

# **DESIGN CONSIDERATIONS FOR IN-SITU CHEMICAL OXIDATION USING HIGH PRESSURE JETTING TECHNOLOGY**

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## **INTRODUCTION**

One of the main challenges for environmental professionals involved in the assessment and remediation of contaminated sites is the development of a remediation strategy to ultimately achieve site closure and allowing for future development of the site with minimal liability for its intended use. When excavation and subsequent treatment and/or disposal is not viable, environmental professionals typically look toward in-situ technologies to achieve this goal. A variety of geologic considerations exist for in-situ remediation. Although many good in-situ remediation technologies exist, to illustrate the factors and evaluate the decision making process, this article reviews one technology (in-situ chemical oxidation) using one delivery method (high pressure jetting ) with two treatment oxidants (hydrogen peroxide and potassium permanganate).

In-situ remediation is the reduction, extraction, removal, stabilization and/or containment of contaminants in the subsurface to a level acceptable for site closure. Site closure is essentially the reduction of risks posed by the presence of contaminants in the subsurface to an acceptable level. In-situ remediation technologies can be divided into two general categories. One category involve a strategy of extraction or removal of contaminants from the subsurface, typically in association with existing conventional approaches such as soil vapor extraction of the vadose zone or pump and treat for groundwater. The other primary category involves a strategy of stabilization/destruction and/or containment of the contaminant in the soil matrix. Where extraction and removal reduces the overall concentration and quantity of contaminant in the subsurface, the latter simply reduces contaminant mobility and in some cases its toxicity.

Regardless of the strategy employed, most in-situ systems designed for the reduction or removal of contaminants incorporate the introduction of some treatment media. Over the past two decades, environmental professionals have been innovative in their approach to in-situ remediate or enhance remediation of subsurface contaminants. They have injected air, water, bacteria, heat, electrical currents, radio frequencies and/or chemicals (i.e., which includes nutrients, oxidants, catalysts, etc.). They have also utilized plants (phytoremediation), pneumatically and hydraulically fractured subsurface materials, or constructed reactive and filtration walls, into or within discrete zones, with varying success to achieve this goal.

## **THE IMPORTANCE OF ADEQUATE HYDROGEOLOGIC CHARACTERIZATION**

In formulating any remedial strategy, understanding of the subsurface environment is essential to development of a practical, efficient, cost-effective and timely in-situ remediation strategy. In performing peer review of numerous remedial histories, it is a common occurrence to encounter ineffective and inefficient in-situ remediation systems due in large part to a greater emphasis placed on engineering design, and less toward subsurface lithologic characterization and basic hydrogeologic understanding. From the client's perspective, characterization does not directly reduce or clean up the site, whereas, actual system design and implementation does. Another factor commonly overlooked is the overall development of a closure strategy in the early phases of the project. It is thus important for environmental professionals to make their client understand that a sound and comprehensive characterization program actually saves money over the course of the project, and allows for smart design of a remedial strategy that will be both effective and efficient.

Before a remedial strategy and system design can be formulated, a thorough understanding of the subsurface environment must be attained. System design is optimized when important geologic factors such as lithology, permeability, porosity, soil and groundwater chemistry, and contaminant type and concentration, and their anticipated fate and transport, are fully evaluated with respect to the design and installation of injection ports, and rates of injection. Geologic factors control the movement, distribution and quality of groundwater as well as contaminants via a combination of several physical, chemical, and biological processes (Testa, 1994; Testa and Winegardner, 2000). Thus, chemical reaction and biological degradation rates must be considered.

The largest percentage of environmentally contaminated sites lie on alluvial and coastal plains consisting of complex interstratified sediments. Lithologic contacts, some abrupt and some gradational, significantly influence permeability, porosity and preferred flow pathways of contaminants in soil and groundwater. The majority of contaminated sites in the world have some component of impacted shallow soil or unconsolidated sediments. Shallow groundwater contamination can result from surface or near-surface activities including unauthorized releases or leaching from landfills, repositories, underground and above-ground storage tanks and pipelines, wells, septic systems, and accidental spills. Contamination can also occur from the application of agricultural chemicals to the land surface, or from non-point sources. Deeper soil or rocks may also become impacted due to preferred flow pathways along fault zones, lack of a competent aquitard or confining layer to inhibit migrating contaminants or via conduits such as abandoned mines or improperly designed or abandoned wells

Since geology is the prime-controlling agent for the movement of groundwater, thus, contaminants, comprehensive understanding of the three-dimensional framework of geologic materials is essential. This understanding provides for a comprehensive assessment of groundwater vulnerability to contamination, and the lateral and vertical extent of hazardous and toxic constituents in the subsurface, and allows for effective design and monitoring of subsurface remedial systems.

Lithology and stratigraphy are the most important factors affecting contaminant movement in soils and unconsolidated sediments. Stratigraphic features including

geometry and age relations between lenses, beds and formations and lithologic characteristics of sedimentary rocks such as physical composition, soil type and chemistry, grain size, grain packing, and cementation, are among the most important factors affecting groundwater and contaminant flow in sedimentary rocks. Igneous-metamorphic rocks are geologic systems produced by deformation after deposition or crystallization. Groundwater and contaminant flow in igneous-metamorphic rocks is most affected by structural features such as cleavages, fractures, folds and faults.

## **IN-SITU REMEDIATION TECHNOLOGIES**

The main benefits of in-situ remediation systems over conventional methods are the lower final cost for remediation, minimum cost for operations and maintenance, no moving parts that could break and no discharge permits or waste disposal of liquids for in-situ groundwater treatment. In-situ remediation programs require detailed understanding of the lithology and hydrogeology of the subsurface. The typical timeline is broken into five main tasks. The first task is the characterization of the subsurface, typically using a direct push technology soil and groundwater sampling rig or hollow stem auger rig. Other specialized rigs might be required, depending on the subsurface lithology. During this phase of work, soil and water samples are collected to evaluate the vertical and lateral extent of contamination and the distribution of contaminants. For remediation using a chemical oxidation technique, chemical parameters such as contaminant concentrations in soil and groundwater, pH, alkalinity, iron content, total organic compounds (TOC), vertical and horizontal porosity and permeability as well as other parameters are evaluated. A specific chemical stoichiometry is determined in the laboratory to determine optimum contaminant treatment. If aerobic bioremediation is an appropriate remediation option, microbial parameter studies (total heterotrophs, specific contaminant degraders), total organic carbon (TOC), alkalinity, dissolved oxygen, pH, and nutrient levels (ammonia nitrogen, ortho-phosphate), as well as other parameters are examined. Anaerobic bioremediation parameter studies include the microbial counts, as well as nitrate, sulfate, ferric iron, pH, and Redox. A typical in-situ remediation program schedule is summarized in Table 1.

In-situ treatment technologies can be an attractive alternative when on-site activities or structure precludes more conventional remediation methods, relatively deeper soils are impacted, and/or when tight time constraints are not an issue. The key to the injection of liquids for in-situ remediation of soil and groundwater is achieving proper exposure of the treatment chemicals and amendments to the contaminated soil and groundwater, regardless of the delivery method used. Treatment chemicals can be injected to favorably enhance a number of chemical and biological processes: chemical oxidation, enhanced biodegradation, soil flushing, pH adjustment and metals stabilization.

### **Chemical Oxidation**

In-situ chemical oxidizers rapidly treat soils contaminated with toxic and recalcitrant organic wastes (Jacobs, 1995, 1996, 1997). In-situ oxidation uses contact chemistry of the oxidizing agent to react with petroleum hydrocarbons, volatile organic compounds, munitions, certain pesticides and wood preservatives. The gasoline additive, methyl

tertiary butyl ether (MTBE) has been shown to break down with Fenton's chemistry (Jacobs et al. , 2000, Leethem, 2002, Kelly et al., 2002). The two most common liquid oxidizers used in soil and groundwater remediation are hydrogen peroxide and potassium permanganate. These oxidizers are non-selective and will oxidize the contaminants, as well as natural organic material (tree roots, organic carbon), reduced metals, carbonates, and sulfides. Liquid oxidants can act as solvents, desorbing contaminants from soil particles. Several sites have been observed where the concentrations in groundwater increase after the first treatment event, while the vadose zone decreases in contaminant concentrations. This rebound effect is noted, however after several treatment events total contaminant concentrations are reduced in both groundwater and vadose zones.

Tables 2 and 3 show how hydrogen peroxide and potassium permanganate relate to other commonly used oxidizers. A summary of the advantages and limitations of these three oxidizers is presented in Table 4. Other oxidants are available, but are less commonly used due to cost, safety and handling issues or potential toxic by-products.

### Hydrogen Peroxide

A common oxidizer used for in-situ applications is hydrogen peroxide ( $H_2O_2$ ). Hydrogen peroxide is the most common peroxide in commerce. Pure hydrogen peroxide and its aqueous solutions are clear liquids resembling water. Unlike water, the hydrogen peroxide has a slightly sharp and distinctive odor. Low concentrations of hydrogen peroxide are sold in drug stores (1-3%) as a mild antiseptic.

Hydrogen peroxide is one of the earliest chemical oxidants to be discovered and used in industry. It was discovered in the late 1700s and was commercialized in the early 1800s. Hydrogen peroxide works as a remedial treatment chemical in two ways: free radical production and direct chemical oxidation using hydrogen peroxide.

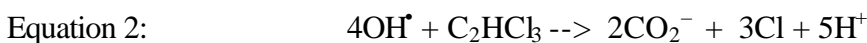
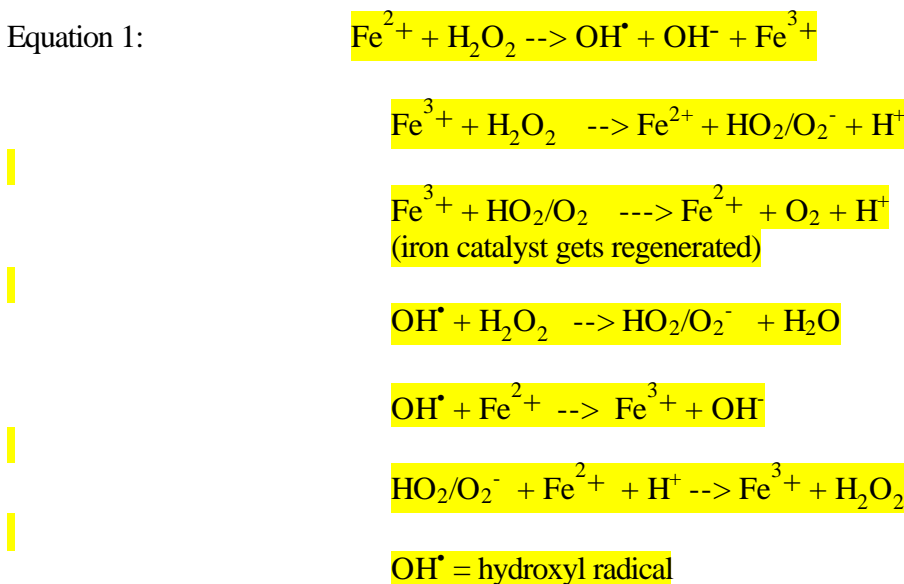
A British Professor H.J.H. Fenton (1893, 1894) described the exothermic and somewhat violent reaction of hydrogen peroxide with iron salts (ferrous sulfate). Fenton's chemistry or Fenton's reagent uses a transition metal catalyst or an acid to enhance the oxidation chemical reaction of hydrogen peroxide by producing the hydroxyl radical.

For in-situ chemical oxidation, the metal catalyst is usually provided by iron oxides within the soil or fill material, or added separately as a solubilized iron salt, such as iron sulfate. In addition, pH adjustment using an acid such as sulfuric ( $H_2SO_4$ ), is common since the chemical oxidation is more rapid and efficient under lower pH conditions (pH 2-4 is optimal). Fenton's chemistry has been well documented for over 100 years and has been in use in water treatment plants for over 50 years. The supportive chemical processes which essentially results in the destruction of petroleum hydrocarbons, and other volatile organic compounds, are well-documented (Watts, 1991, 1992 and 1994). Although Fenton's chemistry has been documented for well over 100 years, it has been employee safety and handling issues that have kept large numbers of environmental contractors from using in-situ chemical oxidation technology. Although this technology can be used safely, significant safety planning, worker training, personal protective

equipment, on-site supervision and monitoring must be an integral part of all oxidation projects.

When chemical oxidant  $\text{H}_2\text{O}_2$  is injected at concentrations of 10 to 35% into the subsurface, it decomposes readily into reactive hydroxyl radicals ( $\text{OH}^\bullet$ ) and water. The hydroxyl radical ( $\text{OH}^\bullet$ ) in the subsurface can be used to rapidly mineralize hydrocarbon, solvent and other contaminants to water and carbon dioxide. This reaction is enhanced in the presence of iron. Iron is naturally occurring in soil and groundwater or can be added during the injection process, if needed. The reaction is based on the principle of Fenton's Chemistry where iron and hydrogen peroxide react to form hydroxyl radicals and other by-products as shown in Equation 1.

The double bonds,  $\text{C}=\text{C}$ , that characterize chlorinated ethenes are more reactive than the single  $\text{C}-\text{C}$  bonds of chlorinated ethanes. Therefore, PCE and TCE are more susceptible to chemical oxidation than TCA. Although all these chemicals are susceptible to chemical oxidation, relative resistance to oxidation from highest to lowest: PCE, TCE, vinyl chloride, phenanthrene, benzene and hexane. The oxidation reaction for a common solvent, trichloroethene (TCE), forms several unstable daughter products (epoxides), then breaks down to ketones and aldehydes, finally yielding carbon dioxide, water and chloride ions (Suthersan, 2002). The oxidation of TCE is shown in Equation 2:



The hydroxyl radical that attacks the carbon-hydrogen bonds is capable of degrading many chlorinated solvents, chloroalkenes, esters, aromatics, pesticides and other recalcitrant compounds such as MTBE, PCP and PCB. The Fenton's chemistry reaction is highly complex. The iron cycles between the Fe(II) and Fe(III) oxidation states yields the hydroxyl radical and other by products (Suthersan, 2002).

Residual  $\text{H}_2\text{O}_2$  not used in the oxidation process breaks-down to water and oxygen in a matter of hours. In addition to the reaction described in Equation 2, there are also a large number of competing reactions including the free radical scavengers, most importantly, carbonate and bicarbonate alkalinity, that will greatly affect the overall reaction scheme. In addition,  $\text{H}_2\text{O}_2$  can serve as an oxygen source for microbes in the subsurface to enhance biodegradation of contaminants.

Although handling hydrogen peroxide and other oxidants requires significant safety training and planning, the oxidant is effective at remediation of a variety of organic contaminants and is relatively inexpensive. The reaction time for hydrogen peroxide in the subsurface is usually within minutes to at most, hours. Rise in temperatures in the subsurface illustrates the exothermic nature of the oxidation process. Rapid degradation of hydrocarbons, solvents and organic compounds is the goal of in-situ chemical oxidation, not the violent decomposition of hydrogen peroxide which does occur at elevated reaction temperatures.

Based on field research, the optimum reaction temperature is relatively low, as measured on the reaction foam in the field using infrared thermal meters is  $35^\circ\text{C}$  to  $41^\circ\text{C}$ . Increases in temperature beyond about  $57^\circ\text{C}$  the peroxide becomes more volatile as it starts to produce a wispy white vapor (Figure 4). The gas is water vapor and carbon dioxide, the end products of chemical oxidation. Subsurface reaction temperatures, as measured using the infrared thermal meter in the range of  $82^\circ\text{C}$  to  $93^\circ\text{C}$  are explosive and unsafe. Temperatures of subsurface chemical reactions can be monitored and lowered by adding water, lowering concentrations of the catalyst or oxidant and reducing injection pressures.

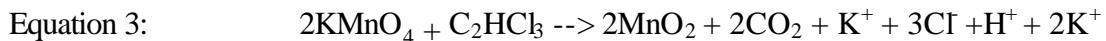
Hydrogen peroxide reacts in an optimal manner in lower pH settings, with lower alkalinity readings. In some cases, acids are used to lower pH. The end products of oxidation are carbon dioxide and water. Trace chloride from chlorinated compounds will likely combine with sodium or calcium ions to form salts or with hydrogen to form weak acids. Careful evaluation of soil and water chemistry using a bench test (Figure 1) with soil and water samples is recommended prior to the start of any injection process. Due to the rapid reaction time, subsurface spacing of injection ports must be relatively close which is dependent on lithology. Clays and silts which are problematic to remediate in-situ, typically require 0.6 to 1 meter spacing, whereas injection ports for clean sand and gravels can be placed at 2 to 3 meter spacing.

### Potassium Permanganate

Potassium permanganate has been used in water treatment plants for several decades because it can oxidize phenols,  $\text{Fe}^{2+}$ ,  $\text{S}^{2-}$  and taste and odor producing compounds (Suthersan, 2002) Although a weaker oxidizer than hydrogen peroxide, potassium permanganate ( $\text{KMnO}_4$ ) lasts longer in the environment (hours to days) and can react in an environment with much higher pH and alkalinity than hydrogen peroxide. For field use, potassium permanganate is shipped as a gray crystalline powder and is mixed with water creating a deep purple liquid. The bright purple color can be used as an indicator

for non-reacted potassium permanganate, whereas the reacted permanganate is dark chocolate brown or black in color, indicating the presence of manganese dioxide ( $\text{MnO}_2$ ) precipitate. Magnesium dioxide is a natural compound commonly found in soils.

The solubility of  $\text{KMnO}_4$  is strongly influenced by temperature and at  $30^\circ\text{C}$ , has a concentration of slightly over 8%. The pH range is critical in being able to determine whether the oxidation reaction will be fast or slow. The chemical formula for chemical oxidation of TCE using potassium permanganate is shown below in Equation 3 (Nickelsen, et. al., 1992):



The oxidation end products when using potassium permanganate include carbon dioxide, water, and the potassium ion ( $\text{K}^+$ ). Under certain conditions, the injection of an oxidant such as potassium permanganate into the subsurface potentially oxidizes and remobilizes certain soluble metals under certain conditions. The highly toxic, oxidized variety of chromium, hexavalent chromium ( $\text{CrVI}$ ) can be formed from the reduced variety, trivalent chromium ( $\text{CrIII}$ ). The amount of ( $\text{CrVI}$ ) mobilized will depend on the background chromium concentrations in the soil. However, any hexavalent chromium formed from the reaction with an oxidant should become reduced and attenuate back to trivalent chromium within a short time frame and distance.

Chemical compatibility of the injection equipment components and safety procedures become critical with the injection of strong acids, bases, oxidants and other chemicals.

## TREATMENT TRAIN APPROACH

Although chemical oxidation can be used as a single technology, in some cases, multiple treatment technologies are more effective. After a chemical oxidation program has been performed to reduce hydrocarbon concentrations, enhanced aerobic biodegradation can be implemented easily with the excess oxygen left in the subsurface from the breakdown of the chemical oxidant. All microbes will be destroyed by chemical oxidation, however reestablishment of bacteria in the soil and groundwater is likely to occur within several weeks.

Natural attenuation is unenhanced physical, chemical and biological processes that act to limit the migration and reduce the concentration of contaminants in the subsurface (Testa, 1996). The most important process in respect to petroleum hydrocarbons is aerobic bioremediation because it is capable of destroying a large percentage of the hydrocarbon contaminant mass. Destruction occurs as a result of bacteria oxidizing reduced materials (i.e., hydrocarbons) to obtain energy. Aerobic biological degradation of fuel hydrocarbons and selected other organic compounds have been well-documented (Rice, et. al., 1995, Mace, et. al., 1997). Supplying the appropriate amount of oxygen, nutrients

and other amendments to the subsurface can enhance the biodegradation process, and significantly increase remediation effectiveness and decrease treatment time.

## DELIVERY METHOD

An integral part of in-situ remediation planning is the evaluation of the delivery method of the treatment chemicals. Jetting is an old groundwater development technology that has been modified for remediation purposes. The technology for high pressure, low to high volume injection of nutrients into the subsurface using a 12.5 mm (1/2-inch) diameter hand-held wand or lance driven into the ground has been widely used for several decades. The jetting technology, at its most basic, uses tree root feeder systems to inject nutrients and other chemicals into the subsurface by means of a high pressure injector tip on the end of a small-diameter, 2 to 5 foot long steel wand. A more powerful and versatile jetting system has been developed to efficiently implement a variety of remediation processes including chemical oxidation, bioremediation, pH adjustment and metals stabilization (Figure 2). The 3 to 4.6 meter long lances use high-pressure liquid pumps to increase flow at the tip of the wand to pressures from 2,109 to 3,515 meters-head (3,000 to 5,000 psi). At these pressures, the lances are pushed downward into the subsurface with little physical effort. The high pressure cuts into the soil and the lances descend at velocities up to one foot per second. High pressure injection points are placed on close spacing, from 1 meter centers for clays to 3 meter centers for clean gravels. The high pressures allow for the treatment liquids to be dispersed into the soil matrix both vertically and laterally, as well as into the groundwater. Field experience shows that clays start to fracture at about 844 meters-head (1,200 psi) tip pressure. At these pressures, the pressure gauges build up and sustain the pressure, and the fracture occurs at breakthrough and the pressure immediately drops significantly until another zone is fractured. The fractures in clays and other low permeability sediments create preferred remedial pathways that may extend 3 meters or more, however, the matrix of the fractured low permeability soil is unlikely to be uniformly treated.

After the reaction occurs, additional treatment events may be required to reduce contaminants to regulatory approved levels. RIP® projects performed for consultants indicated a radius of influence around injection ports up to 8.6 meters. After the liquids are injected and the jetting tool is removed from the subsurface, no pieces or parts are left behind. The injection holes are then either abandoned as is or sealed with cement grout or bentonite, as needed.

The jetting injector wands can be used to remediate limited access areas such as underneath slabs, railways, and buildings, around tanks, pipelines and subsurface utilities; and into hillsides, excavation pits and stockpiles. Jetting technology has the capability to remediate a variety of constituents both in-situ or ex-situ including petroleum hydrocarbons, BTEX, MTBE, chlorinated solvents, soluble inorganics, phenols, PCBs, PAHs, and other organic and inorganic contaminants. The flexibility and accuracy of this injection delivery system provides distinct advantages over both conventional in-situ and ex-situ remediation systems. As a result, the jetting technology can provide appreciable savings in cost and time over traditional remediation technologies. Probe injector rods have been used successfully with direct push technology (DPT) rigs for greater target depths (4.6 meters to 18 meters) (Figure 3).

## CASE HISTORIES

CASE STUDY# 1: Based on previous site investigations, the soil and groundwater beneath a petroleum storage facility in northern California was found to be impacted with, free product consisting of TPH as diesel (TPH-d) and gasoline (TPH-g) range hydrocarbons. As part of a proposed pilot study, four soil borings were initially drilled using a direct push probe sampling rig. Soil samples were collected at 2 and 3.4 meters below ground surface (bgs) to provide pre-treatment data for the pilot scale test.

Groundwater samples were also collected as groundwater was encountered at about 2 meters bgs. The initial investigation detected free product, with concentrations of TPH-d as high as 6,500,000 micrograms per liter ( $\mu\text{g/L}$ ) and TPH-g as high as 770,000  $\mu\text{g/L}$ . The impacted soil extended to a maximum depth of approximately 4.6 meters bgs and generally consisted of fine sand, silts and clays.

Remediation Approach - The pilot study was designed to treat approximately 102 cubic meters of impacted soils buried a few meters below the 3.7-meter by 6.2-meter surface area. A grid pattern was established with 77 lance injection points spaced on 0.6 meter centers. After coring through the concrete and preparing the pilot study area, 1,874 liters of 18% hydrogen peroxide were injected over 4.25 hours. The injection pressure at the lance tip ranged from 1,055 to 2,109 meters-head (1,500 psi to 3,000 psi) during the injection process.

Results - Significant reductions of diesel range hydrocarbons were found to occur in the groundwater. TPH-d was reduced in the groundwater from a maximum concentration of 6,500,000  $\mu\text{g/L}$  prior to the injection treatment down to a maximum detected concentration of 4,700  $\mu\text{g/L}$  following the oxidation process. No free product was detected after treatment. With only 4.25 hours of treatment, the overall average diesel concentration in the groundwater was reduced by greater than 99% and gasoline by greater than 50%.

Discussion - The concentrations of the lighter-end hydrocarbons such as TPH-g did not exhibit the same reductions. The chromatograms from the laboratory analysis of pre- and post-treatment samples were distinctly different. Based on the chemistry of oxidation processes, longer chain aliphatics (C-12 to C-24) such as diesel tend to oxidize before lighter-end hydrocarbons, such as gasoline. Therefore, upon injecting a strong oxidizing agent, such as hydrogen peroxide, into the subsurface where the soil is impacted with petroleum hydrocarbons, larger decreases to existing total organic carbon (TOC) and any oil or diesel range organics should initially be exhibited as these constituents are preferentially oxidized.

During the oxidation process, shorter-chain hydrocarbons are produced from the oxidation of the long-chain hydrocarbons, such as diesel. Some of these may appear as gasoline-range compounds and could explain the difference in chromatograms before and after treatment. It is also likely that various straight-chain

acids, such as acetic acid, would be created during the chemical oxidation process; however, these mild acids are not a threat to groundwater. Both the gasoline range compounds and mild acids would ultimately break down to carbon dioxide and water with further exposure to hydrogen peroxide.

The significant reduction of diesel concentrations in the groundwater indicate the heavier-end diesel chains are being broken apart during the injection of the hydrogen peroxide. The likely by-products of the oxidation of diesel are gasoline-range petroleum hydrocarbons and straight-chain acids. With continued exposure to hydrogen peroxide, the diesel will be preferentially destroyed and the gasoline will start to be consumed at a faster rate. Table 5 summarizes the results.

**CASE STUDY 2:** For another case outside of Olympia, Washington, a manufacturing facility had soil contaminated with volatile organic compounds, including perchloroethylene (PCE), trichloroethylene (TCE), dichloroethylene (DCE) and toluene. The contaminants were reduced in the soil using 15 to 17 percent hydrogen peroxide and a small amount of ferrous sulfate. The TCE, DCE and toluene were destroyed after one treatment event. Approximately 70 percent of the PCE in the soil was destroyed after two treatment events, enough to allow for site closure within 5 months. The actual remediation cost was about eight percent of the alternative which was a dig and haul project with shoring, estimated to cost about \$500,000. Regulatory objectives were met and site closure, property transfer and redevelopment were accomplished within six months of the first injection event. Table 6 summarizes the results.

#### **SUMMARY:**

In-situ remediation requires great geologic skill to perform successfully in a cost effective and time efficient manner. Use of chemical oxidants requires significant planning and on-site monitoring and supervision. Project safety includes worker protection as well as supervising the handling, mixing and injection of these chemicals. Project success is more likely when the regulatory requirements are agreed upon in advance, the optimal site specific treatment chemistry is defined in a bench test, the preferred pathways (porosity, permeability and other geologic parameters) are clearly understood, and the injection port spacing and injection volumes are evaluated within a geologic perspective. When planned with a clear understanding on the site-specific chemistry and hydrogeologic characteristics, in-situ remediation projects have proven to be less time consuming, less disruptive, and less costly than more conventional remediation alternatives.

**NOTES:** The delivery system described is the Remediation Injection Process, (RIP®) which is a trademark of FAST-TEK Engineering Support Services; For more information: [www.fast-tek.com](http://www.fast-tek.com)

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**TABLE 1**  
**AN EXAMPLE SCHEDULE FOR AN IN-SITU**  
**CHEMICAL OXIDATION REMEDIATION PROGRAM**

K	TASK	TIME	OBJECTIVE
	Subsurface Investigation	1 week	Characterize lithology, hydrogeology, contaminant fate and transport
	Bench-Scale Test	1 - 2 weeks	Under laboratory conditions, evaluate contaminated soil and groundwater to determine whether treatment will work. Design optimum specifications for contaminant destruction
	Pilot-Scale Study	1 - 2 weeks	Perform a pilot study in the field to evaluate the treatment and contaminant destruction.
	Full-Scale Remediation	4 – 8 weeks	Based on successful treatment procedures developed in the lab and during the pilot study, design distribution of treatment chemicals for full-scale

			remediation.
	Confirmation Sampling and Site Closure	1 – 2 weeks	Collect adequate number of soil and groundwater samples to confirm successful remediation. Site closure by regulatory agency.
	Note: Specific project requirements may vary.	TOTAL: 9 – 15 weeks	Common approach: typically inject on a grid spacing, then focus on hot spots.

**TABLE 2**  
**COMPARATIVE RELATIVE STRENGTH OF VARIOUS OXIDANTS**

Species	Chemical Formula	Standard REDOX Potential Eo (Volts)	Oxidants commonly used in chemical oxidation remediation
Fluorine	F <sub>2</sub>	3.0	No
Hydroxyl Radical (Created with Fenton's Chemistry)	HO°	2.8	Yes – with acid or iron catalyst
Oxygen Radical	<sup>∞</sup> O <sub>2</sub> <sup>-</sup> (Superoxide)	2.4	No
Ozone	O <sub>3</sub>	2.1	Yes - sparged
Hydrogen Peroxide	H <sub>2</sub> O <sub>2</sub>	1.8	Yes – see *OH
Potassium Permanganate	KMnO <sub>4</sub> <sup>-</sup>	1.7	Yes – mixed with water and injected
Hydrochlorous Acid	HOCl	1.5	No
Chlorine Dioxide	ClO <sub>2</sub>	1.5	No
Chlorine	Cl <sub>2</sub>	1.4	No
Oxygen	O <sub>2</sub>	1.2	No
Bromine	Br <sub>2</sub>	1.1	No
Iodine	I <sub>2</sub>	0.8	No
<b>ACTIVATED OXYGEN SPECIES</b> (Suthersan, 2002)	Formed by action of light on natural organic matter, peroxides or various inorganic catalysts		
Singlet Oxygen	<sup>1</sup> O <sub>2</sub>		
Protonated Superoxide	HO <sub>2</sub> °		
Hydrogen Peroxide	H <sub>2</sub> O <sub>2</sub>		
Hydroperoxide anion	H <sub>2</sub> O <sub>2</sub> /HO <sub>2</sub> <sup>-</sup>		
Hydroxyl Radical	HO°		
Ozone	O <sub>3</sub>		

**TABLE 3**  
**CHEMICAL OXIDATION: OXIDIZING AGENTS**

<b>Commonly used for chemical oxidation</b>	<b>Less Common:</b>
Hydrogen Peroxide (Hydroxyl Radical) (liquid)	Sodium permanganate (solid)
Potassium Permanganate (solid)	Peracetic acid (liquid)
Ozone (gas)	Calcium peroxide (solid)
	Sodium peroxide (solid)
Note: solids soluble in water	Sodium perborate (solid)
	Sodium percarbonate (solid)
	Sodium persulfate (solid)
	Magnesium peroxide (solid)

**TABLE 4**  
**SUMMARY OF ADVANTAGES AND LIMITATIONS**  
**OF TWO COMMON OXIDIZERS**

	HYDROGEN PEROXIDE (H <sub>2</sub> O <sub>2</sub> ) (with acid or iron catalyst as Fenton's Chemistry)	POTASSIUM PERMANGANATE (KMnO <sub>4</sub> )
FACTOR	DESCRIPTION	DESCRIPTION
Reactivity	Very fast, strong reaction	Fast, strong reaction
Reactant half-life	Seconds – minutes	Minutes – hours
Availability	Widely Available	Generally available
Phase	Clear liquid	Gray powder, mixed with water to about 5-6% turns to bright purple color. Over 8% concentration begins to precipitate.
Target Chemicals (Leethem et al., 2002)	Works well with: Chlorinated alkenes, PAHs, MTBE, BTEX, Olefins (Alkenes);	Works well with: Chlorinated alkenes, phenols, sulfide/organosulfur compounds, olefins (Alkenes)
Does not work well on: (Leethem et al., 2002)	Does not work well on Chlorinated alkanes, some alkanes	Does not work well on: gasoline, diesel, MTBE, BTEX, alkanes, methylene chloride, carbon tetrachloride
Safety and Handling	Special handling and safety precautions: PPE for skin, eyes, mucous membranes, lungs. Serious white burns if handled poorly.	Special handling and safety precautions: PPE for skin, eyes, mucous membranes, lungs. Purple staining and burns if handled poorly.

pH requirements	Low pH (2-4) optimal; requires acidic environments with low alkalinity (<200 ppm)	Reactive under neutral pH (7); more flexibility with pH and alkalinity than hydrogen peroxide, pH control and catalysts not needed.
Cost	inexpensive	
Reaction by-products	Non-toxic by-products (CO <sub>2</sub> , H <sub>2</sub> O)	Non-toxic by-products (CO <sub>2</sub> , H <sub>2</sub> O)
Type of oxidizer	Non-selective oxidizer	Non-selective oxidizer
Residuals:	CO <sub>2</sub> , water, iron salts, O <sub>2</sub> , chlorides, if chlorinated compounds present.	Mn, K, MnO <sub>2</sub> , MnO <sub>4</sub> <sup>-</sup>  MnO <sub>2</sub> is an insoluble precipitate that also forms in soil naturally.
Injection Spacing	Close injection port spacing reflects short reaction period (minutes to hours).	Injection spacing can be further apart due to longer reaction time than hydrogen peroxide.
Phase II: Aerobic bioremediation	Kills microbes, reestablished within weeks.	Less toxic to microbes than hydrogen peroxide.
Regulatory Resistance	Low regulatory resistance, as components are H and O.	Higher regulatory resistance due to Mn.
Comments on oxidizing Cr(III) to Cr(VI)	H <sub>2</sub> O <sub>2</sub> : The amount of Cr(VI) mobilized depends on the amount present. Cr(VI) will reattenuate within a short time and distance (Suthersan, 2002).	KMnO <sub>4</sub> : The amount of Cr(VI) mobilized depends on the amount present. Cr(VI) will reattenuate within a short time and distance (Suthersan, 2002).

**TABLE 5- SUMMARY OF CASE STUDY #1**

Contaminants	TPH-diesel; TPH-gasoline
Medium	Groundwater and Soil
Volume	Estimated 60 cubic meters
Depth	0 to 6 meters
Treatment Solution	Hydrogen Peroxide
Reduction	Significant for 4.25 hours
Location	Napa, California

**TABLE 6- SUMMARY OF CASE STUDY #2**

Contaminants	PCE, TCE, DCE, Toluene
Medium	Soil
Volume	1,000 cubic meters
Depth	0 to 5 meters
Treatment Solution	Hydrogen Peroxide
Reduction	> 85%
Location	Tumwater, Washington



Figure 1 - Bench tests are an integral part of the science behind any successful in-situ project (Courtesy FAST-TEK)

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Figure 2 - Injecting hydrogen peroxide on a job site in Tumwater, Washington, (Case 1). (Courtesy FAST-TEK)





Figure 3 - Jetting using hydrogen peroxide with 12-foot long lances in a limited access environment in northern California (Courtesy FAST-TEK).



Figure 4 – Reaction producing water vapor at approximately 57°C signifies reaction is above the optimal temperature range. (Courtesy FAST-TEK)