

ATTACHMENT 10: Oxidant Specific Design Considerations

INTRODUCTION

In addition to general design considerations that are applicable to all ISCO approaches, each individual oxidant has unique features that may require special consideration during the implementation of ISCO. This document provides a brief summary of these characteristics, while more information regarding each oxidant may be found in the ISCO volume of the SERDP / ESTCP Remediation Technology Monograph Series (Springer Science+Business Media, LLC in May 2010), [S1. ISCO Literature Review Summary](#), and the [S2. Annotated ISCO Bibliography](#). It is also important to note that each oxidant may have unique occupational health and safety as well as regulatory concerns that under some circumstances may become a major consideration in selecting a technology. It is beyond the scope of this systematic engineering approach to review all of the health, safety, and regulatory considerations as they relate to these oxidants, but the user is referred to the following guidance for further reading in this important area.

Interstate Technology and Regulatory Council. (2005). "Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater, 2nd ed. ISCO-2." Washington DC. Available at: <http://www.itrcweb.org/guidancedocument.asp?TID=13>

OZONE SPECIFIC CONSIDERATIONS

Ozone has many unique design circumstances due to the fact that it is the only gas-phase oxidant. The systematic engineering approach outlined in this electronic protocol is targeted at the application of ISCO for groundwater remediation, and thus vadose zone processes have largely been excluded. Nonetheless, vadose zone processes and saturated zone processes certainly do interact. For sites where vadose zone contamination is an actionable issue, ISCO using ozone may offer significant benefits over other ISCO oxidants due to the obvious delivery advantage of injecting a gas rather than a liquid. Some important vadose zone transport phenomena are discussed in further detail in the ISCO volume of the SERDP / ESTCP Remediation Technology Monograph Series (Springer Science+Business Media, LLC in May 2010). However, it is beyond the scope of this systematic engineering approach to go into great detail on vadose zone processes, and instead focuses on saturated zone phenomena.

One key design consideration that differs with ozone as compared with the liquid oxidants is that dosing with ozone is typically attained over longer time periods (e.g., months), at low rates of oxidant addition (~50 kg/day). This low rate of oxidant mass addition is a result of the fact that ozone must be produced onsite, and injected at relatively low mass flow rates, and hence long injection times are necessary to achieve significant oxidant doses to the subsurface. As a result, the median duration of an ozone delivery event is 280 days, as opposed to 4-7 days with the other oxidants, as indicated by [Table CD-1](#). This extended duration has obvious implications for costs associated with site mobilization. Unlike the delivery events with the other oxidants, which are short but tend to be labor intensive, much of the equipment involved with ozone ISCO can be fully automated and thus may not require extensive field time from personnel after initial set-up, a major cost driver with respect to field time. Since electricity is the primary consumable instead of wet or dry chemicals, the cost per day in the field may be quite different than with other ISCO oxidants. Also, ozone is generally injected directly from the generator, so there is no need for chemical mixing or diluting equipment. As a result, despite the fact that ozone may require much longer field time the cost for an ozone application may still be quite competitive with other ISCO oxidants. The longer delivery duration also offers a potential effectiveness advantage as there is greater opportunity to refine delivery in the field using the observational approach.

In regards to oxidant delivery, the radius of influence from an ozone sparge point is generally observed to be quite different from other ISCO oxidants. Usually the radius of influence is much wider, but the ozone distribution throughout the radius is also much more heterogeneous. In the subsurface, ozone tends to

travel in discrete gas channels through most media, following high permeability pathways. As the gas channels rise in saturated heterogeneous media, they tend to spread laterally as they encounter low permeability lenses, leading to wide areal extents, but very heterogeneous delivery. It has been suggested that pulsed ozone injection (e.g., injection for 8 hours, then resting for a period) may achieve a better distribution than continuous injection, as the continual establishment and then collapse of gas channels may perturb the distribution periodically, leading to wider media contact.

An additional unique aspect of ozone ISCO is that while liquid ISCO oxidants are typically targeted at source areas, ozone is targeted at plumes and sources with almost equal frequency ([Krembs 2008](#)). This occurs in part because ozone can be injected cheaply at low concentrations for long timeframes. In some instances, ozone has been injected in a curtain or trench to intercept and contain a large plume.

Another important consideration with ozone is that the ozone also results in delivery of large volumes of oxygen to the subsurface, which may enable aerobic biodegradation over long time periods in the otherwise frequently anaerobic subsurface. Thus conceptual design of ISCO using ozone may merit additional exploration of aerobic biodegradation through microcosm studies, if it is desired to optimize this particular degradation pathway.

A final design consideration unique to ozone is that the approach will typically require infrastructure to capture or control VOC emissions in soil gas, such as implementation of soil vapor extraction (SVE). Thus SVE and related gas collection and treatment equipment will need to be considered in the design and costing.

CATALYZED HYDROGEN PEROXIDE (CHP) SPECIFIC CONSIDERATIONS

Catalyzed hydrogen peroxide (CHP) has several important oxidant specific considerations that should be taken into account during conceptual design. Compared with the other liquid oxidants, CHP is generally the shortest-lived within the subsurface. Often, the oxidant may be completely consumed within only a day or two. Stabilization of hydrogen peroxide with chemical amendments is a growing practice that may increase the hydrogen peroxide lifetime in the subsurface, but generally the oxidant still won't persist longer than one week. As a result, the delivery strategy with CHP differs somewhat from other oxidants, as the amount of contact time between the oxidant and the contaminated media is short. This delivery strategy frequently entails the use of higher concentrations of oxidant than is typical of other ISCO oxidants to enable a rapid reaction that speeds contaminant desorption and degradation over short time periods. Elevated oxidant concentrations with CHP also offer chemistry benefits, as some reactive radical species (e.g., superoxide) that enable desorption and degradation are only produced in quantity when the oxidant concentration is high (Watts et al. 1999). However, the elevated concentrations must also be counterbalanced with the need to keep the reaction from getting too vigorous, which may result in excessive heat generation, oxidant surfacing or other undesirable outcomes. As a result, CHP is typically applied in concentrations ranging from 10-15%.

Another consideration with CHP is that generally the oxidant evolves a large amount of gas in the subsurface, which can actually aid delivery. When hydroperoxide decomposes, oxygen gas is a major byproduct, and the displacement of pore water by oxygen gas may increase the radius of influence from an injection point more than would be expected based on fluid injection alone. As a result, CHP sites often apply a lower percentage of the pore volume of oxidant than with other ISCO oxidants. The gas-induced advection may also increase dispersion in the subsurface, improving media contact with the oxidant. However, no modeling or specific quantification of these phenomena are presently available for CHP, and as a result, the ROI with CHP is much harder to predict. Instead, experience must be relied on to determine CHP ROIs and field pilot testing can be used to provide a higher degree of certainty for the achievable ROI.

One final major consideration with CHP is that catalysts or other amendments are delivered with the oxidant to enhance its performance. Amendments may include organic chelating agents, pH adjustments, stabilization aids, dissolved iron and others. Some amendments are used to stabilize the

oxidant to enable longer contact times, while others may enable certain chemical mechanisms that degrade specific contaminants. Regardless, this amendment must be delivered to the subsurface. Some amendments act very quickly and thus must be injected simultaneously with the oxidant while others may entail a sequential injection approach where typically the amendment is injected first, followed by the oxidant. Sometimes the amendment needs only to be added once, while the oxidant may be dosed on multiple occasions. Thus, the conceptual design needs to consider both the amendment injection and the oxidant injection, in terms of the total injection volume, field time, well spacing, and cost of both compounds. CHP is typically applied by specialty contractors, who have developed their own approaches to the selection and use of catalysts/amendments. These specialty contractors should be consulted for more information on the approaches they recommend.

PERSULFATE SPECIFIC CONSIDERATIONS

Persulfate, being a newer arrival to ISCO, presently does not have as long a track record or is as well documented as CHP, permanganate or ozone. For instance, [Krembs \(2008\)](#) lists only 10 sites for persulfate as opposed to 81 for permanganate, 65 for CHP and 24 for ozone. Also, since it is a more recent addition to ISCO, sites that have applied persulfate generally do not have as many years of post-ISCO monitoring data from which to derive conclusions about performance and effectiveness. As a result, the standard of practice for persulfate is much more fluid at present, and will continue to evolve and improve with time. Therefore, the persulfate specific considerations offered herein may be expected to change with time and experience as well.

One major design-specific consideration with persulfate entails activation. Just as with CHP, amendments (activators) are typically injected with persulfate to enhance the reactivity of the oxidant. In fact, the oxidant may not degrade certain contaminants unless it is activated in a specific way. These activators frequently include bases, iron, organic chelating agents, hydrogen peroxide itself, or even heat to raise the temperature of the subsurface. Injection strategies for these activators may vary as the activation aid can be delivered simultaneously with the oxidant, or oxidant delivered and then activator, or vice versa. Persulfate is generally much more persistent in the subsurface than hydrogen peroxide, typically persisting for several weeks to several months, and may in some cases persist longer than the activator. It is also important to note that the activation approach with persulfate can differ from hydrogen peroxide in that sometimes multiple activation doses may be necessary, sometimes without adding more persulfate. Thus, conceptual design must account for addition of these amendments in addition to the injection of the oxidant itself, as it can have significant implications for design and cost considerations. In some applications, installation of more costly permanent wells may be more sensible than direct push points due to the need to periodically reactivate the oxidant.

PERMANGANATE SPECIFIC CONSIDERATIONS

Compared with the other oxidants, the reactive transport of permanganate is much better understood and documented in literature and case studies. Permanganate does not require activation aid or catalysts, and thus only delivery of the oxidant must be considered, though sometimes buffers are mixed with the oxidant to help control manganese solids deposition. Thus, the main permanganate-specific concerns revolve around its persistence in the subsurface, which is reflected by natural oxidant demand (NOD). Compared with the other oxidants, permanganate has the longest persistence (lasting months or even years in the subsurface) its persistence largely dependent on NOD acting as a sink for the oxidant. Thus permanganate can achieve long contact times with the media. However, natural organic matter, minerals and other reductants can exert significant, rapid demands for the oxidant and limit delivery. NOD varies widely from site to site (even within the same site) and thus NOD is a major design concern. NOD cannot be predicted based on normal site characterization data, and so it is highly recommended to conduct a 48 hour NOD test using [ASTM method D7262-07](#) to enable successful conceptual and final design. Many other considerations specific to permanganate are expanded in more detail in the [A5. ISCO Spreadsheet Design Tool](#) and accompanying [A6. ISCO Screening Tool User's Manual](#).

REFERENCES

- [Krembs, F.J. \(2008\)](#). "Critical Analysis of the Field-Scale Application of In Situ Chemical Oxidation for the Remediation of Contaminated Groundwater," Master of Science, Colorado School of Mines, Golden, Colorado.
- Watts, R.J.; Bottenberg, B.C.; Hess, T.F.; Jensen, M.D.; Teel, A.L. (1999). "Role of Reductants in the Enhanced Desorption and Transformation of Chloroaliphatic Compounds by Modified Fenton's Reactions." *Environ. Sci. Technol.*, 33, 3432-3437.