

**CHEMICAL OXIDATION
USING OZONE, HYDROGEN PEROXIDE, AND AIR INJECTION
SYSTEMS
FOR AGGRESSIVE REMEDIATION OF
BTEX, MTBE, AND TBA**

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Chemical Oxidation Using Ozone, Hydrogen Peroxide, and Air Injection Systems for Aggressive BTEX, MTBE, and TBA Remediation

Introduction

There can be many challenges to providing cost-effective and aggressive remediation solutions to sites impacted with contaminants that include benzene, toluene, ethylbenzene, and xylenes (BTEX); methyl tertiary butyl ether (MTBE); tertiary amyl methyl ether (TAME); and tertiary butyl alcohol (TBA) compounds. Groundwater & Environmental Services, Inc. (GES) has developed and utilized various innovative ozone, hydrogen peroxide, and air injection systems that can remediate BTEX, MTBE, and TBA impact at costs significantly below conventional methods and within a relative short time frame.

This paper presents case studies of projects in which BTEX, MTBE, and TBA impact in soil and groundwater (including separate-phase hydrocarbons) was remediated through the combination of ozone and hydrogen peroxide injection or through the combination of hydrogen peroxide and air. Provided is a review of two technologies (GES' patent-pending PulseOx and HypeAir aggressive chemical oxidation techniques) that have been used successfully to remediate contaminated soil and groundwater through monthly and short-term (daily/weekly) events. Case studies discuss the utilization of hydrogen peroxide and air injection systems to remediate soil and groundwater impacted with BTEX and MTBE at relatively low life-cycle remediation costs (\$15,000 to \$200,000). These case studies are from sites exhibiting varying lithologies and within different regulatory environments.

Overview

Max-Ox® is GES' patented technique for aggressive remediation of contaminants in soil and groundwater. The Max-Ox system delivers highly effective oxidants into the subsurface via nested injection wells for maximum reactant distribution. Max-Ox technologies encourage the formation of hydroxyl radicals, powerful oxidizers that quickly break down organic contaminants into end products of carbon dioxide and water. The injection systems can remediate a significantly greater mass of contaminants than oxygen injection and bioremediation systems. The Max-Ox process is effective in the remediation of many dissolved contaminants including MTBE, BTEX, TBA, naphthalene, and chlorinated solvents.

GES has developed two Max-Ox systems: HypeAir (hydrogen peroxide and air) and PulseOx (ozone and hydrogen peroxide).

The HypeAir system, employed for short-term events, uses four processes to remediate soil and groundwater:

- chemical oxidation via hydrogen peroxide injection
- chemical oxidation via hydroxyl radical reaction
- mass transfer of volatile organic compounds via air injection
- enhanced bioremediation via air injection and oxygen-producing chemical reactions following injection events

The PulseOx system, developed jointly by GES and its partner, Applied Process Technology, uses five processes to aggressively remediate soil and groundwater:

- chemical oxidation via ozone injection
- chemical oxidation via hydrogen peroxide injection
- chemical oxidation via hydroxyl radical reactions

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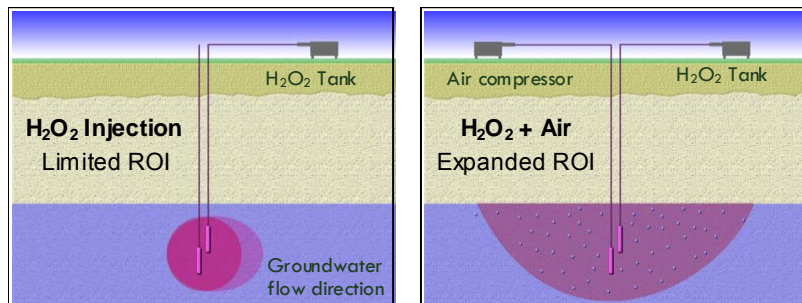
- enhanced bioremediation via high dissolved oxygen levels
- mass transfer of volatile organic compounds via air injection

HypeAir Injection Technique

HypeAir processes are used in short-term remediation events to reduce project life cycle duration and costs. By injecting hydrogen peroxide and air together at varying pressures, the radius of influence for each injection point is greatly increased. Existing monitoring wells, air sparge points, or soil vapor extraction wells can be used to reduce costs.

The HypeAir systems are housed in mobile trailers or trucks, complete with generators. The systems use a variety of injection points and well packer materials to remediate significant source areas in months, weeks, or even days.

This solution achieves effective subsurface distribution of hydrogen peroxide, an oxidizing agent, by combining it with air at varying pressures to increase the radius of influence of each injection point. While hydrogen peroxide reacts directly with organic contaminants to produce carbon dioxide and water, its effects are enhanced when reacting with a metal catalyst or naturally-occurring iron to produce the hydroxyl radical, a very powerful oxidizer.



A significantly expanded radius of influence is achieved by combining oxidants with air

This technique accelerates chemical processes to improve remediation results. Results are further improved with the addition of a catalyst to advance the development of hydroxyl radicals and a supplement to enhance natural bioremediation following chemical oxidation injection events.

The HypeAir chemical reaction is demonstrated by the formula $\text{H}_2\text{O}_2 + \text{C} \rightarrow \bullet\text{OH} + \text{OH}^- + \text{C}^+$, where C = metal catalyst and $\bullet\text{OH}$ = hydroxyl radicals. (Fenton, H.J.H. (1894) J. Chem. Society, 65, 899; Haber, F., and Weiss, J.J. (1934) Proc. Roy. Soc. London, Ser. A, 147, 332). Hydrogen peroxide also reacts directly with organic contaminants and can result in additional mass transfer of contaminants. Unlike conventional Fenton's oxidation applications, the HypeAir process does not result in highly exothermic reactions.

Case Study

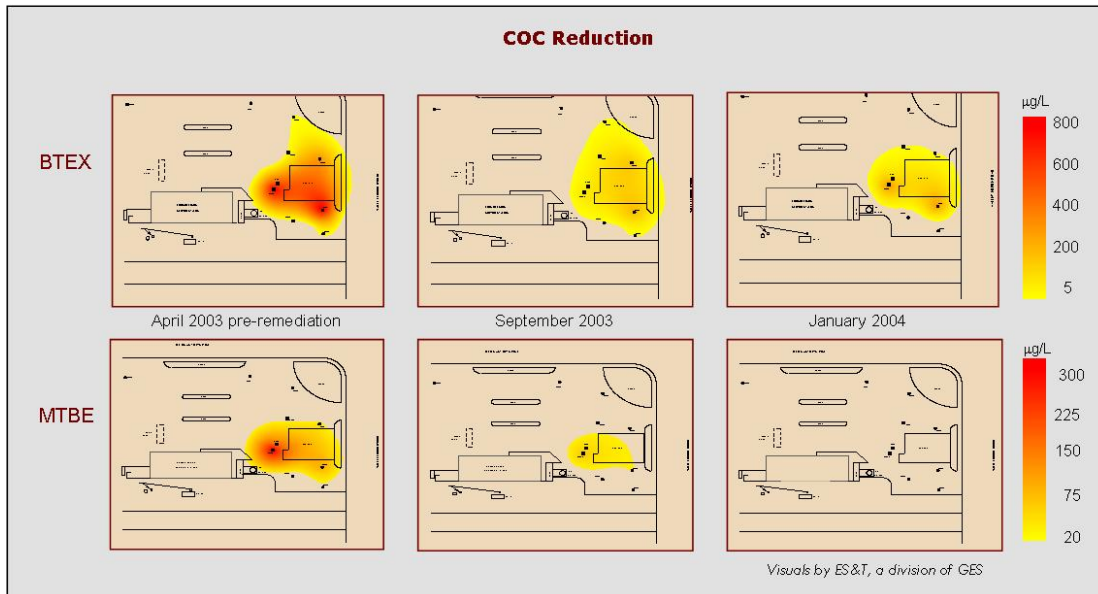
An inactive gasoline service station site was located in an area of silty clay and gravel, with approximately four feet depth to water. The site was impacted with BTEX, MTBE, and Naphthalene. Due to the limited mass present in the subsurface and the presence of permeable gravel fill material in the vicinity of the remaining hydrocarbon mass, it was determined that temporary hydrogen peroxide injection events would be the most cost-effective remediation method. HypeAir, using air to help move the hydrogen peroxide, was selected to more effectively distribute the reactants in the subsurface.

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A total of two injection events, each lasting two days, were performed one month apart, in July and August 2003. A total of 2,550 gallons of hydrogen peroxide at 5 to 10 percent concentration was injected during the two events. Dissolved BTEX and MTBE were significantly reduced after the two events, and continue to decrease over time, as illustrated below.

Well	Dissolved BTEX Concentrations (ug/l)					% Reduction 4/03 – 1/04
	04/22/03	07/07/03	08/12/03	10/02/03	01/06/04	
MW-3	312.2	748.1	10.9	76.5	3.5	99%
MW-4	3.6	ND (5)	ND (5)	2.5	ND (5)	100%
MW-6	793.6	687.4	708.9	302.4	287.9	64%
RW-1A	771.8	87.6	92.9	23.9	284.3	63%
RW-1	ND	118.8	47.5	42.9	2.6	NA
AVERAGE = 81%						

Well	Dissolved MTBE Concentrations (ug/l)					% Reduction 4/03 -1/04
	04/22/03	07/07/03	08/12/03	10/02/03	01/06/04	
MW-3	33.7	31.2	2	9.5	6.2	82%
MW-4	12.3	10.2	ND (5)	ND (5)	ND (5)	100%
MW-6	102	49.8	39.9	24.2	8.7	91%
RW-1A	319	85.8	73	49	6.7	98%
RW-1	157	183	63.7	22.9	16.8	89%
AVERAGE = 92%						



Overall contaminant reduction noted at the five monitoring wells: BTEX 81 percent, and MTBE 92 percent. The total remediation cost was \$15,000.

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PulseOx Injection Technique

Nested Max-Ox stainless steel injection points are used to directly deliver ozone and hydrogen peroxide reactants, with oxygen and air, into groundwater at controlled ratios and locations. This process forms hydroxyl radicals, among the most powerful oxidizers available, with a much greater oxidation potential than either ozone or hydrogen peroxide individually.

Hydrogen peroxide, typically in a 35% solution, is injected from a double-walled holding tank at flow rates up to 200 gpd. Ozone is delivered to injection wells at varying flow rates (up to 30 scfm) at a pressure of 25 psi or more. To achieve maximum distribution with an effective radius of influence at each point, the ozone-oxygen stream is combined with compressed atmospheric air, resulting in a stream capable of delivering up to 30 scfm of ozone, oxygen, and air. Ozone concentration, depending on air cycling frequency, is typically 3,000 - 100,000 ppm_v.

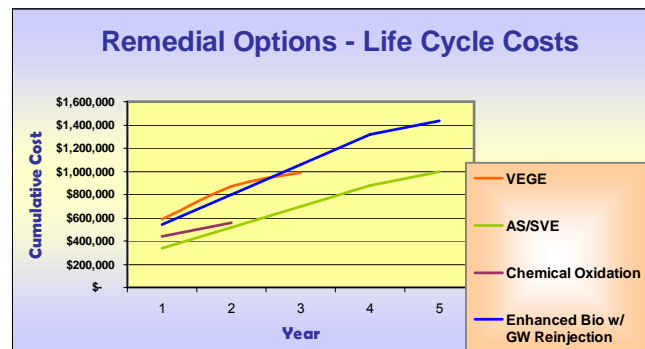
Although ozone will limit microorganism growth in the vicinity of each injection point, dissolved oxygen effects are typically observed at greater distances than the area of ozone influence. The elevated dissolved oxygen concentrations promote the degradation of remaining dissolved contaminants that are aerobically biodegradable. The formation of hydroxyl radicals through the introduction of ozone and hydrogen peroxide is performed by the reaction $2O_3 + H_2O_2 \rightarrow 2OH\cdot + 3O_2$.

Case Study

A PulseOx system using ozone/peroxide/air injection was used at a Delaware site to remediate adsorbed-phase hydrocarbon impact and a dissolved-phase BTEX, MTBE, TAME, and TBA plume that extended 800 feet and impacted eight residential water supply wells. The site, an active gasoline service station in Kenton, DE, was in an area of sandy soil with depth to water of eight to ten feet.

Feasibility testing indicated that chemical oxidation could be very effective since ozone could effectively be distributed into the subsurface (15'-25' ROI observed during testing). Following site characterization and remedial pilot testing, GES prepared a life-cycle cost analysis to determine the most cost-effective remediation approach. This included modeling of potential remedial technologies to evaluate potential results and durations of alternative approaches. Modeling performed by ES&T, GES' division for advanced computer aided technology, supported a determination that chemical oxidation would provide the most cost-effective and shortest life cycle solution. Estimated cost for an estimated 12-months' duration was \$320,000 for 12 months of remediation.

A PulseOx 1000 system, housed in a 16' trailer, was designed to operate continuously for a period of up to nine months. The system control panel cycled injections of ozone, hydrogen peroxide, oxygen, and air to nested stainless steel injection wells. A vapor recovery system was used to prevent the accumulation of vapors in the vadose zone and help remediate an unsaturated adsorbed-phase mass in the vicinity of an existing UST system.



Life-cycle cost analysis assisted in technology selection

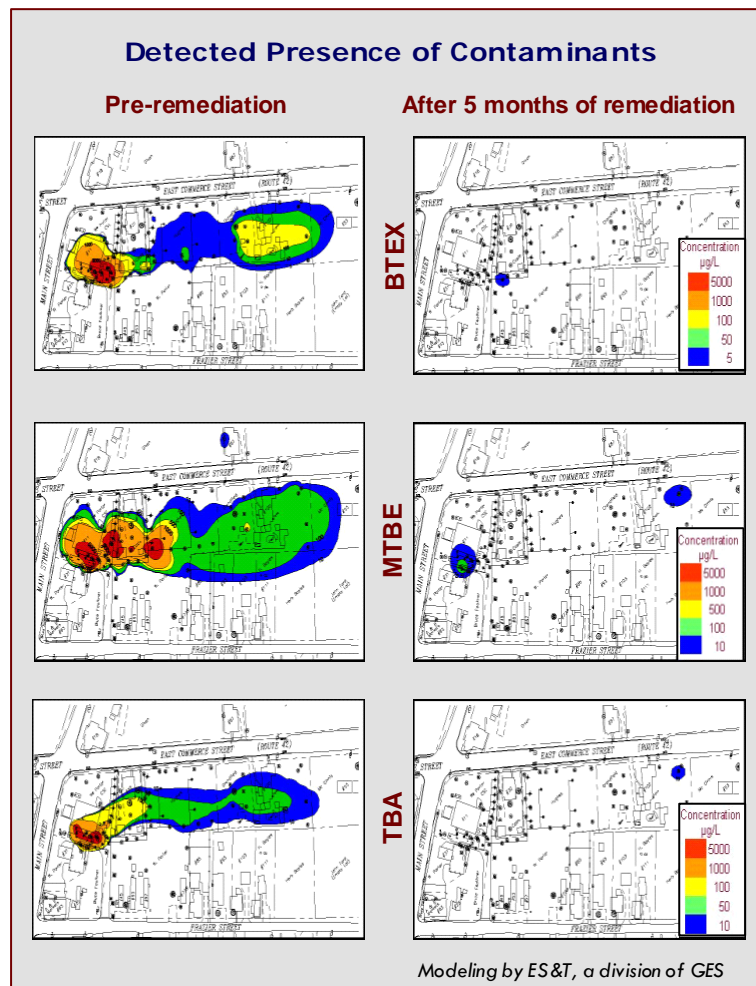
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Formation of hydroxyl radicals in the subsurface accelerated the degradation of contaminants to carbon dioxide and water. Various indicators of contaminant breakdown were noted, including dissolved carbon dioxide levels and elevated levels of carbon dioxide, oxygen, and ozone in the vadose zone headspace.

Dissolved oxygen concentrations in groundwater, below 2 mg/L throughout the plume prior to remediation, were noted at up to 25 mg/L at injection wells and 20 mg/L at nearby observation wells. The ozone injection radius of influence was observed up to 25' from injection wells and up to 15' for low flow and high concentration ozone injection.

After three months of remediation, only three of the 45 sampling locations (all on-site) indicated detectable concentrations of BTEX. Prior to remediation, there was little to no dissolved oxygen throughout the plume, and after three months there were zones as high as 25 ppm. After five months of remediation, BTEX was not detected in any of the sampling locations. Only one well indicated MTBE concentrations greater than 60 µg/L, and only one well indicated TBA concentrations greater than 50 µg/L. After seven months of system operation, DNREC granted approval to deactivate the remediation systems and initiate one year of groundwater monitoring for closure.

After one quarter of post-remediation monitoring, BTEX was not detected in any of the 11 sampling locations. Only one well showed MTBE concentrations above 30 µg/L, and all wells indicated TBA concentrations of less than 50 µg/L. After three quarters of post-remediation monitoring, only one well, located in the original source area, indicated MTBE concentrations above 30 µg/L. Concentrations of BTEX, MTBE, and TBA were not detected or were less than 4 µg/L in the other eight compliance sampling locations. No Further Action designation was achieved in July 2004. Actual remediation cost was \$200,000 for five and one-half months of remediation.



Modeling of plume degradation over time.