



In Situ Chemical Oxidation Fact Sheet

This fact sheet provides an overview of the in situ chemical oxidation (ISCO) technology, when to use it, implementation issues, lessons learned, and useful references for additional information.

What is ISCO?

ISCO is a remediation technology where a chemical oxidant is injected into the subsurface to oxidize or transform contaminants in groundwater or soil into innocuous byproducts.

What are the different types of oxidants used in ISCO?

The different choices of oxidants for ISCO are hydrogen peroxide (H₂O₂), permanganate (MnO₄⁻), persulfate (S₂O₈²⁻), ozone (O₃), perozone (H₂O₂ and O₃ in air), percarbonate

(Na₂CO₃·1.5H₂O₂) and calcium peroxide (CaO₂). As most of the chemical oxidants are strong oxidizing agents, worker and environmental safety are central to effectively designing and managing an ISCO project. Some of the commonly used oxidants and their properties are included in Table 1.

What are the contaminants that can be treated by ISCO?

Table 2 shows contaminant amenability to some of the common oxidants to aid in the selection of an appropriate oxidant. In addition to the contaminants shown in the table, oxidants are also able to treat sites with these contaminants present as non-aqueous phase liquids (NAPLs). A key step in screening an appropriate oxidant for a site is to determine its oxidative capacity with respect to the site contaminant.

Table 1. Summary of Oxidant Types, Key Characteristics, and Safety Considerations

Oxidant	Reactive Species	Form	Activator	Persistence	Electron Potential	Safety Concerns
Permanganate (potassium or sodium)	Permanganate ion (MnO ₄ ⁻)	Powder/liquid	None	Greater than 3 months	1.7 V	Skin and eye contact; inhalation of KMnO ₄ dust must be avoided during storage and handling.
Catalyzed Hydrogen Peroxide (CHP)	Hydrogen peroxide (H ₂ O ₂) Hydroxyl radical (OH·) Perhydroxyl radical (HO ₂ ·) Superoxide radical (·O ₂ ⁻) Hydroperoxide anion (HO ₂ ⁻)	Liquid	None, Fe (II), Fe (III)	Minutes to hours	1.8 V 2.8 V 1.7 V -2.4 V -0.88 V	Decomposition of H ₂ O ₂ generates heat and oxygen that can result in combustion of ignitable material. It can cause chemical/thermal burn on the skin.
Sodium Persulfate (activated or unactivated)	Persulfate anion (S ₂ O ₈ ²⁻) Sulfate radical (·SO ₄ ⁻) Hydroxyl radical (OH·) Superoxide radical (·O ₂ ⁻)	Powder/liquid	None, Fe (II), Fe (III), heat, H ₂ O ₂ , high pH (NaOH)	Weeks to months	2.1 V 2.6 V	Inhalation of sodium persulfate dust must be avoided as it can irritate the respiratory tract.
Ozone	Ozone (O ₃) Hydroxyl radical (OH·)	Gas	None	Minutes to hours	2.1 V 2.8 V	O ₃ has adverse respiratory effects. Safety controls are required to prevent unacceptable exposure pathway.

(Adapted from Huling and Pivetz, 2006 and Siegrist et al., 2011)

Table 2. Oxidant Amenability to Common Contaminant Types

	Contaminant	Oxidant Amenability			Ozone
		Permanganate	CHP	Sodium Persulfate	
Chlorinated aliphatic compounds	Chloroethenes (e.g., PCE, TCE, 1,1-DCE, cis-DCE, trans-DCE, VC)	Degradable	Degradable	Degradable	Degradable
	Chloroethanes (e.g., 1,1,1-TCA, 1,1-DCA)	Negligible	Conditionally degradable	Degradable depending on activation methods	Degradable
	Chloromethanes (e.g., CT)	Negligible	Conditionally degradable	Degradable depending on activation methods	Degradable
Chlorinated aromatic compounds	Chlorophenols (e.g., 2,4-dichlorophenol)	Degradable	Degradable	Possibly degradable – limited data	Degradable
	Polychlorinated biphenyls/dioxins/furans	No	Conditionally degradable	Degradable depending on activation methods	No specific data on kinetics or mechanisms
Hydrocarbon compounds	Benzene, toluene, ethylbenzene, xylene (BTEX)	Conditionally degradable (except benzene)	Degradable	Degradable	Degradable
	Methyl tert-butyl ether (MTBE)	Negligible	Degradable	Degradable	Degradable
	Polycyclic aromatic hydrocarbons (PAH – e.g., benz[a]anthracene, benzo[a]pyrene, pyrene, anthracene)	Conditionally degradable	Conditionally degradable	Degradable depending on activation methods	Degradable

(Adapted from Siegrist et al., 2011)

When is ISCO considered?

ISCO can be considered for source zone (or contaminant mass) removal at sites where groundwater and/or porous media have contaminants of concern (COCs) amenable to common oxidants. Other in situ technologies, such as enhanced bioremediation and in situ chemical reduction, tend to be candidates for many of the same sites where ISCO can be considered. Factors that favor ISCO over these other technologies include: COCs particularly amenable to ISCO (such as chlorinated alkenes and chlorinated phenols), soil with low oxidant demand, and aerobic aquifer (which creates challenges for technologies requiring reducing conditions). Factors that create additional challenges to ISCO implementation include the presence of NAPL or high concentrations of sorbed COCs, heterogeneous and/or low permeability media and current site conditions (e.g., building with sensitive utilities such as gas, steam, petroleum, or communication lines or explosive operations such as research and storage). ISCO typically requires multiple iterations of oxidant application and performance monitoring due to variability in contaminant distribution, subsurface heterogeneity and mass transport mechanisms.

ISCO is best applied as a source zone treatment technology. A database compilation of 242 ISCO case studies implemented from 1996 to 2007 was funded by the Environmental Security Technology Certification Program (ESTCP) (Krembs et al., 2010). The results of the database analysis indicated that goals or metrics such as source reduction (e.g., mass removal/mass flux reduction) and technology performance objectives are met more frequently than standard concentrations such as maximum contaminant levels (MCLs) or alternate contaminant levels (ACLs).

How is ISCO implemented?

ISCO implementation consists of various stages: developing a conceptual site model (CSM), bench-scale treatability testing, screening and selection of oxidant and delivery approach, pilot-scale testing, design development and full-scale implementation. Table 3 illustrates the key activities conducted in ISCO implementation.

How much does ISCO cost?

ISCO costs depend on several factors such as site contaminant (e.g., NAPL), treatment zone volume, subsurface heterogeneity (hydraulic conductivity), stringent treatment goals and remedial approach. The median unit cost (based on 33 projects) was reported as \$94 per cubic yard (cy) of treated aquifer (Krembs et al., 2010). This information is provided for an order of magnitude comparison based on data available through 2010. Site-specific costs based on current pricing and geographic escalation factors should be requested from consultants and technology vendors.

Is there an opportunity to implement green practices in ISCO?

Green and sustainable remediation (GSR) reviews of ISCO indicate that the following activities add to the footprint: production of the oxidant, operation of drill rigs, and personnel and equipment transportation. SiteWise™ (<http://www.ert2.org/t2gsrportal/SiteWise.aspx>) can be used to evaluate the sustainability for ISCO projects. It currently includes only hydrogen peroxide, but users can add other chemicals to the look-up tables or use hydrogen peroxide as a surrogate for the other oxidants

(e.g., assume that they have a similar footprint per pound). The following can be done to reduce the footprint at ISCO sites:

- Robust site characterization, design analysis and treatability testing can optimize the use of oxidant, number of drill rigs and mobilization.
- Develop an appropriate exit strategy to transition from ISCO injections to other technologies such as bioremediation or monitored natural attenuation (MNA) to prevent excessive injections beyond the point of diminishing returns.
- Use green fuels and/or after-treatment technologies to reduce emissions from drill rigs and trucks. Examples of after-treatment technologies include: diesel oxidation catalysts (DOCs), diesel particulate filters (DPFs), selective catalytic reduction (SCR), and/or diesel multistage filters (DMFs). The use of after treatment technologies could potentially increase cost, and also impact

equipment warranties. Careful evaluation of these factors is essential for each application.

- Implement an idle control plan and other operating strategies (reduce the time that drill rigs and trucks are emitting pollutants) to improve efficiency of site activities.
- Optimize the monitoring plans to reduce trips to the site, while still meeting the objectives of the program.

What are the lessons learned from ISCO?

- ISCO is a source zone treatment technology where success is dependent on adequate site characterization, treatability testing, appropriate design (mass, concentration and volume of oxidant), reasonable treatment objectives, oxidant contaminant contact through injection, and post treatment monitoring. ISCO will require multiple delivery events.

Table 3. Key Activities in ISCO Implementation

Stages of ISCO implementation	Key Activities
Conceptual Site Model (CSM) Development	<ul style="list-style-type: none"> a. Site characterization data - distribution and phase (and/or concentration) of contaminants; and its spatial distribution; b. Geochemical parameters - reducing conditions, natural oxidant demand; and c. Subsurface characteristics - geology (lithology, stratigraphy, heterogeneity), hydrogeology (aquifer hydraulic conductivity, porosity, and gradient), location of subsurface structures and underground utilities (ensuring a safe delivery of the oxidant).
Oxidant Screening and Selection	<p>Following factors are used in oxidant screening:</p> <ul style="list-style-type: none"> a. Site COCs; b. Site hydrogeology; c. Nature and extent of COCs; d. Site remediation goals; e. Safety and handling of oxidant (consider underground structures); f. Compatibility with current site conditions; g. Consideration of oxidants based on the potential for production of secondary contaminants.
Design Development	<ul style="list-style-type: none"> a. Bench-scale treatability tests (require up to two months to complete) are conducted to simulate field conditions using site soils and groundwater to evaluate the feasibility of the contaminant oxidant technology. Design parameters are determined as follow: <ul style="list-style-type: none"> • Oxidant and activation selection; • Estimation of oxidant dose (concentration), persistence; • Determine whether the presence of NAPL would hinder the choice of oxidants and performance; • Estimation of byproducts and metal mobilization; • Determine project costs and feasibility of ISCO in comparison to other technologies. b. Oxidant delivery approach is designed based on aquifer heterogeneity, contaminant distribution, and presence of underground utilities. Some design choices include type of injection points (e.g., permanent/temporary wells, direct push probes, trenches, recirculation wells, fracturing, etc.), injection well spacing, number of delivery events, etc. c. Pilot-scale study is used to establish and refine the key design parameters for the full-scale application. Some of the design parameters that will be determined are: injection rate and pressures, oxidant travel times, vertical and horizontal oxidant distribution, persistence of oxidant, contaminant mobilization in groundwater, reaction byproducts.
Full-Scale Implementation	<ul style="list-style-type: none"> a. Evaluate the performance of contaminant degradation/oxidation, contaminant rebound using monitoring program; b. Evaluate different injection strategies to optimize the full-scale implementation; and c. Optimize system design with real-time decision-making. d. Performance evaluation metrics are necessary to evaluate treatment effectiveness and consists of: <ul style="list-style-type: none"> • Process monitoring (concentration, volumes, flow rates and distribution of oxidant, groundwater quality parameters [pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), conductivity]) • Performance monitoring (baseline and post application groundwater and soil concentrations, metal plumes, reaction byproducts, contaminant rebound).

Adapted from Siegrist et al., 2011.

- Accurate oxidant demand based on site characteristic data and treatability tests are critical since significant amounts of oxidant can be consumed due to non-target demand (e.g., non-target contaminants and soil organic matter) and unaccounted sorbed contaminant.
- Heterogeneous subsurface conditions (hydraulic conductivity and media type such as fractured rock) could lead to preferential flow and limited oxidant delivery. Traditional groundwater models (e.g., MODFLOW) may not yield accurate predictions because the oxidant reacts during transport, which can change aquifer hydraulic properties.
- Rebound (an increase in contaminant concentrations post-ISCO application) can be an indication that a refined CSM is needed in order to optimize and target subsequent applications. Some rebound is expected and can be managed by establishing reasonable treatment objectives and transitioning to other less aggressive technologies.
- Coupling ISCO technology with other remediation technologies will enhance treatment efficiencies. ISCO has demonstrated compatibility for coupling with enhanced aerobic and anaerobic bioremediation, MNA and surfactant/cosolvent flushing.
- Factors such as understanding and planning for hazards associated with handling oxidants, real time decision making and optimization are critical to a successful ISCO implementation.
- Performance monitoring program should be consistent with treatment goals (e.g., sampling should include aqueous and soil samples to provide a comprehensive data basis for mass reduction calculations).
- Regulations associated with the implementation of ISCO could vary significantly from federal to state levels. Site-specific applicable or relevant and appropriate regulations (ARARs) should be evaluated early in the planning stage to ensure regulatory compliance for underground injection control, air quality, water quality, and ecological impacts.

Useful Resources and Web Links

NAVFAC T2 Resources

Remediation Innovative Technology Seminar (RITS): Is ISCO Right for Your Site?

<https://portal.navfac.navy.mil/portal/page/portal/963223F2E88C62F1E04400144F414F26>

Cost and Performance Report for Persulfate Treatability Studies

http://www.ert2.org/downloads/final_cp_report_persulfate_06022010.pdf

ISCO Web Tool

<http://www.ert2.org/isco/>

Department of Defense Resources

Siegrist, R.L., Crimi, M., and Simpkin, T.J. 2011. In Situ Chemical Oxidation for Groundwater Remediation Series: SERDP ESTCP Environmental Remediation Technology, Vol. 3, first edition, 678 p.

<http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-200623>

Short Course on Principles and Practices of In Situ Chemical Oxidation

<http://symposium2010.serdp-estcp.org/Short-Courses/SC2>

Other Resources

EPA Clu-in Web site: In Situ Oxidation Web Page

http://www.clu-in.org/techfocus/default.focus/sec/In_Situ_Oxidation/cat/Overview/

Huling, S.G., and B. E. Pivetz. 2006. Engineering Issue: In Situ Chemical Oxidation. United States Environmental Protection Agency, 600-R-06-702.

<http://www.epa.gov/nrmrl/pubs/600r06072/600r06072.pdf>

Krembs, F.J., Siegrist, R.L., Crimi, M.L., Furrer, R.F., and B.G. Petri. 2010. "ISCO for Groundwater Remediation: Analysis of Field Applications and Performance." *Groundwater Monitoring and Remediation*. Vol. 30, Issue No. 4. Fall 2010. p. 42-53.

Interstate Technology Regulatory Council (ITRC). 2005. Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater, second edition.

<http://www.itrcweb.org/Documents/ISCO-2.pdf>