CHAPTER 9

IN SITU CHEMICAL OXIDATION

Robert L. Siegrist,[1] Michelle Crimi,[2] Neil R. Thomson,[3] Wilson S. Clayton[4]
and Michael C. Marley[5]

[1]Colorado School of Mines, 80401 Golden, CO, USA; [2]Clarkson University, 13699 Potsdam, NY, USA; [3]University of Waterloo, Waterloo, ON, Canada, N2L 3G1; [4]TriHydro Corporation 80439 Evergreen, CO, USA; [5]XDD, 03885 Stratham, NH, USA

9.1 TECHNOLOGY DESCRIPTION

This section discusses the topic of *in situ* chemical oxidation (ISCO) including highlights of the overall principles and practices of ISCO for groundwater remediation. Much of the material in this section has been adapted from the recent book *In Situ Chemical Oxidation for Groundwater Remediation* (Siegrist et al., 2011).

9.1.1 Overview of ISCO

In situ chemical oxidation is one of the technologies that have the potential for cost effective remediation of soil and groundwater contaminated by organic chemicals (ITRC, 2005; Huling and Pivetz, 2006; Krembs et al., 2010; Tsitonaki et al., 2010; Siegrist et al., 2011). Many of the most prevalent organic contaminants of concern (COCs) at sites can be destroyed using a chemical oxidant such as catalyzed hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$), activated sodium persulfate ($Na_2S_2O_8$), ozone (O_3), or combinations of oxidants such as ozone and hydrogen peroxide or hydrogen peroxide and sodium persulfate. Under the right conditions, oxidants can transform and often mineralize many COCs including solvents (such as perchloroethene [PCE], trichloroethene [TCE], 1,1,1-trichloroethane [1,1,1-TCA], and 1,4-dioxane), fuels (such as benzene, toluene, methyl tertiary butyl ether), phenols (pentachlorophenol), polycyclic aromatic hydrocarbons (PAHs) (such as naphthalene, phenanthrene), explosives (trinitrotoluene) and pesticides (lindane). Degradation reactions tend to involve electron transfer or free radical processes with simple to complex pathways. Oxidation reactions typically follow second-order kinetics. The need for activation to generate reactive species and the sensitivity to matrix conditions, such as temperature, pH and salinity, vary with the different oxidants and specific contaminants.

An oxidant and amendments (if needed) can be delivered into a target treatment zone (TTZ) within the subsurface at varied concentrations and mass loading rates in liquid, gas or solid phases. Delivery has most commonly been accomplished through permeation by vertical direct-push injection probes or flushing by vertical groundwater wells (Figure 9.1) (Krembs et al., 2010). Other delivery approaches have included horizontal wells, infiltration galleries, soil mixing and hydraulic or pneumatic fracturing.

B.H. Kueper et al. (eds.), *Chlorinated Solvent Source Zone Remediation*,
doi: 10.1007/978-1-4614-6922-3_9, © Springer Science+Business Media New York 2014

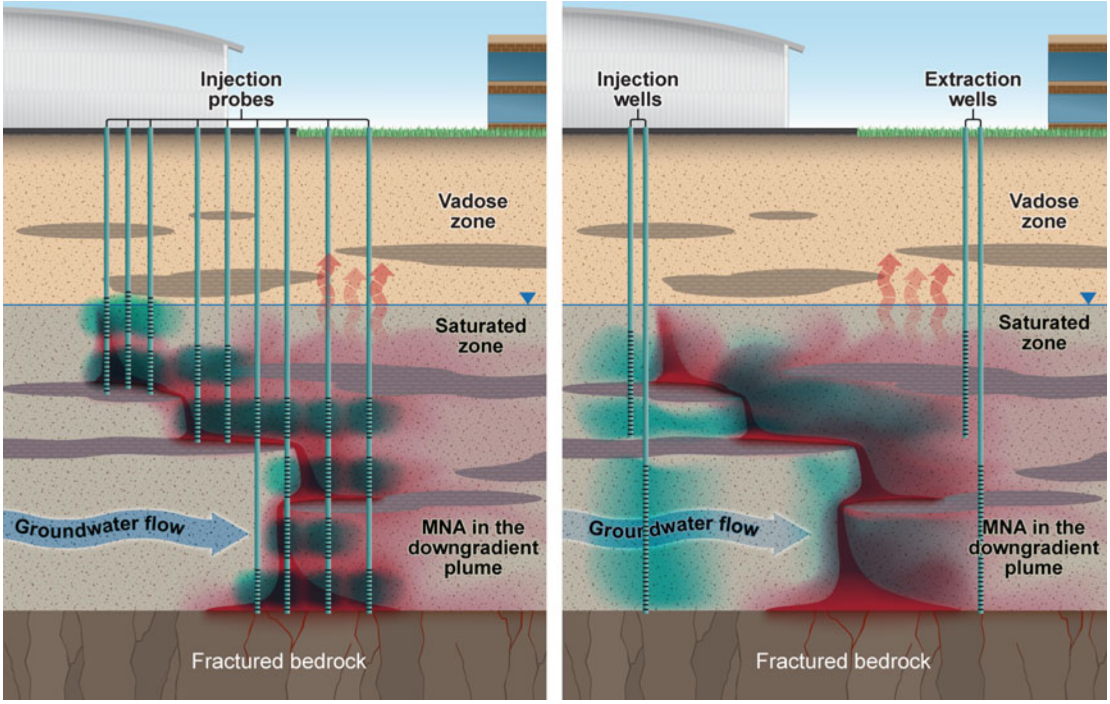


Figure 9.1. ISCO using (*left*) direct-push injection probes or (*right*) well-to-well flushing to deliver oxidants (shown in *blue*) into a TTZ of groundwater contaminated by DNAPL compounds (shown in *red*) (Siegrist et al., 2011).

9.1.2 Historical Evolution of ISCO

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

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

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

To advance the science and engineering of ISCO and resolve questions regarding its design and performance, ISCO research and development efforts were escalated during the early 2000s. This research was catalyzed in a large part by the promising potential of ISCO and growing interest in its use, notably at Department of Defense (DoD) sites across the country. Around 2002, a major ISCO research program was launched within DoD's Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP), as part of its *Dense Nonaqueous Phase Liquid Source Zone Cleanup focus area.*[1]

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

- COC oxidation chemistry and treatment (Gates-Anderson et al., 2001; Jung et al., 2004; Qiu et al., 2004; Smith et al., 2004; Watts et al., 2005a; Forsey et al., 2010)
- Oxidant interactions with subsurface media (Siegrist et al., 2002; Crimi and Siegrist, 2003, 2004a, b; Anipsitakis and Dionysiou, 2004; Shin et al., 2004; Jung et al., 2005; Monahan et al., 2005; Mumford et al., 2005; Bissey et al., 2006; Jones, 2007; Teel et al., 2007; Sun and Yan, 2007; Sirguey et al., 2008; Urynowicz et al., 2008; Woods, 2008; Xu and Thomson, 2008, 2009)
- Destruction of DNAPLs (Crimi and Siegrist, 2005; Heiderscheidt, 2005; Kim and Gurol, 2005; Urynowicz and Siegrist, 2005; Watts et al., 2005b; Siegrist et al., 2006; Smith et al., 2006; Heiderscheidt et al., 2008a; Petri et al., 2008)
- Examination of newer oxidants (Liang et al., 2004a, b; Crimi and Taylor, 2007; Waldemer et al., 2007; Liang and Lee, 2008)
- Oxidant transport processes and deliverability (Choi et al., 2002; Lowe et al., 2002; Struse et al., 2002; Lee et al., 2003; Tunnicliffe and Thomson, 2004; Heiderscheidt, 2005; Ross et al., 2005; Zhang et al., 2005; Petri, 2006; Hønning et al., 2007; Heiderscheidt et al., 2008a; Petri et al., 2008; Smith et al., 2008; Christiansen, 2010, 2011; Christiansen et al., 2010; Silva, 2011)
- Combining ISCO with other remedies (Sahl, 2005; Dugan, 2006; Sahl and Munakata-Marr, 2006; Sahl et al., 2007; Dugan et al., 2010)
- Treatability test methods (Haselow et al., 2003; Mumford et al., 2004; ASTM, 2007)
- Formulation of mathematical models and decision support tools (Kim and Choi, 2002; Heiderscheidt, 2005; Heiderscheidt et al., 2008b)

Research efforts have revealed that the successful use of ISCO for remediation of contaminated soil and groundwater fundamentally depends on the reaction chemistry of the oxidant used and its ability to degrade the COCs. Success also depends on effective delivery of

---

[1] http://www.serdp.org/Featured-Initiatives/Cleanup-Initiatives/DNAPL-Source-Zones, January 24, 2014

oxidants into the subsurface, which is determined by the oxidant reactive transport under the hydrogeological and geochemical conditions present. Oxidant reaction chemistry (both with the COCs and with natural organic matter [NOM] and minerals) and subsurface transport affect ISCO application, COC destruction, and cost effectiveness. In addition, the application of ISCO can be affected by, and can also effect changes in, the pre-ISCO subsurface conditions (such as groundwater flow direction and velocity, redox potential [Eh], pH, temperature, dissolved organic carbon), which should be considered and accounted for during ISCO system design and implementation.

9.1.3 Retrospective Analysis of ISCO Performance and Costs

Field applications of ISCO have continued to grow over the past decade. These field experiences have enabled a retrospective analysis of ISCO system design features and site conditions and the factors affecting performance and cost. Of 242 ISCO projects examined by Krembs et al. (2010), PCE or TCE were the targeted COCs at 70% of the sites, the subsurface conditions were characterized as permeable at 75% of the sites and oxidants were delivered using permanent or temporary injection wells at 70% of the sites. For 99 full-scale ISCO projects that attempted to meet a specific goal and reported success, the results were as follows: 21% of 28 projects attempting to achieve drinking water maximum contaminant limits (MCLs) met this goal (all of these projects were characterized by lower concentrations without reported nonaqueous phase liquids [NAPLs]); 44% of 25 projects attempting to achieve alternative concentration limits (ACLs) met this goal; 33% of six projects attempting to reduce the COC mass by a certain percentage met this goal; 82% of 34 projects attempting to reduce the COC mass and/or time to cleanup met this goal; and 100% of six projects attempting to evaluate effectiveness and optimize future injections met this goal.

Krembs (2008) reported the median total cost for 55 ISCO projects to be $220,000; the median unit cost was $94 per cubic yard (cy) ($123 per cubic meter) treated based on 33 projects with unit cost data. McDade et al. (2005) reported median and unit costs of $230,000 and $125/cy ($163 per cubic meter), respectively, for 13 ISCO projects. It is important to recognize that the cost of an ISCO project can vary by an order of magnitude or more depending on various factors. For example, sites with fuel hydrocarbons and permeable subsurface conditions typically cost less than those with DNAPLs or complex subsurface conditions. High unit costs can also result where ISCO has been used to treat relatively smaller source zones.

The effectiveness of ISCO varies: at some sites, ISCO has been applied and the destruction of the target COCs has occurred, enabling cleanup goals to be met in a cost effective and timely manner, whereas at other sites, ISCO applications have had uncertain or unsatisfactory treatment performance. Poor ISCO performance often has been attributed to application of an inadequate oxidant dose or volume, inadequate oxidant delivery caused by low permeability zones and formation heterogeneity, and excessive oxidant loss due to interaction with natural subsurface materials or the presence of large masses of DNAPLs (Siegrist et al., 2001, 2006, 2008a). In some applications, concerns have arisen over secondary effects, such as mobilization of metals, loss of well screen and formation permeability, and gas evolution and fugitive emissions, as well as health and safety practices (Siegrist et al., 2001; Crimi and Siegrist, 2003; Krembs, 2008; Krembs et al., 2010).

Rebound is a condition where post-treatment concentrations of target COCs in groundwater within a TTZ return to levels near or even above those present prior to treatment. Rebound is a relatively common occurrence with ISCO. It may be a negative condition or could reflect an inherent shortcoming of ISCO or a site-specific performance deficiency. The rebound observed at an ISCO treated site can be beneficial if it is used in an observational approach to refine the conceptual site model (CSM) and refocus subsequent treatment. The use of ISCO can be viewed as an ongoing, iterative process that will take advantage of contaminant rebound rather than view it as an indication that the technology was inappropriate for a site or was applied improperly. It is noted that rebound also can occur with other approaches and technologies that depend on injection of remedial amendments.

9.1.4 ISCO System Selection, Design, and Implementation

In situ chemical oxidation system selection, design and implementation practices should rely on a clear understanding of ISCO and its applicability to a given set of contaminant and site conditions to achieve site-specific remediation objectives. A number of key issues may be relevant and need to be addressed regardless of the oxidant and delivery system being employed, including: (1) amenability of the target COCs to degradation by oxidants; (2) effectiveness of the oxidant for NAPL destruction; (3) requirements for effective implementation (oxidant dose, concentration, volume delivered, method of delivery) for a given TTZ in a given subsurface setting; (4) nonproductive oxidant loss due to interactions with NOM, reduced inorganic species, and some mineral phases in the subsurface; (5) nonproductive oxidant consumption due to auto-decomposition reactions and free radical scavenging reactions; (6) potential adverse effects (mobilizing metals such as chromium, forming toxic byproducts, reducing formation permeability, generating off-gases and heat) and (7) potential to combine ISCO with other remediation technologies and approaches (Siegrist et al., 2011).

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

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

The ISCO systems that can be, and have been, applied in the field are highly varied in their features. Different oxidants and additives (such as stabilizers or activators) have been used. Concentrations and injection flow rates can vary widely, and a variety of subsurface delivery methods can be employed. In addition, overall site remediation goals and regulatory constraints may influence the remediation objectives established for the ISCO technology. To improve the confidence level in the choices and decisions made, treatability studies and field-scale pilot tests are frequently necessary. If ISCO is selected for a site, remedial design and system construction must be accomplished. Finally, ISCO operation and performance monitoring ensues. Given the properties of chemical oxidants, the use of ISCO requires diligent attention to safety and waste management issues (Siegrist et al., 2011). Eventually site closure can be achieved through ISCO alone or in conjunction with another remediation technology or approach.

9.2 KEY CONCEPTS OF ISCO AND DNAPL SOURCE ZONES

While the previous section highlighted the general principles and practices of ISCO for remediation of soil and groundwater, there has been great interest in the potential of ISCO to remediate groundwater where contamination includes DNAPL source zones present in a variety of subsurface geological media. The theoretical basis for the degradation of DNAPL residuals by ISCO is well established, *but* its cost effective realization generally depends on several factors: (1) susceptibility of DNAPL organics to destruction using chemical oxidants, (2) rate and extent of interphase mass transfer of the DNAPL, (3) ability to deliver and transport the oxidant in the subsurface, (4) effects of subsurface conditions on ISCO reactions and (5) ISCO effects on subsurface permeability and biogeochemistry. These issues are discussed in detail in the following sections.

9.2.1 Chemically Reactive Zones and Mass Transfer

In situ chemical oxidation involves the creation of a chemically reactive subsurface environment. This reactive environment is one where a chemical oxidant is introduced with the sole purpose of oxidizing the identified target COCs. By definition, the reaction process results in the oxidation state of a target COC increasing. For example, the oxidation of TCE involves a half reaction where the valence state of carbon is increased from +I to +IV as shown by Equation 9.1 and the associated oxidant is reduced (lowering of oxidation state) as noted below in Section 9.2.2:

$$C_2Cl_3H + 4H_2O \rightarrow 2CO_2 + 3Cl^- + 9H^+ + 6e^- \qquad \text{(Eq. 9.1)}$$

Chemical oxidation can involve more than electron transfer (hydrogen transfer, hydride transfer, oxygen donation) and thus includes all reactions that convert a compound to a higher oxidation state (Stewart, 1964). *In situ* chemical oxidation is an *in situ* mass destructive technology where the objective is to create reaction conditions so that when the COCs are either contacted or intercepted, they are immobilized or degraded into nontoxic end products. The underlying reaction mechanisms and pathways can be very complex and in many cases are unknown. Complete mineralization to CO_2 and H_2O may not occur. Reaction intermediates, which form temporally before they are oxidized to end products, are difficult to identify. Forsey et al. (2010) indicate that ketones and carboxylic acids are potential oxidation reaction end products that may form during the oxidation of coal tars with permanganate. In some cases these end products are nontoxic and can be used as a carbon source for indigenous microbial communities.

A thermodynamic analysis can be used to determine the feasibility of a reaction to take place, but the results provide no information relating to the oxidation reaction rate or kinetics (Schwarzenbach et al., 1993). In some cases the reaction may be deemed feasible, but the kinetics will be far too slow to be useful. In general, the reaction between a chemical oxidant and target COC can be described by a second-order kinetic expression as given by Equation 9.2 (Siegrist et al., 2011):

$$\frac{dC_{COC}}{dt} = -k_{ox}[C_{COC}][C_{ox}] \qquad \text{(Eq. 9.2)}$$

where C_{COC} and C_{ox} are the concentration of the COC and the oxidant, respectively, and k_{ox} is the second-order rate coefficient with respect to the organic compound. As shown by Equation 9.2, the rate of destruction of the COC depends not only on the reaction rate coefficient k_{ox} but also on the product of the concentration of the COC and the oxidant.

To maximize the chemical oxidation reaction, the concentration of the oxidant needs to remain elevated. This can be controlled, in part, by system design. However, as the concentration of the target COC decreases, so will the overall oxidation rate. Second-order rate coefficients for most environmentally relevant DNAPL compounds dissolved in water have been experimentally determined (see IscoKin database at http://cgr.ebs.ogi.edu/iscokin/; accessed January 24, 2014). Reaction rate coefficients are sensitive to temperature variations and pH conditions (Schwarzenbach et al., 1993).

While the *in situ* destruction of DNAPL contaminants (such as PCE and TCE) is one key attribute offered by ISCO, the second attribute is that this technology has the ability to increase mass transfer from DNAPL contaminated regions. There is potential for gas–NAPL or gas–solid reactions, but nearly all reactions of interest that occur between a chemical oxidant and a target organic compound in groundwater take place in the aqueous phase and not in the DNAPL phase. Thus, DNAPL dissolution or mass transfer from the DNAPL phase to the aqueous phase is extremely important since it will, in large part, control the degree of mass destruction and hence source zone treatment effectiveness. The rate at which constituents dissolve from the DNAPL determines the dissolved phase plume concentrations and its longevity. The presence of a DNAPL results in dissolved phase DNAPL constituents that create a concentration gradient across a stagnant boundary layer between the DNAPL and the bulk aqueous solution (Figure 9.2). The larger and more sustained the concentration gradient, the greater the mass of DNAPL depleted.

The mass transfer of a single component DNAPL into the aqueous phase is generally expressed by a macroscopic variation of the stagnant film model given by Equation 9.3 (Schwarzenbach et al., 1993):

$$\frac{dC_{aq}}{dt} = -k_{diss}\left(C^* - C_{aq}\right) \qquad \text{(Eq. 9.3)}$$

where C_{aq} is the aqueous concentration of the COC, C^* is the aqueous solubility limit and k_{diss} is the lumped mass transfer or dissolution rate coefficient. In a porous medium, the lumped mass transfer rate coefficient cannot be determined from first principles, and hence, various methods have been developed to estimate it from system parameters such as pore size distribution metrics, DNAPL saturation, molecular diffusion coefficient and groundwater velocity (Siegrist et al., 2011). As shown by Equation 9.3, the rate at which DNAPL mass is depleted is a product of the dissolution rate coefficient and the concentration difference or gradient between C^* and C_{aq}. Oxidation reactions in the aqueous phase can decrease the concentration of the DNAPL constituents in the bulk solution and, thus, increase or steepen the concentration gradient, which in turn will increase the overall rate of DNAPL mass removal from the system. Results from laboratory studies have shown that a 6 to 10 times increase in the

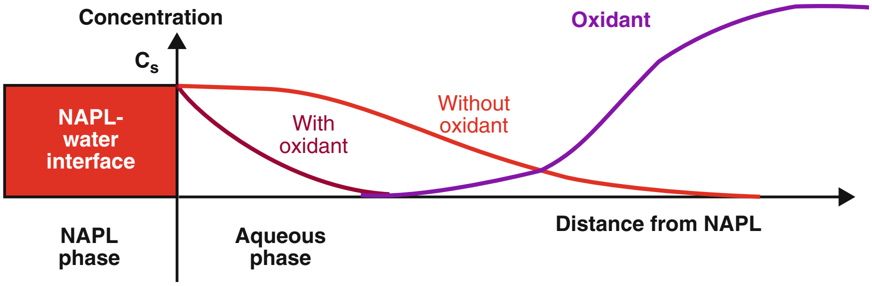


Figure 9.2. Schematic of the dissolved phase concentration gradients near a DNAPL/aqueous phase interface with and without an oxidant present in close proximity.

mass transfer rate is possible to achieve when a DNAPL residual or pool is treated using permanganate (Schnarr et al., 1998; MacKinnon and Thomson, 2002). Research with catalyzed hydrogen peroxide (CHP) has similarly demonstrated increases in mass transfer rates (Watts et al., 2005b; Smith et al., 2006).

In regions of the DNAPL source zone where preferential flow pathways and non-advective locations are present, diffusive dominated transport is the principal mechanism for the migration of DNAPL compounds out of these locations and for the migration of oxidants into these locations. Persistent chemical oxidants, those that are stable in the subsurface for an extended period of time, are particularly advantageous in these situations. When delivered into the treatment zone by way of the preferential flow pathways, these oxidants can diffuse from a preferential pathway into more non-advective regions driven by an oxidant concentration gradient (Figure 9.3). This is in the opposite direction of the gradient associated with the aqueous DNAPL constituents. This counter-diffusion, or two-way diffusion process, increases diffusive mass transfer by decreasing the distance between the DNAPL/aqueous phase interface and the zone where the concentrations of dissolved DNAPL compounds have been reduced as a result of oxidation. Favorable mass transfer rate enhancements have been estimated for these situations, assuming that the chemical oxidant is persistent.

9.2.2 Oxidant Properties

The current chemical oxidants in widespread use are hydrogen peroxide (H_2O_2), potassium or sodium permanganate ($KMnO_4$, $NaMnO_4$), sodium persulfate ($Na_2S_2O_8$), and ozone (O_3). Siegrist et al. (2011) provide a comprehensive overview of these oxidants including chemistry principles and contaminant treatability. The following tables provide insights into some of the key properties of these oxidants. Table 9.1 provides some characteristics of the chemical oxidants in use, while Table 9.2 lists reactive species along with their respective standard electrode potential.

9.2.2.1 Hydrogen Peroxide

Hydrogen peroxide is a strong oxidant that has a high standard reduction potential and is delivered into a source zone as a reagent solution (Table 9.1). Hydrogen peroxide has the potential for direct oxidation of many organic compounds; however, the reaction kinetics are too slow for use (Watts and Teel, 2005). When catalyzed, H_2O_2 can generate a wide range of

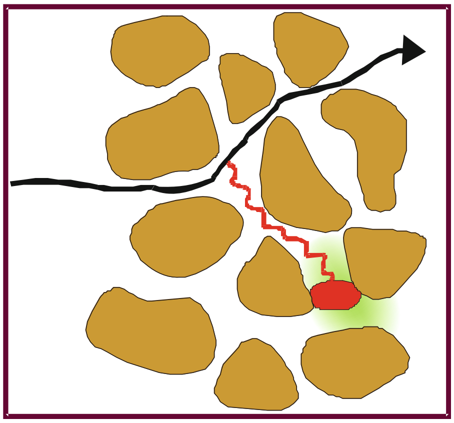


Figure 9.3. Illustration of the two-way diffusion process occurring between a preferential flow pathway (*black arrow*) and an isolated DNAPL residual (*red*).

Table 9.1. Characteristics of Chemical Oxidants Used for Destruction of Organic Contaminants (adapted from Huling and Pivetz, 2006, as presented in Siegrist et al., 2011)

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

Table 9.2. Reactive Species and Their Electrode Potentials (adapted from Huling and Pivetz, 2006, as presented in Siegrist et al., 2011)

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

free radicals and other reactive species that can attack the target organic compound. Hence, hydrogen peroxide is usually applied so that it is catalyzed to generate free radicals such as $OH^\bullet$ (Table 9.1). This can be accomplished by coinjection of a catalyst (such as $FeSO_4$) or through H_2O_2 interactions with naturally occurring minerals. The reactive species formed in a CHP system include oxidants and in some cases reductants. A CHP system should not be confused with the classic Fenton's reagent (Walling, 1975) where dilute hydrogen peroxide and ferrous iron are combined under acidic pH conditions to produce hydroxyl radicals as given by Equation 9.4:

$$H_2O_2 + Fe^{+2} \rightarrow Fe^{+3} + OH^- + OH^\bullet \qquad \text{(Eq. 9.4)}$$

Research has shown that when hydrogen peroxide and ferrous iron are applied *in situ* using a significantly higher H_2O_2 concentration, a much more complex set of reactions occurs (Watts and Teel, 2005). A CHP system involves numerous reactive species and mechanisms that result in significant contaminant transformation or degradation. Notable reactive species are the hydroxyl radical, superoxide anion, perhydroxyl radical and hydroperoxide anion

(Siegrist et al., 2011). Radicals have an unpaired electron and are highly reactive and unstable. Thus, their *in situ* transport distances are short. Therefore, for a CHP system to treat a DNAPL source zone effectively, it must be applied directly in the source zone given that limited transport of the reactive species will occur.

Many stabilizers (chelating agents) have been considered as a means to enhance the transport of hydrogen peroxide and ferrous iron *in situ* (Watts et al., 1999, 2007; Kakarla and Watts, 1997). Ethylenediaminetetraacetic acid (EDTA) is one of the most popular chelating agents used to reduce the decomposition of hydrogen peroxide by suppressing the catalytic activity of naturally occurring transition metals (Jones and Williams, 2002; Ramo, 2003). Sun and Pignatello (1992) assessed the effectiveness of 50 chelating agents and determined that nitrilotriacetic acid (NTA) and hydroxyethyliminodiacetic acid (HEIDA) were the most effective chelating agents for iron. While currently used or proposed chelating agents are poorly biodegradable (e.g., EDTA), associated with health issues (e.g., NTA is a carcinogen), or not very effective (e.g., citrate), Xu and Thomson (2007) explored a newly available and environmentally friendly chelating agent, ethylenediamine disuccinate (EDDS), to stabilize hydrogen peroxide. They found that EDDS was able to reduce hydrogen peroxide decomposition rates in the presence of various aquifer materials by close to 40% in column trials. Schmidt et al. (2011) reported that phytate (25 millimolars [mM]) was effective as a stabilizer for transport of H_2O_2 through iron-coated sand, resulting in H_2O_2 concentrations two orders of magnitude greater than without phytate.

Rapid destruction of DNAPLs, such as TCE, PCE and carbon tetrachloride, has been demonstrated with CHP systems (Watts and Teel, 2005; Yeh et al., 2003). Smith et al. (2004, 2006) demonstrated that the superoxide and hydroperoxide anions are the reactive species responsible for the degradation of some recalcitrant organic contaminants.

Watts et al. (1999) reported that some reactive species formed by CHP may enhance desorption of sorbed contaminants. Corbin et al. (2007) isolated the reactive species in CHP reactions that are responsible for enhanced contaminant desorption – the superoxide species. Therefore, some of the reaction oxygen intermediates formed during CHP oxidation, including superoxide, may act as surfactants or have other properties that enhance solubilization of hydrophobic contaminants. Organic intermediates produced by contaminant degradation reactions may contribute as well. Ndjou'ou and Cassidy (2006) reported that the organic intermediates generated from CHP oxidation of some complex organic wastes, such as NAPL-phase fuel hydrocarbons, may produce organic surfactants as intermediates during the reaction, and these can even become concentrated enough in solution that they exceed the critical micelle concentration. Thus, enhanced solubilization of the remaining contaminant may occur, increasing its availability for aqueous phase degradation reactions.

9.2.2.2 Potassium Permanganate

Potassium permanganate, which is the most commonly used reagent in ISCO applications, is a crystalline solid that is derived from mined potassium ores. Neutral permanganate solutions prepared with water are relatively stable because water is the only solvent that reduces permanganate very slowly in the presence of manganese dioxide (or dust). Manganese species have potential valence states ranging from +1 to +7, of which the +2, +4 and +7 states are the only ones that are stable over a wide range of acidity. Manganese in permanganate has the highest oxidation state. Permanganate is typically delivered into a source zone as a reagent solution, but other applications have used the solid form (see Siegrist et al., 1999).

Because permanganate is highly reactive with compounds containing C=C bonds, the most common use of permanganate-based ISCO is to remediate groundwater contaminated by PCE, TCE, dichloroethene (DCE), and vinyl chloride (VC) (Siegrist et al., 2001). In addition to chlorinated ethenes, recent studies have shown that permanganate is able to oxidize other contaminants such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), some PAHs and pesticides (Tollefsrud and Schreier, 2002; Adam et al., 2004; Waldemer and Tratnyek, 2006; Forsey et al., 2010). Oxidation of target COCs by permanganate occurs by electron transfer and no radicals are involved. Thus, the reaction rate is slower and the range of reactivity is limited.

The most common permanganate reaction employed in environmental engineering is the complete reduction of permanganate (Mn^{7+}) to manganese dioxide (MnO_2) (Mn^{4+}) (Schnarr et al., 1998; Siegrist et al., 2001; Crimi and Siegrist, 2004b), which is a three-equivalent reaction as shown in Equation 9.5. This reaction proceeds differently as a function of pH as shown in Equations 9.5–9.7 (Siegrist et al., 2011):

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2(s) + 4OH^- \quad 3.5 > pH < 12 \tag{Eq. 9.5}$$

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad pH < 3.5 \tag{Eq. 9.6}$$

$$MnO_4^- + 1e^- \rightarrow MnO_4^{2-} \quad pH > 12 \tag{Eq. 9.7}$$

An important product of the reduction of permanganate is manganese oxide, which forms at the point of reaction. Manganese oxide is a water insoluble solid that is highly polar and tends to coagulate by aggregation to form hydrated colloids with high water contents (Perez-Benito and Arias, 1991). The degree to which the colloids will aggregate depends on the presence of other ions as well as the system Eh and pH (Morgan and Stumm, 1963). Laboratory research has demonstrated that the precipitation of manganese oxides and the formation of CO_2, another reaction product, decreased the hydraulic conductivity between 50 and 90% (Schroth et al., 2001) in sand-packed columns, caused flow divergence around regions of higher DNAPL saturations in a two-dimensional physical model (Li and Schwartz, 2004), and resulted in pore plugging and the formation of a distinct manganese oxide layer in the vicinity of the NAPL that reduced the post-treatment mass transfer (Mackinnon and Thomson, 2002; Conrad et al., 2002; Urynowicz and Siegrist, 2005). The longevity of the trapped CO_2 is temporary, but the manganese oxide deposition is believed to be stable as long as the geochemical conditions are conducive ($pH > 3$; Appelo and Postma, 1999). As a result, some have hypothesized that treatment of a DNAPL source zone by permanganate will initially result in some degree of mass destruction until manganese oxide deposition has reached a level to impact hydraulic conductivity and mass transfer. When this point is reached, the manganese oxides will adversely affect the hydraulic performance of the delivery system and/or the rate of mass destruction will decrease.

It has been observed, however, that the deposition of MnO_2 is dependent on the architecture of the DNAPL source zone, the concentration of permanganate delivered and the velocity of the oxidant-amended groundwater across the DNAPL–water interface (Petri et al., 2008; Heiderscheidt et al., 2008a, b). Research findings revealed lower oxidant concentrations and higher flow velocities can result in more dispersed deposition of MnO_2 and limited impacts on mass transfer and DNAPL destruction. Other research has explored the use of additives (hexametaphosphate) to stabilize the MnO_2 solids and limit their deposition at DNAPL–water interfaces (Crimi et al., 2009).

9.2.2.3 Sodium Persulfate

Sodium persulfate is the most common and effective form of persulfate salt for ISCO applications and is delivered into a source zone as a reagent solution. The solubility of sodium persulfate that controls the amount of oxidant mass that can be delivered is high (730 grams per liter [g/L]), although density-driven transport is a concern at higher oxidant concentrations.

The persulfate anion is not affected by sorption (Liang et al., 2008), and it is more stable in the subsurface as compared to peroxide and ozone (Brown and Robinson, 2004; Johnson et al., 2008; Sra et al., 2010).

The chemistry of persulfate is quite complex and not fully understood. Oxidation by persulfate at ambient conditions may occur either by direct oxidation (Equation 9.8) or through the activation of persulfate to sulfate radicals using ferrous iron (Equation 9.9), heat (Equation 9.10), hydrogen peroxide (Equation 9.11), or hydroxide (i.e., base) (Equation 9.12) (House, 1962; Huang et al., 2002):

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-} \tag{Eq. 9.8}$$

$$S_2O_8^{2-} + 1e^- \rightarrow SO_4^{2-} + SO_4^{\bullet-} \tag{Eq. 9.9}$$

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-} \tag{Eq. 9.10}$$

$$S_2O_8^{2-} + OH^{\bullet} \rightarrow SO_4^{2-} + SO_4^{\bullet-} + \frac{1}{2}O_2 + H^+ \tag{Eq. 9.11}$$

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + OH^{\bullet} \tag{Eq. 9.12}$$

Direct persulfate oxidation is not able to destroy some organic contaminants such as saturated chlorinated solvents and normal chain alkanes (Liang et al., 2008). A higher reaction activation energy is required for persulfate to react with these organic compounds. Compared to unactivated persulfate, activated persulfate reacts with a wider range of organic compounds through production of sulfate and hydroxyl free radicals. As shown in Equations 9.9–9.11, sulfate radicals are produced as a result of persulfate activation and initiate a chain of reactions that may form other free radicals and other highly oxidative species such as the hydroxyl radical, superoxide anion, perhydroxyl radical and hydroperoxide anion (Furman et al., 2010; Siegrist et al., 2011). These types of reactive species are very similar to the suite of reactive species generated in a CHP system. However, for activated persulfate, the reactive species generated can vary with the activation approach employed. A free radical reaction, in general, involves a chain of initiation, propagation and termination reactions. Kolthoff and Miller (1951), House (1962) and Liang et al. (2004a, b; 2007) have studied this three-step chain reaction. As a result of persulfate activation and initiation of radical-based chemical reactions, the reaction rate of organic compound degradation can be significantly increased until all reactions are terminated (Liang et al., 2007).

Persulfate has been shown to be an effective oxidant for a variety of DNAPL compounds including chloroethenes (PCE, TCE, DCE, VC). The reactivity of persulfate with halogenated aliphatics is variable and appears to depend on the nature of the carbon bonding, the degree of halogenation and the persulfate activation approach. Literature suggests that persulfate is able to degrade polychlorinated biphenyls (PCBs) and some PAHs (Yukselen-Aksoy et al., 2010).

9.2.2.4 Ozone

Ozone is a gas that is delivered to the TTZ as a mixture with ambient air or pure oxygen. In the saturated zone, the gas distribution is controlled by the same processes that occur during *in situ* air sparging (IAS) (Thomson and Johnson, 2000). Oxidation of the target COC can occur in the gas channel after the contaminant has volatized (gas phase oxidation) or in the aqueous phase once the ozone has dissolved (aqueous phase oxidation). In either case the controlling process is mass transfer between the gas and aqueous phase, which is limited to very near the gas phase channels (Braida and Ong, 2001). Thus, for successful treatment of a DNAPL source zone, closely spaced gas channels are required within the TTZ, and ozone gas delivery must normally occur for an extended period of time (several months).

Oxidation can occur by direct reaction with ozone or by the hydroxyl radical that forms from ozone during the following decomposition reaction (Siegrist et al., 2011):

$$O_3 + H_2O \rightarrow O_2 + 2OH^\bullet \qquad \text{(Eq. 9.13)}$$

When hydrogen peroxide is present in the water or coinjected into the source zone along with ozone (as used in a peroxone ISCO system), then a more aggressive treatment system is possible (Siegrist et al., 2011). Ozone is a short-lived oxidant with a relatively low solubility and high reactivity with a range of nontarget compounds. With minimal transport in the aqueous phase, ozone has to be injected directly into a DNAPL source zone to enable effective treatment.

9.2.3 Oxidant Reactions in the Subsurface

The oxidants in common use for ISCO can react with DNAPL compounds that are prevalent in DNAPL source zones (such as PCE, TCE, DCE). In addition, naturally occurring reductants and catalysts at many contaminated sites can be reactive and, thus, influence oxidant persistence. Typically, the role of the aquifer solids overshadows that of the dissolved groundwater species. Inorganic species containing iron (Fe), manganese (Mn), sulfur (S) and the NOM associated with the aquifer solids are usually of concern. The possibility of multiple inorganic species, as well as a range of NOM, creates an extremely heterogeneous environment in which reactions may occur (Figure 9.4).

The result of the interaction between the selected oxidant and aquifer material leads to either an increase in the consumption of the oxidant by the aquifer solids or an enhancement in the oxidant decomposition rate. When an oxidant is consumed, the reactive species associated

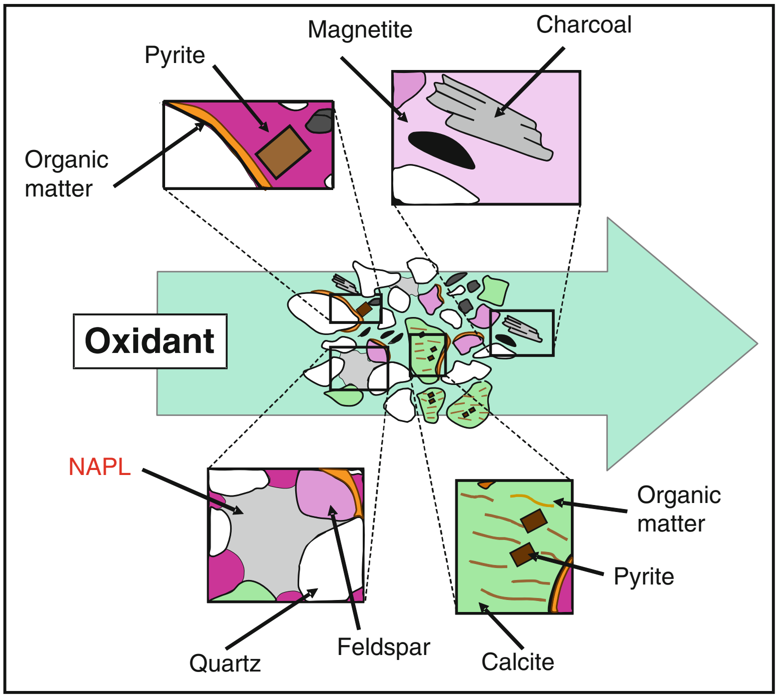


Figure 9.4. Pore-scale conceptual model for natural oxidant interactions showing the possibility of reaction with reduced aquifer solid species, reaction with dissolved DNAPL species, and transport of unreacted oxidant (adapted from Mumford et al., 2005).

with the aquifer solids are finite, and hence there exists a finite consumption or natural oxidant demand (NOD). Once the maximum NOD is satisfied, there is minimal additional oxidant and aquifer material interaction. Conversely, an enhancement in the oxidant decomposition rate implies that infinite interaction capacity is available, that is, all oxidant will eventually be consumed by decomposition reactions. To capture these behavioral differences and the associated underlying processes for all oxidant behavior, the term *nonproductive oxidant depletion* can be used rather than *natural oxidant demand*. Regardless of the way in which nonproductive depletion may manifest itself, it can result in (1) a decrease in the transport of the oxidant within the subsurface, (2) a decrease in the reaction rate with the target COCs and (3) a reduced mass of oxidant available. All of these can result in an inefficient ISCO system. Quantification of the nonproductive oxidant depletion is a requirement for site-specific assessment and the design of cost effective ISCO treatment systems. Table 9.3 describes the observed nonproductive behavior of the four widely used oxidants in the presence of uncontaminated aquifer materials.

To illustrate the inherent differences between the persistence of peroxide, permanganate and persulfate in the presence of aquifer solids, consider the following injection scenario: (1) an uncontaminated aquifer is subject to the injection of an oxidant (peroxide, permanganate or persulfate) in two sequential episodes spaced 30 days apart; (2) following injection the oxidant solution remains immobile as it reacts with the aquifer material; (3) the controlling *in situ* kinetic parameters are taken from bench-scale efforts performed on the same aquifer material and (4) the injection concentration is adjusted so that the oxidation strength is identical for each oxidant. Figure 9.5 depicts simulated oxidant concentration profiles over 60 days, illustrating the following features:

- Peroxide concentration is rapidly reduced.
- The peroxide profiles following injection 1 and injection 2 are identical.
- The permanganate concentration profile following injection 1 decreases quickly and then slows down as it approaches an asymptote.
- The decrease in the permanganate concentration profile following injection 2 is much less than after injection 1, reflecting the consumption of much of the fast reacting NOM.
- The persulfate concentration profile is nearly identical following injection 1 and injection 2.

Table 9.3. Characteristics of the Nonproductive Behavior of Common Chemical Oxidants

Oxidant	Nonproductive Behavior
Ozone	• Enhanced first-order degradation rate • Infinite interaction, infinite NOD
Hydrogen peroxide	• Enhanced first-order degradation rate • Insignificant change in NOM • Repeated decomposition behavior • Infinite interaction, infinite NOD
Permanganate	• Fast initial and slow later consumption rates • Significant change in NOM • MnO_2 catalyzed decomposition • Finite interaction but with increased persistence with each injection • Definitive NOD
Persulfate	• Enhanced first-order degradation rate • Slight to moderate decrease in NOM • Repeated decomposition behavior • Infinite interaction, infinite NOD

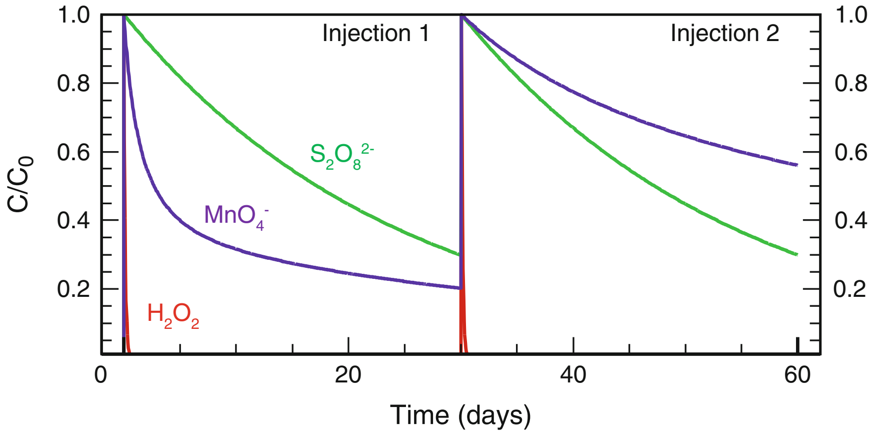


Figure 9.5. Concentration profiles following two sequential injection episodes into a synthetic aquifer for peroxide (*red*), permanganate (*purple*), and persulfate (*green*).

- The persulfate reaction rate is substantially less than peroxide; thus, persulfate is more persistent in this system than peroxide.

Aside from the important nonproductive reactions just noted, other competing and nonproductive reactions occur in ISCO systems. For oxidants involving free radical generation, radical scavenging reactions can decrease the concentration of free radicals available to degrade targeted contaminants. Therefore, scavenging reactions can also result in system treatment inefficiency. Common groundwater anions such as nitrate, chloride, carbonate and bicarbonate are thought to be the most important radical scavengers. Relevant reactions with the bicarbonate ion and the hydroxyl radical or sulfate radical are given below (Buxton et al., 1988; Huie et al., 1991):

$$OH^{\bullet} + HCO_3^- \rightarrow H_2O + CO_3^{\bullet -} \qquad \text{(Eq. 9.14)}$$

$$SO_4^{-\bullet} + HCO_3^- \rightarrow SO_4^{2-} + CO_3^{\bullet -} + H^+ \qquad \text{(Eq. 9.15)}$$

The scavenging effect of carbonate or bicarbonate anions on the efficiency of persulfate reactivity has been observed in experiments (Huang et al., 2002; Liang et al., 2006; Waldemer et al., 2007). Waldemer et al. (2007) used PCE as a model compound with three different concentrations of carbonate to investigate changes in the pseudo first-order kinetic rates. The results showed, as expected, that an increase in the carbonate concentration decreases the rate of PCE oxidation with persulfate.

9.3 CURRENT PRACTICES FOR DNAPL SOURCE ZONE TREATMENT USING ISCO

In this section, the current state of practice for ISCO applied to sites with DNAPL source zones is highlighted. This section conveys what practitioners working at DNAPL sites have normally done, even though this may not represent best practices based on recent research and field experiences. In Section 9.4, remedial design issues are presented with alternative and recommended practices that ideally should be followed to help achieve remedial objectives in a cost effective manner for DNAPL source zones.

To reveal the current state of practice for ISCO applied to DNAPL source zones, it is insightful to examine case studies of field projects. The site conditions and ISCO performance data for ISCO projects at sites with DNAPL source zones are summarized in Example 1. These case studies reveal the general types of approaches that have been and are being used to apply ISCO to achieve varied treatment goals at sites with contrasting site conditions and contamination characteristics.

Example 1. Examples of ISCO Applications to Sites with DNAPL Source Zones

Naval Submarine Base Kings Bay, St. Marys, Georgia. Modified Fenton's reagent was used to treat a chlorinated solvent DNAPL source zone beneath a landfill (reported in NAVFAC, 2000, and Chapelle et al., 2005). After the first application, monitoring data indicated that the source zone had not been completely delineated prior to the design of the first ISCO injection event. Additional modified Fenton's reagent was applied in three additional delivery events. A total of 0.23 pore volumes were applied throughout the course of the project. The cumulative dose of oxidant applied was 24 grams (g) oxidant/kilogram (kg) of impacted media. COC concentrations in the source zone were reduced to below MCLs. However, the offsite plume that was not targeted by ISCO remediation remained and has not attenuated to below MCLs over an approximately 10-year monitoring period.

Sun Belt Precision Products. Four applications of permanganate were applied to a source zone at a site with a known DNAPL release (reported in USEPA, 2003, and ITRC, 2005). The relatively homogeneous sand treatment zone was particularly amenable to ISCO treatment. Only 0.16 pore volumes were delivered over the course of the project, which the design team indicated was intentional to minimize physical displacement. A design radius of influence of 7 feet (ft) (2.1 meters [m]) was used for injections. While NOD was not reported, the sand stratigraphy suggests that it was likely low. Aqueous phase groundwater concentrations were reduced by three to four orders of magnitude throughout the treatment zone. ACLs were met in the treatment zone, allowing the site to obtain closure.

U.S. Department of Energy Portsmouth Gaseous Diffusion Plant. The X-701B site has been treated with permanganate delivered through horizontal wells (West et al., 1997; 1998) and CHP delivered with direct push points (Cross et al., 2006; Cross and Baird, 2008; Wymore et al., 2010). The DNAPL source zone is located in a heterogeneous formation directly overlying low permeability shale. The permanganate recirculation delivered approximately 0.7 pore volumes. While transient COC reductions in groundwater were observed, significant rebound occurred throughout the treatment zone. Catalyzed hydrogen peroxide delivered in multiple injection events was able to reduce aqueous and soil phase COC concentrations in the majority of the treatment zone, but was unable to adequately contact the DNAPL located directly above the shale at the base of the treatment zone. The source zone is currently being remediated by excavation.

U.S. Army Corps of Engineers, Eastland Woolen Mill Superfund Site (Corinna, Maine). Laboratory treatability tests, field pilot tests and full-scale implementation of ISCO were conducted for the site and completed in 2007 (Osgerby et al., 2006). The COCs at the site include 1,2,3-trichlorobenzene; 1,2,4-trichlorobenzene; 1,2-dichlorobenzene; 1,3-dichlorobenzene; 1,4-dichlorobenzene; benzene; and chlorobenzene. The target area is a portion of the site composed of basal till and weathered/fractured bedrock that could not be excavated and contained residual DNAPL. Bench-scale testing showed activated persulfate and CHP to be potentially applicable; however, field pilot testing demonstrated activated persulfate to be a superior ISCO process for the site due to the reactive nature of site soils

(continued)

Example 1. (continued)

that severely limited distribution of the CHP. Full-scale application of activated persulfate was performed between 2005 and 2007 in four phases for treatment of overburden basal till (Phases I and II), weathered bedrock (Phase III), and fractured bedrock (Phase IV). This final phase demonstrated that distribution of the oxidant and treatment of the bedrock would be feasible, though some fracture bedding planes would require high-pressure injections. Tracer tests also indicated that oxidant mass flux into secondary porosity features within the fracture matrix would be an important mechanism to treat the contaminant mass within the bedrock. Nearly 200,000 pounds (lbs) (91,000 kg) of activated persulfate reagents were applied during the four phases of treatment. Over the four phases of injection, an approximate 60% reduction in soil contaminant mass and 90% reduction in groundwater contaminant mass (ISCO objective was an 85% reduction in groundwater COC concentrations) have been achieved.

Industrial Site in New Hampshire, Multiple Source Areas. Remedial investigations identified the contamination as a mixed DNAPL including chlorinated ethanes and chlorinated ethenes. The primary COCs were identified as 1,1,1-TCA and TCE. The contamination was found in silty fine sands; the silt content increased progressively silty with depth. ISCO was selected as the preferred remedial technology. The objective of the remediation was to treat the source and allow the plume to attenuate naturally. As the soils at the site became increasingly silty with depth, the potential existed for preferential flow into the more shallow portions of the injection area that could cause failure of the ISCO to meet its goal. Therefore, modeling of the vertical placement of the injection wells was performed to optimize the distribution of reagents in the subsurface. Bench-scale testing was performed for CHP, which was the ISCO technology selected; the work was completed in 2005–2010 (Smith et al., 2012). During the bench-scale tests, it was determined that H_2O_2 was unstable in the presence of the site soils, which would result in inadequate distribution of the H_2O_2. A variety of CHP stabilization agents were tested to develop a protocol that would allow for better reagent distribution. Direct injection, via installed polyvinyl chloride (PVC) wells, of the stabilized H_2O_2 was selected for the remedial design. The four identified source areas were treated with 76,000 lbs (34,500 kg), 142,000 lbs (64,500 kg), 110,000 lbs (50,000 kg), and 76,000 lbs (34,500 kg) of stabilized H_2O_2, respectively, within 645,200 gallons (gal) of solution. The ISCO application (in most source areas, one or two applications were required) achieved a reduction of $>$80% of dissolved phase chlorinated compounds, which exceeded the ISCO application objective for the site.

Active Manufacturing Facility (New England). The COCs at this facility were 1,1,1-TCA (historical levels over 100 miligrams per liter [mg/L] detected), PCE, and 1, 4-dioxane. The ISCO goal was to reduce COCs concentrations to $<$1 mg/L to allow natural attenuation of the residual plume prior to reaching downgradient receptors. As the DNAPL source area was under an active manufacturing facility, safety concerns eliminated the application of CHP and alkaline activated persulfate (AAP) was selected for the ISCO application. Alkaline activated persulfate required adjustment of the aquifer pH to alkaline conditions (typically $>$pH 10.5). Bench-scale testing demonstrated that the site-specific soils had both a high buffering capacity and nontarget oxidant demand, but that AAP could be successful in achieving destruction of the COCs to below target levels; the work was completed in 2007–2008 (Crawford et al., 2009). The full-scale application required approximately 55,000 gal (208,000 L) of oxidant solution over two separate field events to treat a 30 ft × 60 ft (9 m by 18 m) source zone over a targeted saturated zone thickness of approximately 15 ft (4.6 m), which is equivalent to approximately 0.45 pore volumes of the treatment zone for each event. Two distinct geological

(continued)

Example 1. (continued)

units were identified within the TTZ: an upper sandy silt zone overlying a deeper, lower permeability glacial till zone. This required installation of two separate injection well systems at two discrete depths to optimize oxidant distribution into each soil layer. The post-treatment results showed that the groundwater goals were met in all performance monitoring locations. A year of post-ISCO sampling was completed, and sampling confirmed that a >99% reduction of the target contaminants was achieved, with final concentrations approaching MCLs in many monitoring wells.

To obtain more quantitative insight into ISCO design and performance, databases of project applications have been compiled. Krembs developed a database of ISCO projects that were carried out at 242 sites (Siegrist et al., 2010; Krembs et al., 2010; Krembs, 2008). A subset of these sites was categorized as DNAPL sites. Based on critical review of those sites categorized as having DNAPL contamination, the following general trends were noted for treatment of DNAPL sites using ISCO:

- *In situ* chemical oxidation practitioners use longer delivery events, greater injection volumes and higher oxidant doses for DNAPL sites. The average duration of delivery was longer for DNAPL sites as well.
- A median cumulative injection volume of 0.13 pore volumes was delivered at DNAPL sites. While this number is low, it is more than twice the median volume delivered at sites where DNAPL was not believed to be present (median of 0.056 pore volumes).
- At the 82 DNAPL sites studied, it was more common to use ISCO with other technologies (79%) than to apply ISCO alone (62%), especially post-ISCO (56% vs. 40% of 59 sites).
- Enhanced bioremediation and monitored natural attenuation (MNA) were the most frequently used post-ISCO technologies applied at DNAPL sites (33 and 21% for 34 sites, respectively). In this analysis, MNA was considered as a coupled technology when source documents specifically stated that it would be used, which likely results in an underestimation of the frequency of the use of MNA after ISCO.
- Practitioners attempted to meet MCLs immediately after ISCO at only 14% of 110 DNAPL sites reviewed.
- No DNAPL sites met MCLs following ISCO.
- DNAPL sites were able to attain ACLs in 39% of cases.
- Rebound in COC concentrations in groundwater was observed in at least one monitoring location at 82% of DNAPL sites.

Based on anecdotal reports of technology developers and practitioners, commonly cited reasons for not meeting the desired ISCO performance goals at sites with DNAPL source zones include (1) a lack of contact between the COCs to be treated and the injected reagents (oxidants, catalysts or activators), (2) back diffusion from low permeability and heterogeneous materials, (3) inadequate desorption of sorbed COCs, (4) NAPL solubility and mass transfer limitations and (5) incomplete characterization of the extent or mass distribution of the contaminants (Siegrist et al., 2008b).

9.4 REMEDIAL DESIGN ISSUES AND APPROACHES

9.4.1 DNAPL Source Zones and Viability of ISCO

Dense nonaqueous phase liquid source zones challenge all treatment technologies, particularly where the treatment goals are unrealistic for the site-specific conditions. For example, to date there are no documented cases where DNAPL source zones have been treated and maintained at MCL concentrations by any remediation technology. *In situ* chemical oxidation is applicable to source zones, however, only when treatment goals are realistic and site conditions are amenable; ISCO alone is not recommended for source zones if significant treatment of DNAPL pools is required. Furthermore, ISCO alone is not recommended where >99% concentration, mass, or mass flux reduction is the treatment goal, unless the site is relatively homogeneous (hydraulic conductivity varies by less than a factor of 1,000) and permeable ($>10^{-4}$ centimeters per second [cm/s]) (Siegrist et al., 2011). Concentration, mass and mass flux reductions of 50–90% are achievable and have been well documented in source zones using ISCO; treatment to 99% reduction of concentration, mass or mass flux is feasible but less likely in source zones (Siegrist et al., 2011). The probability of meeting treatment goals, regardless of their stringency, decreases with increasing complexity (such as increasing heterogeneity and/or decreasing permeability) (Krembs et al., 2010; Siegrist et al., 2011). Site complexity reduces the ability to establish contact between oxidants and contaminant – the more challenging the contact of any remediation amendment with contaminants, the less likely successful treatment will be achieved.

Table 9.4 provides an overview of potential oxidant types, delivery methods, potential for rebound and performance goals for various DNAPL source zones (single compound or mixtures), and associated geological subsurface conditions. A discussion of remedial design considerations and approaches is given in the following sections.

9.4.2 Remedial Design Issues

A number of specific issues should be addressed to successfully implement ISCO at DNAPL sites. These issues can be categorized as conceptual site model, site treatment goals, site-specific limitations, effects of source zone treatment, and contaminant rebound (Table 9.5). Further discussion of each of these remedial design issues is given below.

9.4.2.1 Comprehensive Conceptual Site Model

It is well established that geological heterogeneities have a significant impact on source zone architecture (Schwille, 1988; Kueper et al., 1993) (Figure 9.6). Dense nonaqueous phase liquid migration, in particular, has been studied quite extensively as a function of site geology (Pinder and Abriola, 1986; Kueper et al., 1989; Mackay and Cherry, 1989; Kueper and Frind, 1991a, b; Johnson and Pankow, 1992; Poulsen and Kueper, 1992; Held and Illangasekare, 1995a, b; Illangasekare et al., 1995a, b; Ball et al., 1997; Liu and Ball, 2002; Sale et al., 2007). These studies emphasize the complex behavior of DNAPL within source zones, including lateral spread over finer grained media layers as it sinks within the aquifer, entry into and storage within these lower permeability layers, and DNAPL pooling in coarser layers. When ISCO is applied to a DNAPL source zone, for example the DNAPL site depicted in Figure 9.6, it is both efficient and cost effective to deliver the oxidant to regions with high contaminant mass densities. When a site is poorly characterized and complexities are misunderstood or ignored, ISCO systems can bypass zones of high contaminant mass densities. While no site characterization effort will result in a complete understanding of the subsurface conditions, it is important to have a comprehensive CSM. The more geologically complex the site, the higher the degree of characterization that is required.

Table 9.4. Characteristics of DNAPL Source Zones and General Amenability to Successful Application of ISCO

DNAPL Type Subsurface Conditions[a]	Simple Mixtures[b] (Solvents [PCE, TCE, DCE,. . .])		Complex Mixtures[b] (e.g., Solvents w/Fuels, Coal Tars)	
	Globs and ganglia (higher GTP ratio)	Pools (lower GTP ratio)	Globs and ganglia (higher GTP ratio)	Pools (lower GTP ratio)
A. Permeable and homogeneous (21%)	Oxidant type: A Delivery: P, I Rebound: LM Goal: ACL or MF Combined: N	Oxidant type: S Delivery: P Rebound: LM Goal: ACL or MF Combined: Y	Oxidant type: S Delivery: P, I Rebound: LM Goal: ACL or MF Combined: Y	Oxidant type: S Delivery: P, I Rebound: HD Goal: ACL or MF Combined: Y
C. Permeable and heterogeneous (47%)	Oxidant type: A Delivery: P Rebound: LM Goal: MCL, ACL, MF Combined: N	Oxidant type: S Delivery: P, M, O Rebound: HD Goal: MCL, ACL, MF Combined: Y	Oxidant type: A Delivery: P Rebound: LM Goal: MCL, ACL, MF Combined: N	Oxidant type: S Delivery: P, M, O Rebound: HD Goal: MCL, ACL, MF Combined: Y
B. Impermeable and homogeneous (3%)	Oxidant type: S Delivery: M, O Rebound: U Goal: ACL Combined: Y	Conditions not likely to occur	Oxidant type: S Delivery: M, O Rebound: U Goal: ACL Combined: Y	Conditions not likely to occur
D. Impermeable and heterogeneous (15%)	Oxidant type: S Delivery: M, O Rebound: U Goal: ACL Combined: Y	Conditions not likely to occur	Oxidant type: S Delivery: M, O Rebound: U Goal: ACL Combined: Y	Conditions not likely to occur
E. Consolidated material with low matrix porosity (7%)	Oxidant type: A Delivery: I, O Rebound: HD Goal: MF Combined: Y	Conditions not likely to occur	Oxidant type: S Delivery: I, O Rebound: HD Goal: MF Combined: Y	Conditions not likely to occur
F. Consolidated material with high matrix porosity (7%)	Oxidant type: A Delivery: I, O Rebound: HD Goal: MF Combined: Y	Conditions not likely to occur	Oxidant type: S Delivery: I, O Rebound: HD Goal: MF Combined: Y	Conditions not likely to occur

Note: *GTP* ganglia to pool ratio
Oxidant type: A = All oxidants of equal applicability; S = Certain oxidants likely more effective
Delivery method: P = Probes surgically emplaced; I = Injection wells; M = Physical mixing; O = Other enhancements (e.g., well-to-well recirculation)
Rebound potential: *LM* limited and can normally be managed with subsequent targeted injections, *HD* high likelihood and difficult to manage with subsequent injections
Goal achievement: *MCL* maximum contaminant levels, *ACL* alternative concentration limits, *MF* mass flux reduction. Note that for DNAPL source zones, setting a goal of MCLs will almost always require implementation of a remediation approach or technology following ISCO
Combined remedy needed: Y = almost always needed; N = not always necessary; U = uncertain

[a] The classification of subsurface conditions was developed by Krembs et al. (2010) and the percentage listed in parentheses represents the percentage of sites ($n = 209$ sites) compiled by Krembs et al. (2010) where ISCO was applied (includes all types of sites, not just those with DNAPL source zones)

[b] In the opinion of the authors, the general attributes given are associated with more successful applications of ISCO

Table 9.5. Conditions That Challenge Successful ISCO Treatment of DNAPL Source Zones

Category	Challenging Conditions
Conceptual site model	Site can be poorly characterized with respect to contaminant mass density (pools vs. residual) and distribution, total contaminant mass present, and degree of media heterogeneity
	Site geology can be challenging/complex, limiting contact of oxidant and contaminant
	Significant contaminant mass can have moved into lower permeability media via diffusion and/or mass transport
	Prediction of oxidant and/or oxidant amendment distribution at the site can be poor
Site treatment goal	Treatment goal can be unrealistically stringent for a source zone site
Site-specific limitations	Amount of oxidant necessary to treat the mass of contaminant present can be cost prohibitive
	Volume of oxidant necessary to treat the mass of contaminant present at the site can be prohibitive in terms of time onsite (cost) or the ability of the formation to accept the volume
	Project schedule, budget, and timeframe cannot accommodate multiple oxidant delivery events
Effects of source zone treatment	Byproducts of ISCO can be incompatible with aquifer physical or chemical characteristics and/or contribute to implementation/contact challenges
Rebound	Rebound is more prevalent at source zone sites

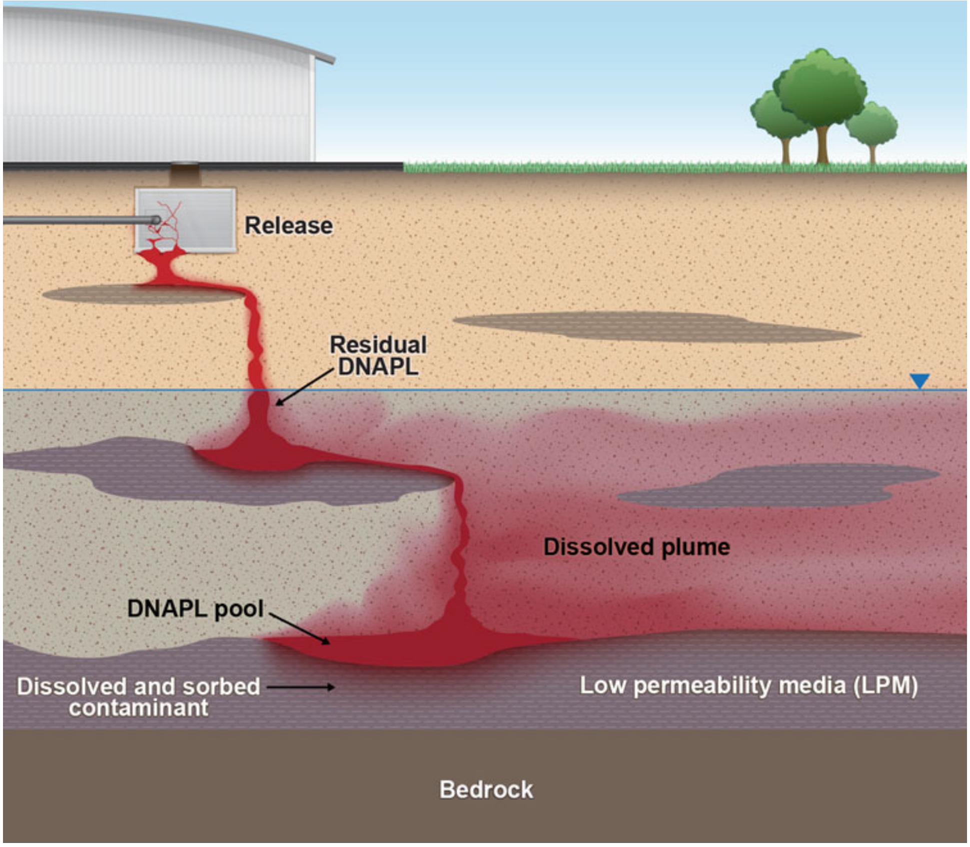


Figure 9.6. Generic contaminated site CSM for a DNAPL source (DNAPL contamination is shown in *red*) (Siegrist et al., 2011).

For source zone treatment, it is critical to understand the contaminant phases, mass, architecture and age, in addition to typical hydrogeology, geochemistry and other site data. At some sites it may be cost prohibitive to attempt to treat all of the mass in a source zone. However, because of the DNAPL architecture, it is often viable to treat enough mass to cost effectively reduce COC mass flux (expressed as mass/time/area) and mass discharge (flux integrated across a cross section of the plume perpendicular to flow) (mass/time). Treatment objectives and monitoring should be established as a function of the phase in which contaminants are present. For example, it is unrealistic and inappropriate to monitor only groundwater concentration within source zones that contain high DNAPL and sorbed phases of contaminant. This is true both for pre-ISCO site characterization and post-ISCO monitoring. Contaminant mass will dictate the chemical oxidant needs for treatment. Dense nonaqueous phase liquid architecture will dictate design features such as the oxidant delivery approach and delivery point spacing. For example, localized DNAPL pools call for closely spaced delivery of oxidants and direct-push injection (multiple events) may be appropriate, whereas residual DNAPL spread relatively uniformly across a site may call for wells installed at a wider spacing. Where contamination has migrated into lower permeability layers, more aggressive delivery approaches, including soil mixing, may be considered. A comprehensive CSM will not only guide ISCO design, it will also serve to guide post-treatment expectations. When it is known that the contaminant is located within lower permeability zones, longer-term back diffusion and site recontamination could be anticipated, and follow-on injections could be planned accordingly.

Current site characterization efforts use systematic planning, dynamic work strategies and real-time field measurements to reduce CSM uncertainty and guide the treatment effort. This dynamic approach is termed the accelerated site characterization process by the American Society for Testing and Materials (ASTM) and the Triad approach by the U.S. Environmental Protection Agency (USEPA) (ITRC, 2003, 2007; ASTM, 2004; Crumbling et al., 2001, 2003; USEPA, 2008). The focus of each of these is managing the uncertainty associated with both the site characteristics and the influence of treatment on site conditions. These approaches are even more valuable to source zone sites because of their complexity. With these iterative data collection and analysis approaches, decisions regarding follow-on data collection efforts can be made near real time to fill data gaps based on information about the site as data is collected. For example, in a source zone where NAPL is suspected, grab sampling can identify a high contaminant concentration location. Follow-on and more refined efforts, where time and budget allow, can be localized in that area with high density data collection rather than moving forward with a grid sampling approach that may be of limited value when a hot spot is identified. During and following ISCO treatment of a site, a similar dynamic approach can and should be used to assess delivery and treatment effectiveness.

Modeling is one tool that can help improve understanding of subsurface conditions and the viability of remediation using ISCO. For example, by simulating possible processes and matching observed data, potential source zone locations and architectures can be estimated. These simulations can help to select appropriate oxidant and delivery approaches for the likely source architecture and hydrogeology. By performing simulations using expected upper and lower limits for site parameters, the effect of uncertainty can also be examined. Examples of ISCO-specific modeling tools include CDISCO and CORT3D.

The conceptual design for ISCO (CDISCO) tool was developed with support from the ESTCP under Projects ER-0626 (Borden et al., 2012) and ER-0623 (Siegrist et al., 2010) and is intended to assist with the conceptual design of injection systems for ISCO using permanganate. The conceptual design for ISCO tool allows the user to evaluate permanganate delivery as a function of aquifer thickness, permeability, total NOD, NOD kinetics, permanganate concentration, injection flow rate and injection duration. It does not, however, model contaminant concentrations and in fact assumes an equal distribution across the treatment zone to which the model is applied.

While CDISCO is an invaluable tool to help design a permanganate delivery system, often models applied to source zones need to consider greater complexity than CDISCO captures. The three dimensional chemical oxidation reactive transport model (CORT3D) was developed with support from SERDP under Projects ER-1290 (Siegrist et al., 2006) and ER-1294 (Illangasekare et al., 2006). CORT3D is based on a modified form of reactive transport in three dimensions (RT3D) version 2.5 (Clement, 1997, 2001; Clement et al., 1998, 2000; Clement and Johnson, 2002; Johnson et al., 2006) and MODFLOW, 2000 (McDonald and Harbaugh, 1988; Harbaugh and McDonald, 1996a, b; Harbaugh et al., 2000). It allows for simulation of three-dimensional (3-D) ISCO reactive transport in groundwater (Heiderscheidt, 2005). CORT3D includes NAPL dissolution, equilibrium or rate-limited sorption, second-order kinetic contaminant oxidation, kinetic oxidation of NOD – both a fast kinetic portion and a slow kinetic portion – and different diffusion coefficients for each aqueous species. The code tracks three aqueous mobile components (contaminant, aqueous chloride and aqueous oxidant) and five immobile components (NAPL, sorbed contaminant, manganese oxide, fast NOD and slow NOD). The code was developed for permanganate, but it may be applicable to other oxidants with further investigation and appropriate oxidant-specific assumptions.

The best predictive tools are only as reliable as the data that is entered into them. Therefore, sophisticated modeling tools are only worth the expense and effort of using them if comprehensive CSM and monitoring plans exist that can be implemented during and after ISCO.

9.4.2.2 Treatment Goals

As discussed in Section 9.3, application of ISCO to DNAPL sites has not been successful in achieving MCLs, though it is capable of meeting less stringent remedial action objectives (such as ACLs). Generally, it is more reasonable to deploy ISCO in the source zone with the intent to reduce the source zone mass and perhaps decrease the mass discharge so that a combined remedy such as ISCO followed by MNA can be effective.

9.4.2.3 Oxidant Type and Concentration

Some oxidants are more viable for treatment of source zones than others based on their stability (longevity) in the subsurface and their ability to be distributed throughout a TTZ. Because of their persistence, permanganate and persulfate, under some activation approaches, tend to be more viable for source zone treatment compared to CHP or ozone (Siegrist et al., 2011). On the other hand, where contaminants such as coal tar or chlorinated solvents are trapped at high saturations, the more aggressive ISCO oxidants, such as CHP or ozone, might facilitate movement of the contaminant, which could increase accessibility and make the DNAPL more amenable to ISCO and combined treatment technologies and approaches.

Where contaminants are present at high concentrations, such as in source zones, it may seem intuitive to deliver high oxidant concentrations in order to rapidly and extensively destroy contaminants. Several factors, in addition to contaminant mass, should be considered when selecting an appropriate oxidant concentration. Extensive nonproductive oxidant depletion occurs due to interaction with the natural constituents of the subsurface, regardless of the oxidant selected. The higher the concentration of oxidant that is delivered, the faster this nonproductive oxidant depletion occurs. Oxidants react more rapidly with most contaminants than with subsurface media; therefore, high concentrations are not problematic where the full contaminant mass is present in the aqueous phase. This is rarely the case, particularly in source zones. It is only efficient to provide oxidant in excess of what is consumed by contaminant reactions and rapid reactions with the media so it can persist long enough to allow for the transfer of remaining mass from the nonaqueous or sorbed phases and to allow for transport into lower permeability areas via diffusion or downgradient via advection and dispersion. In addition to nonproductive oxidant consumption, using a concentration higher than necessary can exacerbate the generation of byproducts, such as gas or acidity/alkalinity, with effects that may be undesirable.

Another issue associated with the need for a large mass of oxidant is that when the large mass is delivered at high concentration, the oxidant solution can experience density-driven flow downward through the aquifer due to gravitational forces. Schincariol and Schwartz (1990) reported that this could happen in subsurface systems when the density difference between fluids is as little as 0.0008 g/cm^3, which is equal to the density difference caused by a concentration of 1,000 mg/L of sodium chloride. This effect has been noted with permanganate by several investigators (Nelson, 1999; Stewart, 2002; Siegrist et al., 2006). While this density effect can be advantageous if expected, treatment can be ineffective in cases where the contaminated zone is completely bypassed.

9.4.2.4 Oxidant Delivery

Certain delivery approaches are more amenable to source zone treatment as well. Typically treatment of source zones requires longer delivery of a greater volume of remediation fluids; therefore, it is advantageous to use a delivery approach that will accommodate this effort. It may ultimately be cost effective to install delivery wells (as opposed to direct push probes) or recirculation systems to accommodate longer delivery periods. Also, soil mixing and hydraulic fracture-emplaced ISCO have the potential to be effective approaches for source zone treatment, particularly where these approaches are closely matched to site conditions. Soil mixing can help overcome heterogeneities through the physical mixing process. Fracturing might be used to facilitate delivery in low permeability formations, although closely spaced fractures will likely be needed to overcome diffusion-limited mass transport. The key point is that more expensive and aggressive delivery approaches improve cost effectiveness as site complexity (hydrogeology and contaminant mass distribution) increases.

Delivery into complex source zones can be enhanced by improved hydraulic delivery and distribution, and improved oxidant stability and reactivity with the COCs. Improved hydraulic delivery can improve contact between the oxidant and COC to increase treatment efficiency and effectiveness. Improved oxidant stability can lead to increased contact duration, which is particularly important where contaminant oxidation is controlled by mass transfer limitations. Oxidant stability can be improved by the addition of amendments to alter its chemical or physical properties. Table 9.6 summarizes methods that are being developed for enhanced ISCO delivery.

Table 9.6. Emerging Approaches for Enhanced ISCO Delivery (after Siegrist et al., 2011)

Approach	Description and Examples
Stabilized oxidants	Phytate, citrate, and malonate have been shown to increase the half-life of H_2O_2 during CHP reactions (Watts et al., 2007)
Encapsulated oxidants	Potassium permanganate in solid microcapsules (Ross et al., 2005) or within a paraffin matrix (Dugan et al., 2009) to achieve controlled release into groundwater (Lee and Schwartz, 2007; Lee et al., 2009)
Polymers and delivery aids	Use of polymers like xanthan to overcome ISCO delivery problems caused by zones of low permeability, site heterogeneity, and excessive NOD (Smith et al., 2008; Crimi et al., 2011)
Density-driven delivery	Density-driven flow was used to deliver permanganate to NAPL located in groundwater on top of an aquitard and a model (MIN3P-D) could simulate the observed behavior (Henderson et al., 2009)
Mechanical mixing	Mechanical mixing of oxidant solutions into shallow soils and subsurface porous media using augers for deep soil mixing or tilling and excavator mixing in shallow soils

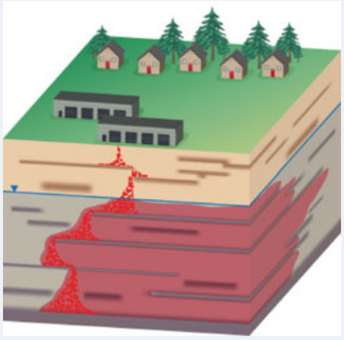
In situ chemical oxidation system design must accommodate the treatment limitations of sorbed and DNAPL phase contaminants in source zones as dictated by the rate and extent of mass transfer into the aqueous phase. In addition to controlling the volume, duration, concentration and approach for oxidant delivery, the number of planned delivery events is another design parameter that can be controlled to accommodate the challenges of treating source zones. In fact, for sites with low rates of mass transfer from the sorbed and DNAPL phases, or from lower permeability media, it may be more cost effective to plan multiple delivery events over time with a lag time between them to accommodate contaminant re-equilibration with the aqueous phase than to plan single, longer duration events where oxidant may be used less efficiently.

9.4.2.5 Cost Considerations

Cost is a key consideration that can influence the viability of successful ISCO for source zone sites. Between the extensive amount of oxidant that can be consumed in DNAPL source zones with high contaminant mass densities and oxidant depletion due to reactions with the media within that treatment zone, chemical costs can be very high for source zone treatment (see Example 2).

Example 2. Oxidant Requirements Using a Mass Balance Approach

Site X contains high concentrations of TCE – up to 100 mg/L in groundwater and 1,000 mg/kg in porous media. Presence of DNAPL is suspected. Permanganate injection via wells has been deemed most viable for the site and multiple injections are planned. The contamination is between 10 ft (3.05 m) and 30 ft (9.1 m) bgs over an area 100 ft (30.5 m) in length and 100 ft (30.5 m) wide.



Assuming a porosity of 0.30 and a bulk density of 1.6 g/cm^3, the total mass of TCE estimated in the treatment zone is approximately 9,250 kg (~20,400 lbs). With a reaction stoichiometry of 1.8 g of permanganate (as MnO_4^-) per g of TCE, approximately 16,650 kg (~36,600 lbs) of permanganate is needed to oxidize the TCE. This mass does not consider the natural demand of the media for permanganate, which would need to be added in excess. Using a simple mass balance approach and an assumption of an NOD of 2 g of permanganate per kg of media, an additional (approximately) 18,160 kg (~40,000 lbs) of permanganate is necessary. If potassium permanganate is used, this translates to 76,600 lbs of $KMnO_4$. At a current cost of \$2.25 per pound of $KMnO_4$, the total cost of permanganate alone is \$172,350. This is \$23/cy of media treated accounting for only the chemical costs. Major assumptions include the following: (1) all of the permanganate is consumed within the target area with no bypass through or around, (2) this mass of oxidant can be delivered uniformly at a reasonable concentration and (3) all contaminant is present in an available aqueous phase within the treatment timeframe. The first assumption presumes a fairly homogeneous formation. Any degree of heterogeneity will cause some extent of bypass. The second assumption depends on numerous design variables. If, for example, a concentration of 1 wt% $KMnO_4$ is used, 1.09 million L (2.9 million gal) is required. This would equal not quite 2 pore volumes of fluid. An underlying concern is whether the formation and budget will accept this volume and associated time onsite. A recirculation approach may be one means to facilitate delivery of this volume/mass of oxidant.

In situ chemical oxidation projects at DNAPL sites have, on average, a higher total cost of treatment relative to other sites (Krembs et al., 2010), which can be attributed to the longer duration of oxidant delivery, greater volume of reagents, greater mass of oxidant and a higher number of delivery events necessary for effective treatment. Sites with large zones of very high contaminant mass density, such as DNAPL pools, are unrealistic to treat with ISCO alone. However, partial mass removal using ISCO followed by alternative treatment approaches that are more cost effective for residual mass may be appropriate. Partial mass removal using ISCO, in fact, may provide enough treatment to reduce mass flux to an acceptable limit, depending on the contaminant architecture. Alternatively, ISCO may be appropriate for residual mass following excavation or other source removal approaches. As discussed earlier, ISCO is best considered as part of a comprehensive approach for source zone remediation.

9.4.2.6 Impacts of ISCO Source Zone Treatment on Aquifer Conditions

Table 9.7 provides an indication of the major subsurface interactions that may occur during ISCO treatment of DNAPL source zone, while Table 9.8 presents some oxidant specific interactions. As discussed below, these interactions can affect aquifer conditions with beneficial or adverse effects.

In situ chemical oxidation can alter subsurface geochemistry (oxidation–reduction potential [ORP], pH) and cause changes to the mobility of metals. Metals of concern include antimony, arsenic, barium, cadmium, hexavalent chromium, copper, iron, lead, mercury, nickel and selenium. Typically, changes are temporary and conditions return to pre-ISCO conditions after the aquifer has re-equilibrated. In source zones containing DNAPL where high oxidant concentrations, oxidant mass, or treatment duration occurs, it is possible for these effects to be amplified over long distances and/or durations.

Gas evolution during ISCO can fill pore spaces and reduce permeability of the formation. For example, gas evolution (CO_2 byproduct) during permanganate ISCO of DNAPL has been reported where groundwater flow has been altered, bypassing zones where significant gas is produced such as the NAPL interface (Reitsma and Marshall, 2000; Lee et al., 2003; Li and Schwartz, 2003). Also, oxygen generation during CHP reactions can be extensive (Watts et al., 1999). While no controlled studies have evaluated the impact in transport systems, it is reasonable to infer that localized O_2 production during CHP reactions can impact permeability much like CO_2. In fact, O_2 generation during CHP reactions is much faster and more aggressive than CO_2 generation during permanganate reactions, so its impact is likely even more pronounced.

Chloride is a byproduct of the reaction of oxidants with many common DNAPLs including TCE and PCE. When oxidation is occurring within source zones, extensive amounts of chloride can be generated local to the point of reaction. For example, Petri (2006) measured concentrations in excess of 3,000 mg/L when treating nonaqueous phase chlorinated solvents with permanganate near the point of reaction. In permanganate systems, chloride does not create challenges to treatment; however, in free radical oxidation systems, such as persulfate and CHP, chloride can act as a free radical scavenger, limiting productive oxidation of contaminants. Furthermore, chloride can form complexes with amendments used to catalyze or facilitate catalysis of free radical oxidation reactions such as iron, impacting oxidation kinetics (Sung and Morgan, 1980). Finally, when present in high concentrations (>3,500 mg/L), chloride can react with contaminants and natural organic carbon to form halogenated intermediates that are potentially more toxic than the parent contaminant (Aiken, 1992; Waldemer et al., 2007).

As discussed in Section 9.2.2.2, manganese dioxide solids (denoted MnO_2, although actually the Mn is in a mixed oxidation state) are a byproduct of ISCO unique to permanganate. Manganese dioxide solids have the potential to alter subsurface hydraulic conductivity and

Table 9.7. Major Subsurface Interactions that Can Potentially Occur During ISCO

Interaction	Type	Comments
Altered behavior of COCs	Organic COCs	Formation of films and rinds due to chemical oxidation at NAPL–water interfaces is possible; this can reduce mass transfer into the aqueous phase where oxidation reactions typically occur
	Metal co-COCs	Oxidation reactions can change the redox state of certain metals and change their toxicity and mobility in groundwater (e.g., Cr^{+3} to Cr^{+6}, more toxic and more mobile; As^{+3} to As^{+6}, less toxic and less mobile)
Permeability loss in injectors and porous media	Particle generation	Formation of reaction products can result in generation of particles, which can clog injectors, well screens, and boreholes (e.g., oxidation using MnO_4^- can generate MnO_2 particles)
	Gas evolution	Oxidation reactions can generate gas (O_2 and CO_2), which can become entrapped in soil and groundwater and reduce effective permeability for flow
Biogeochemical changes	Chemical impurities	Oxidant formulations can include impurities, which can affect groundwater quality (certain permanganate formulations contain metal impurities)
	pH	Oxidation of organics can yield acidity and depress subsurface pH in zones of intense reaction (at NAPL–water interfaces)
	Ion behavior	Permanganate ISCO delivers ions into the subsurface, which can affect sorption and cation exchange sites (e.g., Na^+ can cause dispersion of expandable clays; K^+ and Na^+ can displace sorbed cations)
	Natural organic matter (NOM)	Oxidation of NOM can reduce the f_{oc} and K_d of the subsurface within a TTZ
	Dissolved organic carbon	Oxidation of NOM and hydrophobic organics can generate dissolved organic carbon, which can serve as a substrate for microbial reactions
	Microbiology	Oxidation within a subsurface TTZ can perturb ambient microbial ecology initially depressing biomass, diversity and activity but subsequently stimulating biomass and activity levels to pre-ISCO levels or higher

permeability near the point of oxidant injection and within a TTZ, affecting transport of permanganate in the subsurface. Crimi and Ko (2009) and Crimi et al. (2009) determined that MnO_2 particles in groundwater could be controlled, inhibiting deposition using the amendment sodium hexametaphosphate (SHMP). When SHMP is included in a permanganate oxidation solution, the resulting MnO_2 particles are smaller in size and remain suspended in solution (mobile). During one-dimensional (1-D) transport evaluations of MnO_2 mobility both with and without SHMP in various porous media (organic matter, clay, mineralogy), SHMP enhanced MnO_2 stability in groundwater and resulted in significantly less MnO_2 deposition, particularly within the contaminant source zone. Currently, Crimi et al. (2011) are conducting a field demonstration to evaluate the use of SHMP with permanganate to enhance delivery and

Table 9.8. Subsurface Interactions for Contrasting Oxidants Used for ISCO

Feature	Catalyzed H_2O_2	$KMnO_4$ or $NaMnO_4$	Persulfate	O_3
Subsurface effects on potential rate and extent of oxidation of COCs				
Effect of nonproductive reactions	Can lead to high mass delivery of oxidant solutions	Can lead to high mass delivery of oxidant solutions	Can lead to high mass delivery of oxidant solutions	Can lead to high mass delivery of oxidant solutions
Effect of pH	Optimum <4	Effective at pH 3–12	Optimum >11 for alkaline activation; other activation approaches are less pH dependent	Optimum pH <7
Effect of total dissolved solids	Little to no effect	Little to no effect	Little to no effect	Little to no effect
Effect of CO_3^{-2}	Radical scavenger	No effect	Radical scavenger	Radical scavenger
Effect of temperature	Affects rate of reaction	Affects rate of reaction	Increased temperature increases rate of activation and reaction	Affects rate of reaction
Potential for oxidation to alter pre-ISCO subsurface conditions				
pH in target treatment zone (TTZ)	Can be lowered to acidic conditions depending on buffering capacity	Can be lowered to acidic conditions depending on buffering capacity	High pH can persist following reaction using alkaline pH activation; pH can be lowered to acidic conditions in other activation approaches depending on buffering capacity	Can be lowered to acidic conditions depending on buffering capacity
pH at DNAPL interfaces	Can be lowered toward pH 2	Can be lowered toward pH 2	Can be lowered toward 2	Can be lowered toward pH 2
Temperature	Appreciable increases possible depending on oxidant concentration used	Minor increases possible under normal applications	Minor increases possible under unactivated or iron activated conditions; appreciable increases can result from H_2O_2 or heat activation	Moderate to appreciable increases possible depending on oxidant concentration used
Metal mobilization	Limited potential	Potential for mobilization of redox metals, notably Cr^{+3}	Potential for mobilization of redox metals, notably Cr^{+3}	Potential for mobilization of redox metals, notably Cr^{+3}
Permeability loss	Potential for loss at injection wells and in formation due to gas evolved	Potential for substantial losses at injection wells due to MnO_2 formation	Dependent on activation approach; H_2O_2 activation can lead to permeability losses due to gas evolved; alkaline pH activation could potentially lead to formation of precipitates in/near injection	Potential for loss at injection wells and in formation due to gas evolved
Microbiology	Potential to disrupt biomass levels and activity within TTZ but effects are short term	Potential to disrupt biomass levels and activity within TTZ but effects are short term	Potential to disrupt biomass levels and activity within TTZ but effects are short term	Potential to disrupt biomass levels and activity within TTZ but effects are short term

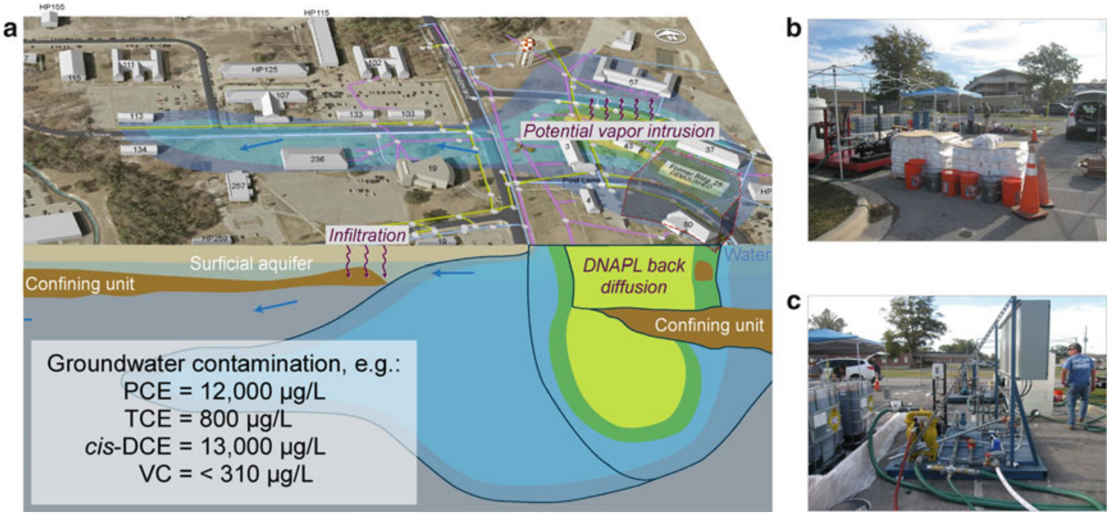


Figure 9.7. Field demonstration Marine Corps Base Camp Lejeune, Jacksonville, North Carolina, of ISCO for remediation of chlorinated solvent contaminated groundwater using coinjection of oxidant and amendments to enhance delivery (from Crimi et al., 2011). The ISCO system includes coinjection of $KMnO_4$ (5 g/L), SHMP (5 g/L), and xanthan gum (0.5 g/L) during a single-well injection event to treat a 10 meter (m) (33 foot) diameter zone of sand and silty sand in the depth interval of 11 to 16 m below ground surface (bgs).

distribution. The demonstration is ongoing at the Marine Corps Base Camp Lejeune in Jacksonville, North Carolina, USA (Figure 9.7). The test area is located within the site of the former base dry cleaning facility, which operated from the 1940s until 2004 when the building was demolished. The subsurface in the test area is comprised of sands of varying permeability with some interbedded silt layers. Perchloroethene contamination has been detected at high concentrations in soil and groundwater samples.

9.4.2.7 Rebound of DNAPL Compound Concentrations

A general rule of thumb used during groundwater monitoring is that a change of < 10% in the field parameters and contaminant concentrations between three consecutive monitoring events can be used to demonstrate re-equilibration or rebound. Re-equilibration may also be presumed to have occurred when geochemical parameter concentrations measured at certain monitoring locations are within the 95% confidence interval for the average baseline condition. A substantial length of time may be required for complete re-equilibration to occur depending on rates of advection versus contaminant desorption, dissolution and back diffusion.

Rebound after an initial ISCO DNAPL source zone treatment event is common. The data presented by Krembs et al. (2010) indicated that rebound (based on an increase of 25% or more) was observed in at least one well following ISCO application at 78% of DNAPL sites and at 56% of the sites where DNAPL was not suspected to be present. While a number of factors may contribute to rebound conditions, the primary reason for rebound at DNAPL sites is because oxidation reactions occur in the aqueous phase (see Section 9.2.1). Dense nonaqueous phase liquid and sorbed contaminants must first dissolve or desorb to be accessible for destruction by oxidants. Once oxidants are depleted due to their reaction with contaminants and/or natural media constituents, any remaining contaminant will continue to partition into the aqueous phase.

While rebound has a negative connotation when associated with performance assessment at treated sites, there are indeed positive attributes of rebound. Rebound marks the transfer of contaminants into a more treatable aqueous phase when identified appropriately as rebound and is not attributable to migration of contaminant into the treated zone from upgradient areas. Rebound itself is an indication that there is untreated mass at the site and additional delivery events are required. Furthermore, rebound data can be used to help locate specific source areas where effort, time and budget can be focused for follow-on treatment.

9.4.3 Remedial Design and Implementation

Implementation of ISCO for treatment of DNAPL source zones should follow the same overall considerations that apply to the general application of ISCO (Siegrist et al., 2011), including:

- Selection of an appropriate approach for delivery that is compatible with site conditions and is consistent with a realistic CSM
- Safe work planning, procedures and equipment
- Provision of appropriate equipment and experienced personnel for chemical handling, mixing and injection operations
- Clear implementation targets for oxidant dose and volume based on a rational design
- An appropriate monitoring program that includes process and performance monitoring
- An adaptive approach that allows dynamic work planning and facilitates use of real-time data in the field

However, since the treatment of DNAPL source zones is inherently challenging, the tolerance for inappropriate application of a technology like ISCO is minimal.

The primary challenge for successful treatment of DNAPL source zones using ISCO is to achieve effective contact between the oxidant and DNAPL. For this reason, careful selection of an implementation approach that is consistent with site geologic conditions is especially critical when treating a source zone. Hence, a realistic CSM is critical because it provides the framework for identifying the specific target locations that require treatment.

Developing an appropriate ISCO implementation approach involves professional judgment as well as technical analysis. Often, several potentially viable implementation approaches exist, and the most favorable approach might consider nontechnical factors related to accessibility of treatment areas, cost, etc. The primary elements of an ISCO implementation approach include the following:

- Consideration of combinations of ISCO and other treatment technologies or use of ISCO as part of a treatment train (such as integrating ISCO with bioremediation, thermal, or MNA)
- Clear treatment objectives defining the TTZ and the treatment endpoints
- Identification of site-specific conditions that may impact the oxidant delivery method or the design oxidant dose and volume
- Selection of an appropriate oxidant and delivery method that overcomes the identified limitations to the maximum extent possible

9.4.3.1 Combining ISCO with Other Technologies and Approaches

Combined remedies often are required for treating DNAPL sources (see Chapter 15). Using ISCO as a component of a combined remedy can be accomplished simultaneously or through various temporal or spatial combinations with other approaches (Siegrist et al., 2011). Enhanced *in situ* bioremediation (EISB) and MNA are most frequently combined with ISCO. ISCO can be an effective pretreatment step to bioremediation by providing partial treatment and making COCs more bioavailable. ISCO has been shown to temporarily decrease microbial abundance and diversity, but these typically rebound with time. In some cases, bioremediation and MNA may actually be enhanced by ISCO as the oxidant may add terminal electron acceptors or partially oxidize contaminants making them more amenable to biodegradation.

In situ chemical oxidation is one component of a comprehensive approach for source zone remediation. A case study review by Krembs et al. (2010) found that sites with NAPL present were more likely to have ISCO coupled with other technologies, especially post-ISCO technologies such as EISB and MNA. Currently, remediation of source zones is increasingly viewed as best accomplished by combining remedies simultaneously or sequentially for different zones of contamination (NRC, 2005) (Figure 9.8). *In situ* chemical oxidation can be appropriately

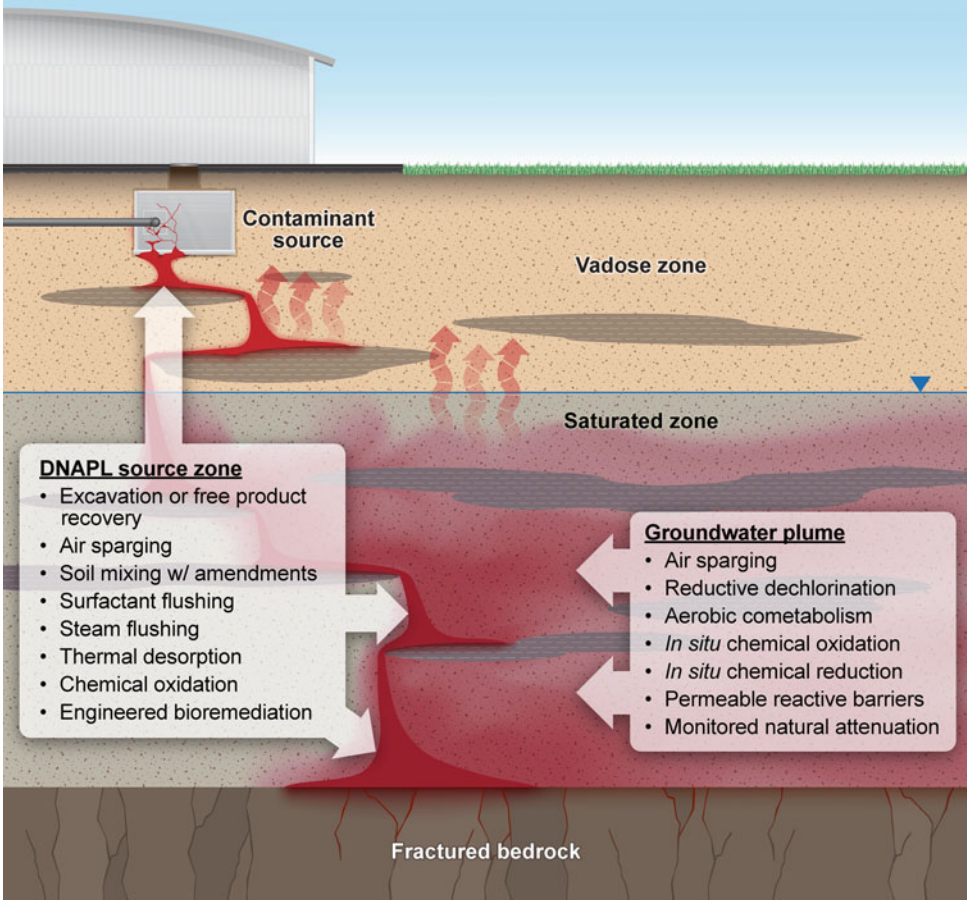


Figure 9.8. Illustration of *in situ* technologies that might be viable for a combined remedy for a site with a DNAPL source zone and associated groundwater plume (DNAPL contamination is shown in *red*) (Siegrist et al., 2011).

coupled with pre-ISCO excavation, air sparging, soil mixing with amendments, surfactant flushing, steam flushing, thermal desorption or engineered bioremediation. On the other end of the treatment train, ISCO can be coupled appropriately with air sparging, reductive dechlorination, aerobic biodegradation, *in situ* chemical reduction (ISCR), permeable reactive barriers or MNA.

Coupling ISCO with different remediation technologies can improve the probability of meeting remediation objectives, especially at sites with unique challenges or aggressive cleanup goals. To optimize the performance of ISCO and the combined remedy, careful consideration of potential interactions is recommended prior to implementation. Siegrist et al. (2011) describe principles of combining ISCO with other approaches, along with key considerations and guidance.

9.4.3.2 ISCO Treatment Objectives

For DNAPL source zone treatment, typically ISCO treatment objectives are related to COC mass reduction although in some situations a numerical concentration-based treatment objective may be adopted. In some cases, an appropriate ISCO treatment objective may stem from an evaluation of the impacts of source zone treatment upon other portions of the site and related exposure pathways. The relationships between source treatment and plume mass discharge or concentration are often an important consideration in developing source area treatment goals (see Chapter 6).

In developing site-specific ISCO treatment objectives, it is critical to differentiate between the vadose zone and saturated zone portions of the source. Vadose zone treatment using ISCO has been largely limited to the application of ozone due to the challenges of applying aqueous oxidant solutions to the vadose zone (Siegrist et al., 2011).

9.4.3.3 Overcoming Site-Specific Limitations on ISCO Application

For ISCO to be successful in treating a DNAPL source zone, several potential limitations must be overcome:

- Difficulty in delivering an adequate mass of oxidant to meet stoichiometric demands uniformly across the TTZ
- Limited persistence of some oxidants and the resulting difficulty of maintaining sufficient oxidant concentrations to sustain elevated COC reaction rates and allow diffusive transport to occur
- Potential for adverse secondary geochemical effects

These limitations form an important framework for selecting an appropriate ISCO implementation approach. When dealt with in a site-specific context, identification and consideration of the potential limitations for ISCO application can lead to the development of a more effective implementation approach. Low permeability media and geologic heterogeneity are two primary potential limitations for ISCO application, particularly within DNAPL source areas. Low permeability conditions in some cases restrict the volume of oxidant that can be delivered, which may prevent an adequate oxidant dose from being applied. Low permeability conditions also require higher injection well density, which increases costs.

When oxidants are injected into the subsurface in a heterogeneous formation, the amendments tend to be transported primarily in the more transmissive zones. Therefore, oxidant delivery into the lower permeability zones occurs more gradually over time by advection or diffusion transport processes. For ISCO, the relative rates of oxidant transport into the lower permeability zones and oxidant consumption are critical implementation considerations. Oxidants that are more persistent will be more amenable to delivery into lower permeability zones in heterogeneous environments.

9.4.3.4 Oxidant Selection and Delivery Methods

The primary oxidant delivery methods are batch injection, continuous injection (constant pressure systems or metered flow systems) and continuous recirculation or mechanical mixing. These are discussed individually below. Although in theory each method can be used with any oxidant, selection of the appropriate oxidant and delivery method should be considered together since in some cases oxidant characteristics may limit the available delivery alternatives. For example, oxidant formulations including percarbonate are typically a solid slurry and will have a limited radius of influence compared to aqueous phase oxidants. Therefore, percarbonate applications may require a higher injection well density or may rely on mechanical soil mixing or other means of delivery such as hydraulic or pneumatic fracturing.

Batch oxidant injection is the most prevalent ISCO implementation approach. Batch injection involves injecting a specified volume of oxidant solution into the subsurface in one or more discrete injection events. For DNAPL source zone treatment, multiple batch injection events should be anticipated to achieve effective COC treatment. Batch injection can be performed using either permanent injection wells or temporary injection points. Direct push drilling of temporary injection points is a common approach, which may facilitate targeting of specific vertical treatment intervals. Proper abandonment of temporary injection points using tremie grouting or other techniques is critical to ensure that the penetrations do not serve as conduits for daylighting or preferential flow of injected fluids.

Continuous oxidant injection systems involve automated delivery systems that maintain a steady delivery of oxidant over a sustained period of time. Ozone gas systems are by default continuous or pulsed injection systems. Similarly, aqueous oxidant solutions can be delivered continuously over extended time periods using either flow metering or constant pressure automated systems. Continuous oxidant delivery may be advantageous for treatment of source zones, where elevated COC concentrations lead to large stoichiometric oxidant dose requirements. Also, continuous oxidant delivery may be advantageous to overcome limitations associated with low permeability and heterogeneous environments.

Oxidant recirculation systems take advantage of groundwater extraction to provide hydraulic control, to increase gradients for oxidant transport through the treatment zone, and to minimize the net addition of water volume to the TTZ. Recirculation systems are generally most practicable in moderate to high permeability environments, although they can still be used in lower permeability environments. Oxidant recirculation systems may require relatively sophisticated fluid handling to mitigate potential impacts of precipitant formation and other secondary geochemical effects related to pH, oxidant presence, potential off-gassing, etc.

Mechanical soil mixing can be accomplished using large diameter augers, rotary drums or other configurations. Mechanical soil mixing has the primary advantage of being able to overcome the delivery limitations in heterogeneous and low permeability settings. However, mechanical soil mixing requires unobstructed access and is limited to a relatively shallow TTZ. Mechanical soil mixing of ISCO reagents involves adding either aqueous oxidant solutions or solid-phase oxidant directly to the soil during the mixing process. Mechanical soil mixing may impact the geotechnical properties of soils, and a geotechnical engineering analysis should be performed to assess the suitability for post-treatment construction, if applicable.

9.5 PROJECT MONITORING AND SYSTEM OPTIMIZATION

9.5.1 Program Components and Elements

In situ chemical oxidation monitoring programs are typically designed to meet several objectives under complex, uncertain and difficult-to-predict conditions. A typical monitoring program includes baseline, delivery and treatment performance monitoring activities, which are conducted to achieve the following goals: (1) collect the necessary data to measure and document achievement of the ISCO treatment operational objectives and treatment milestones, (2) monitor the ISCO process to continually confirm that the design is performing as intended and (3) provide engineering performance parameters for subsequent applications and/or post-ISCO technologies (Siegrist et al., 2011). The elements that are typically addressed in a monitoring plan include:

- Clearly defined data needs and data quality objectives
- Frequency of observations and sampling
- Duration of the monitoring period
- Number and location of monitoring points
- Environmental media to be sampled
- Field and laboratory analytical methods
- Quality assurance/quality control procedures
- Data analysis, evaluation, and documentation

While the types of data collected (contaminant, oxidant, intermediates/byproducts, geochemical changes) for sites where ISCO is being used to treat DNAPL source zones may not differ relative to sites with dilute contaminant plumes, the data collection locations, frequency and duration should be greater for sites with DNAPL source zones. Greater spatial density of data collection will help to ensure that oxidant is transported throughout the TTZ and makes contact with the DNAPL for an adequate time to achieve the expected mass depletion. Also, frequent monitoring will help guide modifications to the ISCO system, if necessary, to achieve target concentrations and oxidant longevity. Long-term monitoring will not only help to assess if treatment objectives have been met, it will also help to establish whether rebound (re-equilibration in the case of source zones) is occurring or likely to occur.

Monitoring only groundwater may underestimate the extent of treatment. Source zones can have contaminant present in multiple phases, including NAPL, sorbed, aqueous and vapor phases. In many cases it is important that monitoring includes each of these phases, although it is common to monitor only the aqueous phase via monitoring wells. However, significant DNAPL mass depletion can occur at a site without significant changes to post-treatment groundwater concentrations after sites have re-equilibrated. Furthermore, monitoring only groundwater provides a limited understanding of potential exposure pathways and associated risk, such as vapor phase concentrations. An integrated monitoring approach will often be required for ISCO applied to DNAPL source zones. Such an approach would include sampling and analysis of COC concentrations in groundwater along with porous media phases complemented by diagnostic techniques such as vertical profiling (using membrane interface probes) and other chemical analyses (chloride concentrations and compound-specific isotopes). Samples collected for analyses need to be carefully handled and preserved to avoid errors and artifacts.

An important foundation for a monitoring program associated with an ISCO project involves the establishment of operational objectives. These are defined as a set of specific delivery and treatment performance-related objectives that, if met, should result in the achievement of the treatment goals for the ISCO remedy. Selecting operational objectives is a project-specific decision. In most cases, they are beneficial for use as a standard against which to compare performance measurements and as a basis for follow-up optimization activities to improve ISCO treatment efficiency. For example, an oxidant recirculation project may include a minimum runtime operational objective to ensure that the treatment system infrastructure is capable of meeting oxidant delivery requirements. If the system runtime does not meet the operational objectives, then optimization activities are needed.

Care should be taken to ensure that the operational objectives are realistic and achievable and, if achieved, lead to successful ISCO treatment. Operational objectives may be established based on bench or field pilot testing, modeling, literature review, previous experience or engineering judgment. Consultation with prospective or contracted ISCO treatment contractors may be beneficial to help define these objectives. Some ISCO contractors have developed unique and proprietary knowledge of ISCO treatments under certain hydrogeochemical and contaminant settings. Typical operational objectives focus on ensuring that the oxidant makes contact with the contaminants within the TTZ for an adequate amount of time to achieve the desired contaminant mass/concentration reduction. Operational objectives that may be considered for an example activated persulfate ISCO application include the following:

- Co-deliver a minimum persulfate concentration of X mg/L and activator concentration of Y mg/L to the zones of highest groundwater contamination within the TTZ.
- Maintain a minimum of Z days of persulfate residence time within the TTZ for the oxidation reaction to occur.
- Minimize loss of oxidant from the TTZ during the delivery process due to daylighting or short-circuiting.
- Maintain hydraulic control and mitigate spread of contamination outside the TTZ.
- Utilize a real-time measurement and data analysis routine to optimize/adapt the injection/monitoring program, ensure cost effective treatment and protect sensitive receptors in the area of treatment.
- Experience zero health and safety incidents.

9.5.2 Monitoring Phases

9.5.2.1 Baseline Monitoring

Baseline monitoring is performed to establish pre-existing conditions and, at a minimum, must include the analysis of environmental samples from impacted media (groundwater, aquifer solids, etc.) at the site for target contaminant(s) and general water quality parameters (dissolved oxygen [DO], ORP, temperature, conductivity) (Siegrist et al., 2011). These baseline analytes are selected because they may affect oxidant performance and may be useful in understanding the ISCO delivery needed; parameters such as ORP, DO and conductivity may be used as surrogate tracers for oxidant migration and distribution. Based on detailed site understanding, the baseline testing may need to be expanded to other parameters, such as potential biological or abiotic interferences, reduced or redox-sensitive metals (if present), products of ISCO treatment (chloride, manganese oxides, acetone, sulfate), fraction organic carbon (f_{OC}) of the sediments and biological sampling to evaluate pretreatment biodiversity.

In general, the baseline monitoring program focuses on characterizing the conditions that affect the injection and monitoring program design, and it is critical to provide a basis for oxidant delivery and contaminant treatment performance assessment. Therefore, much of the baseline sampling focuses on hydrogeological parameters, water chemistry and contaminant phase distribution. Baseline sampling generally should include (1) locations upgradient of the contaminated zone to establish ambient conditions, (2) locations within the TTZ to establish ambient baseline conditions and (3) locations downgradient of the TTZ for treatment performance monitoring (e.g., if downgradient migration of oxidants is expected or if mass flux evaluations are conducted as a treatment cessation criterion). *In situ* chemical oxidation treatment zones are often placed within the core of the contaminated zone and are often subject to some degree of influx or rebound.

Baseline monitoring is typically performed to achieve the following specific objectives:

- Determine pre-existing contaminant concentrations in the different phases.
- Estimate pre-existing contaminant mass.
- Estimate pre-existing mass flux emanating from the contaminant source.
- Estimate ambient variability in water quality concentrations due to natural conditions such as precipitation, seasonal or tidal influence and wet/drought cycles if historical data is available or multiple rounds of baseline monitoring are possible.
- Perform field test for pre-existing geochemical conditions.
- Quantify background metal concentration if metals are at levels of concern.
- Quantify background vadose zone contaminant vapor concentrations if vapor migration is of concern.
- Estimate background biological degradation processes.

Baseline monitoring can be accomplished in many different ways. The most common is to supplement an existing well network and historic database of contaminant concentration data with data collected from a few new borings and wells within the TTZ. Often rapid assessment tools such as a membrane interface probe can assist in developing good data on the contaminant mass and phase distribution. In this way, valuable historical data can be used to aid in assessing the ambient variability of contaminant concentrations, and a one-time analysis of a few key analytes including geochemistry (if missing from historic data set), metals or microbiology can be used to meet the remaining baseline data objectives. Future performance monitoring data can be compared to the historic database to assess treatment efficiency outside the range of historic fluctuation, for example.

Sites seeking to expedite schedules by performing ISCO infrastructure construction and baseline sampling in the same mobilization should be cautious. Well drilling, construction and development activities can cause significant disturbance to the surrounding groundwater. Care must be taken to comply with state requirements, and avoid sampling wells too soon after well development to ensure that baseline samples are representative of the equilibrated formation. Multiple rounds of baseline monitoring can help prevent inaccurate baseline assessment.

Mass flux measurement can be complex and generally requires a detailed understanding of the source and associated dissolved plume geometry and hydrogeological setting. Mass flux measurement requires an understanding of groundwater hydraulics and the dissolved COC distribution. Groundwater hydraulics can be measured using standard slug or pump testing techniques, tracer dilution testing or passive flux meters. The COC distribution can be measured using single or multiple transects of multilevel samplers. Careful consideration should be given to the mass flux measurement methods because method applicability depends upon site conditions.

Baseline monitoring data must be adequate prior to proceeding with the ISCO treatment; ISCO delivery and treatment performance can only be judged after an adequate understanding of the pre-existing conditions.

9.5.2.2 Delivery Performance Monitoring

Delivery performance monitoring is conducted to measure and evaluate the nature and extent of oxidant delivery and hydraulic effects on the water table and includes physical measurements and analysis of environmental samples from the site for parameters indicative of oxidant presence. It does not typically include analysis of target COCs since oxidation reactions are occurring.

In general, the delivery monitoring focuses on characterization of the nature and extent of oxidant delivery for the purposes of evaluating achievement of the design conditions, deciding the scope of continued oxidant injection activities and/or triggering optimization actions. One delivery performance monitoring approach is the observational method (Terzaghi and Peck, 1948). The observational method is an adaptive ISCO implementation method for sites with uncertainty. If the observational method is applied, then delivery performance monitoring data are used to evaluate and optimize the ISCO injection process. The data are compared to trigger levels specified in a site-specific developed implementation or operations plan, and the results are used to determine the next phase of work, whether it be for additional injections, lower pressure application, or delivery cessation because the delivery objectives have been achieved. As such, plans are highly site specific. Delivery performance monitoring is typically performed during and shortly after oxidant delivery for the following purposes:

- Monitor oxidant and activator injection flow rates and volume.
- Monitor water levels and hydraulic controls.
- Monitor injection pressures to ensure aquifers are not plugging or excessive pressures are not applied that could cause well damage, formation deformation or contaminant spreading outside the TTZ.
- Monitor for the appearance of the oxidant to determine if adequate subsurface distribution of the oxidant and activators is occurring; it is very important to recognize the potential for preferential flow and mobile zones in a formation given the pore volumes of oxidant solution delivered and the spacing of observation wells.
- Test changes in ORP, conductivity, pH, DO and temperature to indirectly monitor oxidation reactions and distribution.
- Monitor byproducts to help determine effective radius and the mass of contamination treated.
- Monitor and manage aquifer conditions that affect oxidant chemistry such as pH.
- Monitor nearby utilities for potential breakout (sewer and storm drainage lines).
- Monitor migration/displacement of VOCs in vapor or groundwater during injection.
- Maintain protection of sensitive receptors, human health and the environment.

The timeframe and measurement parameters depend on the oxidant applied, the type of contamination being treated, and the site-specific oxidant persistence. For some oxidants (CHP and ozone), delivery performance monitoring also includes the measurement of oxidant impact on groundwater temperature and off-gas generation in the vadose zone and wellhead space. As such, delivery performance monitoring is also an important component of a comprehensive ISCO health and safety program. Many of the parameters to be monitored are measured using field instrumentation (a YSI 600XL [or similar] water quality meter equipped with a flow-through cell to collect water samples utilizing standard low-flow sampling techniques) or through field kit methods (hydrogen peroxide or persulfate using a CHEMetrics CHEMets® Kit [or similar]).

9.5.2.3 Treatment Performance Monitoring

In situ chemical oxidation, as with any *in situ* technology, is subject to the relatively slow pace of subsurface hydrogeological and contaminant phase distribution equilibrium and mass transfer processes. As such, despite the rapid rates of ISCO contaminant destruction reactions, the re-equilibrated results of an ISCO application are typically not immediately observable. Therefore, most ISCO applications implement treatment performance monitoring. The treatment performance monitoring is typically initiated after oxidant delivery objectives are achieved and the project focus moves toward concentrations of target COCs. Treatment performance monitoring is intended to determine whether the specific treatment goals and milestones established by stakeholders during the design phase are met.

Treatment performance is generally monitored to achieve the following objectives:

- Measure progress toward, and achievement or failure to achieve, the ISCO treatment goals (the degree of source removal or source mass flux reduction)
- Evaluate the extent and uniformity of COC treatment within the TTZ
- Evaluate changes in aquifer solids and aquifer conditions due to the treatment process
- Evaluate effects of recontamination and/or rebound
- Monitor conditions for system optimization through additional applications of ISCO or polishing using another technology within a treatment train approach

Common ISCO treatment goals, as discussed previously, typically include the following:

- Reducing the contaminant mass in the source zone and/or mass discharge
- Numerical standard in a specific phase (soil gas, groundwater or aquifer solids)
- Removal of visible or mobile NAPL
- Achieving a risk-based contamination target

Treatment performance monitoring is often designed to include evaluation of the impact to the contaminant mass whether it is a specific ISCO treatment goal or not because ISCO is most commonly used as a mass reduction technology and evaluation of the impacts to mass is typically the most direct measurement of the effectiveness of the treatment technology. If mass flux reduction is the ISCO treatment goal, it may become important to understand the relationship between mass reduction and mass flux. At many sites, the relationship is not linear, and a large mass reduction may be needed to reduce the mass flux and meet the ISCO treatment goal. Different approaches can be used to estimate contaminant concentrations and mass levels in a target treatment zone and locations downgradient from it. For performance assessment related to ISCO, it is important to pay careful attention to (1) general issues and concerns with sampling and analysis of volatile organic compounds (e.g., West et al., 1995; Oesterreich and Siegrist, 2009) and (2) the effects of ISCO on NOM and associated changes in partitioning behavior (e.g., Woods et al., 2012).

Monitoring dissolved contaminant concentrations in the presence of oxidant requires appropriate sample preservation to prevent further oxidation reactions that may degrade contaminants within the sample container and introduce a negative bias to laboratory results (Huling et al., 2011). Several emerging and innovative tools are available to support an evaluation of ISCO effectiveness. Compound-specific isotope analysis is a useful tool to evaluate whether contaminant destruction has occurred; it may be especially useful to document contaminant mass destruction in source areas where dissolved concentration rebound through dissolution of NAPL or sorbed phase mass into groundwater masks treatment effectiveness. In addition, measurement of chloride concentrations can be used as an indicator of chlorinated solvent mineralization.

Depending upon site-specific concerns of the stakeholders and others involved in the project, an objective of the treatment monitoring plan may also include monitoring the impact of ISCO on subsurface conditions. This may be a concern in site-specific cases as ISCO has the potential to result in changes to microbial populations, geochemical conditions, nontarget organic compounds and aqueous concentration of metals (Siegrist et al., 2011).

In addition, ISCO is often used as part of a treatment train, and other remediation technologies, such as EISB or MNA, may follow ISCO treatment. In this situation, one of the objectives of the treatment performance monitoring may be to establish a baseline condition for follow-up remedy. Therefore, additional parameters beyond those discussed here, such as microbiological analysis, may need to be added to the ISCO treatment performance monitoring.

9.6 STATUS AND AREAS FOR ADVANCEMENTS

9.6.1 Status

In situ chemical oxidation has been developed and deployed for *in situ* remediation of organically contaminated soil and groundwater. The principles and practices associated with ISCO applied to treat dissolved and sorbed phase contamination are generally well established and documented in design manuals and reference texts (ITRC, 2005; Huling and Pivetz, 2006; Siegrist et al., 2011). The application of ISCO to treat DNAPL source zones is not as well established, and field applications for this purpose have had mixed results. While there is a theoretical basis for the degradation of DNAPL residuals by ISCO, cost effective remediation generally depends on the following: (1) susceptibility of DNAPL organics to oxidative destruction, (2) rate and extent of interphase mass transfer of the DNAPL, (3) delivery of an adequate amount of oxidant that contacts DNAPL in the TTZ, (4) effects of subsurface conditions on ISCO reactions and (5) ISCO effects on subsurface permeability and biogeochemistry. These issues have been discussed in the previous sections.

The theoretical considerations related to the application of ISCO to treat DNAPL source zones can be summarized as follows:

- DNAPL source zones tend to be present in highly heterogeneous subsurface settings, both physical and chemical, and delivery of oxidants and amendments is challenging to accomplish and difficult to predict.
- Chemical oxidants, by nature, are nonselective and thus reactions are competitive; in some cases nontarget reactions (nonproductive reactions) can dominate the overall oxidant use.
- A large mass of oxidant is necessary to treat a DNAPL source zone; because use of high concentrations of oxidant can result in greater nonproductive consumption due to NOD and faster decomposition, high fluid volumes are generally necessary.
- Higher oxidant concentrations can give rise to density-driven transport.
- Delivery must overcome physical heterogeneities.
- DNAPL/oxidant contact will maximize treatment. Due to mass transfer limitations of DNAPL, this requires a longer duration of oxidant delivery and/or persistence than a typical aqueous phase application.

- Preferential pathways will cause non-ideal conditions and increase diffusion mass transfer limitations. DNAPL sites will often have significant mass trapped in lower-permeability zones. Over time, DNAPL compounds can back-diffuse into more transmissive zones, and thus, greater oxidant persistence is advantageous.
- Dense nonaqueous phase liquid architecture must be suitable for reagent delivery.

The key challenges to the successful application of ISCO for treatment of DNAPL source zones include:

- Inappropriate goals, schedule, and budget for the site
- Lack of a comprehensive CSM
- Inadequate understanding of site-specific limitations related to contaminant and hydrogeological characteristics
- Limited availability of appropriate predictive tools
- Limited understanding of the effects of ISCO reactions on aquifer physical and biogeochemical processes
- Incomplete and/or inappropriate monitoring (such as groundwater concentrations only) to determine mass depletion
- Contaminant rebound

Successful implementation of ISCO depends on understanding and anticipating these challenges. Approaches for managing these challenges include:

- Coupling ISCO with other site management approaches
- Setting appropriate goals and performance metrics
- Using dynamic characterization and assessment approaches and striving to effectively monitor the right locations and phases to assess DNAPL destruction
- Applying appropriate predictive tools
- Applying enough oxidant solution (volume) at an appropriate concentration for long enough to reflect contaminant mass transfer limitations
- Enhanced delivery approaches
- Multiple delivery events
- Use of rebound data to plan future injections

9.6.2 Areas for Advancement

9.6.2.1 Emerging Approaches and Technologies

Areas for advancement of ISCO, including effective application for DNAPL source zones, have been summarized by Siegrist et al. (2011) and include emerging approaches and technologies in areas such as:

- Using ISCO as part of an integrated approach coupled with other approaches or technologies for improved treatment efficiency and effectiveness
- Enhanced delivery methods for ISCO
- Improved ISCO monitoring and assessment

Interest in using ISCO combined with other technologies is increasing. Using ISCO as a component of a combined remedy can be accomplished simultaneously or through temporal or spatial implementation approaches. *In situ* chemical oxidation and other technologies can be applied sequentially to the same zone, such as ISCO followed by bioremediation, or ISCO can be used to treat a portion of a site, with different technologies applied to other portions. For example, ISCO may be used to treat the source zone, and ISCR may then be used to treat the associated groundwater plume. Potential benefits of combining technologies include improved effectiveness, shorter treatment times, less rebound, and lower overall treatment costs. Examples of emerging approaches and technologies coupled with ISCO include the following: (1) ISCO via multiple oxidants, (2) ISCO with EISB, (3) ISCO with MNA, (4) ISCO with ISCR, (5) ISCO with surfactants and (6) ISCO with thermally enhanced recovery. Issues to consider when selecting and designing a coupled remedy include compatibility of reactants, particularly if used simultaneously (e.g., surfactants and oxidants), and the implication of the byproducts of one technology serving as the inputs for follow-on approaches (such as ISCO followed by MNA – ISCO byproducts will serve as inputs for bioprocesses and other geochemical interactions).

Improving and advancing oxidant delivery approaches is of particular interest because delivery effectiveness is strongly affected by certain hydrogeological and geochemical conditions. Oxidant delivery can be enhanced by improving hydraulic delivery and distribution of the solution containing the oxidant and/or improving oxidant stability and targeted reactivity toward contaminants. An array of approaches are under development, including investigation into oxidant stabilization and/or encapsulation, the use of polymers and other delivery aids to enhance contact between oxidant and contaminant, density-driven delivery and mechanical mixing approaches.

Successful ISCO application also requires appropriate monitoring and assessment of oxidant delivery and treatment effectiveness. The integrated use of field methods and real-time analysis in an expedited approach (Triad) can enhance ISCO system design and implementation. The development and deployment of *in situ* sensors and continuous data logging also can aid in understanding how an ISCO application is progressing.

9.6.2.2 Research Needs and Breakthrough Areas

Research needs and breakthrough areas to enhance ISCO development and deployment include ISCO process chemistry, ISCO delivery, ISCO system design and ISCO process control and assessment (Siegrist et al., 2011). While extensive knowledge about ISCO-related reaction and transport processes is available to guide design and implementation, knowledge gaps need additional attention. Research is needed to more effectively and predictably apply ISCO to a broader range of sites and achieve equal or better outcomes in less time and expense. Additional understanding of reaction mechanisms and kinetics for complex contaminant conditions (pesticides) and/or complex mixtures (manufactured gas plant residuals) is needed. The understanding of oxidant interactions with subsurface constituents needs to improve, along with approaches to minimize nonproductive oxidant consumption. The applicability of ISCO to large, dilute plumes can be improved through such development. The long-term impacts of ISCO on water quality and on specific subsurface constituents (NOM), including influences on post-ISCO natural attenuation, need further attention. Innovative methods for delivering oxidants that will improve movement into or control contaminant migration out of lower permeability zones are necessary. Advances in delivery need to be coupled with tools to understand and predict delivery and treatment effectiveness. Finally, the development of robust sensors to understand oxidant delivery, contaminant treatment, contaminant migration and biogeochemical impacts (which can be deployed *in situ* and transmit data for real-time decision making) would have a beneficial impact on ISCO success.

REFERENCES

Adam ML, Comfort SD, Morley MC, Snow DD. 2004. Remediating RDX-contaminated ground water with permanganate: Laboratory investigations for the Pantex perched aquifer. J Environ Qual 33:2165–2173.

Aiken G. 1992. Chloride interference in the analysis of dissolved organic carbon by the wet oxidation method. Environ Sci Technol 26:2435–2439.

Anipsitakis GP, Dionysiou DD. 2004. Radical generation by the interaction of transition metals with common oxidants. Environ Sci Technol 38:3705–3712.

Appelo CAJ, Postma D. 1999. Geochemistry, Groundwater and Pollution. A.A. Balkema Publishers, Leiden, The Netherlands.

ASTM (American Society for Testing Materials). 2004. Standard Guide for Accelerated Site Characterization for Confirmed or Suspected Petroleum Releases. E1912-98. ASTM International, West Conshohocken, PA, USA.

ASTM. 2007. Standard Test Method for Estimating the Permanganate Natural Oxidant Demand of Soil and Aquifer Solids. D7262-07. ASTM International, West Conshohocken, PA, USA. 5 p.

Ball WP, Liu C, Xia G, Young DF. 1997. A diffusion-based interpretation of tetrachloroethene and trichloroethene concentration profiles in a groundwater aquitard. Water Resour Res 33:2741–2757.

Barbeni M, Nfinero C, Pelizzetti E, Borgarello E, Serpon N. 1987. Chemical degradation of chlorophenols with Fenton's reagent. Chemosphere 16:2225–2237.

Bellamy WD, Hickman PA, Ziemba N. 1991. Treatment of VOC-contaminated groundwater by hydrogen peroxide and ozone oxidation. J Water Pollut Control Fed 63:120–128.

Bissey LL, Smith JL, Watts RJ. 2006. Soil organic matter-hydrogen peroxide dynamics in the treatment of contaminated soils and groundwater using catalyzed H_2O_2 propagations (modified Fenton's reagent). Water Res 40:2477–2484.

Block PA, Brown RA, Robinson D. 2004. Novel activation technologies for sodium persulfate *in situ* chemical oxidation. Proceedings, Fourth International Conference on the Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, USA, May 24–27, Paper 2A-05.

Borden RC, Cha KY, Simpkin T, Lieberman MT. 2012. Development of a Design Tool for Planning Aqueous Amendment Injection Systems Soluble Substrate Design Tool. Final Report and User's Guide, ESTCP Project ER-200626. June. 40 p. http://www.serdp.org/. Accessed January 25, 2014.

Bowers AR, Gaddipati P, Eckenfelder WW, Monsen RM. 1989. Treatment of toxic or refractory wastewaters with hydrogen peroxide. Water Sci Technol 21:477–486.

Braida WJ, Ong SK. 2001. Air sparging effectiveness: Laboratory characteristics of air-channel mass transfer zone for VOC volatilization. J Hazard Mater 87:241–258.

Brown RA, Norris RD. 1986. Method for Decontaminating a Permeable Subterranean Formation. U.S. Patent 4,591,443. U.S. Patent Office, Washington, DC, USA.

Brown RA, Robinson D. 2004. Response to naturally occurring organic material: Permanganate versus persulfate. In Gavaskar AR, Chen ASC, eds, Remediation of Chlorinated and Recalcitrant Compounds, Proceedings, Fourth International Conference, Monterey, USA, Battelle Press, Columbus, OH, USA, May 24–27.

Brown RA, Norris RD, Westray M. 1986. *In situ* treatment of groundwater. Presented at Haz Pro '86, Baltimore, MD, USA, April 1–3.

Brown RA, Skaladany G, Robinson D, Fiacco RJ. 2001. Comparing permanganate and persulfate treatment effectiveness for various organic contaminants. Proceedings, The First International Conference on Oxidation and Reduction Technologies for In-Situ Treatment of Soil and Groundwater, Niagara Falls, Ontario, Canada, June 25–29.

Buxton GV, Greenstock CL, Helman WP, Ross AB. 1988. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (OH·/O·−) in aqueous solution. J Phys Chem Ref Data 17:513–886.

Chapelle FH, Bradley PM, Casey CC. 2005. Behavior of a chlorinated ethene plume following source-area treatment with Fenton's reagent. Ground Water Monit Remediat 25:131–141.

Choi H, Lim H-N, Hwang T-M, Kang J-W. 2002. Transport characteristics of gas phase ozone in unsaturated porous media for in-situ chemical oxidation. J Contam Hydrol 57:81–98.

Christiansen CM. 2010. Methods for Enhanced Delivery of *In Situ* Remediation Amendments in Contaminated Clay Till. PhD Thesis. Technical University of Denmark, Kgs. Lyngby, Denmark.

Christensen KE. 2011. Evaluating Dense Non-aqueous Phase Liquid Dissolution Kinetics and Chemical Oxidation in a Three-dimensional Bench-scale Fracture Network. PhD Thesis. Colorado School of Mines, Golden, CO, USA.

Christiansen CM, Damgaard I, Broholm MM, Kessler T, Klint KE, Nilsson B, Bjerg PL. 2010. Comparison of delivery methods for enhanced *in situ* remediation in clay till. Ground Water Monit Remediat 30:107–122.

Clement TP. 1997. A Modular Computer Code for Simulating Reactive Multi-Species Transport in 3-D Groundwater Systems. PNNL-11720. Pacific Northwest National Laboratory, Richland, WA, USA, 59 pp.

Clement TP. 2001. Generalized solution to multispecies transport equations coupled with a first-order reaction network. Water Resour Res 37:157–163.

Clement TP, Johnson CD. 2002. What's New in RT3D Version 2.5. Pacific Northwest National Laboratory, Richland, WA. 20 p. http://www.eng.auburn.edu/~clemept/Computer_codes/RT3Dv25_Update.pdf. Accessed January 25, 2014.

Clement TP, Sun Y, Hooker BS, Petersen JN. 1998. Modeling multispecies reactive transport in ground water. Ground Water Monit Remediat 18:79–82.

Clement TP, Johnson CD, Sun Y, Klecka GM, Bartlett C. 2000. Natural attenuation of chlorinated solvent compounds: Model development and field-scale application. J Contam Hydrol 42:113–140.

Conrad SH, Glass RJ, Peplinski WJ. 2002. Bench-scale visualization of DNAPL remediation processes in analog heterogeneous aquifers: Surfactant floods and *in situ* oxidation using permanganate. J Contam Hydrol 58:13–49.

Corbin JF III, Teel AL, Allen-King RM, Watts RJ. 2007. Reactive oxygen species responsible for the enhanced desorption of dodecane in modified Fenton's systems. Water Environ Res 79:37–42.

Crawford S, Smith BA, O'Shaughnessy K, Hagelin N, Jacobson R. 2009. Application of alkaline activated persulfate and evaluation of treatment residuals. Conference on Design and Construction Issues at Hazardous Waste Sites, Philadelphia, PA, USA.

Crimi M, Ko S. 2009. Control of manganese dioxide particles resulting from *in situ* chemical oxidation using permanganate. Chemosphere 74:847–853.

Crimi ML, Siegrist RL. 2003. Geochemical effects associated with permanganate oxidation of DNAPLs. Ground Water 41:458–469.

Crimi ML, Siegrist RL. 2004a. Association of cadmium with MnO_2 particles generated during permanganate oxidation. Water Res 38:887–894.

Crimi ML, Siegrist RL. 2004b. Impact of reaction conditions on MnO_2 genesis during permanganate oxidation. J Environ Eng 130:562–572.

Crimi ML, Siegrist RL. 2005. Factors affecting effectiveness and efficiency of DNAPL destruction using potassium permanganate and catalyzed hydrogen peroxide. J Environ Eng 131:1716–1723.

Crimi ML, Taylor J. 2007. Experimental evaluation of catalyzed hydrogen peroxide and sodium persulfate for destruction of BTEX contaminants. Soil Sediment Contam 16:29–45.

Crimi M, Quickel M, Ko S. 2009. Enhanced permanganate *in situ* chemical oxidation through MnO_2 particle stabilization: Evaluation in 1-D transport systems. J Contam Hydrol 105:69–79.

Crimi M, Silva JAK, Palaia T. 2011. Cooperative Technology Demonstration: Polymer-Enhanced Subsurface Delivery and Distribution of Permanganate. ESTCP Project ER-0912. http://www.serdp.org/. Accessed November 2, 2012.

Cross PE, Baird D. 2008. Initial Results of ISCO for a Large TCE DNAPL Source Area. Presentation at the Sixth International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2008). In Sass BM (Conference Chair), Remediation of Chlorinated and Recalcitrant Compounds – 2008. ISBN 1-57477-163-9, Battelle Press, Columbus, OH, USA, Abstract C-018.

Cross PE, Baird D, Wymore R. 2006. Modified Fenton's Reagent Remediation of a Large TCE Source Zone. Presentation at the Fifth International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2006). In Sass BM (Conference Chair), Remediation of Chlorinated and Recalcitrant Compounds – 2006. ISBN 1-57477-157-4, Battelle Press, Columbus, OH, USA, Abstract D-68.

Crumbling DM, Groenjes C, Lesnik B, Lynch K, Shockley J, VanEe J, Howe R, Keith L, McKenna G. 2001. Applying the concept of effective data to contaminated sites could reduce costs and improve cleanups. Environ Sci Technol 35:405A-409A.

Crumbling DM, Griffith J, Powell DM. 2003. Improving decision quality: Making the case for adopting next-generation site characterization practices. Remediat 13:91–111.

Dugan P. 2006. Coupling *In Situ* Technologies for DNAPL Remediation and Viability of the PITT for Post-Remediation Performance Assessment. PhD Thesis. Colorado School of Mines, Golden, CO, USA.

Dugan PJ, Vlastnik E, Ivy S, Swearingen L, Swearingen J. 2009. Micro-encapsulated oxidant technology: Enhancing *in situ* chemical oxidation (ISCO) with selective oxidation using controlled-release permanganate. Proceedings, Annual Conference on Soils, Sediments, Water, and Energy, Amherst, MA, USA, October 19–22. http://www.umasssoils.com/posters2009/chem_ox.htm. Accessed November 2, 2012.

Dugan PJ, Siegrist RL, Crimi M. 2010. Coupling surfactants/cosolvents with oxidants for enhanced DNAPL removal: A review. Remediat J 20:27–50.

ESTCP (Environmental Security Technology Certification Program). 1999. Technology Status Review: *In Situ* Oxidation. ESTCP, Arlington, VA, USA. 50 p. http://www.serdp.org/. Accessed June 25, 2012.

Forsey SP, Thomson NR, Barker JF. 2010. Oxidation kinetics of polycyclic aromatic hydrocarbons by permanganate. Chemosphere 79:628–636.

Furman O, Teel AL, Watts RJ. 2010. Mechanism of base activation of persulfate. Environ Sci Technol 44:6423–6428.

Gates DD, Siegrist RL. 1993. Laboratory Evaluation of Chemical Oxidation Using Hydrogen Peroxide. Report from The X-231B Project for *In Situ* Treatment by Physicochemical Processes Coupled with Soil Mixing, ORNL/TM-12259. Oak Ridge National Laboratory, Oak Ridge, TN, USA.

Gates DD, Siegrist RL. 1995. *In situ* chemical oxidation of trichloroethylene using hydrogen peroxide. J Environ Eng 121:639–644.

Gates DD, Siegrist RL, Cline SR. 1995. Chemical Oxidation of Contaminants in Clay or Sandy Soil. Proceedings, American Society of Civil Engineering (ASCE) National Conference on Environmental Engineering, Pittsburgh, PA, USA, July 1995.

Gates-Anderson DD, Siegrist RL, Cline SR. 2001. Comparison of potassium permanganate and hydrogen peroxide as chemical oxidants for organically contaminated soils. J Environ Eng 127:337–347.

Glaze WH, Kang JW. 1988. Advanced oxidation processes for treating groundwater contaminated with TCE and PCE: Laboratory studies. J Am Water Works Assoc 5:57–63.

Harbaugh AW, McDonald MG. 1996a. User's Documentation for MODFLOW-96: An Update to the U.S. Geological Survey Modular Finite-Difference Ground-Water Flow Model. Open-File Report 96-485. U.S. Geological Survey, Reston, VA, USA. 56 p.

Harbaugh AW, McDonald MG. 1996b. Programmer's Documentation for MODFLOW-96: An Update to the U.S. Geological Survey Modular Finite-Difference Ground-Water Flow Model. Open-File Report 96-485. U.S. Geological Survey, Reston, VA, USA, 56 p.

Harbaugh AW, Banta ER, Hill MC, McDonald MG. 2000. MODFLOW-2000: The U.S. Geological Survey Modular Ground-Water Model – User Guide to Modularization Concepts and the Ground-Water Flow Process Model. Open-File Report 00-92. U.S. Geological Survey, Reston, VA, USA, 130 p.

Haselow JS, Siegrist RL, Crimi ML, Jarosch T. 2003. Estimating the total oxidant demand for *in situ* chemical oxidation design. Remediat J 13:5–15.

Heiderscheidt JL. 2005. DNAPL Source Zone Depletion During *In Situ* Chemical Oxidation (ISCO): Experimental and Modeling Studies. PhD Thesis. Colorado School of Mines, Golden, CO, USA.

Heiderscheidt JL, Siegrist RL, Illangasekare TH. 2008a. Intermediate-scale 2D experimental investigation of *in situ* chemical oxidation using potassium permanganate for remediation of complex DNAPL source zones. J Contam Hydrol 102:3–16.

Heiderscheidt JL, Crimi ML, Siegrist RL, Singletary M. 2008b. Optimization of full-scale permanganate ISCO system operation: Laboratory and numerical studies. Ground Water Monit Remediat 28:72–84.

Held RJ, Illangasekare TH. 1995a. Fingering of dense non-aqueous phase liquids in porous media: 1. Experimental investigation. Water Resour Res 31:1213–1222.

Held RJ, Illangasekare TH. 1995b. Fingering of dense non-aqueous phase liquids in porous media: 2. Analysis and classification. Water Resour Res 31:1223–1231.

Henderson TH, Mayer KU, Parker BL, Al TA. 2009. Three-dimensional density-dependent flow and multicomponent reactive transport modeling of chlorinated solvent oxidation by potassium permanganate. J Contam Hydrol 106:195–211.

Hønning J, Broholm M, Bjerg P. 2007. Role of diffusion in chemical oxidation of PCE in a dual permeability system. Environ Sci Technol 41:8426–8432.

House DA. 1962. Kinetic and mechanisms of oxidations by peroxydisulfate. Chem Rev 62:185–203.

Huang KC, Couttenye RA, Hoag GE. 2002. Kinetics of heat-assisted persulfate oxidation of methyl tert-butyl ether (MTBE). Chemosphere 49:413–420.

Huie RE, Clifton CL, Neta P. 1991. Electron transfer reaction rates and equilibria of the carbonate and sulfate radical anions. International Journal of Radiation Applications and Instrumentation, Part C: Radiat Phys Chem 38:477–481.

Huling SG, Pivetz BE. 2006. Engineering issue paper: In-situ chemical oxidation. EPA 600-R-06-072. U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Cincinnati, OH, USA. 60 p. http://www.epa.gov/tio/tsp/issue.htm#EF. Accessed November 3, 2012.

Huling SG, Ko S, Pivetz B. 2011. Groundwater sampling at ISCO sites: Binary mixtures of volatile organic compounds and persulfate. Ground Water Monit Remediat 31:72–79.

Illangasekare TH, Armbruster EJ III, Yates DN. 1995a. Non-aqueous-phase fluids in heterogeneous aquifer: Experimental study. J Environ Eng 121:571–579.

Illangasekare TH, Ramsey JL, Jensen KH, Butts M. 1995b. Experimental study of movement and distribution of dense organic contaminants in heterogeneous aquifers. J Contam Hydrol 20:1–25.

Illangasekare TH, Munakata Marr J, Siegrist RL, Soga K, Glover KC, Moreno-Barbero E, Heiderscheidt JL, Saenton S, Matthew M, Kaplan AR, Kim Y, Dai D, Gago JL, Page JWE. 2006. Mass Transfer from Entrapped DNAPL Sources Undergoing Remediation: Characterization Methods and Prediction Tools. CU-1294. ER 1294. Final Report. Strategic Environmental Research and Development Program (SERDP), Arlington, VA, USA. 435 p. http://www.serdp.org/. Accessed November 2, 2012.

ITRC (Interstate Technology & Regulatory Council). 2001. Technical and Regulatory Guidance for *In Situ* Chemical Oxidation of Contaminated Soil and Groundwater (ISCO-1). Washington, DC, USA. http://www.itrcweb.org/guidancedocument.asp?TID=13. Accessed November 2, 2012.

ITRC. 2003. Technology and Regulatory Guidance for the Triad Approach: A New Paradigm for Environmental Project Management. SCM-1, December. ITRC, Washington, DC, USA. http://www.itrcweb.org/guidance/getdocument?documentid=90. Accessed June 19, 2013.

ITRC. 2005. Technical and Regulatory Guidance for *In Situ* Chemical Oxidation of Contaminated Soil and Groundwater, 2nd ed (ISCO-2). Prepared by the ITRC *In Situ* Chemical Oxidation Team. http://www.itrcweb.org/guidancedocument.asp?TID=13. Accessed December 6, 2009.

ITRC. 2007. Triad Implementation Guide. SCM-3. ITRC Sampling, Characterization, and Monitoring Team, Washington, DC, USA. http://www.itrcweb.org. Accessed November 2, 2012.

Johnson CD, Truex MJ, Clement TP. 2006. Natural and Enhanced Attenuation of Chlorinated Solvents Using RT3D. PNNL-15937. Pacific Northwest National Laboratory, Richland, WA, USA.

Johnson RL, Pankow JF. 1992. Dissolution of dense chlorinated solvents into groundwater. 2. Source functions for pools of solvent. Environ Sci Technol 26:896–901.

Johnson RL, Tratnyek PG, O'Brien Johnson R. 2008. Persulfate persistent under thermal activation conditions. Environ Sci Technol 42:9350–9356.

Jones LJ. 2007. The Impact of NOD Reaction Kinetics on Treatment Efficiency. MS Thesis. University of Waterloo, Waterloo, Ontario, Canada.

Jones PW, Williams DR. 2002. Chemical speciation simulation used to assess the efficiency of environment-friendly EDTA alternative for use in pulp and paper industry. Inorg Chim Acta 339:41–50.

Jung H, Kim J, Choi H. 2004. Reaction kinetics of ozone in variably saturated porous media. J Environ Eng 130:432–441.

Jung H, Ahn Y, Choi H, Kim IS. 2005. Effects of in-situ ozonation on indigenous microorganisms in diesel contaminated soil: Survival and regrowth. Chemosphere 61:923–932.

Kakarla PKC, Watts RJ. 1997. Depth of Fenton-like oxidation in remediation of surface soils. J Environ Eng 123:11–17.

Kim J, Choi H. 2002. Modeling *in situ* ozonation for the remediation of nonvolatile PAH-contaminated unsaturated soils. J Contam Hydrol 55:261–285.

Kim K, Gurol MD. 2005. Reaction of nonaqueous phase TCE with permanganate. Environ Sci Technol 39:9303–9308.

Kolthoff IM, Miller IK. 1951. The chemistry of persulfate. I. The kinetics and mechanism of the decomposition of the persulfate ion in aqueous medium. J Am Chem Soc 73:3055–3059.

Krembs FJ. 2008. Critical Analysis of the Field Scale Application of *In Situ* Chemical Oxidation for the Remediation of Contaminated Groundwater. MS Thesis. Colorado School of Mines, Golden, CO, USA.

Krembs FJ, Siegrist RL, Crimi M, Furrer RF, Petri BG. 2010. ISCO for groundwater remediation: Analysis of field applications and performance. Ground Water Monit Remediat 30:42–53.

Kueper BH, Frind EO. 1991a. Two-phase flow in heterogeneous porous media. 1. Model development. Water Resour Res 27:1049–1057.

Kueper BH, Frind EO. 1991b. Two-phase flow in heterogeneous porous media. 2. Model application. Water Resour Res 27:1059–1070.

Kueper BH, Abbot W, Farquhar G. 1989. Experimental observations of multiphase flow in heterogeneous porous media. J Contam Hydrol 5:83–95.

Kueper BH, Redman D, Starr RC, Reitsma S, Mah M. 1993. A field experiment to study the behavior of tetrachloroethylene below the water table: Spatial distribution of residual and pooled DNAPL. Ground Water 31:756–766.

Lee BS, Kim JH, Lee KC, Kim YB, Schwartz FW, Lee ES, Woo NC, Lee MK. 2009. Efficacy of controlled-release KMnO4 (CRP) for controlling dissolved TCE plume in groundwater: A large flow-tank study. Chemosphere 74:745–750.

Lee ES, Schwartz FW. 2007. Characteristics and applications of controlled-release $KMnO_4$ for groundwater remediation. Chemosphere 66:2058–2066.

Lee ES, Seol Y, Fang YC, Schwartz FW. 2003. Destruction efficiencies and dynamics of reaction fronts associated with the permanganate oxidation of trichloroethylene. Environ Sci Technol 37:2540–2546.

Li XD, Schwartz FW. 2003. Permanganate Oxidation Schemes for the Remediation of Source Zone DNAPLs and Dissolved Contaminant Plumes. In Henry SM, Warner SD, eds, Chlorinated Solvent and DNAPL Remediation. American Chemical Society, Washington, DC, USA, pp 73–85.

Li XD, Schwartz FW. 2004. DNAPL mass transfer and permeability reduction during *in situ* chemical oxidation with permanganate. Geophys Res Lett 31:L06504, doi:10.1029/2003GL019218.

Liang C, Lee IL. 2008. *In situ* iron activated persulfate oxidative fluid sparging treatment of TCE contamination: A proof of concept study. J Contam Hydrol 100:91–100.

Liang C, Bruell CJ, Marley MC, Sperry KL. 2004a. Persulfate oxidation for *in situ* remediation of TCE. I. Activated by ferrous ion with and without a persulfate-thiosulfate redox couple. Chemosphere 55:1213–1223.

Liang C, Bruell CJ, Marley MC, Sperry KL. 2004b. Persulfate oxidation for *in situ* remediation of TCE. II. Activated by chelated ferrous ion. Chemosphere 55:1225–1233.

Liang C, Wang Z S, Mohanty N. 2006. Influences of carbonate and chloride ions on persulfate oxidation of trichloroethylene at 20 C. Sci Total Environ 370:271–277.

Liang C, Huang CF, Mohanty N, Lu CJ, Kurakalva RM. 2007. Hydroxypropyl-β-cyclodextrin-mediated iron-activated persulfate oxidation of trichloroethylene and tetrachloroethylene. Ind Eng Res 46:6466–6479.

Liang C, Lee I-L, Hsu I-Y, Liang C-P, Lin Y-L. 2008. Persulfate oxidation of trichloroethylene with and without iron activation in porous media. Chemosphere 70:426–435.

Liu C, Ball WP. 2002. Back diffusion of chlorinated solvent contaminants from a natural aquitard to a remediated aquifer under well-controlled field conditions: Predictions and measurements. Ground Water 40:175–184.

Lowe KS, Gardner FG, Siegrist RL. 2002. Field pilot test of *in situ* chemical oxidation through recirculation using vertical wells. Ground Water Monit Remediat 22:106–115.

Mackay DM, Cherry JA. 1989. Ground water contamination: Limits of pump-and-treat remediation. Environ Sci Technol 23:630–636.

MacKinnon LK, Thomson NR. 2002. Laboratory-scale *in situ* chemical oxidation of a perchloroethylene pool using permanganate. J Contam Hydrol 56:49–74.

Marvin BK, Nelson CH, Clayton W, Sullivan KM, Skladany G. 1998. *In Situ* Chemical Oxidation of Pentachlorophenol and Polycyclic Aromatic Hydrocarbons: From Laboratory Tests to Field Demonstration. In Wickramanayake GB, Hinchee RE, eds, Physical, Chemical, and Thermal Technologies: Remediation of Chlorinated and Recalcitrant Compounds. Battelle Press, Columbus, OH, USA, pp 383–388.

McDade JM, McGuire TM, Newell CJ. 2005. Analysis of DNAPL source-depletion costs at 36 field sites. Remediat J 15:9–18.

McDonald MG, Harbaugh AW. 1988. A Modular Three-Dimensional Finite-Difference Ground-Water Flow Model. Techniques of Water-Resources Investigations, Book 6, Chapter A1. U.S. Geological Survey, Reston, VA, USA, 586 p.

Monahan MJ, Teel AL, Watts RJ. 2005. Displacement of five metals sorbed on kaolinite during treatment with modified Fenton's reagent. Water Res 39:2955–2963.

Morgan JJ, Stumm W. 1963. Colloid-chemical properties of manganese dioxide. J Coll Sci 19:347–359.

Mumford KG, Lamarche CS, Thomson NR. 2004. Natural oxidant demand of aquifer materials using the push-pull technique. J Environ Eng 130:1139–1146.

Mumford KG, Thomson NR, Allen-King RM. 2005. Bench-scale investigation of permanganate natural oxidant demand kinetics. Environ Sci Technol 39:2835–2840.

NAVFAC (Naval Facilities Engineering Service Center). 2000. Site 11, Old Camden County Landfill Remedial Action Operation: NSB Kings Bay, GA. Remedial Action Operation Optimization Summary Report. NFESC, Port Hueneme, CA, USA, 8 p.

Ndjou'ou A-C, Cassidy D. 2006. Surfactant production accompanying the modified Fenton oxidation of hydrocarbons in soil. Chemosphere 65:1610–1615.

Nelson MD. 1999. The Geochemical Reactions and Density Effects Resulting from the Injection of $KMnO_4$ for PCE DNAPL Oxidation in a Sandy Aquifer. MSc Thesis. University of Waterloo, Waterloo, ON, Canada.

Nelson CH, Brown RA. 1994. Adapting ozonation for soil and ground water cleanup. Chem Eng 11:EE18-EE22.

NRC. 2005. Contaminants in the Subsurface: Source Zone Assessment and Remediation. National Academies Press, Washington, DC, USA. 372 p.

Osgerby IT, Smith BA, Crawford SC, Sperry K, Boeckeler AJ, Getchell SA, McGrath D, Acone SE, Hathaway E. 2006. Case Study: History of a Successful ISCO Project: Eastland Woolen Mills Superfund Site (Corinna, Maine). Proceedings, The 5th International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, USA.

Oesterreich RC, Siegrist RL. 2009. Quantifying volatile organic compounds in porous media: Effects of sampling method attributes, contaminant characteristics and environmental conditions. Env Sci Technol 43:2891–2898.

Perez-Benito JF, Arias C. 1991. Occurrence of colloidal manganese dioxide in permanganate reactions. J Colloid Interface Sci 152:70–84.

Petri BG. 2006. Impacts of Subsurface Permanganate Delivery Parameters on Dense Nonaqueous Phase Liquid Mass Depletion Rates. MS Thesis, Environmental Science and Engineering Division, Colorado School of Mines, Golden, CO, USA.

Petri B, Siegrist RL, Crimi ML. 2008. Effects of groundwater velocity and permanganate concentration on DNAPL mass depletion rates during *in situ* oxidation. J Environ Eng 134:1–13.

Pinder GF, Abriola LM, 1986. On the simulation of non-aqueous phase organic compounds in the subsurface. Water Resour Res 22:109S-119S.

Poulsen MM, Kueper BH. 1992. A field experiment to study the behavior of tetrachloroethylene in unsaturated porous media. Environ Sci Technol 26:889–895.

Qiu Y, Kuo CH, Zappi ME, Fleming EC. 2004. Ozonation of 2,6- 3,4- and 3,5-dichlorophenol isomers within aqueous solutions. J Environ Eng 130:408–416.

Ramo J. 2003. Hydrogen Peroxide-Metals-Chelating Agents: Interactions and Analytical Techniques. Oulu University Press, Oulu, Finland.

Ravikumur JX, Gurol M. 1994. Chemical oxidation of chlorinated organics by hydrogen peroxide in the presence of sand. Environ Sci Technol 28:394–400.

Reitsma S, Marshall M. 2000. Experimental Study of Oxidation of Pooled NAPL. In Wickramanayake GB, Gavaskar AR, Chen ASC, eds, Chemical Oxidation and Reactive Barriers: Remediation of Chlorinated and Recalcitrant Compounds. Battelle Press, Columbus, OH, USA, pp 25–32.

Ross C, Murdoch LC, Freedman DL, Siegrist RL. 2005. Characteristics of potassium permanganate encapsulated in polymer. J Environ Eng 131:1203–1211.

Sahl J. 2005. Coupling *In Situ* Chemical Oxidation (ISCO) with Bioremediation Processes in the Treatment of Dense Non-Aqueous Phase Liquids (DNAPLs). MS Thesis, Environmental Science and Engineering Division, Colorado School of Mines, Golden, CO, USA.

Sahl J, Munakata-Marr J. 2006. The effects of *in situ* chemical oxidation on microbial processes: A review. Remediat J 16:57–70.

Sahl JW, Munakata-Marr J, Crimi ML, Siegrist RL. 2007. Coupling permanganate oxidation with microbial dechlorination of tetrachloroethene. Water Environ Res 79:5–12.

Sale T, Illangasekare T, Zimbron J, Rodriguez D, Wilking B, Marinelli F. 2007. AFCEE Source Zone Initiative. Final Report. Submitted to Air Force Center for Engineering and the Environment, Brooks City-Base, TX, USA.

Schincariol RA, Schwartz FW. 1990. An experimental investigation of variable density flow and mixing in homogeneous and heterogeneous media. Water Resour Res 26:2317–2329.

Schmidt JT, Ahmad M, Teel AL, Watts RJ. 2011. Hydrogen peroxide stabilization in one-dimensional flow columns. J Contam Hydrol 126:1–7.

Schnarr MJ, Truax CL, Farquhar GJ, Hood ED, Gonullu T, Stickney B. 1998. Laboratory and controlled field experiments using potassium permanganate to remediate trichloroethylene and perchloroethylene DNAPLs in porous media. J Contam Hydrol 29:205–224.

Schroth MH, Oostrom M. Wietsma TW, Istok JD. 2001. In-situ oxidation of trichloroethene by permanganate: Effects on porous medium hydraulic properties. J Contam Hydrol 44:185–201.

Schwarzenbach RP, Gschwend PM, Imboden DM. 1993. Environmental Organic Chemistry. John Wiley & Sons, Inc., New York, NY, USA.

Schwille F. 1988. Dense Chlorinated Solvents in Porous and Fractured Media. Translated by JF Pankow. Lewis Publishers, Chelsea, MI, USA. 146 p.

Shin W-T, Garanzuay X, Yiacoumi S, Tsouris C, Gu B, Mahinthakumar G. 2004. Kinetics of soil ozonation: An experimental and numerical investigation. J Contam Hydrol 72:227–243.

Siegrist RL, Lowe KS, Murdoch LD, Slack WW, Houk TC. 1998a. X-231A Demonstration of *In Situ* Remediation of DNAPL Compounds in Low Permeability Media by Soil Fracturing with Thermally Enhanced Mass Recovery or Reactive Barrier Destruction. Oak Ridge National Laboratory Report ORNL/TM-13534. U.S. Department of Energy Office of Technology Development, Washington, DC, USA. 407 p.

Siegrist RL, Lowe KS, Murdoch LC, Case TL, Pickering DA, Houk TC. 1998b. Horizontal Treatment Barriers of Fracture-Emplaced Iron and Permanganate Particles. In North Atlantic Treaty Organization (NATO)/Committee on the Challenges for Modern Society (CCMS) Pilot Study Special Session on Treatment Walls and Permeable Reactive Barriers. EPA 542-R-98-003. Washington, DC, USA, pp 77–82.

Siegrist RL, Lowe KS, Murdoch LC, Case TL, Pickering DL. 1999. *In situ* oxidation by fracture emplaced reactive solids. J Environ Eng 125:429–440.

Siegrist RL, Urynowicz MA, West OR, Crimi ML, Lowe KS. 2001. Principles and Practices of *In Situ* Chemical Oxidation Using Permanganate. Battelle Press, Columbus, OH, USA. 336 p.

Siegrist RL, Urynowicz MA, Crimi ML, Lowe KS. 2002. Genesis and effects of particles produced during *in situ* chemical oxidation using permanganate. J Environ Eng 128:1068:1079.

Siegrist RL, Crimi ML, Munakata-Marr J, Illangasekare T, Lowe KS, Van Cuyk S, Dugan P, Heiderscheidt J, Jackson S, Petri B, Sahl J, Seitz S. 2006. Reaction and Transport Processes Controlling *In Situ* Chemical Oxidation of DNAPLs. ER-1290 Final Report. DoD Strategic Environmental Research and Development Program (SERDP), Washington, DC, USA. 235 p. http://www.serdp.org/. Accessed November 2, 2012.

Siegrist RL, Crimi ML, Munakata-Marr J, Illangasekare T, Dugan P, Heiderscheidt J, Petri B, Sahl J. 2008a. Chemical Oxidation for Clean Up of Contaminated Ground Water. In Annable MD, Teodorescu M, Hlavinek P, Diels L, eds, Methods and Techniques for Cleaning-Up Contaminated Sites. NATO Science for Peace and Security Series. Springer Publishing, Dordrecht, The Netherlands, pp 45–58.

Siegrist RL, Petri B, Krembs F, Crimi ML, Ko S, Simpkin T, Palaia T. 2008b. *In Situ* Chemical Oxidation for Remediation of Contaminated Ground Water. Proceedings, ISCO Technology Practices Workshop. ESTCP ER-0623. Golden, CO, USA, March 7–8, 2007. 77 p. http://www.serdp.org/. Accessed November 2, 2012.

Siegrist RL, Crimi ML, Petri B, Simpkin T, Palaia T, Krembs FJ, Munakata-Marr J, Illangasekare T, Ng G, Singletary M, Ruiz N. 2010. *In Situ* Chemical Oxidation for Groundwater Remediation: Site Specific Engineering and Technology Application. ER-0623. Version PRv1.01, October 29, 2010). Final Report. Version PRv1.01, October 29, 2010). ESTCP, Arlington, VA, USA. http://www.serdp.org/. Accessed January 25, 2014.

Siegrist RL, Crimi M, Simpkin TJ, eds. 2011. *In Situ* Chemical Oxidation for Groundwater Remediation. Springer, New York, NY, USA. 678 p.

Silva JAK. 2011. The Utility of Polymer Amendment for Enhancing *In Situ* Remediation Effectiveness. PhD Thesis. Colorado School of Mines, Golden, CO, USA.

Sirguey C, de Souza e Silva PT, Schwartz C, Simonnot M. 2008. Impact of chemical oxidation on soil quality. Chemosphere 72:282–289.

Smith BA, Teel AL, Watts RJ. 2004. Identification of the reactive oxygen species responsible for carbon tetrachloride degradation in modified Fenton's systems. Environ Sci Technol 38:5465–5469.

Smith BA, Teel AL, Watts RJ. 2006. Mechanism for the destruction of carbon tetrachloride and chloroform DNAPLs by modified Fenton's reagent. J Contam Hydrol 85:229–246.

Smith BA, Marley MC, O'Shaughnessy K, Maclean DA, Santos DA. 2012. In-Situ Chemical Oxidation (ISCO) Using Catalyzed Hydrogen Peroxide to Remediate a DNAPL Source Area. Proceedings, 8th International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, May 19–22.

Smith MM, Silva JAK, Munakata-Marr J, McCray JE. 2008. Compatibility of polymers and chemical oxidants for enhanced groundwater remediation. Environ Sci Technol 42:9296–9301.

Sra KS, Thomson NR, Barker JF. 2010. Persistence of persulfate in uncontaminated aquifer materials. Environ Sci Technol 44:3098–3104.

Stewart CL. 2002. Density-Driven Permanganate Solution Delivery and Chemical Oxidation of a Thin Trichloroethene DNAPL Pool in a Sandy Aquifer. MSc Thesis. University of Waterloo, Waterloo, Ontario, Canada.

Stewart R. 1964. Oxidation Mechanisms. W.A. Benjamin, New York, NY, USA.

Struse AM, Siegrist RL, Dawson HE, Urynowicz MA. 2002. Diffusive transport of permanganate during *in situ* oxidation. J Environ Eng 128:327–334.

Sun H, Yan Q. 2007. Influence of Fenton oxidation on soil organic matter and its sorption and desorption of pyrene. J Hazard Waste Hazard Mater 144:164–170.

Sun Y, Pignatello JJ. 1992. Chemical treatment of pesticide wastes. Evaluation of Fe(III) chelates for catalytic hydrogen peroxide oxidation of 2,4-D at circumneutral pH. J Agric Food Chem 40:332–337.

Sung W, Morgan JJ. 1980. Kinetics and product of ferrous iron oxygenation in aqueous systems. Environ Sci Technol 14:561–567.

Teel AL, Finn DD, Schmidt JT, Cutler LM, Watts RJ. 2007. Rates of trace mineral-catalyzed decomposition of hydrogen peroxide. J Environ Eng 133:853–858.

Terzaghi K, Peck RB. 1948. Soil Mechanics in Engineering Practice. John Wiley & Sons, New York, NY, USA.

Thomson NR, Johnson RL. 2000. Air distribution during *in situ* air sparging: An overview of mathematical modeling. J Hazard Mater 72:265–282.

Tollefsrud E, Schreier CG. 2002. Effectiveness of chemical oxidation to remove organochlorine pesticides from soil. Proceedings, Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, USA. Battelle Press, Columbus, OH, USA, Paper 2C-16.

Tratnyek PG, Johnson TL, Warner SD, Clarke HS, Baker JA. 1998. *In Situ* Treatment of Organics by Sequential Reduction and Oxidation. In Wickramanayake GB, Hinchee RE, eds, Physical, Chemical, and Thermal Technologies: Remediation of Chlorinated and Recalcitrant Compounds. Battelle Press, Columbus, OH, USA, pp 371–376.

Tsitonaki A, Petri B, Crimi M, Mosbæk H, Siegrist RL, Bjerg PL. 2010. *In situ* chemical oxidation of contaminated soil and groundwater using persulfate: A review. Crit Rev Environ Sci Technol 40:55–91.

Tunnicliffe BS, Thomson NR. 2004. Mass removal of chlorinated ethenes from rough-walled fractures using permanganate. J Contam Hydrol 75:91–114.

Tyre BW, Watts RJ, Miller GC. 1991. Treatment of four biorefractory contaminants in soils using catalyzed hydrogen peroxide. J Environ Qual 20:832–838.

Urynowicz MA, Siegrist RL. 2000. Chemical Degradation of TCE DNAPL by Permanganate. In Wickramanayake GB, Gavaskar AR, Chen ASC, eds, Chemical Oxidation and Reactive Barriers: Remediation of Chlorinated and Recalcitrant Compounds Series C2-6. Battelle Press, Columbus, OH, USA, pp 75–82.

Urynowicz MA, Siegrist RL. 2005. Interphase mass transfer during chemical oxidation of TCE DNAPL in an aqueous system. J Contam Hydrol 80:93–106.

Urynowicz MA, Balu B, Udayasankar U. 2008. Kinetics of natural oxidant demand by permanganate in aquifer solids. J Contam Hydrol 96:87–194.

USEPA (U.S. Environmental Protection Agency). 1998. Field Applications of *In Situ* Remediation Technologies: Chemical Oxidation. EPA 542-R-98-008. USEPA OSWER, Washington, DC, USA. http://www.epa.gov/swertio1/download/remed/chemox.pdf. Accessed November 2, 2012.

USEPA. 2003. The DNAPL Remediation Challenge: Is There a Case for Source Depletion?. 600-R-03-143. USEPA Office of Research and Development, Washington, DC, USA. December.

USEPA. 2008. Triad Central Website. http://www.triadcentral.org. Accessed January 25, 2014.

Vella PA, Veronda B. 1994. Oxidation of Trichloroethylene: A Comparison of Potassium Permanganate and Fenton's Reagent. In *In Situ* Chemical Oxidation for the Nineties, Vol 3. Technomic Publishing, Inc., Lancaster, PA, USA, pp 62–73.

Vella PA, Deshinsky G, Boll JE, Munder J, Joyce WM. 1990. Treatment of low-level phenols with potassium permanganate. Res J Water Pollut Control Fed 62:907–914.

Venkatadri R, Peters RW. 1993. Chemical oxidation technologies: Ultraviolet light/hydrogen peroxide, Fenton's reagent, and titanium dioxide assisted photocatalysis. J Hazard Waste Hazard Mater 10:107–149.

Waldemer RH, Tratnyek PG. 2006. Kinetics of contaminant degradation by permanganate. Environ Sci Technol 40:1055–1061.

Waldemer RH, Tratnyek PG, Johnson RL, Nurmi JT. 2007. Oxidation of chlorinated ethenes by heat-activated persulfate: Kinetics and products. Environ Sci Technol 41:1010–1015.

Walling C. 1975. Fenton's reagent revisited. Account Chem Res 8:125–131.

Watts RJ, Smith BR. 1991. Catalyzed hydrogen peroxide treatment of octachlorodibenzo-pdioxin (OCCD) in surface soils. Chemosphere 23:949–955.

Watts RJ, Teel AL. 2005. Chemistry of modified Fenton's reagent (catalyzed H2O2 propagation-CHP) for *in situ* soil and groundwater remediation. J Environ Eng 131:612–622.

Watts RJ, Rausch RA, Leung SW, Udell MD. 1990. Treatment of pentachlorophenol contaminated soils using Fenton's reagent. J Hazard Waste Hazard Mater 7:335–345.

Watts RJ, Leung SW, Udell MD. 1991. Treatment of contaminated soils using catalyzed hydrogen peroxide. Proceedings, First International Symposium on Chemical Oxidation. Technomic, Nashville, TN, USA. February 20–22.

Watts RJ, Jones AP, Chen P, Kenny A. 1997. Mineral-catalyzed Fenton-like oxidation of sorbed chlorobenzenes. Water Environ Res 69:269–275.

Watts RJ, Foget MK, Kong SH, Teel AL. 1999. Hydrogen peroxide decomposition in model subsurface systems. J Hazard Mater B69:229–243.

Watts RJ, Sarasa J, Loge FJ, Teel AL. 2005a. Oxidative and reductive pathways in manganese-catalyzed Fenton's reactions. J Environ Eng 131:158–164.

Watts RJ, Howsawkeng J, Teel AL. 2005b. Destruction of a carbon tetrachloride dense nonaqueous phase liquid by modified Fenton's reagent. J Environ Eng 131:1114–1119.

Watts RJ, Finn DD, Cutler LM, Schmidt JT, Teel AL. 2007. Enhanced stability of hydrogen peroxide in the presence of subsurface solids. J Contam Hydrol 91:312–326.

West OR, Siegrist RL, Mitchell TJ, Jenkins RA. 1995. Measurement error and spatial variability effects on characterization of volatile organics in the subsurface. Env Sci Technol 29:647–656.

West OR, Cline SR, Holden WL, Gardner FG, Schlosser BM, Thate JE, Pickering DA, Houk TC. 1997. A Full-Scale Field Demonstration of *In Situ* Chemical Oxidation through Recirculation at the X-701B Site. ORNL/TM-13556. Oak Ridge National Laboratory, Oak Ridge, TX, USA. 114 p.

West OR, Cline SR, Siegrist RL, Houk TC, Holden WL, Gardner FG, Schlosser RM. 1998. A Field-Scale Test of *In Situ* Chemical Oxidation through Recirculation. Proceedings, Spectrum '98 International Conference on Nuclear and Hazardous Waste Management, Denver, CO, USA, September 13–18, pp 1051–1057.

Woods LM. 2008. *In Situ* Remediation Induced Changes in Subsurface Properties and Trichloroethene Partitioning Behavior. MSc Thesis. Environmental Science and Engineering Division, Colorado School of Mines, Golden, CO, USA.

Woods PL, Siegrist RL, Crimi M. 2012. Effects of *in situ* remediation using oxidants or surfactants on subsurface organic matter and sorption of trichloroethene. J Ground Water Monit Remediat 32:96–105.

Wymore R, Cross PE, Baird D. 2010. Case Study: CHP Treatment of a TCE DNAPL Plume. Presentation at the Seventh International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2010). In Fields KA, Wickramanayake GB (Chairs), Remediation of Chlorinated and Recalcitrant Compounds – 2010. ISBN 978-0-9819730-2-9. Battelle Memorial Institute, Columbus, OH, USA, Abstract D-005.

Xu X, Thomson NR. 2007. Stability of hydrogen peroxide in the presence of aquifer solids using a green chelating reagent, Chemosphere 69:755–762.

Xu X, Thomson NR. 2008. Estimation of the maximum consumption of permanganate by aquifer solids using a modified chemical oxygen demand test. ASCE J Environ Eng134:353–361.

Xu X, Thomson NR. 2009. A long-term bench-scale investigation of permanganate consumption by aquifer materials. J Contam Hydrol 110:73–86.

Yan YE, Schwartz FW. 1998. Oxidation of Chlorinated Solvents by Permanganate. In Wickramanayake GB, Hinchee RE, eds, Physical, Chemical, and Thermal Technologies: Remediation of Chlorinated and Recalcitrant Compounds. Battelle Press, Columbus, OH, USA, pp 403–408.

Yan YE, Schwartz FW. 1999. Oxidative degradation and kinetics of chlorinated ethylenes by potassium permanganate. J Contam Hydrol 37:343–365.

Yeh CK-J, Wu H-M, Chen T-C. 2003. Chemical oxidation of chlorinated non-aqueous phase liquid by hydrogen peroxide in natural sand systems. J Hazard Mater 96:29–51.

Yukselen-Aksoy Y, Khodadoust AP, Reddy KR. 2010. Destruction of PCB 44 in spiked subsurface soils using activated persulfate oxidation. Water Air Soil Pollut 209:419–427.

Zhang H, Ji L, Wu F, Tan J. 2005. *In situ* ozonation of anthracene in unsaturated porous media. J Hazard Mater 120:143–148.