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## **Assessment of the Applicability of Chemical Oxidation Technologies for the Treatment of Contaminants at Leaking Underground Storage Tank (LUST) Sites**

### **ABSTRACT**

The total number of confirmed releases from underground storage tanks is increasing rapidly. In addition, the treatment of contaminants in soil and groundwater at leaking underground storage tank (LUST) sites presents complex technical challenges. Research efforts focused on developing LUST site remediation technologies have produced a variety of physical treatment methods including: 1) in-situ treatment technologies such as soil vapor extraction (SVE), radio frequency (RF) heating, steam stripping (SS), soil flushing, and air sparging (AS), and 2) ex-situ treatment technologies such as soil washing, thermal desorption, and solvent extraction. Most of these technologies involve the separation of contaminants from soil or groundwater. The separated contaminants may be adsorbed on activated carbon, condensed to liquid, or separated from the extracting solvents by distillation. The destruction or disposal of these waste mixtures is a tedious and expensive task. Furthermore, most of the in-situ remediation technologies are only effective for removing volatile organic compounds (VOCs) and only certain semivolatiles from the vadose zone. The combination of SVE with either SS or AS is being studied and developed, and indications are that these integrated systems may be effective for removing the same contaminants for the saturated zone. However, the efficiencies of the combined techniques has not been established. The most commonly applied methods for the treatment of contaminants of high molecular weight is excavation of the soil or pumping and treating the groundwater.

Biodegradation has been used for both in-situ and ex-situ destruction of organic contaminants. Because of the slow and complicated bioreactions, however, the mechanisms and efficacy of such treatments are not easy to establish.

Recently, new treatment methodologies have been investigated. Processes involving chemical oxidation have the potential to treat all types of organic contaminants (volatile, semivolatile, and nonvolatile) in both vadose and saturated zones either in-situ or following excavation or, under certain conditions, to detoxify the hazard-

ous materials that may be present in the off-gases that result from the use of vapor extraction or thermal desorption technologies. The oxidative processes can entail complete mineralization, transformation of complex substances into simple compounds, or conversion of hazardous materials to more water-soluble compounds that are typically less toxic and amenable to biodegradation.

## INTRODUCTION

### OBJECTIVE

The objective of this paper is to provide an overview of the published reports regarding chemical oxidation processes for degrading organic pollutants and to discuss in detail some of these processes that appear to have the greatest potential for detoxifying hazardous materials at LUST sites. These technologies are of interest if they can more completely degrade the contaminants, provide a reduction in the time necessary to remediate a LUST site, or provide a cost savings over the existing remediation methods. The goal is to identify which process applications might be most worthy for further development as LUST remediation technologies.

### CHEMICAL OXIDATION TECHNOLOGY

Chemical oxidation technologies, as discussed in this paper, involve the conversion of environmental contaminants to nonhazardous or less toxic compounds that are ideally more stable, less mobile, and/or inert. This paper will assess the potential for treating chemicals that have leaked from underground storage tanks by using chemical oxidation to degrade hydrocarbons, chlorinated hydrocarbons, or other organic chemicals to simpler molecules with the ultimate goal of complete oxidation to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{HCl}$ . Incomplete or partial oxidation of molecules may occur that typically renders them less toxic and in many instances more biodegradable; for some contaminated sites, however, the combination of chemical oxidation/bioremediation may yield acceptable results.

Chemical oxidation technologies have the following general advantages [1]:

- Simple, readily available equipment and reagents.
- They typically have low capital, operating, and maintenance costs.
- They are capable of a high level of treatment at low concentrations.
- Oxidants may have a positive effect on microbial degradation.

Chemical oxidation technologies have the following general limitations [1, 2, 3]:

- Systems must be designed for the specific contaminant and soil type and thus initial laboratory or pilot testing is required.
- Some oxidants have safety and environmental concerns.
- Oxidants are not discriminating and may react with nontarget compounds; they are most suited to media with low concentrations of contaminants.

The major cost of oxidation treatment is due to the cost of the oxidants. The economics vary based on the contaminant and the media being treated. Contaminants in water or soil are the primary waste form treatable by chemical oxidation. Chemical oxidation is applicable to both concentrated and dilute waste streams, but the competing processes are more numerous for the concentrated streams [4].

## UNDERGROUND STORAGE TANK (UST) CHARACTERIZATION

The EPA estimates that as many as 15 to 20 percent of the approximately 1.8 million regulated UST systems nationwide either are leaking or are expected to leak in the near future [5]. Underground storage tanks in the United States primarily are used to store gasoline and other petroleum products. However, other organic and inorganic chemical substances such as solvents and various hydrocarbons may also be stored in USTs [5, 6]. USTs typically fail due to corrosion of the tank or associated piping system.

Corrective actions that have been used or are being developed include the following:

- In-situ soil treatment - soil vapor extraction, soil flushing, radio frequency heating, bioventing, hydrogen peroxide bio-oxidation, etc.
- Ex-situ soil treatment - incineration, thermal desorption, soil washing, solvent extraction, biodegradation, recycle and reuse (asphalt, cement and brick manufacturing), etc.
- In-situ groundwater treatment - air sparging, biodegradation, steam stripping, chemical oxidation, etc.
- Free product recovery.
- Groundwater extraction and treatment by air or steam stripping, carbon adsorption, chemical oxidation, physical separation, biodegradation, etc.

## EVALUATION CRITERIA FOR ASSESSING CHEMICAL OXIDATION TECHNOLOGY

During the evaluation of published reports, descriptions of chemical oxidation processes were reviewed to ascertain the state of the art of chemical oxidation technology and the potential for its use in treating contaminants at LUST sites. A literature search was conducted of published literature including journal articles, conference papers, computer data bases, vendor reports, and EPA documents. The following criteria were used to evaluate the technologies:

- Type, number, and completeness of the studies found.

- Safety or environmental impacts including toxicity of oxidant or products formed and releases to all media.
- Complexity of the process including range of physical conditions under which the reactions occur and labor required to implement the process.
- Estimated cost of the technology versus existing alternatives.
- Applicability of the technology to LUST sites, and the extent of adaptation necessary.

## OVERVIEW OF CHEMICAL OXIDATION TECHNOLOGIES DESCRIBED IN LITERATURE

Literature was reviewed to gather data pertaining to the following oxidants: chlorine, chlorine dioxide, hydrogen peroxide, hypochlorite, ozone, and ozone/ultraviolet light (UV). Table I presents information found on the advantages and limitations of the oxidants that could be used in the treatment of contaminants at LUST sites.

### COMMON CHEMICAL OXIDANTS

After the turn of this century, chlorine gas was applied as part of the drinking water treatment process. In areas centrally supplied with drinking water in the USA and Europe, this process reduced the typhoid mortality rate to an insignificant level. With the recent advancements of analytical methods for performing trace analysis, however, the presence of chloroform and other chlorinated compounds were detected in chlorinated drinking water. These findings have prompted a search for other drinking water treatment options.

Chlorine dioxide is an effective alternative to chlorine because it chemically converts contaminants to salts and nontoxic organic acids. Chlorine dioxide (an unstable gas requiring on-site generation) is generated by reacting sodium chlorite solution with chlorine gas or by reacting sodium chlorite solution with sodium hypochlorite and hydrochloric acid [7]. Concentrated aqueous solutions of chlorine dioxide (0.5 to 3 g/L) may be stored for a few hours before application. In soil treatment applications, the chlorine dioxide may be applied in-situ through conventional injection wells or surface flushing [7]. If chlorine dioxide is used in place of chlorine, chlorinated hydrocarbons are not created during the oxidation of organic compounds. However, chlorine dioxide does give rise to other, unwanted substances. Large amounts of chlorite are formed and in some cases 50 to 70 percent of the chlorine dioxide consumed is converted to chlorite [8].

Hydrogen peroxide is a powerful oxidizing agent whose reaction by-products (water and oxygen) are nontoxic [12]. Solutions of hydrogen peroxide are relatively safe, effective, and easy to use (with a natural decomposition rate of just 1 percent per year in commercial storage) [12]. Hydrogen peroxide is a source of hydroxyl radi-

TABLE I. SUMMARY OF ADVANTAGES AND LIMITATIONS OF COMMON CHEMICAL OXIDANTS FOR USE AT LUST SITES

Oxidant Technology	Advantages	Limitations
Chlorine	<ul style="list-style-type: none"> <li>- Low initial cost</li> <li>- Long history of use in water treatment</li> </ul>	<ul style="list-style-type: none"> <li>- Biological activity may be killed by chlorine [9].</li> <li>- Chlorine can convert organics to chlorinated compounds which may be carcinogenic or difficult to biodegrade [9].</li> <li>- Not previously used at LUST sites.</li> <li>- Chlorine gas is highly corrosive.</li> </ul>
Chlorine dioxide	<ul style="list-style-type: none"> <li>- Does not react with organics to form organo-chlorine compounds as does chlorine [10].</li> <li>- May be generated on site [7].</li> </ul>	<ul style="list-style-type: none"> <li>- <math>\text{ClO}_2</math> is a relatively unstable gas which is not to be compressed and liquified without danger of explosion and therefore must be generated on site [10].</li> <li>- Chlorine dioxide generates some undesirable side products, namely chlorites.</li> <li>- Aliphatic hydrocarbons do not react significantly with chlorine dioxide in practical conditions of water treatment [10].</li> </ul>
Hydrogen peroxide	<ul style="list-style-type: none"> <li>- Economical and readily available [11].</li> <li>- Oxygen from disproportionation is available for use by microorganisms [11].</li> <li>- Can be added to environment at high concentration, providing an oxygen supply several orders of magnitude more concentrated than possible and saturating water with pure oxygen [11].</li> <li>- Does not persist in the environment [11].</li> <li>- Hydrogen peroxide is infinitely soluble in water [12].</li> </ul>	<ul style="list-style-type: none"> <li>- Toxic to microorganisms [11].</li> <li>- Use in conjunction with in-situ bioremediation is not well developed [11].</li> <li>- Its decomposition in the subsurface may be so rapid that much of the resulting oxygen will bubble out of solution, becoming unavailable to microorganisms [11].</li> </ul>
Hypochlorite	<ul style="list-style-type: none"> <li>- Low cost.</li> <li>- Readily available, and the aqueous solution is easily transported, stored, and metered into the reacting system [13].</li> </ul>	<ul style="list-style-type: none"> <li>- Forms chlorinated by-products.</li> </ul>

(continued)

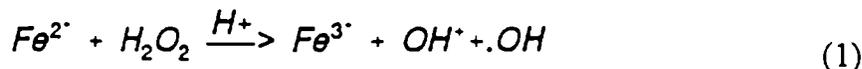
TABLE 1 (continued)

Oxidant Technology	Advantages	Limitations
Ozone	<ul style="list-style-type: none"> <li>- Ozonation in the presence of UV irradiation, ultrasound and/UV H<sub>2</sub>O<sub>2</sub> causes organic oxidations to proceed at significantly increased rates.</li> <li>- Generated on site from air; used immediately; no storage or handling of strong oxidants; stop generating by turning off power [14].</li> <li>- Very strong oxidant; reacts with a large variety of organics; does not form chlorinated organics; residuals react with constituents or revert back to oxygen; short reaction time; lower dose rates than other oxidants; makes some organics more biodegradable [14].</li> <li>- Temperature and pH less critical than with other oxidants; treated effluents are normally oxygen rich [14].</li> </ul>	<ul style="list-style-type: none"> <li>- Cannot be stored due to short half life.</li> <li>- Ozonation of organic compounds rarely proceeds completely to CO<sub>2</sub> and water. Instead, intermediate oxidation products form [15].</li> <li>- Ozone is produced on site. The total equipment (air preparer, ozone generator, contact chambers) represent substantial capital and operational costs [14].</li> <li>- Will not degrade low-molecular weight chlorinated organics; must treat off-gas if ozone present [14].</li> </ul>
Ozone/UV	<ul style="list-style-type: none"> <li>- Ozonation in the presence of UV irradiation causes organic oxidations to proceed at significantly increased rates, especially for compounds normally refractory to ozone alone [16].</li> </ul>	<ul style="list-style-type: none"> <li>- Cost of both UV and ozone generators may be high.</li> <li>- UV is not amenable to in-situ application.</li> </ul>

cals, one of the most potent oxidizers known. The hydroxyl radical is second only to fluorine in oxidation potential among the common oxidants.

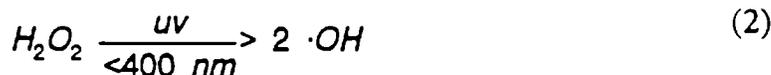
There are two main methods of producing hydroxyl radicals with hydrogen peroxide:

- 1) By Fenton's method which involves the use of ferrous ion to enhance the production of hydroxyl radicals.

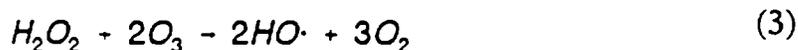


- 2) By "Advanced Oxidation Processes" [18, 19]

- $H_2O_2$ /ultraviolet light



- $H_2O_2$ /ozone



- $H_2O_2$ /ozone/ultraviolet light (e.g., Ultrox system [20]).  
(Molar ratio of  $H_2O_2/O_3$  is varied by waste with at least 13 possible reactions [21])

Sodium hypochlorite is a widely used oxidant. It is therefore readily available in the form of aqueous solutions that are easily transported, stored, and metered into the reacting system. One of the major uses of hypochlorite solutions is for the treatment of cyanide-containing wastes from ore extraction, synthetic organic-chemical manufacture, and metal finishing. However, chlorinated by-products may be formed.

Ozone is a powerful oxidant that has the ability to oxidize a great number of organic and inorganic materials. Ozone oxidation reactions in aqueous media usually are dependent upon pH [15]. At higher pH ranges (8 to 9), ozone decomposes to form hydroxyl free radicals ( $\bullet\text{OH}$ ), which are stronger oxidizing agents than free ozone. At low pH, ozone reacts as the free ozone molecule, which has a slower reaction rate than  $\bullet\text{OH}$ . Ozonation of organic compounds rarely proceeds completely to  $\text{CO}_2$  and water. Instead, intermediate oxidation products form. These will contain more oxygen than did the starting organic materials. Because of this, the oxidized materials are more polar, have a greater solubility in water, and are usually more readily biodegradable. Saturated aliphatic hydrocarbons are unreactive toward ozone. Unsaturated aliphatic compounds generally are readily reactive with ozone, unless they have been halogenated to high levels. Alcohols are slowly oxidized to acids. Oxalic acid and  $\text{CO}_2$  are the most stable reaction products of organic oxidation. Benzene is slowly oxidized with ozone. Other aromatic compounds generally are easily oxidized by ozone, except when electron-withdrawing substituents are present on the aromatic ring.

Ozonation in the presence of UV irradiation, ultrasound, and/or  $\text{H}_2\text{O}_2$  causes organic oxidations to proceed at significantly increased rates. Reaction times can be 100 to 1000 times faster in the presence of UV light [2].

## POTENTIAL CHEMICAL OXIDATION TECHNOLOGIES FOR USE AT LUST SITES

There are four types of treatment operations for which chemical oxidation technologies may be implemented at LUST sites: ex-situ water treatment, in-situ soil and water treatment, ex-situ soil treatment, and treatment of gaseous emissions generated by soil vapor extraction (SVE), thermal desorption and radio frequency heating systems. Table II summarizes the characteristics of chemical oxidation technologies that, on the basis of this review, appear to have the greatest potential for use at LUST sites. In the following sections each of these four types of treatment operations and the corresponding chemical oxidation processes which may be applicable are discussed.

The discussion below emphasizes primarily technologies involving the use of  $\text{H}_2\text{O}_2$ , ozone, and UV. Other chemical oxidation technologies ( $\text{Cl}_2$ ,  $\text{ClO}_2$ , hypochlorite) are not included here due to the lack of information regarding their application to most common LUST contaminants as well as potential safety and environmental concerns arising from the possible formation of chlorinated by-products.

### EX-SITU WATER TREATMENT

Ex-situ water treatment at LUST sites may entail treatment of contaminated groundwater or treatment of water generated on the site by processes such as soil flushing. Since chemical oxidation processes have been used in wastewater treatment and drinking water treatment for many decades, knowledge in this area is

TABLE II. CHEMICAL OXIDATION TECHNOLOGIES WITH POTENTIAL FOR USE AT LUST SITES

Oxidation Technology	Type of Studies, Extent of Use	Potential Safety or Environmental Impacts	Complexity of Process	Estimated Cost Versus Existing Alternatives	Adaptation to LUST Sites	References
<b>Ex-Situ Water Technology</b>						
UV/H <sub>2</sub> O <sub>2</sub> (Perox-pure™)	Used at over 70 sites	Minimal	System is complex, but is commercially available	Cost-effective for toxic contaminants	Has been used at LUST sites	21, 22, 23
UV/H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> (ULTROX)	Used at over 20 sites	Ozone must be treated before release to ambient air	System is complex, but is commercially available	Cost-effective for toxic contaminants	Has been used at LUST sites	20, 22
UV/O <sub>3</sub> , O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> , UV/laser/H <sub>2</sub> O <sub>2</sub>	Bench-scale and laboratory studies	Ozone must be treated before release to ambient air	Systems are complex	Unknown	Must be scaled up and field tested	18, 24, 25, 26, 27, 28, 29
<b>In-Situ Soil and Water Technology</b>						
H <sub>2</sub> O <sub>2</sub> (Venture)	Pilot scale study	Minimal	Medium Complexity	Low	Considerable work is necessary to understand best conditions for use	50
O <sub>3</sub>	Laboratory and pilot scale studies	Unknown	Medium Complexity	Medium	Considerable work is necessary to understand best conditions for use	49, 51
H <sub>2</sub> O <sub>2</sub> /Bioremediation	Laboratory and bench-scale with some inconclusive use in the field	High concentrations of H <sub>2</sub> O <sub>2</sub> toxic to microbes	Process is not complex, but best conditions of use are not well understood	Unknown. May have cost advantage if time is important or very toxic chemicals are present	Considerable work is necessary to understand best conditions for use	17, 30, 31, 32, 33, 34, 35, 36, 37, 38, 40

(continued)

TABLE 2 (continued)

Oxidation Technology	Type of Studies, Extent of Use	Potential Safety or Environmental Impacts	Complexity of Process	Estimated Cost Versus Existing Alternatives	Adaptation to LUST Sites	References
<b>PX-Situ Soil Technology</b>						
H <sub>2</sub> O <sub>2</sub>	Laboratory and bench-scale studies. Some field tests.	Minimal	Not developed enough to ascertain complexity	Unknown. May have cost advantage if time is important or very toxic chemicals present	Considerable work is necessary to identify best conditions for use	17, 39, 41, 52
UV/O <sub>3</sub> (Excalibur Enterprises)	Pilot scale	Ozone must be treated before release to ambient air	System is complex	Unknown	Must be field tested	16, 42
<b>Technology to Treat Air From SVE Systems</b>						
UV (Purus)	Laboratory and bench-scale studies	Minimal	Medium complexity	May have cost savings for smaller LUST sites where the capital cost of carbon adsorption is high	May be problem in treating surges in containment release	45, 46
UV/TiO <sub>2</sub> (Nutech Environmental)	Bench and pilot scale	Minimal	Medium complexity	Unknown	Must be scaled up and field tested	47, 48
Air sparging with O <sub>3</sub>	Theoretical	Potential release of O <sub>3</sub>	Medium complexity	Unknown	Considerable work needed	49

comparatively advanced, and commercial systems are in use to oxidize organics and chlorinated organics.

Several commercially available chemical oxidation water treatment technologies are briefly described below:

- The Perox-pure™ system developed by Peroxidation Systems Inc. employs UV and H<sub>2</sub>O<sub>2</sub> and has been used at over 70 sites [21, 22, 23]. The system produces the hydroxyl radical and has degraded numerous water contaminants including chlorinated solvents, pesticides, polychlorinated biphenyls, phenolics, and fuel hydrocarbons in concentrations ranging from a few thousand milligrams per liter to one microgram per liter [21, 23]. The system can also be used as a pre-treatment to detoxify contaminants prior to biological treatment.
- The Ultraviolet Radiation/Oxidation system developed by Ultrox International uses UV, H<sub>2</sub>O<sub>2</sub>, and O<sub>3</sub> and has been used at over 20 sites [20, 22]. The system decomposes the ozone prior to release to ambient air [20].
- Bench-scale investigations have shown that UV/laser/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, and UV/O<sub>3</sub> can decompose waterborne contaminants such as chlorinated solvents, benzene, phenol, and other organics [18, 24-29].

## IN-SITU SOIL AND WATER TREATMENT

In a recent pilot scale study, hydrogen peroxide solution (35% in water) was injected into the saturated zone of a gasoline contaminated site (2,000 cubic yards) with a porosity of 0.45. The total BTEX (benzene, toluene, ethyl benzene and xylene) decreased from 10820 ppm to 580 ppm within 1-1/2 months. Four more injections were conducted and the final BTEX was reduced to 384 ppb (52). The characteristics of the site are not clear and the test results were not verified.

Hydrogen peroxide (in conjunction with bioremediation) was the chemical oxidant most often used for in-situ treatment of contaminated soils. Numerous articles were reviewed describing bench-scale and field applications of H<sub>2</sub>O<sub>2</sub> in conjunction with bioremediation to treat fuel and chlorinated hydrocarbon spills in soil [17, 31-35]. While the results of the studies are inconclusive, it appears that under the proper conditions, the combination of H<sub>2</sub>O<sub>2</sub> and bioremediation can result in a significant reduction in the time necessary for remediation.

In situ aerobic biotransformation of underground organic pollutants is well known and complete mineralization of many hydrocarbons is achieved under oxidant-rich conditions [11]. Dissolved oxygen availability frequently limits the biotransformation of organic compounds in the subsurface due to the limited aqueous solubility of oxygen, the relatively slow rate of reaeration of groundwater in the saturated

zone, and the significant biological oxygen demand caused by aerobic metabolism. In biological systems, hydrogen peroxide can supply dissolved oxygen and therefore can be used to augment the oxidant capacity of the aquifer.  $H_2O_2$  is disproportionated by the action of microbial catalase and several inorganic catalysts such as iron oxide species to give 0.5 mole of oxygen per mole of  $H_2O_2$  consumed.



The resulting dissolved oxygen should then be available for microbial respiration. Injections of hydrogen peroxide and bacterial nutrients, such as nitrogen and phosphorus, into contaminated soil and groundwater has been performed to provide oxygen and nutrients for bacteria that metabolize hydrocarbon contaminants. This technology has been used to clean up soil and groundwater near leaking diesel and gasoline tanks [31, 33, 34, 35].

The process generally entails passing a water solution through the contaminated soil, collecting the water downstream (downgradient), and possibly reinjecting upgradient. Suitable biological nutrients or other amendments are added to the water prior to injection. It is often necessary to treat the water prior to reinjection to remove contaminants. The previous section on water treatment described the use of chemical oxidation in such cases.

In-situ bioremediation with hydrogen peroxide involves optimization of several controlling variables including pH, catalysts, temperature, contact time, application rate, and reactivity of the contaminants [17]. The optimum value for these factors varies with the compound being oxidized. While the process is not complex, the optimum conditions seem difficult to predict and identify. Other problems encountered include decomposition of peroxide near the distribution point, major growth of bacteria near the injection point, obstruction of regular groundwater flow by biomass, and inadequate penetration and availability across the contaminated area [8, 32, 35, 40]. Iron catalyzes the decomposition of peroxide. Since iron appears in many soils around LUST sites, this can be a recurring concern. However, the addition of phosphates will passivate iron and limit the effect on peroxide [32, 35, 39].

Bacterial enzymes (catalase) can also cause premature decomposition of peroxide [40]. These enzymes can collect in the water/solution injection galleries, resulting in a rapid loss of peroxide effectiveness. One method which has been used to inhibit this effect is to filter water through charcoal beds, or not to use recycled solution [8, 40]. Because these may not be cost-effective solutions, they may be difficult to resolve if catalase-enhanced decomposition occurs.

Whether inhibited or not, decomposition of peroxide still occurs. Even with phosphate addition and the lack of any catalase activity, peroxide, after being released into the environment, decomposes by 80 percent over as little as four hours [11,

40]. Since solution flow is generally quite slow across a contaminated zone (due primarily to the relatively low fluid porosity of subsurface soils), it often is difficult for active peroxide solution to reach much of the contaminated area. For that reason, multiple injection points are often advisable to provide suitable oxidant activity to the zones of interest.

In order for peroxide to be effective in the chemical oxidation mode only, it must decompose to form the OH radical, which is a potent oxidizer. Several studies (3, 36, 37) achieved substantial degradation of soil contaminants with peroxide at a pH of 2-3. In most cases it would be difficult and expensive to acidify large volumes of soil. Based on the published data, a further expense would be the extremely high dosage utilized in the experiments, over 10,000:1, peroxide to contaminant, in some cases.

Other research studies involving peroxide for soil remediation (39, 41) were performed at neutral or slightly basic pH's (i.e., 9), where the concentration of OH radical would be much higher (over 4 orders of magnitude higher than in the previously described study). These tests were in the form of a pretreatment of refractory constituents prior to bioremediation. Such an approach would be simpler, and thus more feasible, to arrange in an ex-situ system. As such, it will be described in the following section.

Another type of reaction is direct oxidation of organic compounds by  $H_2O_2$  in the presence of enzymes (peroxidases) or metal oxide catalysts [11]. Molecular oxygen is not evolved as a result of this latter type of  $H_2O_2$ -consuming reaction.

In any case, the aqueous solution containing the oxidant must come into intimate contact with the contaminant before oxidation/bioremediation can occur. Non-wettable solids or contaminants or inaccessible soil pores and clay will retard and limit the effectiveness of this approach. Contaminants in the vadose zone would be difficult to access and treat by this approach.

The information which was reviewed indicated that  $H_2O_2$  does not persist in the environment. No reports were found which indicated that  $H_2O_2$  reacts with environmental constituents to form toxic by-products. At high  $H_2O_2$  concentrations (between 0.05 and 0.2 percent)  $H_2O_2$  is toxic to the microorganisms [35].

The primary limitation in the use of this technology at LUST sites is the lack of specific information regarding the concentrations of  $H_2O_2$  which are optimal for site specific conditions. The technology would be more costly than use of bioremediation alone due to the cost of the hydrogen peroxide; however, the reduction in cleanup time and the ability to degrade more complex contaminants may result in a net cost savings. The method could also be cost prohibitive if large quantities of  $H_2O_2$  are required due to a large contaminant concentration or other organic matter in the soil that would consume the  $H_2O_2$ .

On the plus side, hydrogen peroxide is the preferred oxidant for in-situ treatment of contaminated soil because it is a liquid and is miscible with water, is relatively inexpensive, and does not persist in the environment. Although it can be added to the environment at high concentration, it can be injurious to microorganisms. Even in somewhat lower concentrations, it can inhibit the growth of microorganisms [11].

The greatest difficulty in the use of hydrogen peroxide (or any other chemical oxidants) in situ is that the oxidant will not selectively oxidize the desired contaminant but rather will react with organic substances, toxic or benign, in the soil, thereby consuming  $H_2O_2$ . This makes the quantity of oxidant required prohibitively expensive in some cases.

The oxidation of some PAHs in dry soil by ozone has been observed in laboratory tests. Phenanthrene was completely removed, while pyrene and chrysene were partially removed (33% - 94%) (49). Experiments for the ozone treatments of contaminated soils have been conducted in laboratory and pilot scales. In laboratory, two kilograms each of PAH (2,250 mg/kg) and mineral oil (12,000 mg/kg) contaminated soils were tested. The PAHs were reduced to 2.9 mg/kg in 20 days and mineral oil was reduced to 3.5 mg/kg in 60 days. The pilot scale test was conducted on 3 tons of contaminated soil, no test result is available. An in-situ treatment was just started at a former gasoline station (51).

## EX-SITU SOIL TREATMENT

In the literature reviewed, it was found that both hydrogen peroxide and ozone/UV have been used in integrated treatment systems for treating contaminated soil. One of the difficulties in evaluating the application of chemical oxidation to ex-situ treatment of soil is that few of the literature references discuss applications to LUST types of contaminants. The discussions below emphasize what fuel hydrocarbons and similar materials have been tested, but also draws upon work with other compounds which may be relevant in evaluating LUST remediations.

Experiments with hydrogen peroxide (Fenton's reagent) involved mainly percolating a peroxide solution through a bed of the contaminated soil. These were conducted at neutral or slightly basic conditions, up to a pH of 9 [39, 41, 42]. After 15 to 20 days of treatment of the contaminants under consideration, concentrations had fallen to the level at which bioremediation or landfarming could begin. Benefits included accelerated degradation, production of intermediate products which were more amenable to biological attack (primarily due to reduced structures which could more readily be absorbed into the cell), and reduction of contaminant to levels below that toxic to the bioorganisms.

Another study [43] blended a peroxide solution in with the contaminated soil using rototilling. This likely resulted in volatilization of substantial amounts of the contaminant (gasoline, in this case), and very little actual oxidation occurred. One of

the difficulties in dealing with ex-situ treatment of soils from UST sites is volatilization, which can occur even during the excavation process. Any further handling and soil turning or cultivation during treatment processes can result in almost total loss of volatile constituents. Since volatilization is not an oxidation process, such experiments cannot be utilized to evaluate chemical oxidation.

A pilot scale test was conducted on VOC (volatile organic compound) contaminated soil with aqueous  $H_2O_2$ . Seven cubic yards of the soil was agitated with 1,000 pounds of 35%  $H_2O_2$  for 15 minutes and let the mixture stand for one hour. The concentration of methylene chloride reduced from a maximum of 14,000 ug/kg to under the detection limit (11 ug/kg), toluene from 25,000 ug/kg to less than 5 ug/kg ethyl benzene from 24,000 ug/kg to less than 5 ug/kg, xylene from 133,000 ug/kg to less than 5 ug/kg (52).

UV/ozone offers some unique advantages for chlorinated aromatic compounds, such as pesticides and herbicides. For example, UV most readily attacks the chlorine-carbon bond and ozone attacks the aromatic ring. Most work with UV/ozone has been with water solutions. One ex-situ treatment involves washing soil with water, followed by UV/ $O_3$  treatment of the leachate. Thus, if complicated chlorinated organics or polynuclear aromatic hydrocarbons (PAHs) are present, UV/ozone may be a viable alternative [16, 39, 44].

Generally, LUST soils contain simpler hydrocarbon fuel materials, which are readily degraded by less expensive methods. However, final treatment of soil washing solutions prior to disposal (for any solution not being recycled) may benefit from chemical oxidation to treat to very low concentration levels, providing an alternative to carbon beds.

The information found indicated that  $H_2O_2$  did not persist in the environment and did not form toxic products. Ozone, if present in the off-gas, must be treated prior to release to the ambient air.

The ex-situ oxidation technology appears to be promising and may have a cost advantage in cases where soils contain chemicals that are difficult to degrade. Considerable work is necessary to identify the best conditions for the use of this technology.

#### TREATMENT OF AIR GENERATED FROM SOIL VAPOR EXTRACTION (SVE) SYSTEMS

Finally, soil vapor extraction (SVE) systems generate air streams which contain organic contaminants that require treatment prior to release to the atmosphere. At high organic concentrations, combustion is normally utilized. At lower organic concentrations, carbon adsorption is typically used to remove the contaminant prior to disposal. UV technologies may also be used to treat air streams containing contaminants in the lower concentration range. The reason for substitution of UV

technologies for carbon adsorption is that there may be a cost savings in some cases.

The literature contains several reports which describe bench- and pilot-scale assessments of chemical oxidation technologies. These systems include the Photolytic Oxidation Process by Purus, Inc. [45, 46], and the TiO<sub>2</sub>/Photolytic Air Treatment System by Nutech Environmental [47, 48]. These systems use air (oxygen) or UV and TiO<sub>2</sub>/UV.

Another bench-scale experiment proposed pumping ozonated air or oxygen instead of air into a conventional vapor extraction system [49]. Ozone may present an environmental hazard if not treated prior to release. No toxic reaction products were identified. The processes are fairly complex and it is not clear if they could handle surges in contaminant release as a conventional carbon adsorption system could. The rationale for the use of these systems is that the high capital cost of a carbon adsorption unit could be avoided in certain circumstances. However, no cost data was identified to confirm this. In addition, no adaptation is necessary to develop this technology for use at LUST sites.

## CONCLUSIONS AND RECOMMENDATIONS

The primary data gaps for three of the four treat operations (except ex-situ water treatment) is the lack of cost data and the lack of field experience at LUST sites. The lack of cost data and field experience are serious impediments for selecting these potentially useful technologies.

## CONCLUSIONS

The following conclusions can be made regarding the potential use of the oxidation technologies in each of the four LUST treatment operations.

### Ex-situ water treatment using UV/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> and UV/H<sub>2</sub>O<sub>2</sub> technologies.

- Commercial systems using these technologies are in use.
- The technology appears best for low concentrations of contaminants that are not amenable to biological treatment.
- Other systems using UV/O<sub>3</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, and UV/laser/H<sub>2</sub>O<sub>2</sub> are being investigated.
- Market forces will determine the most cost effective technology.

### In-situ or ex-situ soil and water treatment using aqueous H<sub>2</sub>O<sub>2</sub>.

- The technology has been field or pilot scale tested, the characteristics of the site, contaminated soils and water are not clear.

- The conditions for the reactions to occur are not understood.
- Considerable work is needed to identify the best conditions and soil or water types for use of this technology.
- The possibility of the detoxification of high molecular weight compounds is unknown.

In-situ soil and water treatment using  $H_2O_2$ /bioremediation.

- The technology has been field tested with inconclusive results.
- The mechanisms are complex and not well understood in site-specific applications.
- Considerable work is needed to identify the best conditions and soil types for use of this technology.
- Cost versus other alternatives is a major unresolved question.
- Very low pH (2-3) and higher pHs (9) as studied for Fenton's solution application would be difficult to attain for in situ applications.

\* In-situ or ex-situ soil treatment using  $O_3$ .

- The preliminary experiments showed that this technology is very effective for the removal of some semi-volatile organic compounds (SVOCs) with inconclusive results.
- The reaction mechanisms are not understood.
- Considerable work is needed to the applicability of this technology for various compounds contained in USTs.
- Cost and effectiveness versus other technologies have to be evaluated.

\* Ex-situ soil treatment using  $H_2O_2$  or UV/ $O_3$ .

- With ex-situ treatment, losses of the contaminant due to volatilization can distort the reported results.
- Considerable work is needed to identify the best conditions for use of this technology.
- The technology appears best for low concentrations of contaminants that are not amenable to biological treatment.

- Cost versus other alternatives is a major unresolved question.

#### Treatment of air from SVE systems using UV, UV/TiO<sub>2</sub>:

- Technologies destroy contaminants completely.
- The technology appears best for low concentrations of contaminants that are not amenable to carbon adsorption/desorption or incineration.
- Lower capital costs may give technology a cost advantage over alternatives.
- Work is needed to identify the best conditions for use.

### RECOMMENDATIONS

Technologies using UV/H<sub>2</sub>O<sub>2</sub> and UV/ozone to treat contaminated water streams are well advanced. Sufficient cost information generally is available so that market forces will determine which technologies are preferable and in which situations.

For in-situ soil and water treatment using H<sub>2</sub>O<sub>2</sub>/bioremediation, the technology appears to have potential in certain circumstances. However, since the mechanisms, best conditions for use, and cost parameters are uncertain, further investigation is recommended.

For ex-situ soil treatment using H<sub>2</sub>O<sub>2</sub> or UV/O<sub>3</sub>, the technology appears to have potential in certain circumstances. However, since the best conditions for use and cost parameters are uncertain, further investigation is recommended. Ex-situ applications should minimize soil movement to reduce contaminant volatilization. Soil washing applications, possibly in conjunction with a subsequent H<sub>2</sub>O<sub>2</sub> enhanced bioremediation step, thus appear to be the most fruitful for additional work.

The use of H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> for in-situ and ex-situ treatments of soil and water have shown faster remediation possibility. However, the data were inconclusive. Further investigation on the applicability of these technologies to all the constituents contained in UST and the conditions necessary for their effectiveness is recommended.

For treatment of air from SVE systems using UV or UV/TiO<sub>2</sub>, the technology appears to have potential for treating low concentrations of contaminants that are not amenable to other conventional treatment methods. Since the best conditions for use and cost parameters are uncertain, further investigation is recommended. Stringent air emission regulations may provide further impetus to apply chemical oxidation in these applications. The adaption of these technologies for the treatment of the off-gas from steam stripping and radio frequency heating also need further investigation.

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