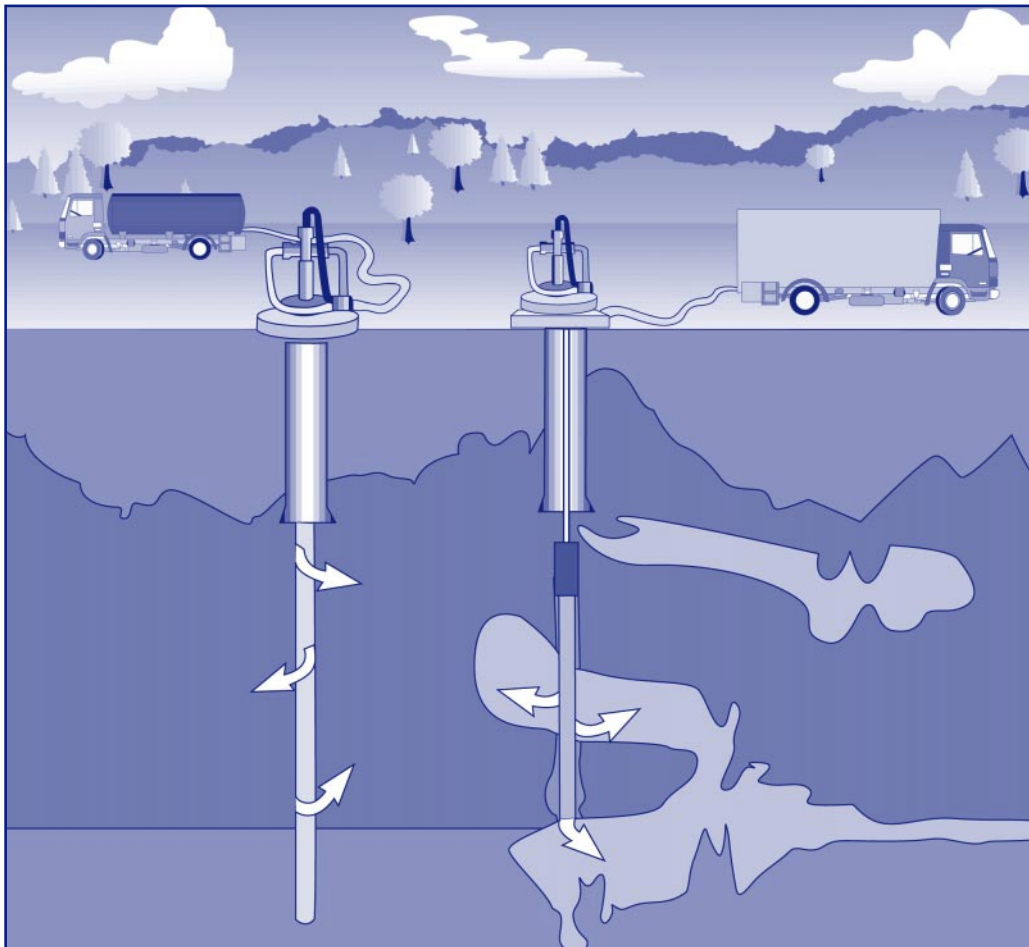




Technical/Regulatory Guidelines

Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater



June 2001

Prepared by
Interstate Technology and Regulatory Cooperation Work Group
In Situ Chemical Oxidation Work Team

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EXECUTIVE SUMMARY

The contamination of groundwater and subsurface soil in the United States is a challenging problem. There are estimated to be 217,083 sites requiring some form of remediation (U.S. EPA, 1997). All of these sites potentially threaten groundwater resources. They are frequently impediments to the reuse of “brownfield” sites. Conventional treatment methods, such as pump-and-treat technology, are often costly and less than effective. Emerging in situ groundwater and subsurface soil treatment technologies may provide effective, lower-cost alternatives. It is important to fully understand all aspects of any innovative technology. This guidance document was developed to outline the technical and regulatory requirements of In Situ Chemical Oxidation (ISCO). ISCO refers to a general group of specific technologies, with each technology representing specific combinations of oxidants and delivery techniques. Specific primary oxidants addressed in this document are hydrogen peroxide, potassium and sodium permanganate, and ozone. Additionally this document is intended to expedite movement to a consensus on regulatory requirements through the ITRC concurrence process. It should prove useful to regulators, stakeholders, consultants, and technology implementers.

The document is divided into sections consisting of technology overview, remedial investigations, safety concerns, regulatory concerns, applicability, injection design, monitoring, and stakeholder concerns. From a regulatory perspective, the most important sections of the document are identification of injection restrictions, implementation and post closure monitoring. Appendix B provides case studies of ISCO implementations, and the reference list includes documents with additional case study data.

Site characterization is a critical step in effectively applying ISCO or any other remedial technology. A complete understanding of the site geology, hydrogeology, and geochemistry, as well as the contaminant profile, is necessary. Specifics on field and laboratory analytical parameters are provided in Section 2. Once a complete understanding of the site has been accomplished, it is important to develop a conceptual site model in order to relate the data in three-dimensions. Numerous hydrogeological and geochemical models are available to further evaluate site conditions.

Regulatory issues associated with ISCO include the state or federal programs associated with Underground Injection Control (UIC), and Air Quality. Permitting will typically not be an extensive process in ISCO deployment, as required permits may be limited to UIC concerns. Air Quality concerns are limited to controlling fugitive vapors that may be produced by the heat of reaction. Monitoring issues are discussed in this document.

Health and safety issues for ISCO include the following: (1) safely handling the oxidants, as hydrogen peroxide, potassium permanganate, and sodium permanganate solutions are strong nonspecific oxidants; (2) permanganate dust is hazardous; (3) the presence of ozone will increase the flammability of many materials; and (4) the generation of ozone usually includes high-voltage equipment concerns.

Tribal and stakeholder concerns should be addressed in detail. This requires frank public discussion about the potential risks and benefits of the technology and about site-specific issues. This document provides detail on tribal and stakeholder concerns in Section 7.

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TECHNICAL AND REGULATORY GUIDANCE FOR IN SITU CHEMICAL OXIDATION OF CONTAMINATED SOIL AND GROUNDWATER

1.0 INTRODUCTION AND TECHNOLOGY OVERVIEW

This document is intended to serve as a technical and regulatory guide for stakeholders, regulators, and technology implementers involved in selecting and implementing ISCO as a remedial action. The In Situ Chemical Oxidation (ISCO) Work Team of the ITRC is composed of members from six state regulatory agencies (New Jersey, Louisiana, Florida, Kansas, California, and Massachusetts), plus stakeholders, federal agencies, and private sector individuals. The ISCO Work Team has prepared this document to provide guidance for the implementation of ISCO techniques. Wherever possible, the team has identified potential regulatory issues and recommended regulatory guidance for ISCO.

Remediation of groundwater contamination using ISCO involves injecting oxidants and other amendments as required directly into the source zone and downgradient plume. The oxidant chemicals that are commonly used with ISCO are described in Section 1.2. The oxidant chemicals react with the contaminant, producing innocuous substances such as carbon dioxide (CO₂), water (H₂O), and inorganic chloride. However, the full spectrum of reaction intermediates and products is not fully understood at this time for all contaminants. Because this is an emerging technology, the number of laboratory and pilot-scale tests exceeds the number of full-scale deployments. This ratio is improving as the techniques are applied and gain acceptance. Examples of potential contaminants that are amenable to treatment by ISCO include BTEX (benzene, toluene, ethylbenzene, and xylenes), tetrachloroethylene (PCE), trichloroethylene (TCE), dichloroethylenes, vinyl chloride (VC), MTBE (methyl-tert-butyl-ether), PAH (polyaromatic hydrocarbons) compounds, and many other organic contaminants. References to journal articles and guidance documents that provide technical information on these contaminants are included in Section 9 of this document.

ISCO offers several advantages over conventional treatment technologies such as pump and treat. For instance, the technology does not generate large volumes of waste material that must be disposed of and/or treated. ISCO is also implemented over a much shorter time frame. Both of these advantages should result in savings on material, monitoring, and maintenance. This technology also has various limitations and should not be considered a magic bullet for every site. Furthermore, application of ISCO may actually disrupt other remedies. For example, application of ISCO on a site that is benefiting from natural reductive dehalogenation may temporarily upset the geochemistry that facilitates the process.

Because this is an evolving technology, this document is intended as a guide only and may become obsolete as new technologies and applications of ISCO evolve. Suggestions concerning future revisions and comments can be sent to any of the team members using the contact information in the appendix. In addition, current research should always be reviewed when considering the guidelines outlined in this document. Users of this document are encouraged to consult the references listed in Section 9 for background and technical information on this technology. Much of the information presented in this document was based upon work plans and operational experience at many projects where ISCO has been used to remediate contaminated soil and groundwater. The team used these work plans as a reference and evaluated regulatory issues using the collective experience within the group. Where possible, the team tried to use regulatory expertise to reach a consensus. Regulatory examples are provided in Appendix A.

As indicated by the title, this document focuses on providing technical and regulatory guidance for ISCO. The object is to provide guidance for state and federal regulators, consultants, and project managers. This document points out important considerations to take into account during site

characterization, remedial design, implementation of the remedy, implementation monitoring, and post-closure monitoring. Case studies have also been included to demonstrate the implementation of ISCO techniques.

Users of this document are encouraged to refer to the ITRC's website (<http://www.itrcweb.org>) or Appendix E to order additional copies of this document and other ITRC publications.

1.1 Brief Descriptions of the Technologies

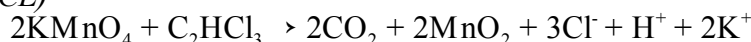
1.1.1 Potassium and Sodium Permanganate

Permanganate is an oxidizing agent with a unique affinity for oxidizing organic compounds containing carbon-carbon double bonds, aldehyde groups or hydroxyl groups. As an electrophile, the permanganate ion is strongly attracted to the electrons in carbon-carbon double bonds found in chlorinated alkenes, borrowing electron density from these bonds to form a bridged, unstable oxygen compound known as a hypomanganate diester. This intermediate product further reacts by a number of mechanisms including hydroxylation, hydrolysis or cleavage. Under normal subsurface pH and temperature conditions, the carbon-carbon double bond of alkenes is broken spontaneously and the unstable intermediates are converted to carbon dioxide through either hydrolysis or further oxidation by the permanganate ion. There are two forms of permanganate, KMnO_4 and NaMnO_4 . The balanced oxidation-reduction reactions of KMnO_4 with the various species of chlorinated ethenes can be written as follows:

Perchloroethene (PCE)



Trichloroethene (TCE)



Dichloroethene (DCE)



Vinyl Chloride (VC)



The by-products of the reactions shown above are reaction end-points. Yan and Schwartz (1999) identified the intermediate reaction products of TCE oxidation using permanganate ion as being ephemeral, and consisting mainly of esters and short-chain acids. Carbon dioxide (CO_2) exists naturally in subsurface from biological processes and bicarbonate partitioning in the groundwater. Manganese dioxide (MnO_2) is a natural mineral already found in the soils in many parts of the country. If the precipitation of manganese dioxide in the soils is excessive, it can reduce the permeability of the soil, thus limiting injection of the aqueous oxidant. Although the manganese dioxide is insoluble in groundwater, manganate (Mn^{+4}) may be reduced to dissolved divalent manganese (Mn^{+2}) under low-pH or redox conditions. The effect of this reaction on dissolved manganese levels in the immediate treatment area is not well understood. The chloride ion (Cl^-) released by the oxidation reaction may be converted into chlorine gas (Cl_2) due to the high-redox conditions. Chlorine gas reacts immediately with groundwater and pore water to form hypochlorous acid (HOCl). This hypochlorous acid may react with methane to form trace concentrations of chloromethanes in the groundwater immediately after treatment. However, this phenomenon is typically short-lived as the subsurface conditions are converted from an anoxic state to an oxidized state.

Permanganate can also be used to treat organic compounds that contain hydroxyl functional groups such as primary and secondary alcohols, as well as some organic acids such as phenol. These oxidation reactions occur best at higher pH values where hydrogen abstraction creates a negative

charge on the oxygen atom. The permanganate is attracted to the negative charge, resulting in an oxidation reaction that converts the compound into an aldehyde, ketone or carboxylic acid. Saturated aldehydes, methyl ketones, and aliphatic carboxylic acids can be further oxidized by permanganate, but incomplete oxidation may occur with more complex oxygenated hydrocarbons.

1.1.2 Hydrogen Peroxide

This process involves free radical generation and direct oxidation with hydrogen peroxide. Hydrogen peroxide, which can be delivered at depth using lance permeation or soil mixing techniques or injected water amendments, is an effective oxidizing agent. However, to achieve the desired contaminant reductions in a reasonable time, a metal catalyst is required. Iron is most commonly used, and, when mixed with hydrogen peroxide, the catalyst is known as Fenton's reagent. The terms "Fenton's reagent" and "hydrogen peroxide" are used interchangeably in this document. The basic reaction is as follows:



The process is well documented for producing hydroxyl radicals by the reaction of hydrogen peroxide and ferrous iron (Fe^{+2}). The hydroxyl radicals ($\text{OH}\bullet$) serve as very powerful, effective, and nonspecific oxidizing agents, second only to fluorine in oxidizing power. Many reactions occur during the oxidation of a contaminant, and either ferrous or ferric iron can react with the peroxide to produce oxidizing radicals.

The Fenton process is relatively fast acting, taking only days or weeks. The contaminants are treated in situ, converted to innocuous and/or natural occurring compounds [e.g. H_2O , CO_2 , O_2 halide ions]. By acting/reacting upon the contaminant in place, the reagent serves to eliminate the possibility of vertical movement of the contaminant other than that resulting from the act of vertical injection itself, which is often a concern with other remediation technologies. As a side benefit, aerobic biodegradation of contaminants can benefit from the presence of O_2 released during H_2O_2 decomposition, if large quantities of reagent need to be applied.

At a number of sites, a "top-down" injection approach has been implemented with Fenton's reagent when significant contamination exists just below the surface. By delivering the reagents into the groundwater at a shallow depth, a "blanket" can be created to consume organics as they rise due to volatilization from the heat generated by the exothermic reaction.

Technologies utilizing the Fenton process have shown some success with DNAPL remediation. For example, at the Naval Submarine Base at King's Bay, Georgia, this technology was shown to be successful in remediating DNAPL (dense, nonaqueous-phase liquids) to below 100 ppb in the primary treatment zone; this trend has been confirmed by subsequent sampling results.

The usefulness of Fenton's reagent may be limited by low soil permeability, incomplete site delineation, subsurface heterogeneities, and highly alkaline soils where carbonate ions are free radical (hydroxyl) scavengers.

1.1.3 Ozone

Ozone (O_3) is one of the strongest oxidants available for ISCO. It can be delivered via horizontal or vertical wells. Currently, it is most commonly used to remediate PAHs, BTEX, and chlorinated VOCs (volatile organic compounds). It can also oxidize phenol to less toxic products. Ozone can oxidize organic contaminants in two ways, either with direct oxidation by ozone or by the generation of free radical intermediates. The hydroxyl radicals are nonselective oxidizers, which rapidly attack organic contaminants (typically in less than 10 seconds) and break down their carbon-to-carbon bonds. Ozone can oxidize compounds such as aromatics and chlorinated alkenes. However, oxidation by hydroxyl radicals is faster than oxidation by the ozone itself.

Ozone must be generated on site, and this eliminates the storage and handling problems associated with other oxidants. Typical application ratios for ozone range from 1 to 10 lb of ozone per 1 lb of contaminant. Generally, moderate ozone gas saturation in the subsurface achieves optimum treatment effectiveness.

Ozone application is particularly effective for use at facilities using, storing, and/or disposing of chlorinated or nonchlorinated solvents and/or pesticides and at military facilities where ordnance compounds were manufactured, used, stored, or disposed. It may also assist bioremediation by breaking down complex compounds into simpler compounds that are more easily degraded. When it decomposes, ozone provides oxygen to the microbial community, which can aid in bioremediation. However, it is also a sterilizing agent in high concentrations or long residence times so the ozone must be carefully controlled if bioremediation is to be encouraged.

1.2 Appropriate and Applicable Uses of the Technology

In situ chemical oxidation is useful for source area mass reduction and intercepting of plumes to remove mobile contaminants. Each oxidant chemical is effective for different contaminants. Applicable contaminants include chlorinated solvents, polyaromatic hydrocarbons, and petroleum products. These include PCE, TCE, vinyl chloride, and the BTEX compounds as well as naphthalenes. Commonly used oxidants are not effective with saturated aliphatic hydrocarbons (octane, hexane, etc.) or chlorinated alkanes (chloroform, carbon tetrachloride, etc.). Permanganate may have limited effectiveness against BTEX.

The appropriateness of ISCO technology at a site also depends on matching the oxidant and delivery system to the site contaminants and site conditions. For example, permanganate is not effective against BTEX while peroxide and ozone are. This requires careful site characterization and screening. For instance, oxidation is dependent on achieving adequate contact between oxidants and contaminants. Failure to account for subsurface heterogeneities or preferential flow paths can result in extensive pockets of untreated contaminants. The applied reagents could also be consumed by natural organic matter or dissolved iron (rather than the contaminants), thereby compromising the remediation effectiveness. In summary, the most critical success factors are:

1. the effectiveness of, and ability to control, the ISCO reaction with the contaminants, and
2. the effective delivery of the reagents to the zone to be treated.

Important advantages of ISCO include its relatively low cost and speed of reaction; however, the design must account for the hazards of the chemicals and potential for vigorous uncontrolled reactions in the subsurface that may occur with Fenton's reagent. Volatile compounds may be released by even moderate changes in temperature. There could be a significant change in both the concentration and distribution of flammable vapors and/or toxic non-flammable vapors when using an in situ chemical oxidation method. This dynamic environment is less predictable than most other cleanup situations, where less powerful remediation methods are unable to drive the cleanup by greatly changing a site's established equilibrium of contaminants that are distributed amongst the vapor, liquid, and adsorbed phases.

For chlorinated hydrocarbon remediation via chemical oxidation methods, the risk of a fire is reduced since those compounds are less flammable than BTEX. However, caution should be exercised in order to prevent the release or migration of quantities and concentrations of chlorinated vapors that may be harmful from a toxicological or environmental standpoint.

Design and implementation considerations related to safety may include (1) venting or negative pressure system with ozone or Fenton's reagent to accommodate off-gasses and relieve pressure and buildup of organics, especially if the ground surface is paved and (2) utility surveys to account for the effect of underground piping, utilities, or trenches on preferential pathways and/or pockets for organic decomposition, explosive liquids and vapors, and oxygen. For more information on safety

concerns, see Section 3, “Health and Safety Issues.”

Table 1-1 provides some considerations for in situ treatment. Site-specific information is needed for field application.

TABLE 1 -1

Considerations for In Situ Treatment With ISCO

Treatable Compounds: Chlorinated alkenes, polyaromatic hydrocarbons, and petroleum products. Not effective for chlorinated alkanes and saturated aliphatic hydrocarbons.

Natural Organic Matter (NOM) and Other Reduced Species: Any reduced species in the system can exert a demand for oxidant. Of particular importance are NOM, anthropogenic organic matter, and reduced inorganics.

Permeability: Prefer high permeability, but feasible for low permeability with use of advanced oxidant delivery techniques, such as deep soil mixing and soil fracturing.

Depth of Application: With use of the advanced delivery techniques, depth is generally not a limitation.

Potential Detrimental Effects: Gas evolution, toxic byproducts, resolubilization of metals and reduction of biomass.

Other factors: Optimal pH and degradation characteristics for each oxidant are as follows:

	<u>Fenton's Reagent</u>	<u>Permanganate</u>	<u>Ozone</u>
pH	Prefer low pH of 2 to 4, but feasible up to near neutral pH.	Prefer neutral pH of 7 to 8, but effective over a wide range.	Effective at natural soil pH.
Degradation	Easily degraded in contact with soil/groundwater.	The oxidant is very stable.	Ozone degradation in soils is limited.

2.0 REMEDIAL INVESTIGATION AND FEASIBILITY STUDIES

A site must be thoroughly characterized in order to design and implement ISCO. The physical setting and the site's regulatory constraints must be accounted for before this technology can be considered feasible. Important features of the physical setting include topography, structures at the surface, underground utilities and structures, surface water features, and ecological resources. All sources of existing information should be researched including permits and radiation licenses, operating records, waste disposal records, interviews, site reconnaissance maps and aerial photographs, and previous reports. This existing information may need to be enhanced by acquiring and properly analyzing additional site-specific data needed to develop an appropriate design. A Sampling and Analysis Plan based on specific Data Quality Objectives should be developed for each site.

2.1 Specific Geologic and Chemical Data Needs

Site specific geochemical data are required to estimate chemical dosage, to establish a baseline condition prior to treatment and to evaluate the effectiveness of treatment in soil and/or groundwater. A baseline condition should be established for measurement of initial contaminant concentrations and other indicator parameters prior to treatment in soil and groundwater. For chemical oxidation technologies of interest in this document, Table 2-1 lists parameters that should be measured. Note that ordering of the parameters does not imply any ranking.

TABLE 2-1

Geologic and Chemical Data NeedsData Needs For All ISCO Agents

Volatile Organic Compounds
Contaminant Mass
Natural Organic Matter
Chemical Oxygen Demand
pH of Soil and/or Groundwater
Hydraulic Conductivity
Soil Characterization
Groundwater Gradient
Vadose Zone Permeability
Oxidation Reduction Potential
Dissolved Oxygen in Groundwater
Conductivity/Resistivity of Groundwater

Additional Data Needs For Permanganate

Soluble Manganese Concentration in
Groundwater
Permanganate Impurities

Additional Data Needs For Fenton's Reagent

Lower Explosive Limit
Carbon Dioxide
Oxygen
Iron content of soil and/or groundwater
Alkalinity of Soil and/or Groundwater

Additional Data Needs For Ozone

Lower Explosive Limit
Carbon Dioxide
Oxygen
Alkalinity of Soil and/or Groundwater
Moisture Content of Vadose Zone

Each of the above parameters is discussed in the following paragraphs.

Contaminant Mass. Estimation of contaminant mass including the presence of free-phase: Attempts should be made to accurately estimate the contaminant mass in aqueous and nonaqueous phases. Such estimation is essential to determine chemical dosing and for placement of oxidant distribution points (or wells).

Natural Organic Matter. Natural organic matter (NOM) in soil and/or groundwater: NOM would consume oxidant and therefore should be used to estimate chemical dosage. For soils with high values of NOM, chemical oxidation, solely, may not be an economical technology (Weeks et al., 2000).

Chemical Oxygen Demand (COD). COD is an essential parameter to estimate chemical dosing for all oxidant technologies. COD value would incorporate the oxidation potential of media including oxidant demand imposed by NOM, iron, manganese, arsenic, carbon monoxide (CO), methane, and acetate and therefore is a useful indicator of oxidant demand.

pH of Soil and/or Groundwater. pH values are necessary to check suitability of an oxidant especially if the contaminated zone is altered by chemical addition to suit an oxidation technology. pH should be measured to establish baseline conditions.

Hydraulic Conductivity. Hydraulic conductivity measurements help estimate a zone of influence and groundwater velocity. This information, along with the rate of decomposition of an oxidant, is necessary to estimate spacing between injection wells, frequency of application, concentration of an oxidant, etc.

Soil Classification. A qualitative evaluation of soil, including heterogeneity, is necessary to evaluate the applicability of an oxidant. For example, for clay soils most of the treatment techniques would be unfavorable since oxidant contact with the contaminant would be limited by diffusion. Soil

porosity is necessary to estimate groundwater velocity and is rarely measured. Based on a qualitative evaluation of soil, a value for soil porosity may be assumed and used for groundwater velocity estimation. The degree of heterogeneity of the medium influences the mode of oxidant application.

Groundwater Gradient. Gradient is necessary for estimation of groundwater flow, zone of influence, spacing between wells, etc. The natural gradient can be modified (ex: recirculation) to increase the zone of influence.

Vadose Zone Permeability. Permeability is required to determine an acceptable rate of a liquid dosing and to determine a zone of influence for ozone application and spacing of injection points.

Oxidation Reduction Potential (ORP) and Dissolved Oxygen (DO). ORP and DO of groundwater should be measured to assess applicability of an oxidant and to establish baseline conditions. This helps determine potential impacts on speciation and mobility of nontarget metals (e.g., chromium).

Conductivity/Resistivity of Groundwater. This is important to establish baseline conditions, to monitor and map the extent of the “reaction zone.”

Volatile Organic Compounds (VOCs), Lower Explosive Limit (LEL), Carbon Dioxide (CO₂) and Oxygen(O₂). If an inhabited structure is present on the site or in proximity to the site, the basement and/or indoor air of the building should be screened for the presence of VOCs, LEL, CO₂, and O₂ before and during chemical dosage. These measurements help establish baseline conditions and to monitor migration of gases.

Iron Content of Soil and/or Groundwater. The initial iron content of soil and/or groundwater should be factored to estimate the dosing requirements of iron. If the presence of initial iron content is ignored, there is a potential of overdosing iron and therefore reducing permeability due to formation of iron oxides after the treatment. Also, the presence of high levels of iron (specifically in ferrous form) has been reported to “scavenge” H₂O₂ due to undesirable reactions that may not oxidize target organics. Iron should be measured along with other metals.

Alkalinity of Soil and/or Groundwater. In general, field representative alkalinity measurements are essential to determine the amount of chemical addition to control pH. Hydroxyl radicals are reportedly scavenged by the presence of carbonates and bicarbonates. Therefore, estimates of chemical dosage should account for the presence of carbonates and bicarbonates in soil and/or groundwater.

Manganese Concentration in Soil and/or Groundwater. Background measurements of manganese concentration may have value to establish existing conditions prior to remediation. At sites that are adjacent to drinking water supplies, the affect of permanganate application to the unsaturated and saturated zones should be evaluated, including precipitation of manganese dioxide in the aquifer.

Permanganate Impurities. Commercially available permanganates have heavy-metal impurities, including chromium. If a site is adjacent to a drinking water supply, the potential for groundwater contamination due to metals from permanganates should be evaluated.

Moisture Content of Vadose Zone. It has been reported that the effectiveness of ozone gas reduces with increase in moisture. It was noted that presence of high moisture content would reduce the air-filled porosity and therefore would restrict advective flow of ozone gas to the contaminated zone.

2.2 Bench-Scale and Pilot-Scale Studies

A full-scale remediation is rarely designed and implemented based solely on site characterization data collected during a remedial investigation. This is particularly the case when in situ treatment

technologies, such as ISCO, are employed. Site-specific complexities and the nuances of specific technologies demand that a more in depth analysis of at least feasibility, if not optimization, be conducted. Site-specific technology feasibility testing is typically conducted during the remedial investigation or a subsequent technology-screening phase, while optimization testing is typically conducted during the engineering feasibility or early design stages.

Technology feasibility testing is typically first conducted at the laboratory scale, commonly referred to as a treatability study. Site materials (e.g., soil and groundwater) are properly packaged and shipped to the laboratory facility. Measurement of critical physical and chemical parameters is conducted and the resulting measurement data are reviewed to determine general suitability of the technology and to identify issues that may require further investigation. Typically, the bench-scale testing results are used to complete technology selection and to prepare for a field test of the technology at the site in question. Occasionally, the bench-scale testing is deemed adequate to support full-scale design and no further testing is performed. In this situation, the bench-scale testing has not only addressed the issue of technology applicability, but has also generated information to allow a measure of full-scale optimization.

Optimization testing is typically conducted in the field setting at what is referred to as the pilot scale. Pilot studies are conducted at a scale that is commensurate with a more comprehensive analysis of technology effectiveness and testing of optimization schemes. ISCO technology vendors may choose to perform pilot-scale testing as the initial step towards full-scale design and implementation if site and contaminant features are believed to be adequately represented in their experience base. Full-scale design typically follows pilot testing, although on occasion the pilot study results in the discovery of unique and adverse site features that cause a specific technology to be rejected.

The results of bench-scale testing of an ISCO technology may or may not be directly (linearly) applied to the design of a corresponding pilot-scale study. The same may be said for pilot studies as they relate to full-scale design. The process of nonlinear scaling up of the results from a small scale to a larger scale may be required. Scaling up is usually applicable to bench-scale studies while pilot-scale studies are often performed at a scale that is essentially the same as the full system under consideration. Bench-scale results are often based on extremely small volumes of disturbed soil and/or groundwater relative to the volume that requires treatment. The test apparatus may not adequately recreate the geometric nature or flow characteristics of the physical system observed in the field. For example, one-dimensional flasks or columns and two-dimensional tanks are often utilized as convenient means to simulate the three dimensional environment. Often the dimensions of the apparatus are such that test boundary conditions (e.g., wall effects) that are not present in the field become important. Also, bench-scale tests often are based on well mixed static systems while the field implementation involves dynamic plug flow. Additional discussion on laboratory- (bench-), pilot-, and full-scale demonstration of an ISCO technology can be found in Greenberg, et al., 1998, and in Siegrist, et al., 2000. Although a few sophisticated tools have been developed and applied against ISCO field data with success (Zhang and Schwartz, 2000), it is anticipated that these tools will not be applied on a regular basis to ISCO applications for several more years.

Objectives of bench-scale studies of ISCO technologies as a group, or technical considerations that should be addressed in planning for bench-scale testing, are listed in Table 2-2.

TABLE 2-2

ISCO Bench-Scale Studies

1. Isolate one or more physical or chemical processes to assess basic feasibility of the technology (e.g., remove rate-limiting transport processes by establishing a well-mixed system for evaluating basic chemical compatibility).

2. Assess the effects of NAPL (mobile and/or residual phase) on treatment effectiveness.
3. Determine the time for various levels of contaminant removal.
4. Determine if enough soil and water samples have been obtained to perform the desired testing, including all controls required for adequate statistical analysis.
5. Assess treatment effectiveness against all significant contaminants of concern (COCs).
6. Identify formation of intermediates that may be hazardous or deleterious in fulfillment of the treatment process.
7. Assess volatilization potential, including potential for carbon dioxide gas formation.
8. Assess impact on the biogeochemical environment.
9. Evaluate the effects of pH and redox adjustment on metal ion mobility (e.g., arsenic, lead and chromium) and treatment activity.
10. Assess survivability of free radicals (from Fenton's and ozone technologies) against scavengers such as carbonate ions and acids.
11. Assess the potential for permeability reduction by MnO_2 colloids, iron oxide precipitates, and/or gas bubbles.
12. Estimate reagent stoichiometry for optimal performance at the implementation scale.

A pilot-scale test should be of sufficient duration to demonstrate the effectiveness of the technology in the field. General technical considerations that should be addressed in planning for pilot-scale testing of ISCO technologies follow in Table 2-3.

TABLE 2-3

ISCO Pilot-Test Considerations

1. Site the pilot test in the location that is most representative of site conditions.
2. Assure site infrastructure, utilities, and waste management systems are sufficient to allow for uninterrupted operation.
3. Determine the technology assessment performance criteria and evaluate short-term attainment of cleanup standards or criteria, whether numerical goals or performance-based.

As a final note, bench-scale and pilot-scale studies are subject to environmental and occupational and transportation safety laws and guidelines established by local, state, and federal jurisdictions. In some cases, exemptions to specific regulations may apply. These exemptions may be offered under the following circumstances:

- where the volumes of contaminated media to be utilized are small,
- where the testing period is short, or
- when specific activities (treatability testing) are conducted under the auspices of certain regulatory programs (federal Superfund).

Special care must be given to the transportation and TSD (treatment, storage, and disposal) of contaminated media.

3.0 HEALTH AND SAFETY ISSUES

Hydrogen peroxide and potassium permanganate are relatively safe chemicals with respect to toxicity. However, the typical dangers associated with the handling of any oxidizing chemical are present with these chemicals. Skin contact with oxidizing chemicals should be avoided, and special care should be taken to avoid breathing the chemicals in the form of a dust or mist. Also, oxidizing

chemicals should never be directly mixed with combustible materials or reducing agents. Oxidizing chemicals will not only react violently with combustible materials, but they may also release oxygen gas during decomposition that could help fuel a fire. In addition, some oxidizing agents are incompatible. For example, potassium permanganate should never be mixed with hydrogen peroxide because the peroxide readily donates electrons to the permanganate ion, creating an immediate and violent reaction. Product labeling typically warns against these dangers. However, personnel who lack experience and skill with the chemicals may be prone to mishandling of the chemicals. Therefore, inexperienced personnel should not work directly with the chemicals since this presents the greatest potential for injury.

The primary toxicity risk associated with oxidizing chemicals is through direct inhalation of the chemicals. Inhalation of hydrogen peroxide mist or potassium permanganate dust can irritate the respiratory tract. Inhalation of large quantities of permanganate dust can result in pulmonary edema, which could develop several hours to several days after the exposure. Severe inhalation exposure could potentially result in death from oxidation of the lung tissue. Since the above oxidizing chemicals are not volatile, inhalation of the chemicals should only occur if the chemicals are handled in a manner that would create airborne mist or dust. Workers should therefore handle the chemicals in a manner that minimizes the creation of mist or dust. Proper respiratory protection should always be worn when working directly with the chemical. Once the chemicals are placed into the subsurface, exposure to the chemicals through inhalation pathways is very unlikely. Therefore, the threat of toxic exposure is primarily limited to those individuals working directly with the unreacted chemical. The life span of the above oxidizing chemicals is short after the chemicals are introduced into the subsurface for in situ oxidation. The life span of hydrogen peroxide may last from several hours up to several days before it is completely depleted. Potassium permanganate, on the other hand, may remain in the subsurface for several months, depending on the organic content and mineral composition of the soils. Once reacted, the threat of toxic exposure is eliminated since the by-products of the reaction are considered safe and non-toxic.

As oxidizing chemicals, potassium permanganate and hydrogen peroxide are either potentially flammable or explosive when mixed with combustible chemicals. Oxidizing chemicals not only react violently with combustible materials, but they also release oxygen gas during decomposition, which could help fuel a fire or explosion. In addition, hydrogen peroxide can rapidly self-decompose when in contact with metals or combustible compounds at elevated temperatures. During decomposition, hydrogen peroxide releases heat and oxygen gas. The rate of hydrogen peroxide decomposition can be controlled by using low concentrations of peroxide (i.e., less than 11%). When higher concentrations of hydrogen peroxide are used, the exothermic breakdown of the peroxide generates heat and oxygen gas that tends to volatilize contaminants from the soil and/or groundwater. This rapid decomposition reaction could foreseeably create an explosive condition if used for treatment of flammable or combustible compounds due to the resulting mixture of heat, oxygen, and flammable compound. In fact, the United States EPA suspected that this type of hydrogen peroxide reaction may have contributed to a sewer and home explosion at a remediation site in Wisconsin that resulted in one fatality and three injuries. As a result, the United States EPA has advised caution before approving the use of hydrogen peroxide for in situ chemical oxidation of flammable compounds such as for gasoline remediation. A similar project conducted at an underground storage tank (UST) project in Cherry Point, North Carolina resulted in buckling of an asphalt parking lot and a subsequent fire and explosion. These case studies demonstrate the potential dangers of using high-strength peroxide for in situ remediation applications.

Potassium permanganate is a more stable oxidizing agent than hydrogen peroxide, so the risks associated with rapid decomposition of the chemical are not as prevalent. However, fire or explosion risks still exist if an individual or contractor improperly mixes permanganate with combustible or flammable compounds. Examples of such incompatibility include a barn fire that occurred when a farmer mixed formaldehyde and potassium permanganate together for fumigation purposes. In another incident, a fire and subsequent plane crash occurred when a crop duster mixed permanganate

with elemental sulfur in the crop dusting bins. In each of these examples, the injured individuals apparently did not possess the required chemical knowledge or expertise to be working directly with the chemicals. A remediation worker recently received thermal burns while working on a permanganate ISCO project at a DOE facility in Piketon, Ohio. These examples demonstrate why environmental contractors must have adequate training and knowledge of oxidizing chemicals prior to implementation of ISCO in the field.

Since ozone is generated on site, handling and transportation concerns do not apply to its use. However, pure ozone is an explosive gas in addition to being an oxidizer. High concentrations of ozone (greater than 2 ppm) can cause irritation or damage to the eyes and respiratory tract. When used for in situ chemical oxidation, the ozone is typically mixed with air prior to injection, but nearly pure ozone may be present in the generating apparatus or build up in the enclosure containing the equipment. Therefore, adequate ventilation of this enclosure is necessary, and all ignition sources should be kept away from the equipment.

Potassium permanganate and hydrogen peroxide will cause burns to the skin, eyes, and mucous membranes upon contact. As with all oxidizing chemicals, the severity of the chemical reaction depends on the concentration of the oxidant in solution. The dangers of high-strength peroxide were illustrated earlier, but similar dangers may result from the use of high-strength permanganate solutions. The solubility of potassium permanganate in water is typically limited to between 3% and 6% (depending on the temperature of the water). This lower concentration of permanganate will cause burns to the skin upon prolonged exposure. However, sodium permanganate has a much higher solubility and can therefore cause immediate and severe burns upon contact.

ISCO may have some adverse effects to native soil and groundwater conditions that may adversely affect other remedial applications. For instance, the oxidizers may inhibit some of the indigenous anaerobic bacteria in the soil that are capable of utilizing the contaminants as a source of energy. This effect may temporarily restrict natural degradation that may be occurring in the soils and groundwater.

4.0 REGULATORY BARRIERS

The ITRC mission to promote safe and effective innovative environmental technologies is in part accomplished by reducing regulatory barriers to the deployment of technologies. In situ chemical oxidation offers significant benefits over conventional pump-and-treat technology, but its use may be limited by perceived regulatory barriers.

The ITRC document entitled *Technical and Regulatory Requirements for Enhanced In Situ Bioremediation (EISB) of Chlorinated Solvents in Groundwater* (December 1998) presents a detailed discussion of regulatory and policy issues (section 3.0). Included in this document are two surveys; State Regulatory and Underground Injection Control (UIC) Program, as well as regulatory issues and solutions.

This section will revisit some of these same issues, as well as attempt to update the status of regulatory barriers associated with in situ chemical oxidation (ISCO). Lastly and more importantly, an attempt will be made to provide solutions to these barriers associated with ISCO projects. States appear to be modifying permits as well as granting variances in a manner that promotes the use of Innovative Treatment Technologies (ITTs) like ISCO.

As defined in the March 2000 EPA document entitled *An Analysis of Barriers to Innovative Treatment Technologies: Summary of Existing Studies and Current Initiatives* (EPA 542-B-00-003), regulatory and legislative barriers “are imposed by legislature and government agencies through

specific statutes, regulations, policies and programs.” Three consistently mentioned barriers were as follows:

- Permitting processes are inconsistent, involve numerous levels and are time- and resource-intensive.
- Permitting and manifesting requirements under the Resource Conservation and Recovery Act (RCRA) often inhibit the development of ITTs.
- Contractors and others are concerned about financial liabilities they might incur through the use of ITTs.

Since the most common application of ISCO is aquifer remediation via an injection well, a typical regulatory barrier is the UIC program of the Safe Drinking Water Act (SDWA). Other possible barriers are the RCRA, the Comprehensive Emergency Response, Compensation and Liability Act (CERCLA), and the Emergency Planning and Community Right to Know Act (EPCRA).

4.1 Permitting/Manifesting Barriers

4.1.1 SDWA/UIC

Injection wells are regulated by the UIC program, which falls under the federal SDWA. Under the UIC program, injection of any fluid into a well is prohibited, except as authorized by permit or rule. State UIC programs may be delegated complete or partial enforcement responsibility (or primacy) by EPA.

Injection wells incidental to aquifer remediation and experimental technologies are distinguished from hazardous waste injection wells and are designated as Class V under the UIC program. Class V wells covered by the federal UIC program are authorized by rule and do not require a separate UIC permit. A Class V well regulated by a state UIC program may require a permit. While permit requirements are not a direct barrier to in situ groundwater remediation, examples of states' UIC variances (from permits) for subsurface injection of fluids in conjunction with an ISCO project can be found in Appendix A. In fact, states appear to be issuing these types of permits in a manner that actually streamlines the permit process and in doing so promotes the use of an ITT such as ISCO.

The purpose of the UIC program is to protect underground sources of drinking water (USDW) by prohibiting injections that may affect water quality. Commonly mentioned regulatory concerns noted in the June 2000 ITRC DNAPL document related to UIC are reiterated below in Table 4-1:

TABLE 4-1

Potential UIC Concerns for ISCO

1. Constituents in the injected fluid exceed a primary or secondary drinking water standard
2. Formation of toxic intermediate products
3. Unknown toxicity of a constituent of the oxidant/catalyst
4. Formation/mobilization of colloids due to breakdown of NOM
5. Migration of contaminants away from the plume or source area

Contaminated aquifers at Superfund sites may not serve as a USDW. For this reason, UIC requirements may not apply to wells at CERCLA sites.

4.1.2 RCRA

ISCO may take place via injection methods or mixing methods. When mixing techniques are used and potential hazardous wastes are treated, the need for a permit for treatment, storage, and disposal (TSD) is an issue. Although RCRA remediation staging piles and Corrective Action Management Units (CAMUs) presently allow for on-site treatment of wastes, the permit requirements for these management plans can be time-consuming and expensive.

4.1.3 CERCLA

As part of this act, releases of certain quantities of hazardous chemicals are required to be reported to the National Response Center (NRC). In regards to in situ chemical oxidation (of contaminated soils), it is likely that the treatment would be considered a “process” rather than a “release” and therefore would be exempt from CERCLA reporting. It is strongly recommended, however, that the appropriate regulatory agency be contacted prior to the commencement of an ISCO project to make certain that all reporting requirements are satisfied.

4.1.4 EPCRA

This act created a national program for emergency planning, notification and reporting for releases of extremely hazardous or toxic chemicals. There are mainly three sections (310, 311, and 312) of EPCRA that would deal with ISCO treatment. Section 302 requires facilities to prepare a comprehensive emergency response plan if an extremely hazardous substance will be stored or handled in quantities greater than established limits. For example, if 1,000 pounds or greater of H_2SO_4 is stored at a facility for in situ Fenton's oxidation, a comprehensive emergency response plan must be prepared. Section 311 requires the submission of MSDS sheets to state and local planning commissions and to fire departments if extremely hazardous substances and/or CERCLA hazardous substances are stored in quantities greater than the established limits. Section 312 requires an emergency and hazardous chemical inventory form to be submitted to state and local planning commissions and to the local fire department for hazardous substances and/or CERCLA hazardous substances stored in quantities greater than the established limits. It should be noted that Section 311 reporting requirements are not much of a burden; whereas Section 312 may not be applicable for most ISCO projects if chemical storage no longer occurs once chemical injection into the subsurface takes place.

4.2 Liability Barriers

In addition to the safety considerations inherent to ISCO projects (see Section 3.0), users of ITTs such as ISCO may be concerned about liabilities incurred through the licensing and transferring of ITTs. Other liability concerns are usually related to RCRA permitting and manifesting requirements (see above).

4.3 Solutions to Regulatory Barriers

State variances have been granted from the various rules that prohibit “zones of discharge” for discharges through remediation well. Typically, these variances are contingent upon the following:

- A corrective action plan must be approved by the agency.
- The discharge (of treatment chemicals) must be through an underground injection control well which meets all of the applicable construction, operating, and monitoring requirements of the state agency.

- The zone of discharge must be acceptable to the state agency, typically a ten-foot radius from the point of injection, but always within the contamination plume.
- The rate and volume of reagent injection must not cause undesirable migration either of the reagents or of contaminants already present in the aquifer.
- The corrective action plan must address groundwater monitoring requirements associated with the use of the technology based on site-specific hydrogeology and conditions.

Federal EPA initiatives to reduce regulatory (and legislative) barriers have been implemented such as:

- Since 1992, EPA has been granting states the authority to implement the Treatability Exclusion Rule; the Research, Development, and Demonstration Permit Program and the Subpart X Permit Program. Those authorities are granted to states to simplify the approval process for technologies and to allow flexibility in testing and demonstrating ITTs.
- In further promoting the use of innovative technologies, in 1994 EPA revised its Treatability Study Sample Exclusion Rule (59 F.R. 8362) to allow treatability studies on up to 10,000 kg of media contaminated with nonacute hazardous waste without the requirement for permitting and manifesting.
- In addition, EPA encouraged streamlining RCRA permits and orders for innovative treatment technology development and use, encouraged state adoption and streamlining of EPA authorization to administer the treatment study sample exclusion rule.
- In 1993, EPA issued the Superfund Response Action Contractor Indemnification Rule (58 Federal Register [F.R.] 5972). The rule was designed to help contractors who use ITTs obtain lower deductibles under their liability insurance.
- EPA's Area of Contamination (AOC) policy allows soils to be excavated, moved, treated and redeposited within the AOC without triggering RCRA regulatory requirements.

Individual state regulations may be more restrictive than the above-mentioned EPA requirements. Thus, individual state regulations must always be reviewed.

5.0 APPLICATION, POST-TREATMENT, AND CLOSURE MONITORING

This section describes the issues related to field application and documentation of in situ oxidation projects, including design approaches, field process and performance monitoring, post-treatment monitoring, and closure monitoring. The discussion provided herein generally applies to all in situ oxidation technologies, but unique considerations for specific oxidants are presented separately, where applicable.

5.1 Design of Oxidant Injection Concentration and Volume

The oxidant injection concentration and volume should be determined by considering both the total oxidant dose required and the subsurface hydrogeology of the site. In order to achieve adequate contact between the oxidant and the contamination, the injected volume should represent an adequate fraction of a subsurface pore-volume of the target area. However, injection of excessive volumes can cause displacement of the groundwater contamination. Determining the appropriate injection volume is largely dependent on site-specific conditions, and is of course dependent on the oxidant being used.

5.1.1 Fenton's Reagent

In commercial applications of Fenton's reagent, a mixture of approximately 5–35% H_2O_2 (wt./wt.) is applied. The initial weight (or equivalent volume) of H_2O_2 and ferrous ions is based on contaminant levels, subsurface characteristics, soil and/or groundwater volume to be treated, and the specific stoichiometry of $H_2O_2: Fe^{2+}$ determined during a laboratory study. Sometimes, additional reagent may be applied to account for heterogeneity of the medium and unanticipated rate of decomposition of H_2O_2 to provide additional contact time for the contaminants. If the natural pH of the contaminated zone is not low enough for efficient hydroxyl radical generation, acids may be added to adjust the pH of the subsurface prior to the Fenton's reagent application.

There are several advantages of applying H_2O_2 at lower concentrations below 35% (e.g., 10%). Low-concentration applications reduce the chance of excessive heat and gas generation and reduce the potential of simply stripping of contaminants from aqueous phase to the vapor phase without oxidizing them (Frisbie, 1992). In addition, excess application of H_2O_2 may not be economical due to undesirable reactions including those of the hydroxyl radicals with H_2O_2 (Baker, 1997). However, bulk H_2O_2 is generally available in 35% or 50% concentrations (at a lower cost per pound) and a 10% application may mean additional chemical handling at the site. Currently, staff reviewers of Massachusetts DEP are typically recommending application of H_2O_2 at no greater than 10% at sites.

5.1.2 Permanganate

Potassium permanganate ($KMnO_4$) can be readily mixed in concentrations of about 3–4%. The actual concentration obtained may vary depending on temperature and the dissolved solids in the make-up water. Sodium permanganate ($NaMnO_4$) is available in liquid form at a 40% (by weight) concentration. Typical concentrations for injection range up to approximately 25%. The permanganate concentration needed at the site can be determined by dividing the required total permanganate dose (either estimated or based on bench or pilot tests) into the appropriate injection volume (based on site hydrogeology and other constraints).

5.1.3 Ozone

Ozone is a gas that is generated on site from either atmospheric or compressed oxygen. The ozone concentration and gas flow rate produced by an ozone generator is fixed within fairly narrow ranges. The ozone concentrations are in the range of 5% (by weight) when generated from oxygen and about 1% when generated from atmospheric air. Ozone generator capacities are typically expressed in terms of mass output (i.e., lbs. ozone per day). Since the ozone generators produce a continuous ozone stream, the in situ oxidation process using ozone is more of a continuous process, compared to the batch injection approaches that are common with permanganate and Fenton's reagent. The ozone generator capacity required is determined from the overall oxidant loading required, the gas flow rates that the subsurface will accept, and the allowable time frame for treatment. For example, if 7,000 lbs. of ozone is required to meet the matrix demand and the contaminant demand at the site, and if one year is allowed for treatment, then the ozone generator capacity is determined from $7,000 \text{ lbs.} \div 365 \text{ days} = \text{approx. } 20 \text{ lbs. ozone per day}$.

5.2 Oxidant Injection and Subsurface Delivery/Transport

In general, oxidants should be applied at a sufficient number of points/wells such that there is adequate overlap of "effective zones" where an oxidant is in contact with contaminants. With in situ oxidation, it can be difficult to design a full-scale treatment system that will fully treat all contamination in a single treatment phase. The uncertainty in subsurface characterization data frequently leads to a more optimum approach of treating the site in several phases. In this manner, treatment results can be used to guide adjustments and additions to the system design. This allows

for treatment of difficult hot spots, without delivery of an excess of oxidant to other areas of the site. Such an approach may offer both technical and cost advantages.

The primary factors that control the effectiveness of oxidant contact with contaminants in the subsurface relate to subsurface geologic conditions (i.e., heterogeneity) and transport of the oxidant. Oxidant transport is reaction limited, because the oxidants are being depleted as they move through the subsurface. Therefore, the effective radius of oxidation treatment may be substantially less than the hydraulic (or pneumatic in the case of ozone gas) radius of influence. Faster rates of oxidant reaction (i.e., shorter half-lives) lead to more limited transport distances.

Modeling of the reactive transport of oxidants is promising but not yet developed to the level where it is applicable to project designs on a routine basis. However, modeling has been used to assess the sensitivity of oxidant transport to various parameters. Clayton (1998) developed numerical and analytical models of reactive oxidant transport and evaluated the effects of hydraulic parameters and first- and second-order reaction kinetics. The rates of oxidant transport and the oxidant concentration profiles are highly dependent on the reaction kinetics as well as the hydraulic parameters such as fluid saturation, heterogeneity, and dispersion. The modeling results showed that the oxidant would tend to move outward as a reaction front. As oxidizable materials are consumed near the injection point, the oxidant can move over larger distances. Clayton (1998) provides an analytical solution for the maximum steady-state oxidant distribution around an injection point, based on combining the equation for radial flow and simple first-order oxidant decay. This analytical solution provides a simplified analysis of oxidant transport for uniform radial flow around a single injection point. It is useful for screening purposes, but there can be many cases where it is not valid such as in cases where flow is nonradial or where fracture or other preferential flow is involved. Where preferential flow is involved, oxidant transport out of the preferential flow zones is predominantly by diffusion.

Given the limitations of reactions on oxidant transport, there are several options for oxidant delivery. The options for oxidant delivery are as varied as the range in techniques for drilling, well construction, and solution injection. Common options include injection into existing wells (i.e., former SVE or pump and treat wells), specially installed wells, temporary direct-push points (i.e., Geoprobe™ or cone penetrometer), and permanent direct-push wells. The oxidant injection pressure and flow conditions are also important and relate closely to oxidant transport. Injection at low to moderate flow rates under Darcian-flow conditions (i.e., nonturbulent, porous-media flow conditions) usually involves gravity feed into an injection point. If an oxidant is injected under substantial pressure or velocity, the injection conditions may potentially be hyper-Darcian (i.e., hydraulic fracture or soil jetting conditions). Pressurized injection may be advantageous because it can result in less plug-flow displacement and better lateral transport. However, if the soil fracture pressures are exceeded, then caution is needed to ensure that the fracture geometry is controlled so that the fractures do not move upward to a nontarget zone or potentially breach to the ground surface.

For heterogeneous media, recirculation of oxidant may be more effective than single injections. However, oxidant recirculation systems are prone to fouling and plugging due to solids generated because of the oxidation process.

5.2.1 Fenton's Reagent

There are several patented and commercial approaches for applying Fenton's reagent. In one method, before the application, it is verified that the formation is capable of accepting a certain liquid flow rate. Once an acceptable liquid flow rate is established, a 35% H₂O₂ solution and ferrous ions are injected at the same location so that chemical mixing occurs once the chemicals have reached the zone of treatment. In this patented delivery device, the injector is designed to prevent mixing of chemicals inside the injector tube.

In another patented method, an organically complexed and more mobile form of a ferrous ion catalyst is initially applied to the subsurface. The subsurface is allowed to equilibrate to ensure that conditions (pH, level of iron, etc.) are favorable for the Fenton's reactions. A 50% H₂O₂ is finally applied under pressure to mix with the iron in the subsurface to generate the hydroxyl radicals.

In a third patented Fenton's approach, a mixture of up to 5% hydrogen peroxide, an iron catalyst, and several proprietary compounds is injected in one step through a direct-push probe. The oxidant solution is injected while driving the probe, liquefying the soil around the probe tip and enabling the probe to be advanced by hand.

5.2.2 Permanganate

Since permanganate is more persistent in the subsurface than peroxide, there is a wider range of options for field application and subsurface delivery. These applications can include injection of a wide range of permanganate solution concentrations as well as emplacement of permanganate solution or potassium permanganate solids (Siegrist et al., 1999) into hydraulic fractures. Emplacement of permanganate solids can serve to form a reactive barrier that will provide a long-term source of oxidant. Alternately, the hydraulic fractures may serve as a primary delivery mode for treatment of clays. In this case, oxidant transport away from the fractures is primarily by diffusion. Struse (1999) evaluated the diffusive transport involved in the field project described by Siegrist et al. (1999). These studies both indicated that the diffusive transport of an oxidant is dependent on a high level of overall oxidant persistence. Diffusive permanganate transport treatment distances of 0.4 meters (1.3 ft) were observed over a period of 10 months.

For delivery of aqueous solutions of permanganate, selection of the solution injection concentration and volume are key to the resulting subsurface oxidant delivery. Injection of higher concentrations of permanganate can promote greater diffusion and can result in greater permanganate persistence. However, injection of greater permanganate concentrations can also result in lower treatment efficiency because the matrix demand is generally greater at larger oxidant concentrations. There is considerable room for professional judgment in determining an appropriate volume and concentration of solution to be injected to achieve adequate subsurface transport and ensure complete contaminant treatment.

5.2.3 Ozone

Subsurface delivery and transport of ozone gas is substantially different from that involved with aqueous-phase oxidants. In situ ozonation involves mass transfer from the gas phase to the aqueous phase, where the oxidation reactions primarily occur. Ozone gas can be injected into the vadose zone or into the saturated zone. Both cases involve consideration of flow under variably saturated conditions. The distribution of ozone gas injected in the vadose zone depends strongly on the existing moisture conditions and geologic heterogeneity. Ozone injection into the saturated zone involves the gas flow mechanisms of in situ sparging, where injected gases displace groundwater to form an unsaturated region of gas flow. In this scenario, subsurface heterogeneity can lead to preferential gas flow, and ozone transport may be limited by mass transfer and aqueous-phase diffusion in regions that remain water-saturated.

5.3 Process and Performance Monitoring

From the regulatory perspective, one of the most important topical areas within ISCO remediation is process and performance monitoring. Process and performance monitoring is important to all stakeholders in ISCO remediation projects because it addresses the following basic concerns:

- Technology applicability
- Remediation design

- Safety
- Technical performance

As a remediation plan is implemented, the remediation process should be monitored to continually confirm that the specific ISCO technology and remediation design are in fact applicable to the site. Process monitoring is also an important component of a comprehensive health and safety program. Finally, one of the most challenging aspects of conducting a remediation is determining whether the remedial action was a success or failure. This determination can be made in a defensible way only through an adequately designed performance monitoring and assessment process, which includes a clear definition of success. The performance monitoring and assessment process must provide information that is compatible with the agreed upon regulatory framework.

Process monitoring is done as a quality control measure before, during and immediately after the injection operation. Process monitoring consists primarily of the following:

- Confirmation of oxidant injection concentrations, volumes, and flow rates
- Measurement of oxidant concentrations in groundwater or soil gas samples
- Measurement of oxidant persistence

Performance monitoring is done primarily after the injection operations, although preinjection data must be gathered to establish a baseline.

Analysis for organic contaminants in soil and groundwater is important for in situ oxidation. Analysis of groundwater alone will not allow determination of the mass of contaminant degraded. Groundwater analytical data obtained during the in situ oxidation process can be highly dynamic and frequently shows transient increases and decreases in contaminant levels. Since the reaction kinetics with TOC are generally faster than the reaction kinetics with contaminants, contaminants can be released from soils during the initial stages of treatment. A common observation is that dissolved organic contaminant levels will increase for a short period, followed by a permanent decrease as the contaminant mass is degraded. This reinforces the importance of a comprehensive groundwater monitoring program.

Analysis of dissolved metals in groundwater is also important, since certain redox-sensitive metals can be oxidized to a more soluble state. The primary metals of concern include chromium, uranium, vanadium, selenium, lead, and molybdenum. These metals are all more mobile in an oxidized state. They may currently be in a chemically reduced, insoluble state at a particular site and therefore not detected in groundwater. However, because they are more soluble under oxidizing conditions, these metals can be mobilized by in situ oxidation. Sites where this could be a potential problem can include sites where either (1) naturally occurring metals concentrations in soils are elevated or (2) historical metals contamination was attenuated by naturally occurring chemical reduction processes.

In most cases, field and laboratory data have shown that the metals liberated by oxidation are readily attenuated back to background conditions. However, this may not always be the case. In order to minimize the possible risk of mobilizing metals at a site where in situ chemical oxidation is implemented, several steps can be implemented for site screening. Soil laboratory data of total metals content can indicate if the site contains sufficient metals to be problematic. More detailed evaluation can be performed by conducting laboratory treatability tests using samples of soil and groundwater from the site. In these bench-scale tests, aquifer materials are subjected to oxidation, and the solution water is analyzed for metals content before and after treatment. If metals are liberated into the aqueous solution, this solution can then be contacted with site soils to determine the ability of the soils to attenuate the metals to background conditions. At the field scale, metals analysis of groundwater samples is important to verify that metals mobilization is not occurring.

Common field monitoring parameters are summarized in Table 5-1.

TABLE 5-1
Field Monitoring Parameters

Analyte	Suggested Technique
Contaminants	EPA SW 846 8260B
Oxidant	Field test kit
Metals	EPA Method 200.7 (ICP), SM 3120B
Major ions (Na, K, Ca, Mg, Fe,	EPA Method 200.7 (ICP) SM 3120B
Nitrate, sulfate, and chloride	EPA Method 300 – Ion chromatography
Alkalinity, as CaCO ₃	EPA Method 310.1, SM 2320B
ORP (Eh)	Field measurement SM 18 th ED 2580B -
pH, hydrogen ion	Field measurement EPA Method 150.1, 18 th ED
Temperature	Field measurement EPA Method 170.1, 18 th ED
Specific conductance	Field measurement EPA Method 120.1, 18 th ED

Insensitive settings such as a site with occupied buildings, as a precautionary measure, monitoring of key parameters including VOCs, temperature, etc., must continue for three additional hours after the last application for the day. This monitoring is particularly important for application of Fenton's reagent. For ozone, continuous monitoring of ozone gas, VOCs, and O₂ should be conducted.

5.4 Post-Treatment and Closure Monitoring

Subsurface conditions after oxidation processes should be stabilized. Prior to determining the final level of treatment obtained, monitoring for temperature, presence of residual oxidant level, LEL (for indoor air and utility areas), etc. would help determine if chemical reactions are completed. To determine the effectiveness of treatment and to evaluate if the desired degree of oxidation is achieved, oxidant level, contaminant level, and geo chemical conditions should be monitored. Due to adsorption and desorption equilibrium, contaminant concentrations often rebound. Therefore, monitoring should be conducted for a few years to evaluate the final level of treatment obtained.

6.0 COST ESTIMATES

Chemical oxidation can be an effective remedial option, but it is not a universal solution for soil or groundwater contamination. Projects exist where in situ chemical oxidation may be ineffective and/or uneconomical based on site-specific conditions. In particular, if the carbonate or bicarbonate content or the COD of the site soil or groundwater is elevated, in situ treatment may not be cost-effective due to excessive chemical demand for the oxidant. The geochemistry of both the soil and groundwater must be considered for in situ application since the oxidant will react with both.

As with any remediation technology, the costs of treatment may vary widely depending on the scale of the project and the nature and distribution of the contaminants. The costs associated with in situ chemical oxidation typically fall into the following categories:

- Thorough characterization of the subsurface to determine the stratigraphy, hydrogeology, and mass of contaminants. However, these costs are often part of the remedial investigation (RI), and are not directly related to implementation of ISCO.

- Drilling of monitoring wells for performance monitoring. Again, at least part of this cost is usually associated with the RI.
- The oxidant chemical itself. Equations for calculating the amount and cost of each type of oxidant based on site-specific conditions are included in Appendix D.
- Laboratory analysis of water and/or soil samples to establish a baseline and evaluate the performance of the oxidant.
- Contractor costs for labor, mobilization and demobilization, injection of the oxidants, and collection of confirmation samples.
- Infrastructure necessary to implement ISCO, including utilities, fencing, improvements necessary for site access, etc.
- Permits and/or regulatory oversight required for the project.

Some cost estimates from actual ISCO implementations are available in Appendix B, “Case Studies.” Relative cost comparisons of ISCO and other innovative in situ technologies are presented in the ITRC document “*Dense Non-Aqueous Phase Liquids (DNAPLs): Review of Emerging Characterization and Remediation Technologies.*”

7.0 TRIBAL AND STAKEHOLDER CONCERNS

Stakeholders and representatives of any affected tribes should be involved at every stage of the evaluation, selection, and permitting of treatment systems and in the selection and performance evaluation of vendors. Such involvement will lead to better, more defensible solutions and will expedite the cleanup of contaminated sites. One of the objectives of the responsible parties must be to integrate tribes and stakeholders into all of their processes.

Since chemical oxidation methods are a relatively new technology, when such technology is being considered for permitting or deployment for the first time in a given area, stakeholders and tribal representatives should be given the opportunity to comment on it and to make their issues, needs, and concerns known. Information about the technology, including alternatives analysis, should be made widely available for public comment.

Chemical oxidation methods may have the potential benefit of cleaning up a contamination problem quickly and therefore may be regarded favorably by tribes and stakeholders. However, since chemical oxidation methods involve the introduction of a chemical reagent into the environment, tribes and stakeholders will have the obvious question “Will it do any harm?” This question must be addressed carefully and honestly.

In some instances, one can cite the examples where the technology has been tried before and report on its success or failure in each situation. In the case of an immature technology, one may be in a situation where one is proposing a solution that is believed to be likely to work but has not been tried previously in a parallel situation. In this type of case, one must give accurate and honest information. Explain all of the reasons why you believe that the technology is likely to work. Give the details of what you believe to be the possible failure scenarios. How likely is the technology to fail? What damage might be done? Have public discussion about the alternatives. It is possible that tribes and stakeholders will embrace an opportunity to try a new solution to a contamination problem, particularly if there is a good chance that it may succeed where other solutions are likely to fail. Be open about the potential risks and benefits. The affected tribes and stakeholders must be given the opportunity to weigh the potential risks against the potential benefits, since they are often the ones

most directly affected by the contamination and by the success or failure of the cleanup technology. In certain cases, they are also the ones who bear the cost of the cleanup or, at the very least, as taxpayers in practice serve as the insurer of last resort.

In 1997, the Tribal and Stakeholder Working Group (TSWG), working with the U.S. Department of Energy (DOE) Office of Science and Technology (OST), developed a set of principles for the integration of tribes and stakeholders into the process of evaluating and developing new technologies for the treatment of mixed low-level waste. Below we discuss the applicable TSWG principles and how they translate to a situation where in situ chemical oxidation is being considered for the remediation of subsurface contamination.

1. Minimize effluents: Clean up contamination as quickly as possible. Avoid fouling. Avoid the generation of reaction side products and new contaminants.
2. Minimize effects on human health and the environment: Protect present and future drinking water supplies. Minimize the potential for accidents.
3. Minimize waste generation: Avoid the production of waste from the cleanup effort.
4. Address social, cultural, and spiritual considerations: Minimize land use in the cleanup process. Discuss the transport of chemical reagents with the tribes and stakeholders and adapt such transport to address their concerns. Respect the social, cultural, and spiritual values of specific sites. Minimize noise and traffic. Protect local vistas. Include the costs of tribal and stakeholder participation in cost estimates and budgets. Include the costs of compliance with intergovernmental agreements in cost estimates and budgets.
5. Provide timely, accurate, complete, and understandable information: Explain the technology screening and evaluation process. Provide information about any previous applications of the technology. Provide information about the hazards and risks and also potential hazards and risks, as well as benefits and potential benefits. Keep the tribal and stakeholder representatives involved and informed throughout the evaluation, selection, permitting and deployment processes. Independent technical advisory resources should be made available to the tribes and stakeholders whenever feasible.
6. Incorporate tribal and stakeholder involvement into the responsible parties' procurement process, the permitting process, and the performance evaluation of contractors.

One of the current uncertainties about ISCO is that the radii of influence for different types of injections have not been established yet for all soil types and hydrogeological conditions. Recent case studies suggest that, for situations where the soil is tight, the number, geometry, and technique of injection are probably critical to the success or failure of the ISCO treatment. Thus, in turn, the motivation level of the responsible party can be a key factor in the success or failure, since some experimentation and multiple attempts with injection configuration and injection method may be necessary.

When a new technology such as ISCO is considered for application to a difficult problem such as DNAPL contamination of subsurface water and soil, there necessarily will be uncertainties about the efficacy and risks of the technology in a given situation. Public acceptance of a new technology will be more likely if tribes and stakeholders are involved in a timely and meaningful manner in the evaluation process. Such involvement will enable the early identification of significant issues and the joint resolution of these issues. In turn, public involvement will promote faster and more efficacious cleanup of contamination and will increase public acceptance of novel approaches to such cleanup.

8.0 CASE STUDIES

The following previously unpublished case studies are presented in greater detail in Appendix B. Previously published collections of case studies are noted in the References section.

Site: **Former Laundry and Cleaning Company, 7th Street Site, Garden City, KS**
Technology: Ozone
Summary: A linear array of four KV Associates ozone sparge/soil vapor extraction wells was installed into a shallow, unconfined aquifer of alluvial sand and gravel to stop a dissolved plume of perchloroethylene contamination originating at a closed dry cleaning facility from reaching a public water supply well.

Site: **Dry Cleaning Site, 25th and Main, Hutchinson, KS**
Technology: Ozone
Summary: A linear array of six KV Associates ozone sparge/soil vapor extraction wells was installed into a shallow, semiconfined aquifer of fluvial sands to reduce the concentration of a dissolved perchloroethylene plume threatening private water wells to below the Maximum Contaminant Level (MCL).

Site: **Quick-N-Easy/Former Artistic Site, Wichita, KS**
Technology: Sodium Permanganate
Summary: An aqueous solution of sodium permanganate was injected through an array of direct-push probes, in two treatment phases, into a shallow, semiconfined aquifer of fluvial sand and gravel to reduce the concentrations of a dissolved perchloroethylene and trichloroethylene plume to below their MCLs.

Site: **Former Isleta Chevron Filling Station, Albuquerque, NM**
Technology: Hydrogen Peroxide/Fenton's Reagent
Summary: A modified Fenton's Reagent solution (BiOx®) containing 5% hydrogen peroxide was injected through an array of direct-push probes into a shallow, unconfined sandy aquifer to clean up a plume of gasoline-derived contaminants existing in both dissolved and free-product phases to below their MCLs.

Site: **Former Manufactured Gas Plant, Long Beach, CA**
Technology: Ozone
Summary: An array of both vertical and horizontal injection wells was used to supply ozone to both the shallow aquifer and the unsaturated zone to clean up heavy petroleum hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) to below regulatory limits.

Site: **Former Wood Treatment Facility, Sonoma County, CA**
Technology: Ozone
Summary: An array of injection wells was used to supply ozone over a one-year period to both a very shallow sand and clay aquifer and the vadose zone to clean up pentachlorophenol and PAHs existing as both dissolved and free-phase contamination to below regulatory limits.

Site: **San Francisco Bay, CA**
Technology: Potassium Permanganate or Hydrogen Peroxide
Summary: In several pilot- or full-scale projects, oxidants were injected through direct-push probes into shallow, low-permeability aquifers consisting of silts, sands, and clay to clean up contaminants including perchloroethylene, trichloroethylene, vinyl chloride, and benzene from various industrial sites to below regulatory limits.

Site: **Service Station Site in Madison, WI**
Technology: Hydrogen Peroxide
Summary: An operating gasoline service station had a petroleum release. Following site characterization, the selected remedial alternative was hot-spot removal and injection of hydrogen peroxide/ferrous sulfate. 45 injection wells and 14 vent wells were installed, and treatment was conducted from August to September 1998. Results indicate that remediation was successful.

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Many Internet sites include some useful information on chemical oxidation. The following sites are listed only to provide a beginning point for readers to start their own research:

www.estcp.org

DOD program site

http://www.estcp.org/documents/techdocs/ISO_Report.pdf

PDF file: “Technology Status Review, In Situ Oxidation”

www.gwrtac.org

<http://www.gwrtac.org/html/topics/inchemox.htm>

PDF file: “Field Applications of In Situ Remediation Technologies: Chemical Oxidation”

<http://clu-in.org>

EPA site

<HTTP://www.clu-in.org/PRODUCTS/siteprof/remdctg.cfm>

Site profiles of remedial technologies

<http://www.civil.uwaterloo.ca/groundwater/oxlitrev.html>

Comprehensive bibliography by Eric Hood, Univ. of Waterloo)

<http://www.itrcweb.org>

ITRC home page

<http://apps.em.doe.gov/ost/pubs/itsrs/itsr2161.pdf>

PDF file: “Fenton’s Reagent Innovative Technology Summary Report”

<http://apps.em.doe.gov/ost/pubs/itsrs/itsr167.pdf>

PDF file: “In Situ Chemical Oxidation Using Potassium Permanganate Innovative Technology Summary Report”

<http://bigisland.ttclients.com/frtr/info/abstracts.html>

Federal Remediation Technologies Roundtable case studies

APPENDIX A

Regulatory Examples

APPENDIX A – Regulatory Examples

Example 1 – New Jersey

In New Jersey, we are required to issue New Jersey Pollution Discharge Elimination System (NJPDES) Discharge to Groundwater (DGW) permits for any actual or potential discharge of pollutants to the ground (this would include the federally initiated Underground Injection Control permits). Injection or placement on/in the ground of any chemical has historically been interpreted to be a discharge of pollutants. However, for projects such as ISCO technologies, NJ has been using the permit-by-rule (PBR) provisions for pilot tests/feasibility studies to allow the RP to do this with out a final NJPDES permit. PBRs are initially for 90 days, an additional 90 days can be granted for modifications. However, 180 days is the maximum time period allowed - after which a full NJPDES-DGW is required. A PBR allows the NJDEP to permit certain discharges just by writing a letter with certain conditions (sampling/technical requirements) to the Responsible Party (RP).

An example of the PBR letter can be found below.

* = Industrial Establishment

RE: Permit-by-Rule Discharge Authorization
*
Municipality, County

Dear _____ :

This permit-by-rule discharge authorization is hereby issued pursuant to the New Jersey Pollutant Discharge Elimination System (NJPDES), N.J.A.C. 7:14A-1 et seq. Pursuant to N.J.A.C. 7:14A-22.4(b)5, a Treatment Works Approval is not required for the discharge to groundwater authorized in this letter. The discharge approved through this permit-by-rule shall be conducted in conformance with the following requirements:

1. * is authorized to discharge to the groundwaters of the State of New Jersey (State) from:

a pilot treatment plant for the purpose of obtaining engineering design data where the discharge will not last more than 90 days from the first date of discharge, except for discharges related to in situ biotreatability studies where the discharge will not last more than 180 days from the first date of discharge.

monitoring well(s) used to measuring aquifer characteristics where the discharge will not last more than 30 days from the first date of discharge.

a facility or equipment used for monitoring, engineering remedial alternatives analysis, or design studies necessary to evaluate a contaminated site where the discharge will not last more than 90 days from the first date of discharge.

2. The discharge shall follow the proposed scope of work as outlined in the _____ dated: _____ as approved by the New Jersey Department of Environmental Protection (NJDEP) on _____ (oversight document). Failure to comply with the requirements of the oversight document will revoke the permit-by-rule authorization to discharge to the groundwaters of the State.

3. * shall comply with all provisions of the Additional Conditions Applicable to all UIC Permits of the NJPDES regulations, N.J.A.C. 7:14A-5.9, et seq.

4. All design plans and specifications for the treatment and/or reinjection system(s) shall be retained and made available to the NJDEP upon request. System performance will be evaluated against the effluent limits outlined in the oversight document. * shall meet all effluent limits as outlined in the oversight document.
5. * shall inspect the discharge weekly for evidence of malfunction including, but not be limited to, breakout, wet areas, ponding, odors, or an overabundance or loss of vegetative cover. At the first indication of a malfunction, * shall notify the NJDEP pursuant to N.J.A.C. 7:14A-2.5(a)14vi.
6. Seasonal application of water to the land surface via an overland flow or spray irrigation system shall be to a vegetated area, and shall not erode the land surface. The application rate must allow for infiltration prior to the property boundary and prior to reaching any surface water body or other receptor. All applications shall cease when the ground is frozen or snow/ice covered.
7. The discharge of water via any discharge to groundwater unit shall not adversely impact the behavior of the plume, create an unpermitted discharge to any surface water of the State, create a persistent standing, ponded or surface-flowing fluid condition, or adversely impact a water supply well. The permittee shall take any and all action necessary to prevent groundwater contamination from impacting a water supply well.
8. * is advised that this permit-by-rule authorization is limited to the timeframe noted above. Any discharges after this timeframe will require a full NJPDES permit pursuant to N.J.A.C. 7:14A-1 et seq.
9. Upon completion of the remediation, all temporary discharge to groundwater units shall be properly closed and abandoned. Closure plans for the unit(s) shall be submitted to the Case Manager for review and approval under the oversight document. All temporary UIC-Class V injection wells shall be properly abandoned in accordance with N.J.A.C. 7:14A-5.10(a)6.

Example 2 – California

California does not have any statewide policy regarding the use of In Situ Chemical Oxidation at groundwater cleanup sites. However, one of the Regional Water Quality Control Boards (North Coast Region) has recently adopted a General Permit for such activities.

Background

Responsibility for groundwater cleanup in California is delegated to two CalEPA agencies. The State Water Resources Control Board (State Water Board) regulates groundwater cleanup through its 9 semiautonomous Regional Water Quality Control Boards (Regional Water Board). The California Department of Toxic Substances Control (DTSC) regulates groundwater cleanup through its four Regions.

The State and Regional Water Boards and DTSC each have jurisdiction over separate groundwater programs but share responsibilities in some areas. The State and Regional Water Boards designate groundwater beneficial uses and are the lead agency regarding regulation of leaking underground storage tanks and municipal landfills. DTSC is the lead agency regarding regulation of hazardous waste (i.e., RCRA) and remediation of Department of Defense Sites. Areas where both agencies share responsibilities concern cleanup of nonfuel groundwater plumes (e.g., VOCs, metals). Typically, a lead agency is appointed to avoid duplication.

Regulatory Case Study

On July 27, 2000, the North Coast Regional Water Board Adopted Order No. R1-2000-51 prescribing general permitting requirements for addition of oxygen releasing compounds to groundwater. The North Coast Regional Water Board covers an area bounded the Oregon state line to the north, Pacific Ocean to the West, the San Francisco Bay Region to the south, and Great Central Valley to the east.

The permit includes the following summary:

The addition of oxygen releasing compounds to groundwater can be an effective treatment technology capable of reducing the levels of contaminants in groundwater. Oxygen releasing compounds generally consist of magnesium peroxide, calcium peroxide, hydrogen peroxide, permanganates, or other similar compounds. All the compounds are applied to aid in the remediation of petroleum hydrocarbons and other similar contaminants found in groundwater. The addition of any oxygen-releasing compound to groundwater may result in unintended secondary impacts to water quality. Any potential adverse water quality impacts are localized, short-term, and do not impact any current or prospective uses of groundwater. Groundwater quality will be monitored before addition of the oxygen releasing compounds, during treatment, and after treatment is completed to verify no adverse impact to water quality.

Conditions of application for the General Permit are as follows:

1. The discharger shall submit a complete report of waste discharge describing the proposed action including, but not limited to the following: the backgroundwater quality of the aquifer into which the oxygen releasing compounds will be added, including contaminant types, chemical oxygen demand, pH, nutrients, dissolved oxygen, dissolved carbon dioxide, groundwater temperature, iron, oxygen reduction potential, and hydraulic conductivity; characterization of the nature of the groundwater plume; description of the treatment system; and description of the nature and volume of any chemical additives. The report of waste discharge also needs to include information on the possibility of any adverse impacts to groundwater quality, and whether the impacts will be localized and short-term, and not adversely affect any current or projected uses of the water during the time that impacts are being realized.
2. The discharger shall submit a monitoring proposal to monitor the effectiveness of the treatment system and groundwater quality. The monitoring proposal shall describe the locations to be sampled and will include, but not be limited to the following: an up gradient sampling point, a down gradient sampling point, and sampling points within the contaminated zone, and address the nature of the oxygen releasing compounds and the treated chemicals and any associated breakdown products.
3. The discharger shall submit a sensitive receptor study that includes, but is not limited to: identifying all sensitive receptors within 1500 feet, all beneficial uses of groundwater, and other pertinent information for the specific site.
4. The discharger shall publish a Notice of Intent to comply with these waste discharge requirements in a newspaper of general circulation in the affected area, post a copy of the notice at the site in a prominent location(s), and shall provide notice to contiguous property owners and any interested parties.
5. These Waste Discharge Requirements shall not take effect until the Executive Officer notifies the Discharger in writing that the Waste Discharge Requirements have been issued. The Executive Officer shall not issue the Waste Discharge Requirements until

thirty days after the discharger has filed a complete Report of Waste Discharge and published the Notice of Intent. The Waste Discharge Requirements shall not be issued if the Executive Officer finds that there may be significant impacts to water quality, or finds that significant public controversy has arisen or will likely arise from the issuance of these requirements and that these requirements should be considered at a regularly scheduled Regional Water Board meeting.

Example 3 – Florida

EXHIBIT A

Memorandum

Proposed Injection Well(s) for In Situ Aquifer
Remediation at a Hazardous Waste Remedial Action Site

TO: Richard Deuerling, Mail Station 3530
Division of Water Resource Management
Bureau of Water Facilities Regulation
Underground Injection Control Section

FROM: _____

DATE: _____

SUBJ: Proposed Injection Well(s) for In Situ Aquifer
Remediation at a Hazardous Waste Remedial Action Site

Pursuant to Rule 62-528.630(2)(c), F.A.C., inventory information is hereby provided regarding the proposed construction of temporary injection well(s) for the purpose of in situ aquifer remediation at a hazardous waste contaminated site.

Site name: _____
Site address: _____
City/County: _____
Latitude/Longitude: _____
FDEP Facility Number: _____

Site owner's name: _____
Site owner's address: _____

Well contractor's name: _____ (Note 1)
Well contractor's address: _____

Brief description of the in situ injection-type aquifer remediation project:

Summary of major design considerations and features of the project:

Areal extent of contamination (square feet): _____
Number of injection wells: _____
Composition of injected fluid (See note2)
(ingredient, wt. %): _____

Injection volume per well (gallons): _____
Single or multiple injection events: _____
Injection volume total (all wells, all
events): _____

A site map showing the areal extent of the groundwater contamination plume and the location and spacing of injection wells and associated monitoring wells, is attached.

The following is a summary description of the affected aquifer:

Name of aquifer: _____
Depth to groundwater (feet): _____
Aquifer thickness (feet): _____

The injection well(s) features are summarized below, and/or a schematic of the injection well(s) is attached.

Direct-push or Conventional (circle the appropriate well type)
Diameter of well(s) (i.e., riser pipe & screen) (inches): _____
Total depth of well(s) (feet): _____
Screened interval: _____ to _____ feet below surface
Grouted interval: _____ to _____ feet below surface
Casing diameter, if applicable (inches): _____
Cased depth, if applic.: _____ to _____ feet below surface
Casing material, if applic.: _____

The in situ injection-type aquifer remediation plan for this contaminated site is intended to meet the groundwater cleanup criteria set forth in the site Decision Memo. Additionally, all other groundwater standards will be met at the time of project completion for any residuals associated with the ingredients of the injected remediation products, and any by-products or intermediates produced as a result of the chemical or biochemical transformation of those ingredients or the contaminants during their use. Applicable primary and secondary drinking water standards are set forth in Chapter 62-550, F.A.C., and additional

groundwater quality criteria are set forth in Chapter 62-520, F.A.C.

The remediation plan estimates that site remediation will take _____ months. We will notify you if there are any modifications to the remediation strategy which will affect the injection well design or the chemical composition and volume of the injected remediation product(s).

The proposed remediation plan was approved on _____ by a RAP approval memo (or other enforceable document). A copy is attached. The remediation system installation is expected to commence within 60 days. Please call me at _____ if you require additional information.

Note 1. If an injection well installation contractor has not yet been selected, then indicate the name and address of the project's general remediation contractor/consultant.

Note 2. Complete chemical analysis of injected fluid is required by Chapter 62-528, Florida Administrative Code. Proprietary formulations shall make confidential disclosure. Injected fluids must meet drinking water standards of Chapter 62-550, F.A.C., unless an exemption or variance has been granted.

Example 4 – Kansas

CLASS V UNDERGROUND INJECTION CONTROL PERMIT APPLICATION FOR SUBSURFACE INJECTION OF FLUIDS IN CONJUNCTION WITH A GROUNDWATER REMEDIATION PROJECT

In conformity with K.S.A. 65-164, 65-165 and 65-171d, the undersigned representing (name of company, corporation or person applying) hereby makes application to the Kansas Department of Health and Environment (KDHE) for a permit to inject non-hazardous fluids into or above an underground source of fresh or usable water by means of an injection well(s) for the purpose of remediation of contamination. This application shall be signed by an executive officer of a level of at least Vice-President.

1. The applicant shall provide documentation with this application that KDHE's Bureau of Environmental Remediation has approved a remediation plan that includes the use of the proposed injection well(s). Describe the contamination problem proposed for remediation, including a discussion of the source of the contamination.
2. Describe in detail the function of the well(s) within the scope of the remediation project.
3. Describe the fluids to be injected. Include predicted concentrations of the parameters of concern in the injection fluid. Provide information for each unique injection material or additive including Material Safety Data Sheets. If materials or additives are mixed prior to injection, provide an analysis of the batch conditions. Otherwise provide an analysis for each material if materials are to be injected sequentially, or manifold mixed during injection. Additional testing of the fluid to be injected may be required after review of the application and pertinent information. All analyses shall be conducted by a laboratory certified by the State of Kansas.

4. Provide a description of the injection zone including lithology, hydrology, porosity, permeability, groundwater flow velocity, transmissivity, specific capacity and coefficient of storage. Include geologic maps, diagrams, geologic cross-sections, contamination concentration maps, a piezometric surface map, and results of aquifer pump tests. Provide references for the information submitted.

5. Injection Zones: Depth to: Geologic Name(s) Top Bottom

6. Well Completion

Borehole, casing and cement or grout information.

Borehole Casing Material Weight Wall Casing Type Amount Cement Size lbs/ft Thickness Seat Cement or Gauge Depth or Grouted no.

Grout Interval from to

Screen or perforation material: _____

Type of screen or perforation openings: _____

Screen or perforations intervals:

from _____ to _____ from _____ to _____

from _____ to _____ from _____ to _____

Gravel pack intervals:

from _____ to _____ from _____ to _____

from _____ to _____ from _____ to _____

To facilitate grouting, the grouted interval of the well bore shall be drilled to a minimum diameter at least three inches greater than the maximum outside diameter of the well casing. Provide information describing the seal to be used on top of the well casing. This seal shall be air and water tight. If a pitless well adapter shall be so designed and fabricated to prevent soil, subsurface or surface waters from entering the well. If the wellhead is to be completed below the finished ground level the wellhead shall be enclosed in an approved water tight vault. The top of the vault shall be sloped to allow drainage away from the vault. Provide information describing the design of the vault. Provide an explanation describing why it is necessary to complete the wellhead below ground level.

7. Provide a detailed schematic drawing indicating the proposed well(s) completion at the surface and subsurface.

8. Fluid Injection Rate:

Fluids are to be injected at a minimum rate of _____ gallons/day to a maximum rate of _____ gallons/day. Demonstrate by appropriate calculations the well(s) is capable of receiving the proposed maximum fluid injection rate. Provide references for sources of all values used in the calculations.

9. Injection Pressure:

Maximum wellhead injection pressure will be _____.

Minimum wellhead injection pressure will be _____.

Demonstrate by appropriate calculations the proposed maximum injection pressure will not fracture the injection zone or damage the well components.

10. Discuss the stimulation program for the well(s), including chemical treatments and mechanical means.

11. Discuss the proposed injection procedure for the well(s) and provide a diagram. Describe the injection well pattern. Submit a design plan for the injection system including any pumps, filters, lines, and tanks used in the injection system.

12. Describe the meters or gauges that will be used to measure injection volume, injection rate, and injection pressure. Include the frequency of calibration.
13. Provide a plugging and abandonment plan for the well(s). The plugging plan must include the type of grout, estimated volume of grout, and a description of the grout emplacement procedure. Include a diagram of how the well will be plugged. Guidelines are attached.
14. Provide a map showing the well(s) to be permitted, surface water bodies, springs, mines, quarries, water wells, monitoring wells, withdrawal wells, any other penetrations of the aquifer and other pertinent surface features within the 1/4 mile radius area of review. The map must be clear and readable with the 1/4 mile radius area of review drawn on the map. A tabulation of data on all the wells within the area of review must be provided including the status, type, construction, date of drilling, location, depth and plugging or completion data. Key the tabulated wells to their location on the map.
15. Provide modeling results for the proposed injection - withdrawal scenario. The model used shall be approved by KDHE's Bureau of Environmental Remediation. Documentation of this approval shall be provided with this application. Provide a plan for monitoring the effects of injection on the groundwater system in the vicinity of the remediation project. Describe the monitoring wells to be used for this purpose. Include the data to be collected from the monitoring wells, frequency of data collection, data presentation format, and frequency of reporting the data to KDHE.
16. The well(s) shall be constructed by a water well contractor licensed by KDHE. Provide the contractor's name, business address, and KDHE license number.
17. The following must be submitted to and approved by KDHE upon completion of the well(s).
 - A. A log(s) for the well(s)
 - B. KDHE water well record form WWC-5
 - C. Complete casing, cementing or grouting, and screening information. Include work reports, work tickets or other documentation.
 - D. A schematic drawing showing the actual completion of the well(s) at the surface and subsurface, if different from the proposed completion.

AUTHORITY

To whom should future correspondence be addressed:

(signed) _____

I hereby certify that the statements herein are true and correct to the best of my knowledge and belief.

Signature of Applicant or Duly Authorized Agent Title

Subscribed and sworn to before me this _____ day of _____,

19 _____

Notary Public

My Commission Expires _____

6/94

APPENDIX B

Case Studies

APPENDIX B - Case Studies

1. Former Garden City Laundry and Cleaning Company, 7th Street Site, Garden City, KS

Background

The former Garden City Laundry and Cleaning Company was located at 410 North 8th Street in Garden City, Kansas. This dry-cleaning establishment was in operation from 1952 to 1970, and was demolished in the mid-1970s. Releases of perchloroethylene (PCE) occurred through spills and generally poor operating procedures after the facility switched from petroleum-based (stoddard) solvents to PCE. The contamination was discovered by testing Garden City Public Water Supply (PWS) well 18 for volatile organic compounds (VOCs) in January, 1986, as part of a state-wide effort to test PWS wells for VOCs. Further sampling of PWS well 18 was done in 1993 as part of a preliminary assessment (PA) and screening site inspection (SSI). An expanded site investigation (ESI) involving additional sampling and collection of background information on site activities was conducted in 1995. This ESI identified the Garden City Laundry as the source of the contamination in PWS well 18. Levels of PCE in this well have remained relatively steady, below the 5 microgram per liter (ug/L) maximum contaminant level (MCL). After the ESI was completed, the site was transferred to the State Dry-cleaning Trust fund in 1995. Further characterization of the groundwater plume was done by the Dry-cleaning Trust fund in 1997-1998 as a follow-up to the ESI.

Site Hydrogeology

The surface geology around the site consists of sandy loam soils of the Las Animas association, underlain by as much as 56 feet of sand and gravel alluvial deposits which make up the upper aquifer beneath the site. The samples containing PCE were taken from this upper aquifer. This alluvium overlies a confining layer of silt approximately 30 to 60 feet thick, with a vertical conductivity of 0.01 to 0.0001 feet per day. Beneath the confining layer is a lower aquifer of stratified sands and gravel with some clay and silt. This lower aquifer is more than 100 feet thick and includes the Ogallala aquifer, which supplies most of the PWS wells in Garden City. The hydraulic conductivity of the lower aquifer has been calculated at 80 to 150 feet per day. Beneath the lower aquifer is bedrock of Cretaceous age consisting primarily of shales and limestones, although some sandstone lenses are present in the bedrock and are tapped by a few wells. Bedrock is found 250-300 feet below ground surface (bgs). The Arkansas River is located approximately three-quarters of a mile south of the site.

Groundwater flow direction in the shallow aquifer, in the vicinity of the site, appears to be towards one of the PWS wells, apparently due to the well's cone of depression in the water table. The water table is found approximately 20 feet bgs. Groundwater flow direction in the deep aquifer is to the south.

Receptors Impacted

Most of the population of Garden City (27,036 persons as of 1995) receives water from 11 PWS wells. None of these wells provide more than 40% of the total water supply, so contamination from PWS wells 10 and 18 is substantially diluted before reaching any receptors. Numerous private and community wells exist within four miles of the site; water from these wells, if impacted by contaminants from the site, would not be treated or diluted prior to consumption by receptors.

Remedial Objectives

Investigation by KDHE defined the extent of the PCE plume migrating away from the site and its concentration gradient. Pumping of PWS well 18 is drawing the plume towards the well, indicating that PCE concentrations in the well may increase over time. Therefore, the objective was to install

a treatment system across the central, high-concentration lobe of the plume to halt its advance and reduce concentrations in the distal portions of the plume.

Selection of Technology and Design Parameters

This site was selected for implementation of innovative remedial technology, in the form of in situ chemical oxidation, because the contamination plume was relatively small and well-defined, and the subsurface geology was simple, well characterized, and suitable for the process. The high hydraulic conductivity of the contaminated aquifers simplifies the delivery of oxidants to the affected zones. The site's hydrogeology is relatively simple and well-defined, so very little untreated contaminant should remain in impermeable zones, minimizing the potential for contaminant rebound after in situ treatment ceases.

Ozone sparging, combined with soil vapor extraction, was chosen as the remedial technology to serve as a technology demonstration project. The equipment selected consists of a KV Associates C-Sparger control system with dual Spargepoint wells. These wells combine dual ozone sparging points, dual well screens, inflatable packer, and a recirculating pump. During operation, ozone is released first from the lower spargepoint, then the upper. Following these two sparging intervals, the in-well pump is activated to circulate ozonated water surrounding the well through the two screened intervals, increasing the well's radius of influence. This cycle is repeated for each well in series.

Soil vapor extraction was implemented by connecting a suction line to the top of the four-inch C-sparge well to extract excess ozone and gaseous breakdown products of PCE bubbling out of the saturated zone. SVE control equipment, also supplied by KV Associates, consisted of a vacuum blower exhausting all four wells in parallel, with a flowmeter and pressure gauge to monitor system performance.

Implementation of Technology

A linear array of four sparging / SVE wells was placed across the path of the highest-concentration portion of the advancing plume, spaced at 60-foot intervals. The radius of influence of these wells were determined to overlap, based on SVE vacuum tests of one of the wells which created differential pressures in all other wells. Two nearby monitoring wells were installed to help characterize the effectiveness of the remediation. The system was brought on-line in August of 1998. The ozone-air mixture was supplied to the sparging wells (one at a time) at approximately 2 cubic feet per minute, at pressures of 5-10 psi, with an ozone concentration of 1.5-2.5 ppm.

Operational Performance and Problems

The performance of this system cannot be adequately determined, due to numerous equipment failures that prevented the system from working for more than a few days or weeks at a time. Most of these failures were attributable to the C-Sparger control system. The control unit is very complex and installed in a relatively small enclosure that led to overheating problems. In addition, the ozone compressor created substantial vibration, which caused failures of electronic components, electrical connections, and mechanical fittings. Follow-up sampling to evaluate reductions in PCE concentration have not yet been conducted.

Costs

Purchasing, installing, and maintaining the components of the C-Sparger and SVE systems, as well as two monitoring wells near the linear sparging / SVE array, cost approximately \$81,000. Costs can be broken down as follows:

C-Sparger controller, SVE controller, and downhole components - \$31,000

Installation of four sparge wells and two monitoring wells - \$25,000
Operation, maintenance, and repairs, August 1998-December 1999 - \$25,000

Follow-up Activities

After extensive consultation with KV Associates on the design of their C-Sparger controller, the manufacturer changed the design to better isolate the mechanical and electrical components from each other. The controller is now housed in two separate enclosures. The new controller was installed at the site in January 2000. Minor adjustments have been performed on the system, and it is currently operating. Follow-up sampling for preliminary evaluation of the system's ability to remediate the plume will be conducted in the near future.

Point of Contact

M. Saqib Khan
Kansas Department of Health and Environment
(785) 296-8025

2. 25th and Main Dry Cleaning Site, Hutchinson, KS

Background

The 25th and Main site in Hutchinson encompasses three former facilities at two locations: the former Ideal Cleaners at 2500 N. Main, the former American Uniform at 2500 N. Main, and the former One Hour Martinizing at 2522 N. Main. Public water supply (PWS) wells in Hutchinson were tested for volatile organic compounds (VOCs) in 1982 as part of a statewide effort, and PWS wells 2, 8, 9, and 12 were found to contain perchloroethylene (PCE). PWS wells 9 and 12 were removed from service in 1989 due to levels of PCE in excess of the federal maximum contaminant level (MCL).

KDHE conducted a PA/SI on PWS well 12 in 1991 and PWS well 9 in 1992, which identified the dry-cleaning facilities at 25th and Main as one potential source of PCE contamination in groundwater. An expanded site investigation (ESI) of these wells was completed in 1993 to better define the site hydrogeology and the extent of the contaminant plume. The site was transferred to the State Dry-cleaning Trust fund in 1995.

In 1998, this site was chosen to implement a pilot test of KV Associates' C-Sparge ozone sparging system. The objective of the initial test phase was to determine the efficiency of removal with this technology, its radius of influence around the sparging well, and other parameters necessary to plan a full-scale installation. A four-inch ozone sparging well was drilled to a depth of 35 feet, and five two-inch monitoring wells were drilled at different distances from the well and screened at progressively deeper depths, to determine the radius of influence of the C-Sparge well and its effect on the downgradient concentrations of PCE. System operation started June 10, 1998.

After three days of system operation, fine bubbles of air/ozone were observed in all wells within 40 feet, indicating the well created a substantial radius of influence. Sampling of the sparging well and monitoring wells occurred daily for the first five days of operation, and approximately biweekly thereafter, concluding on August 27, 1998. Data on PCE concentration and dissolved oxygen from these samples indicated the system was remediating a portion of the plume. Estimates of the radius of influence, based on the site hydrogeology and sampling results, indicate that the well could treat an elliptical region 90 feet long (in the direction of flow), 80 feet wide, and 50 feet deep. Based on these results, a full-scale ozone sparging system was designed and installed.

Site Hydrogeology

Surface geology at the site consists of unconsolidated Pleistocene-age fluvial deposits overlying Permian-age bedrock. The uppermost bedrock member beneath the site is the Ninescah shale. Surface topography is very flat, dipping only a few feet per mile towards the Arkansas River, which is approximately 3 miles south of the site. The fluvial deposits consist of sand, silt, and clay near the surface and progressively coarser sands at depth. Lenticular silt or clay bodies are present in the deeper sands. The relatively impermeable surface silts and clays range in thickness from 7 to 12 feet, and are underlain by a downward-coarsening sequence of sands to a depth of 60 to 65 feet, where bedrock is encountered. These sands compose the regional High Plains aquifer, which is generally unconfined. Groundwater is encountered at 18 to 19 feet below ground surface (bgs), and groundwater flow direction is generally to the southeast. The hydraulic conductivity of this aquifer is estimated at 650 feet per day.

Impacted Receptors

Of the four PWS wells in which PCE was detected in 1982, three have been removed from service, and the fourth no longer shows PCE contamination. New PWS wells drilled to replace the old ones were drilled upgradient in an uncontaminated area; therefore, PWS customers should not be impacted. However, several domestic and numerous irrigation wells are present within one mile of the groundwater plume.

Remedial Objectives

The 25th and Main site was one of three dry cleaning sites in Hutchinson selected to evaluate different innovative technologies for remediating groundwater contaminated with PCE. The objective of this remediation is to reduce concentrations of PCE in the groundwater plume below the MCL using one of these innovative technologies.

Selection of Technology and Design Parameters

This site was selected for implementation of innovative remedial technology, in the form of in situ chemical oxidation, because the contamination plume was well defined, and the subsurface geology was simple, well characterized, and suitable for the process. The high hydraulic conductivity of the contaminated aquifer simplifies the delivery of oxidants to the affected zones. The site's hydrogeology is relatively simple and well-defined, so very little untreated contaminant should remain in impermeable zones, minimizing the potential for contaminant rebound after in situ treatment ceases.

This site was chosen to implement KV Associates' C-Sparge ozone sparging system, combined with soil vapor extraction (SVE). Each four-inch C-Sparge well combines dual ozone sparging points, dual well screens, an inflatable packer, and a recirculating pump. During operation, ozone is released first from the lower sparge point, then the upper. Following these two sparging intervals, the in-well pump is activated to circulate ozonated water surrounding the well through the two screened intervals, increasing the well's radius of influence. In addition, an SVE port at the top of the well extracts excess ozone and gaseous PCE degradation products from the upper well screen, which is installed across the water table.

Implementation of Technology

The four-inch C-Sparge wells, installed in a barrier-fence configuration across the plume, were drilled to a depth of 40 feet, with the lower sparge point at 35 feet below ground surface (bgs) and the upper at 25 feet. The wells were spaced at approximately 70 foot intervals to allow for sufficient overlap of their radii of influence. Six additional two-inch monitoring wells were drilled at different

locations on the downgradient side of the barrier fence at shallow and deep depths to monitor the effectiveness of the remediation. Four of these wells were installed in two pairs of shallow and deep wells, to depths of 23 and 35 feet, respectively. The remaining two wells at the ends of the barrier fence were installed to 28 feet bgs. Since each C-Sparger control panel can operate a maximum of four sparging wells, two control panels were installed, with one controlling the two middle wells, and the other controlling the four outer wells. The ozone-air mixture was supplied to the sparging wells (one well per controller at a time) at approximately 2 cubic feet per minute, at pressures of 5-10 psi, with an ozone concentration of 1.5-2.5 ppm. One SVE vacuum blower was installed and connected to all six C-Sparger wells in parallel for continuous vapor extraction. System operation started August 26, 1998.

Operational Performance

Prior to system startup, on August 17, 1998, baseline samples were taken from four of the six downgradient monitoring wells. PCE concentrations ranged from 5.82 micrograms per liter (ug/L) to 21.6 ug/L.

Operation of the KVA C-Sparger system at this site was plagued by the same types of equipment failures that occurred at the Garden City Laundry site, which used identical control equipment. Despite the non-continuous operation of the system, follow-up sampling events were conducted in October and December 1999. Dissolved oxygen levels in nearly all of the monitoring wells were found to have increased by 1 ppm or more (a 50-100% increase) by the December sampling event. PCE concentrations ranged from non-detect to 19 ug/L in the previously sampled monitoring wells. Concentrations in wells near the southwest end of the sparge well array showed decreases in both follow-up sampling events, while other wells showed no clear trend. One well showed a threefold decrease in concentration between the October and December events (15 ug/L to 5 ug/L) that may be unrelated to the operation of the sparging wells.

Problems

As with the installation of the KV Associates C-Sparger system in Garden City, Kansas, numerous mechanical and electrical problems with the control system resulted in intermittent failures of the sparging system. These failures resulted from blown fuses, leaks in fittings, split hoses, and problems with electrical and electronic components of the controllers. These reliability problems are similar to those encountered during the pilot test; therefore, the ability of this system to carry out a long-term remediation project is unproven.

In addition, a change in contractors midway through the operational phase of the project resulted in a year-long interruption in sample collection and analysis (October 1998 to October 1999). This lack of data complicates further any evaluation of the system's performance.

Costs

Installing and operating this barrier-wall sparging and SVE array cost \$133,500, not including the costs of the pilot study or previous work to determine the extent of the plume and the site hydrogeology. These costs can be broken down as follows:

C-Sparger controllers and downhole components - \$50,000
Installation of six monitoring wells and six sparge wells - \$30,500
SVE system components - \$25,000
SVE and C-Sparger controller installation - \$17,000
Operation, maintenance, and repairs - \$11,000

Follow-up Actions

While it is apparent that the system is reducing the concentration of PCE in the groundwater plume, it is not clear that the system is suited for long-term operation, or that it can fully remediate the plume by itself. Modifications to the C-Sparge control system (as installed at Garden City) may be made to this system, depending on the performance of the modified system in Garden City. Whether or not these modifications are made, further sparging and sampling will yield better data on the effectiveness of the system. At present, the system is shut down, and no further sampling is being conducted.

Point of Contact

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(785) 296-8025

3. Quick-N-Easy / Former Artistic Site, Wichita, KS

Background

The Quick-N-Easy Cleaners and former Artistic Cleaners are located at 1557 South Hydraulic Ave. and 1612 East Harry Street, respectively, in the central portion of Wichita, Kansas. In September 1995, the contaminant plume originating from this site was first identified, and Quick-N-Easy and Artistic were found to be responsible parties. Also in 1995, monitoring wells for an adjacent service station were found to contain perchloroethylene (PCE), trichloroethylene (TCE), and cis-1,2-dichloroethylene (DCE) above their maximum contaminant levels (MCLs). Further sampling by hydraulic push probes in 1996 better defined the leading edge of the contaminant plume and yielded information on the site's hydrogeology.

An Expanded Site Investigation (ESI) in 1998 using a soil gas survey and further hydraulic probe investigation of soil and groundwater at the site yielded a detailed map of contaminant concentrations at the site, which was used to plan treatment of the site with soil-vapor extraction (SVE) and in situ chemical oxidation techniques. The main release mechanism was apparently improper disposal of used PCE by dumping into the sanitary sewer system, and migration into the surrounding soils and groundwater through cracks in the system.

Site Hydrogeology

The stratigraphy of the site includes Quaternary deposits of unconsolidated clay, silt, sand, and gravel. These deposits make up four depositional cycles from the Arkansas River, which is located approximately one mile west of the site. Underlying the Quaternary materials is bedrock, the uppermost member of which is the Permian-age Wellington shale.

Groundwater is one of the primary sources of water in the county, and the stream-valley Quaternary deposits are tapped by wells in the region. As the site is within the floodplain of the Arkansas River, the Quaternary alluvial aquifer is present and readily accessible beneath the site. Large-capacity wells drilled into the alluvial aquifer yield high flow rates. Some water in the area is very hard and has high chloride content, so the City of Wichita no longer uses this water for its municipal water supply.

Hydrogeologic characterization of the site in the 1998 ESI revealed that groundwater flow at the site is generally northwest to southeast, towards Chisholm Creek. The water table was found to be approximately 15 feet below ground, and the depth to bedrock was 45 to 50 feet. Above and below the alluvial aquifer lie relatively impermeable layers of silts and clays 5 to 10 feet thick.

Contamination by PCE and TCE was found throughout the thickness of the alluvial aquifer downgradient of the site at concentrations exceeding MCLs.

Impacted Receptors

Although the City of Wichita does not use water from the affected aquifer for municipal water supply, a few domestic wells were identified within one mile of the site. In addition, several irrigation wells tapping the affected aquifer are present in Linwood Park and surrounding areas, posing inhalation and contact risks to the public.

Remedial Objectives

The objective of remedial actions at this site is to reduce groundwater concentrations of PCE and TCE to levels at or below their MCLs. Further, PCE and TCE present in the vadose zone must be removed to prevent recontamination of the aquifer.

Selection of Technology and Design Parameters

This site was selected for implementation of innovative remedial technology, in the form of in situ chemical oxidation, because the contamination plume was relatively small and well defined, and the subsurface geology was simple, well characterized, and suitable for the process. Injection of a liquid solution of sodium permanganate (NaMnO_4) was selected as the remedial technology, based on its relatively low cost (compared to traditional pump-and-treat systems), ease of implementation, and demonstrated ability to oxidize PCE and TCE in groundwater. However, this technology was not deemed effective at oxidizing these contaminants in the unsaturated zone, due to low permeability and inability to evenly distribute the oxidant. Therefore, to remove PCE and TCE in the vadose zone, a system of SVE wells was employed.

To remediate contaminated groundwater, the sodium permanganate was injected through an array of hydraulic push probes at the source area. A 4% solution (25 mg/L permanganate) was used based on a laboratory treatability study; however, this study did not take into account the chemical oxygen demand of the aquifer sediments.

To deal with vadose-zone contamination, an array of four SVE wells was installed around the foundations of the buildings at the site, and piping was run from these wells to a master exhaust blower. These wells were screened in the shallow clayey soils from approximately 8 to 13 feet below ground surface (bgs), which places them just above the static groundwater level. Emissions permitting from the SVE system were not required as the mass of contaminants removed was anticipated to be less than 50 pounds per day.

Implementation of Technology

Prior to implementing the in situ chemical oxidation process, an array of 11 additional monitoring wells was installed around and downgradient of the source areas to be treated. Wells were installed in pairs, with one screened in the shallow portion of the aquifer and one in the deep portion of the aquifer. These wells, along with existing monitoring wells adjacent to the site, were sampled prior to and at intervals after treatment to evaluate the effectiveness of the remedy. Samples were tested for PCE and TCE concentration, oxidation-reduction potential, pH, dissolved oxygen concentration, conductivity, and temperature, and were examined for any free-phase oxidant solution present.

The sodium permanganate solution was injected into an array of 33 hydraulic push probes on November 1 to November 5, 1999. Injection depths were staggered throughout the source areas to ensure even dispersion throughout the affected aquifer. A total of 757 gallons of 4% solution were used, for an average of 23 gallons per well. However, due to local variations in hydraulic

conductivity, the actual volumes per well varied significantly. After waiting 6 days for the oxidant to degrade the PCE and TCE, confirmation samples were taken on November 11 to evaluate the reduction of contamination. Another round of confirmation samples was taken November 18. Estimates of the radii of influence of each injection point were calculated based on the volume of oxidant injected, the hydrogeology at each injection point, and field screening for permanganate by titration.

Operational Performance

Analytical data from the monitoring wells taken before and after the injection of oxidant does not show a clear, consistent pattern of contaminant decrease or increase. Two wells showed marked declines of PCE and TCE concentration immediately after dosing, followed by significant rebound. Two wells showed increases in contaminant concentration after dosing. Several wells showed opposite concentration trends of PCE and TCE, with PCE concentration decreasing and TCE concentration increasing (in all but one well). One well showed concentrations increasing and then decreasing.

TCE concentrations in the deep wells overall appeared to increase, while PCE concentrations decreased. Chloride concentrations in the deep wells increased, while those at shallow depth generally decreased or were relatively steady (in all but one well, which showed increases at both depths).

Overall, it is apparent that PCE concentrations were reduced by the introduction of the oxidant. However, several confounding factors can be identified. First, the radii of influence of the injection points do not overlap in general, so untreated contaminants are present adjacent to treated areas, and can contribute to rebound. Second, silt lenses and/or gravels were found in many of the monitoring wells, so it is likely that preferential migration of the oxidant solution due to variable hydraulic conductivity occurred. This may have allowed the oxidant to bypass some volumes of the aquifer. Third, injection of the oxidant solution may have forced contaminants out of low-permeability zones, increasing the average concentration in the aquifer.

Problems

Since the calculated radii of influence of the injection points did not always overlap, there was incomplete treatment of the source area. The fact that contaminant concentrations increased in several monitoring wells may indicate that contaminants in low-permeability zones, which may not have been represented in pre-treatment estimates, were released as oxidant injection disturbed the aquifer. In addition, the chemical demand of the aquifer was not taken into account in calculating the amount of oxidant required. Therefore, the pre-treatment estimates of the amount of contaminant present were too low, and insufficient oxidant solution was supplied to the aquifer. Existing hydrogeologic data on the subsurface in the treated area may be insufficient to generate better estimates of the radii of influence of injection points, preferential migration pathways, and the mass of contaminant present, so additional study may be needed.

Costs

Costs of implementing this in situ oxidation treatment (not including previous site characterization studies) total \$49,500 and can be broken down as follows:

Installation of 11 monitoring wells - \$4,500
Injection event materials and labor - \$10,000
Purchase and Installation of SVE system - \$21,000
Pre-and post-injection sample collection and analysis - \$14,000

Follow-up Actions

A second round of permanganate injections was performed in early August of 2000. A permit for operating Class V injection wells was obtained from KDHE's Bureau of Water (see Appendix ??). For this event, the concentration of permanganate was increased to 15%, and a total of 1,472 gallons of oxidant solution was injected through an array of 64 probes in an area of 270 by 120 feet directly adjacent to the building. The injection of oxidant in each probe was targeted at specific depths, with 3-4 gallons of oxidant injected at five-foot intervals between 15 and 40 feet below ground surface. Post-treatment sampling was conducted at 5, 10, 17, 30, and 60 days after injection, with a sampling event 90 days after injection pending.

The results from the early post-treatment sampling events do not present a clear picture of the effects of the injection event. One monitoring well showed a 99% decrease in contaminant concentrations, while the remaining wells showed increases in contaminant concentrations of up to a factor of ten. Analysis of titration data for permanganate in the monitoring wells and injection points indicates that the radii of influence of the injection points probably did not overlap in most cases. A full analysis of the performance of the second injection event will be conducted after all post-treatment monitoring data is available.

Point of Contact

Robert Jurgens
Kansas Department of Health and Environment
(785) 291-3250

4. Former Isleta Chevron Filling Station, Albuquerque, NM

Background

This site was a gasoline filling station that had closed. In 1994, the New Mexico Environmental Department (NMED) had the building demolished and removed five underground storage tanks (USTs) from the property. These tanks, as well as the dispenser islands, showed evidence of long-term leakage that had created substantial volumes of contaminated soil. Monitoring wells on the site showed concentrations of benzene in excess of 10,000 parts per billion (ppb). Approximately 1500 tons of contaminated soil were removed, as well as 5000-6000 gallons of a mixture of water and free product. The excavations were backfilled, and an air sparging and soil vapor extraction system was installed over the source area. However, the system was never operated due to problems with utility hookups.

Approximately four months after the removal of the source material, the monitoring wells were resampled. The contaminant concentrations had decreased markedly with the removal of the source, to levels of 1000-3000 ppb. This reduction was attributed to natural attenuation processes. It was decided not to activate the sparging / extraction system, and the vacant site sat in this condition for the next 5 years. Periodic sampling showed a relatively constant concentration of the contaminants in groundwater.

In 1999, this site was selected for a pilot test of in situ chemical oxidation using a variant of Fenton's reagent (hydrogen peroxide and iron catalyst). This pilot test was intended in part to gain state acceptance for this process.

Site Hydrogeology

The uppermost two feet of the soil column at the site is primarily fill materials, including some broken asphalt and concrete. Below this is a thick layer of coarse-to-medium sand that is fairly homogeneous. The water table is approximately 8 feet below ground in this sand layer. Annual fluctuations in the water table are on the order of six inches above and below the average depth. Through this fluctuation and other factors, a smear zone of free product has developed above and below the water table a distance of two feet. Groundwater flow direction is consistently to the south.

Impacted Receptors

None identified at present. However, the property is slated for redevelopment, raising the possibility of exposures in the future.

Remedial Objectives

The objective of this pilot test was to clean up the remaining plume of groundwater contaminated with light nonaqueous phase liquid (LNAPL). Contaminants encountered include benzene, toluene, ethylbenzene, and xylene (BTEX) and naphthalene. The plume is about 100 by 150 feet in size.

Selection of Technology and Design Parameters

This site was selected for implementation of in situ chemical oxidation in part because of its relatively small, well-defined plume, and the suitability of the site hydrogeology to injection of oxidants (permeable sands with relatively high hydraulic conductivity). In addition, the presence of monitoring wells on-site for evaluation of the process, and the extensive data on historical contaminant concentrations, allowed detailed evaluation of the effectiveness of the oxidation process. Finally, the site is vacant, so gaining access to the necessary injection points was not an issue.

The technology implemented at this site was BioManagement Services' BiOx process, which uses a modified Fenton's reagent chemistry. A solution of 5% hydrogen peroxide, an iron catalyst, and other proprietary ingredients is mixed on-site and injected into the ground through a direct-push probe at the desired depth or depth range. The mixture of chemicals can be tailored for specific site conditions.

Implementation of Technology

Two days prior to implementation of the in situ treatment, NMED performed a complete sampling of all monitoring wells on the site for volatile organic compounds (VOCs), total cations, nitrate, phosphate, and total dissolved solids. Dissolved oxygen was not measured, as the necessary field equipment was not available.

As this was a technology demonstration for state regulators, the contractor selected all parameters for the test to achieve complete remediation of the plume, based on his experience at previous sites. Within a 25-foot circle around MW-8, the monitoring well with the highest concentrations of contaminants (assumed to be the center of the plume), 39 injections of the oxidant solution were placed in a square grid array. At each injection point, the injector probe was pushed to a depth of four feet while injecting water through the probe to aid in penetration of the soil. At a depth of four feet, the oxidant solution began to be injected, and the probe was advanced while injecting to a depth of twelve feet. This provided oxidant to the soil zone four feet above and below the water table.

The spacing of the grid of injection points, and the amount of oxidant injected per hole, was adjusted in the field based on observation of other injection points. Bubbling or "geysering" of fluid from previous, adjacent holes was used as an indication that overlap of the radii of influence of the injections had been achieved. The final grid of injections was spaced 3 feet apart. A total of

approximately 1000 gallons of oxidant solution was injected for an average of 25.5 gallons per injection point. The complete injection program took place in one day.

Operational Performance

Forty-eight days after injection, all of the monitoring wells at the site were purged and resampled, and the same suite of analytes as performed prior to the injection was run by the same analytical laboratory. The results for MW-8 indicated a 35% decrease in benzene concentrations, from 2300 to 1500 ppb. However, concentrations of toluene, ethylbenzene, xylenes, and naphthalene increased by amounts ranging from 69% to 560%. A similar pattern was found at the next most contaminated well, with benzene and naphthalene concentrations decreasing somewhat and the remaining contaminants' concentrations increasing. At more distant, less contaminated wells, effects were mixed, but the overall changes in concentration were relatively small.

Problems

As indicated by the comparison of analytical results from before and after treatment, injection of the oxidant solution did not significantly reduce the overall contaminant concentrations in the groundwater. NMED believes that, due to the injection of oxidant above the water table, some degree of soil washing or flushing occurred which removed adsorbed contaminants or free product from the vadose zone and delivered it to the groundwater. The additional mass of contaminants delivered to the groundwater through this process may have counteracted any reductions in groundwater concentrations due to oxidation. In addition, the rapid introduction of the oxidant solution into the sandy aquifer may have formed preferential pathways that allowed the solution to bypass some volumes of the soil. Finally, the rapid reaction of the oxidant solution with its catalyst, the contaminants, and naturally occurring organic compounds in the soil may have prevented "active" oxidants from reaching all contaminated areas of the aquifer.

Although NMED purged three to five well volumes from each monitoring well prior to sampling, the contractor is concerned that the samples taken from the wells were not truly representative of the overall groundwater concentrations.

Costs

As this pilot project was performed by the contractor in part to gain state acceptance for the process, the true costs were not calculated. However, the reagents are fairly inexpensive, and labor costs are low (one person completed the injection program in one day). Monitoring well installation and analytical costs for follow-up sampling are expected to account for the majority of project costs.

Follow-up Actions

NMED is currently in negotiations with the contractor for additional treatment of the area using the BiOx process. If the effects of soil washing or flushing by the oxidant solution are largely responsible for the observed contaminant concentrations in the groundwater, as is suspected, then subsequent treatments with this technology should produce more dramatic reductions in groundwater concentrations as the mass of contaminants in the vadose zone is reduced. Future groundwater sampling methodology may be modified to deal with concerns about the representativeness of the samples taken.

Point of Contact

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5. Former Manufactured Gas Plant, Long Beach, CA

A full-scale, in situ ozonation project to remediate polycyclic aromatic hydrocarbons (PAHs) in soil and groundwater began operating in early 1999 at a former manufactured gas plant (MGP) site in Long Beach, California. The site is under an elevated roadway interchange, requiring in situ remediation. Residues generated from the original gas manufacturing operations consist of tar, oils, and lampblack containing PAHs. Initial concentrations of the primary constituents were as high as 2,484 mg/kg for total PAHs, 100 mg/kg for benzo(a)pyrene (BaP), and 27,800 mg/kg for total petroleum hydrocarbons (TPH) in soil. Baseline dissolved contaminant concentrations ranged as high as 912,000 ug/l for TPH, 4,820 ug/l for benzene, 20,000 ug/l for naphthalene, and 340 ug/l for BaP.

A total of 33 vertical sparge wells, constructed of Teflon, Viton, and 316 stainless steel and screened at a depth of 25 feet, were installed throughout the contamination plume. In addition, a single 360-foot horizontal well with a 135-foot screened section in the middle was installed through the center of the plume at about 6 feet below the water table. Ozone, generated on site, was pulsed into the wells in both the saturated and vadose zones to promote chemical oxidation and enhanced biodegradation.

After the first quarter of ozone treatment, groundwater sampling revealed that initial dissolved contaminant concentrations were reduced to below detectable levels. In particular, BaP was reduced to below the MCL level of 0.2 $\mu\text{g/l}$. Concentrations remained below detectable levels through three successive quarterly sampling events. Separate phase mixtures of heavy oils and PAHs accumulated in wells after three months of ozone treatment, indicating significant desorption from soil of MGP residues. In addition, the character of the oils changed during the remediation, showing enrichment of the light fractions along with depletion of the heavy fractions. After two quarters of soil sampling showed no consistent trends, soil concentrations began to sharply decrease during the third and fourth quarter events. Decreasing trends in the variability of the targeted contaminant concentrations were noted. These trends were observed in all boring locations. Concentrations in over half of the samples were reduced to below the effective treatment target of 1 mg/kg BaP equivalents for soil.

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6. Former Wood Treatment Facility, Sonoma County, CA

An intensively monitored field-scale application of in situ ozonation was performed at a former wood treatment and cooling tower manufacturing facility, located in Sonoma County, California (Clayton, 2000b). Primary contaminants are pentachlorophenol (PCP) and creosote (i.e., polycyclic aromatic hydrocarbons [PAHs]). The site subsurface consists of stratified silty sands and clays, and the depth to water varies from 4 to 15 feet seasonally. Field operation and monitoring of the in situ ozonation system was conducted from December 1997 through December 1998.

Maximum pretreatment soil contamination was 220 mg/kg PCP and 5,680 mg/kg total PAHs. High levels of dissolved contamination and non aqueous phase liquid (NAPL) existed in the vadose zone prior to treatment. For example, one vadose zone lysimeter produced liquid NAPL and water which contained >20,000 ug/l total dissolved PCP and PAHs.

Approximately 8,000 lbs. of ozone were injected into the subsurface over a 12-month period. In general, effective ozone transport and ozone gas mass transfer to the aqueous phase were observed. Ozone concentrations ranging from less than 1 ppm to several hundred ppm were measured in soil gas over the entire area of the monitoring network. These concentrations were several orders of magnitude below the injection concentration of 5 percent (50,000 ppm), which reflects rapid subsurface ozone reaction and degradation. Dissolved ozone concentrations up to 1.4 ppm were measured in soil moisture samples collected from pressure-vacuum lysimeters.

Soil samples collected at paired locations prior to in situ ozonation, and during February, June, and October 1998 showed an average 93 percent reduction in PCP and PAHs. The maximum pretreatment soil contamination was reduced greater than 98 percent, from an initial value of 220 mg/kg PCP and 5,680 mg/kg total PAHs, to below detection limits.

Significant contaminant mass reduction was reflected not only in soils data, but also in substantial reductions in aqueous-phase concentrations of PCP and PAHs. The lysimeter data showed several orders of magnitude reduction in dissolved PCP and PAHs at the first sampling event, conducted after approximately one month of ozone injection in the 5-spot area. In addition, an individual lysimeter produced liquid NAPL at the beginning of the project but not after one month of treatment.

Ozone consumption was calculated at approximately 7 pounds of ozone per pound of PCP and PAHs destroyed. This number is highly conservative, because the system was optimized for maximum ozone loading, and not for efficient ozone usage. Combining in situ ozonation and bioremediation can significantly decrease ozone consumption.

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7. San Francisco Bay Sites managed by the California Regional Water Quality Control Board

Five pilot- or full-scale applications of in situ chemical oxidation (using potassium permanganate or hydrogen peroxide) were performed in 1999 at industrial sites in the San Francisco Bay area. The contaminants of concern included perchloroethylene, trichloroethylene, vinyl chloride, chloroethane and benzene. The soils at these sites are typical of the South Bay area, and consist of a mix of silts, sands, and clay which is fairly tightly packed and therefore not particularly permeable. Direct-push injectors were used to deliver the oxidants to the subsurface. Pre- and post-injection monitoring was performed to evaluate the performance of the oxidants.

Based on the results of the post-injection monitoring, which indicated either a significant rebound or negligible reduction of contaminant concentrations, the Regional Water Quality Control Board concluded ISCO was “ineffective” at cleaning up the groundwater at four of these sites, and “somewhat effective” at the fifth site. However, several aspects of these projects contributed to the poor performance of ISCO. First and foremost, the low permeability of the soils at the sites did not allow adequate dispersion of the oxidants or sufficient contact with the contaminants. It is likely that preferential flow pathways were the dominant method of transport of the oxidant, thus bypassing large volumes of the subsurface.

The methods of oxidant delivery were not optimized for the sites. At one site, an injection lens was used which resulted in uneven distribution of the oxidants, while at another site, the radius of influence of each injection point was not known or estimated, leaving some volumes of the aquifer between the injections untreated. "Widely scattered" contamination was present at a third site which could not be fully addressed by the system of injection locations.

The dedication of the responsible parties at these sites to the successful implementation of ISCO was also suspect in several cases. The impression of some of the State's project managers was that the responsible parties were mainly interested in leaving the problem to natural attenuation, and were only implementing ISCO because they were required to attempt some sort of remediation. As a result, the work done at these sites was likely not designed for maximum efficiency and was based on a poor understanding of the site conditions.

In April 2000, the San Francisco Bay Regional Water Quality Control Board completed a survey of 47 innovative groundwater remediation projects in its region. A total of 10 sites were found to have used chemical oxidation (including the 5 previously mentioned sites), and the survey results from these 10 sites are listed below in Table B-7-1. The contaminants of concern included perchloroethene, trichloroethene, vinyl chloride, chloroethane, MTBE and benzene. The soils at these sites are alluvial deposits consisting of discontinuous lenses of silts, sands, gravels and clay. Shallow groundwater conditions occur at all of the sites with the contamination typically found in aquifers at a depth of between 10 and 50 feet below the ground surface. Groundwater direct-push injectors were used to deliver the oxidants to the subsurface in most of the sites. Pre- and post-injection monitoring was performed to evaluate the performance.

Based on this limited set of projects surveyed, Regional Board staff have drawn several preliminary conclusions on the effectiveness of ISCO in the San Francisco Bay Area. In general, the ISCO technology is more effective in higher permeability soils because the oxidant can more easily reach sorbed contaminants. The level of hydrogeologic investigation may need to be increased to implement ISCO compared to traditional pump-and-treat methods.

Projects where ISCO was deemed ineffective typically showed a significant rebound in pollutant concentrations within several months after the injection period. This is probably due to contaminants that are sorbed in low permeability aquifer material and not easily accessible to injected oxidants. It is believed that the conceptual model of some of these sites, which would have thoroughly characterized the subsurface in terms of its stratigraphy, porosity and permeability, soil and water chemistry, and the temporal and spatial variation in these parameters, was not well developed.

Lessons learned from these ISCO implementations are threefold. First, a thorough understanding of the site is essential to a successful implementation of any remedial technology, especially ISCO. The migration of both the contaminants and the oxidants is highly dependent on the hydrogeology of the subsurface, so this information must be available prior to planning for a cleanup. Second, ISCO is not a panacea, and there are sites where it is not a viable remedial technology. The information gathered during site characterization should indicate whether or not ISCO could be reasonably expected to succeed. Third, as an innovative technology, ISCO is not well understood by many responsible parties, contractors, and regulators, and therefore further work is needed to optimize ISCO performance for site-specific conditions. In order to maximize the effectiveness and acceptance of the technology, all stakeholders must understand the process and its limitations, and must be given the opportunity for close involvement throughout the project.

TABLE B-7-1

Chemical Oxidation Projects
 Survey of Innovative Groundwater Remediation Projects
 San Francisco Bay Regional Water Quality Control Board
 April 2000

Site Name (City)	Project Stage	Effectiveness Rating*	Comments
Synertek Bldg. 3 (Santa Clara)	Full Scale	1	Using KMnO4 for vinyl chloride
Siltec aka MSA (Menlo Park)	Pilot	1	KMnO4 injection for DNAPL
Siemens 639 N. Pastoria (Sunnyvale)	Pilot	3	Inject KMnO4 for TCE, plan full scale
McKesson (Union City)	Pilot	2	Inject H2O2 for TCE
H.B. Fuller (Newark)	Full Scale	1	Inject ORC for CVOCs and benzene
TRW Microwave (Sunnyvale)	Planning	0	Inject H2O2 for TCE
National Semiconductor (Santa Clara)	Planning	0	Fenton's reagent and ozone sparging
HP 1501 PMR (Palo Alto)	Pilot	1	Inject KMnO4 at 2 locations
American Microsystems (Santa Clara)	Pilot	2	Inject KMnO4 for TCE in source area
Chevron Berryessa (San Jose)	Pilot	0	Inject "Iso-Gen" for benzene/MTBE

* 3 = very effective, 2 = somewhat effective, 1 = ineffective, and 0 = too soon to tell

Point of Contact

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8. Service Station Site in Madison, WI

Background

The service station site located in Madison, Wisconsin, is an operating gasoline service station. The existing underground storage tank (UST) system consists of one 4,000-gallon gasoline tank, one 4,000-gallon diesel tank, and two dispenser islands. In addition, one 550-gallon waste oil tank and one 550-gallon fuel oil tank exists on the property. On August 14, 1995, one 8,000-gallon gasoline tank was removed from the site. The remaining four USTs are proposed to be removed prior to remedial activities. All of the USTs are registered with the Wisconsin Department of Commerce (DCOM).

A petroleum release was detected on May 11, 1994, from a soil sample collected from beneath the east unleaded dispenser island and analyzed for Gasoline Range Organics (GRO). The test results indicated a GRO concentration of 4,200 mg/kg, which is above the soil cleanup standards for GRO of 100 mg/kg. The WDNR was immediately notified of the release.

Site Hydrogeology

Soil types encountered during the investigation consisted of silty clay native to fill material with sand and gravel and organic matter extending to depths ranging from 6 to 11 feet below ground surface (bgs). These fill soils are underlain by brown to grey brown to red-brown silty sand to sand and gravel. This sandy gravelly soil extends to depths ranging from 15 to 17 feet bgs. Beneath the dense sandy/gravelly soil is friable light brown to white to pink sandstone bedrock to the maximum explored depth of 26 feet bgs. Groundwater is present at 16 to 20 feet below ground surface.

Depth to groundwater in the site monitoring wells ranges from 16 to 20 feet below ground surface with a hydraulic conductivity of 10^{-5} . As evidenced during water sample collection, recharge is moderate, which is typical of saturated silty sand. The groundwater flow direction is predominantly toward the north/northwest. The flow direction is consistent with local topography.

Design/Implementation

Following the completion of the subsurface investigation, a remedial alternatives comparison was prepared and submitted to the DCOM for review and approval. The selected and approved remedial alternative was a limited hot-spot contaminated soil excavation with the injection of Hydrogen Peroxide/Ferrous Sulfate (HP/FS) injection to remediate contaminated groundwater within shallow bedrock. A wordplay was prepared and submitted to the WDNR for approval. Approval for the remedial approach was granted by the WDNR in March, 1998.

Approximately 2,100 tons of contaminated soil were excavated and transported to the Madison Prairie Bio-Site on July 6 and 7, 1998. The chemical oxidation vendor performed a HP/FS injection pilot-test during the week of July 13, 1998. Based on the results of the pilot test, including contaminant destruction, the absence of vapor migration based on screening of vent wells and subsurface utilities and neighboring basements; as well as other factors, full-scale treatment was determined to be feasible utilizing this technology. In late July/early August, 1998, 45 injector wells (15 foot to 17 foot radius), and 14 vent wells were installed at the site covering an area of 220 foot by 200 foot. Full-scale chemical oxidation treatment of the petroleum-contaminated groundwater, saturated soils (including capillary fringe), and bedrock was performed from late August to September 11, 1998. Approximately 15,000-gallons of Fenton's

reagent were injected over a 15-day period. The average concentration of H₂O₂ injected was 25 percent.

Post-remediation groundwater monitoring has been performed quarterly for 1 year. Results indicate that groundwater remediation has been successful.

Operation and Performance

Prior to site remediation, three complete rounds of groundwater sampling were performed. Pre-remediation samples were collected in February and October, 1996; February 1997; and August 1997. Post-remediation quarterly groundwater sampling was performed in September 1998, December 1998, April 1999, and July 1999. Eleven monitoring wells were present on-site and off-site were utilized for groundwater monitoring. Analytical parameters included in the sampling program were Petroleum Volatile Organic Compounds (PVOCs).

Of the 11 monitoring wells installed during subsurface investigation at the site, five (MW-1 through MW-5) of the wells are located on-site. The remaining wells were installed to define the extent of potential off-site impacts to groundwater and to monitor groundwater quality during the HP/FS remediation performed on-site.

MW-1

Total PVOC concentrations in MW-1 decreased from 23,770 milligrams per liter (mg/L) before treatment to 24 mg/L in July 1999.

MW-2

Total PVOC concentrations in MW-2 decreased from 1,979 mg/L before treatment to 140 mg/L in July 1999.

MW-3

Total PVOC concentrations in MW-3 decreased from 283 mg/L before treatment to 2.6 mg/L in July 1999.

MW-4

Total PVOC concentrations in MW-4 decreased from 23,189 mg/L before treatment to 114 mg/L in July 1999.

MW-5

Total PVOC concentrations in MW-5 decreased from 1,179 mg/L before treatment to 346 mg/L in July 1999.

The PVOC concentrations in all off-site monitoring wells have also decreased to a lesser degree following site remediation. The site obtained closure 1 year after treatment.

Costs

The approximately costs of the treatment portion of the project was \$270,000. This included the costs for drilling, chemical, labor, and a pilot test.

Contact

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APPENDIX C

Acronyms

APPENDIX C – Acronyms

AOC	Area of Contamination
ARAR	Applicable or Relevant and Appropriate Requirement
ASTM	American Society of Testing and Materials
BNA	Base/Neutral/Acid
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
CAMU	Corrective Action Management Unit
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CEM	Continuous Emissions Monitor
CFR	Code of Federal Regulations
CLP	Contract Laboratory Program
CO	Carbon Monoxide
COC	Contaminant of Concern
COD	Chemical Oxygen Demand
DCA	Dichloroethane
DCE	Dichloroethene
DGW	Discharge to Groundwater
DNAPL	Dense Non-Aqueous Phase Liquid
DO	Dissolved Oxygen
DOD	Department of Defense
DOE	Department of Energy
DTSC	California Department of toxic substances control
ECOS	Environmental Council of the States
EISB	Enhanced <i>in-situ</i> bioremediation
EPA	Environmental Protection Agency
EPCRA	Emergency Planning & Community Right to Know Act
ERIS	Environmental Research Institute of the States
GC/ECD	Gas Chromatograph/Electron Capture Detector
GC/MS	Gas Chromatograph/Mass Spectrometer
GRO	Gasoline Range Organics
ITRC	Interstate Technology and Regulatory Cooperation (Work Group)
ISCO	In Situ Chemical Oxidation
ITT	Innovative Treatment Technology
KDHE	Kansas Department of Health and Environment
LEL	Lower Explosive Limit
LNAPL	Light nonaqueous phase liquid
MCL	Maximum Contaminant Level
MGP	Manufactured Gas Plant
MTBE	Methyl-Tert-Butyl-Ether
NAPL	Non-Aqueous Phase Liquid
NJPDES	New Jersey Pollution Discharge Elimination System
NMED	New Mexico Environmental Department
NOM	Natural Organic Matter
NPL	National Priority List
NRC	National Response Center
ORP	Oxygen Reduction Potential
OSHA	Occupational Safety and Health Administration
OST	Office of Science and Technology (DOE)
PAH	Polycyclic Aromatic Hydrocarbon
PBR	Permit By Rule
PCB	Polychlorinated Biphenyl

PCE	Perchloroethene or Tetrachloroethene
PCP	Pentachlorophenol
PIC	Products of Incomplete Combustion
POC	Point of Contact
POP	Proof of Process
POTW	Publicly Owned Treatment Works
PVOC	Petroleum Volatile Organic Compounds
PWS	Public water supply
QA/QC	Quality Assurance/Quality Control
RCRA	Resource Conservation and Recovery Act
RI	Remedial Investigation
RP	Responsible Party
RTDF	Remediation Technology Development Forum
SDWA	Safe Drinking Water Act
SSEB	Southern States Energy Board
SVE	Soil Vapor Extraction
TCE	Trichloroethene
TPH	Total Petroleum Hydrocarbons
TRPH	Total Recoverable Petroleum Hydrocarbons
TSCA	Toxic Substances Control Act
TSWG	Tribal and Stakeholder Working Group
TSD	Treatment, Storage and Disposal
UIC	Underground Injection Control
USDW	Underground Source of Drinking Water
UST	Underground Storage Tank
VC	Vinyl Chloride
VO	Volatile Organic
VOC	Volatile Organic Compound
WGA	Western Governor's Association

APPENDIX D

Cost Estimates

APPENDIX D – Cost Estimates

Although many of the costs for ISCO are site-specific, generic cost equations may be used to at least calculate the chemical costs associated with ISCO treatment based on site-specific soil and groundwater carbonate and COD values. These equations can provide a first step in evaluating if the cost of ISCO remediation is cost-prohibitive based merely on the cost of the treatment chemicals. However, in using these equations, one must keep in mind that the chemical costs typically constitute between 15 to 30 percent of the total remediation life-cycle costs. The equations for estimating the ISCO treatment chemical costs are summarized below, and are based on the following assumptions:

One mg/kg COD calculated by chromic acid titration is equivalent to a 2.5 mg/kg KMnO_4 demand based on carbon to carbon dioxide stoichiometry;

One mg/kg COD calculated by chromic acid titration is equivalent to 2.1 mg/kg H_2O_2 demand based on carbon to carbon dioxide stoichiometry;

The specific gravity of 11% hydrogen peroxide is 1.1;

Carbonate/bicarbonate concentration refers to total calcium carbonate alkalinity as determined by acid titration to a pH value of 4.0;

1.07 grams of sulfuric acid neutralizes one gram of calcium carbonate;

The soil density is 1.85 g/cc (1,400 kg/yd³);

The ferrous iron demand is 0.5 percent of the total peroxide demand;

Ferrous sulfate heptahydrate is comprised of 20 percent ferrous iron;

The cost of hydrogen peroxide is \$0.25/lb (1999 vendor quote);

The cost of potassium permanganate is \$1.60/lb (1999 vendor quote);

The cost of sulfuric acid is \$0.10/lb (1999 vendor quote); and

The cost of ferrous sulfate heptahydrate is \$1.00/lb (1999 vendor quote).

Chemical cost per cubic yard of subsurface treatment zone using Fenton's oxidation:

$$\begin{aligned} \text{H}_2\text{O}_2 (\$/\text{yd}^3) &= [(\text{COD}_{\text{gw}}/1.85) \times (.25) + (\text{COD}_{\text{soil}}) \times (.75)] \times (2.1 \text{ mg H}_2\text{O}_2/\text{g soil}) \times (1,400 \text{ kg/yd}^3) \times (1 \text{ lb H}_2\text{O}_2/453,600 \text{ mg}) \times (\$/0.25/\text{lb}) \\ &= [(\text{COD}_{\text{gw}}/1.85) \times (.25) + (\text{COD}_{\text{soil}}) \times (.75)] / 617 \end{aligned}$$

$$\begin{aligned} \text{H}_2\text{SO}_4 (\$/\text{yd}^3) &= [(\text{Alkalinity}_{\text{gw}}/1.85) \times (.25) + (\text{Carbonate}_{\text{soil}}) \times (.75)] \times (1.07) \times (1,400 \text{ kg/yd}^3) \times (1 \text{ lb H}_2\text{SO}_4/453,600 \text{ mg}) \times (\$/0.10/\text{lb}) \\ &= [(\text{Alkalinity}_{\text{gw}}/1.85) \times (.25) + (\text{Carbonate}_{\text{soil}}) \times (.75)] / 3028 \end{aligned}$$

$$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} (\$/\text{yd}^3) = [(\text{H}_2\text{O}_2 \text{ costs}) \times (0.5) \times (\$/1.00/\$0.25) / 0.2]$$

Chemical cost per cubic yard of subsurface treatment zone using permanganate oxidation:

$$\begin{aligned} \text{KMnO}_4 (\$/\text{yd}^3) &= [(\text{COD}_{\text{gw}}/1.85) \times (.25) + (\text{COD}_{\text{soil}}) \times (.75)] \times (2.5 \text{ mg KMnO}_4/\text{g soil}) \times (1,400 \text{ kg/yd}^3) \times (1 \text{ lb KMnO}_4/453,600 \text{ mg}) \times (\$/1.60/\text{lb}) \\ &= [(\text{COD}_{\text{gw}}/1.85) \times (.25) + (\text{COD}_{\text{soil}}) \times (.75)] / 81 \end{aligned}$$

Ozone is generated on-site from ambient air using an electrical discharge or similar means. Therefore, the costs associated with its use include the purchase of the generating equipment and the electricity required to operate it. Information on the cost of the generating equipment is included in the Case Studies section of this document.

APPENDIX E

**ITRC Contacts, ITRC Fact Sheet, ITRC Product List, and
Document Evaluation Survey**

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