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How To Evaluate Alternative Cleanup Technologies For Underground Storage Tank Sites

A Guide For Corrective Action Plan Reviewers

Chapter XIII

Chemical Oxidation

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Chapter XIII
Chemical Oxidation

Overview

Petroleum contaminant decomposition and in-situ destruction may be accomplished using chemical oxidation technologies. In contrast to other remedial technologies, contaminant reduction can be seen in short time frames (e.g., weeks or months). As discussed in this chapter, a variety of chemical oxidants and application techniques can be used to bring oxidizing materials into contact with subsurface contaminants to remediate the contamination. With sufficient contact time with the organic contaminants, chemical oxidants may be capable of converting the petroleum hydrocarbon mass to carbon dioxide and water and ultimately irreversibly reduce concentrations of petroleum hydrocarbons in soil and groundwater. While many of the chemical oxidants have been used in wastewater treatment for decades, only recently have they been used to treat hydrocarbon-contaminated groundwater and soil *in-situ*.

Chemical oxidation technologies are predominantly used to address contaminants in the source area saturated zone and capillary fringe. Cost concerns can preclude the use of chemical oxidation technologies to address large and dilute petroleum contaminant plumes. More frequently, chemical oxidation technologies are employed to treat smaller source areas where the petroleum mass is more concentrated. However, where excessive petroleum contaminant mass exists in the source area and where there is a significant thickness of mobile non-aqueous phase liquids (NAPLs), other remedial technologies (e.g., free product recovery) may need to precede chemical oxidation for the remediation to be safe and cost-effective.

Concurrent treatment of source area saturated and unsaturated zones usually requires the integration of chemical oxidation with other remedial technologies that target unsaturated zone contamination (e.g., soil vapor extraction). Frequently, soil vapor extraction, which is used to treat the unsaturated zone, is included as a component of chemical oxidation remedial solutions even if there is no specific need to treat unsaturated soils in the source area. Use of soil vapor extraction in conjunction with chemical oxidation can help alleviate safety issues associated with controlling and recovering off-gas containing volatile organic carbons (VOCs), oxygen, oxidants and other reaction byproducts that can be generated by various chemical oxidants.

As discussed in greater detail below, each chemical oxidant and application technology has advantages and disadvantages. Some oxidants are stronger than others, yet some weaker oxidants may persist in the subsurface, allowing longer contact times with the contaminants. Careful evaluation of the contaminants of concern is needed before selecting a chemical oxidation technology. Certain

contaminants (e.g., benzene) that are frequently remedial drivers at petroleum UST release sites are unable to be readily chemically oxidized *in-situ* using some chemical oxidants (e.g., permanganate).

Understanding the site hydrogeologic conditions is important when considering chemical oxidation technologies because these conditions often determine the extent to which the chemical oxidants may come into contact with the petroleum contaminants. Chemical oxidants may not be able to penetrate low permeability homogenous soils or horizons in heterogeneous soils that contain the bulk of petroleum contaminant mass.

Soil reactivity with chemical oxidants is also important when considering the costs of the use of chemical oxidation. Excessive loss of a chemical oxidant that is reacting with organics in soil, instead of reacting with the contaminants, may preclude the use of the technology as an economically viable approach to site remediation. Different chemical oxidation technologies are most appropriate for particular hydrogeologic conditions. For example, Fenton's Reagant may not be ideal for groundwater with high concentrations of carbonate. The carbonate ion preferentially scavenges the hydroxyl radicals created by Fenton's Reagant reactions before they have a chance to react with the petroleum contaminants. By contrast, the presence of carbonate minerals in the geologic matrix has generally positive effects on permanganate oxidation.

Remedial strategies for petroleum UST sites that include a combination of active source zone treatment with enhanced natural attenuation outside the contaminant plume core may consider chemical oxidation technologies. Many chemical oxidation techniques also provide residual dissolved oxygen that is used by aerobic microorganisms to biodegrade contaminants. In addition, these technologies may also oxidize reduced electron acceptors (e.g., nitrogen to nitrate, sulfides to sulfate), which are then used by anaerobic microorganisms to biodegrade contaminants. For more information on enhanced aerobic remediation technologies, see "How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers" (EPA-510-B-95-007, 1995). For specific information on aerobic remediation technologies, see Chapter III, *Bioventing*, Chapter VIII, *Biosparging*, and Chapter X, *In-situ Groundwater Bioremediation*.

Exhibit XIII-1 summarizes the general advantages and disadvantages of chemical oxidation technologies.

Several chemical oxidants have been used to remediate petroleum contaminated UST sites. The most commonly used (and most effective) are Hydrogen Peroxide/Fenton's Reagent and Ozone. Sodium or Potassium Permanganate have been used, but experience with these compounds is more limited, although some recent bench-scale and field studies are showing promise.

EXHIBIT XIII-1
Chemical Oxidation
Primary Advantages and Disadvantages

Advantages	Disadvantages
# Contaminant mass can be destroyed in-situ.	# Potentially higher initial and overall costs relative to other source area solutions.
# Rapid destruction/degradation of contaminants (measurable reductions in weeks or months).	# Contamination in low permeability soils may not be readily contacted and destroyed by chemical oxidants.
# Produces no significant wastes (VOC off-gas is minimal), except Fenton's.	# Fenton's Reagant can produce significant quantity of explosive off-gas. Special precautions (i.e., SVE system) are required for appropriate implementation of remedial action involving Fenton's Reagent/hydrogen peroxide.
# Some oxidants (not Fenton's) are capable of completely oxidizing MTBE (but production of degradation products may be problematic).	# Dissolved contaminant concentrations may rebound weeks or months following chemical oxidation treatment.
# Reduced operation and monitoring costs.	# Dissolved contaminant plume configuration may be altered by chemical oxidation application.
# Compatible with post treatment monitored natural attenuation and can even enhance aerobic and anaerobic biodegradation of residual hydrocarbons.	# Significant health and safety concerns are associated with applying oxidants.
# Some oxidation technologies cause only minimal disturbance to site operations.	# May not be technically or economically able to reduce contaminants to background or very low concentrations.
	# Significant losses of chemical oxidants may occur as they react with soil/bedrock material rather than contaminants.
	# May significantly alter aquifer geochemistry; can cause clogging of aquifer through precipitation of minerals in pore spaces.

There has also been recent interest in and some field applications using sodium persulfate ($Na_2S_2O_8$) to oxidize organic contaminants or to reduce the oxidant demand of native soils before other oxidants are applied to the contamination. Some research has demonstrated that when mixed with ferrous iron as a catalyst, the sulfate free radical (SO_4^-) can be produced, which has an oxidation potential only slightly less than Fenton's Reagent. Field testing of this oxidant to date has primarily involved the destruction of chlorinated organics rather than petroleum hydrocarbons. Given the experimental status of this oxidant, it is not further described or discussed in this chapter.

A brief description of the three main petroleum hydrocarbon oxidants and associated application technologies is provided below. Exhibit XIII-2 compares the relative advantages and disadvantages of these chemical oxidation technologies.

Hydrogen Peroxide and Fenton's Reagent

Hydrogen peroxide is a strong oxidant that can be injected into a contaminated zone to destroy petroleum contaminants. When injected to groundwater, hydrogen peroxide is unstable, and reacts with organic contaminants and subsurface materials. It decomposes to oxygen and water within hours of its introduction into groundwater generating heat in the process. Peroxide is typically shipped to a remediation site in liquid form at dose concentrations ranging from five percent to 50 percent by weight.

The reactivity of hydrogen peroxide can limit the extent to which it may be distributed in the subsurface before it decomposes. Injecting concentrations of hydrogen peroxide as low as 100 ppm (a small fraction of one percent) can cause oxygen concentrations in groundwater to exceed the solubility limit of oxygen in groundwater (typically 9-10 mg/L). When this occurs, oxygen gas is formed, and is lost in the form of bubbles that rise through the saturated zone to the water table and into the unsaturated zone.

Hydrogen peroxide is particularly effective when it reacts with ferrous iron (Fe^{2+}) to produce Fenton's Reagent. Ferrous iron may be naturally present in the subsurface soils and/or groundwater, or it can be added as a catalyst solution together with the hydrogen peroxide to produce this aggressive chemical reaction.

Hydrogen peroxide in the presence of ferrous iron (Fe^{2+}) reacts to form hydroxyl radicals (OH•), ferric iron (Fe^{3+}), and hydroxyl ions (OH^-). The hydroxyl ions are very powerful oxidizers, and react particularly with organic compounds. The hydroxyl radicals break the petroleum hydrocarbon bonds of common petroleum constituents such as benzene, toluene, ethylbenzene, and xylene, as well as petroleum aromatic hydrocarbons (PAHs) and methyl tertiary butyl ether (MTBE), a common gasoline additive.

Fenton's Reagent requires soluble Fe^{2+} to form OH•. This optimal reaction occurs under relatively low pH conditions (e.g., pH of 2 to 4). pH adjustment in the treatment area is often necessary to enable the oxidation process to proceed efficiently. This can be accomplished by either acidifying the hydrogen peroxide or by adding a chelating acid. Using a ferrous sulfate solution `simultaneously adjusts aquifer pH and adds the iron catalyst needed for Fenton's Reagent. Because of the low pH requirement, Fenton's Reagent treatment may not be efficient or effective in limestone geology or sediments with elevated pH levels or with significant capacity to buffer these reactions. In addition, reaction between hydrogen peroxide and ferric iron can consume hydrogen peroxide, reducing the effectiveness of the oxidant dose. The same effect may also occur in soils with high ferric iron content.

Exhibit XIII-2
Chemical Oxidation Technologies Comparative Matrix

	Hydrogen Peroxide/ Fenton's Reagant	Permanganate	Ozone
Advantages			
Potential to complete remediation in shortest time	x		
Capacity to oxidize MTBE and benzene	x		x
No significant VOC off-gas produced by heat of reaction	x [1]	x	
Oxidizes over extended period, increasing possibility of contact with contaminants		x	
Increases dissolved oxygen levels for potentially enhanced aerobic bioremediation	x		x
Reduced health and safety concerns during application		x [2]	
Can be applied using automated system			x

[1] If solid peroxide is injected below 10% strength, the heat of dilution is mitigated and VOC generation typically avoided.

[2] Note that sodium permanganate is often applied as a liquid at 40% strength, which poses a significant handling and explosion risk.

Exhibit XIII-2 Chemical Oxidation Technologies Comparative Matrix (continued)			
	Hydrogen Peroxide/ Fenton's Reagant	**Permanganate**	**Ozone**
Disadvantages			
Inability to effectively oxidize benzene or MTBE		x	x
Increased risk of fugitive vapors entering building structures, utility conduits, particularly in absence of adequate vapor recovery technology (e.g., soil vapor extraction)	x		x
Increased risk of plume reconfiguration	x		x
Low permeability soil horizons less likely to be penetrated by oxidant over short injection period	x	x	x
On-site reactive chemical handling and storage required	x	x	x
On-site gas production and delivery equipment (e.g., ozone generator) required			x
Few petroleum remediation projects completed using this technology due to limited effectiveness		x	
Possible production of unwanted compounds or by-products in the subsurface[3]	x	x	x
Potential to precipitate solids and clog aquifer pores	x	x	

Fenton-like reactions produce the hydroxyl radical (OH•) which is one of the strongest oxidants, but the reaction proceeds so quickly that the radicals may not have sufficient time to come into contact with contaminant molecules so that they can be destroyed before the hydrogen peroxide decomposes. Also, some

[3] Chemical oxidation may cause some may create some toxic or highly mobile secondary products. Ensure that analyses for potential secondary products are included in any corrective action plan that proposes the use of chemical oxidants.

contaminants may sorb so tightly to organic material in the soil that they are effectively protected from destruction.. This may be particularly true for sites with significant layers or lenses of low permeability that results from high clay content. In such cases, the oxidant may successfully address contaminants in more permeable layers or lenses of soil while leaving the bulk of the contamination that resides in the low permeability soils.

Difficulty in addressing contamination in low permeability soils may be alleviated to some degree by controlled pneumatic or hydraulic fracturing of the soil. However, engineered hydraulic fractures generally cannot be spaced more closely than about 5 feet, which means that chemical oxidants must still penetrate a substantial thickness of low permeability soil to come into contact with the contamination. Deep soil mixing with large diameter drill augers is the most effective method currently available to increase contact between adsorbed contaminants and the oxidants. In any case, long term post-injection monitoring of contaminant levels in groundwater is critical to evaluating the success of putting Fenton's Reagent into contact with adsorbed contaminants. If inadequate contact occurs, contaminant levels in groundwater samples will rebound as the adsorbed contaminant mass gradually (typically over months) bleeds back into groundwater.

Controlled oxidation is increasingly being practiced using solid peroxides, pH modifiers, and catalysts that promote the generation of free radicals. This new approach moderates the rate of dissolution and peroxide generation, which in turn controls that rate of reaction between peroxide and the petroleum contaminants. The use of slurried peroxides creates the opportunity to release oxidants and oxygen over a longer period, which can promote subsequent aerobic remediation.

“Modified” Fenton-type systems use pH-neutral and even higher pH conditions along with slurried solid peroxides and metallic or organo-metallic catalysts. The reaction of the oxidants with the catalysts generate hydroxyl radicals, which react with the organic contaminants within the subsurface. The advantage to this approach is the ability to use Fenton’s Reagant under neutral pH conditions, requiring no acidification of the aquifer. It leads to a mix of reducing and oxidizing reactions in the subsurface, which moderates the rate of dissolution and peroxide generation, which moderates the rate of reaction between the peroxide and the petroleum contaminants. This releases oxidants and oxygen over a longer period, and may promote subsequent aerobic remediation.

Fenton-like reactions are exothermic and can raise the temperature of groundwater, produce steam and generate significant pressures in the application area, particularly when the Fenton’s is added at strengths approaching 10-12%. Especially in deep vadose zones and in monitoring or injection wells where pressures may be elevated, Fenton’s-like reactions can lead to explosive conditions and present safety concerns that need to be promptly and effectively managed. In addition, migration of explosive vapors along preferential pathways may pose an explosion hazard.

Several incidents resulting in spontaneous explosions of subsurface vapors have occurred during Fenton's Reagent treatment of petroleum contaminated sites. Other incidences have involved VOC vapor migration and intrusion into buildings and contaminant plume expansion. To manage these risks, at a minimum, it is important before a chemical oxidation strategy is selected and implemented to:

- Locate pockets of high levels of petroleum contamination in the treatment area.
- Identify and evaluate preferential flow paths.
- Clear the area of subsurface utilities, basements or other enclosed spaces that could accumulate and transmit vapors.
- Ensure that no petroleum storage tanks or lines are in the treatment area.

During application of an oxidation technology, consider the following to manage risks:

- Use a field photo-ionization or flame ionization detector (PID/FID) and explosimeter to monitor for explosive conditions.

- Install and operate a soil vapor collection system during Fenton's Reagent treatment until such time it can be demonstrated that there is no significant threat.

- Use a heat probe to monitor subsurface temperatures. Hydrogen peroxide, for example, decomposes at temperatures above 65°C, so as reactions progress in the subsurface, it is important to control the temperature to ensure maximum efficacy of the oxidation process.

- Closely monitor hydrogen peroxide and catalyst injection into the treatment area and adjust levels based on field analyses of soil gas and groundwater samples.

- Consider hydraulically containing groundwater during the treatment process to minimize the possibility of the chemical reaction pressures expanding the contaminant plume. Note, however, that dissolved gases in groundwater often prevent this approach from being as effective as predicted.

Other safety concerns include those associated with storing and using concentrated hydrogen peroxide on site. Many applications of the technology have involved the storage and use of thousands of gallons of fifty-percent hydrogen peroxide. Skin burns and blindness can result from contact with this chemical at this concentration. Safety precautions include the use of skin protection and safety glasses during application of these chemicals. A shower and eye wash facility may need to be constructed for the duration of the application.

Hydrogen peroxide and catalyst solutions needed for Fenton's Reagent are usually added to the treatment area by pressure injection into one or more designated chemical oxidation injection wells, or gravity injection into one or more monitoring or other wells.

In pressure injection, compressed air is used to sparge the ferrous iron catalyst and relatively large volumes of peroxide solution (e.g., hundreds to thousands of gallons) into the contaminated soil and groundwater over a short period of time (e.g., days). The sparged air forces the chemical reactants down the injection well point(s) and out into the impacted saturated soil. This is an aggressive approach that poses inherent increased risks of VOC vapor production and migration as well as plume re-configuration. Plume re-configuration may occur because the zone of influence during injection is limited, and permeability decreases with application of the technology, which may create preferential flowpaths with continued injection. Operation of a soil vapor extraction system concurrently with oxidant injection is a sensible precaution.

In gravity injection, small volumes of reagents are gravity-fed into injection well(s) over a longer application period. The distribution and dissipation of the reagents in the saturated zone is largely controlled by the site hydrogeologic conditions. The gravity injection approach may reduce some of risks associated with chemical oxidation technologies. Additionally, given its prolonged application period, the oxidants may be able to penetrate into more of the lower permeability soils to address contaminants in these areas.

In both cases, multiple injection events, separated by extended periods of groundwater monitoring, may be required in order to approach cleanup objectives. Establishing which injection or application approach is likely to be most efficient or cost effective for a given site is challenging, given the recent emergence of this technology and the limited volume of scientifically defensible information that is currently available for the two basic application methods. Site-specific safety concerns may be a key determining factor of the most appropriate injection approach.

An additional benefit of hydrogen peroxide and Fenton's Reagent is the temporary increase of oxygen levels in and around the treatment area. The increased oxygen levels at the fringes of the treatment area can enhance naturally occurring aerobic biodegradation processes that reduce contaminant mass. While there may be concerns about oxidizing hydrocarbon-degrading bacteria in the chemical oxidation treatment area, many studies have shown that soil cannot be readily sterilized by Fenton's Reagent and that microbial populations rapidly rebound following chemical oxidation treatment. In addition to enhancing aerobic biodegradation, reduce nitrogen and sulfur are oxidized to nitrate and sulfate, which can be used by anaerobic microbes.

Permanganate

Permanganate is emerging as a chemical oxidant that can be used to destroy petroleum and other organic compounds in soil and groundwater, and has successfully treated MTBE in recent laboratory and bench-scale studies. This oxidant is weaker than hydrogen peroxide. Its inability to oxidize benzene can lead to the early elimination of permanganate as a candidate for oxidation technology at petroleum cleanup sites.

However, permanganate has several advantages over other oxidants. It:

- Oxidizes organics over a wider pH range.
- Reacts over a prolonged period in the subsurface allowing the oxidant to more effectively permeate soil and contact adsorbed contaminants.
- Does not normally produce heat, steam and vapors or associated health and safety concerns.

Permanganate may be applied to sites as either potassium permanganate ($KMnO_4$) or sodium permanganate ($NaMnO_4$). Where cost dominates over engineering factors at a site, potassium permanganate is the preferred chemical form because it is more widely available, less costly, and is available in solid form, which facilitates transport and handling. Where other factors are more important, the liquid form of sodium permangante is preferable.

When choosing potassium permanganate for application at a site, be aware of three properties that can cause concern to owner, operators or state regulators.

First, potassium permanganate is derived from mined potassium ores which, by their nature, typically contain salt and metal impurities (e.g., arsenic, chromium, lead). Depending on water quality criteria in the state in which the site occur and the quality and concentration of potassium permanganate used to oxidize the site contaminants, these impurities may generate concern. (This is also true of sodium permanganate, which is mined and processed in similar fashion.)

Second, potassium permanganate is used to produce pharmaceuticals and should be used and monitored carefully.

Third, potassium permanganate in flowable form contains silica, which can accumulate in wells and plug the screen.

As with other chemical oxidation technologies, the success of the use of permanganate relies heavily on its ability to come into contact with the site contaminants. The delivery mechanism must be capable of dispersing the oxidant throughout the treatment zone. To accomplish this, permanganate may be delivered in solid or liquid form in a continuous or cyclic application schedule using injection probes, soil fracturing, soil mixing, groundwater re-circulation or treatment fences.

Dissolved permanganate has been delivered to injection or re-circulation wells at concentrations ranging from 100 to 40,000 milligrams per liter (mg/L). Contaminated soils have been successfully oxidized through slurry injection, deep soil mixing or hydraulic fracturing using concentrated permanganate solutions ranging from 5,000 to 40,000 mg/L or up to 50 percent by weight solid permanganate.

In-situ permanganate reactions can yield low pH (e.g., pH 3) and high Eh conditions (e.g., +800 mV), which can temporarily mobilize naturally-occurring metals and metal contaminants that may also be present in the treatment area. The release of these metals from the aquifer formation, however, may be offset by sorption of the metals onto strongly sorbent MnO_2 solids that are precipitated as a byproduct of permanganate oxidation. In addition, high sodium permanganate concentrations can create sodium problems with clay permeability at the edges of the injection zone due to swelling clays and potential aquifer clogging. $Cr(OH)_3$ in soils may be oxidized to hexavalent chromium, which may persist for some time. This may generate concern if the aquifer is being used for drinking water. Questions remain about the mass of MnO_4 that is generated, and the effect, if any, the mass may have on subsurface permeability and remediation performance.

Ozone

Ozone (O_3) is a strong oxidant with an oxidation potential about 1.2 times greater than hydrogen peroxide. It can be used to destroy petroleum contamination in-situ. Ozone, a gas, is typically generated on-site using a membrane filtration system and typically delivered to the subsurface through sparge wells. Delivery concentrations and rates vary, however, because of the high reactivity of ozone and associated free radicals. Ozone needs to be generated in close proximity to the treatment area, and sparge wells generally need to be spaced closely in the target remedial zone.

Ozone can also be injected into the subsurface in a dissolved phase. The gas may be transferred to the dissolved phase on-site by sparging upgradient water with ozone. Groundwater that is extracted upgradient from the area to be treated may be amended with ozone, then re-injected or re-infiltrated into the subsurface, where it transports the dissolved phase ozone and oxygen into the contaminated area. (Check with appropriate state groundwater authorities to learn whether groundwater re-injection is allowed in the state.) More commonly, gaseous ozone is injected or sparged directly into contaminated groundwater.

Typically, air containing up to five percent ozone is injected into strategically placed sparge wells. Ozone then dissolves in the groundwater, reacts with subsurface organics, and ultimately decomposes to oxygen. Ozone can oxidize site contaminants directly or through formation of hydroxyl radicals (OH•), strong nonspecific oxidants with an oxidation potential that is about 1.4 times that of

ozone. It is capable of oxidizing BTEX constituents, PAHs, and MTBE (with limited effectiveness).

Heat and VOC vapors may be generated as a result of ozone sparging and the oxidation reactions when ozone concentrations are high. As a result, vapor control equipment (e.g., a soil vapor extraction and treatment system) is often needed to operate in conjunction with the ozone sparging system to capture and prevent the vapors from migrating to, entering and impacting subsurface utilities or nearby structures.

Ozone is also effective in delivering oxygen to enhance subsurface bioremediation of petroleum-impacted areas. Ozone is 10 times more soluble in water than is pure oxygen. Consequently, groundwater becomes increasingly saturated with dissolved oxygen as the unstable ozone molecule decomposes into oxygen molecules. About one-half of dissolved ozone introduced into the subsurface degrades to oxygen within approximately 20 minutes. The dissolved oxygen can then be used by indigenous aerobic hydrocarbon-degrading bacteria.

The oxidizing properties of injected ozone can temporarily suppress subsurface biological activity in the immediate injection area. However, this suppression has been found to be temporary, and sufficient bacteria survive in-situ ozonation to resume biodegradation once ozone has been applied. Additionally, aerobic bacteria along the fringes of the treatment area may thrive under the oxygen rich conditions produced during ozone treatment. Biodegradation enhancement is a primary benefit of this oxidation technology.

Special Considerations for MTBE

As mentioned above, any of the three oxidation approaches may be applicable for remediating MTBE, either in the presence or absence of other gasoline hydrocarbons. Hydrogen peroxide and ozone addition have both been used on a number of MTBE-impacted field sites, with successes reported at many of them. The success of these techniques may be attributable to the combined effects of the oxidation, increased dissolved oxygen levels in the groundwater, and generated heat.

The available field data on these chemical oxidation projects for MTBE treatment is somewhat sparse. Some literature reports do not contain enough time-series sampling data on groundwater concentrations to ensure that the beneficial reductions of MTBE are not short-lived and that groundwater concentrations do not later rebound.

Very little published data exists on using permanganate on MTBE-impacted field sites, but recent laboratory batch testing looks promising. The method's ability to oxidize MTBE, but not benzene, may have application where an active remediation technology is desired for treating the MTBE, but the benzene is to be

addressed by monitored natural attenuation. Further development and field confirmation of potassium permanganate's effectiveness for MTBE is needed.

With any oxidation method, the potential for creating unwanted intermediary products or other unwanted by-products always needs to be considered. In studies of aboveground oxidation of MTBE-impacted groundwater, the primary byproducts of concern were found to be acetone, tertiary butyl alcohol (TBA) and tertiary butyl formate (TBF), and bromate (for ozone-based oxidation). The possible in-situ formation of these by-products, as well as their potential fate and possible impacts, should be considered as part of any plan to conduct subsurface chemical oxidation of MTBE. Several laboratory studies that addressed the oxidation of MTBE-impacted water have indicated that combining ultraviolet light with hydrogen peroxide may oxidize MTBE more effectively, with fewer byproducts. Although the UV light requirement may render this application infeasible for in-situ chemical oxidation projects, the effectiveness of ex-situ treatment technologies may be enhanced.

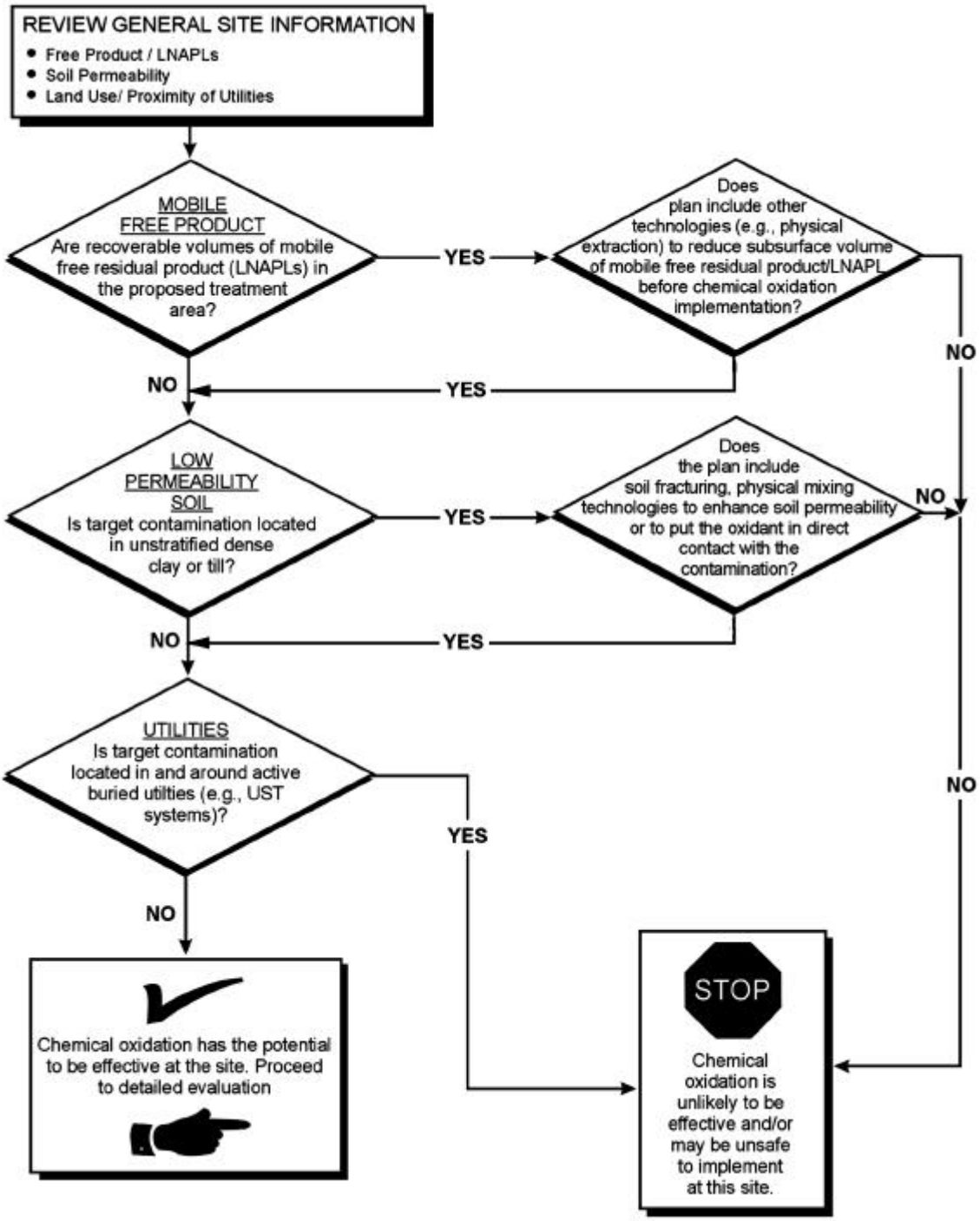
Another consideration for MTBE is whether chemical oxidation technologies can be cost effective for a highly soluble compound like MTBE and that is often found to exist in laterally extensive, mobile groundwater plumes. Chemical oxidation can be quite effective on the high hydrocarbon concentrations typically seen in groundwater and soils in source areas, but may not be applicable to the expansive, lower-concentration, dissolved-phase plumes often associated with MTBE-impacted sites.

Chemical Oxidation Technology Effectiveness Screening Approach

The descriptions of the various chemical oxidation technologies in the overview should provide the basic understanding needed to move forward with evaluation of a corrective action plan that proposes to use chemical oxidation. To assist with evaluation of the chemical oxidation corrective action plan, a step-by-step technology effectiveness screening approach is provided in a flow diagram in Exhibit XIII-3. This exhibit summarizes the evaluation process and serves as a roadmap for the decisions to be made during evaluation of a corrective action plan that proposes chemical oxidation technologies. A checklist has been provided at the end of this chapter for use as a tool to both evaluate the completeness of the chemical oxidation corrective action plan and to focus attention on areas where additional information may be needed.

Note that the first step in this screening includes information that can only be gleaned from a thorough assessment of the site, such as soil permeabilities and the nature of the aquifer geology, including heterogeneity, the presence of preferred pathways, and other characteristics. Before embarking on the selection of a chemical oxidation technology, be sure that a complete, and preferably three-dimensional, delineation of the subsurface and contaminant plume has been conducted.

Exhibit XIII-3
Initial Screening for Potential Effectiveness of Chemical Oxidation



The evaluation process can be divided into the four steps described below.

- **Step 1: An initial screening of chemical oxidation effectiveness** allows quick determination of whether chemical oxidation should be considered as a remedial approach for the site.

- **Step 2: A detailed evaluation of chemical oxidation effectiveness** provides further screening criteria to confirm whether chemical oxidation is likely to be effective. First, extract from the corrective action plan certain site-specific data on the nature/extent of contamination, potential risk to human health/the environment, subsurface geology and hydrogeology, and other relevant site characteristics. Then, compare the site-specific data to the criteria provided in the Exhibit to assess whether chemical oxidation is likely to be effective.

- **Step 3: An evaluation of the chemical oxidation system design in the corrective action plan** allows determination of whether basic design information has been defined, necessary design components have been specified, the construction process flow designs are consistent with standard practice, and adequate feasibility testing has been performed.

- **Step 4: An evaluation of the operation and monitoring plans** allows determination of whether baseline, start-up and long-term system operation and monitoring are of sufficient scope and frequency and whether remedial progress monitoring and contingency plans are appropriate.

Step 1: Initial Screening of Chemical Oxidation Effectiveness

This section allows you to perform an initial screening of whether chemical oxidation is likely to be an effective approach to remediate the petroleum-impacted areas at a site. Before selecting chemical oxidation as the preferred remedial approach, determine whether the corrective action plan has taken into account key site-specific conditions. In addition, evaluate several "bright lines" defining the limits of chemical oxidation overall viability as a remedial technology. These bright lines will assist in evaluating the corrective action plan and in determining the appropriateness of chemical oxidation as the site remedial solution. After establishing the overall viability of an chemical oxidation approach, basic site and petroleum contaminant information can be examined to further determine the expected effectiveness of chemical oxidation as the remedial choice.

Overall Viability

The following site conditions are considered to be the “bright lines” defining the general limits of chemical oxidation viability at a site. If review of the corrective action plan indicates that any of the following conditions exist, chemical oxidation is not likely to be a feasible or appropriate remedial solution for the site.

- **Free mobile product is present and the corrective action plan does not include other means for its recovery.** Chemical oxidation is not likely to

cost-effectively address free product. Significant thickness and volumes of free product may need to be recovered using conventional approaches before oxidizing the residual hydrocarbons. For some chemical oxidation technologies, free product poses a safety issue, increasing chances of an explosion.

- **Utilities (active gas mains, petroleum USTs/piping, sewers, etc.) lie in the immediate vicinity of the treatment area.** Concerns associated with the heat, VOC vapors, elevated oxygen levels and potential corrosion that can occur from the induced chemical reactions during application of oxidants may preclude the use of this technology until the utilities can be removed or relocated. Potential risks associated with the use of chemical oxidation in the presence of buried utilities include explosion, combustion, and vapor intrusion into buildings.

- **The target contaminant zone is comprised of or includes unstratified dense clay.** With the low permeabilities inherent to clay or clay-rich soils, chemical oxidants cannot easily come into contact with the adsorbed contaminants. Without adequate contact, the petroleum contaminants will remain adsorbed to the low permeability soil, which often contains most of the contaminant mass, rendering remediation unsuccessful. Soil fracturing, use of slow reaction oxidants (e.g., permanganate) or multiple oxidant applications may be used to help bring the oxidants into contact with the contaminants, but technical and cost considerations may lead to consideration of other remedial approaches or technologies.

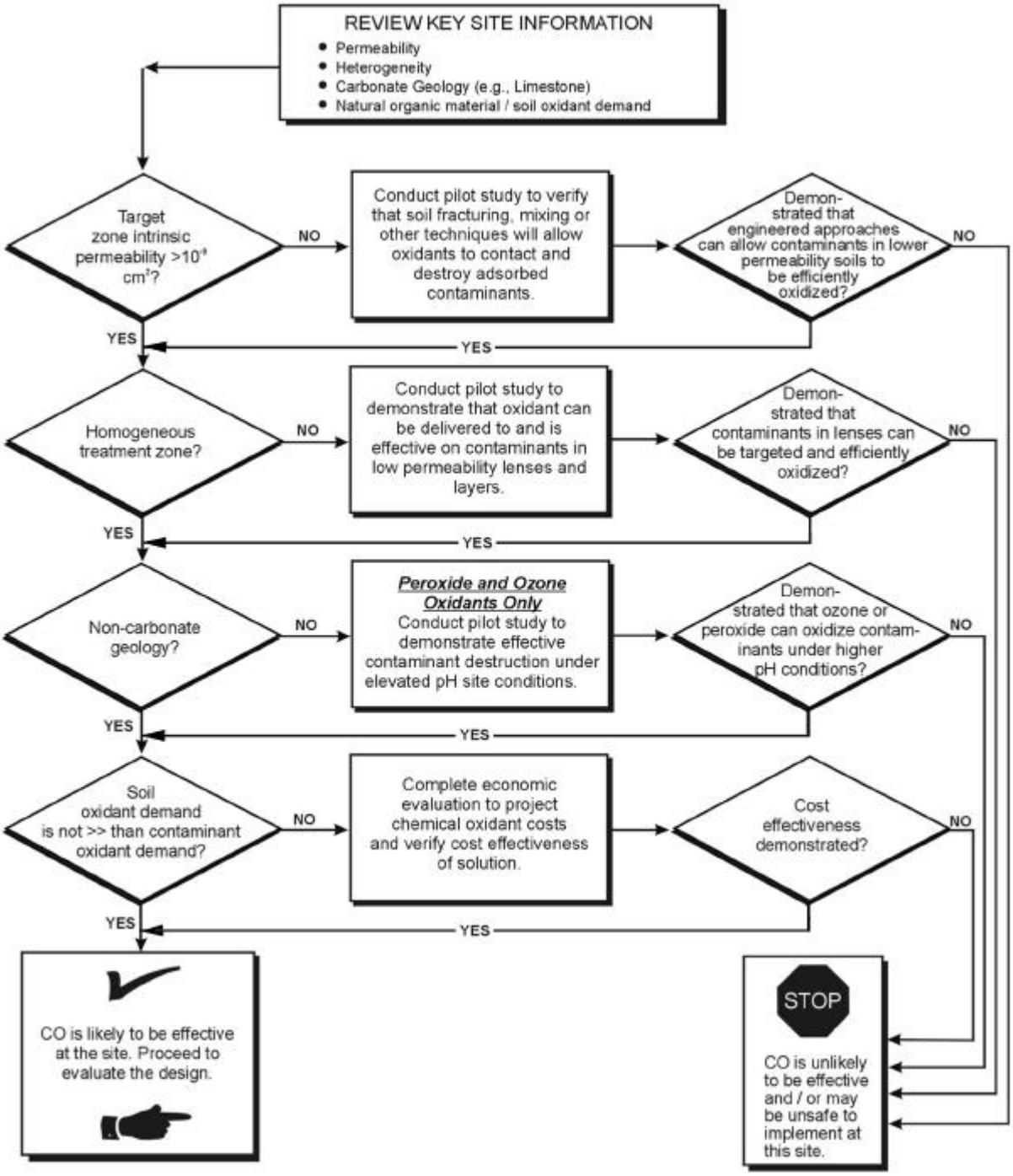
Potential Effectiveness of Chemical Oxidation

Before performing a more detailed evaluation of chemical oxidation's potential remedial effectiveness and future success at a site, it is useful to review several key indicators. One key factor that influences the effectiveness of chemical oxidation at a site is soil permeability.

Chemical oxidation of contaminants in fine-grained soils, or in clays and silts with low permeabilities, is likely to be less effective than chemical oxidation of contaminants in coarse-grained soils (e.g., sand and gravels) because it is more difficult to effectively contact chemical oxidants with organic contaminants in low-permeability materials.

It is also important to determine whether the chemical oxidant that may be used to address site contaminants is able to readily oxidize the chemical constituents of concern. For example, permanganate cannot readily oxidize benzene or MTBE, which may be target contaminants. The detailed chemical oxidation effectiveness evaluation section of this chapter considers the oxidizing strength of various oxidants and the resistance of specific petroleum hydrocarbon constituents to oxidation. The flowchart in Exhibit XIII-4 outlines the factors that

Exhibit XIII-4
Detailed Screening for Potential Effectiveness of Chemical Oxidation



should be evaluated in the detailed screening for the use of chemical oxidation technologies.

Step 2: Detailed Evaluation of Chemical Oxidation Effectiveness

If initial screening of the corrective action plan indicates that chemical oxidation may be feasible and potentially effective for the site, then a more detailed evaluation of the proposed chemical oxidation remedy should be performed to confirm this assessment. To help with this more detailed evaluation, this section covers a number of important site-specific characteristics influencing the potential effectiveness of chemical oxidation that were not considered or fully explored in your initial screening of the remedial approach. Additionally, this section provides a more detailed discussion of key contaminant characteristics influencing the potential effectiveness of chemical oxidation.

Key site and contaminant factors that should be explored in the detailed evaluation of chemical oxidation are listed in Exhibit XIII-5. The remainder of this section details each of the parameters described in Exhibit XIII-5. After reviewing and comparing the information provided in this section with the corresponding information in the corrective action plan, it should be possible able to evaluate whether chemical oxidation is likely to be effective at the site.

Exhibit XIII-5
Key Parameters Used to Evaluate Chemical Oxidation Applicability

Site Characteristics	Constituent Characteristics
# Oxidant Demand Factors # Advective and Dispersive Transport Factors – Intrinsic Permeability – Soil Structure and Stratification – Hydraulic Gradient – Iron and Other Reduced Inorganic Compounds Dissolved in Groundwater	# Chemical Class and Susceptibility to Chemical Oxidation # Solubility Characteristics – Solubility – K_{oc} Factor

Site Characteristics That Affect Chemical Oxidation

This section addresses three factors at a site that can affect the ability of chemical oxidants to treat petroleum-contaminated groundwater at a site:

- Oxidant Demand Factors
- Advective and Dispersive Transport Factors
- Constituent Characteristics Factors

Each of these factors is described in detail below.

Oxidant Demand Factors. Once introduced into the saturated zone, chemical oxidants and catalysts may be distributed by advection and dispersion to address the target treatment zone. Ideally, the oxidant concentrations are sustained from the point of application until the oxidants contact the contaminants. However, the concentrations of oxidant more typically decrease by dilution through mixing with subsurface pore water and through consumption via chemical reactions that are not related to the degradation of the target constituents of concern. The loss of oxidant due to subsurface reactions unrelated to contamination oxidation, often referred to as the natural oxidant demand (NOD), is a significant consideration in determining the economic viability of chemical oxidation and in engineering the appropriate oxidation application dose and approach.

NOD stems from reaction with organic and inorganic chemical species naturally present in the subsurface. Oxidants that react with the natural organic material (NOM) are lost and are, therefore, subsequently unable to react with the target contaminants. In certain soil types (e.g., peat), the NOM and therefore the NOD can be extremely high. Inorganic oxidant demand may exist if naturally-occurring reduced mineral species (e.g., ferrous iron) are present in the groundwater or saturated soils. These reduced compounds can also react with the oxidants to remove oxygen available for reaction with the target contaminants. Exhibit XIII-6 presents a sample of some common inorganic processes that consume oxygen and oxidants in groundwater.

NOD almost always exceeds contaminant oxidant demand. If insufficient doses of oxidants are not provided to satisfy both demands, the target contaminants may not be degraded to the desired level. Bench testing should be used to determine the NOD for the saturated zone.

Exhibit XIII-6
Inorganic Oxidation Processes That Consume Dissolved Oxygen in Groundwater

Process	Reaction
Sulfide Oxidation	$O_2 + ½HS \rightarrow ½\ SO^{2-} + ½H^+$
Iron Oxidation	$¼O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + ½H_2O$
Nitrification	$O_2 + ½NH^{4+} \rightarrow ½NO^{3-} + H^+ + ½H_2O$
Manganese Oxidation	$O_2 + 2Mn^{2+} + 2H_2O \rightarrow 2MnO_2\ (s) + 4H^+$
Iron Sulfide Oxidation	$15/4O_2 + FeS_2\ (s) + 7/2H_2O \rightarrow Fe(OH)_3\ (s) + 2SO_4^{2-} + 4H^+$

Exhibit XIII-7 explores the theoretical oxygen demand of a number of petroleum hydrocarbon constituents common to petroleum UST cleanup sites. The exhibit outlines the stoichiometric reactions for the complete oxidation of the typical target hydrocarbons. In theory, oxygen levels of at least 3 to 3.5 times the amount of subsurface petroleum mass that needs to be removed to meet cleanup goals must be delivered to the groundwater and distributed over the planned remedial period.

Exhibit XIII-7
Organic Compound Oxidation Stoichiometry

Petroleum Hydrocarbon	Oxidation Reaction	Oxygen Requirement (g O_2 per g Contaminant)
MTBE	$C_5H_{12}O + 7.5\ O_2 \rightarrow 5CO_2 + 6H_2O$	2.7
Benzene	$C_6H_6 + 7.5\ O_2 \rightarrow CO_2 + 3H_2O$	3.1
Toluene	$C_6H_5CH_3 + 9\ O_2 \rightarrow 7CO_2 + 4H_2O$	3.1
Ethylbenzene	$C_2H_5C_6H_5 + 10.5\ O_2 \rightarrow 8CO_2 + 5H_2O$	3.2
Xylenes	$C_6H_4(CH_3)_2 + 10.5\ O_2 \rightarrow 8CO_2 + 5H_2O$	3.2
Cumene	$C_6H_5C_3H_7 + 12O_2 \rightarrow 9\ CO_2 + 6H_2O$	3.2
Naphthalene	$C_{10}H_8 + 12O_2 \rightarrow 10CO_2 + 4H_2O$	3.0
Fluorene	$C_{13}H_{10} + 15.5O_2 \rightarrow 13CO_2 + 5H_2O$	3.0
Phenanthrene	$C_{14}H_{10} + 16.5O_2 \rightarrow 14CO_2 + 5H_2O$	3.0
Hexane	$C_6H_{14} + 9.5\ O_2 \rightarrow 6CO_2 + 7H_2O$	3.5

A number of experiments and field tests have determined that site NOD is highly variable and not easily predicted. For example, NOD associated with permanganate application has been found to vary from two to over 100 mg MnO_4^- per mg of total organic carbon (TOC) in the treatment area soil, and equal to or greater than the contaminant oxygen demand.

Oxidizing reactions associated with the NOD can produce solid precipitates that can accumulate in soil pore spaces. Particles may be produced by shearing off fragments of natural soil or by yielding reaction products (e.g., iron or manganese oxides). Permanganate oxidation results in the production of MnO_2 solids as a reaction product. These precipitates can potentially decrease soil permeability and remediation system function and performance; however, their effects in this regard have not been fully examined and are not well understood.

Advective and Dispersive Transport Factors. The site conditions affecting advection and dispersion of dissolved oxygen are:

- # Intrinsic Permeability
- # Soil Structure and Stratification
- # Groundwater Velocity
- # Iron and Other Reduced Inorganic Compounds Dissolved in Groundwater

Each of these conditions is described in detail below.

Intrinsic Permeability. Intrinsic permeability is a measure of the ability of soil to transmit fluids. Intrinsic permeability often decreases near injection wells or infiltration galleries. This is also commonly a result of the precipitation of carbonate species, such as calcite. In general, oxygen is more easily distributed in soils with higher soil permeabilities (e.g., sands and gravels) than in soils with lower permeabilities (e.g., clays or silts). Intrinsic permeability can be calculated from hydraulic conductivity measurements taken from on-site pump testing. Pump test or slug test-derived permeability ranges are representative of average hydraulic permeability conditions for heterogeneous conditions. Alternatively, intrinsic permeability can be estimated from soil boring logs and laboratory tests. Intrinsic permeability values obtained through empirical means are less accurate and result in a wider range of permeability estimates. In any case, derived permeabilities are only approximations of actual subsurface conditions and should be regarded as such in the evaluation of chemical oxidation as a remediation technology. Intrinsic permeability can vary over 13 orders of magnitude (from 10^{-16} to 10^{-3} cm^2) for the wide range of earth materials. Exhibit XIII-8 provides general guidelines on the range of intrinsic permeability values over which chemical oxidation is likely to be effective.

Exhibit XIII-8
Intrinsic Permeability and Chemical Oxidation Effect

Hydraulic Conductivity (K) (in ft/sec)	Intrinsic Permeability (k) (in ft^2)	Chemical Oxidation Effectiveness
$K > 10^{-6}$	$k > 10^{-12}$	Effective to generally effective
$10^{-6} \leq K \leq 10^{-7}$	$10^{-12} \leq k \leq 10^{-13}$	Possibly effective; needs further evaluation
$K < 10^{-7}$	$k < 10^{-13}$	Marginally effective to ineffective

It is important to note that the intrinsic permeability of a soil can decrease as chemical oxidation progresses. The most likely cause of reduced intrinsic permeability while implementing chemical oxidation is the precipitation of inorganic complexes that form during oxidation of reduced, naturally occurring mineral species such as ferrous iron. If the soil intrinsic permeability indicates borderline potential effectiveness (i.e., $10\text{-}9 \leq k \leq 10\text{-}10$), the geochemistry should be further evaluated. It may be necessary to determine the concentration of

reduced inorganic species, primarily iron, in the soil to assess whether subsurface flow pathways could become constricted by precipitation of inorganic compounds, such as ferric oxides.

Soil Structure and Stratification. Soils in a target treatment area are not uniformly permeable (i.e., heterogeneous), but rather have large-scale and small-scale variations in permeability (i.e., heterogeneous). Heterogeneity controls movement of fluids in the subsurface. Soil heterogeneity plays a very important role in chemical oxidation technologies because oxidants and catalyst reagents introduced to the subsurface are distributed preferentially along higher permeability layers in the saturated soil. For example, in a heterogeneous soil comprised of sand, silt and clay layers, oxidants may be effectively distributed through the sand layer to successfully reduce petroleum hydrocarbons there, but will be ineffectively delivered and distributed to the silt and clay layers. If the silt and clay layers are thick relative to the sand horizon and contain significant petroleum hydrocarbon mass, chemical oxidation technologies may be inefficient or ineffective. In addition, the tendency for the development or enhancement of preferential flow paths may be increased by the addition of Fenton's reagant or the use of ozone sparging.

Unless site soils are homogeneous, average soil intrinsic permeability may not adequately determine the viability of chemical oxidation approaches because discrete low permeability soil horizons may exist, and these horizons might contain a large fraction of the subsurface petroleum mass. In most cases, it is prudent to evaluate petroleum mass distribution across all soil types to determine whether chemical oxidation is likely to be effective and will achieve cleanup objectives. If select soil horizons containing hydrocarbon mass are not expected to be effectively treated using chemical oxidation, chemical oxidation may not be viable for the site. For example, if 50 percent of the contaminant mass is contained and isolated in low permeability soil horizons, and the site cleanup goals is a 95 percent reduction in petroleum contaminant concentrations, then it is reasonable to conclude that the goal cannot be achieved using chemical oxidation. However, in such circumstances, combining chemical oxidation with other technologies that enhance the permeability of low permeability horizons in the contaminated zone (e.g., soil fracturing) could be considered. Or, alternatively, following source removal addition of peroxides could be employed to increase the rate of aerobic biodegradation to achieve remediation objectives. For more information about enhanced aerobic bioremediation, refer to Chapter XII in this manual.

Groundwater Velocity. Chemical oxidation technologies may rely on groundwater advection and dispersion to distribute oxidants and catalyst reagents in the subsurface. Distribution of oxidants and reagents can be most readily accomplished under hydrogeologic conditions conducive to higher groundwater flow rates. True groundwater velocity is referred to as the seepage velocity (q_s) and can be calculated from the equation at the top of the next page:

$$q_s = \frac{K(dh/dl)}{n_e}$$

where: dh/dl = aquifer hydraulic gradient (maximum difference in water table elevation or potentiometric surface (L)/distance between upgradient and downgradient measurement points (L)
K = hydraulic conductivity (L/T)
n_e = soil effective porosity (dimensionless)

As the hydraulic gradient increases, groundwater velocity increases proportionately. This same relationship exists between groundwater velocity and soil permeability. Groundwater velocity is inversely proportional to soil porosity. As porosity increases, groundwater velocity decreases. When a significant hydraulic gradient exists, targeted delivery of oxidant to the contaminant zones may require injection and extraction wells.

In addition, transport of dilute dissolved contaminants is a function of advection, dispersion, and chemical and physical reactions. Advection refers to the movement imparted by flowing groundwater, and the rate of transport is usually taken to be equal to the *average* linear groundwater velocity. Hydrodynamic dispersion occurs as a result of molecular diffusion and mechanical mixing and causes the dissolved contaminant plume to spread out with distance from the source. Molecular diffusion is generally only significant when groundwater movement is very slow. Mechanical mixing occurs as groundwater flows through the aquifer matrix twisting around individual grains and through interconnected pore spaces at differing velocities. The movement of some dissolved contaminants may also be affected by chemical and physical reactions, such as sorption and biodegradation, which act to reduce the transport velocity and decrease concentrations in the plume.

Iron and Other Reduced Inorganic Compounds Dissolved in Groundwater. The effective intrinsic permeability of the saturated zone can be significantly reduced if the chemical oxidation treatment zone contains naturally elevated levels of reduced iron (e.g., ferrous iron, or Fe^{2+}) or other mineral species. For example, when dissolved iron is exposed to chemical oxidants, it may be oxidized to ferric iron (Fe^{3+}) oxide that can precipitate within the saturated zone and occlude soil pore space. On a large scale, this could reduce effective soil porosity, and oxidant delivery efficiency and availability. In such cases, decreases in soil porosity can be expected to occur closest to the oxidant delivery locations (i.e., near oxidant injection wells). Bench-scale tests may need to be performed to evaluate the inorganic NOD of the aquifer material and determine the feasibility of the remedial approach.

In addition to being considered in evaluating the potential effectiveness of chemical oxidation, hydraulic gradient can be an engineering design issue. If the

gradient is not steep enough to provide adequate flow and oxidant transport through the contaminated zone, then certain engineering provisions (e.g., spacing application points more closely, creating artificial hydraulic gradients) can be added to the design to enhance oxidant distribution.

Constituent Characteristics That Affect Chemical Oxidation. It is important to evaluate the potential impacts of site contaminants on the performance of the proposed chemical oxidation approach. In particular, it is important to review how the chemical structure, chemical properties, concentrations and toxicities of the petroleum contaminants can influence remedial performance.

Petroleum products are complex mixtures of hundreds or even thousands of hydrocarbon chemical constituents, other chemical constituents and additives. Each of these constituents has a different atomic structure that determines, in part, how easily it may be chemically oxidized.

With the notable exception of benzene, most petroleum hydrocarbons have been demonstrated to be oxidized by all three primary chemical oxidants. Benzene is not readily oxidized by permanganate, and oxidation of MTBE has only been demonstrated to be oxidizable by permanganate at bench scale.

The two factors related to chemical classes, and their susceptibilities to chemical oxidation, are their solubility characteristics and their K_{oc} values. Each is discussed in more detail below.

Solubility Characteristics. Solubility is the maximum concentration of a chemical that can be dissolved in water at a given temperature without forming a separate chemical phase on the water (i.e., free product). Most petroleum compounds have low solubility values, thus limiting the concentrations of contamination that can be dissolved in groundwater. The solubility values for petroleum hydrocarbons range over four orders of magnitude, as shown in Exhibit XIII-9.

Compounds with higher solubility values are generally smaller, lower molecular weight molecules (e.g., benzene). When spilled, these compounds exist in groundwater at higher relative concentrations and move more quickly through the aquifer than do compounds of higher molecular weights. Larger and higher molecular weight hydrocarbon molecules are generally less soluble in water; therefore, their dissolved concentrations in groundwater tend to be limited (e.g., naphthalene). Long-chain hydrocarbons are often saponified by chemical oxidation, making them more soluble, particularly in the presence of any free product.

Exhibit XIII-9
Solubility Values and Organic Carbon Partition Coefficients For Select Petroleum Hydrocarbon Constituents

Compound	Molecular Weight (g/mol)	Solubility in Water (g/L)	Organic Carbon Coefficient (K_{oc} - ml/g)
MTBE	88	51	12
Benzene	78	1.79	58
Toluene	92	0.53	130
Ethylbenzene	106	0.21	220
Xylenes (total)	106	0.175	350
Cumene	120	50	454
Naphthalene	128	0.031	950
Acenaphthene	154	.0035	4,900

Solubility is also an indicator of likely contaminant sorption onto soil. There is an inverse relationship between a chemical compound's solubility and its organic carbon partition coefficient (K_{oc}). A compound with a high solubility has a reduced tendency to adsorb to soil that is in contact with contaminated groundwater and may be more readily contacted by chemical oxidants. Conversely, contaminants with low solubility values will likely have an increased tendency to adsorb to soil that is in contact with contaminated groundwater and may be less readily chemically oxidized. Note that some compounds are less predictable in this relationship, such as cumene. Cumene has a strong ability to sorb to soils, despite its very high solubility. If cumene is a key target contaminant, chemical oxidation may not be the most appropriate technology for removing it from groundwater. The relationship between solubility and K_{oc} is described in more detail below.

K_{oc} Factor. When groundwater is contaminated by a petroleum UST release, the proportion of hydrocarbon mass in the soil is often far greater than that dissolved in groundwater. This is due in part to the low solubility thresholds for petroleum contaminants. However, another factor is the strong tendency for most petroleum hydrocarbons to adsorb to naturally occurring organic carbon material in the soils. This tendency along with the sheer mass of soil relative to groundwater in a contaminated area can lead to hydrocarbon mass distributions that are so unevenly distributed that they can make the mass in the dissolved-phase appear insignificant. Because of the high proportionate amount of contaminant mass in the adsorbed phase, it is important to understand the ability of the chemical oxidant to come into contact with the soil contamination.

K_{oc} is a compound-specific property that helps define the equilibrium condition between organic carbon and the contaminant concentrations in an aqueous solution. Using site-specific soil organic carbon content data (i.e., fraction of organic content or foc), K_{oc} can be used to determine the equilibrium contaminant concentrations between groundwater and soil below the water table. The typical organic carbon content in surface soils ranges from 1 to 3.5 percent. In aquifer soils, organic carbon content is an order of magnitude lower – from 0.1 and 0.01 percent – because most organic residues are either incorporated into the soil matrix or deposited on the surface.

Higher K_{oc} and Kd values indicate that more contaminant mass is likely to be retained in soil, and therefore potentially less readily contacted by chemical oxidants. Conversely, lower K_{oc} and Kd values indicate that lower contaminant concentrations will exist in equilibrium in soil for given concentrations in groundwater. A comparison of the solubility and K_{oc} values for the sample group of petroleum hydrocarbons reveals the inverse relationship between the two parameters (i.e., compounds with higher solubility values have lower K_{oc} constants).

In the absence of site-specific data that reveal the distribution of contaminant mass, solubility and K_{oc} data can be used to obtain a general understanding of the likelihood that chemical oxidation is applicable at the site. Petroleum contaminants with high solubility limits and low K_{oc} values are more likely to come in contact with chemical oxidants and to be destroyed by chemical oxidation technologies. When contaminant solubility constants are low and K_{oc} values are high, chemical oxidants may not have adequate contact with the contaminants to effectively destroy contaminant mass, particularly in low permeability soils.

Step 3: Evaluation of Chemical Oxidation Design

This section provides guidance on reviewing and evaluating a chemical oxidation remediation system's design. This section focuses on identifying and reviewing key elements of corrective action plans to help ensure they demonstrate a coherent understanding of the basis for the chemical oxidation system design**.** This section provides information on typical chemical oxidation technology components to help verify that the corrective action plan has included the basic equipment requirements for the remedial system.

It is assumed that it has already been verified, through the detailed technology screening process described in Steps 1 and 2, that chemical oxidation appears appropriate and is expected to be an effective cleanup approach, given site-specific conditions. If chemical oxidation effectiveness evaluation has not been completed, it is strongly recommended that this be done prior to evaluating the design.

Two important factors that need to be considered in evaluating the design of chemical oxidation treatment are (1) the design basis and (2) the site cleanup goals. Each of these factors is discussed in more detail below.

Design Basis

A review of the corrective action plan should find consistency between site characterization work and information that is presented as the basis for the chemical oxidation design in the corrective action plan. It is important that during the chemical oxidation effectiveness evaluation a reviewer has a solid understanding of the nature and extent of the site-specific petroleum constituents of concern, including an understanding of the contaminant phases present and the relevant site chemical, physical, and biological properties. When preparing and reviewing the corrective action plan design, it is important to understand the site geology and hydrogeology, and the risks associated with the contamination. These data, which should have been developed and interpreted as part of the site characterization effort, serve as the foundation for the remedial system design.

While site characterization data provide the core raw materials for the design, further refinement is often needed and useful. For example, while the site characterization work may identify potential human or ecological receptors that may be exposed to contamination, specific cleanup goals may not have been established. In such cases, the specific remedial goals would need to be developed and identified in the corrective action plan through one or more established approaches. These approaches may include adopting state-published cleanup standards, developing site-specific risk-based standards acceptable to the state, or employing other state-specific and approved methods.

A corrective action plan may also include the results and interpretation of follow-up studies completed after the original site characterization. The need for such studies is often identified after a review of the site characterization shows that additional information is needed to complete the remedial system design. For example, the site characterization may suggest that one or more of the constituents of concern is believed to be marginally degradable, either chemically or biologically, and the level of expected degradation is difficult to predict from the existing data.

Examples of typical information expected to be developed during the site characterization, or as a result of follow-up studies that should be completed to support the basis for the technology selection and design of the corrective action plan, are summarized in Exhibit XIII-10.

Cleanup Goals

The evaluation of alternative remedial approaches and the subsequent design of the selected approach are strongly influenced by the cleanup goals that the remediation program must achieve. Often, preliminary goals identified during the

site characterization evolve as a better understanding of site conditions and potential receptors is attained. However, owing to their importance to remediation planning and design, the cleanup goals should be fully evolved and solidified in the corrective action plan.

These goals usually provide the end-point concentrations for petroleum constituents in soil and groundwater that are acceptable to state or other regulatory agencies. These cleanup thresholds could be goals that represent any of the following:

- Health-based numeric values for petroleum chemical constituents published by the respective regulatory agency.
- Cleanup goals developed and proposed by the contractor specifically for the contaminated site.
- Goals derived from site-specific risk assessment involving contaminant fate and transport modeling coupled with ecological and human-health risk assessment.

Additional project goals that may be regulatory requirements include hydraulic control of the contamination, a cleanup time frame, or other performance goals established in the corrective action plan. Regardless of the cleanup goals and how they are established, the state-sanctioned goals should be noted in the corrective action plan and recognized as a fundamental basis for the technology selection and design.

The cleanup goals presented in the corrective action plan answer important questions about the viability of the selected remedial approach and the adequacy of the remedial design. The critical question is, Can the cleanup concentration goals be economically met by the designed chemical oxidation approach? It is important to understand how much oxidant will be consumed by NOD reaction, and how much will be lost attempting to permeate low permeability soils, in order to weigh the economics and technical feasibility of the approach. Multiple applications of the chemical oxidants may be required in order to accomplish the site objectives. Many logistical, political, risk-related, and cost issues are associated with successive attempts to oxidize the site contamination, and should be considered when such a proposal is put forth in a corrective action plan. Verification that the target petroleum constituents of concern can be chemically oxidized by the oxidant of choice should be completed.

Exhibit XIII-10 Chemical Oxidation Design Basis Factors	
Design Basis Factor	**Source(s) of Design Information**
Cleanup Goals # Target contaminant levels (soil and groundwater) # Remediation timeframe # Plume control # Others	Receptor survey, pre-design exposure or risk assessment analyses (potentially including numerical modeling), or state requirements.
Geology # Uniformity (homogeneity, heterogeneity) # Stratigraphy (vertical profile of sand, silt, clay, etc.) # Geochemistry (reduced mineral content, organic content, mineral demand for ferrous iron, sulfite, nitrite, dissolved oxygen, etc.) # Bedrock (description, depth, strike, dip, fracturing, etc.) # Soil permeabilities	Site characterization, soil borings, well installations, sampling and analysis, and site observations. Local geologic studies.
Hydrogeology # Depth to groundwater # Groundwater elevation and gradient # Aquifer/water bearing unit class (confined, unconfined, perched, bedrock, etc.) # Hydraulic parameters (conductivity, transmissivity, storativity, effective porosity, etc.) # Geochemistry (aqueous demand for ferrous iron, sulfite, nitrite, dissolved oxygen, etc.) # Modeling (simulation of groundwater flow and effects of manipulation of hydraulic head)	Site characterization, well gauging, aquifer pump testing, data analyses, and local hydrogeologic studies.
Petroleum Contamination # Target chemical constituents # Concentrations of other contaminants that can consume oxygen # Mass estimates (adsorbed, dissolved, liquid and vapor phases) # Extent (vertical and lateral) # Fate and transport characteristics (solubility, partition coefficients) # Vapor pressure and Henry's law constant for contaminants, especially if these contaminants are driven into the vapor phase by the remediation process # Modeling (simulation of contaminant transport under various scenarios)	Soil, groundwater and other media sampling/laboratory analysis, review of published data on contaminants and data interpolation and analysis. Materials Safety Data Sheets can provide this information.

Chemical Oxidation Technology Selection

With the design basis established in the corrective action plan, it is now possible to review the corrective action plan to confirm that the proposed candidate chemical oxidation technology is a reasonable site-specific choice. Depending on project-specific circumstances, there may be a few chemical oxidation technologies equally viable and appropriate for a site. Alternatively, site-specific or project-specific circumstances may suggest that one of the chemical oxidation technologies would address the on-site contamination far better than any of the others.

Exhibit XIII-2 presented a comparative summary of each of the chemical oxidation technologies. These factors can be used to help evaluate the appropriateness and feasibility of the chemical oxidation approach outlined in the corrective action plan. Other differences among alternative chemical oxidation technologies can also help to distinguish their most appropriate application(s). Two characteristics that can be useful in evaluating the feasibility and appropriateness of a proposed chemical oxidation technology are (1) oxygen production for enhancement of aerobic biodegradation, and (2) chemical oxidation potential. Each of these is described in more detail below.

Oxygen Enhanced Biodegradation and Chemical Oxidation Potential. Another distinguishing characteristic of some chemical oxidation technologies is their ability to impart oxygen to the groundwater, which enhances aerobic biodegradation of contaminants while chemically oxidizing petroleum contaminants. In particular, both ozone and hydrogen peroxide are strong oxidizers. During their decomposition, these oxidizers may also generate the hydroxyl radical, an even more powerful chemical oxidizer of organic compounds. As these chemical oxidants react in the subsurface, oxygen is produced which may help enhance aerobic biodegradation processes occurring along the fringes of the treatment area. These chemical oxidation technologies not only chemically oxidize the contaminants in the treatment area but also provide oxygen to promote biodegradation of petroleum contamination. In addition, chemical oxidants can oxidized ferrous iron minerals to ferric iron, and transform other reduced forms to oxidized forms that anaerobic microbes can use.

Ozone and hydrogen peroxide can help to fully or partially chemically oxidize the recalcitrant subsurface petroleum contamination while providing oxygen for in-situ bioremediation of the contamination. Either of these technologies may be applied to sequentially treat the contamination via oxidation, followed by bioremediation, or configured for concurrent treatment relying on oxidation for core treatment with bioremediation as the treatment approach in the peripheral reaches of the plume.

Exhibit XIII-11 Relative Power of Chemical Oxidants[4]		
Compound	**Oxidation Potential (volts)**	**Relative Oxidizing Power (Cl_2 = 1.0)**
Hydroxyl Radical	2.8	2.1
Sulfate Radical	2.6	1.9
Ozone	2.1	1.5
Hydrogen Peroxide	1.8	1.3
Permanganate	1.7	1.2
Chlorine Dioxide	1.5	1.1
Chlorine	1.4	1.0
Oxygen	1.2	0.90
Bromine	1.1	0.80
Iodine	0.76	0.54

However, both ozone and hydrogen peroxide are non-selective with respect to reaction with subsurface organic material. If naturally occurring organic materials (e.g., humic substances) are present in the site subsurface, injected ozone or infiltrated hydrogen peroxide may be lost through the oxidation of these organics, leaving fewer of the oxidants available to react with (and oxidize) the petroleum contaminants. The relative oxidizing power of the chemical oxidants may also be helpful in determining the most appropriate chemical oxidant for site conditions. Exhibit XIII-11 shows that the hydroxyl radical (Fenton's Reagent), ozone, hydrogen peroxide and permanganate, in order of decreasing oxidation strength, are among the strongest chemical oxidizers.

Design Components

Although the design elements of alternative chemical oxidation technologies can vary, Exhibit XIII-12 describes common ones. Several of the more important elements are discussed below to assist with evaluation of the corrective action plan. Each of the major headings in the exhibit above is discussed in more detail below.

[4] Note that these compounds are provided for comparative purposes only. Many of these compounds are not typically used for in-situ chemical oxidation.

Exhibit XIII-12
Common Chemical Oxidation Remediation Design Elements

- Oxidant and Catalyst Delivery Design
  - Theoretical oxidant mass requirement
  - Natural oxidant demand estimates
  - Application delivery rate
  - Number and depth of application points/position
  - Equipment
- Permit Requirements and Thresholds
  - Underground injection/well installation
  - Groundwater (wastewater) discharge
  - Air (soil vapor) discharge
- Performance Monitoring Plan
  - On-going distribution of oxidants
  - Reduction in contaminants (adsorbed and dissolved phases)
- Contingency Plan
  - Inadequate oxidant distribution
  - Lower-than-expected petroleum mass reduction rates
  - Excessive contaminant migration
  - Build-up of excessive recalcitrant petroleum constituents
  - Fugitive (soil vapor) emissions
  - Difficult-to-treat/fouling of treated wastewater discharge
  - Aquifer clogging with precipitates or biomass

Oxidant Application Design should be based primarily on contaminant mass reduction requirements, site characteristics and cleanup goals. Oxidants need to be applied at concentrations and total mass levels that satisfies both the NOD and the oxidant demand of the petroleum hydrocarbons. Note that state regulations may either require permits for oxidant or catalyst injection or prohibit them entirely.

Permit Requirements and Thresholds should be identified in the design so that the system can be constructed to comply with permit requirements and constraints. Depending on the specific chemical oxidation technology and the state in which the site is located, permits may be required for underground injection, treated groundwater discharge (to sanitary or storm sewer, or air (soil vapor) discharge. Several federal, state and local programs either directly manage or regulate aquifer remediation wells (ARWs). Many of these programs require permits for underground injection of oxygen. On the federal level, management and regulation of these wells fall primarily under the underground injection control program authorized by the Safe Drinking Water Act (SDWA). Some states and localities have used these authorities, as well as their own, to extend the controls in their areas to address concerns associated with ARWs.

Aquifer remediation injection wells are potentially subject to at least three categories of regulation. First, a state's underground injection control program (or

in direct implementation states, the federal UIC program) may have jurisdiction over such wells. Second, in some states without UIC programs, the state's program for groundwater protection or national pollution discharge elimination system (NPDES) requirements may apply to remediation wells. Third, remediation wells may be regulated by federal and state authorities through Superfund programs, corrective action programs under RCRA, the UST program, or other environmental remediation programs. In the case of remediation programs, the regulatory requirements typically address the selection of aquifer remediation as a cleanup alternative and establish the degree of required cleanup in soil and groundwater, while deferring regulation of the injection wells used in the remediation to other programs.

Performance Monitoring should be accounted for in the form of a written data quality objective plan that can be used to objectively evaluate chemical oxidation system performance. The monitoring plan should outline a data quality objective process that defined the criteria that the data collection should satisfy, including when to collect samples, where to collect samples, the tolerable level of decision error for the study, and how many samples to collect, balancing risk and cost in an acceptable manner. It should describe the approaches and methods that will be used to evaluate chemical oxidation system effectiveness in each of the following:

- Delivering the oxidant and catalyst to the subsurface.
- Distributing the oxidant throughout the contaminated area.
- Reducing adsorbed and dissolved phase petroleum concentrations.
- Achieving other performance requirements consistent with site-specific cleanup goals.
- Confirming chemical oxidation effectiveness through long-term monitoring.

Contingency Plans should also be prepared as part of the remedial design. The design should anticipate low-likelihood problems and potentially changing environmental conditions, as well as outline specific response actions that may be taken. Examples include response actions to take if performance monitoring data indicate any of the following:

- Inadequate oxidant distribution
- Inadequate permeation of low permeability soil zones
- Low petroleum mass reduction rates
- Excessive contaminant migration
- Recalcitrance of constituents
- Production of excessive fugitive emissions
- Rebound in contaminant levels measured during long term post-application monitoring
- Evidence of oxidant moving in wrong direction

Components of Chemical Oxidation Systems

Having briefly covered factors that affect the selection and design of a particular chemical oxidation technology and the critical elements that should be included in the corrective action plan chemical oxidation design, it is now appropriate to discuss major components of various chemical oxidation systems. This discussion should help in the evaluation of the corrective action plan chemical oxidation design.

Exhibit XIII-13 summarizes some of the major equipment components associated with each of the more common chemical oxidation technologies. Note that this exhibit continues across three pages. Depending on which chemical oxidation technology has been selected in the corrective action plan, a subset of these major system components should be presented and discussed and schematically depicted (e.g., process flow diagram) in the corrective action plan. The design should relate capacities of these equipment components to design requirements (e.g., required oxidant production and delivery rates).

Exhibit XIII-13
Major Components of Chemical Oxidation Systems

Component	Function
Hydrogen Peroxide/Fenton's Reagent Injection Systems	
Extraction Wells	Wells may be used to capture soil vapor generated by the oxidation process that may be heated and contain elevated levels of VOCs and oxygen (i.e., soil vapor extraction). Can also be used to help control groundwater flow during oxidant and catalyst delivery (i.e., groundwater extraction).
Injection Wells or Infiltration Galleries	Injection wells, infiltration galleries or a combination of these may be used to inject hydrogen peroxide catalyst solution, and compressed air for reagent contact with the treatment zone contaminants. Diluted peroxide and peroxide slurries can be injected via lance points.
Extraction, Injection, Transfer, and Metering Pumps and Tanks	Extraction, injection, transfer, and metering pumps may be used for various purposes including: transferring groundwater from and back into the ground; transferring extracted groundwater between different components of the treatment system; and metering hydrogen peroxide and catalyst into the infiltration system to maintain design concentrations. Note that pumps can be damaged by hydrogen peroxide and may need frequent replacement.
Blowers	Extraction blower(s) may be used to draw soil vapor from extraction wells to capture fugitive VOC vapors and oxygen.

Exhibit XIII-13 Major Components of Chemical Oxidation Systems (continued)	
Component	**Function**
Hydrogen Peroxide/Fenton's Reagent Injection Systems (continued)	
Groundwater and Vapor Treatment Equipment	Extracted groundwater or soil vapor may be treated to remove petroleum hydrocarbons by various means such as: granular activated carbon adsorption, air stripping or others.
Instrumentation and Controls	Used to integrate and activate/deactivate system components. Help maintain the balance of flows consistent with the design and to safeguard against inadequate treatment or inappropriate discharges.
Monitoring Wells	Used to collect environmental samples analyzed in laboratories and field to evaluate on-going effectiveness of remediation. Groundwater well samples tested for peroxide and contamination to evaluate overall effectiveness of oxidant delivery/dispersal and the contaminant reductions over time. Long term monitoring of contaminant concentrations is essential to evaluating the effectiveness of the technology.
Permanganate Injection Systems	
Extraction Wells	Wells may be used to enhance hydraulic gradient across the treatment area so that permanganate can be more rapidly delivered to and put in contact with site contaminants.
Injection Wells or Infiltration Galleries	Injection wells, infiltration galleries or a combination of these may be used to inject permanganate or permanganate amended groundwater into the treatment zone. Upgradient injections of amended groundwater with downgradient extraction of groundwater may enhance the hydraulic gradient across the treatment zone, thereby accelerating permanganate delivery to the contamination.
Extraction, Injection, Transfer, and Metering Pumps and Tanks	Extraction, injection, transfer, and metering pumps may be used for various purposes including: transferring groundwater from and back into the ground; transferring extracted groundwater between different components of the treatment system; and metering permanganate into the infiltration system to maintain design concentrations.
Groundwater Treatment Equipment	Extracted groundwater may be treated to remove petroleum hydrocarbons by various means such as: granular activated carbon adsorption, chemical oxidation, air stripping or others.
Instrumentation and Controls	Used to integrate and activate/deactivate system components to maintain the balance of flows consistent with design and to safeguard against inadequate treatment or inappropriate discharges.

Exhibit XIII-13 Major Components of Chemical Oxidation Systems (continued)	
Component	**Function**
Permanganate Injection Systems (continued)	
Lance Injection Points	Permanganate in slurry form may be injected into the subsurface over a grid using push-point technologies.
Large Diameter Auger Deep Soil Mixing	Permanganate may be mixed deeply into the contaminated soil and groundwater using large diameter augers in patterned drilling over contaminated areas.
Monitoring Wells	Used to collect environmental samples tested in laboratories and the field to evaluate on-going effectiveness of remediation. Comparative analyses over time of groundwater samples from these wells for dissolved oxygen and petroleum contamination indicates how effectively oxygen is being delivered/dispersed and contaminant reductions are occurring.
Ozone Injection Systems	
Sparging Wells	Used as a conduit to inject ozone into contaminated groundwater. The ozone is sparged near the base of the soil and groundwater petroleum contamination so that it may contact the contaminants and provide oxygen to the hydrocarbon degrading bacteria.
Air Compressing Equipment	Used to pressurize ambient air needed to generate ozone and to provide the pressure needed to inject the ozone beneath the water table. Oil-less compressors are preferred, because air compressor equipment must supply oil- and contaminant-free air to minimize in-line reactions with and pre-mature decomposition of ozone.
Ozone Generating Equipment	Used to generate ozone gas on-site, typically at concentrations of about 5%.
Soil Vapor Extraction/ Treatment Equipment (optional)	Used, if necessary, to control fugitive soil vapor ozone and volatilize organic compounds emissions in the unsaturated zone. May consist of low vacuum/flow blower to generate vacuum conditions in unsaturated zone and collect the vapors. Off-gas treatment may be necessary and may be accomplished using granular activate carbon, biofilters or other technologies.
Instrumentation and Controls	Used to integrate and activate/deactivate system components to maintain the balance of flows consistent with the design and to safeguard against inadequate treatment or inappropriate discharges.
Monitoring Wells	Used to collect environmental samples tested in laboratories and the field to evaluate on-going effectiveness of remediation. Comparative analyses over time of groundwater samples from these wells for dissolved oxygen and petroleum contamination indicates how effectively oxygen is being delivered/dispersed and contaminant reductions are occurring.

While the sets of major equipment components used by the chemical oxidation technologies differ significantly, the use of wells by each different approach warrants recognition and further discussion. In particular, the orientation, placement, number and construction of this common design element is worthy of a brief review. wells or gravity-fed into vertical delivery wells. Additionally, hydrogen peroxide-amended groundwater can be re-infiltrated using either vertical or horizontal wells. Although vertical sparge wells are more common for ozone injection, horizontal sparge wells can be used. Permanganate amended groundwater can similarly be re-infiltrated using vertical wells, horizontal wells, infiltration trenches or combined approaches. Well orientation should be based on site-specific needs and conditions. For example, horizontal systems should be considered when evaluating sites that require re-infiltration of amended groundwater into shallow groundwater at high flow rates. They are also readily applicable if the affected area is located under a surface structure (e.g., a building), or if the thickness of the saturated zone is less than 10 feet.

Injection, Extraction and Re-infiltration Wells. Three important considerations are well orientation, well placement and number, and well construction.

- **Well Orientation.** Both horizontal and vertical wells can be used to treat subsurface petroleum releases with any of the various chemical oxidation systems. However, hydrogen peroxide and a catalyst (Fenton's Reagent) is most commonly injected into vertical sparge wells.

- **Well Placement and Number of Wells**. The number and location of wells are determined during the design to accomplish the basic goals of (1) optimizing reliable oxidant and catalyst delivery to the contaminated area, and (2) providing conduits to measure chemical oxidation system performance. For permanganate re-infiltration systems this typically means placing re-injection wells in the upgradient portion of the source area(s) while extracting groundwater from downgradient locations. This approach simultaneously provides an enhanced hydraulic gradient, which can accelerate oxidant distribution across the impacted area. The number, location and design of the extraction wells will largely be determined from site-specific hydrogeology, the depth(s) and thickness(es) of the contaminated area(s), and the results of field-scale pilot testing and hydraulic modeling. Note that well placement may need to be changed as remediation progresses, as wells often generate preferential flow paths over time.

Determining the number and spacing of the wells for ozone injection may also be determined through field-scale pilot testing. However, the following general points should be considered.

- Closer well spacing is often appropriate in areas of high contaminant concentrations to enhance contaminant contact and oxidant delivery/distribution where the oxidant demand is the greatest.

- Direct delivery of oxidant into the contaminated material using closer well spacings can deliver, disperse, and significantly decrease the treatment timeframe through groundwater advection/dispersion more quickly than oxidant delivery.

At sites with stratified soils, wells screened in strata with low permeabilities often require closer well spacing than wells screened in strata with higher permeabilities.

Well Construction. Chemical oxidation system wells are constructed of 1- to 6-inch diameter PVC, galvanized steel, or stainless steel pipe, although caution should be exercised in the use of stainless steel pipe in low-pH conditions. Ozone injection sparge wells have screened intervals that are normally 1-3 feet in length and situated within the contaminated zone. Injection sparge points must be properly grouted to prevent the oxidants from moving directly up the well annulus to the unsaturated zone rather than being forced into the contaminated aquifer ("short circuiting" of the injected oxygen) when horizontal injection oxidant exits along the entire screen length. Exhibit XIII-14 shows a cross-section typical ozone or hydrogen peroxide (Fenton's Reagent) sparge well.

Re-infiltration wells typically have screen lengths that extend from the base of the wells into the unsaturated zone. Groundwater extraction wells should ideally be screened in the saturated interval containing the greatest mass of hydrocarbons. Field-scale pilot studies and subsequent data analysis and hydraulic modeling can greatly assist one in determining the configuration and construction design of groundwater extraction and injection wells.

Step 4: An Evaluation of the Operation and Monitoring Plan

Remedial Progress Monitoring

Significant uncertainties associated with site conditions can remain even as remedial designs are completed and implemented. In the start-up period, these unknowns frequently can result in operations that vary from the original design. These variances often require adjustments to account for unforeseen conditions and to optimize system performance. Unfortunately, in many cases, the need for these adjustments can go unrecognized for a long time.

In some cases, the delay in recognizing that remedial system adjustments are necessary may be attributed to slow responses in subsurface conditions to the applied technology. Because these subsurface responses to the applied remedial technology can be delayed, there is often the tendency to give the remedial program more time to work (sometimes years) before making system

modifications or adjustments. In other cases, the delay may stem from misuse or misinterpretation of site data, which can lead to the conclusion that the remedial system is performing well when it is, in fact, not. An example of this misuse is the practice of using groundwater analytical data from chemical oxidant delivery wells as an indicator of remedial progress. In this case, an assessment is biased by the localized effects of concentrated chemical oxidation in the immediate vicinity of the oxidant delivery wells, but does not provide an objective measure of the chemical oxidation system's ability to distribute the oxidant and contact the adsorbed contaminants throughout the treatment area.

However, at many sites remedial system or application operational efficiencies are not optimized simply because an adequate performance monitoring plan has either not been developed or has not been fully implemented. In such cases, the designed remedial system may be installed, implemented, and allowed to run its course with insufficient numbers or types of samples to determine whether the remedial system is performing in accordance with design expectations. The result of such monitoring approaches can be the discovery of a sub-standard or failed remediation program years after its implementation.

The previous section discussed the importance of developing a comprehensive remedial progress monitoring plan. This covers the topics that should be addressed in such a plan to ensure objective gauging of remedial system performance. Necessary optimization adjustments can be made early in the remediation program as well as throughout the duration of a chemical oxidation remedial program. The following section provides a focused discussion on evaluation sampling and chemical oxidation evaluation criteria that should be examined during review of a operations and monitoring plan that proposes to use chemical oxidation.

Evaluation Sampling

Evaluation sampling is performed to gauge the effectiveness of the chemical oxidation program relevant to design expectations. Based on a comparison of the actual field sampling data to design and operational expectations, timely modifications to the system or operating procedures can be made to optimize the application of chemical oxidants early in the remediation program. Projects with regular performance reviews guided by the results of such sampling and monitoring programs have a greater chance of achieving the design remedial goals within desired timeframes and, potentially, at a lower cost.

Various environmental media are sampled to evaluate system performance. Groundwater, soil, and soil vapors from the treatment area and vicinity are commonly sampled to determine the degree to which the chemical oxidation program is meeting the basic objectives of the approach, including:

- Delivering oxidants to the treatment zone at required design rates.

- Distributing the oxidants across the target contaminated area to contact the contaminants.

- Reducing concentrations of petroleum hydrocarbons in soil and groundwater at design rates through chemical oxidation of the petroleum compounds.

Exhibit XIII-14 identifies those parameters that are commonly measured in groundwater, soil and soil vapor samples to help evaluate chemical oxidation progress and system performance. A brief description of the respective sampling frequencies and the relevance and significance of each parameter to the performance evaluation are also provided in the exhibit. A key element is the location(s) where performance evaluation sampling takes place relative to subsurface oxidant delivery points. As stated in the exhibit, performance evaluation samples should not normally be collected from oxidant delivery locations.

Exhibit XIII-14
Common Performance Monitoring Parameters and Sampling Frequencies

Analytical Parameter	Sampling Frequency			Purpose
	Start-up Phase (7-10 days)	Remediation/ Post-Application Long-Term Monitoring Phase		
	Daily	*Weekly to Monthly*	*Quarterly to Annually*	
GROUNDWATER *Samples should be collected from monitoring wells located in and around the treatment area and from extraction wells (if used). Samples should not be collected from oxidant delivery wells for evaluating system performance because they represent highly localized effects of the remediation program.*				
Dissolved Oxygen	X	X		Determines the effect of the oxidants on dissolved oxygen levels and potential to boost aerobic biodegradation as a secondary benefit.
Redox Potential	X	X		Yields data on system's ability to increase the extent of aerobic subsurface environment.

Exhibit XIII-14
Common Performance Monitoring Parameters and Sampling Frequencies (continued)

Analytical Parameter	Sampling Frequency: Start-up Phase (7-10 days)	Sampling Frequency: Remediation/ Post-Application Long-Term Monitoring Phase		Purpose
	Daily	***Weekly to Monthly***	***Quarterly to Annually***	
GROUNDWATER (continued) *Samples should be collected from monitoring wells located in and around the treatment area and from extraction wells (if used). Samples should not be collected from oxidant delivery wells for evaluating system performance because they represent highly localized effects of the remediation program.*				
pH	X	X		Confirms pH conditions are stable and suitable for Fenton's Reagent, or identifies trends of concern.
H_2O_2, Ozone, or Permanganate	X	X		Provides information on distances the oxidizing compounds are able to be transmitted by the remedial system before decomposing.
Petroleum COCs			X	Indicates remedial progress.
Degradation Daughter Constituents (e.g., TBA)			X	Could indicate incomplete oxidation process.
Water Table Elevations	X	X		Determines if hydraulic conditions (groundwater flow) are consistent with design intent or if chemical oxidation has had an unanticipated affect on these conditions.

Exhibit XIII-14 Common Performance Monitoring Parameters and Sampling Frequencies (continued)				
Sampling Frequency				
Analytical Parameter	**Start-up Phase (7-10 days)**	**Remediation/ Post-Application Long-Term Monitoring Phase**		**Purpose**
	Daily	***Weekly to Monthly***	***Quarterly to Annually***	
SOIL VAPOR *Samples should be collected from monitoring wells located in and around the treatment area that are screened in the unsaturated zone and from soil vapor extraction wells (if used). Samples should <u>not</u> be collected from oxidant delivery wells for evaluating system performance because they represent highly localized effects of the remediation program.*				
Carbon Dioxide	X	X		Provides evidence of chemical oxidation.
Oxygen	X	X		Indicates potential losses of introduced oxygen through the unsaturated zone.
Volatile Petroleum Contaminants (Constituents) of Concern (COCs)	X	X		Suggests residual sources in soil or fugitive emissions associated with the remedial effort.
Fugitive Ozone or Hydrogen Peroxide	X	X		Determines losses of oxygen-yielding reagents delivered to the subsurface.
SOIL *Samples should be collected from borings or using push point or drill rig sampling equipment in and around the treatment area. Soil samples should consistently be collected from same contaminated sections of stratigraphic interval for comparison to earlier samples from same locations and depths.*				
Petroleum COCs			X	Provide a measure of remedial progress, contaminant mass reducions and the extent to which chemical oxidation of adsorbed contaminants is limited.

The performance of the chemical oxidation system should be determined by the chemistry of soil and groundwater located between, around and downgradient of oxidant delivery locations rather than inside or in the immediate vicinity of the oxidant delivery points. Conditions inside or in the immediate vicinity of oxidant injection locations have been preferentially altered by chemical oxidation to destroy the petroleum contaminants. Therefore, data from these locations are not representative of the subsurface conditions that exist beneath most of the site. To understand the effect the chemical oxidation system is having on the subsurface conditions as a measure of its performance, samples of soil, groundwater and soil gas should be collected from alternate locations. In review of the performance monitoring plan in the corrective action plan, it should be verified that a sufficient number of sampling locations exist between oxidant application points to provide the necessary performance sampling data. A description of how these data may be used to evaluate the chemical oxidation system performance is provided below.

Evaluation Criteria

The evaluation sampling described above provides the evidence needed to assess the chemical oxidation system performance. This evidence requires examination and interpretation to confirm chemical oxidation system effectiveness and whether system or application modifications may be warranted. A discussion of these data and how system performance can be interpreted is provided below. In particular, an evaluation of performance is examined from the following two broad chemical oxidation system requirements:

- Oxidant Delivery and Distribution
- Permanent Contaminant Mass Reduction and Attainment of Cleanup Goal

Each of these is discussed in more detail below.

Oxidant Delivery and Distribution. Performance sampling may indicate that the chemical oxidation system is meeting design specifications for oxidant delivery and distribution if the data show the following:

- Oxidant and catalyst are being delivered to the subsurface at the design mass delivery rate or design adjusted rate based on analysis of field monitoring data; and
- The oxidant and catalyst are detected in samples from the treatment area at the design concentrations.

If the performance monitoring data suggest that one or more of these conditions is not met, the system may not be meeting the requirements of the design, and system adjustments or modifications may need to be made. As previously discussed, the remedial system design should include contingency planning that explores performance deficiency scenarios and identifies possible solutions.

Oxidant delivery deficiencies may be overcome by simply adjusting system flow rates, upgrading equipment capacities or increasing oxidant dose concentrations. However, occasionally, oxidant delivery rates may be limited by the capacity of the subsurface to transport the delivered oxidant mass.

Perhaps the most challenging performance problem is when a chemical oxidation system or program is unable to deliver oxidants to a portion or multiple portions of a contaminated area. There are many ways that oxidants distributed from delivery points could fail to reach target contaminated area. These may include:

- Low permeability heterogeneous soils.
- Low hydraulic gradient and groundwater flow.

Possible remedies to the performance problem include adding additional oxidant delivery points; increasing oxidant delivery rates; increasing dose concentrations; or enhancing hydraulic gradients and groundwater flow.

Permanent Contaminant Mass Reduction And Attainment of Cleanup Goal. The effectiveness of a chemical oxidation program can only be determined after examining the reduction in contaminant mass, and after identifying whether the contaminant mass reduction is sufficient for the soil and groundwater to permanently meet cleanup standards.

It is not sufficient to simply review groundwater monitoring data collected during and weeks or even months after completing a chemical oxidation program. These data are often biased, reflecting the successful oxidation of the most readily contacted contaminants, predominantly contaminants in the most permeable soil zones. False positive evaluations of chemical oxidation program performance can result from reliance on short-term post-chemical oxidation application groundwater monitoring data. These false positive evaluations may become evident during long-term groundwater monitoring when contaminant levels rebound as untreated contaminant mass in the less permeable soil bleeds back out and re-contaminates the more permeable zones. Long term (e.g., months to years), post-chemical oxidation groundwater monitoring is needed to evaluate the effectiveness of a chemical oxidation program.

Program effectiveness may also be evaluated by estimating the mass of contaminants destroyed, which can be accomplished using sample analytical data. Provided that a sufficient number of soil samples are collected and analyzed for the treatment area, soil sampling using identical methods before and after implementation of a chemical oxidation program may indicate the volume of contaminant mass destroyed by the oxidants. Comparing the estimated actual mass destruction with the projected mass destruction (as predicted in the corrective action plan) will reveal the relative effectiveness the oxidant application program. If the contaminant mass destroyed is roughly the amount predicted during the design, the chemical oxidation program can be considered a success.

Should significantly more contaminant mass be destroyed than predicted, the program might be characterized as highly successful, but if significantly less contaminant mass is destroyed than predicted, it may be more accurately characterized as a failure. As the remediation program progresses, it may be necessary to review the project goals, particularly if the source has been effectively reduced (e.g., 70-90%), but significant contaminant mass remains in the associated plume. It may be necessary to perform a second phase of remediation (e.g., apply a different oxidant, move to monitored natural attenuation) to determine whether site cleanup has been achieved or is feasible.

The most direct measurement of the success of a chemical oxidation program is to determine whether the groundwater and soil remedial objectives have been met and can be sustained indefinitely following chemical oxidation treatment. Post-application monitoring should be conducted for a minimum of one year following chemical oxidation treatment to confirm that short-term reductions can be sustained, indicating that contaminant levels have been adequately reduced throughout the contaminated soil and groundwater.

References

Baker, Katherine H. and D.S. Herson. Bioremediation. McGraw-Hill, Inc. 1994.

Brown, Richard, Chris Nelson, M. Leahy. Combining Oxidation and Bioremediation for the Treatment of Recalcitrant Organics. In Situ and On Site Bioremediation. Battelle Press. 1997.

Brown, R. A., R.D. Norris, R.L Raymond. Oxygen Transport in Contaminated Aquifers With Hydrogen Peroxide. API Conference "Petroleum Hydrocarbon and Organic Chemicals in Groundwater: Prevention, Detection and Restoration", Houston, TX. 1984.

Brown, R.A. Bioremediation of Petroleum Hydrocarbons: A Flexible, Variable Speed Technology. *Remediation*. Summer/1996.

Brown, R. A. and R. D. Norris. The Evolution of a Technology: Hydrogen Peroxide in *In-situ* Bioremediation. In Situ Hydrocarbon Bioremediation. Hinchee, R.E. Ed., CRC Press, Boca Raton. 1994.

Carter, Sean. Enhanced Biodegradation of MTBE and BTEX Using Pure Oxygen Injection. In Situ and On Site Bioremediation. Battelle Press. 1997.

Chapman, Steven W. Semi-Passive Oxygen Release Barrier for Enhancement of Intrinsic Bioremediation. In Situ and On Site Bioremediation. Vol. 4. 1997.

California MTBE Research Partnership. Treatment Technologies for Removal of Methyl Tertiary Butyl Ether (MTBE) from Drinking Water, National Water Research Institute, Fountain Valley, California, February 2000.

Chapelle, Francis H. Bioremediation of Petroleum Hydrocarbon-contaminated Ground Water: The Perspectives of History and Hydrogeology. *Ground Water*, Vol. 37, No. 1. Jan.-Feb. 1999.

Chien Chin. Assessment of the Applicability of Chemical Oxidation Technologies for the Treatment of Contaminants at LUST Sites, Chemical Oxidation, Technologies for the Nineties. Technomic. 1993.

Christian, B.J, L.B. Pugh and B.H. Clarke. Aromatic Hydrocarbon Degradation in Hydrogen Peroxide- and Nitrate-Amended Microcosms. In Situ and On Site Bioremediation Symposium. Battelle Press. 1995.

Cole, G. Mattney. Assessment and Remediation of Petroleum Contaminated Sites. CRC Press. 1994.

Droste, Edward. Observed Enhanced Reductive Dechlorination After *In-situ* Chemcial Oxidation Pilot Test. Proceedings, Remediation of Chlorinated and Recalcitrant Compounds. Battelle Press. 2002.

Dupont, Ryan R. and Robert E. Hinchee. *Assessment of In-Situ Bioremediation Potential and the Application of Bioventing at a Fuel-Contaminated Site*, and Brown, R. A. and R. D. Norris. *Oxygen Transport in Contaminated Aquifers*. Presented a NWWA and API Conference "Petroleum Hydrocarbon and

Organic Chemicals in Groundwater: Prevention, Detection and Restoration". Houston, TX. 1984.

Fry, Virginia A., J. D. Istok, K. T. O'Reilly. Effect of Trapped Gas on Dissolved Oxygen Transport - Implications for In Situ Bioremediation. *Ground Water*, Vol. 34, No. 2. Mar-Apr 1996.

Groundwater Remediation Technologies Analysis Center. Trends in Applying Innovative *In-situ* Chlorinated Solvents Remediation Technologies - Poster. Battelle Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey CA, 2002.

Hinchee, R.E., D.C. Downey, P.K. Aggarwal. Use of Hydrogen Peroxide as an Oxygen Source of *In-situ* Biodegradation: Part I. Field Studies. *Journal of Hazardous Materials*. 1991.

Johnson, R, J. Pankow, D. Bender, C. Price and J. Zogorski. MTBE, To What Extent Will Past Releases Contaminate Community Water Supply Wells? *Environmental Science and Technology/News*. 2000.

Nelson, C.H. and R. A. Brown. Adapting Ozonation for Soil and Groundwater Cleanup. *Chemical Engineering*. November 1994.

Norris, R. D., K. Dowd and C. Maudlin. The Use of Multiple Oxygen Sources and Nutrient Delivery Systems to Effect *In-situ* Bioremediation of Saturated and Unsaturated Soils. In Situ Hydrocarbon Bioremediation. Hinchee, R.E. Ed. CRC Press, Boca Raton. 1994.

Prosen, B. J., W.M. Korreck and J. M. Armstrong. Design and Preliminary Performance Results of a Full-scale Bioremediation System Utilizing on On-site Oxygen Generation System. *In-situ* Bioreclamation: Applications and Investigations for Hydrocarbon and Contaminated Site Remediation. Eds., R. E. Hinchee. Butterworth-Heinemann. 1991.

Riser-Roberts, Eve. Remediation of Petroleum Contaminated Soils. Lewis Publishers. 1998.

Siegrist, Roberts L., et al. Principles and Practices of *In-situ* Chemical Oxidation Using Permanganate. Battelle Press. 2001.

USEPA. In Situ Remediation Technology: In Situ Chemical Oxidation. EPA 542-R-98-008. 1998.

USEPA. Cost and Performance Report, Enhanced Bioremediation of Contaminated Groundwater. 1998.

USEPA. The Class V Underground Injection Control Study, Volume 16, Aquifer Remediation Wells, EPA/816-R-99-014, 1999.

Checklist: Can Chemical Oxidation Be Used At This Site?

This checklist can help you to evaluate the completeness of the corrective action plan and to identify areas that require closer scrutiny. As you go through the corrective action plan, answer the following questions. If the answer to several questions is "no", you will most likely want to request additional information to determine if the proposed chemical oxidation technology and approach will accomplish the site cleanup goals.

1. Site Factors

Yes	No	
o	o	Is the soil intrinsic permeability greater than 10^{-9} cm^2?
o	o	Is the soil generally free of impermeable or low permeability layers that could retain significant petroleum contaminant mass and limit the bioavailability of this mass?
o	o	Is the soil profile determined from geologic boring logs generally free of natural organic material (e.g., layers of peat or humic material)?
o	o	Is the soil temperature expected to be 10°C or higher during remediation?
o	o	Is the pH of site groundwater between 5 and 9?
o	o	Is the dissolved iron concentration in the site groundwater < 10 mg/L?
o	o	Have imminent likely excessive risks to human health or the environment (if any, associated with the petroleum contamination) been eliminated?
o	o	Does the state have specific permitting requirements?

2. Chemical Oxidation Design

Yes	No	
o	o	Has the mass of petroleum hydrocarbons requiring biodegradation been estimated?
o	o	Has the mass of dissolved oxygen required to biodegrade the petroleum contaminants been estimated?
o	o	Can the proposed chemical oxidation approach deliver the necessary oxygen mass to the treatment area within the estimated cleanup time?
o	o	Is the capacity of the chemical oxidation treatment system sufficient to generate and deliver oxygen at the required design rate?
o	o	Is the density and configuration of oxygen delivery points adequate to uniformly disperse dissolved oxygen through the target treatment zone, given site geology and hydrologic conditions?

3. Permitting Issues

Yes	No	
o	o	Does the state have specific permitting requirements? If so, are they addressed in the plan?

4. Written Performance Monitoring Plan

Yes	No	
o	o	Will a comprehensive set of baseline sampling be performed prior to chemical oxidation system start-up?
o	o	Does the plan specifically exclude sampling from oxygen delivery wells when collecting data to evaluate chemical oxidation system performance?
o	o	Are monitoring wells adequately distributed between oxygen delivery locations to collect groundwater and soil vapor samples to evaluate the performance of the chemical oxidation system?
o	o	Does the written plan include periodically collecting soil samples from the contaminated interval(s) at locations between oxygen delivery locations?
o	o	Will the soil, soil vapor and groundwater samples be analyzed for the majority of the recommended performance monitoring parameters?
o	o	Will frequencies of performance monitoring correspond to those identified in Exhibit XIII–14?