

IN SITU CHEMICAL OXIDATION

This fact sheet provides an overview of in situ chemical oxidation (ISCO) remediation technology, including when to use it, design and implementation best practices, new innovations, lessons learned, a case study, and references.

Introduction What is ISCO?

ISCO is a remediation technology in which a chemical oxidant is injected into subsurface soil and/or groundwater to oxidize target contaminants. This is an abiotic process that converts organic contaminants into innocuous byproducts such as carbon dioxide, chloride, or water. These reactions can occur rapidly, so ISCO can be used to quickly reduce contaminant mass and concentration, particularly in source areas.



At what type of sites is ISCO used?

ISCO is most commonly used to treat chlorinated compounds, but can also treat 1,4-dioxane, fuel-related compounds, chlorinated benzenes, and other organic compounds. It is typically applied to source areas or higher concentration areas within groundwater plumes. ISCO works best in geologic conditions (more permeable and more homogeneous) that are optimal for most in situ technologies. Sites with low permeability, high heterogeneity, and/or fractured rock require more careful design.

How is ISCO used along with other technologies?

ISCO is usually applied as part of a treatment train and is very rarely a "one-and-done" technology that leads immediately to site closure. ISCO can be applied at the front end of the remediation program, with less aggressive technologies such as in situ bioremediation (ISB) or monitored natural attenuation (MNA) used after ISCO. Alternatively, ISCO can be used after more aggressive source removal such as excavation or in situ thermal treatment. ISCO may be preferred over anaerobic ISB because of a need for fast treatment, because of the presence of compounds that are recalcitrant to bioremediation.

What are the different types of oxidants used in ISCO?

The most common oxidants for ISCO are permanganate (MnO_4) , persulfate $(S_2O_8^2)$, hydrogen peroxide (H_2O_2) , and ozone (O_3) . Additional chemical activators are added along with some oxidants. The oxidant and activator react to form even more reactive chemical species called free radicals. Because free radicals are so reactive, they are short-lived, so the oxidant and activator must be mixed in situ or in a tank immediately before injection. Some of the commonly used oxidants and their properties are strong oxidizing agents, worker and environmental safety are central to effectively designing and managing an ISCO project.

How do I select an oxidant?

A key step in screening an appropriate oxidant for a site is to verify that it can degrade the contaminants at the site. Table 2 shows contaminant amenability to

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some of the common oxidants to aid in the selection of an appropriate oxidant. Oxidants are also able to treat sites with these contaminants present as non-aqueous phase liquids (NAPLs), though this represents a substantial additional challenge. NAPLs are very difficult to locate during site characterization and are similarly difficult to contact with oxidants due to their unknown and small location. NAPLs can also slowly dissolve over time, leading to contaminant rebound after treatment.

Oxidant persistence is another important attribute (see Table 1), with more persistent oxidants typically being more successful as they can mitigate against back-diffusion, contaminant desorption, NAPL dissolution, and other processes that can redistribute contaminants after ISCO injection. Persistence under site-specific conditions may be variable, and laboratory bench tests can be used to compare the persistence of multiple oxidant options.

ISCO Design

The following elements should be considered when designing an ISCO program.

- The **oxidant selected** (with an activator, if required) must be capable of degrading the target contaminants (see Table 2).
- A sufficient mass of oxidant, termed as **oxidant dose**, must be delivered to the treatment zone. This is typically represented as oxidant mass per mass of soil in the treatment zone (see callout box). It can be estimated with site-specific laboratory bench test data, though stoichiometric equations and practitioner experience may also be used.

$$Oxidant \ Dose = \frac{Mass \ Oxidant}{Mass \ Soil} = \frac{Mass \ Oxidant}{L \ x \ W \ x \ H \ x \ Bulk \ Density}$$
$$Treatment \ Zone \ ePV = L \ x \ W \ x \ H \ x \ Eff. Porosity$$
$$Injection \ ePV = \frac{Volume \ Injected}{Treatment \ Zone \ ePV}$$

Oxidant	Activator	Form	Reactive Species	Standard Reduction Potential	Persistence	Safety Concerns
Permananate (potassuim or sodium)	None	Powder/ Liquid	Permanganate anion (MnO_4^-)	+1.7 V	Months	Skin and eye contact; inhalation of KMnO ₄ dust must be avoided. NaMnO ₄ typically procured in highly concentrated 40% solution.
Persulfate (soduim or potassium)	None, high pH (NaOH), Fe (II), Fe (III), H_2O_2 , heat	Powder	Persulfate anion $(S_2O_8^{2-})$ Sulfate radical (SO_4^{-}) Hydroxyl radical (OH^{-}) Superoxide radical (O_2^{-})	+2.1 V +2.6 V +2.8 V -2.4 V	Weeks to Months	Inhalation of persulfate dust must be avoided as it can irritate the respiratory tract. Persulfate solutions can be highly corrosive to many metals.
Catalyzed Hydrogen Peroxide (CHP)	Fe (II), Fe (III)	Liquid	Hydrogen peroxide (H_2O_2) Hydroxyl radical (OH•) Perhydroxyl radical (HO2•) Superoxide radical (O2•) Hydroperoxide anion (HO2•)	+1.8 V +2.8 V +1.7 V -2.4 V -0.88 V	Minutes to Hours	Decomposition of H_2O_2 generates heat and oxygen that can result in combustion of ignitable material. It can cause chemical/thermal burns on the skin.
Ozone	None, Hydrogen Peroxide	Gas	Ozone (O₃) Hydroxyl radical (OH•)	+2.1 V +2.8 V	Minutes to Hours	O ₃ has adverse respiratory effects. Safety controls are required to prevent unacceptable exposure pathway.

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

Note: "None" in activator column refers to injecting oxidant without additional activator. Persistence of oxidants under actual field conditions is highly site-specific.

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- Laboratory bench testing can be used to determine oxidant persistence in the presence of site soils, to verify contaminant degradation by oxidants, and to evaluate the oxidant dose under site-specific conditions. The amount of oxidant that is consumed through reaction with the soil matrix is termed the natural oxidant demand (NOD). The NOD is typically greater than the demand for oxidant from reactions with site contaminants, thus NOD is very important in determining the proper oxidant dose. Note that laboratory bench tests are typically conducted under well-mixed conditions and are therefore best-case results from a contaminant degradation perspective. Being wellmixed, oxidant bench tests do not account for challenges associated with geologic heterogeneity and incomplete contact between the oxidant and target contaminants.
- To achieve adequate contact between the oxidant and the contaminated media, an appropriate volume of oxidant solution must be delivered to the subsurface. The fraction of an effective pore volume (ePV) to be injected must be specified. This is calculated through a two-step process:
 1) the total ePV in the treatment zone as a whole is calculated; and 2) the fraction of that which will be replaced by oxidant solution during injection is calculated (see callout box on page 2). This concept is also illustrated in Figure 1.
- The distance that oxidant travels from an injection point, termed the **radius of influence** (ROI), must be estimated (shown in Figure 1). Estimating ROI can be done by calculating the volume of a cylinder (Volume = π *radius²*thickness*effective porosity). Spreadsheet-based tools (e.g., Conceptual Design for ISCO [CDISCO] tool

	Permanganate	Persulfate - No Activator	Persulfate - Iron Activation	Persulfate - Peroxide Activation	Persulfate - Base Activation	Ozone	Hydrogen Peroxide- Iron Activation
PCE, TCE, cDCE, VC	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
TCA, DCA, Chloroethane	Poor	Poor	Fair	Good	Good	Good	Good
1,4-Dioxane	Good*	Excellent	Excellent	Excellent	Excellent	Good	Excellent
PFAS**	Poor	Poor	Poor	Poor	Poor	Poor	Poor
BTEX	Poor	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
MTBE and TBA	Poor	Poor	Fair	Good	Good	Fair	Fair
Light hydrocarbons (gas, diesel, jet fuel)	Fair	Good	Excellent	Excellent	Excellent	Good	Good
Heavy hydrocarbons (fuel oils, bunker oil)	Poor	Poor	Poor	Good	Good	Fair	Fair
Tri-, Di-, and Mono- chlorobenzene	Poor	Good	Good	Excellent	Excellent	Fair	Fair
Carbon Tet., Chloroform, DCM, MeCl	Poor	Poor	Poor	Good	Good	Poor	Good

Table 2. Oxidant Amenability to Common Contaminant Types

Notes: Table from RITS 2019, modified from Table A8 of ISCO Technology Practices Manual, ESTCP Project ER-0623

- * = 1,4-Dioxane degradation by permanganate will proceed to very low concentration endpoints only if natural oxidant demand (NOD) is low and/or oxidant concentration is high.
- ** = Based on current knowledge, ISCO oxidants do not degrade the full suite of PFAS compounds. In addition, attempting ISCO for treatment of PFAS in soil or groundwater is not advised without adequate testing, due to the potential for transformation of relatively immobile PFAS compounds ("precursors") into more mobile PFAS end products such as PFOA or PFOS.





Notes: The oxidant is shown in purple and the oxidant ROI as the distance from the injection point to the perimeter of the purple color indicating the area of influence. Target contaminants are shown in dark red (higher concentration) and light red (lower concentration). The target treatment zone is shown as the dashed yellow box. The number of ePVs injected is the ratio of purple (oxidant) to the yellow (treatment zone).

developed by ESTCP project ER-200626) can also be used, and in rare instances at complex sites, numerical models could be developed. Because of geologic heterogeneity, oxidant transport distance from an injection point is not uniform in each lateral direction and at each depth across the vertical interval being treated. **The oxidant will travel farther from the injection point when greater volume is delivered.** The target ROI is a key factor in determining the volume of oxidant required for injection.

• Injection **pressures** and **flow rates** should be estimated during the design phase. These are a function of the permeability of the soil being treated: low-permeability soils will have lower flow rates with higher pressures, while the opposite is true for high-permeability soils. Injection flow rates are highly site-specific, for example, for a 5-ft vertical injection interval, flow rates may range from 0.1 to 1 gallons per minute (gpm) for a clay or silt, and 1 to 5 gpm for a sand or gravel. Actual flow rates may be more or less than these general ranges and will depend on the pressure applied to the injection point. Greater injection pressures and flow rates are typically acceptable in deeper treatment zones.

- **Pilot testing** can be performed to collect design information under actual field conditions, including ROI, injection pressures and flow rates, oxidant persistence, and contaminant degradation.
- Common oxidant **delivery methods** are injection through dedicated injection wells and through temporary direct push points. Newer innovations for oxidant delivery include recirculation (coupled injection and extraction), in situ

soil mixing (blending of powder or liquid oxidant into soil matrix using specialized mixing tools), and permeability enhancement (increasing local permeability by injection of oxidant and/or sand "proppant" at very high pressure; sand holds open new pore space after the pressure dissipates). Recirculation may improve treatment in sites with complex geology, where the transmissive portion of the aquifer through which oxidants are distributed is limited. Soil mixing (e.g., blending of oxidant with impacted media in situ using specialized mixer or large diameter augers) provides an effective means to overcome contaminant/reagent contact limitations and is most frequently applied at highconcentration source zones. Permeability enhancement may be used to improve the ROI at low-permeability sites. These methods require more specialized equipment and expertise and are likely more costly to implement.

ISCO Implementation And Monitoring

ISCO implementation requires specialized knowledge and equipment. There are many logistical and safety considerations, including the following: chemical hazards posed by the oxidant; pressurized systems; heavy equipment; chemical compatibility, including materials used in injection equipment and subsurface infrastructure that may be present at the site; heat generation due to chemical reactions; and potential adverse impacts resulting from excursions of oxidant solution to unintended areas.

Equipment often includes the following: tanks with industrial mixers for preparing oxidant solution; pumps that move the oxidant solution to injection points; manifolds that split flow and allow for measurement and adjustment of injection pressures and flow rates; and hoses connecting this equipment to injection points. Care must be taken to ensure that equipment is constructed of materials that are compatible with the oxidant and activator being used. For example, most oxidant suppliers have technical data sheets explaining which metals, plastics, and sealants are compatible with their products.



Photo of injection system manifold (provided courtesy of Trihydro Corporation)



Photo of field monitoring of oxidant concentration with test kit (provided courtesy of Trihydro Corporation)

Process monitoring involves data collection during implementation to document injection performance relative to design specifications. Typical process monitoring data include injection flow rates, pressures, and total volumes at each injection point. These measurements should be collected multiple times at each injection point to document consistency or changes over time. In addition, oxidant concentration should be measured at monitoring wells within and around the ISCO treatment zone periodically during injection to document the subsurface distribution of oxidant. Oxidant concentrations should be measured directly with an oxidant-specific method (e.g., using a field test kit for persulfate or colorimeter for permanganate concentrations). Oxidant influence should not be inferred from secondary lines of evidence such as changes in oxidation-reduction potential (ORP), dissolved oxygen, or conductivity. Secondary lines of evidence can produce spurious results because byproducts of reactions such as dissolved oxygen or heat can move greater distances through the subsurface during injection than the oxidant itself, particularly when the oxidant is highly reactive. Changes in fluid levels in a monitoring well can be measured to assess the hydraulic influence of injection, but as with reaction byproducts, observing a change in head in a monitoring well during injection does not necessarily mean that oxidant traveled to that well.

Performance monitoring occurs after ISCO has been implemented. Target compounds are measured to verify the extent that concentrations decreased as intended. Oxidant concentrations should be measured as well to evaluate the persistence of the oxidant within the treatment zone and provide additional context for contaminant concentration data. Contaminant concentrations may be biased low if measurements are collected while oxidant is still present in the treatment zone, due to reaction occurring between the time of sample collection and analysis. Special preservatives can be used when groundwater samples contain residual oxidant (see Ko et al., 2012).

Lessons Learned

Several recurring issues have challenged ISCO applications over the years. These are discussed briefly below, with more details available in RITS 2019 and the citations provided.

- ISCO projects often under-designed in terms of total volume injected. The cumulative number of ePVs injected over the course of an ISCO program has historically been 0.1 to 0.2 (i.e., 10% to 20%) on average based on multiple independent case study reviews (Clayton, 2007; Krembs et al., 2010). Concentration reductions for target contaminants have been approximately 50%, with some sites showing negligible change. To improve performance results, a greater volume of fluids should be injected to more thoroughly contact contaminants in the subsurface.
- ISCO challenged by low-permeability sites. Injection of any reagents, including oxidants, is difficult at lowpermeability sites as it can result in injection volumes that are much lower than optimal, reagent surfacing, or long durations of injection. Soil mixing or permeability enhancement are two delivery methods that have been more recently developed to increase performance at lowpermeability sites.
- Groundwater concentrations are only part of the story. At most ISCO sites, the purpose of remediation is to reduce groundwater concentrations in monitoring wells to below a regulatory standard. Soil concentrations and/ or the presence of NAPL source material are generally not a regulatory driver. However, continued presence of soil or NAPL-phase contaminants can sustain elevated groundwater concentrations after ISCO is implemented, leading to contaminant "rebound." Furthermore, lowpermeability zones of subsurface soil can store large fractions of contaminant mass. Once oxidants are depleted after ISCO injection, back diffusion can sustain elevated groundwater concentrations. At high concentration sites, soil sampling or other site characterization methods (e.g., MIP or LIF) can be used to assess non-aqueous

concentrations over time and thereby document the progress that ISCO is making toward reducing contaminant mass. At many sites, substantial mass reductions have been achieved even though groundwater concentrations are not substantially changed.

• **ISCO is challenged by LNAPL.** While some ISCO reagents can treat petroleum LNAPL, the presence of LNAPL is challenging to ISCO because: a) there is typically much higher contaminant mass present at LNAPL sites relative to chlorinated solvent sites; and b) petroleum LNAPL compounds require much more oxidant for complete mineralization (for example, 50 lbs of persulfate are required to completely mineralize 1 lb of diesel based on reaction stoichiometry). Furthermore, chemical oxidants tend to move in the aqueous phase, and attaining sufficient contact with LNAPL (by definition, a non-aqueous phase) may be challenging. Lastly, some oxidants, particularly hydrogen peroxide, generate heat which could result in unintended consequences such as LNAPL mobilization to unintended areas or increased volatility. These risks may be mitigated with appropriate selection of oxidant and stabilizers.

• Measure oxidant concentration to determine oxidant distribution. Determining oxidant distribution and persistence is key to monitoring ISCO programs. Methods that measure the concentration of the oxidant directly (e.g., oxidant-specific test kit) should be used. Use of secondary lines of evidence such as reaction byproducts (high ORP, dissolved oxygen, heat, etc.) can produce the false impression that the oxidant has traveled farther or persisted longer than it actually has. If the oxidant concentration is present above the range of the test kit, the sample should be repeatedly diluted in the field (i.e., serial 10x dilutions) to bring the concentration within the test kit's range.

• ISCO requires multiple injection events. To achieve permanent groundwater concentration reductions, ISCO requires multiple injection events to overcome the contact limitations described previously (ITRC, 2005; ESTCP, 2010; NAVFAC, 2015). Incremental progress with each step should be demonstrated/evaluated through performance monitoring and re-evaluation of the ISCO program and conceptual site model as needed. It is not advisable to proceed with a second or third injection event if performance monitoring indicates that ISCO is not making incremental progress toward the overall objective.

 Mid-course corrections typically necessary. Due to uncertainty associated with field conditions such as geology, hydrology and chemistry, there are deviations encountered during field-scale ISCO implementation. These may be reduced through detailed site characterization and planning and obtaining process monitoring data. Process monitoring data help the team to implement changes as ISCO is being implemented, which is sometimes termed the Observational Approach or Adaptive Site Management. The Design-Build Approach discussed in NAVFAC 2015 may offer a mechanism to build such changes into the contract under which ISCO is performed.

ISCO and Emerging Contaminants

ISCO has applicability to some emerging contaminants such as 1,4-dioxane. 1,4-Dioxane can be treated by oxidants that generate free radicals (persulfate and catalyzed hydrogen peroxide {CHP}). It may also be treatable with permanganate and ozone if the reactivity of the oxidant with site soil is low (i.e., the site has low NOD) (see Tables 1 and 2 for information on reactive species associated with each oxidant

and 1,4-dioxane treatability). Though 1,4-dioxane may be treated with oxidants, this compound is challenging for ISCO because of: a) very low typical target endpoints such as 0.46 µg/L EPA regional



screening level or $<1 \mu g/L$ state-specific standards; and b) 1,4-dioxane is often present in large, dilute plumes that are challenging to treat efficiently with ISCO.

The currently available ISCO reagents do not treat the entire suite of per- and polyfluoroalkyl substances (PFAS). The carbon-fluorine backbone of the PFAS molecule is not degraded by oxidants. Therefore, some PFAS compounds can be modified by oxidants, including partial degradation of precursors, which converts the original PFAS to other PFAS compounds. Caution should be used if considering ISCO for a site where PFAS may be present. At this time, chemical oxidants are not capable of complete degradation of PFAS.

However, chemical oxidants may stimulate transformation of some PFAS compounds, referred to as precursors,



into more stable end products such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). In many cases, the end-product compounds are more mobile in groundwater, and potentially more toxic, than the precursor compounds from which they were formed.

Case Study

This case study presents a robust design leading to substantial concentration reduction. This information is from an industrial site impacted by TCE (trichloroethylene) that was present in a low-permeability silt. Elevated TCE concentrations in groundwater and observations of staining on soil cores suggested the presence of residual TCE dense non-aqueous

phase liquid (DNAPL). The goal of ISCO was to reduce TCE concentrations to below 10,000 µg/L in groundwater (an approximate 50% to 95% reduction from pre-remediation concentrations) such that a more passive technology could be used as a polishing phase. A 10-day bench study determined that the permanganate NOD at the site was low (1.3 g permanganate / kg of soil). NOD data were used in the CDISCO model to evaluate injection well spacing and permanganate dosing. Permanganate was injected through permanent injection wells. The design details and performance results are shown in Table 3 and Figure 2. Note that injection Rounds 3 through 5 were conducted in conjunction with treatment of other areas at the site, and that these polishing events were smaller in scope than Rounds 1 and 2 (i.e. reduced number of injection wells; focused on areas with presistent elevated TCE concentrations.

The ISCO program was successful in reaching the project goals of lowering TCE to below 10,000 µg/L and allowing transition to more passive technologies (ISB and MNA). In addition, groundwater concentrations were reduced by 92% on average, and much greater reductions were observed at some individual wells. Total mass was reduced by 99%.

Few key elements:

- Greater than 1 ePV was injected during each event. The periphery of the treatment zone to mitigate against plume displacement.
- The applied oxidant dose exceeded the NOD in each injection event (safety factor). An increase in the amount of reagent did not result in substantial overall project cost increases as cost of reagents is a small percentage of total costs.
- Injection events included mid-course corrections based on review of process-monitoring data. Oxidant concentration data were collected toward the end of each injection event to determine where permanganate had been consumed most quickly and areas where permanganate had not been delivered at all. Additional permanganate was injected to address these as-yet untreated or permanganatedepleted areas during the same mobilization. Additional permanganate injections at undetermined locations were addressed contractually by defining a small number of "To Be Determined" wells that would receive a pre-determined quantity of permanganate solution.

	Round 1 May 2014	Round 2 March 2015	Round 3 Sept. 2015	Round 4 July 2016	Round 5 July 2017
Effective Pore Volumes (ePVs) Injected (-)	1.0	1.2	1.3	1.2	1.0
Oxidant Dose (g permanganate / kg soil)	1.5	2.0	1.5	2.1	1.1
Number of Injection Wells Used (-)	22	20	12	14	11
Oxidant Concentration (g/L)	22	25	17	26	16
Reduction in Average GW Concentration	25%	71%	60%	93%	92%
Reduction in TCE Footprint >10,000 µg/L	33%	47%	60%	99%	99.5%
Reduction in TCE Mass	64%	80%	87%	99%	99%

Table 3. Case Study - Design Parameters and Performance Results

Note: (-) = dimensionless parameter

Figure 2. Case Study - TCE Concentration Map Before and After ISCO



Note: Graphics based on data provided courtesy of Russ Bunker and Jack Spadaro (Wood PLC).



Useful Resources and Web Links

NAVFAC T2 Resources

Best Practices for Injection and Distribution of Amendments (Battelle for NAVFAC 2013) https://www.navfac.navy.mil/content/dam/ navfac/Specialty%20Centers/Engineering%20and%20Expeditionary%20Warfare%20Center/Environmental/Restoration/er_pdfs/b/ navfacexwc-ev-tr-1303-injectamnd-20130319.pdf

Design Considerations for In Situ Chemical Oxidation (Battelle for NAVFAC 2015) https://www.navfac.navy.mil/content/dam/ navfac/Specialty%20Centers/Engineering%20and%20Expeditionary%20Warfare%20Center/Environmental/Restoration/er_pdfs/d/ navfacexwc-ev-tm-1502-isco-design-201503f.pdf

Remediation Innovative Technology Seminar (RITS): In Situ Chemical Oxidation - Best Practices and New Innovations. 2019. https://www.navfac.navy.mil/navfac_worldwide/specialty_centers/exwc/products_and_services/ev/erb/rits.html

Remediation Innovative Technology Seminar (RITS): Is ISCO Right for Your Site? https://portal.navfac.navy.mil/portal/page/portal/ 963223F2E88C62F1E04400144F414F26

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Clayton, W.S. 2007. Engineering Delivery of Soluble Amendments. Presentation at 2007 SERDP Symposium, Washington, DC, December 4-6, 2007. https://symposiumarchive.serdp-estcp.org/symposium2007/upload/drwilsonclayton.pdf

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. https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-200623/ER-200623/(language)/eng-US

Other Resources

Huling, S.G., and B.E. Pivetz. 2006. Engineering Issue: In Situ Chemical Oxidation. United States Environmental Protection Agency, 600-R-06-702. https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NRMRL&dirEntryId=156513

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