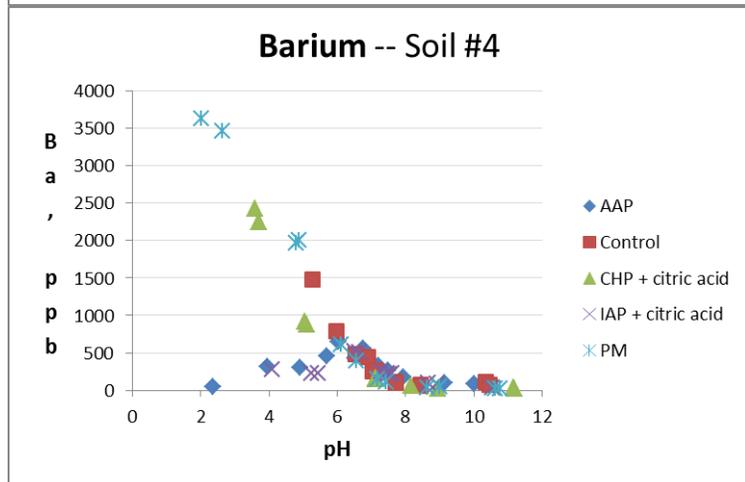
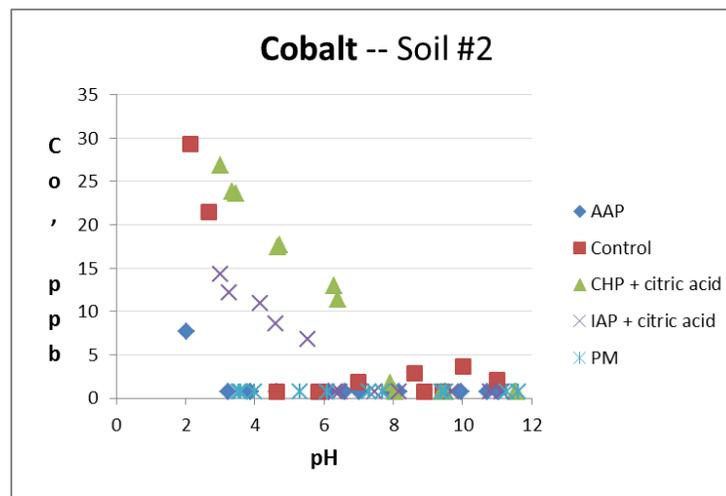
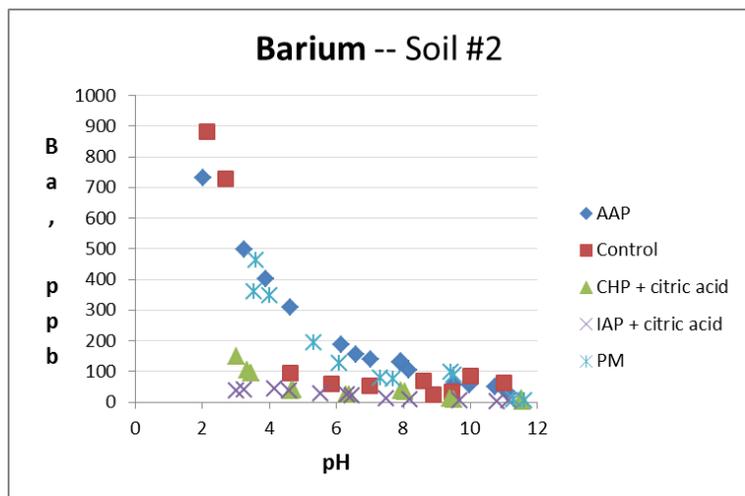
(AAP = alkaline-activated persulfate; CHP and IAP = iron-activated hydrogen peroxide and sodium persulfate, respectively; PM = permanganate); oxidant doses used are shown in Table 4.2.

Figure B.5 The pH-dependent release of Cadmium and Lead in Soil #1 and #4 due to the application of various ISCO chemistries



(AAP = alkaline-activated persulfate; CHP and IAP = iron-activated hydrogen peroxide and sodium persulfate, respectively; PM = permanganate); oxidant doses used are shown in Table 4.2.

Figure B.6 The pH-dependent release of Barium and Cobalt in Soil #2 and #4 due to the application of various ISCO chemistries



(AAP = alkaline-activated persulfate; CHP and IAP = iron-activated hydrogen peroxide and sodium persulfate, respectively; PM = permanganate); oxidant doses used are shown in Table 4.2.

References

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