



## Chemical Oxidation Guidance

# LEAKING UNDERGROUND STORAGE TANK PROGRAM: Use of In-Situ Chemical Oxidant Compound Injection

## SUMMARY

In-situ chemical oxidation involves the introduction of a chemical oxidant into the subsurface for the purpose of transforming contaminants in groundwater or soil into less harmful species. With sufficient contact time, oxidants are capable of converting petroleum hydrocarbons (fuels, solvents, and pesticides) into carbon dioxide and water. In many cases, chemical oxidation is chosen when bioremediation is not effective due to limited microbial growth, contaminant characteristics, or site conditions.

The commonly used oxidants are hydrogen peroxide and iron (Fenton's reagent), permanganate, ozone, and persulfate. Each of these oxidants has advantages and disadvantages. Some oxidants are more appropriate depending on the site-specific conditions. For example:

1. High concentrations of carbonate in the groundwater have a negative effect on Fenton's reagent. By contrast, permanganates have more positive effects when carbonates are present in the groundwater;
2. Permanganates are unable to chemically oxidize benzene; and
3. Persulfate is a relatively new form of oxidant whose field-scale effectiveness is still being determined.

Chemical oxidation offers the advantages of being rapid and aggressive, as well as providing residual dissolved oxygen (DO).

The primary obstacles for chemical oxidation are effective delivery and distribution to the contaminant in the subsurface environment. Chemical oxidation requires contact between the oxidant and the contaminant. Without such contact, no remediation will occur.

Another obstacle for chemical oxidation is posed by high levels of ferrous iron ( $\text{Fe}^{++}$ ) and other oxygen-reducing metals in the subsurface soil. These metals will increase the amount of chemical oxidants needed to remediate the contaminated area, thereby reducing the oxidant's cost effectiveness. In contrast, Fenton's reagent requires ferrous iron to increase the strength and speed of the chemical reaction.



In general, chemical oxidation is ideally suited to treat small areas, where the petroleum mass is more concentrated. As such, chemical oxidation has been predominantly used to address contaminants in the source area saturated zone and capillary fringe, while treatment of the source area's unsaturated zone requires another remedial technology (e.g., soil vapor extraction). However, where free product exists, other remedial technologies (e.g., free product recovery) need to be conducted prior to chemical oxidation for the remediation to be safe and cost effective.

Chemical oxidation can be dangerous, since oxidants are corrosive and can explode under the right conditions. Soil vapor extraction can help alleviate this safety issue by recovering off-gases while treating the source area's unsaturated zone.

## **INTRODUCTION**

This guidance is intended to provide enough basic information to form a design decision that has a reasonable chance of remediating a site. This information is provided as a guide in reviewing in-situ chemical oxidation proposals to provide the Leaking Underground Storage Tank Section with a consistent approach to site investigation and design requirements for these activities.

### **A. PRELIMINARY SITE CONSIDERATIONS**

The following conditions can limit the success of chemical oxidation at the site and should be considered in the initial assessment and the design. Site conditions that do not comply with these general criteria should be taken into account in the design. Soil (below the groundwater) and groundwater samples required for these determinations can be collected during the Site Investigation or Corrective Action phase. The presence of free product amounts, pH of the groundwater, soil porosity, and heavy metal levels in the groundwater are important considerations for the design of the remediation and are discussed below:

#### **1. Free Product**

Free product must not be present to any great extent (not beyond a sheen). Free product recovery should precede chemical oxidation.

#### **2. pH**

The upper foot of the groundwater surface should be tested (one sample). This sample should be collected from an area of the contaminant plume with the highest levels of contaminants. In most cases the pH should be between six and eight. If it is not, the designer must address what impact the pH will have on the chemical oxidation process.

#### **3. Soil Porosity**

A soil sample from the contaminated zone should be collected and tested for soil porosity. This soil sample should be collected at or near the groundwater surface in the saturated zone. Porosity is a measure of the void space between soil particles and is used to estimate the volume of dissolved contaminants in the saturated zone.

#### 4. Iron

A groundwater sample should be analyzed for dissolved iron levels. These levels should be considered in the design of a chemical oxidation process requiring iron addition (Fenton's reagent). Oxygen demand by iron, as well as all other metals, should be considered in the oxygen demand calculations using the chemical oxygen demand analysis results. Also, the potential for oxidized metals to interfere with the movement of groundwater during the remediation process (fouling of well screens, decrease in hydraulic conductivity, etc.) should be considered.

### **B. WHAT ARE THE CONTAMINANTS OF CONCERN (COC)?**

The COC for leaking underground storage tanks (USTs) are defined in the regulations. The focus of this guidance is primarily benzene, ethylbenzene, toluene and xylenes (BTEX), methyl tertiary-butyl ether (MTBE), and polynuclear aromatics (PNAs). The goal is to achieve the appropriate remediation objectives.

### **C. HAS THE PLUME BEEN DELINEATED?**

The groundwater plume must be delineated and should include:

1. The dissolved level of contaminants in the groundwater.
2. The adsorbed level of contaminants on soil below the groundwater table (this includes the capillary fringe). The adsorbed levels and dissolved levels must be considered (levels above the soil sorption capability will eventually be desorbed to the groundwater).
3. The level of contaminants in the unsaturated soil zone above the groundwater. If this soil is not removed, it will continue to act as a source of contaminants and should be considered in the design. Modeling (i.e., TACO) of the concentration of these contaminants can be used to predict their impact on the groundwater concentrations. Based on the information provided to the Illinois EPA to date, the remediation of the unsaturated zone with chemical oxidation compounds is generally ineffective.

### **D. HYDRAULIC CONDUCTIVITY**

This information is required for all impacted zones that are saturated with groundwater and are going to be chemically oxidized. A hydraulic conductivity of greater than  $1 \times 10^{-7}$  cm/sec is recommended. The hydraulic conductivity will affect the amount of time that will be required to inject the remediation material and the number of injection points.

### **E. WHAT ARE THE CONTAMINATION LEVELS?**

For contaminant plumes of one-half acre or less, five borings should be completed and groundwater and soil samples (below the water table – upper one foot of the saturated zone) collected. One boring should be located at the upgradient (based on groundwater flow direction) edge of the contaminant plume, one from the downgradient edge, and three across the center of the plume (perpendicular to the direction of groundwater flow). These five groundwater and saturated soil samples should be tested for total petroleum hydrocarbons

(TPH), chemical oxygen demand (COD), and eight heavy metals (total in soil, dissolved in groundwater). The eight heavy metals are arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. If the plume is greater than one-half acre, one additional boring (for a saturated soil and groundwater sample) should be collected for each additional one-half acre, or portion thereof. Additional samples can be located based on the plume shape, dimensions, and locations of previous borings to best characterize the contaminant levels in the plume.

## F. WHAT IS THE MASS OF CONTAMINANTS TO BE TREATED?

Using the information obtained from the borings, find an average concentration of contaminants in the saturated soil and groundwater. The higher level of either TPH or COD should be used to find this average. The amount of oxygen required to remediate the site must satisfy the oxygen demand of all oxygen users (COD) found in the borings, not just the petroleum constituents (TPH). In most cases the COD will be higher than the TPH values at a leaking UST site. Once the average concentration in the saturated soil and groundwater is known, the mass of contaminants to be treated can be calculated. Although a portion of the contaminants adsorbed to the saturated soil will not dissolve into the groundwater, use of the average amount in the saturated soil is conservative. The mass of contaminants in the saturated soil samples should be greater than the mass found in the groundwater samples. Then calculate the mass of contaminants requiring remediation using the higher of the saturated soil or groundwater TPH or COD concentrations. The following example demonstrates how to calculate this amount:

Highest average concentration (TPH or COD)	= 5.4 ppm
Volume of contaminated mass (groundwater plume)	= 1,000 cy

[Assume saturated clay weighs 118 lb/cf (3,186 lb/cy) and sand weighs 124 lb/cf (3348 lb/cy)]

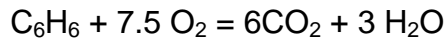
The **total mass of contaminants** is conservatively estimated to be:

$$\frac{5.4}{1 \times 10^6} \times (3200 \text{ lb/cy} \times 1000 \text{ cy}) = 17 \text{ lbs}$$

This approach assumes an average concentration of TPH/COD in both the soil and groundwater in the saturated zone. Porosity can be used to better define the mass of impacted soil and groundwater separately. In this case, the average saturated soil concentration and average groundwater concentration are used to estimate the mass of contaminants in the soil and groundwater. The total mass of contaminants is then the sum of the calculated soil and groundwater mass.

## G. WHAT AMOUNTS OF OXYGEN ARE REQUIRED TO REMEDIATE THE COC?

Once the total mass of contaminants is known, the amount of oxygen required can be calculated. As a rule of thumb, three pounds of oxygen are required per one pound of hydrocarbon. The stoichiometric amount of oxygen required for each contaminant could be calculated and added together to get the amount of oxygen required. As an example, the amount of oxygen needed to degrade benzene is:



[Molecular weights: C = 12, H = 1, and O = 16]

$$\begin{aligned}\text{C}_6\text{H}_6 (12 \times 6) + (1 \times 6) &= 78 \\ 7.5 \text{ O}_2 [7.5 \times (16 \times 2)] &= 240\end{aligned}$$

Therefore, it would take 240 pounds of oxygen to degrade 78 pounds of benzene, or 3.08 (240/78) pounds of oxygen per pound of benzene.

Illinois EPA assumes three pounds of O<sub>2</sub> are required per pound of contaminant (TPH or COD). From the example in paragraph F, it was determined that 17 lbs of contaminants require remediation; therefore, **51 lbs** (17 lb X 3 lb O<sub>2</sub>/lb of contaminant) **of oxygen** would be needed.

## H. HOW MUCH PRODUCT IS REQUIRED?

1. The amount of oxygen by weight (in percent) in the product and an estimate of how much will actually be released for chemical oxidation should be provided. Manufacturers provide the amount of oxygen contained in their product. Normally this information is provided in a lb/lb ratio (solid) or percent by weight (liquid) basis. For example, if a manufacturer claims the product contains ten percent oxygen by weight, the product will have one pound of oxygen available for every ten pounds of product.

The difficult part is estimating how much of this actual oxygen content will be released during the process. Using the calculated oxygen requirement of 51 lbs from paragraph G above, the amount of this product that will be required is 510 lbs [51 lb / 0.1 (10 percent)], assuming all available oxygen is released. A reasonable discussion of the amount of oxygen available in the product versus the amount released under field conditions is required. Since it is unlikely the total amount of oxygen available will be released, Illinois EPA will allow a **factor of safety of 20 to 30 percent** increase in the amount of product required. So if 510 lbs of a product are required from the calculations, this amount may be increased to 665 lbs [510 lbs x 1.3 (30 percent)].

2. Always ensure the products injected will not cause violations of the groundwater quality standards for constituents in the product. A thorough knowledge of the impurities and additives in a product and their potential impact on the groundwater is required.

## I. RADIUS OF INFLUENCE, NUMBER OF INJECTIONS, AND LAYOUT OF INJECTION PATTERN

1. What radius of influence can be achieved?

Four feet in one hour may be acceptable; however, four feet in six hours may make for an extremely long remediation. There are design changes that can improve delivery time such as changing the injection pressure.

Determining the location and number of injection wells required for a one-time application is the critical factor in the design of in-situ chemical oxidation. The design considerations are based on a one-time injection of oxygen. Injection wells should be located to provide distribution of the electron ( $O_2$ ) acceptor throughout the area targeted for remediation. Determining the area of influence is a key parameter for proper distribution of the product into the ground. Injection pressure, hydraulic conductivity (K), hydraulic gradient (i), and porosity (n) are important elements to calculate an approximate area of influence. Darcy's Law can be used to estimate the area of influence. Assuming the length ( $\Delta l$ ) is half of the radius of influence, use the injection pressure (psi) and an initial estimate of the radius of influence (ft) to calculate the time required to achieve this radius. The amount of time required should be evaluated for reasonableness. An example of this type of calculation follows:

$v = K \Delta h / \Delta l$ , where  $v$  = Darcy Velocity

$v_a = Ki/n$ , where  $v_a$  = Interstitial Velocity, (ft/sec)  
 $K$  = Hydraulic Conductivity, (ft/sec)  
 $i$  = Hydraulic Gradient,  $\Delta h / \Delta l$  (ft/ft)  
 $n$  = Porosity of Aquifer Material, (percent)

Generally, the products are injected into the ground with a pressure ranging from 250 to 2500 psi. To simplify the calculations, several assumptions are made to calculate the area of influence and interstitial velocity. Assuming a pressure of 1500 psi, an approximate area of influence of 4 feet, and  $K = 1 \times 10^{-4}$  cm/sec, as well as the given density of water, 62.4 lb/ft<sup>3</sup>:

$v_a = Ki/n = 3.28 \times 10^{-6}$  ft/sec  $\times$  3847 = 0.0126 ft/sec = 0.76 ft/min

where  $K = 1 \times 10^{-4}$  cm/sec =  $3.28 \times 10^{-6}$  ft/sec  
 $\Delta h = (1500 \text{ lb/in}^2 \times 144 \text{ in}^2/\text{ft}^2) / (62.4 \text{ lb/ft}^3) = 3462 \text{ ft}$   
 $\Delta l = 2 \text{ ft}$  (half of the design influence)  
 $i = \Delta h / \Delta l = 3462 \text{ ft} / 2 \text{ ft} = 1731 \text{ ft/ft}$   
 $n = 45\%$  (assumed)  
 $i/n = 1731 / 0.45 = 3847$

Based on the assumptions, it is calculated that a four-foot (0.76 ft/min.  $\times$  5 min. = 3.80  $\approx$  4 feet) radius of influence can be achieved in *five minutes* with an injection pressure of 1500 psi. Is this time frame reasonable? Is it reasonable to expect the design pressure (psi) to be applied for the required time (in this example, five minutes) at each injection point? The time required per injection can be decreased by increasing the injection pressure and/or reducing the design radius of influence. Location of the injection points should maximize the area of influence from each injection point (i.e., offset or staggered centers).

## 2. How many injections are required?

Knowing the radius of influence, a layout of an injection pattern can be developed to cover the plume that has been defined. Generally, it is recommended that injections be first advanced along the outside of the contamination plume.

3. How much is injected per point?

The initial plume samples can then be used to lay out (estimate) the amounts of product required in each area (based on the levels of contaminants).

**J. WHAT MONITORING WILL BE REQUIRED?**

It is recommended that sampling of the groundwater occur within a month prior to the injection date and one sampling after six months. Additional injections would only be allowed if it is demonstrated that a reasonable level of remediation has been achieved, or if the designer has provided justification for the lack of success. The initial injection report should include a plan to improve the results. If the failure of the initial injection cannot be addressed, future injections are discouraged. Sampling and analysis should be conducted for the contaminants of concern (BTEX, PNAs, etc.) during these events.

**K. USE OF MANUFACTURER'S CALCULATION SHEETS**

Illinois EPA will not accept the calculation sheets provided from the manufacturer without additional documentation. The documentation should present a step-by-step breakdown of each equation used in the spreadsheet, an explanation of each input parameter for each equation, and where the parameter comes from (site-specific and/or default numbers). The inputs must be specific to the site in question. If the source of an input parameter cannot be checked for accuracy or the calculations cannot be duplicated, Illinois EPA will request additional information.

**L. CLOSURE**

Sampling of the groundwater must show compliance with the applicable Part 742 remediation objectives.

**M. OTHER ITEMS TO CONSIDER**

The proposed injection points are considered Class V wells and are regulated by the Underground Injection Control (UIC) Program pursuant to 35 Ill. Adm. Code 704.148. Therefore, a Class V Injection Well Inventory Form must be submitted. The form, instructions, and well codes may be downloaded from <http://www.epa.state.il.us/land/regulatory-programs/underground-injection-control.html>.

For additional information regarding the UIC Program, please contact Bur Filson at 217-782-6070.