

*IN SITU* CHEMICAL OXIDATION  
- STATE OF THE ART

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## ABSTRACT

This article describes the current status for ISCO as a remediation technology with focus on the critical parameters for a successful application. ISCO has been greatly developed and expanded in recent years. Focus has shifted from finding out which contaminants are amenable towards overcoming implementation limitations, such as oxidant delivery, effective and timely activation, and competing reactions. Coupled approaches (treatment trains) have shown a promising potential for achieving higher contaminant reductions at lower remediation costs.

## INTRODUCTION

*In situ* chemical oxidation (ISCO) is based on oxidation methods originating from the drinking water and waste water treatment. Strong oxidants were introduced around 1930 in order to remove organic contaminants from municipal and industrial waters, as well as to act as disinfection agents against. On site or ex situ treatment in reactor systems, for the removal of organic contaminants from soil or groundwater was the next step /1/. *In situ* chemical oxidation is the descendant of this technology and it involves the introduction of strong oxidants in the subsurface where they can *in situ* destroy the contaminants of concern. Over the last 10 years there has been a significant development in the field of ISCO. Methods and knowledge on the interactions between the oxidants, the contaminants, and the subsurface are constantly emerging /2/. Figure 1 displays a conceptual application of ISCO, where the oxidant is delivered in the subsurface by probe injection and activated by the use of heat. This paper provides a brief overview of ISCO technology and application status.

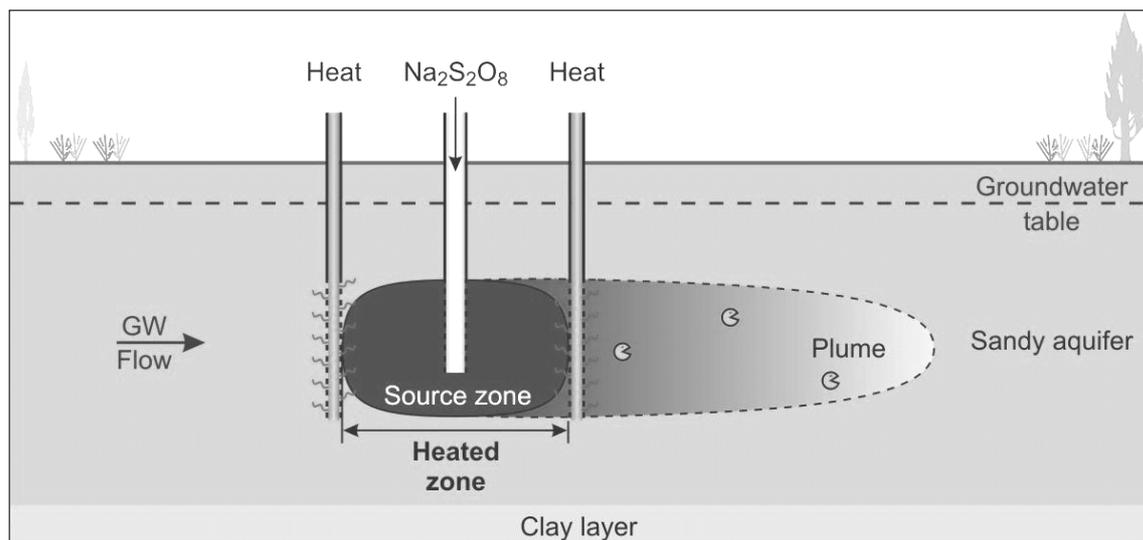


Figure 1 Example of an ISCO application in the field. Sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) is used as an oxidant and heat is used as an activation aid /3/.

## STATUS

The most commonly oxidants used for *in situ* chemical oxidation are /2/:

- Hydrogen peroxide and catalyzed hydrogen peroxide (CHP) also referred to as modified Fenton's reagent
- Ozone
- Permanganate
- Persulfate and activated persulfate

Oxidants can generally be grouped to radical and non-radical oxidants depending on whether they propagate the formation of free radicals. Persulfate and hydrogen peroxide can function both directly and through radical formation. Ozone is primarily used in the unsaturated zone and will not be discussed further in this paper. Table 1 offers an overview of the different oxidizing agents and the reactions involved. A detailed description of each oxidant and oxidation chemistries is given elsewhere /1,2,3/.

Oxidant	Reactions	Potential (V)
Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	$H_2O_2 + H^+ + e^- \rightarrow OH^- + H_2O$	1.78
Catalyzed hydrogen peroxide (Fe <sup>2+</sup> + H <sub>2</sub> O <sub>2</sub> )	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^-$	2.8
Ozone (O <sub>3</sub> )	$O_3 + 2H^+ + 2e^- \rightarrow O_2 + 2H_2O$ $O_3 + OH^- \rightarrow O_2 + HO_2^\bullet$	2.07
Persulfate (S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> )	$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$ or $S_2O_8^{2-} + 2Fe^{2+} \text{ (or heat)} \rightarrow 2SO_4^{\bullet-} + 2Fe^{3+}$	2.01
Activated persulfate (SO <sub>4</sub> <sup>-•</sup> )	$2SO_4^{\bullet-} + 2H_2O \rightarrow 2HSO_4^- + 2OH^\bullet$	2.6
Permanganate (MnO <sub>4</sub> <sup>-</sup> )	$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 \text{ (s)} + 2H_2O$	1.68

Table 1. Common oxidants and most important oxidant reactions

ISCO has been widely used in the US, and the state of science and practice has increased dramatically /2/. Today, permanganate is the most used oxidant technology with many well documented field applications. Fenton-driven oxidation is the next most popular application and has been used in a large number of sites with various modifications. Persulfate (activated persulfate) is an emerging oxidant with increasing field applications and a variety of implementation approaches /2/. The effectiveness of different oxidants towards common contaminants of concern has been established through lab and field studies. Focus has therefore shifted towards design and implementation issues such as:

- Selection of oxidant dose

- Selection of oxidant delivery method
- Development and delivery of activation aid
- Treatment trains

## CRITICAL ISSUES

### Oxidant selection

The success of ISCO applications largely depends on several parameters besides the oxidants' ability to degrade the contaminant. Once the type of contamination is known, several decision schemes can assist in selecting a suitable oxidant /2,4/. Oxidants have varying persistency in the subsurface. Permanganate and non-activated persulfate are more suitable for low permeability layers and diffuse contamination while CHP and activated persulfate are more suitable in high permeability layers and hotspots /5,6,7/.

### Oxidant dose and overcoming natural oxidant demand

The total costs of ISCO applications are often dependant on the amount of injected oxidant. Three key parameters for selecting oxidant dose are: The contaminants' oxidant demand, the natural oxidant demand, and the oxidant persistency in the subsurface. Bench scale treatability tests and field pilot tests can assist in selecting the right amount of oxidant /8/. It is recommended to use iterative injection events as opposed to single injections of high oxidant doses /2,5,8/.

Overcoming natural oxidant demand is one of the major challenges for ISCO. Although NOD has been extensively studied, it has been impossible to create generalized values for NOD mainly due to NOD dependence on both sediment composition and oxidant dose. NOD is primarily an issue for stable oxidants such as permanganate and non activated persulfate. CHP and activated persulfate are decomposing and reacting at such fast rates that oxidant transport is mainly controlled by their decomposition rather their reaction with the sediment /2,9/.

The majority of NOD values stem from well-mixed bench scale experiments where there is maximum contact between oxidant and sediment. The duration of those experiments is also a critical factor for the precision of the estimation. Hønning et al. /10/ found that the sediment was not an instantaneous oxidant sink for permanganate. Instead, after a significant initial consumption, the sediment continued to exert an oxidant demand.

NOD increases with increasing oxidant concentration. In low permeability geological settings the diffusion of  $MnO_4$  will be overcome by the consumption of NOD by the sediment and will render ISCO ineffective. Up to 90% of oxidant consumption may be due to NOD in diffusion limited systems /11/. These findings must be taken into account when upscaling from bench scale tests to field scale applications

#### **GUIDELINES FOR NOD BENCH SCALE TESTS**

1. Use a representative soil water ratio
2. Use a representative soil sample with regards to its chemistry
3. Use the oxidant concentrations and time scales that will also be used in the field
4. Run treatability tests with and without contaminant. Note that oxidant-sediment and oxidant-contaminant reactions occur simultaneously. It is therefore not necessary to completely meet NOD on order to remove the contaminants

See also:

[http://www.epa.gov/ada/research/waste/research\\_52.pdf](http://www.epa.gov/ada/research/waste/research_52.pdf).

## **Oxidant delivery**

Oxidant delivery is critical for the success and cost efficiency of ISCO, as it controls oxidant-contaminant contact. Site permeability, level of site characterization, depth of contamination and budget considerations are input parameters for selecting a delivery method. The most common methods and their applicability are discussed below:

- *Direct push technology (e.g. GeoProbe)* allows for density driven and diffusive transport of the oxidant between the vertical injection layers. If the contaminated zone is well characterized, this technique can be very effective as it allows for targeted injections [12]. This technology is however unsuitable for geologic environments that include rocks/cobbles and boulders, as these can prevent the tool from advancing into the subsurface [2].
- *Injection wells and recovery or recirculation*, allow for directing oxidant transport in the subsurface and are therefore suitable for low permeability layers. However pumping wells and potential treatment of the recovered groundwater can increase the expenses [2]. Moreover, high permeability zones within the treated low permeable layer may result in preferential flow pathways that bypass the contaminant.
- *Solid mixing*, where oxidant solutions or particles are mixed into the soil with an auger. This method can treat contaminants in low permeability media, but its suitability depends largely on the depth of the contaminated zone [12]. Treatment of depths up to fourteen meters has been documented [13].
- *Emplacement of oxidant particles* in natural or engineered fractures or vertical wells [14]. Groundwater flow would slowly allow the diffusion of the oxidant into the aquifer.
- *Infiltration* allows the treatment of large areas, provided that the media is has a moderate to high permeability and that the infiltration surface should be well graded to achieve uniform distribution [2].

Additional factors to be considered when choosing an oxidant delivery method are oxidant solubility and stability. CHP is very unstable and therefore most suitable for targeted injections rather than emplacement-diffusion controlled transport. Injections of highly concentrated oxidant solutions may trigger solubility limitations. Moreover, oxidant transport can be limited by the aquifer's natural oxidant demand and products of the oxidation reactions. Specifically, precipitates such as  $MnO_2$  from  $MnO_4^-$ ,  $FeOOH$  from iron activation aids used for CHP or persulfate, or  $CO_2$  and other gases from the oxidized contaminants can cause clogging of the media and hinder oxidant delivery.

Table 2 compiles information regarding the suitability of different delivery technologies for different oxidants under various site conditions. The need for activation can complicate oxidant delivery. In order to select the appropriate delivery approach and activation method the principles behind the different activation methods must be understood.

Technology	Oxidants	Type of media (permeability)
Direct push	All	High (not suitable for rocky material)
Injection & Recovery or Recirculation	All	High/Low
Soil mixing	Permanganate, Persulfate	High/Low
Emplacement in fractures	Permanganate ,Persulfate	Fractured media/clay
Infiltration	Permanganate ,Persulfate	High

Table 2. Oxidant delivery under different site conditions

### Development and delivery of activation aids

Modified Fenton's and activated persulfate applications involve an activation aid that propagates the generation of the reactive species (mainly hydroxyl and sulfate radicals). The most common activation aids and the challenges associated to them are presented in Table 3. Detailed description of how these methods can or have been implemented in the lab and the field is available in other reports /2,15/. Successful and timely activation is a key issue for ISCO efficiency. Therefore development of ISCO has focused on this issue.

Activation aid	Oxidants	Challenges
Heat	Persulfate	Energy and equipment required Too high temperatures can result in unproductive decomposition
Iron	Persulfate/peroxide	Keep iron soluble/available Finding a suitable iron/oxidant ratio Achieving activation when the oxidants are in contact with the contaminants
pH manipulation	Persulfate (alkaline), or acidification combined with iron activation	Overcoming the aquifers neutralizing capacity Achieving activation when the oxidants are in contact with the contaminants Emerging technology with few experiences
Peroxide*	Persulfate	Achieving activation when the oxidants are in contact with the contaminants Emerging technology with few experiences

Table 3. Activation aids and related challenges

## DEVELOPMENT POTENTIAL

Chemical oxidation is one of the most popular technologies for *in situ* remediation because it has the potential of achieving large reductions of concentration and mass flux within a short time frame. Several aspects of ISCO are under current development and hold a promising potential. These include:

- Development of new oxidants that are safer/easier to handle, such as solid peroxides ( $\text{MgO}_2$ ,  $\text{CaO}_2$ ,  $\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ ) /16/.
- Development of new activation aids, more effective iron chelates, innovative heating methods, recently alkaline activation. Activation of persulfate by naturally occurring iron is another promising alternative but field applications are lacking. Another aspect is directing radical reaction towards specific radicals that are more reactive with specific contaminants and less reactive towards natural (in)organic matter. This aspect needs to be further explored in bench scale.
- New delivery methods for the oxidants in order to overcome low permeability and diffusion constraints as well as methods of delivering the activation aids timely and in the targeted area.
- Treatment train approaches where a type of pre- or simultaneous treatment is used in order to prime the site for accepting the oxidant (e.g. fracturing, surfactant flushing, thermal) or a post treatment is used as a polishing step (often bioremediation) /3/.

At present, a group of researchers, authorities and engineers in the United States are working towards comprising a Technology Practices Manual for ISCO. This protocol will assist in screening whether ISCO is suitable for a site and offer tools for detailed design and planning, implementation and performance monitoring. The protocol will be available in early 2009 /17/.

## ISCO IN TREATMENT TRAINS

ISCO can be used in combination with other technologies in order to increase treatment efficiency. In fact, 74% of the study sites for the development of the ISCO Technology Practice Manual had used a treatment train approach. Of the sites that reached concentration reductions higher than 90%, 84% had used a treatment train approach /8/.

A list of possible technology combinations is given below:

- ISCO can be combined with physical source removal technologies such as excavation or SVE of the source and/or unsaturated zone prior to ISCO. This could reduce the contaminant mass to be treated by ISCO and prevent recontamination of the aquifer by infiltration [2]. Application of persulfate ISCO after thermal treatment could be employed as a cost effective way of achieving heat activation of persulfate /3/.
- Other chemical treatments such as the introduction of a surfactant can also be used together with ISCO, in order to increase the solubility of sorbed contaminants /18,19/.
- ISCO can be combined with hydraulic or pneumatic fracturing in tight soil media in order to ease the delivery of oxidant in low permeability zones /14/.
- ISCO can be combined with a subsequent natural or stimulated bioremediation to be used as a polishing step for rebound/intermediate contamination. This can assist in a

cost effective remediation by limiting the amount, area and period of applying expensive oxidizing reagents to the subsurface. Recent studies have shown that the inhibiting affects of ISCO on natural aquifer microorganisms are only temporary, and biodegradation processes can resume soon after ISCO. Tsitonaki et al. /20/ studied the effects of heat activated persulfate on indigenous soil microorganisms and found that although live cell numbers were not affected at concentrations up to 10 g/L, microbial activity was inhibited (Figure 2). In a later experiment /21/ it was shown that aerobic biodegradation of creosote compounds in soil columns could recover after treatment with heat activated persulfate (30 g/L). Aerobic processes recover faster because they are favored by the post ISCO aerobic conditions.

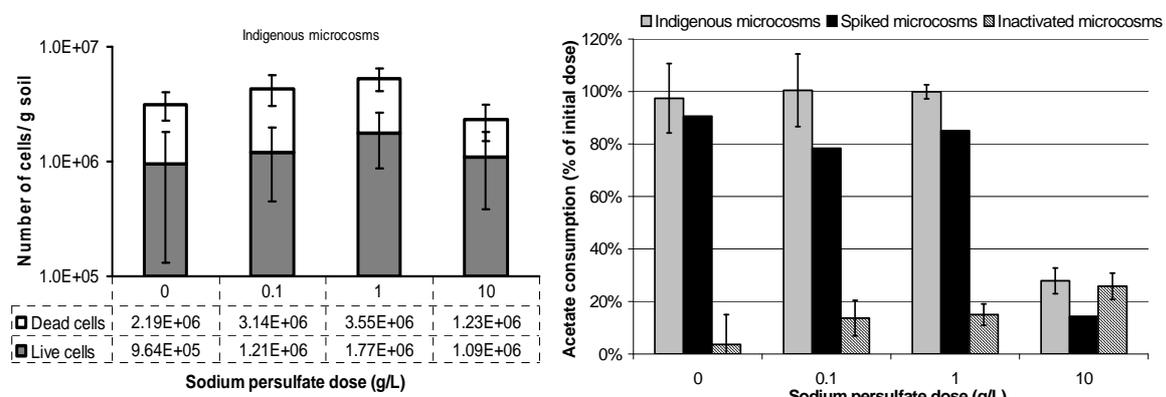


Figure 2. Effects of heat activated persulfate on the number or viable microorganisms and on bacterial ability to use acetate as studied in laboratory microcosms with indigenous and laboratory microorganisms /20/.

## CONCLUSIONS AND PERSPECTIVES

ISCO is a viable technology for the remediation of soil and groundwater. In recent years continuous development of new methodologies and increasing field applications have helped to overcome some of the limitations of ISCO. However, documentation and communication of such efforts is necessary in order to achieve optimal results and increase the spectrum of site conditions for which ISCO is suitable. The combination of ISCO with other remediation technologies also holds a great potential for increasing cost efficiency and effectiveness under difficult site conditions.

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