Ex Situ Treatment of MTBE-Containing Groundwater by a UV Peroxide System

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This article describes the design, implementation, and operating results for an ex situ ultraviolet/hydrogen peroxide (UVP) system to treat methyl tert-butyl ether (MTBE) in extracted groundwater. The UVP modification was designed to reduce the operation and maintenance costs of an existing groundwater pump-and-treat treatment system that relied on air stripping and carbon adsorption. The UVP system is relatively inexpensive and can easily be scaled to cope with different groundwater extraction rates up to 80 gpm by adding UV lamps in series or in parallel at the higher groundwater extraction rates. The MTBE concentration in the effluent from the UVP system to the carbon vessels decreased from an average of 590 µg/L to approximately 2 µg/L on average over 33 months of operation of the UVP. Incorporation of this UVP modification as a second-stage treatment to the groundwater pump-and-treat/soil vapor extraction system, after the air stripper and prior to the carbon vessels, significantly increased the usable life of the carbon (from two months previously to about two years after installation) and completely resolved the issue of frequent MTBE breakthroughs of the carbon that had plagued the remediation system since its inception. © 2006 Wiley Periodicals, Inc.

INTRODUCTION

MTBE in groundwater is difficult to treat by conventional ex situ treatment methods. Ultraviolet/peroxide (UVP) systems have been successfully applied to treatment of methyl tert-butyl ether (MTBE) in water. However, these systems require large capital expenditures and are not easily scalable and, therefore, are not cost-effective at small sites such as the typical gasoline station leaking underground storage tank. Furthermore, while laboratory studies of MTBE destruction with UVP systems under carefully controlled conditions have been published, there is very little if any published data on actual operational systems in the field (i.e., in the presence of other dissolved gasoline constituents).

This article documents the application of a low-cost, expedient, scalable UVP system that has been successfully applied at a gasoline station, together with destruction efficiency data useful for design of such a treatment system.

MTBE is a gasoline constituent that, in large measure because of its high solubility in water, is viewed as a widespread environmental problem and a potential threat to groundwater in several areas of the country (Lince et al., 2001; Squillace et al., 1998). The treatment of gasoline contamination in groundwater, and consequently of MTBE, has relied for the most part on the standard groundwater pump-and-treat system, often coupled with soil vapor extraction (SVE) or dual-phase extraction systems. In many of these remediation systems, the extracted groundwater is passed through virgin coconut carbon to adsorb MTBE...
and other dissolved gasoline constituents from the extracted groundwater so as to allow for the discharge of the treated water to sewer or stormwater runoff collection systems.

The adsorption of MTBE onto carbon is inefficient and expensive due to its low adsorption coefficient and is usually accompanied by breakthroughs of unpredictable frequencies due to coadsorption of other gasoline constituents, bicarbonates, and dissolved solids, as well as the relative ease with which MTBE partitions into water. Thus, overall remediation is hampered by costs of frequent carbon changeouts and violations of regulatory discharge requirements. These factors act in concert to prolong the time and raise the operation and maintenance expenditures required to achieve site cleanup and regulatory closure.

Air stripping is sometimes used for MTBE treatment, as at the subject site. At ambient groundwater temperature, air-stripping efficiency is too low to be effective, but increasing the water temperature can enhance the partitioning of MTBE from water to air. Unfortunately, the monthly energy bill for operation of a water heater is high. The air stripper at the subject site operates at about 90 to 98 percent destruction efficiency because of the use of a heater to boost water temperature. At 98 percent efficiency, if the influent MTBE concentration is greater than 25 µg/L, a carbon-polishing unit is required to achieve an effluent concentration below the detection limit (0.5 µg/L MTBE). The adsorption isotherms provided by carbon vendors are proprietary. However, the vendor used here (Barneby-Sutcliffe) provided Freundlich isotherms for the MTBE adsorption performance of their carbon in the form of:

\[
q = k \cdot C^n
\]

where \(q\) is the adsorbed concentration in mass of contaminant per mass of activated carbon (mg/g), \(C\) is the dissolved concentration in mass of contaminant per volume of water (µg/L), and \(k\) and \(n\) are dimensionless constants. A representative range of published values for the adsorption isotherm of MTBE and coconut carbon is \(k = 0.01\) to 0.04 and \(n = 0.7\) to 1.0 at 20° C. For an MTBE influent concentration of 100 µg/L, an adsorption on the order of about 1 mg of MTBE per gram of carbon can be expected.

With an MTBE influent concentration of 100 µg/L, 6,000 lbs of carbon, and a flow rate of 10 gpm, the maximum breakthrough time should be 500 days, or about 16 months. Prior to installation of the UVP treatment stage, breakthrough times of only two to three months were observed in the field, presumably due to the presence of total petroleum hydrocarbons (TPH) and other constituents (i.e., dissolved solids) in the groundwater and due to nonuniform advance of the mass transfer zone within the carbon vessels. Due to the high cost of carbon changes and water heating, an intermediate treatment stage was needed to improve destruction efficiency.

A low-cost, scalable UVP system was installed at a gasoline station site in South Lake Tahoe, California, which already had operational pump-and-treat and SVE remediation systems. The extracted groundwater was passed through an air stripper followed by second-stage carbon treatment before being tested and discharged into the stormwater runoff system under a special-use discharge permit. However, the cost of carbon replacement was unacceptably high, and carbon replacement was costing an average of over $2,500 a month, even after more than three years of remediation. MTBE concentrations in groundwater were initially well over 100,000 µg/L. The goal, therefore, was to devise a simple, economical approach to reduce operation and maintenance costs and control breakthroughs through the design and installation of the UVP system described here.
Over the past few years, reports discussing the use of advanced oxidation processes (AOPs) as a means of remediating organic chemicals, including MTBE, have emerged in the literature (Acero et al., 2001; Huber et al., 2003). AOPs typically use ozone alone, ozone and ultraviolet (UV) radiation, or ozone and hydrogen peroxide ($\text{H}_2\text{O}_2$). Commercially available systems using AOPs are often sold as “black boxes” and are typically out of the price range of remediation efforts associated with gasoline stations.

The AOP reactions generate the highly reactive hydroxyl radical ($\cdot\text{OH}$), which then oxidizes MTBE (Stefan et al., 2000).

\[
\begin{align*}
\text{C}_5\text{H}_{12}\text{O} & \rightarrow 4\cdot\text{OH} \rightarrow \text{C}_5\text{H}_{10}\text{O}_2 \text{ (tert-butyl formate)} + 3\cdot\text{H}_2\text{O} \\
\text{C}_5\text{H}_{10}\text{O}_2 & + 2\cdot\text{OH} \rightarrow \text{C}_4\text{H}_{10}\text{O} \text{ (tert-butyl alcohol)} + \text{CO}_2 + 1\cdot\text{H}_2\text{O} \\
\text{C}_4\text{H}_{10}\text{O} & + 8\cdot\text{OH} \rightarrow \text{C}_3\text{H}_6\text{O} \text{ (acetone)} + \text{CO}_2 + 6\cdot\text{H}_2\text{O} \\
\text{C}_3\text{H}_6\text{O} & + 6\cdot\text{OH} \rightarrow \text{C}_2\text{H}_4\text{O} \text{ (acetaldehyde)} + \text{CO}_2 + 4\cdot\text{H}_2\text{O} \\
\text{C}_2\text{H}_4\text{O} & + 6\cdot\text{OH} \rightarrow \text{CH}_2\text{O} \text{ (formaldehyde)} + \text{CO}_2 + 4\cdot\text{H}_2\text{O} \\
\text{CH}_2\text{O} & + 4\cdot\text{OH} \rightarrow \text{CO}_2 + 3\cdot\text{H}_2\text{O} \\
\text{C}_5\text{H}_{12}\text{O} & + 30\cdot\text{OH} \rightarrow 5\cdot\text{CO}_2 + 21\cdot\text{H}_2\text{O}
\end{align*}
\]

The stoichiometry shows that a molar ratio of approximately 15 moles of $\text{H}_2\text{O}_2$ to 1 mole of MTBE is required for complete breakdown. Incomplete breakdown can yield tert-butyl formate (TBF), tert-butyl alcohol (TBA), acetone, acetaldehyde, and formaldehyde.

The slowest kinetic reaction rate is the transformation of TBA to acetone (Stefan et al., 2000). Therefore, TBA can be monitored in the system effluent as an indicator of incomplete MTBE breakdown. TBA is also often present in MTBE-contaminated groundwater as a gasoline additive, a feedstock for the synthesis of MTBE, and/or a natural breakdown product. At the subject site, the system influent and effluent were analyzed for a list of fuel oxygenates, including TBA. Effluent sampling indicated that either the reaction was going to completion or that the carbon was adsorbing all unreacted breakdown products.

MTBE has been successfully treated using UV/$\text{H}_2\text{O}_2$ (Cater et al., 2000; Stefan et al., 2000). The UV/$\text{H}_2\text{O}_2$ process involves the photolytic breakdown of $\text{H}_2\text{O}_2$ to generate the $\cdot\text{OH}$ radical, which is indiscriminate in its ability to promote the oxidation and mineralization of a wide range of organic compounds, including MTBE, chlorinated solvents, and other organic pollutants (Vorhach, 2002). A notable advantage of the UV/$\text{H}_2\text{O}_2$ process over the UV/ozone process, especially where drinking water is concerned, is that the former does not generate the bromate ion, a suspected carcinogen, from naturally occurring bromide in groundwater (Damm et al., 2002; Symons & Zheng, 1997). These emerging oxidation technologies offer the promise of expedited and less costly cleanups as understanding of them improves with experience and documentation of sites cleaned up to regulatory mandates.
AOP reactors are assumed to follow first-order or pseudo-first-order kinetics that can be described as follows (Kuo, 1998):

$$\frac{C_{\text{out}}}{C_{\text{in}}} = e^{-k(V/Q)} = e^{-kt}$$

where \( C \) is contaminant concentration in groundwater, \( V \) is the reactor volume, \( Q \) is the groundwater flow rate, \( k \) is the rate constant, and \( t \) is the hydraulic retention time.

It can be seen from the formula above that MTBE destruction efficiency is proportional to hydraulic retention (exposure) time. Retention time can be increased by either decreasing the flow rate or increasing the number of UV lamps in a series. In the field, increasing the number of lamps is the more practical choice. The rate constant is proportional to the power applied—that is to say, the higher the wattage of the lamp, the more rapid and complete the dissociation of •OH and the more rapid and complete the resulting destruction of MTBE (and TBA).

For electrical energy, the equation can be rewritten (Chang & Young, 2000) as:

$$k = \frac{P}{(V \times E_{E0})}$$

$$E_{E0} = \frac{(P \times t)}{(V \times \ln (C_{\text{out}}/C_{\text{in}}))}$$

where \( E_{E0} \) is electrical energy per order, \( P \) is power (watts), \( t \) is time (minutes), \( V \) is reactor volume (liters), and \( k \) is pseudo-first-order rate constant. Rearranging:

$$\frac{C_{\text{out}}}{C_{\text{in}}} = e^{-\left\{\frac{P}{V \times E_{E0}}\right\} \times t}$$

There are some problems with applying the rate constant approach to system design in the field. At gasoline station release sites, MTBE is seldom the only constituent present in the reaction vessel, and is accompanied by varying concentrations of dissolved aliphatic and aromatic petroleum hydrocarbons, other fuel oxygenates, and, occasionally, iron. Furthermore, the groundwater extraction rates, along with transfer pump rates and dosing rates within the treatment system, are often variable. There is a difference, therefore, between MTBE destruction that can be achieved under controlled conditions in the laboratory and what can practically be achieved at an operational reformulated gasoline release site. Unfortunately, published field data are hard to come by.

**MATERIALS AND METHODS**

The design and implementation of the UVP system is based on a controlled laboratory study by Chang and Young (2000). In essence, these authors designed an in vitro experimental system consisting of the photolysis of \( \text{H}_2\text{O}_2 \) using a low-pressure UV lamp to generate the •OH radical, which then oxidized MTBE in a recirculating system. These authors studied the breakdown of MTBE using \( \text{H}_2\text{O}_2 \) to MTBE in molar ratios of 4:1, 7:1, and 15:1. Over a 120-minute observation period, they reported a 99.9 percent degradation of MTBE, with optimal results at a molar ratio of \( \text{H}_2\text{O}_2 \) to MTBE of 15:1 (the stoichiometric ratio discussed earlier). The authors reported a corresponding increase in the formation of TBF such that at the end of one hour, the TBF concentration remaining in the reaction vessel exceeded the MTBE concentration. The reaction rates for breakdown products TBF and
TBA are slower than the reaction rate for MTBE. Therefore, accumulation of these degradation intermediates is possible and must be accounted for in any remediation system, as discussed later. An excess molar ratio sufficiently above the 15:1 ratio and an increased retention time should eliminate these breakdown products and drive the reaction to completion.

With this in mind, an intermediate-stage UVP treatment system was designed with a molar ratio assured to be greater than 15:1 to destroy MTBE not removed by the air stripper. The carbon treatment stage was retained only because the local utility district required that the treated discharge to the sewer system always be below the detection limit of 0.5 µg/L. The tertiary carbon stage therefore assured this would never occur but was no longer relied on as a treatment stage, as, by design, the treated effluent from the UVP system was near or below the detection limit.

Exhibit 1 is a simplified schematic of the remediation system, including the air stripper and the pump-and-treat system, modified to include the UVP system. The extracted groundwater (influent) passes through an oil-water separator and a water heater and then travels through an air-stripping tower containing packing material. Air is blown through this tower, and water percolates down into the air stripper sump. A transfer pump then pumps the water through the UVP system and through each of the carbon vessels in series before being discharged to the sewer system.

In order to achieve adequate mixing of the H₂O₂ with the air stripper effluent water following initial trials, the H₂O₂ was delivered directly into the air stripper water effluent holding sump. H₂O₂ (30% w/v) was pumped from a holding tank at a rate of 25 mL/min (7.5 g/min) based on the dissolved MTBE concentration from a 100-gallon tank into this sump, and the effluent water (containing H₂O₂) from the air stripper sump was then pumped through a series of UV lamp units before entering the carbon-containing vessels, as illustrated in Exhibit 1. The holding tank below the air-stripping column had a capacity of 140 gallons. The transfer pump was regulated so that it began pumping when the tank was full and stopped pumping when 100 gallons had been removed from the tank. The pumping rate was adjusted to the system influent flow rate so that the transfer pump cycled on and off about every eight minutes, to maintain a flowthrough rate of about 12.5 gpm, on average, to match the groundwater extraction rate.

The optimum dose of H₂O₂ delivered during this eight-minute period was determined to be 200 mL, or 7.5 grams per minute, at an MTBE influent concentration of 2,000 µg/L. This resulted in an effective H₂O₂ concentration of approximately 0.158 percent or about 158 µg/L at an extraction rate of 12.5 gpm in the air stripper effluent holding tank just before this water entered the UV lamp units. In principle, as the influent MTBE concentration declines, the H₂O₂ dose rate could likewise be reduced, but this is difficult to accomplish in practice. Therefore, the system has an inherent tendency to overdose, but this is not seen as a problem so long as underdosing does not occur. The dosing is done by continuous feed, so
that the concentration at the end of the pumping cycle when the tank is nearly empty is higher than at the beginning of the pumping cycle when the tank is full. The variability in dose rate due to pump-cycling and variable pumping rates is not considered important, but these factors do introduce some variability into the measured MTBE destruction efficiency, a factor that cannot be controlled as in laboratory studies.

The UV lamps used were purchased from Quality Marine in Los Angeles, California, and were manufactured by Tropical Marine Centre in the United Kingdom. These UV lamp units are marketed as water sterilizers for aquariums. Each UV lamp unit consists of four (P-4) or eight (P-8) three-foot long, 30-watt UV lamps. The lamps are individually chambered in fused 1.5-inch quartz glass sleeves, which in turn are contained within a two-inch tube made of a specially formulated UL1018 PVC and operate at a recommended maximum flow rate of 40 gpm. Scalability is achieved by simply adding or removing the number of lamps needed to achieve the desired destruction efficiency given the influent concentration and pumping rate.

The UV lamps were added incrementally so that the MTBE destruction efficiency as a function of energy and peroxide dose rate could be computed and adjustments made to the system. The incremental addition of UV lamps increased the residence time of the extracted water within the UVP system. Four UV lamp units consisting of four lamps each (16 lamps × 30 watts per lamp) were installed initially. Additional UV lamps were added incrementally. After five weeks of testing with varying doses of H₂O₂, an additional 24 UV lamps were installed. Following the installation of nine additional groundwater extraction wells, the groundwater extraction rate consistently exceeded 15 gpm, and 16 additional UV lamps were added to increase the residence time of the extracted groundwater in the UVP system. Exhibit 2 is a photograph of the UVP modification to the remediation system.
The MTBE degradation efficiency of the system was assessed weekly (and later bi-monthly) by sampling contaminants in the air stripper effluent and in the UV effluent. As shown in Exhibit 1, the effluent from the UVP pretreatment unit flows through the carbon vessels in series, and the effluent from carbon vessel #4 is discharged to the sewer. In the 33 months since installation of the UVP system, no MTBE breakthrough has occurred and no carbon changeout has been necessary in 665 days of operation.

RESULTS AND DISCUSSION

Field conditions were highly variable. However, treatment systems in the field generally experience decreasing rather than increasing influent concentration over time, resulting in overtreatment rather than undertreatment. Discharge limit exceedence then is unlikely with this system, but overtreatment at times is likely, calling for periodic reductions in hydrogen peroxide dose rate and lamp removals. Following the end of the first month of pilot testing, the average quarterly MTBE effluent from the UVP system ranged from 145 ± 127 µg/L of MTBE during the first three months of operation to 2 ± 3 µg/L of MTBE after 33 months of operation, with corresponding MTBE destruction efficiencies increasing from 40 ± 27 percent to 78 ± 6 percent (Exhibit 3). This MTBE degradation by the UVP system compares quite favorably against the 636 ppb of MTBE entering the carbon vessels prior to installation of the UVP system.

Exhibit 4 shows the increase in MTBE destruction efficiency (in percent) in the UV effluent plotted against the duration of exposure (retention) time to the UV light. Customarily, MTBE concentration is plotted against UV dose (energy applied per volume). However, in this case, the power applied was a constant 30 watts, and the volume and retention time both varied directly with the number of lamps added. Therefore, exposure or retention time rather than power was plotted for simplicity. MTBE reaction rate and destruction efficiency are proportional power not simply retention time, but since power applied was held constant, the simpler relationship holds.

The residence time (exposure) and, hence, the reaction rate, vary with the transfer pumping rate and the number of lamps. The variables include \( \text{H}_2\text{O}_2 \) dosing rate (fed at a constant rate into the pump-and-treat system, with variable flow due to variable groundwater extraction rates) and flow rates through the UV lamps as determined by

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**Exhibit 3.** Destruction efficiency for MTBE in extracting water using a UV peroxide system

<table>
<thead>
<tr>
<th>Period</th>
<th>UV Influent Concentration MTBE (µg/L)</th>
<th>UV Light Effluent Concentration MTBE (µg/L)</th>
<th>UVP Efficiency (%)</th>
<th>Volume Extracted (Liters)</th>
<th>Average Flow (lpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Q-02</td>
<td>217 ± 108</td>
<td>145 ± 127</td>
<td>40 ± 27</td>
<td>4,642,982</td>
<td>33.9</td>
</tr>
<tr>
<td>3Q-02</td>
<td>114 ± 74</td>
<td>26 ± 31</td>
<td>78 ± 12</td>
<td>5,923,454</td>
<td>44.7</td>
</tr>
<tr>
<td>4Q-02</td>
<td>113 ± 74</td>
<td>26 ± 16</td>
<td>76 ± 13</td>
<td>8,150,420</td>
<td>48.3</td>
</tr>
<tr>
<td>1Q-03</td>
<td>43 ± 29</td>
<td>13 ± 9</td>
<td>72 ± 13</td>
<td>8,308,158</td>
<td>61.4</td>
</tr>
<tr>
<td>2Q-03</td>
<td>37 ± 22</td>
<td>8 ± 6</td>
<td>79 ± 6</td>
<td>7,533,173</td>
<td>58.1</td>
</tr>
<tr>
<td>3Q-03</td>
<td>22 ± 4</td>
<td>4.6 ± 1.3</td>
<td>79 ± 5</td>
<td>6,761,936</td>
<td>51.0</td>
</tr>
<tr>
<td>4Q-03</td>
<td>4 ± 1.4</td>
<td>1.4 ± 0.5</td>
<td>64 ± 5</td>
<td>6,575,088</td>
<td>47.6</td>
</tr>
</tbody>
</table>
transfer pump cycling. A simple presentation of the data is a plot of pumping rate versus destruction efficiency for the treatment system as configured (Exhibit 5). Note that the destruction efficiency is independent of influent concentration. Hence, using Exhibit 4 and given an MTBE influent concentration and groundwater extraction rate, the number of 30-watt UV lamps required for treatment can be determined to achieve a desired destruction efficiency. Exhibit 5 demonstrates that 100 percent destruction efficiency is possible with this treatment system (unlike air stripping) and shows the rate of reduction of destruction efficiency for a given configuration as a function of increasing extraction rate.

Based on the in vitro results of Chang and Young (2000) regarding the generation of tert-butyl formate, the remediation system influent and the UVP effluent was tested at least once per quarter over the 33-month study period for by-products of MTBE degradation, including TBF. No TBF was detected in the influent groundwater (detection limits varied from 2 to 16 µg/L due to dilution factors), and no TBF was detected (< 2.0 µg/L) in the air stripper effluent or the UVP effluent during these same sampling events. Thus, the potential generation of TBF by the UVP system could not be precisely evaluated but did not appear to be an issue at the detection limits obtained.

In summary, the ex situ treatment of MTBE in extracted groundwater by a simple UVP treatment system provides a scalable and economical solution for treatment of MTBE-contaminated groundwater at gasoline stations with leaking underground storage tanks and relatively low groundwater extraction rates. The simplicity of the design of the UVP system allowed it to be operational in the field within three months. The system was so effective in reducing MTBE that it was turned off in three years, with no breakthrough of MTBE through the carbons. In fact, in many instances, the installation of the UVP system may make the use of carbon unnecessary. While we describe its use in treating MTBE in extracted groundwater, the system can also be used as described to treat
chlorinated solvents such as perchloroethylene (PCE), trichloroethylene (TCE), and similarly recalcitrant compounds in extracted groundwater, because the active component of the UVP system, the hydroxyl free radical, is highly effective against many organic contaminants.

REFERENCES


Ijaz S. Jamall, PhD, is a principal scientist with Risk-Based Decisions, Inc., in Sacramento, California. He has conducted research on the role of oxygen free radicals in health and disease and has used this background to design and implement a variety of oxidative systems for the remediation of organic compounds in soil and groundwater.

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