

**Treatment of Recalcitrant Chlorinated Organic Contaminants
Utilizing a Proprietary Oxidation Technique**

VTX

"Liquid Incineration for a Cleaner Environment"

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Introduction

A proprietary catalyst and reactant are employed in a method for degrading organic contaminants, such as chlorinated solvents, petroleum hydrocarbons and pesticides, in soil, wastewater and groundwater. Soil or water containing an organic compound having at least one oxidizable aliphatic or aromatic functional group is contacted with an active catalyst and a reactant in amounts effective to achieve mineralization of the compound in the presence of water in normal pH ranges.

The VTX technique has been demonstrated to treat several recalcitrant pesticides and chlorinated organic chemicals, including TCE, MtBE, PCE, 2,4-D, BTEX and many others.

Successful treatment of target contaminants *in situ* involves implementation of a strategy that places the catalyst and reactant in contact with the soil, wastewater and/or groundwater. The delivery system selected, therefore, becomes a critical factor. Treatment of wastewater and extracted groundwater is a simple matter of mixing the catalyst and hydrogen peroxide inline prior to a retention tank to provide the necessary time for the reactions to occur. Typically, two to three hours of

contact time is necessary for complete oxidation of target contaminants.

It should also be noted that treatment of contaminants *ex situ* is quite feasible. The system for treating soil and groundwater *ex situ* is highly effective and will, almost always, be cheaper than existing remedies. Existing case studies offer impressive results for the treatment of TCE, TCA and BTEX.

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Chemical Oxidation

Hydrogen peroxide, potassium permanganate and ozone are typical reagents used in the destruction of selected hydrocarbons. However, the oxidative power of these compounds is not sufficient to oxidize the vast variety of environmental contaminants. The following table illustrates the relative oxidation potential (as compared to chlorine at 1.0) for commonly known oxidants.

Relative Oxidation Power

<u>Reactive Species</u>	<u>Relative Oxidation Power</u>
Fluorine	2.23
Hydroxyl Radical	2.06
Atomic Oxygen (singlet)	1.78
Ozone	1.52
Persulfate	1.48
Hydrogen Peroxide	1.31
Permanganate	1.24
Hypochlorous Acid	1.10
Chlorine	1.00

Fluorine and hydroxyl radicals (free radicals) are capable of oxidizing most commonly found environmental contaminants. However, fluorine exhibits far too aggressive traits to be used on most environmental cleanup projects. Hydroxyl radicals are very

effective in treating most environmental contaminants. Typically, for environmental treatment purposes, hydroxyl radicals are produced by a technique known as Fenton's reaction.

Fenton-type systems, employing ferrous/ferric salts and hydrogen peroxide in acidified soil or water suspensions at pH ~2 to 3, have been studied as potential oxidants of soil and water contaminants. The reaction is unique in that ferric and ferrous iron are cycled between the two valence states in the presence of hydrogen peroxide simultaneously at low pH. With each cycle there is production of a hydroxyl radical. Numerous studies have been conducted which indicate that the hydroxyl radicals produced in Fenton's reaction can successfully oxidize contaminants in soil and water. For example, pentachlorophenol and trifluralin were shown to be extensively degraded in soil suspensions when treated with $\sim 4 \times 10^{-3} \text{M}$ ferrous ion and 3.5M (120 g/L) hydrogen peroxide; hexadecane and Dieldrin were partially transformed under similar conditions. Tetrachloroethene was mineralized in silica sand suspensions treated with $5 \times 10^{-3} \text{M}$ ferrous ion and 2.1M hydrogen peroxide. Numerous other studies exist. The drawback to Fenton's style treatment is that it is cumbersome, exhibits significant health and safety risks and requires costly materials of special construction to conduct. The process also produces significant sludge in water based treatment systems, which adds significantly to the cost. In soil decontamination, the need to acidify the soil is a serious drawback to use of Fenton's reaction. In the case of soil treatment, acidification to an optimum pH of 3 is difficult and clumsy because soil has a high buffering capacity. Moreover, acidification itself can be viewed as a pollutant.

At neutral pH, ferrous ion can rapidly reduce hydrogen peroxide to a hydroxyl radical.

However, there is a major disadvantage of using ferrous ion in this way in that it is required in stoichiometric amounts. Further, peroxide demand and, therefore, ferrous ion demand can be high due to competitive oxidation of soil/water organic matter and soil-catalyzed decomposition. A further disadvantage of ferrous ion is that the ions are oxidized by hydroxyl radicals and, therefore, competes with the target compounds unless its concentration is kept low by gradual addition in dilute form.

Description of the VTX Chemical Oxidation Process

The VTX process is based upon the finding that certain catalysts and peroxide or similar reactant can be employed to degrade soil and/or water borne contaminants at **normal pH levels**. VTX process accomplishes destruction of contaminants by producing free radicals on a similar scale to Fenton's reaction at neutral pH.

With the VTX technique, soil or water containing an organic compound having at least one oxidizable aliphatic or aromatic functional group such as pesticides, petroleum hydrocarbons or chlorinated solvents, are contacted with an active, soluble catalyst and an oxidizing reagent in amounts effective to achieve degradation of the target compound in the presence of water at neutral pH levels.

The preferred catalyst is safe, (i.e., does not add to the contamination of the soil or water to be decontaminated). The catalyst uses very small amounts of an environmentally acceptable metal as its chief catalysis point within the VTX complex. However, unlike Fenton's type reactions, the VTX complex allows for free radical generation at neutral pH. The non-metallic portion of the VTX complex is

environmentally safe and is degraded in the process.

Since the process is self-consuming to a large degree, only CO₂, low levels of non-toxic metal, sodium chloride, some remaining partially oxidized catalyst in the case of incomplete oxidation, and water are produced as final products. All breakdown products of the catalyst are readily biologically degradable and environmentally safe.

As mentioned, an advantage of the process is that the catalyst/reactant combination itself substantially oxidizes the VTX catalyst, but only after the catalyst has degraded the target compound. The catalyst is used in combination with a reactant (oxidant) in concentrations effective to degrade the target compound. Hydrogen peroxide is typically utilized with the catalyst. The amount required depends upon the concentration of contaminant to be degraded, the type of contaminant and can also depend upon the natural organic matter content of the soil and/or water.

The degradation reaction proceeds at normal pH ranges, which can be from about 3.5 to about 8.5, more typically around pH 7. It is an advantage that no acidification of the soil or water is required as with the Fenton's type reaction. Degradation occurs even where the soil and/or water buffers the reaction. This would include carbonate buffer within typical environmental ranges.

Low concentrations of reactant and catalyst may be employed, and yet provide relatively rapid degradation (i.e., within three hours or less). Reactant to pesticide, petroleum hydrocarbon or chlorinated solvent mass ratios can be low, (i.e. peroxide dosing on the order of about 1.0 to 3.0 times the contaminant mass as measured by Chemical Oxygen Demand). Catalyst concentration is much lower than contaminant

concentration. Remediation thus takes place under very mild conditions.

As previously mentioned, a variety of organic compounds containing at least one oxidizable aliphatic or aromatic functional group can be degraded using this method. The process is especially useful for the degradation of chlorinated solvents (e.g. TCE, PCE) and recalcitrant organics like MtBE.

In-house investigation of the effectiveness of the process on TCE and PCE were quite impressive. TCE in soil was reduced from 836 ppm to <1 ppm in one study and from 38 ppm to <1 ppm in a second study. In a separate study, PCE in soil was reduced from 31 ppm to <5 ppb. Water contaminated with TCE at 100 ppm was treated with a single application of catalyst and reactant. TCE concentrations dropped to non-detection levels after treatment. Also, no detectable levels of intermediary organics (i.e., vinyl chloride) were found in the soil or water with a proper dose of catalyst. All studies of soil and water were conducted at neutral pH. The time allowed for treatment was 3-4 hours.

The following is a table of selected results from bench scale testing. Complete oxidation of targeted chemicals can be achieved in nearly all cases by increasing the VTX process chemistry.

Selected Chemical Oxidation Results of the VTX Process

Target Compounds	Before Treatment	After Treatment	
	ppb	ppb	

<u>MTBE</u>	85,000	< 5
<i>Benzene</i>	294,875	< 5
<i>Toluene</i>	153,678	< 5
<i>1,2-Dichloropropane</i>	120,450	<
<i>Trichloroethylene</i>	500,000	< 5
<i>1,1-Dichloroethane</i>	84,346	< 5
<i>Tetrachloroethylene</i>	33,000	<10
<i>cis 1,2-Dichloroethylene</i>	4,550	<10
<i>Vinyl chloride</i>	40	<5
<i>Ethylbenzene</i>	55,273	< 5

Dose rate (mass/mass): 3 to 5 Parts Oxidant: 1 Part Contaminant as COD

A limited amount of large-scale field application of the VTX process are ongoing. Case study information can be made available upon request.

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A General Description of Treatment Techniques

Successful use of this technology for cleaning soil, wastewater and/or groundwater will require a procedure which contemplates complete contact of the contaminant with the catalyst and reactant. As mentioned previously, treatment of water is a simple matter of making contact through a mixing scenario and providing the correct amount of retention time.

For *ex situ* soil contamination, soil should be put through a hammermill/screen (i.e. Powerscreen, Extec or equivalent) to break the soil up into small particles. Liquid catalyst is delivered under pressure into the soil as it travels up the conveyor belt. The delivery of this product would contemplate contact of the catalyst evenly through

the soil. Diluted reactant would follow the addition of the catalyst and would proceed until saturation of the soil is attained. Treatment of soil using this technique has worked very well.

In situ treatment of soil using this technique is difficult unless assurances of contact of the catalyst and reactant can be made. A system for groundwater injection is most often installed utilizing screened well points. Catalyst and reactant are injected into the contaminated aquifer under pressure to affect dispersion. Treatment occurs upon contact. However, the most efficient approach for treating groundwater zones containing heavy levels of contaminant is to pull the groundwater up into a reactor vessel, treat it to non-detect levels and return the treated water to the groundwater with excess catalyst and reactant to the outside edges of the plume from which the groundwater was removed in order to attack adsorbed contaminant. The remedial objective is to create a cone of depression around the collection well and return groundwater with excess VTX treatment from the outside edge of the plume back towards the collection point.