SUPPLEMENTAL INFORMATION
ISCO Literature Review Summary

SUMMARY OF THE STATE OF THE SCIENCE OF ISCO

In situ chemical oxidation (ISCO) has evolved from a novel remediation technique into a well-established technology over the course of the last 15 years. The technology consists of the introduction of a chemical oxidant into the subsurface, which in turn initiates a series of chemical reactions that detoxify and degrade organic contaminants. The initial applications of this technology had variable results, where some excellent successes confirmed the promise of the technology, but some unexpected failures indicated the need for improved understanding and application. As a result, much was invested in ISCO research and development by both private and public funding sources, with the objective of probing the causes of these successes and failures. Through these efforts, much has been learned about oxidation chemistry, the nature of the subsurface environment, the interactions between oxidants and the subsurface, and the strengths and limitations of ISCO. This body of knowledge provides the scientific basis for ISCO, in combination with relevant experience gained from the related fields of advanced oxidation processes in water treatment, ex situ soil treatment with chemical oxidants, and the general chemistry literature. Through this scientific knowledge, many useful inferences may be made about when ISCO will or will not work for a particular site, as well as assist with informed decision-making and design when applying the technology.

As part of ESTCP project ER-0623, a comprehensive review of the literature was performed to gather the necessary technical information to develop the protocol contained on this CD. This document contains a summary of this effort, and the present state of scientific knowledge. Two products of this effort are a series of chapters within an ISCO volume of the SERDP / ESTCP Remediation Technology Monograph Series (slated for publication by Springer Science+Business Media, LLC in May 2010) on the science and function of each major ISCO oxidant, as well as a series of tables containing summary information about each study identified during the literature review. These tables have been prepared in the format of an S2. Annotated ISCO Bibliography and are included on this CD for reference.

COLLECTION OF SCIENTIFIC LITERATURE

Extensive searches of the literature were conducted to assemble as broad and comprehensive a selection of relevant literature as possible. This thorough review ensures that a representative fraction of the available scientific knowledge was included in the protocol development and the production of the chapters in the ISCO volume of the SERDP / ESTCP Remediation Technology Monograph Series (Springer Science+Business Media, LLC in May 2010). Literature collection methods included extensive searches of online abstract search engines, library catalogs, table of contents of major journals, and manual search of indexes and reference lists. The bulk of this collection effort was conducted in fall and winter of 2006, although occasional searches of more limited scope were conducted after this to account for more recent publications up to the time of this writing in summer of 2008. Information was gathered from a diversity of backgrounds, as sources were drawn not only from remediation and environmental science fields, but also chemistry, chemical engineering, and other fields that have investigated facets of oxidation processes and technologies with relevance to ISCO. Sources include a variety of peer-reviewed journal articles, conference proceeding papers, government publications, academic reports and theses, and other relevant forms of information. A breakdown of the collected sources by the publication type is presented in Figure S2-1.
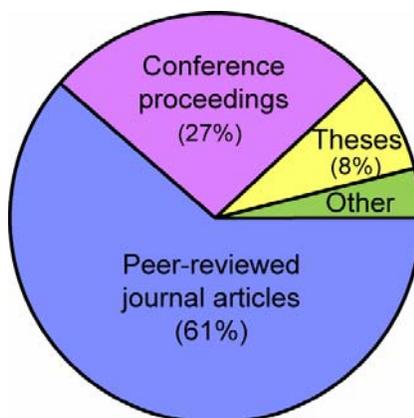
Figure S2-1: Sources Within the Collected Literature.

To limit the scope of information collection to practical bounds relevant to ISCO, the search was initially limited to four major ISCO oxidants, including persulfate, permanganate, hydrogen peroxide, and ozone, though percarbonate was added at a later date. References were gathered that were related to these oxidants and had important implications to any facet of ISCO, including reaction chemistry in water or soil systems, field applications of ISCO, coupling oxidants with other technologies or processes, subsurface oxidant or contaminant transport, and others. This review effort initially recovered approximately 600 publications with relevance to ISCO and related chemical oxidation processes.

EVOLUTION OF ISCO OVER TIME

The collected literature indicates that ISCO has developed rapidly over the last 15 years, with a major expansion of ISCO research and field application beginning in the mid to late 1990s. Since the dawn of site remediation in the early 1980s with the passage of Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and the Resource Conservation and Recovery Act (RCRA), many clean-up actions focused initially on either physical removal or containment of contaminants within the subsurface. Thus, conventional remediation technologies such as pump and treat, soil vapor extraction, air sparging and excavation became widely applied. However, by the mid-1990s, the experience with these technologies had demonstrated that in many cases, they were not capable of meeting remediation goals or site closure within reasonable cost constraints or timeframes. Thus, in situ remediation technologies gained popularity because they could achieve treatment of contaminants within the subsurface where removal by conventional methods was infeasible, and could also reduce the costs associated with extraction, treatment and disposal of contaminated media, such as soil or groundwater. Furthermore, they offered the potential to treat contaminant source zones directly, decreasing their mass, concentration and longevity, rather than focusing on containment. Advanced oxidation processes (AOPs) had already been developed for the water and wastewater treatment fields to deal with organic contaminants, and had been applied to soils and groundwater extracted from remediation sites. Thus with increasing demand for in situ remediation methods it was logical to see if oxidants could be injected into the subsurface to treat contaminated soil and groundwater. Much of the initial research was focused on the oxidants hydrogen peroxide and potassium permanganate, in part because of the commonplace usage and already extensive experience with these oxidants in water treatment and the innocuous nature of their byproducts. In water systems, hydrogen peroxide will decompose to oxygen and water, while permanganate will decompose to manganese dioxide, a common soil mineral. Ozone developed as an ISCO oxidant along a similar path, where it was incorporated as a method for enhancing the performance of methods such as SVE and air sparging. Thus many ozone studies have looked at the degradation of fuel hydrocarbon contaminants, where SVE and air sparging have been widely applied. From these early applications in situ ozonation has evolved its own place as a technology for degrading contaminants in situ. In comparison, the use of persulfate and percarbonate for ISCO is a more recent development. These oxidants have not been used as extensively in environmental applications as permanganate, hydrogen peroxide or ozone, and thus have a smaller knowledge base. As a result, many environmental

professionals are unfamiliar with them. However, as the experience base with ISCO grew with time, it was realized that a key limitation of permanganate was its limited reactivity with some common organic contaminants, while hydrogen peroxide and ozone were often challenged by short persistence in the subsurface, which limits their injection options and contact time with contaminants. Thus a search began for new oxidants having wide reactivity but longer lifetimes, and this has generated interest in persulfate and percarbonate. Hence, much of the research in recent years has begun to focus on better understanding of these two oxidants. Figure S2-1 displays the development of these oxidants over time for ISCO applications as they show the cumulative number of ISCO-related studies versus oxidant and time for the studies that were found during the literature collection effort.
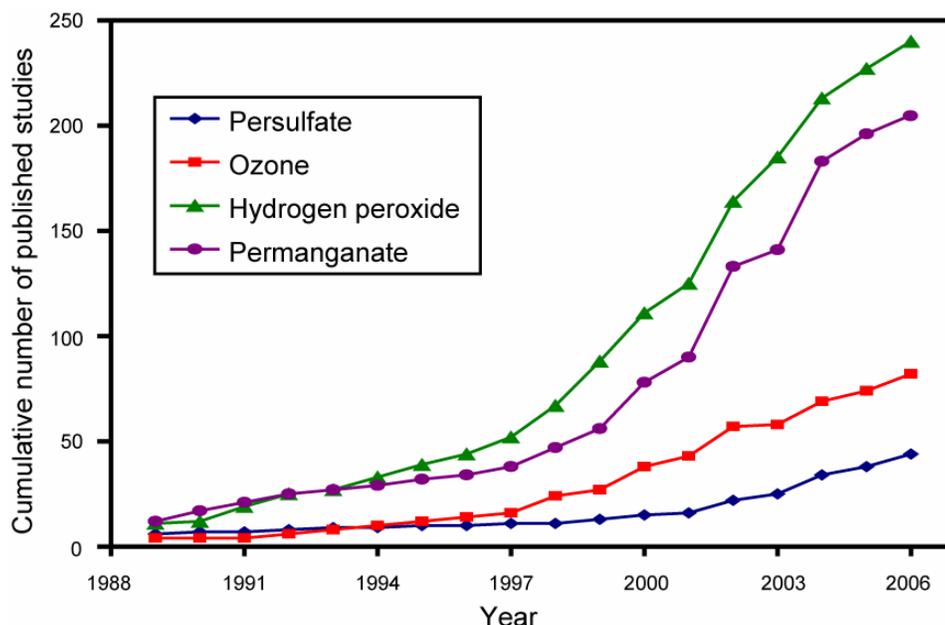

Figure S2-2: Development of ISCO Knowledge Base vs. Time by Oxidant.

PROFILE OF INFORMATION AVAILABLE IN THE LITERATURE

While a large number of studies on each oxidant were uncovered during the literature collection effort, the nature of the knowledge base varies significantly by oxidant. This discrepancy is due to the distinctive chemistry and fate of each of these oxidants in the subsurface. As the literature was collected, the studies were broadly categorized by the specific oxidant and the types of processes that were investigated by each study. These categories were defined by the methodology employed by each study and were determined as follows.

Aqueous reaction chemistry – Aqueous chemistry studies investigate reaction processes in fairly simple systems with no porous media present. These studies often utilize highly controlled reaction conditions to study process fundamentals. The experiments may be homogeneous, meaning strictly water phase is present, or heterogeneous, where other solid or liquid phases are present, such as NAPLs, humic matter or pure minerals. However, no porous media is present.

Soil slurry reaction chemistry – Soil slurry studies investigate ISCO within the presence of a porous media. The introduction of porous media introduces more uncertainty into an oxidation system as the wide variety of soil minerals and organic matter within the media may interact with the oxidant and alter chemical kinetics and reaction pathways. These tests are always batch reactor systems, which are typically completely mixed.

Oxidant transport studies – These are studies that investigate oxidant use within a system that simulates oxidant and contaminant transport processes that occur in subsurface systems. Major

processes include advection, dispersion and diffusion. These experiments include 1-D column studies and 2-D and 3-D tank studies, as well as other unique apparatus studying field transport. Other apparatus include laboratory mock-ups of field injection rigs, diffusion cells and others.

Metal mobility studies – These are studies that explicitly evaluate the impact of ISCO on metal mobility and transport during or after an ISCO application. These tests may include laboratory research of bench scale systems or field monitoring of metals after an ISCO application.

ISCO coupling studies – These are studies to evaluate the impact of ISCO on other remediation technologies and processes that occur in the subsurface. The most extensively studied technology is that of bioremediation and monitored natural attenuation, as these processes are most commonly applied during or after ISCO. Examples of less extensively investigated technologies include surfactant enhanced aquifer remediation (SEAR), thermal remediation, zero valent iron, and others.

Modeling studies – These are studies that try to simulate certain aspects of an ISCO application, such as reaction efficiency, oxidant transport, contaminant degradation, contaminant transport, or others. Models may include analytical models based on mathematical solutions to fundamental quantitative relationships or numerical models, which approximate solutions based on iteration.

Field applications – These are field case studies that have been reported in the literature, often through conference proceedings but sometimes through peer reviewed technical journals as well. These studies are included here in an overall discussion of the ISCO literature, but specific analysis of these field applications is included the Database of Field Aplications and Experiences with ISCO sites (a.k.a. Database of ISCO or DISCO).

ISCO application guidance – These are publications that provide guidance as to how to make decisions surrounding ISCO technology selection, design or implementation. These publications may include guidance documents on the technology as a whole, or specific aspects of the technology.

Figure S2-3 displays conceptually how these studies represent different processes and scales within a conceptual site model, from the pore scale to the site-wide scale.

Figure S2-4 displays the breakdown of the literature into these categories by oxidant type. As can be seen, the nature of the knowledge base varies by each oxidant. Hydrogen peroxide and permanganate are the two most extensively studied oxidants with over 200 studies each due in part these two oxidants widespread use in industrial and water treatment applications. Some of the literature developed for water treatment applications has direct relevance for ISCO. Percarbonate and persulfate had comparatively fewer studies focusing on ISCO or ISCO-like processes. This is likely an artifact of these oxidants being newer to implementation in ISCO applications, as well as their being less commonly used oxidants in industry or water treatment. Thus the knowledge base has not had as much time or driving force to grow for these oxidants. However, as with all scientific fields, they continue to grow over time, and the more recent attention on persulfate in particular indicates that the nature and extent of the scientific understanding of this oxidant will grow in the future.
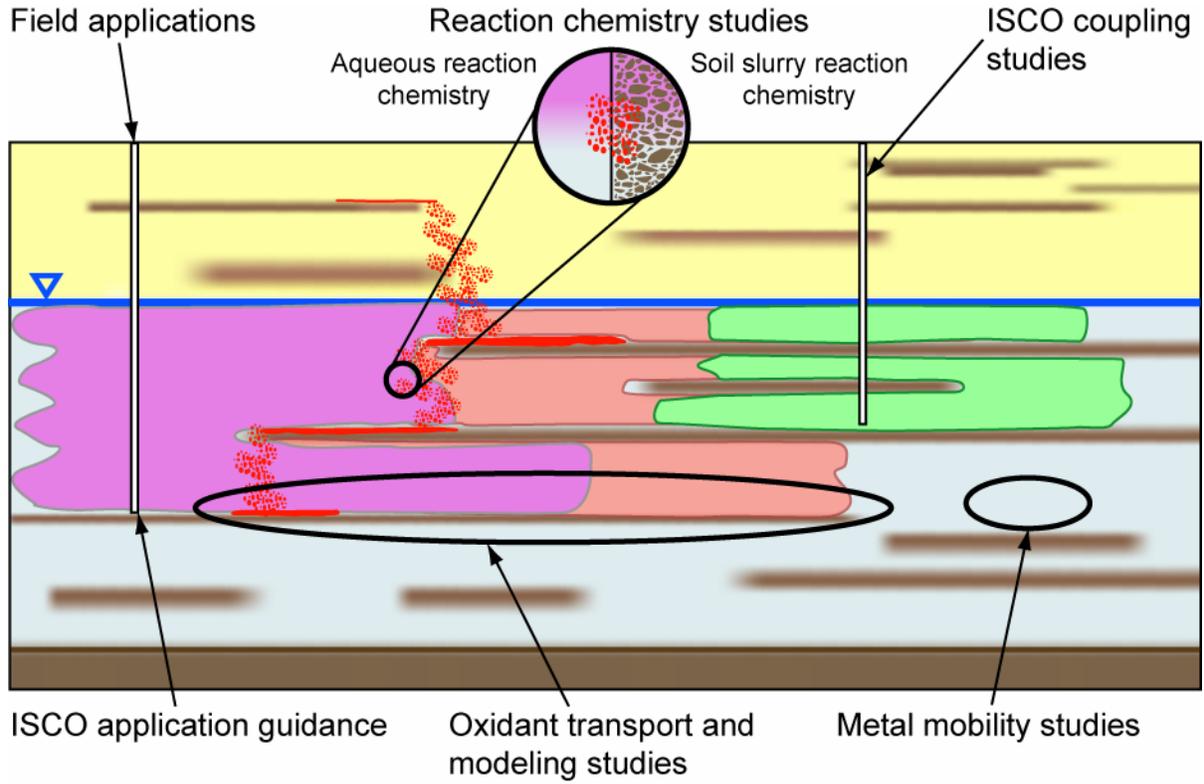
Figure S2-3: Conceptual Diagram of Relating Study Types to a Conceptual site Model.
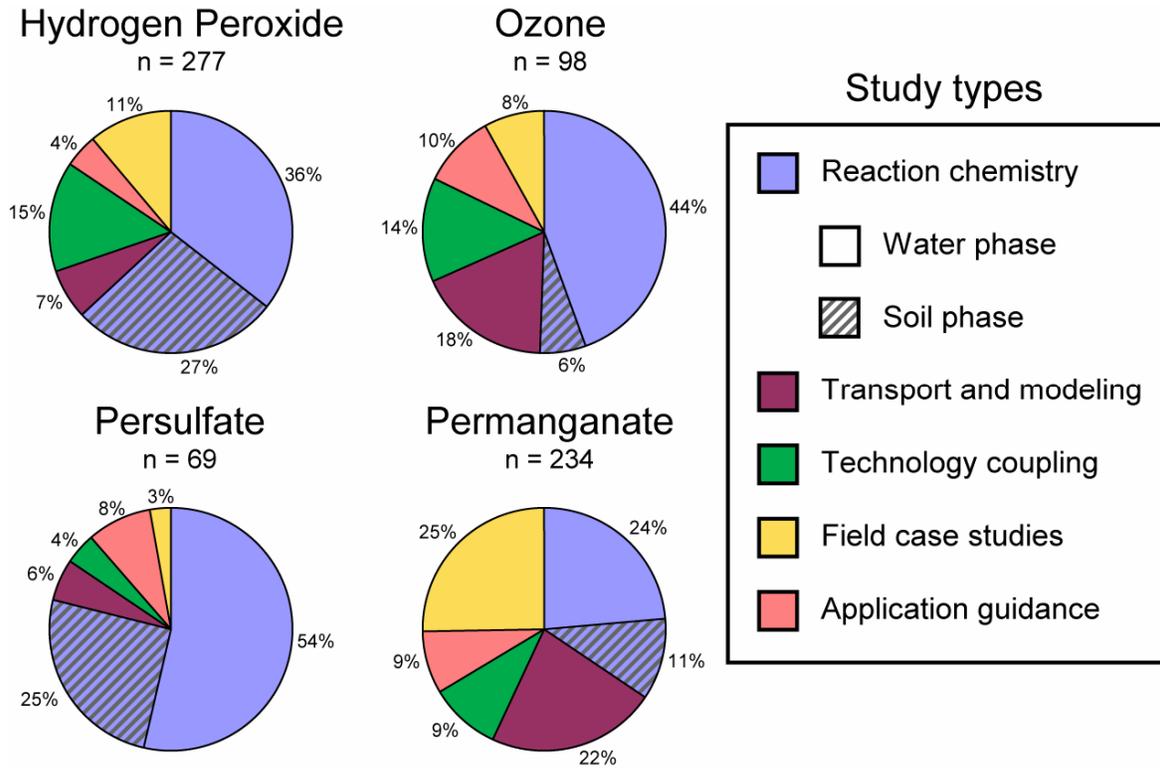

Figure S2-4: Breakdown of the ISCO Knowledge Base by Oxidant.

Looking at Figure S2-4, it is apparent that persulfate and hydrogen peroxide are largely dominated by studies of their chemistry, whether in aqueous systems or soil slurries. This is due in part to the very complex chemistry of these two oxidants, as they involve multiple oxidant activation approaches and a variety of free radical species. However, the percentage of studies evaluating oxidant transport is much smaller for these two oxidants, representing only about 6-7% of total publications reviewed by the authors as of September of 2008.   This is likely due to the still-developing knowledge base of these two oxidants, as well as difficulties in assessing the reactive transport of oxidants with such complex chemistry. In contrast permanganate has comparatively fewer studies focusing on chemistry and a much larger proportion evaluating oxidant transport.   Permanganate has a much simpler and more predictable chemistry, and thus has less need for chemistry research. This simpler chemistry also lends itself more easily to laboratory study in transport domains. One key impetus for study of permanganate in transport domains is that it is the only oxidant that generates a solid phase byproduct (manganese dioxide), which can impact flow and reactive transport within the subsurface. In the case of both ozone and hydrogen peroxide, a fairly large number of studies have evaluated their impact on coupling with other remediation processes, especially bioremediation and natural attenuation. Part of the interest for this research is not just driven by ISCO needs. In addition to being industrial oxidants, hydrogen peroxide and ozone are also present in the natural environment at very low concentrations, especially in environments exposed to sunlight. These compounds have long been of interest because of their potential toxicity to biological organisms, and the natural mechanisms that organisms have to defend from attack from these compounds have been well researched and are well understood. In contrast, permanganate and persulfate are not commonly found in the natural environment and thus research on their impacts to biologic organisms is driven almost exclusively by ISCO and related technologies. In the case of persulfate, very little information is presently available on this facet of the technology.

With respect to the prevalence of field applications of ISCO in the published literature, permanganate has the most instances, followed by peroxide, ozone, and persulfate and percarbonate had the least. However, this is not a true indication of the frequency of application of one oxidant versus another, as most remediation field sites do not publish data or findings in journals or conference proceedings. Furthermore, sites that do publish results are often those that are either highly successful or utilize unique approaches, and may not be representative of the overall experience base with ISCO in the field. The very small number of studies for persulfate is likely due to the relatively recent emergence of this oxidant as an ISCO technology. With scientific literature, there is always a lag period between the time data is collected and analyzed, and actual publication of the research, as it must often clear a lengthy peer process. With field experimentation, this period is even longer as ISCO must first be applied, followed by collection of monitoring data for analysis, and finally publication. As a result, the small number of field case studies detailed in the literature is not very surprising given this oxidant's recent emergence in the last 5 years as a major ISCO oxidant. The amount of guidance in the published literature available for each oxidant is also proportional to the amount of research that has been done on each oxidant. Thus, permanganate and hydrogen peroxide have the most application guidance publications available, while the newer oxidants such as persulfate or percarbonate have only been included in the most recent guidance publications. Thus there is considerably more guidance available for the oxidants with a longer track record than on the novel ones, where science and experience are still refining their application.

OXIDANT-SPECIFIC LITERATURE SUMMARY

With the gathering of this large body of research, several key observations may be made with respect to the nature of the knowledge base for each oxidant, based on what is available in the literature. This is summarized in the following sections. A comprehensive description of the science and function of permanganate, hydrogen peroxide, persulfate and ozone is available in the ISCO volume of the SERDP / ESTCP Remediation Technology Monograph Series (Springer Science+Business Media, LLC in May 2010).

Permanganate

A key feature of permanganate as an ISCO oxidant is that in comparison to the other ISCO oxidants, its chemistry is simple, predictable, and selective. Permanganate is largely understood to participate in oxidation reactions by direct electron transfer between the oxidant and the reductant, rather than through radical intermediates as is common with other oxidants. Because the reaction is direct, no activation aids or catalysts are needed to enable the degradation reactions. Many reaction mechanisms are well understood, and the chemistry of the oxidant has been found to be predictable and consistent within environmentally relevant ranges of major geochemistry parameters, such as pH or ionic strength. However, the selective nature of the oxidant also limits the applicability to only those contaminants that will degrade by permanganate reaction. While there are many contaminants that permanganate will degrade, there are also many which permanganate is effectively unreactive and may not degrade to any extent. For instance, permanganate is known to fully degrade trichloroethene (TCE) or tetrachloroethene (PCE) to carbon dioxide and chloride, but contaminants such as 1,1,1-trichloroethane or benzene are known to be effectively inert to the oxidant, and thus permanganate cannot be used to treat these two latter contaminants.   Therefore permanganate ISCO applicability is limited to only those that react at appreciable rates with permanganate; as a result, permanganate ISCO is limited to the smallest number of contaminants of all ISCO oxidants. However, this selective reactivity is also an advantage, as permanganate is stable for very long time periods once reductants such as contaminants or natural oxidant demand in the aquifer are depleted. This long persistence can promote a wide variety of transport phenomena within subsurface environments, such as diffusion into low permeability media as well as long contact times needed to degrade some contaminants such as DNAPLs.

The reactive transport of permanganate, in comparison to other oxidants, is well investigated and important to consider for deliverability. In addition the typical hydrologic processes that govern solute transport (e.g. advection, dispersion, heterogeneity, etc), permanganate subsurface transport is strongly impacted by two unique facets of oxidation using permanganate. These are natural oxidant demand (NOD) and manganese oxides deposition, and are described in more detail below. Many of these transport phenomena, such as NOD, contaminant oxidation and even manganese oxides deposition have been suitably quantified such that they have been included in reactive transport models with success.

Natural Oxidant Demand - When permanganate is injected into a porous media, it reacts with soil organic matter and reduced minerals which exert a "demand" for the oxidant. This demand is generally observed to be finite but rate-limited, and represents a non-productive oxidant sink. This is termed NOD. If the NOD is too high, then permanganate ISCO can be challenged by either limited delivery and short oxidant persistence, or the need for a cost-prohibitive mass or volume of permanganate injections. NOD is known to be site-specific, but at present there is no reliable correlation of NOD to typically measured site characterization data, and thus a site-specific test procedure remains the only accurate way of characterizing NOD. Considerable guidance has been developed to assist in determining if NOD will or will not be a problem with a site, and is addressed in the E-protocol on this CD, and elsewhere (e.g., ASTM method D7262-07).

Manganese Oxides - The other major factor impacting permanganate transport is the deposition of manganese oxides, the solid manganese product of permanganate reactions. Deposition of manganese oxides has the potential to impact subsurface permeability, altering transport patterns in the subsurface, particularly with high NOD media or with DNAPLs. This is because the extense zones of reaction in high NOD media or at a DNAPL interface result in intensive production and deposition of MnOx. The result of this can be increased backpressures (impacting implementation) and can also affect the ultimate distribution and contact of permanganate with contaminants of concern. Particularly with DNAPLs, the DNAPL depletion rates can decline from resulting flushing inefficiencies, as large amounts of injected permanganate mass may begin to bypass rather than contact the DNAPL. It has been proposed that this deposition of manganese dioxide solids at the DNAPL-groundwater interface may effectively encapsulate the DNAPL over time, and serve as an in situ stabilization method, but the long term stability remains unknown. Alternatively, some have proposed alternate physical or chemical methods to inhibit or control manganese oxides deposition, with some success. However, while this phenomenon is well investigated,

there is still considerable uncertainty on the degree of impact it may have on site-specific performance due to the heterogeneous nature of manganese oxides deposition.

Hydrogen Peroxide

In comparison to permanganate, hydrogen peroxide has much more complex chemistry, which is demonstrated by the fact that nearly 60% of the published studies evaluated hydrogen peroxide reaction chemistry in some facet. Furthermore, although many different contaminants, reaction mechanisms, byproducts and kinetics have been investigated, the chemistry behind hydrogen peroxide is still an active field of research where there are still a number of unknowns. Hydrogen peroxide reactions involve the catalysis of hydrogen peroxide to form a wide variety of radicals, which are highly reactive non-selective chemical intermediates that are short-lived. Due to their non-specific nature, they may react with a wide variety of organics, and thus hydrogen peroxide ISCO is relevant to the treatment of a very large number of organic contaminants. Because the reaction is catalytic, many different catalysts have been explored in hydrogen peroxide reactions. The most common and active catalysts include iron salts and iron and manganese soil minerals. Often, activity of these catalysts is moderated by the addition of organic chelating agents, pH adjustments and other additives. Geochemistry can also complicate the reactivity and effectiveness of hydrogen peroxide, as factors such as salinity, buffer capacity and pH may impact the chemistry. The body of literature on hydrogen peroxide has identified many of the mechanisms and responses involved with these reactions, both in water and in soil systems. However, there are still some knowledge gaps, and even where phenomena are well understood, the complexity of the chemistry due to the occurrence of a large number of simultaneous reactions can still impart uncertainty in the outcome. As a result, treatability studies that optimize hydrogen peroxide chemistry for site-specific conditions can be beneficial in maximizing performance.

Compared with permanganate, the transport of hydrogen peroxide and its catalysts is much less investigated. Hydrogen peroxide is known to have short oxidant persistence in the subsurface, due largely to catalytic decomposition with iron and manganese soil minerals. This short persistence, often with half-lives on the order of hours to several days, limits oxidant delivery options and the oxidant contact time within the subsurface. Additionally, many transport phenomena involved with hydrogen peroxide ISCO have not been investigated to a large degree, in part due to its short persistence. Field applications have noted that hydrogen peroxide ISCO involves the evolution of significant volumes of oxygen gas within the subsurface, but the impact of this on oxidant and contaminant transport is not well understood. Furthermore, impacts to contaminant mass transfer processes such as DNAPL dissolution or sorption have not been extensively evaluated. Because such effects have not been extensively investigated or quantified, reactive transport modeling for hydrogen peroxide ISCO is not presently feasible beyond simple prediction based on oxidant persistence.

Persulfate

Like hydrogen peroxide, persulfate chemistry is complex and an active field of research and development. As previously mentioned, the body of research with persulfate is considerably smaller than that of hydrogen peroxide, permanganate or ozone, and thus there are many more unknowns. This smaller knowledge base is in part due to the more recent arrival of persulfate in the ISCO arena, as well as the less common use of persulfate in traditional water treatment applications. Thus at the time of this publication preparation, there have been fewer published studies evaluating ISCO relevant processes and shorter monitoring records of field applications. Like hydrogen peroxide, persulfate is known to act through radical intermediates, including many of the same radicals found within hydrogen peroxide systems, along with the introduction of some unique to persulfate. However, there is strong evidence that persulfate may also react through direct reaction with some organics, such as with permanganate. The production of radicals is achieved through activation, which initiates the oxidant to form radicals. A wide variety of methods are available for persulfate activation, including the addition of transition metal salts (especially ferrous iron), heat, alkaline pH, the use of hydrogen peroxide itself and possibly others. While the mechanisms involved with these activation processes have received more attention recently, there still remains considerable uncertainty in their chemistry, such as which radicals are produced or dominant and under what chemistry conditions. Again, since radicals are non-specific reactive species, persulfate oxidation is known to degrade a very wide variety of organic contaminants, similar to hydrogen peroxide.

While the degradability of a number of organics and some of the major chemistry mechanisms involved with persulfate oxidation has been determined, the reactive transport of persulfate within porous media is much less investigated. As with all oxidants, persistence is a major factor as it determines the contact time the oxidant has in the subsurface, and thus the time available for oxidant transport and reaction with contaminants. However, the factors that impact persulfate persistence are not well investigated. For instance, it is not known what role soil minerals play in persulfate reactions or their impact on persulfate persistence. With hydrogen peroxide, mineralogy is often the controlling factor for oxidant persistence as well as a major catalyst for radical production, but it is unknown if the same applies to persulfate. The role of soil organic matter is also unknown, although persulfate oxidation has long been used in total organic carbon analysis for complete oxidation of organics to carbon dioxide. Furthermore, very few studies have evaluated the transport of persulfate and its activation aids within a porous media system, and thus there may be considerable unknowns in how the oxidant moves through and interacts with the subsurface. The lack of investigation and quantification of transport phenomena renders it difficult to model persulfate reactive transport, and at present no modeling studies are known to the authors.

Ozone

Ozone for use in ISCO operations is also less widely studied in comparison to hydrogen peroxide or permanganate. However, ozone has been extensively studied for its application in advanced oxidation processes (AOPs) as well as its relevance in atmospheric and environmental science research. Some of the findings from these other fields may be useful to make determinations about ozone ISCO. Ozone, like hydrogen peroxide and persulfate, is known to have a complex chemistry. It is known to work through both direct oxidation and radical reaction mechanisms, and many reaction mechanisms may be active simultaneously. In addition to solution-phase reactions, reactions may also occur in the gas-phase, especially with volatile contaminants. Again, because of the non-selective nature of radicals, a very large variety of COCs is known to be degradable by ozone ISCO.

Invariably, the injection of a gas into the saturated zone causes partial desaturation, and thus reactive transport of ozone is always a multiphase process. The persistence of ozone in either gas- or aqueous-phase is known to be short, but because ozone is generally injected over long time periods, breakthrough behavior can be more relevant. Soil organic matter and contaminant mass act as finite oxidant sinks that slow breakthrough, while increasing water saturation increases mass transfer to aqueous phase and limits the ultimate transport distance that can be achieved. Soil minerals may act as catalysts, while water quality parameters (especially pH), impact the mass transfer and decomposition rates. As a result, breakthrough or transport behavior can be expected to vary widely from site to site depending on the conditions present.

Many of the studies of in situ ozonation have focused on treatment and transport within unsaturated zone soils (vadose zone) and several models are available for prediction of vadose reactive transport. However, at present much less information or modeling tools are available for saturated zone injections. While some studies have evaluated ozone in the saturated zone, much of the prediction of how ozone transports and reacts within the subsurface must be based on information from the air sparging literature, where there are more studies. Presently, numerical modeling is available for prediction of ozone transport within unsaturated systems (vadose zone), but not in saturated systems.

Percarbonate

Percarbonate is the newest oxidant to receive consideration for ISCO processes. Percarbonate involves the release of hydrogen peroxide under strongly alkaline conditions that helps stabilize the oxidant. As such, the chemistry of percarbonate has many similarities to hydrogen peroxide ISCO, in that the many radicals that are involved may be the same, and many different contaminants may be degradable by percarbonate. However, the chemistry is unique from most hydrogen peroxide applications because it occurs under alkaline conditions, which impacts the reactivity of hydrogen peroxide and the derived radicals in a number of ways. The chemistry is complex, and given that this is the newest oxidant, there is less information about it with regard to soil interactions or its reactive transport. Thus there are many data gaps. However, percarbonate has long been used as a non-chlorine bleaching agent, and there is

information about its reaction chemistry in chemistry and chemical engineering literature, especially with regard to detergents. The present status of results from field demonstrations of the technology indicate that this oxidant has much promise for successful application, but the nature of its interactions with the subsurface environment are not well understood and thus it is difficult to anticipate the site-specific performance at this time.

COUPLING ISCO WITH OTHER IN SITU REMEDIATION METHODS

A large volume of literature has evaluated the impacts of ISCO on other important remediation processes and technologies, as it is not uncommon for multiple methods to be employed to meet success at a remediation site. Much of this coupling literature has focused on the impacts of ISCO on biologic processes, and has implications for bioremediation and monitored natural attenuation. The amount of coupling studies in the literature varies greatly by oxidant, and is the most extensive for hydrogen peroxide and permanganate, and the least extensive for persulfate. The very low number of studies with persulfate indicates there is still a fair amount of uncertainty in how this oxidant may be expected to impact these processes. However, overall the investigations of the interactions of ISCO with biological processes have typically confirmed five major phenomena, regardless of oxidant. These are:

- ISCO does NOT sterilize the subsurface
- Anaerobic processes within ISCO treatment zones are typically disrupted by ISCO, but the disruption is temporary and ambient activity eventually rebounds with time
- The diversity of the microbial community can be reduced after application of ISCO
- Oxidation of soil organic matter and contaminants may release organic acids and other dissolved organic compounds that may support biological processes
- Oxidants and their breakdown products may provide microbes with terminal electron acceptors, such as oxygen, manganese, or sulfate

These factors indicate that biological processes may be coupled with ISCO both within ISCO treated zones as well as in down-gradient areas. Some adverse impact to the microbial community and natural attenuation processes may be observed within the treatment zone, but there are also mechanisms that can enhance these biological processes, especially in down-gradient zones. Thus natural attenuation or bioremediation may certainly be incorporated into ISCO remediation strategies.

The interactions of ISCO with other remediation technologies have also been investigated. Perhaps the most investigated non-biologic technology is that of surfactant enhanced aquifer remediation, where it has been observed that surfactants can enhance the solubility of DNAPL compounds and improve their contact with ISCO oxidants. However, the surfactants themselves can be degraded by the oxidant possibly reducing oxidant persistence, and the potential consequences of the mobilization of DNAPL must be considered. Some have evaluated oxidation reactions at elevated temperature, which has implications for interactions of thermal remediation methods with ISCO. Higher temperatures generally increase kinetic rates of reaction, and can enable the degradation of contaminants that are resistant to oxidation at lower temperatures. But higher temperature can also decrease oxidant persistence and therefore contact times. Investigations into interactions between ISCO and other remediation technologies indicate that the impacts are very oxidant-specific and technology-specific. Often, there are very few or no studies of specific oxidant technology couplings, and thus only inferences based on experience and knowledge of the oxidant and the other technology may be used.

SUMMARY

Overall the ISCO literature indicates a large body of scientific information is available and many processes are understood. However, the body of information for each specific oxidant varies in both depth and content. Furthermore, many processes remain to be understood. Thus the scientific basis for ISCO applications will continue to evolve as research on ISCO processes continues.