3.0 Advanced Oxidation Processes

*Literature Review*

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3.1 Background and Objectives of Evaluation

Organic compounds, including MTBE, have been treated in drinking water using AOPs at several sites across the United States over the past five years. The largest system (3,000 gpm) is a medium pressure H$_2$O$_2$/MP-UV system installed in Salt Lake City, Utah to remove up to 10 µg/L PCE from drinking water (Crawford, 1999). Other systems are installed in Canada for the removal of N-nitroso dimethyl amine (NDMA) and several are planned for installation at Suburban Water Company (Los Angeles, CA) and La Puente (Los Angeles, CA) (Crawford, 1999). AOPs represent an alternative drinking water treatment option to air stripping (see Chapter 2), GAC adsorption (see Chapter 4), and resin sorption (see Chapter 5) processes, which may be inefficient for MTBE removal in certain cases due to MTBE’s relatively low Henry’s constant and high solubility. Unlike air stripping and adsorption, which are phase-transfer processes, AOPs are destructive processes. AOPs destroy MTBE and other organic contaminants directly in the water through chemical transformation, as opposed to simply transferring them from the liquid phase into a gas phase (in the case of air stripping) or solid phase (in the case of GAC and resins). However, despite this advantage, there are significant limitations and challenges in the full-scale application of AOPs. In general, AOPs are much less well understood than air stripping and sorption due to the complex chemical and physical processes involved in oxidation reactions.

The implementation of AOPs and the determination of their effectiveness are difficult for several reasons. As with all treatment technologies, the effectiveness of AOPs will be largely determined by the specific water quality matrix of the contaminated water. However, in the case of AOPs, the effects of background water quality on contaminant removal are much less well understood than for other technologies. For example, the presence of high bromide concentrations or NOM can result in the formation of regulated oxidation by-products that may cause water quality to deteriorate beyond its initial state of contamination. Similarly, the presence of nitrates, NOM, and carbonates can interfere with the destruction of the target contaminant(s) and ultimately reduce the effectiveness of the selected AOP. In general, most of the technical difficulties associated with AOPs stem from the fact that oxidation processes are non-selective with the potential for significant interference. To compensate for these limitations, more energy or higher chemical dosages may be required, potentially resulting in higher costs.

The primary objective of this chapter is to evaluate the feasibility of using AOPs for the removal of MTBE from drinking water. This feasibility evaluation will include a review of the chemical and physical principles behind AOPs, a discussion of the various established and emerging AOP technologies that have potential for MTBE removal, an analysis of the effects of water quality on the effectiveness of these AOPs, and a cost analysis based on information gathered from manufacturers, vendors, and actual pilot tests. Based on the findings of the review and results of the cost analysis, this chapter will conclude with overall recommendations for implementation of AOPs for MTBE removal and recommendations for future work.
3.2 Process Definition

Oxidation is defined as the transfer of one or more electrons from an electron donor (reductant) to an electron acceptor (oxidant), which has a higher affinity for electrons. These electron transfers result in the chemical transformation of both the oxidant and the reductant, in some cases producing chemical species with an odd number of valence electrons. These species, known as radicals, tend to be highly unstable and, therefore, highly reactive because one of their electrons is unpaired. Oxidation reactions that produce radicals tend to be followed by additional oxidation reactions between the radical oxidants and other reactants (both organic and inorganic) until thermodynamically stable oxidation products are formed. The ability of an oxidant to initiate chemical reactions is measured in terms of its oxidation potential. The most powerful oxidants are fluorine, hydroxyl radicals (•OH), ozone, and chlorine with oxidation potentials of 2.85, 2.70, 2.07 and 1.49 electron volts, respectively (Dorfman and Adams, 1973). The end products of complete oxidation (i.e., mineralization) of organic compounds such as MTBE or benzene are carbon dioxide (CO₂) and water (H₂O).

AOPs involve the two stages of oxidation discussed above: 1) the formation of strong oxidants (e.g., hydroxyl radicals) and 2) the reaction of these oxidants with organic contaminants in water. However, the term advanced oxidation processes refers specifically to processes in which oxidation of organic contaminants occurs primarily through reactions with hydroxyl radicals (Glaze et al., 1987). In water treatment applications, AOPs usually refer to a specific subset of processes that involve O₃, H₂O₂, and/or UV light. However, in this analysis, AOPs will be used to refer to a more general group of processes that also involve TiO₂ catalysis, cavitation, E-beam irradiation, and Fenton’s reaction. All of these processes can produce hydroxyl radicals, which can react with and destroy a wide range of organic contaminants, including MTBE. Although a number of the processes noted above may have other mechanisms for destroying organic contaminants, in general, the effectiveness of an AOP is proportional to its ability to generate hydroxyl radicals. The various chemical and physical mechanisms through which AOP technologies produce hydroxyl radicals are discussed in Section 3.3.
3.3 General Process Principles and Implementability Issues

As with the other treatment technologies discussed in this report, the design of an AOP is governed by the influent contaminant concentration, target effluent contaminant concentration, desired flow rate, and background water quality parameters such as pH, bromide concentration, and alkalinity. The key design parameters for AOPs include: chemical dosages and ratios with other chemicals, reactor contact time, and reactor configuration. The optimum dosages, ratios, and contact time are water-specific and treatment scenario-specific, and are often determined through pilot studies using the water matrix of interest. As can be expected, higher chemical dosages and contact times are typically expected to result in higher removal rates; however, increasing dosages results in higher O&M costs and possible by-product formation. However, in some cases, the formation of by-products can be limited by higher chemical ratios. This issue will be discussed in more detail in the discussions of specific AOP technologies. While AOPs have been found to be effective for a wide variety of organic contaminants, this analysis will focus on the practical implementation of AOPs in drinking water treatment specifically for removal of MTBE.

3.3.1 Water Quality Impacts

As previously mentioned, there are many water quality parameters that may impact the effectiveness of any particular AOP. For example, nearly all dissolved organic compounds present in the source water will serve to reduce the removal efficiency of the target compound by consuming •OH (Hoigne, 1998). Below is a brief discussion of each of these water quality parameters and the mitigation measures that can be taken to limit the detrimental impact of these parameters on AOP effectiveness.

Alkalinity. The detrimental impact of alkalinity on the effectiveness of AOPs has been extensively studied (AWWARF, 1998). As mentioned previously, the hydroxyl radical is non-selective and, thus, can be exhausted by the presence of organic or inorganic compounds other than the contaminants of concern. Both carbonate and bicarbonate will scavenge hydroxyl radicals to create carbonate radicals which, in turn, react with other organic or inorganic compounds present, albeit at a much slower rate (Hoigne and Bader, 1976; AWWARF, 1998). The reaction for the scavenging of hydroxyl radicals by bicarbonate ions is shown below (Morel and Hering, 1993):

\[
•\text{OH} + \text{HCO}_3^- \rightarrow \text{CO}_3^- + \text{H}_2\text{O}
\]

The rate constants, \(k\), for the reactions of the hydroxyl radical with carbonate and bicarbonate are \(3.8 \times 10^8\) and \(8.5 \times 10^6\) M\(^{-1}\)s\(^{-1}\), respectively (Buxton et al., 1988). These rate constants are much slower than the reaction rate constant of hydroxyl radicals with MTBE (\(10^9\) M\(^{-1}\)s\(^{-1}\)). However, for these second order reactions, the actual reaction rate, \(r\), is a function of both the rate constant and the concentration of the reactant, \(C\): \(r = k [C]\). Waters with medium to high alkalinitities (>100 mg/L as CaCO\(_3\)) likely contain carbonate and bicarbonate ions at
concentrations several orders of magnitude greater than MTBE and, thus, the reaction of hydroxyl radicals with carbonate and bicarbonate can proceed as fast or faster than their reaction with MTBE. Consequently, MTBE-impacted waters high in bicarbonate ions may require a lowering of alkalinity (e.g., pH adjustment or carbon dioxide stripping) prior to treatment by AOP (AWWARF, 1998) or higher doses of oxidants coupled with increased reaction time.

**TOC and NOM.** TOC measurement incorporates all organic compounds present in the water, both dissolved organic carbon (DOC) and particulate organic carbon (POC). Drinking water supplies typically contain TOC concentrations ranging from <1 mg/L to >7 mg/L and include naturally occurring compounds and anthropogenic compounds (e.g., pesticides, gasoline components, and chlorinated compounds). NOM, a subset of TOC, is commonly used to describe large macromolecular organic compounds present in water. These macromolecules can include humic substances, proteins, lipids, carbohydrates, fecal pellets, or biological debris (Stumm and Morgan, 1996) and, while not highly reactive, often contain reactive functional groups (Hoigne, 1998). Organic matter present in the water, whether anthropogenic or natural, will scavenge hydroxyl radicals and, thus, limit the effectiveness of AOPs. The rate constants reported in the literature for hydroxyl radical reactions with NOM range from $1.9 \times 10^4$ to $1.3 \times 10^5$ (mg/L)$^{-1}$s$^{-1}$ (AWWARF, 1998). Given the high molecular weight of NOM (5,000 to 10,000 g/mole), these rate constants are comparable to the reaction rate constant for MTBE and, thus, high concentrations of NOM can result in significant reduction of MTBE destruction potential. The effects of high concentrations of NOM may be mitigated by the addition of higher dosages of oxidant and longer reaction times.

**Nitrates and Nitrites.** Hydroxyl radicals can be formed by several mechanisms, including UV photooxidation of hydrogen peroxide. Any constituent present in the water that adsorbs UV light will decrease the formation of hydroxyl radicals and the subsequent destruction of MTBE. Nitrates and nitrites adsorb UV light in the range of 230 to 240 nm and 300 to 310 nm and, consequently, high nitrate (>1 mg/L) or high nitrite (>1 mg/L) concentrations have been shown to limit the effectiveness of UV technologies (see Section 3.4.2 for a comparative discussion of UV lamps) (Calgon, 1996; Cater, 1999).

**Phosphates and Sulfates.** While phosphates and sulfates are commonly present in low concentrations in source waters, these compounds have the potential to scavenge hydroxyl radicals. However, they are extremely slow in reacting with •OH, and their scavenging effect can usually be neglected (Hoigne, 1998) for ozone/peroxide/UV systems. For TiO$_2$ systems, sulfates have been noted to significantly decrease the destruction rate of organic contaminants at concentrations above approximately 100 mg/L (Crittenden et al., 1996).

**Iron (II), Copper (I), or Manganese (II).** While not well understood, the presence of these reduced metals in combination with NOM and hydroxyl radicals may lead to the formation of iron or copper organic complexes or the oxidation of Mn (II) to form permanganate (Hoigne, 1998; Calgon, 1996). The formation of permanganate has been observed to occur
with a rate constant of $3 \times 10^3$ to $2 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ (Reckhow et al., 1991). In addition, the presence of iron (absorptivity 200 to 400 nm) and other scaling agents may result in fouling of UV systems.

**Turbidity.** Systems relying on UV irradiation for the dissociation of $\text{H}_2\text{O}_2$ or $\text{O}_3$ exhibit a decrease in efficiency as turbidity increases. Turbidity lowers the transmittance of the source water and, thus, lowers the penetration of the UV radiation into the source water.

In addition to possible interference with AOPs by the compounds described above, the recent emergence of UV irradiation as a disinfection technology has prompted the investigation of possible negative side effects of UV irradiation on drinking water containing NOM. In particular, there have been concerns regarding the potential effects of UV irradiation on by-product formation when UV is used in conjunction with chlorine addition. Chlorine is sometimes added at plant headworks as a pre-treatment step or, more likely, used as a primary or secondary disinfectant farther down the treatment train. The use of chlorine is associated with the formation of by-products, such as THMs and haloacetic acids (HAA$_9$: HAA$_5$ plus tribromo-, bromochloro-, bromodichloro- and dibromochloroacetic acid), from NOM normally present in water. These by-products are suspected human carcinogens and are regulated by the EPA. A number of researchers have investigated the potential of UV irradiation to change the composition or distribution of these by-products by promoting the photolysis of NOM (e.g., humic acids) into smaller molecules that have higher potential for THM and HAA$_9$ formation (e.g., Stewart et al., 1993; Hengesbach et al., 1993).

Zheng et al. (1999a) recently showed that UV irradiation at a dosage of 100 mJ/cm$^2$ (the expected maximum UV dosage used for water disinfection applications) of water pre-chlorinated at 6 to 48 mg/L can result in a one to seven percent decrease in the THM concentration and a change in the HAA$_9$ concentration ranging from -3 to 4 percent. These results suggest that under typical treatment conditions, where pre-chlorination is usually less than 5 mg/L, there will be negligible changes in THM and HAA$_9$ formation. It was suggested that UV irradiation might have caused a fraction of the $\text{Cl}_2$ residual to decompose into chlorine radicals ($\text{Cl}^*$), which then reacted with THM precursors and converted them into HAA$_9$ precursors. In a parallel study, Zheng et al. (1999b) also studied the effect of UV irradiation prior to chlorine addition on the subsequent formation of THMs and HAA$_9$s after chlorine is added. The study found that UV irradiation (dosage range from 0 to 3,000 mJ/cm$^2$) had insignificant effects on the formation of THMs after the addition of chlorine at a dosage of 5 to 10.5 mg/L. Similar results were observed for HAA$_9$ formation. Thus, it could be inferred that the use of UV, especially at doses less than 100 mJ/cm$^2$, either prior to or after a chlorination process, has a minor impact on THM and HAA$_9$ formation.

Zheng et al. (1999b) investigated the effects of pre-chlorination combined with $\text{H}_2\text{O}_2$/UV on THM and HAA$_9$ formation. Upon exposure of drinking water to a UV dose of 100 mJ/cm$^2$ and $\text{H}_2\text{O}_2$ dosages ranging from 3.6 to 51 mg/L, THM concentrations increased between two to six percent compared to values observed without $\text{H}_2\text{O}_2$/UV treatment. THM and HAA$_9$
formation generally increased linearly for UV doses up to 2,000 mJ/cm². At a UV dosage of 2,000 mJ/cm², the THM concentrations increased between 37 percent and 146 percent and HAA₉ concentration increased between 39 percent and 128 percent. UV doses for MTBE removal applications are expected to be greater than 2,000 mJ/cm² and, thus, increases in THM and HAA₉ formation may be significant. Consequently, these preliminary results suggest that the combined effects of H₂O₂ and UV irradiation on THM and HAA₉ formation potentials should be considered in drinking water situations.

3.3.2 General Advantages

The specific advantages of each AOP will be discussed later in this chapter. The following list describes the advantages that are common to all AOPs.

**MTBE Destruction**

AOPs represent an alternative drinking water treatment option to air stripping, GAC adsorption, and resin sorption. Air stripping and sorption are phase-transfer processes in which organic contaminants like MTBE are physically transferred to a gas phase (air stripping) or solid phase (GAC and resins). Actual destruction of MTBE requires additional processes, such as thermal or catalytic oxidation of the off-gas from an air stripper or incineration of the GAC. In contrast, AOPs destroy primary organic contaminants directly in water through chemical reactions. Furthermore, the effectiveness of AOPs is facilitated by the relatively high solubility of MTBE while air stripping and sorption onto GAC and resins are limited by MTBE’s high solubility.

**Disinfection Capability**

Several AOP technologies — namely ozonation, ozonation combined with H₂O₂, and certain types of UV irradiation — are currently used for disinfection purposes in the water treatment industry. Currently, ozonation and MP-UV irradiation are the only state or federally approved disinfection technologies; (Reynolds and Richards, 1996; EPA/600R-98/160VS, 1999). Disinfection credit can be given for peroxide/ozone systems depending on the ozone residual remaining in the effluent water; this residual will decrease as the peroxide to ozone ratio increases. The EPA and NSF International verified the performance of a MP-UV system (Sentinel™, Calgon Carbon, Markham, Ontario) under the Environmental Technology Verification (ETV) program and certified it for 3.9 log₁₀ removal of *Cryptosporidium* (EPA/600/R-98/160VS, 1999; Bukhari et al., 1999).

**Established Technologies for Drinking Water Treatment**

Although the use of AOPs for organic contaminant removal from drinking water has been limited in the past, many of the components of AOPs have been used by the water community and industry (e.g., UV and ozone for disinfection). Consequently, treatment plant operators
may already be familiar with operation and implementation of these established AOP components, suggesting that the implementation of some AOPs will be feasible with minimal training.

3.3.3 General Disadvantages

Specific disadvantages of each AOP will be discussed later in this chapter. The following list describes some common disadvantages of AOP technologies.

Oxidation By-products

The reaction between •OH and many organic contaminants occurs rapidly; however, this reaction by itself does not directly result in the mineralization of these contaminants but produces organic oxidation by-products, which can further react with •OH. There are at least two proposed mechanisms in the literature for the complete oxidation of MTBE to carbon dioxide and water (Barreto et al., 1995; Kang and Hoffmann, 1998). If the reaction rate for a particular by-product is slower, it may be the rate limiting step in the complete mineralization of the target compound and that by-product will accumulate. Ideally, AOP systems are designed to completely mineralize the organic contaminants of concern to CO\(_2\) and H\(_2\)O, but this may require more energy and greater chemical dosages and, ultimately, may prove to be cost prohibitive in certain applications.

While highly dependent on the specific water quality, Table 3-1 shows experimentally determined hydroxyl radical rate constants for MTBE and its various oxidation by-products (water quality varies, as discussed in the literature). A possible mechanism for the oxidation of MTBE involves either direct conversion to TBA or oxidation of the methyl group to form tertiary-butyl formate (TBF). TBF can then be hydrolyzed to TBA and formaldehyde. TBA can lose a methyl group to form isopropyl alcohol, which can be further oxidized to acetone. In some AOPs, further oxidation of these by-products was found to be the rate-limiting step in the ultimate mineralization of MTBE. Finally, acetone may be converted to formaldehyde or formate, which can be mineralized to CO\(_2\) and H\(_2\)O. As stated above, economic considerations can limit the complete mineralization of MTBE, leaving short-chained carboxylic acids, alcohols, aldehydes, and/or acetone in the effluent water (Karpel Vel Leitner et al., 1994; Liang et al., 1999a). These residual oxidation compounds are also produced by the partial oxidation of NOM (Hoigne, 1998). These compounds represent a source of concern in drinking water applications due to their high solubility and uncertain toxicity. In addition, the presence of these more easily degradable compounds can promote biological growth and fouling in the distribution system. Thus, these compounds are often further treated with a biological activated filter or some other polishing treatment step.
Bromate Formation

In addition to organic oxidation by-products, inorganic by-products can also be formed. Bromide concentrations in raw drinking water can range from non-detect to several hundred µg/L to several mg/L in brackish water (Hoigne, 1998). During the use of AOPs that employ ozone, bromate can be formed when bromide is present in the source water (Krasner, 1993; von Gunten and Hoigne, 1994; Siddiqui et al., 1999). The conversion of bromide to bromate can proceed as follows (Krasner, 1993; Siddiqui et al., 1994):

\[
\text{Br}^- \rightarrow \text{BrO}^- \rightarrow \text{BrO}_2^- \rightarrow \text{BrO}_3^-
\]

\[
\text{Br}^\ast \rightarrow \text{BrO}^\ast \rightarrow \text{BrO}_2^- \rightarrow \text{BrO}_2^\ast \rightarrow \text{BrO}_3^-
\]

When bromide concentrations in the source water exceed 0.1 mg/L, bromate has been found to be produced at concentrations above the Stage 1 Disinfection/Disinfection By-product (D/DBP) MCL of 10 µg/L (Liang et al., 1999a). However, prior studies of ozone-based AOPs, specifically H_2O_2/O_3 systems, have shown that varying the chemical ratio of O_3 to H_2O_2 is effective at minimizing bromate formation (Song et al., 1997). In addition, research has demonstrated that bromate formation is reduced by approximately 20 percent at a slightly acidic pH (~6.5), when compared to the ambient pH (Liang et al., 1999a).

Interfering compounds

As mentioned previously, alkalinity and/or the presence of TOC (including NOM), nitrites, and other inorganics can limit the effectiveness of AOPs due to their scavenging of hydroxyl radicals that would otherwise be used to destroy MTBE. Thus, as the concentrations of these
parameters increase, chemical dosages and contact times will also increase to maintain effluent concentrations at the treatment goal. Increasing chemical dosages will raise operational costs while increasing contact times will raise initial capital costs. The sensitivity of operational and capital costs to changing source water qualities is discussed in more detail in Section 3.7.

3.3.4 AOP Technologies

AOPs can be divided into established and emerging technologies based on the existing literature and the water treatment industry’s experience with the technology. Emerging technologies are defined here as technologies that have very limited, if any, full-scale applications in drinking water treatment. The following AOP technologies are discussed in this report:

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<tr>
<th>Established Technologies</th>
<th>Emerging Technologies</th>
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<tbody>
<tr>
<td>• Hydrogen Peroxide/Ozone (H₂O₂/O₃)</td>
<td>• High Energy Electron Beam</td>
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<td></td>
<td>Irradiation (E-beam)</td>
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<td>• Ozone/Ultraviolet Irradiation (O₃/UV)</td>
<td>• Cavitation (Sonication &amp;</td>
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<td></td>
<td>Hydrodynamic)</td>
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<tr>
<td>• Hydrogen Peroxide/</td>
<td>• TiO₂-catalyzed UV Oxidation</td>
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<tr>
<td>Ultraviolet Irradiation (H₂O₂/UV)</td>
<td>• Fenton’s Reaction</td>
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Each of the above AOP technologies is evaluated in Section 3.4 on the basis of its performance reported in the engineering literature, results of manufacturer or vendor studies, and the industry’s experience with the technology. The following sections include detailed discussions of each technology’s chemistry, advantages and disadvantages, key variables and design parameters, and available performance data from bench-, pilot-, and field-scale tests. Tables 3-2 to 3-5 present summaries of these discussions. A summary including brief descriptions, system components, and advantages and disadvantages of established and emerging AOP technologies is presented in Table 3-2. Table 3-3 lists the reactions, by-products, interfering compounds, and oxidant hierarchy associated with the various AOP technologies. Table 3-4 presents a summary of pilot and field studies and Table 3-5 lists vendor information for each AOP technology.
<table>
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<tr>
<th>AOP Technology</th>
<th>Brief Description</th>
<th>System Components</th>
<th>Advantages</th>
<th>Disadvantages</th>
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</thead>
</table>
| General AOPs   | Oxidation of organic contaminants including MTBE occurs primarily through reactions with highly reactive radicals such as $\cdot$OH. The formation of these radicals can occur through several different processes that are discussed below. | See below. | • AOPs are destructive processes.  
• Several AOPs have disinfectant capabilities.  
• Many AOP components have been utilized in the water community and industry. | • Potential for accumulation of oxidation by-products.  
• Potential for bromate formation.  
• Radical scavenging by interfering compounds can reduce effectiveness of AOPs. |
| Established Technologies |  |  |  |  |
| $H_2O_2/O_3$  | $H_2O_2$ and $H_2O_2$ are simultaneously applied to water, they react to form hydroxyl radicals. These $\cdot$OH can oxidize most dissolved organic matter to form by-products. | $H_2O_2$ Storage and Injection System  
$O_3$ Generator and Diffusers  
Contactor and Mixing Vessels  
Ozone Off-gas Catalytic Decomposer  
Supply and Discharge Pumps and Piping  
Monitoring & Control Systems | $H_2O_2$ Storage and Injection System  
$O_3$ Generator and Diffusers  
Contactor and Mixing Vessels  
Ozone Off-gas Catalytic Decomposer  
Supply and Discharge Pumps and Piping  
Monitoring & Control Systems | Efficient in treating waters with high MTBE concentrations.  
Supplemental Disinfectant.  
More effective than $O_3$ or $H_2O_2$ alone.  
Established technology for remediation applications. | Potential for bromate formation  
(controllable through adjustment of $O_3/H_2O_2$ ratio and pH).  
May require treatment of excess $H_2O_2$ due to potential for microbial growth.  
May require ozone off-gas treatment and/or permitting. |
| $O_3/UV$       | Hydroxyl radicals are generated when low-pressure UV light is applied to ozonated water. Destruction of organic compounds occurs by hydroxyl radical reactions, coupled with direct photolysis and oxidation by molecular ozone. | Ultraviolet Lamps, Lamp Sleeves, and Lamp Cleaning System  
$O_3$ Generator and Diffusers  
Liquid $O_3$ or compressed air tank  
Contactor and Mixing Vessels  
Ozone Off-gas Catalytic Decomposer  
Temperature Controller  
Supply and Discharge Pumps and Piping  
Monitoring & Control Systems | Supplemental disinfectant.  
More effective than $O_3$ or UV alone.  
More efficient at generating $\cdot$OH than $H_2O_2/UV$ process for equal oxidant concentrations. | Energy and cost intensive process.  
Potential for bromate formation  
(controllable through adjustment of $O_3/H_2O_2$ ratio and pH).  
Turbidity can interfere with UV light penetration.  
Ozone diffusion can result in mass transfer limitations.  
May require ozone off-gas treatment and/or permitting.  
Interfering compounds (e.g., nitrate) can absorb UV light.  
UV lamp and sleeve failures can potentially contaminate water with mercury.  
Potential increase in THM and HAA5 formation when combined with pre- and/or post-chlorination. |
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<td><strong>Established Technologies continued</strong></td>
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<tr>
<td><strong>H₂O₂/UV</strong></td>
<td>As in the O₃/UV process, several synergistic oxidation mechanisms result in the destruction of organics. The •OH radical route is the predominant removal mechanism. For H₂O₂, a greater number of radicals are produced when MP-UV lamps are used compared to the LP-UV lamps.</td>
<td>• Ultraviolet Lamps, Lamp Sleeves, and Lamp Cleaning System  • Hydrogen Peroxide Storage and Injection System  • Reactor Chamber  • In-Line Mixer  • Temperature Controller  • Supply and Discharge Pumps and Piping  • Monitoring &amp; Control Systems</td>
<td>• No potential for bromate formation.  • Can oxidize &gt;95% MTBE compared to &lt;10% for UV or H₂O₂ alone.  • MP-UV and pulsed-UV irradiation can serve as disinfectant.  • Full scale drinking water treatment system exists in Salt Lake City, UT.  • No off-gas treatment required.  • Not limited by mass transfer relative to O₃ processes.</td>
<td>• Turbidity can interfere with UV light penetration.  • Less stoichiometrically efficient at generating •OH than O₃/UV process  • Interfering compounds (e.g., nitrate) can absorb UV light.  • Potential increase in THM and HAA₅ formation when combined with pre- and/or post-chlorination.</td>
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<td><strong>Emerging Technologies</strong></td>
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<td><strong>High Energy Electron Beam</strong></td>
<td>Electrons react with water molecules and produce intermediates such as hydroxyl radicals, hydrated electrons and hydrogen atoms. These intermediates react with organic compounds, including MTBE, to form by-products.</td>
<td>• Insulated Core Transformer  • Electron Accelerator  • Concrete Vault  • Water Distribution Device  • Resistance Temperature Devices  • Temperature Controller  • Power Source  • Supply and Discharge Pumps and Piping  • Monitoring &amp; Control Systems  • Lead Shielding</td>
<td>• No potential for bromate formation.  • May actually reduce bromate.  • Minimal organic by-product formation potential.  • Can supplement the disinfection process.  • Turbidity has minimal effect on the system performance.  • No off-gas treatment required.</td>
<td>• Public perception may prove to be significant obstacle to drinking water implementation.  • No full-scale applications exist.  • Energy intensive process; costs not fully evaluated.  • Requires specially trained operators, which would likely increase labor costs.</td>
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<td>Emerging Technologies continued</td>
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**Sonication / Hydrodynamic Cavitation**
- Sonication or hydrodynamic processes induce the formation of cavitation microbubbles. These bubbles implode violently after reaching a critical resonance size and generate high temperatures and highly reactive radicals. Removal of organics occurs by thermal decomposition at the bubble-water interface and by reaction with the radicals. Oxidation by cavitation is enhanced by the addition of O₂ or H₂O₂.
- **System Components** |
  - Hydrodynamic/Ultrasound Cavitation Generator
  - Reactor Chamber
  - Chemical Feed Tanks and Pumps
  - Power Source
  - Temperature Controller
  - Supply and Discharge Pumps and Piping
  - Monitoring & Control Systems
- **Advantages** |
  - Simple design resulting in minimal maintenance costs.
  - Energy usage comparable to AOPs using UV.
  - No bromate formation potential if O₂ is not added.
  - Less heat transfer relative to UV system.
  - No off-gas treatment required if O₂ is not used.
- **Disadvantages** |
  - No full-scale applications exist.
  - Supplemental oxidants such as O₂ and H₂O₂ may be required to achieve target removal efficiencies, resulting in increased costs.

**TiO₂-Catalyzed UV Oxidation**
- When TiO₂ is illuminated by UV light, valence band electrons are excited to the conduction band, resulting in the formation of holes. These holes react with water molecules to produce hydroxyl and other radicals that in turn oxidize organic compounds. Formation of H₂O₂ intermediate can also assist the overall oxidation process.
- **System Components** |
  - TiO₂ Slurry Injection and Extraction System (Option-1)
  - TiO₂ Impregnated Resin Fluidized Bed Reactor (Option-2)
  - Ultraviolet Lamps, Lamp Sleeves, and Lamp Cleaning System
  - Static Mixer
  - Supply and Discharge Pumps and Piping
  - Monitoring & Control Systems
- **Advantages** |
  - No potential for bromate formation.
  - Can be performed at higher (300-380 nm) wavelengths than other UV oxidation processes.
  - No off-gas treatment required.
- **Disadvantages** |
  - No full-scale applications exist.
  - Pre-treatment necessary to avoid fouling of the TiO₂ catalyst.
  - If TiO₂ is added as a slurry, then a separation step is required.
  - Potential for rapid loss of TiO₂ activity, requiring catalyst on-site storage or regeneration method.
  - Rigorous studies needed to determine the optimum TiO₂ dose.
  - May require oxygen sparging.
  - Reaction efficiency is highly pH-dependent, requiring close monitoring and control.

**Fenton’s Reaction**
- Radicals, including •OH, are produced when Fe(II) reacts with H₂O₂. Destruction of organic matter occurs by reaction with these radicals. Iron acts as a catalyst for this reaction.
- **System Components** |
  - Fe(II) and Hydrogen Peroxide Storage and Injection Systems
  - Completely Stirred Tank Reactor
  - pH Controllers
  - Iron Removal System
  - Supply and Discharge Pumps and Piping
  - Monitoring & Control Systems
- **Advantages** |
  - No potential for bromate formation.
  - Not an energy intensive process compared to AOPs that utilize O₂ or UV.
  - No off-gas treatment required.
- **Disadvantages** |
  - No full-scale applications exist.
  - Requires iron extraction system.
  - Very low pH (<2.5) is required to keep the iron in solution.
  - pH adjustment will increase operation and maintenance costs.
<table>
<thead>
<tr>
<th>AOP PROCESS</th>
<th>MAJOR REACTIONS AND BY-PRODUCTS</th>
<th>INTERFERING COMPOUNDS</th>
<th>OXIDANT HIERARCHY</th>
</tr>
</thead>
</table>
| $\text{H}_2\text{O}_2/\text{O}_3$ | $\text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{HO}_2^+ + \text{H}_3\text{O}^+$  
$\text{O}_3 + \text{HO}_2^- \rightarrow \bullet\text{OH} + \text{O}_2^- + \text{O}_2$  
$\bullet\text{OH} + \text{MTBE} \rightarrow$ Oxidation By-products  
(TBA, TBF, acetone, aldehydes) | • Br⁻  
• Radical Scavengers  
(e.g. $\text{HCO}_3^-$, $\text{PO}_4^{3-}$)  
• TOC/NOM | 1. $\bullet\text{OH}$  
2. Other Radicals (e.g. $\bullet\text{O}_2$)  
3. $\text{O}_3$  
4. $\text{H}_2\text{O}_2$ |
| $\text{O}_3/\text{UV}$ | $\text{O}_3 + \text{H}_2\text{O} \xrightarrow{\text{h}u} \text{O}_2 + \text{H}_2\text{O}_2$ ($\lambda < 300 \text{ nm}$)  
$2 \text{O}_3 + \text{H}_2\text{O}_2 \rightarrow 2 \bullet\text{OH} + 3 \text{O}_2$  
$\bullet\text{OH} + \text{MTBE} \rightarrow$ Oxidation By-products  
(TBA, TBF, acetone, aldehydes) | • Br⁻  
• Scaling Agents  
(e.g. $\text{Fe}^{2+}$, $\text{Mg}^{2+}$)  
• Radical Scavengers  
(e.g. $\text{HCO}_3^-$, $\text{PO}_4^{3-}$)  
• TOC/NOM | 1. $\bullet\text{OH}$  
2. Other Radicals (e.g. $\bullet\text{O}_2$)  
3. $\text{O}_3$  
4. UV |
| $\text{H}_2\text{O}_2/\text{UV}$ | $\text{H}_2\text{O}_2 \xrightarrow{\text{h}u} 2 \bullet\text{OH}$ ($\lambda < 300 \text{ nm}$)  
$\bullet\text{OH} + \text{MTBE} \rightarrow$ Oxidation By-products  
(TBA, TBF, acetone, aldehydes) | • Scaling Agents  
(e.g. $\text{Fe}^{2+}$, $\text{Mg}^{2+}$)  
• Radical Scavengers  
(e.g. $\text{HCO}_3^-$, $\text{PO}_4^{3-}$)  
• TOC/NOM | 1. $\bullet\text{OH}$  
2. Other Radicals (e.g. $\bullet\text{O}_2$)  
3. UV  
4. $\text{H}_2\text{O}_2$ |
| $\text{E-beam}$ | $\text{H}_2\text{O} + \text{h}h \rightarrow 2.7 \bullet\text{OH} + 0.6 \bullet\text{H} + 2.6 \text{e}_{aq}^-$  
0.45 $\text{H}_2 + 0.7 \text{H}_2\text{O}_2 + 2.6 \text{H}_3\text{O}^+$  
$\bullet\text{OH} + \text{MTBE} \rightarrow$ Oxidation By-products  
(TBA, TBF, acetone, aldehydes)  
$\text{MTBE} + \text{e}_{aq}^- \rightarrow (\text{CH}_3)_2\text{C}^- + \text{OCH}_3$  
$\text{OCH}_3 + \text{H}_2\text{O} \rightarrow \text{HOCH}_3 + \text{OH}$  
$\text{MTBE} + \text{H}^- \rightarrow$ Reduction By-products | • Radical Scavengers  
(e.g. $\text{HCO}_3^-$, $\text{PO}_4^{3-}$)  
• TOC/NOM | 1. $\bullet\text{OH}$  
2. $\text{e}_{aq}^-$  
3. $\text{H}^-$  
4. $\text{H}_2\text{O}_2$ |

Note: $\text{h}u$ represents UV radiation.
<table>
<thead>
<tr>
<th>AOP PROCESS</th>
<th>MAJOR REACTIONS AND BY-PRODUCTS</th>
<th>INTERFERING COMPONDS</th>
<th>OXIDANT HIERARCHY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cavitation</td>
<td>O₃ + H₂O → O₂ + 2 •OH&lt;br&gt;O₃ + •OH → HO₂ + O₂&lt;br&gt;O₃ + HO₂⁻ → •OH + O₂⁻ + O₂&lt;br&gt;•OH + MTBE → Oxidation By-products (TBA, TBF, acetone, aldehydes)</td>
<td>• Radical Scavengers (e.g. HCO₃⁻, PO₄³⁻)&lt;br&gt;• TOC/NOM</td>
<td>1. •OH&lt;br&gt;2. Other Radicals (e.g. H•)</td>
</tr>
<tr>
<td>TiO₂⁺ Catalyzed UV Oxidation</td>
<td>O₂ + H⁺ + 2eubit + H₂O₂&lt;br&gt;2H₂O + 2h⁺ → 2H⁺ + H₂O₂&lt;br&gt;O₂ + H⁺ + eubit → HO₂•&lt;br&gt;HO₂• → H₂O + •O₂²&lt;br&gt;H₂O₂ + •O₂ → OH⁻ + O₂ + •OH&lt;br&gt;H₂O₂ + eubit → OH⁻ + •OH&lt;br&gt;OH⁻ + h⁺ → •OH&lt;br&gt;•OH + MTBE → Oxidation By-products (TBA, TBF, acetone, aldehydes)&lt;br&gt;h⁺ubit : Valence-band holes&lt;br&gt;eubit : Conduction-band electrons</td>
<td>• Radical Scavengers (e.g. HCO₃⁻, PO₄³⁻)&lt;br&gt;• TOC/NOM&lt;br&gt;• UV Scaling Agents (e.g. Fe⁷+, Mg⁷⁺)</td>
<td>1. •OH&lt;br&gt;2. Other Radicals (e.g., HO₂•)&lt;br&gt;3. UV</td>
</tr>
<tr>
<td>Fenton’s Reaction</td>
<td>Fe⁷⁺ + H₂O₂ → Fe⁵⁺ + OH⁻ + •OH&lt;br&gt;Fe⁷⁺ + H₂O₂ → Fe⁵⁺ + •O₂⁻ + 2H⁺&lt;br&gt;•O₂ + Fe⁷⁺ → Fe⁵⁺ + O₂&lt;br&gt;•OH + MTBE → Oxidation By-products (TBA, TBF, acetone, aldehydes)</td>
<td>• Radical Scavengers (e.g. HCO₃⁻, PO₄³⁻)&lt;br&gt;• TOC/NOM</td>
<td>1. •OH&lt;br&gt;2. Other Radicals (e.g. •O₂⁻)</td>
</tr>
<tr>
<td>VENDOR</td>
<td>STUDY LOCATION</td>
<td>TYPE OF TECHNOLOGY</td>
<td>INFUENT CONC. (µg/L)</td>
</tr>
<tr>
<td>--------</td>
<td>----------------</td>
<td>-------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>Applied Process Technology, Inc.</td>
<td>Valley County Water District, Lantez Well</td>
<td>H₂O₂/Co</td>
<td>5,340 (TCE)</td>
</tr>
<tr>
<td>Applied Process Technology, Inc.</td>
<td>Los Angeles Department of Water Works, Headworks Well Field, Griffith Park</td>
<td>H₂O₂/Co</td>
<td>297 (TCE)</td>
</tr>
</tbody>
</table>

Table 3-4
Summary of AOP Pilot and Field Studies
<table>
<thead>
<tr>
<th>VENDOR</th>
<th>STUDY LOCATION</th>
<th>TYPE OF APPLICATION</th>
<th>TYPE OF TECHNOLOGY</th>
<th>FLOW RATE (gpm)</th>
<th>DURATION OF STUDY</th>
<th>INFLUENT CONC. (µg/L)</th>
<th>EFFLUENT CONC. (µg/L)</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Applied Process Technology, Inc.</td>
<td>Chevron Oil Co. Newark, CA</td>
<td>Remediation</td>
<td>H₂O₂/O₃</td>
<td>10</td>
<td>Field evaluation: 12/98 Commercial installation: 11/98.</td>
<td>33,000 (MTBE) 3,200 (TBA) 3,000 (TAME) 1,800 (TPHg)</td>
<td>ND:&lt;5 (MTBE) ND:&lt;100 (TBA) ND:&lt;10 (TAME) ND:0.5 (TPHg)</td>
<td>Groundwater</td>
</tr>
<tr>
<td>Applied Process Technology, Inc.</td>
<td>Shell Oil Co. Service Station</td>
<td>Remediation</td>
<td>H₂O₂/O₃</td>
<td>10</td>
<td>Field evaluation: 4/98.</td>
<td>3,200 (MTBE) 1,400 (TBA) 2,500 (TBF) 10,590 (BTEX)</td>
<td>ND:&lt;25 (MTBE) ND:&lt;10 (TBA) ND:&lt;25 (TBF) ND:&lt;10 (BTEX)</td>
<td>ND below limits of detection for Del Mar Lab's EPA Methods 8260, 8015, 8315, and 300-B as of 4/98.</td>
</tr>
<tr>
<td>Applied Process Technology, Inc.</td>
<td>Evaluation of Charnock Well Water at Santa Monica, CA</td>
<td>Potable</td>
<td>H₂O₂/O₃</td>
<td>10</td>
<td>Evaluation: 1998.</td>
<td>50 spiked to 1,100 (MTBE) 321 spiked to 1,033 (Br')</td>
<td>&lt;1 (MTBE) &lt;10 (BrO₂)</td>
<td>Groundwater</td>
</tr>
<tr>
<td>Applied Process Technology, Inc.</td>
<td>Kinder Morgan Energy Partners, Chico, CA</td>
<td>Industrial</td>
<td>H₂O₂/O₃</td>
<td>1</td>
<td>Field evaluation 2/99</td>
<td>680,000 (MTBE) 320,000 (TBA) 57,000 (TAME) 6,400 mg/L (COD)</td>
<td>2.3 (MTBE) &lt;1.0 (BTEX) 740 (TPHg) 2,600 (TBA) &lt;1.0 (TAME) 372 mg/L (COD)</td>
<td>Refinery tank draw-down and process waste water.</td>
</tr>
<tr>
<td>Applied Process Technology, Inc.</td>
<td>Kinder Morgan Energy Partners, Vacaville, CA</td>
<td>Remediation</td>
<td>H₂O₂/O₃</td>
<td>10</td>
<td>Field evaluation 12/98</td>
<td>26,000 (MTBE) 300 (Benzene) 250 (TBA)</td>
<td>&lt;0.5 (MTBE) &lt;0.5 (Benzene) &lt;10 (TBA)</td>
<td>Groundwater</td>
</tr>
</tbody>
</table>
Table 3-4 (Continued)
Summary of AOP Pilot and Field Studies

<table>
<thead>
<tr>
<th>VENDOR</th>
<th>STUDY LOCATION</th>
<th>TYPE OF TECHNOLOGY</th>
<th>TYPE OF APPLICATION</th>
<th>EFFLUENT CONC. (µg/L)</th>
<th>INFUENT CONC. (µg/L)</th>
<th>DURATION OF STUDY</th>
<th>FLOW RATE (gpm)</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Applied Process Technology, Inc.</td>
<td>San Gabriel Basin Water Quality Authority, El Monte, CA</td>
<td>Remediation</td>
<td>Hydroxyl Systems</td>
<td>140 (PCE), 4 (TCE), &lt;2 (TCE), &lt;1 (1,1,1-TCA), &lt;5 (MTBE), 10 (1,1,1-DCA)</td>
<td>100-300 mg/L (MTBE)</td>
<td>Starting in early 2000.</td>
<td>20-60</td>
<td>NA</td>
</tr>
<tr>
<td>Hydroxyl Systems Inc.</td>
<td>JFK Airport, New York</td>
<td>Remediation</td>
<td>Hydroxyl Systems</td>
<td>10-30</td>
<td>500 (MTBE)</td>
<td>Finished Phase I field studies.</td>
<td>100-300</td>
<td>NA</td>
</tr>
<tr>
<td>OXIDATION Systems Inc.</td>
<td>March Air Force Base, El Centro, California</td>
<td>Remediation</td>
<td>Hydroxyl Systems</td>
<td>10-30</td>
<td>50-140 spilled to 1,000 to 500 (MTBE)</td>
<td>Since 1997.</td>
<td>100-300</td>
<td>NA</td>
</tr>
<tr>
<td>Calgon Carbon</td>
<td>Santa Monica, CA</td>
<td>Remediation</td>
<td>E-beam</td>
<td>100-300</td>
<td>50-140 (MTBE)</td>
<td>170 to 224 (MTBE)</td>
<td>100</td>
<td>NA</td>
</tr>
<tr>
<td>Haley Aldrich</td>
<td>Miami-Dade County, Florida</td>
<td>Research</td>
<td>E-beam</td>
<td>120</td>
<td>NA</td>
<td>1.4 to 91.4 (MTBE)</td>
<td>100</td>
<td>NA</td>
</tr>
<tr>
<td>Haley Aldrich</td>
<td>Orange County, FL</td>
<td>Remediation</td>
<td>E-beam</td>
<td>120</td>
<td>NA</td>
<td>170 to 224 (MTBE)</td>
<td>100</td>
<td>NA</td>
</tr>
</tbody>
</table>

Groundwater pretreatment to air stripping
Other organics, such as BTEX, present.
Kennedy-Jenks is the Consulting Company.
Electron Beam Research Facility
Removal dependent upon water quality (e.g., TOC, salinity).
<table>
<thead>
<tr>
<th>VENDOR</th>
<th>CONTACT INFORMATION</th>
<th>TYPE OF TECHNOLOGY</th>
<th>TOTAL NUMBER OF APPLICATIONS</th>
<th>NUMBER OF MTBE APPLICATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Applied Process Technology, Inc.</td>
<td>Mr. Terry Applebury Chief Technical Officer 3333 Vincent Road, Suite 222 Pleasant Hill, California 94523 Phone: (925) 977-1811 Fax: (925) 977-1818</td>
<td>H₂O₂/O₃, in-line, at-pressure, multi-injection, HiPOX Reactor</td>
<td>10 Applications 2 x 1,000-gpm systems installed 3 x &lt; 100 gpm systems installed 2 mobile systems in the field</td>
<td>11 field evaluations 4 commercial installations</td>
</tr>
<tr>
<td>Hydroxyl Systems</td>
<td>Mr. Chris Harp Project Manager 9800 McDonald Park Road Sidney, British Colombia Canada, V8L5W5 Phone: (250) 655-3348 Fax: (250) 655-3349</td>
<td>H₂O₂/UV O₃/UV O₃, H₂O₂/UV H₂O₂/O₃ UVTiO₃-Fluidized Bed Reactor</td>
<td>&gt; 50 installations</td>
<td>1 extensive bench-scale testing</td>
</tr>
<tr>
<td>US Filter</td>
<td>Mr. Bill Himebaugh Industrial Wastewater Manager 1100 E. Willow Street Signal Hill, CA 90806 Mr. Rick Woodling Senior Applications Engineer 2805 Mission College Boulevard Santa Clara, CA 92054 Phone: (408) 588 200 Fax: (408) 567-0397</td>
<td>H₂O₂/UV O₃/UV O₃, H₂O₂/UV H₂O₂/O₃ Ultrox UV System D-TOX Vapor Phase System</td>
<td>Total Installations: &gt;50 Ultrox Installations: &gt;20</td>
<td>None</td>
</tr>
<tr>
<td>Calgon Carbon</td>
<td>Mr. Stephen Carter Manager, Research and Technical Services 130 Royal Crest Court Markham, Ontario, Canada, L3R0A1 Phone: (905) 477-9242, x331 Fax: (905) 477-4511 Mr. Martin Crawford Calgon Carbon Suisun City, CA Phone: (707) 435-9390</td>
<td>UV /H₂O₂ UV/Fenton’s H₂O₂ UV Photolysis UV Reduction UV/O₃</td>
<td>Total Installations: 250 (US: 200; Canada: 25) MTBE Installations: 12 MTBE is likely to be present at the BTEX installations.</td>
<td>2 in-depth field studies in Santa Monica, CA: 1) groundwater contaminated with MTBE &amp; BTEX and 2) drinking water aquifer.</td>
</tr>
<tr>
<td>VENDOR</td>
<td>CONTACT INFORMATION</td>
<td>TYPE OF TECHNOLOGY</td>
<td>TOTAL NUMBER OF APPLICATIONS</td>
<td>NUMBER OF MTBE APPLICATIONS</td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>--------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------------------</td>
</tr>
</tbody>
</table>
| Trojan Technologies                         | Dr. Bill Dewaal  
Director of Marketing AOPs  
3020 Gore Road  
London, Ontario  
Canada, INSV477  
Phone: (519) 457-3400  
Fax: (519) 457-3030                                                                                                                                   | UV/H₂O₂  
UV/TiO₂-Substrate Attached  
UV Photolysis                                                                                                                                   | 3 Installations in North America  
1 Installation in Hong Kong  
>100 Installations for Drinking Water Disinfection in Europe  
>2,000 Applications in North America for Municipal Wastewater Disinfection                                                                 | Pilot Studies in collaboration with Hydroxyl Systems, Inc.                                                                                      |
| Oxidation Systems Inc.                      | Mr. Joe Pisani  
President, OSI  
250 W. Colorado Boulevard  
Suite 190, Arcadia, CA 91007  
Phone: (626) 446-1482  
Fax: (626) 446-1493                                                                                                                                  | Hydrodynamic Cavitation (HYDROX)                                                                         | ~30 Installations                                                                                                                                  | 1 bench/pilot study                                                                                                                                  |
| HGC-UV                                      | Dr. Harold Bentley  
President, GeoChem  
51 W. Wetmore, Suite 101  
Tucson, AZ 85705  
Phone: (520) 293-1500  
Fax: (520) 293-1550                                                                                                                                    | UV + H₂O₂/O₃                                                                                           | Start-up firm                                                                                                                                       | Preliminary bench-scale studies                                                                                                                     |
| High Voltage Environmental Applications / Haley & Aldrich | Dr. Bill Cooper  
Dept of Chemistry, University of North Carolina Wilmington  
Phone: (910) 962-3450                                                                                                                                   | E-beam                                                                                                  | Total Disinfection Installations: 700  
Pilot and Demonstration Remediation Applications: 200                                                                                           | MTBE, TBA, TBF & Formaldehyde Studies: 10  
Case Study: Orange County Water District  
Pilot Testing: Miami, Florida                                                                                                                                   |
| Pulsar Environmental Technologies           | Mr. James Bender  
President  
Pulsar Environmental Technologies  
11802 Kemper Road  
Auburn, California, 95603  
Phone: (530) 823-1434  
jbender@pulsar-environmental.com                                                                                                        | Pulsed UV Technologies  
Riptide™ Pulsar UV Reactors                                                                                                      | 1 installation of 30-60 gpm capacity for treating landfill leachate (Oregon)  
No drinking water applications – currently applying for NSF approval/certification.  
Some ultra-pure water applications for semiconductor industry.                                                                                      | Preliminary bench-scale studies                                                                                                                       |

Table 3-5 (Continued) Summary of Vendor Information
3.4 Established Technologies

3.4.1 Hydrogen Peroxide/Ozone (H$_2$O$_2$/O$_3$)

**Process Description**

When O$_3$ is added to water, it participates in a complex chain of reactions that result in the formation of radicals such as the hydroxyl radical (•OH) and the superoxide radical (O$_2$•) (Hoigne, 1998). Like O$_3$, these radical products (•OH and O$_2$•) are oxidants capable of MTBE destruction. Of the radical intermediates formed in ozonated water, •OH is the most powerful MTBE oxidant, even more powerful than O$_3$ itself. Direct oxidation of ethers by O$_3$ is known to occur very slowly; this reaction’s second-order kinetic rate constant is less than 1 M$^{-1}$s$^{-1}$ (Buxton et al., 1988). By contrast, oxidation of ethers by radical oxidants is extremely rapid. Hydroxyl radicals react with MTBE according to a rate constant of 1.6 x 10$^9$ M$^{-1}$s$^{-1}$ (Buxton et al., 1988).

H$_2$O$_2$ can be combined with ozone to enhance the transformation of O$_3$ to •OH in solution. H$_2$O$_2$ is a weak acid, which partially dissociates into the hydroperoxide ion (HO$_2^-$) in water. H$_2$O$_2$ reacts slowly with O$_3$, whereas the HO$_2^-$ ion can rapidly react with O$_3$ to form •OH (Hoigne, 1998):

\[
\begin{align*}
H_2O_2 + H_2O & \leftrightarrow HO_2^- + H_3O^+ \\
O_3 + HO_2^- & \rightarrow •OH + O_2^- + O_2 
\end{align*}
\]

These reactions and possible by-products are summarized in Table 3-3. Also listed in this table are the interfering compounds and oxidant hierarchy.

**System Description/Design Parameters**

In an H$_2$O$_2$/O$_3$ system, H$_2$O$_2$ is used in conjunction with O$_3$ to enhance the formation of hydroxyl radicals. Since O$_3$ decomposes rapidly, it is typically produced on-site using a generator fed with dried compressed air or oxygen (Hoigne, 1998). The gas mixtures produced from air and oxygen by an ozone generator usually consist of 0.5 to 1.5 percent and 1 to 2 percent by volume O$_3$, respectively (Montgomery, 1985). The use of air to generate ozone requires dehumidification, which may be cost prohibitive relative to the use of pure liquid oxygen. In addition, larger quantities of ozone can be produced from a unit of liquid oxygen (14 percent O$_2$ by weight) compared to a unit of compressed air (2 percent O$_2$ by weight), which facilitates greater mass transfer of the ozone into the source water. Finally, ozone can be generated from liquid oxygen using less energy relative to compressed air.

For AOPs, O$_3$ gas is fed through spargers, porous piping or plates, or Venturi-type injectors at dosages equivalent to 1 to 2 mg/L ozone per mg/L DOC; however, higher dosages are recommended for source waters with high alkalinity (>100 mg/L as CaCO$_3$) or NOM.
Ozone transfer efficiencies from the gas to the water of up to 90 to 95 percent can be achieved (Montgomery, 1985). H$_2$O$_2$ is fed from an aqueous solution, at peroxide to ozone ratios ranging from 0.3:1 to 3:1 (Liang, 1999a, b; Applebury, 1999). The specific ratio will be a function of disinfection requirements, bromide concentration, contaminant concentration, and other water quality parameters.

Since ozone residual can provide disinfection credit, a lower peroxide to ozone ratio is typically applied to source waters requiring disinfection (e.g., surface waters) in order to leave some ozone residual. However, researchers have shown that bromate formation is a strong function of the H$_2$O$_2$ to O$_3$ ratio, and that H$_2$O$_2$ to O$_3$ ratios can effectively reduce the concentration of bromate generated (Siddiqui et al., 1994; Liang et al., 1999a and 1999b; White, 1999). These counter-acting effects should be considered when trying to determine the optimal peroxide to ozone dosage ratio to apply for a specific water source with significant influent bromide concentrations (>0.1 mg/L). For source waters requiring minimal disinfection (e.g., some groundwaters), a higher peroxide to ozone ratio can be applied to minimize bromate formation. In the case of waters requiring disinfection, alternative bromate formation mitigation measures may be required if a high peroxide to ozone ratio is used for disinfection credit or an alternative disinfectant (e.g., Cl$_2$) may be used to fully meet disinfection standards.

Two types of ozone contact configurations exist for application: 1) conventional 3 to 5 meter deep continuously stirred reactor basins, and 2) long (>100 feet) plug flow reactors. In a conventional ozone reactor, ozone is bubbled through the base of the reactor and allowed to diffuse through the reactor until it either escapes through the top or is completely reacted. This results in high ozone concentrations at the base of the reactor, independent of the contaminant concentrations, which promote the reaction of ozone with other chemical constituents to form regulated by-products (e.g., bromate). These reactors are typically covered so that excess O$_3$ can be collected and directed to an off-gas decomposer. Automatic monitoring and control systems are used to regulate chemical feed rates, pH, and other parameters. In addition, a variety of safety, monitoring, and control systems are included to facilitate operation. A schematic of a conventional H$_2$O$_2$/O$_3$ system equipped with UV lamps is shown in Figure 3-1a.
The second type of H₂O₂/O₃ contact system, referred to as HiPOx, has been commercialized by Applied Process Technology, Inc. (APT) (San Francisco, CA). HiPOx is a continuous, in-line plug flow reactor where O₃ and H₂O₂ are injected into the water stream in precisely controlled ratios at multiple ports along the flow reactor (see Figure 3-1b). The primary advantage of this system is that high dosages can be applied at the beginning of the flow reactor, where contaminant concentrations are high. As contaminant concentrations are reduced along the line, decreasing dosages can be applied, thereby controlling formation of regulated by-products (e.g., bromate). Using multiple injection ports, the concentration of molecular ozone in solution can be maintained at a lower concentration, typically below 0.5 mg/L, than in a large continuously stirred reactor. This keeps the H₂O₂ to O₃ ratio high.

Figure 3-1a. A schematic of a conventional (continuously stirred tank reactor) H₂O₂/O₃ system equipped with UV lamps (drawing provided by Komex H2O Science, 1998).
which, in turn, increases the rate of molecular ozone being converted to the hydroxyl radical and increases the rate of hypobromite reduction to bromide (Staehelin and Hoigne, 1982; von Gunten and Oliveras, 1997). As a result, the HiPOx system has been shown to effectively reduce bromate formation, even under high concentrations of influent bromide (1,000 µg/L), by minimizing the molecular ozone available to oxidize the bromide to hypobromite and having excess hydrogen peroxide available to reduce any hypobromite produced (Applebury, 1999). In addition, this system can be operated without the loss of pressure experienced by bringing the source water in contact with the atmosphere, thereby reduce pumping costs.

The major components of both a continuously stirred tank reactor and a plug flow reactor include:

- A H₂O₂ storage tank
- A H₂O₂ injection system
- An ozone generator
- Liquid oxygen or compressed air tank
Advantages and Disadvantages

The advantages and disadvantages of the H$_2$O$_2$/O$_3$ system are briefly summarized in Table 3-2. The benefits of using an H$_2$O$_2$/O$_3$ system are:

- The combined H$_2$O$_2$/O$_3$ process has been demonstrated to be more effective at removing MTBE and other natural and synthetic organics than O$_3$ or H$_2$O$_2$ alone. In addition, using a combination of O$_3$ and H$_2$O$_2$ to produce hydroxyl radicals, rather than just O$_3$, allows a lower dosage of O$_3$ to be used. This is desirable for reducing costs and bromate formation potential.

- The theoretical yield of hydroxyl radicals via H$_2$O$_2$/O$_3$ technology is less than that of the H$_2$O$_2$/UV technology; however, the yield is less affected by water quality (i.e., turbidity, iron, and nitrates lower the yield for UV processes but not H$_2$O$_2$/O$_3$ processes). Once the hydroxyl radicals are formed, however, the chemical destruction and interferences are the same for both technologies.

- According to this literature review, H$_2$O$_2$/O$_3$ systems appear to be the most tested and applied AOP in remediation applications for groundwaters, relative to the other AOPs. Thus, the implementation of H$_2$O$_2$/O$_3$ systems has a field-proven history of operation and regulatory acceptance.

The disadvantages and limitations of the H$_2$O$_2$/O$_3$ system are:

- The use of O$_3$ can result in the potential formation of bromate; however, bromate formation can be mitigated by lowering the pH to $<$6.5, increasing the H$_2$O$_2$ to O$_3$ ratio, or adding another radical scavenger that will react with hydroxyl radicals prior to the bromide (e.g., ammonia).

- The H$_2$O$_2$/O$_3$ process typically requires an air permit for ozone emissions in addition to an off-gas treatment system for ozone destruction. The hydrogen peroxide reacts rapidly with most of the applied ozone and, thus, the air exiting the contactor has been observed to typically contain ozone concentrations less than 1 mg/L (Applebury, 1999). This concentration is significantly higher than the 1-hour Clean Air Act standard of 0.12 ppmv (CFR Title 40, Part 50). Current methods for removal of ozone in the off-gas include thermal destruction, catalytic reduction, or a combination of the two (Horst, 1982; White, 1999).
Thermal destruction takes advantage of the fact that ozone decomposes rapidly at high temperatures. Catalytic reduction involves passing the ozone off-gas across a surface (commonly iron or manganese oxide) that catalyzes the decomposition of ozone to elemental oxygen. These controls will add to the operational and capital cost of the system (AWWA/ASCE, 1997).

- Residual H$_2$O$_2$ can serve as an oxygen source for microorganisms and can promote biological re-growth in the distribution system. Although there are currently no federal or state standards for residual H$_2$O$_2$ in treated drinking water, drinking water purveyors are not likely to allow any detectable levels of H$_2$O$_2$ in treated drinking water (detection limits range from 1 µg/L to 100 µg/L depending on the method and concentration) because of concerns over biological growth. Thus, depending on the effluent concentration, post-treatment of excess H$_2$O$_2$ may be required to limit downstream biological fouling. However, if residual H$_2$O$_2$ concentrations are limited to less than a few mg/L, treatment systems already in place for the removal of oxidation by-products from the H$_2$O$_2$/O$_3$ system effluent will also remove the residual H$_2$O$_2$. In cases where residual H$_2$O$_2$ generally exceeds a few mg/L, a treatment system specifically for H$_2$O$_2$ removal (e.g., catalytic activated carbon) will need to be employed (Crawford, 1999).

**Bench-scale Studies**

Karpel Vel Leitner et al. (1994) studied the reaction of ozone combined with hydrogen peroxide on gasoline additives such as MTBE in a dilute aqueous solution. Experiments conducted in a semi-continuous reactor with MTBE showed that the use of H$_2$O$_2$/O$_3$ is a more effective treatment process than ozone alone. Applied dosages of 3.0 and 1.7 mg ozone per mg of MTBE were found to result in 80 percent reduction of MTBE under ozone alone (at pH 8) and under H$_2$O$_2$/O$_3$, respectively. TBA, TBF, and formaldehyde were identified as the by-products of the H$_2$O$_2$/O$_3$-MTBE reactions.

**Pilot/Field Studies and Vendor Information**

Dyksen et al. (1992) performed pilot tests using in-line application of ozone and hydrogen peroxide to evaluate process issues for the removal of organic chemicals such as TCE, PCE, cis-1,2 dichloroethylene (cis-1,2 DCE), and MTBE. The results indicated that H$_2$O$_2$/O$_3$ is more effective than ozone alone for removal of TCE, PCE, cis-1,2 DCE, and MTBE. Non-detectable levels of MTBE were recorded using an ozone dosage of 8 mg/L, a contact time of 3 to 6 minutes, and a hydrogen peroxide to ozone ratio of 0.5.

Liang et al. (1999a) conducted a pilot-scale study to investigate the effectiveness of ozone and H$_2$O$_2$/O$_3$ processes for MTBE removal in surface water. Using two treatment trains with a total flow capacity of 12 gpm, H$_2$O$_2$/O$_3$ was found to be more effective than ozone alone for MTBE removal under their tested conditions. The results indicated that 4 mg/L of ozone
and 1.3 mg/L of hydrogen peroxide can achieve average MTBE removals of approximately 78 percent for both source water supplies tested.

Liang et al (1999b) also investigated the removal of MTBE from contaminated groundwater through the use of ozone and H₂O₂/O₃. Experiments conducted in a large-scale semi-batch reactor again demonstrated that H₂O₂/O₃ (at a H₂O₂ to O₃ ratio of 1.0) was consistently more effective in oxidizing MTBE than ozone alone, even at ozone doses as high as 10 mg/L. Applied ozone doses greater than 10 mg/L were necessary to reduce MTBE concentrations from approximately 200 and 2,000 µg/L to concentrations below the California secondary drinking water standard of 5 µg/L. However, at this dosage, both ozone and H₂O₂/O₃ were also found to completely oxidize MTBE oxidation by-products, such as TBF and TBA.

Most vendors who provide ozone technologies can also provide H₂O₂/O₃ systems by adding H₂O₂ injection systems to their oxidation reactors. There are several vendors who currently exclusively provide H₂O₂/O₃ technology, but few have applied their process for MTBE removal (see Table 3-4). APT (San Francisco, CA) has performed several pilot/field-scale studies of their patented H₂O₂/O₃ system, HiPOx. As mentioned previously, unlike more conventional H₂O₂/O₃ systems, the HiPOx system has multiple oxidant injection ports and the reaction is carried out under pressure. Three of the APT studies involved MTBE removal applications (see Table 3-4). In one APT study involving highly brominated (bromide >1,000 µg/L) coastal water, a 10-gpm HiPOx system was able to reduce the MTBE concentration from 1,000 µg/L to 1 µg/L while maintaining the bromate concentration at less than 10 µg/L (Waters, 1999). TBA concentrations in the effluent were measured at approximately 60 µg/L. In a second field study, a 10-gpm HiPOx system was able to reduce MTBE (in a solution containing a mixture of BTEX compounds) from 33,000 µg/L to <5 µg/L MTBE. The third study (0.25 gpm) showed reduction of 660,000 µg/L MTBE to 2.3 µg/L. TBA and by-product concentrations were not measured for the latter two studies.

Hydroxyl Systems (HSI) (Sidney, British Columbia, Canada) is currently conducting a remediation field study using H₂O₂/O₃ at the JFK Airport in New York. The objective of the study is to reduce MTBE from an initial concentration of 100 to 300 mg/L to a final effluent goal of 50 µg/L (local action level), at a flow rate of 20 to 60 gpm (Harp, 1999). Phase 1 of the field study is scheduled to commence in early 2000. The flow rates at this treatment facility will be gradually increased from 20 gpm to 60 gpm (Harp, 1999). U.S. Filter (Santa Clara, CA) also has several H₂O₂/O₃ installations across the nation but currently has no installations designed specifically for MTBE removal applications (Himebaugh, 1999; Woodling, 1999). Refer to Tables 3-4 and 3-5 for a summary of these case studies and vendor information, respectively.

**Summary**

H₂O₂/O₃ systems have been well studied at the bench-, pilot-, and field-scale levels for the removal of organic contaminants such as BTEX, TCE, and PCE. There are currently a
number of full-scale H$_2$O$_2$/O$_3$ systems in use for MTBE remediation (Table 3-4); however, use of this technology for drinking water applications has only been performed at the pilot scale. While concerns have been raised about the formation of bromate with these systems, this concern can be mitigated by increasing the peroxide to ozone ratio, decreasing the pH, or raising the concentration of other radical scavengers. The chemistry behind H$_2$O$_2$/O$_3$ systems is well understood; however, as with all AOPs, more pilot- and field-scale demonstration sites under a variety of water quality matrices are needed prior to general regulatory acceptance.

### 3.4.2 UV Systems

UV light is in the high-energy end of the light spectrum with wavelengths less than that of visible light (400 nm) but greater than that of x-rays (100 nm). UV radiation (h\_u) can destroy organic contaminants, including MTBE, through direct and indirect photolysis (Zepp, 1988). In direct photolysis, the absorption of UV light by MTBE places it in an electronically excited state, causing it to react with other compounds, and eventually degrade. In contrast, indirect photolysis of MTBE is mediated by hydroxyl radicals that are produced when ozone or peroxide is added to the source water either prior to or during UV irradiation.

The most common sources of UV light are continuous wave low pressure mercury vapor lamps (LP-UV), continuous wave medium pressure mercury vapor lamps (MP-UV), and pulsed-UV (P-UV) xenon arc lamps. Both LP-UV and MP-UV mercury vapor lamps produce a series of line outputs, whereas the xenon arc lamp produces a continuous output spectra. The characteristics of typical LP-, MP-, and pulsed-UV lamps are presented in Table 3-6.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Low Pressure</th>
<th>Medium Pressure</th>
<th>Pulsed-UV</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Emission</strong></td>
<td>Monochromatic</td>
<td>Polychromatic</td>
<td>Polychromatic</td>
</tr>
<tr>
<td>(85-90% at 253.7 nm)</td>
<td></td>
<td>(185-1,367 nm)</td>
<td>(185-1,000 nm)</td>
</tr>
<tr>
<td><strong>Peak Output Wavelength [nm]</strong></td>
<td>253.7</td>
<td>200-400</td>
<td>~450</td>
</tr>
<tr>
<td><strong>Mercury vapor pressure (torr)</strong></td>
<td>$10^{-3}$ to $10^{-2}$</td>
<td>$10^{7}$ to $10^{8}$</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Operating temperature</strong></td>
<td>40 to 60 °C</td>
<td>500 to 800 °C</td>
<td>~15,000 °C</td>
</tr>
<tr>
<td><strong>Arc length (cm)</strong></td>
<td>40 to 75</td>
<td>5 to 195</td>
<td>15</td>
</tr>
<tr>
<td><strong>Lifetime</strong></td>
<td>8,000 to 10,000 hrs</td>
<td>2,000 to 5,000 hrs</td>
<td>&gt; 100 x 10$^6$ pulses</td>
</tr>
<tr>
<td><strong>Light intensity (relative)</strong></td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
</tbody>
</table>
For most traditional applications of UV irradiation with $H_2O_2$ or $O_3$, LP-UV and MP-UV have been used; however, MP-UV is receiving increasing attention because of its greater potential for direct photolysis. In addition, MP-UV lamps radiate over a wider range of wavelengths (200 to 400 nm) than LP-UV lamps, which better facilitates the formation of hydroxyl radicals when hydrogen peroxide is present; hydrogen peroxide absorbs more in the higher wavelengths (250 to 300 nm). Furthermore, while an LP-UV lamp is more electrically efficient than an MP-UV lamp, the latter produces a greater UV output per lamp. Thus, MP-UV systems can be expected to use fewer lamps, take up less space, and require less maintenance. Finally, after extensive ETV testing, the EPA has recently credited Calgon Carbon’s (Markham, Ontario, Canada) MP-UV lamp system (Sentinel™) with 3.9 log$_{10}$ inactivation for Cryptosporidium parvum (EPA/600/R-98/160VS, 1999; Bukhari et al., 1999. Calgon Carbon (Markham, Ontario) has decided not to use P-UV lamps due to their short lifetimes and minor observed benefits relative to MP-UV (Crawford, 1999).

To describe the removal efficiency for organic contaminants using UV lamps, Calgon Carbon (Markham, Ontario, Canada) has defined the term Electrical Energy per Order of Removal (EE/O) as the kilowatt-hours (kWh) of electricity required to reduce the concentration of a compound (e.g., MTBE) in 1,000 gallons by one order of magnitude (or 90 percent) (Calgon AOT Handbook, 1996). The unit for EE/O is kWh/1,000 gal/order of removal and is defined at the optimum $H_2O_2$ or $O_3$ concentration. According to Calgon Carbon, the EE/O provides a convenient way to compare the effectiveness of removal of various organic compounds, using UV irradiation for a single source water (i.e., the EE/O will change depending on the water quality). The higher the EE/O value of a contaminant, the more difficult and/or more costly it is to remove that contaminant relative to those with lower EE/O values. For example, MTBE is more difficult to treat than BTEX, with EE/O values of around 10 for MTBE and 2 to 5 for benzene. An EE/O of 10 for MTBE means that it would take ~10 kWh to reduce MTBE from 600 µg/L to 60 µg/L in 1,000 gal of water. It will take another 10 kWh to reduce the MTBE from 60 µg/L to 6 µg/L, and so on (Calgon AOT Handbook, 1996).

**Ozone/UV ($O_3$/UV)**

- **Process Description**

Due to the relatively high molar extinction coefficient of ozone, LP-UV or MP-UV radiation can be applied to ozonated water to form highly reactive hydroxyl radicals (Wagler and Malley, 1994). The use of UV irradiation — whether MP-UV, LP-UV, or P-UV — to produce hydroxyl radicals with ozone occurs by the following reaction:

$$\text{O}_3/\text{UV process: } O_3 + H_2O \overset{h\nu}{\rightarrow} O_2 + H_2O_2 \quad (\lambda <300 \text{ nm})$$

$$2 O_3 + H_2O_2 \rightarrow 2 \cdot OH + 3 O_2$$

As the above reactions illustrate, photolysis of ozone generates hydrogen peroxide and, thus, $O_3$/UV involves all of the organic destruction mechanisms present in $H_2O_2/O_3$ and $H_2O_2/UV$.
AOPs (Table 3-3). These mechanisms include direct reaction with ozone, direct photolysis by UV irradiation, or reaction with hydroxyl radicals (Calgon AOT Handbook, 1998). In most past applications of O₃/UV, LP-UV lamps have been used (AWWA, 1990; Calgon AOT Handbook, 1996); however, MP-UV and P-UV are receiving increased attention due to their disinfection capabilities and direct photolysis benefits.

**System Description/Design Parameters**

Two basic UV reactor design configurations are used for the removal of organic contaminants from water. Calgon Carbon, Inc. (Markham, Ontario, Canada) currently uses both reactor designs for MTBE removal, depending on the flow rate (Crawford, 1999). For large-scale drinking water applications (>500 gpm), a tower design is typically utilized. In the tower configuration, multiple UV lamps are arranged horizontally within a single large reactor vessel with the contaminated water flowing perpendicularly past the UV lamps. For example, a tower system may consist of 12 20-kW UV lamps arranged horizontally throughout the tower. Heat transfer for MP-UV lamps is typically <1°C for every 4 kWh/1,000 gallons. Therefore, no cooling systems are needed for the large-scale tower configuration.

For small-scale systems (<500 gpm), Calgon Carbon (Markham, Ontario, Canada) employs reactors where a single UV lamp per reactor vessel is arranged vertically. For example, a small-scale system may consist of three individual reactor vessels in series, each containing one 30-kW UV lamp in a vertical position. For very small systems (<50 gpm), these higher watt lamps operate at a higher temperature and, thus, require a cooling fan to effect heat transfer (Crawford, 1999). Safety interlocks are provided on Calgon UV reactors to protect personnel from both the UV radiation and high voltage supply (Calgon AOT Handbook, 1996).

U.S. Filter (Santa Clara, CA) markets a LP-UV oxidation system, referred to as Ultrox, which can use either ozone, peroxide, or a combination of both as supplemental oxidants (Gruber, 1994). A typical Ultrox system can consist of a combination of the following four components: 1) a stainless steel reaction chamber with LP-UV lamps; 2) an air compressor/ozone generator; 3) a hydrogen peroxide feed system; and 4) a catalytic ozone decomposition unit. As a first step in the treatment process, the contaminated source water is mixed with peroxide and then fed into the reaction chamber where ozone is added, if necessary. The reaction chamber ranges in size from 325 to 3,900 gallons and is divided into a series of parallel sub-chambers, each housing a bank of LP-UV mercury vapor lamps (Gruber, 1994). As the water flows through each sub-chamber, it passes in front of each bank of UV lamps (the number of sub-chambers and the number of lamps depend on the size of the system and type of contaminant being destroyed). The Ultrox system employs low-intensity UV lamps; hence, the surface temperatures of the quartz sheath surrounding each lamp rarely exceeds 90°F (Gruber, 1994).
For O3/UV applications, ozone is introduced into the system at the bottom of each chamber by a stainless steel sparger. The ozone generator employed in the Ultrox system can electrically generate ozone from either air or liquid oxygen. Any ozone that is present in the off-gas is put through a fixed bed catalytic scavenger. This ozone decomposition unit operates at 150°F and uses a proprietary nickel-based catalyst to convert ozone to oxygen (Gruber, 1994). Ultrox systems can operate from flow ranges of 5 gpm to 1,200 gpm. Higher flowrates are attainable with multiple treatment trains (Himebaugh, 1999).

To minimize problems associated with potential fouling of the UV lamp sleeves in cases where the influent water has high concentrations of fouling agents (e.g., iron, calcium, and magnesium), UV systems are equipped with automated cleaning devices. Quartz sleeves that separate the water from the UV lamps are periodically cleaned by pneumatically driven wipers. Quartz sleeve cleaning devices are common in UV oxidation technologies, and the costs are generally included in the total costs of the system (Crawford, 1999). The frequency of UV lamp cleaning is a function of the presence of iron and other scaling agents in the water. However, the wiping mechanisms used today are well designed and allow for trouble-free operation for source waters containing concentrations of iron and other fouling agents.

The two primary design variables that must be optimized in sizing a UV AOP system are the UV power radiation per unit volume of water treated — more commonly referred to as UV dose — and the concentration of hydrogen peroxide or ozone. UV dose, when applied to AOP, is a measure of the total lamp electrical energy applied to a fixed volume of water. The units are measured in kWh/1,000 gallons treated. This parameter combines flowrate, residence time and light intensity into a single term. The dose of UV light and peroxide/ozone required per unit volume of water treated may vary from one type of water to another. For a flow-through system, the UV dose (kWh/1,000 gal) is given by:

$$ UV \text{ Dose} = \frac{1,000 \times \text{lamp power}}{\text{flow (gpm)} \times 60} $$

Design tests are typically performed to measure the UV dosage required to achieve the desired effluent concentration. The dosage to be applied is determined in an iterative manner by examining the effect on treatment of selected process variables such as pH, oxidant concentration and retention time.

The major components of an O3/UV system include:

- UV lamps, lamp sleeves, and lamp cleaning system
- Ozone generator and diffusers
- Ozone contactor
- Ozone off-gas decomposer
• Liquid oxygen or compressed air tank
• Supply and discharge pumps and piping
• Monitoring and control systems

Figure 3-1a previously showed a schematic of a conventional H₂O₂/O₃ system equipped with UV lamps. An O₃/UV system is similar, with the exception of the H₂O₂ feed system.

• Advantages and Disadvantages

The advantages and disadvantages of the O₃/UV system are briefly summarized in Table 3-2. The benefits of using the O₃/UV system are:

• The removal efficiency of the combined O₃/UV process is typically higher than the additive removal efficiencies of ozone and UV alone (Prado and Esplugas, 1999). The magnitude of this synergistic effect varies depending on the contaminant of interest (Prado and Esplugas, 1999).

• The combined O₃/UV process is more efficient at generating hydroxyl radicals than the combined H₂O₂/UV process for equal oxidant concentrations using LP-UV. This is because the molar extinction coefficient of O₃ at 254 nm is two orders of magnitude greater than that of H₂O₂, indicating that a lower UV intensity or a higher H₂O₂ dose is required to generate the same number of hydroxyl radicals for these two processes (Glaze et al., 1987). However, for MP-UV lamps, H₂O₂/UV processes will generate more hydroxyl radicals than O₃/UV processes, assuming the peroxide absorbs greater than 17 percent of irradiated light (200 nm to 300 nm) (Cater, 1999).

The disadvantages of the O₃/UV system are:

• As mentioned previously, the use of ozone for source waters with high bromide concentrations (>0.1 mg/L) can result in the formation of bromate.

• The O₃/UV process typically requires an air permit for ozone emissions in addition to an off-gas treatment system for ozone destruction. These controls will add to the operational and capital cost of the system (AWWA/ASCE, 1997).

• Despite the fact that O₃/UV is more stoichiometrically efficient at generating hydroxyl radicals than H₂O₂/UV or H₂O₂/O₃, the O₃/UV process is less energetically efficient than H₂O₂/UV or H₂O₂/O₃ for generating large quantities of hydroxyl radicals due to the low solubility of O₃ in water compared to H₂O₂. Thus, operational costs are expected to be much higher than these comparative processes. The hydroxyl radical yield can be decreased further by the presence of interfering parameters (e.g., nitrates, turbidity, or iron) in the source water.
• Gaseous O$_3$ must be diffused into the source water, resulting in potential mass transfer limitations relative to H$_2$O$_2$, which is fed as a liquid solution (Wagler and Malley, 1994).

• UV light penetration into the source water — and, thus, process efficiency — can be adversely affected by turbidity (Prado and Esplugas, 1999).

• As mentioned previously, there are many interference compounds that absorb UV light (e.g., nitrate and iron) and, thus, reduce process efficiency.

• UV lamp and sleeve failures can potentially contaminate treated water with mercury, although all lamp failures to date have resulted in aqueous Hg concentrations below drinking water standards (Crawford, 1999).

• Research suggests that the use of UV combined with pre- and/or post-chlorination can potentially result in the increased formation of THM and HAA$_9$ at UV dosages >100 mJ/cm$^2$ (Zheng et al., 1999a,b).

• **Bench-scale Studies**

To date, no bench-scale studies of MTBE destruction with the O$_3$/UV process have been identified.

• **Pilot/Field Studies and Vendor Information**

The O$_3$/UV process has been employed for the following applications (Rice, 1997):

• Groundwater treatment to destroy TCE, PCE, and PCP.

• Remediation at Superfund sites to destroy VOCs and benzidines.

• Remediation at U.S. Army Ammunition plants to destroy explosive compounds such as 2,4,6-trinitrotoluene (TNT) and cyclonite (also referred to as RDX).

Most O$_3$/UV systems in place are for destruction of ordinance compounds. Currently, there are no field or pilot applications of O$_3$/UV technology for MTBE remediation. This is likely because this technology is economically prohibitive relative to other AOPs for easily degradable compounds (Crawford, 1999). Some of the known vendors for O$_3$/UV systems include: Hydroxyl Systems (Sidney, British Columbia, Canada), Calgon Carbon (Markham, Ontario, Canada), U.S. Filter (Santa Clara, CA) and HGC-UV Incorporated (Tucson, AZ). Table 3-5 summarizes vendor information for these technologies.
Summary

The applications of ozone and UV are energy intensive processes and, hence, a combined O_3/UV process may not be cost effective for treating waters with high TOC and MTBE concentrations. In addition, O_3/UV process requires the expending of significantly more (electrical) energy than H_2O_2/UV or H_2O_2/O_3 processes. The use of ozone in potable water applications can result in the generation of bromate at concentrations above the Stage 1 D/DBP Rule of 10 µg/L. In conclusion, due to these economic and practical constraints, this technology will not be considered further for MTBE removal from drinking water in the remainder of this chapter.

Hydrogen Peroxide/UV (H_2O_2/UV)

Process Description

As in the O_3/UV process, the effectiveness of the H_2O_2/UV process relies on several synergistic oxidation mechanisms for the destruction of MTBE. The oxidation of organics can occur by either direct photolysis or reactions with hydroxyl radicals. Hydroxyl radicals are produced from the photolytic dissociation of H_2O_2 in water by UV irradiation (Wagler and Malley, 1994; Calgon AOT Handbook, 1998). As in the O_3/UV and H_2O_2/O_3 systems, the degradation of MTBE is primarily due to the oxidation reactions initiated by the highly reactive hydroxyl radicals:

\[ \text{H}_2\text{O}_2/\text{UV process: } \text{H}_2\text{O}_2 \xrightarrow{\text{h}_{\nu}} 2 \cdot \text{OH} \ (\lambda < 300 \text{ nm}) \]

\[ \cdot \text{OH} + \text{MTBE} \rightarrow \text{Oxidation by-products} \]

System Description/Design Parameters

For the H_2O_2/UV system, higher radical generation results from the use of MP-UV lamps relative to the LP-UV lamps, due to the better absorptivity of H_2O_2 at lower wavelengths (Cater, 1999). Peroxide dissociates to form hydroxyl radicals at wavelengths of 250 nm and below. Thus, while peroxide dissociation occurs with LP-UV, MP-UV emits a broader spectrum that promotes the dissociation of peroxide better than LP-UV. Calgon Carbon (Markham, Ontario, Canada) uses MP-UV lamps exclusively in its H_2O_2/UV processes due to the requirement for fewer lamps, the potential for direct photolysis, and smaller resulting system size (Cater, 1999).

All of the reactor configurations discussed for the O_3/UV process are applicable for the H_2O_2/UV process. H_2O_2/UV systems are equipped with hydrogen peroxide storage and injection systems in place of an ozone generator and diffuser system. Hydrogen peroxide is injected upstream of the reactor using metering pumps and mixed by in-line static mixers (Crawford, 1999).
The key design and operating parameters include the H$_2$O$_2$ dose, the UV lamp type and intensity, the reactor contact time, and the control systems (pH and temperature). The low molar extinction coefficient for H$_2$O$_2$ (Wagler and Malley, 1994) results in the use of MP-UV lamps for higher hydroxyl radical yields. UV doses typically range from 2.5 kWh/1,000 gallons to 15 kWh/1,000 gallons depending on water quality and contaminant concentrations (Crawford, 1999). The UV quartz sleeve cleaning frequency is a function of iron and other scalants that are present in the water.

Hydrogen peroxide can be added either as a single slug dose or at multiple points in the system. The optimum dose of H$_2$O$_2$ should be determined for each water source based on bench and pilot-scale testing, but is commonly estimated at twice the TOC and not less than 1 to 2 mg/L (e.g., TOC for drinking water ranges from less than 0.1 mg/L to greater than 7 mg/L, which would suggest a peroxide concentration of up to 14 mg/L). As previously noted, currently, there are no federal or state regulations for H$_2$O$_2$ residual in treated drinking water; however, drinking water purveyors are not likely to allow any detectable levels of H$_2$O$_2$ in treated drinking water because of concerns over biological growth. Thus, if H$_2$O$_2$ is added at very high concentrations (>10 mg/L), effluent treatment will be required. Consequently, Calgon Carbon (Markham, Ontario, Canada) commonly keeps H$_2$O$_2$ doses at less than 3 to 5 mg/L to minimize H$_2$O$_2$ residuals. Once the optimum H$_2$O$_2$ dose is determined, the EE/O for the target compound is applied to determine energy costs.

Pulsar Environmental Remediation Technologies, Inc. (Auburn, CA) markets modular, P-UV reactors — known as Riptide™ systems — for remediation applications. These Riptide™ reactors are available in three different sizes: 1 to 10 gpm (Riptide-8), 10 to 60 gpm (Riptide-20), and 60 to 400 gpm (Riptide-350) (Bender, 1998). The large Riptide™ reactor (Riptide-350) is a 6-foot vertical chamber with a 20-inch diameter (Bender, 1999). The Riptide™ system is comprised of a multi-pass reaction chamber containing a high-energy UV flashlamp. These Pulsar (Auburn, CA) UV lamps radiate UV light in a broad spectrum ranging from 185 nm to 400 nm, in a radiation profile known as blackbody or continuum radiation (Bender, 1998). The Pulsar (Auburn, CA) lamps also radiate visible and infrared light from 400 to 3,000 nm, in accordance with the blackbody profile (Bender, 1998).

The major components of a H$_2$O$_2$/UV system include:

- UV lamps, lamp sleeves, and lamp cleaning system
- Hydrogen peroxide storage and injection system
- Reactor chamber
- In-line mixer
- Supply and discharge pumps and piping
- Monitoring and control systems
Figure 3-1a shows a schematic of a system capable of using O₃, H₂O₂, and UV. A H₂O₂/UV system would look very similar, except for the absence of the O₃ feed system.

- **Advantages and Disadvantages**

The advantages and disadvantages of the H₂O₂/UV system are briefly summarized in Table 3-2. The advantages of the H₂O₂/UV system are:

- No potential for bromate formation in the H₂O₂/UV process because the system does not rely on ozone for organic destruction (Siddiqui et al., 1999).

- Prior studies have demonstrated that the H₂O₂/UV process can oxidize >95 percent MTBE compared to <10 percent for UV or H₂O₂ alone under similar test conditions (Wagler and Malley, 1994).

- Currently, the only full-scale drinking water treatment AOP in the United States is a H₂O₂/MP-UV system installed in Salt Lake City, Utah. According to this literature review, H₂O₂/UV systems appear to be the most tested and applied AOP in drinking water applications relative to the other AOPs, although not for MTBE. Thus, the implementation of H₂O₂/UV systems for drinking water applications has a history of operation and regulatory acceptance.

- MP-UV and P-UV irradiation can serve as an effective disinfectant for a variety of microorganisms (e.g., viruses); however, there is currently no regulatory authority for receiving disinfection credit as a result of using MP-UV or P-UV.

- H₂O₂ is highly soluble and can be added to the source water at high concentrations, whereas O₃ is a much less soluble gas that must be bubbled into the source water. Consequently, H₂O₂/UV processes can generate larger amounts of hydroxyl radicals than O₃/UV processes for equal amounts of energy used to add the oxidants to the source water. Furthermore, assuming the peroxide absorbs greater than 17 percent of the 200 to 300 nm light, H₂O₂/MP-UV processes will generate more hydroxyl radicals than O₃/UV for equal concentrations of O₃ and H₂O₂ in the source water (Cater, 1999).

The disadvantages of the H₂O₂/UV system are:

- UV light penetration — and, therefore, process efficiency — can be adversely affected by high turbidity and elevated nitrate concentrations (Prado and Esplugas, 1999).

- UV lamp and sleeve failures can potentially contaminate treated water with mercury, although all lamp failures to date have resulted in aqueous Hg concentrations below drinking water standards (Crawford, 1999).
• Research suggests that the use of H₂O₂/UV combined with pre- and/or post-chlorination can result in the increased formation of THM and HAA₉, especially at high UV dosages (>2,000 mJ/cm²). Note: 2,000 mJ/cm² translates to approximately 0.6 kWh/1,000 gallons for a Calgon system (Cater, 1999) and thus, is well within the range of UV used for AOP applications.

• The theoretical yield of hydroxyl radicals via the H₂O₂/UV process is greater than that for the H₂O₂/O₃ process; however, due to interfering compounds in the water, this theoretical yield can be decreased to below that of the H₂O₂/O₃ process. Once the hydroxyl radicals are formed, however, the chemical destruction and interferences are the same for both technologies.

• The presence of residual hydrogen peroxide in the treated effluent will promote biological re-growth in the distribution system. Currently, there are no federal or state regulations for H₂O₂ residual in drinking water; however, drinking water purveyors are not likely to allow any detectable levels of H₂O₂ in treated drinking water (detection limits range from 1 to 100 µg/L depending on the method and concentration) because of concerns over biological growth. Thus, depending on effluent concentrations, post-treatment of excess H₂O₂ may be required to limit downstream biological fouling. High concentrations of residual peroxide (exceeding a few mg/L) can be treated using catalytic activated carbon (Crawford, 1999).

• **Bench-scale Studies**

Wagler and Malley (1994) conducted bench-scale studies to determine the effectiveness of UV light, H₂O₂, and UV combined with H₂O₂ in removing MTBE from contaminated groundwater in New Hampshire. In general, treatment of a simulated groundwater with pH between 6.5 and 8.0 by UV alone or by H₂O₂ alone produced less than 10 percent removal of MTBE after 2 hours of exposure. In contrast, the combination of UV and H₂O₂ within the pH range of 5.5 to 10 produced more than 95 percent removal of MTBE after only 40 minutes of exposure time. This study confirmed that the hydroxyl radical formed in the H₂O₂/UV process is the primary oxidant responsible for the oxidation of MTBE. During these oxidation experiments, methanol, formaldehyde, TBA, and 1,1-dimethylethyl-formate were identified as by-products of the H₂O₂/UV process. Furthermore, H₂O₂/UV oxidation of an actual groundwater containing MTBE and other VOCs resulted in 83 percent removal of MTBE after 2 hours of contact time.

Chang and Young (1999) determined the kinetics of H₂O₂/UV degradation of MTBE by using a recirculating batch reactor with a LP-UV lamp. With a spiked MTBE concentration of 10 mg/L, H₂O₂/UV treatment resulted in 99.9 percent removal. The major by-product identified was TBF. The second order rate constant for the MTBE/•OH reaction under the H₂O₂/UV treatment process was found to be 4.82 x 10⁹ M⁻¹ s⁻¹. The mean second order rate constant for the reaction of TBF with •OH was found to be 1.19 x 10⁹ M⁻¹ s⁻¹. The yield for
TBF formation from the MTBE/OH reaction was calculated to be 27 percent under the conditions of this experiment.

In preliminary bench-scale studies, peroxide-assisted Pulsar (Auburn, CA) P-UV systems successfully reduced the MTBE from influent concentrations ranging from 40 to 2,000 µg/L to less than 5 µg/L (Bender, 1998). Presence of high turbidity, large particles and excess total dissolved solids (TDS) can affect the performance of P-UV systems (Bender, 1999), similar to other UV-dependent AOPs. Pulsar Environmental (Auburn, CA) is currently working with NSF International for certification of the Riptide™ system for use in drinking water applications (Bender, 1999).

- Pilot/Field Studies and Vendor Information

In July 1998, a pilot treatment plant was constructed at the Charnock well field in Santa Monica, California to evaluate treatment technologies for removal of MTBE and TBA from drinking water. The treatment plant included several treatment processes, including an H₂O₂/UV oxidation system (for MTBE, TBA destruction), several carbon adsorption systems (for by-product destruction and polishing), and a packed tower air stripper. Additional systems, including a granular media filter and bag filter with an oxidant injection system, were installed to evaluate iron and manganese removal for pre-treatment to the H₂O₂/UV system.

Calgon Carbon (Markham, Ontario, Canada) provided the H₂O₂/UV system, which consisted of a tower reactor with three MP-UV lamps. The reactor was approximately 42-inches in diameter and 6 feet in height. The pilot facility began operation on July 31, 1998 at a design flow of 140 gpm, but testing was conducted at flows as high as 350 gpm. The pilot testing was conducted over a period of approximately 12 months and included an optimization phase, a reliability phase, and a sensitivity phase for MTBE, TBA, and other by-product testing (Rodriguez, 1999).

Raw groundwater from the Charnock well field was spiked at concentrations of approximately 1,000 µg/L MTBE and/or 200 µg/L TBA. MTBE and TBA were removed to less than 10 µg/L; however, the results of the pilot testing indicated that the costs were significantly higher than expected and the removal efficiencies were lower than predicted. The detection of by-products in the treated water (TBA, TBF, and acetone) mandated the use of an additional treatment unit, which would further increase the cost of treatment. Finally, residual H₂O₂ in the treated water would require installation of a carbon system for its removal. Testing conducted indicated that the H₂O₂/UV technology worked for MTBE removal, but the high energy requirements, complications caused by several sleeve/lamp failures, formation of by-products, and requirement for additional treatment processes significantly reduced the advantages of this technology (Rodriguez, 1999).
Currently, Calgon Carbon (Markham, Ontario, Canada) has two installations where MTBE is being treated (Cater, 1999). One of these installations treats heavily contaminated wastewater with high concentrations of MTBE (100 mg/L), BTEX (40 mg/L), and chemical oxygen demand (COD) (2,000 mg/L). The other installation is for pipeline rinse water that contains BTEX (4 mg/L) along with MTBE (11 mg/L). Both these units were designed for BTEX treatment (Cater, 1999).

While not for MTBE treatment, there are several full-scale drinking water applications of H$_2$O$_2$/MP-UV. Calgon Carbon (Markham, Ontario, Canada) currently maintains two full-scale AOP applications for drinking water treatment. These systems in Eastern Canada and Salt Lake City, Utah use H$_2$O$_2$/MP-UV to remove NDMA and PCE, respectively, at low concentrations. The Salt Lake City installation uses a 12-foot tower (4-foot diameter) with 12 layers of lamps aligned perpendicular to the flow to treat groundwater at 3,000 gpm. Treated water is discharged directly into the distribution system. Calgon Carbon (Markham, Ontario, Canada) is currently in the process of installing two additional H$_2$O$_2$/MP-UV systems in La Puente, California and a second in Southern California.

Some of the known vendors for H$_2$O$_2$/UV systems include: Hydroxyl Systems (Sidney, British Columbia, Canada), Calgon Carbon (Markham, Ontario, Canada), U.S. Filter (Santa Clara, CA), Pulser Environmental Remediation Technologies (Auburn, CA), and Trojan Technologies (London, Ontario, Canada). Table 3-5 summarizes the vendors, their technologies and number of installations. U.S. Filter (Santa Clara, CA) has a patented H$_2$O$_2$ — and/or O$_3$ — enhanced oxidation system known as Ultrox (Gruber, 1994). Ultrox systems are currently being used at more than 20 groundwater remediation applications and 10 wastewater treatment applications. None of these Ultrox systems treat MTBE (Himebaugh 1999; Woodling 1999). Trojan Technologies (London, Ontario, Canada) has more than 2,000 H$_2$O$_2$/UV systems for disinfection of wastewaters (Dewaal, 1999) and is currently planning to perform bench-scale studies in collaboration with HSI at the JFK Airport site discussed earlier (Dewaal, 1999).

**Summary**

H$_2$O$_2$/UV oxidation is one of the few AOPs used in drinking water treatment (e.g., Salt Lake City, Utah). In addition, a large amount of bench- and pilot-scale research has been conducted on the removal of MTBE and other gasoline contaminants using this AOP. A low potential for bromate formation — coupled with compact reactor design — makes the H$_2$O$_2$/UV system an attractive AOP option for treating potable waters. For highly turbid waters and for waters with high concentrations of scaling agents, appropriate pre-treatment may be required to enhance MTBE removal efficiency. As with all AOPs, more pilot- and field-scale demonstration sites under a variety of water quality matrices are needed prior to general regulatory acceptance.
3.5 Emerging Technologies

3.5.1 E-beam Treatment

Process Description

E-beam treatment refers to the use of ionizing radiation from an electron beam source to initiate chemical changes in aqueous contaminants. In contrast to other forms of radiation, such as infrared and UV, ionizing radiation from an E-beam is absorbed almost completely by the target compounds’ electron orbitals, thus increasing the energy level of its orbital electrons. The energy level of radiation is sufficiently high to produce changes in the molecular structure of compounds, but is too low to induce radioactivity (Siddiqui et al., 1996; HVEA, 1999). Electron beam processes use the portion of the electromagnetic spectrum between 0.01 eV and 10 eV (Siddiqui et al., 1996).

Within 10^-16 to 10^-12 seconds, E-beam irradiation of water results in the formation of electronically excited species, including ions and free radicals, along the path of the electrons. The products of direct reactions of water molecules with the electron beam are formed in isolated volumes referred to as “spurs.” As these spurs expand through diffusion, a fraction of the initial products escape into the bulk solution and transfer their energy to other aqueous chemical species, causing more reactions to occur (Nickelsen et al., 1992). After approximately 10^-7 s, oxidizing species, such as hydroxyl radicals, and reducing species, such as aqueous electrons and hydrogen atoms, are formed from the E-beam irradiation of water (Nickelsen et al., 1992; Allen, 1961). The net reaction is shown below:

\[
\text{H}_2\text{O} + \text{e}^{-} \rightarrow 2.7 \cdot \text{OH} + 0.6 \cdot \text{H} + 2.6 \text{e}_{\text{aq}}^{-} + 0.45 \text{H}_2 + 0.7 \text{H}_2\text{O}_2 + 2.6 \text{H}_3\text{O}^+ 
\]

The combination of products that result from this reaction creates a unique environment where oxidizing and reducing reactions occur simultaneously (Allen, 1961). In particular, note that the oxidizing species, \(\cdot \text{OH}\), and the reducing species, \(\text{e}_{\text{aq}}^{-}\), are expected to be present in similar steady-state concentrations. These two species, along with another reducing species, the hydrogen atom (\(\cdot \text{H}\)), are the most reactive products of this reaction and control the rate of the electron beam process for MTBE destruction. The reactions of these species with MTBE are as follows (Cooper and Tornatore, 1999):

\[
\text{MTBE} + \text{e}_{\text{aq}}^{-} \rightarrow (\text{CH}_3)_3\text{C}\cdot + \cdot\text{OCH}_3 \\
\cdot\text{OCH}_3 + \text{H}_2\text{O} \rightarrow \text{HOCH}_3 + \text{OH}^+ \\
\text{MTBE} + \cdot \text{H} \rightarrow \text{Reduction by-products} \\
-\text{H}_2 \\
\cdot \text{OH} + \text{MTBE} \rightarrow \text{Oxidation by-products}
\]
The above-mentioned reactions are summarized in Table 3-3. The aqueous electron reacts with MTBE according to a rate constant of $1.75 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$, while the rate constant for the reaction of MTBE with hydrogen atoms was found to be less than $8.0 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ (Cooper and Tornatore, 1999). The reaction rate of MTBE with hydroxyl radicals is approximately 90 and 20,000 times faster than with aqueous electrons and hydrogen atoms, respectively (Buxton et al., 1988; Cooper and Tornatore, 1999).

**System Description/Design Parameters**

In the E-beam process, a continuous stream of high-energy electrons irradiates contaminated water. The generation of high-energy electrons is accomplished through the use of an electron accelerator in which electrons emitted by a hot cathode (e.g., tungsten filament) are accelerated by means of a voltage differential (Nickelsen et al., 1998). The accelerated electrons are then deflected magnetically by a scanner to produce an E-beam, which scans the water surface with a particular radiation pattern and frequency. Once in the water, the electrons react with water molecules to form reactive intermediates, such as hydroxyl radicals, hydrated electrons, and hydrogen atoms, as discussed above (Cooper, 1999). The shape and frequency of this pattern is controlled to apply a uniform amount of electrons (dose) to the source water stream. A common unit of electron dose is the rad, defined as the energy absorption of 100 ergs per gram of material. The maximum depth of penetration of an E-beam is directly proportional to the energy of the incident electrons and inversely proportional to the density of the falling stream, the beam power, and the length of time the water is exposed to the electron beam. Most E-beam systems for drinking water treatment are designed such that the electron beam infiltrates less than a centimeter into the source water. For example, 1.5 MeV electrons have a depth of penetration of approximately 7 mm in water (Nickelsen et al., 1994).

Currently, there is only one E-beam configuration used to treat drinking water. In this configuration, an E-beam scans in a raster pattern over a thin (approximately 4 mm) sheet of water. This configuration is designed to apply radiation doses up to several thousand krad and scanned at 200 Hz by 60 Hz to cover an area 1.2 m wide by 5 cm deep (Nickelsen et al., 1994). A key piece of equipment for the application of E-beam is the water distribution system. For E-beam to be effective, the source water must be spread over a plate at a sufficiently shallow thickness to allow electrons to penetrate most of the water. If the water thickness is too deep because of higher flow rates or limitations of the distribution system, multiple water passes through the electron beam may be required to meet effluent goals. Because E-beam systems can potentially emit x-rays, the electron accelerator, the beam scanner, and the contact chamber are usually completely surrounded by lead of varying thickness to attenuate any emitted x-rays to less than 0.2 mRem/h (Nickelsen et al., 1998).

The major components of the E-beam system include:

- Electron accelerator with an insulating core transformer
- Power source
- Beam scanner
- Contact chamber (concrete vault)
- Water distribution device
- Supply and discharge pumps and piping
- Resistance temperature devices (RTDs)
- Monitoring and control systems
- Lead shielding

A schematic of the various components of an E-beam system is shown in Figure 3-2.

**Figure 3-2.** A schematic of a high energy electron beam system (drawing provided by Komex H2O Science, 1998).
Advantages and Disadvantages

The advantages and disadvantages of the E-beam system are briefly summarized in Table 3-2. The advantages of the E-beam system are:

- Little potential for inorganic by-product formation (e.g., bromate) due to the large number of radicals produced. Some studies have indicated that E-beam irradiation can actually reduce the concentration of bromate in water (Siddiqui et al., 1996).

- Recent laboratory E-beam studies have demonstrated minimal organic by-product formation compared to other AOPs (Cooper, 1998; Cooper et al., 1999; Tornatore 1999); however, further studies are required to confirm this preliminary finding.

- The E-beam system can supplement the disinfection process, providing additional protection against pathogenic microorganisms (Kurucz et al., 1991).

- Studies have indicated that interference and turbidity have minimal effects on the performance of the E-beam treatment system (Cooper, 1998).

The disadvantages of the E-beam system are:

- There are currently no full-scale drinking water applications of E-beam systems, although there have been many pilot-scale systems over the past several years.

- E-beam relies on irradiation of drinking water, a term synonymous in the public to radiation. Despite the relatively safe nature of this technology, radiation shielding is still required and, thus, there is significant public perception challenges that must be overcome prior to the implementation of E-beam. This is likely the largest disadvantage of E-beam, relative to the other AOPs evaluated in this chapter.

- E-beam systems are energy intensive and may prove to be cost prohibitive.

- The E-beam system requires specially trained skilled operators who are able to work near a radiation source. While not necessarily dangerous, this would likely require increased labor costs.

Pilot/Field Studies and Vendor Information

Over 700 E-beam systems have been implemented in materials applications and food and drug industry disinfection applications worldwide (Tornatore, 1999). There are presently no electron beam processes in continuous drinking water service, but over 200 pilot and demonstration studies have been performed on over 60 different organic contaminants. Some of the targeted contaminants include benzene (Nickelsen et al., 1992; Nickelsen et al., 1994),
phenol, TCE, and PCE (Lin et al., 1995; USEPA, 1998), THMs and THM precursors (Cooper et al., 1996), and MTBE (Cooper et al., 1998). Of the 200 pilot and demonstration studies, more than 10 have been designed to evaluate performance on MTBE, TBA, TBF, and formaldehyde (Tornatore, 1999).

Many of these pilot scale studies have been completed using the mobile E-beam treatment system designed and built by High Voltage Environmental Applications (HVEA). This system can have process flow rates of up to 40 gpm at an applied power of 20 kW (Cooper et al., 1999; HVEA, 1999). HVEA also has a research station, formerly known as EBRF (Electron Beam Research Facility), at the Miami Dade Central District Wastewater Treatment Plant in Miami, Florida (HVEA, 1999). At this (EBRF/HVEA) facility, there is an E-beam reactor designed for large scale research. The E-beam Reactor in Miami Dade is comprised of a horizontal 1.5 MeV insulated-core transformer (ICT) electron accelerator capable of delivering up to 60 mA of beam current (Nickelsen et al., 1994).

Test results from MTBE pilot and demonstration studies have shown the ability of E-beam systems to reduce MTBE concentrations from 1,000 µg/L to less than 5 µg/L (Tornatore, 1999). Tornatore et al. (1999) also conducted large-scale E-beam experiments for MTBE destruction with a flow rate of 100 gallons per minute in a recycle mode. MTBE was reduced to below the detection limit (87 µg/L) after cumulative doses of 665 and 2,000 krads applied to initial MTBE concentrations of 2,300 and 31,000 µg/L, respectively. At the equivalent energy dose, primary reaction intermediates (TBA, TBF) were also treated to low residual concentrations. A dose response curve for TBA and TBF has been developed which suggests that the energy required for removal of these compounds to below detection levels is approximately equal to the energy requirement for MTBE removal. TBA and TBF reactions use reducing chemistry, and, thus, these reactions proceed concurrently with the process of MTBE destruction (Tornatore, 1999).

A series of experiments were performed with the electron beam technology at Orange County Water District (Fountain Valley, CA) to treat MTBE and a variety of other contaminants in a number of different water sources (Cooper et al., 1999). The results indicate that MTBE was readily treated in all experiments, and that treatment efficiency was dependent upon basic water chemistry, delivery system limitations, and the presence of competing organic and inorganic compounds. MTBE removal efficiencies of greater than 99.5 percent, with final concentrations less than 5 µg/L, were reported in several experiments (Cooper et al., 1999). Primary reaction intermediates (TBA, TBF) were reduced concurrently with MTBE, suggesting that the oxidizing and reducing chemistry involved is efficient in treating MTBE and its by-products. Background water quality was shown to have an impact on the treatment efficiency of MTBE and other compounds. Waters lower in TOC and pH demonstrated higher removal efficiencies. Researchers concluded that the application of the electron beam process is best suited for high flow rate, single or multiple constituent treatment scenarios where complete oxidation or mineralization of contaminants is the desired endpoint (Cooper...
et al., 1999). Tables 3-4 and 3-5 present summaries of on-going field studies and vendor information, respectively.

Summary

E-beam systems are used widely in the food and drug industry for disinfection; however, over the past several years, a large number of pilot-scale studies have been completed at drinking water facilities. Due to the nature of the reducing and oxidizing species created in a E-beam reactor, MTBE concentrations can be reduced to well below action levels with minimal to no by-product formation. Despite this fact, the negative public perception resulting from the use of radiation combined with the requirement for skilled operators and the expected high capital and O&M costs for E-beam systems will likely result in their limited application. However, because this technology has been used in the past, there may be some treatment or remediation scenarios where E-beam will be selected because it may provide advantages relative to other treatment options.

3.5.2 Cavitation

Process Description

Cavitation is described as the formation of microbubbles in solution that implode violently after reaching a critical resonance size. These microbubbles can be produced by a number of mechanisms: 1) local increase in water velocity as in eddies or vortices, or over boundary contours; 2) rapid vibration of the boundary through sonication; 3) separation or parting of a liquid column owing to water hammer; or 4) an overall reduction in static pressure. The rapid implosion of cavitation microbubbles results in high temperatures at the bubble/water interface, which can trigger thermal decomposition of the MTBE in solution or thermal dissociation of water molecules to form extremely reactive radicals. The extreme conditions generated during cavitation decomposes water to create both oxidizing (•OH) and reducing (•H) radical species (Skov et al., 1997; Kang and Hoffman, 1998). As in other AOPs, the primary mechanism for MTBE removal by cavitation is through reaction with hydroxyl radicals.

There are three known methods of producing hydroxyl radicals using cavitation — namely, ultrasonic irradiation or sonication, pulse plasma cavitation, and hydrodynamic cavitation. Sonication causes the formation of microbubbles through successive ultrasonic frequency cycles until the bubbles reach a critical resonance frequency size that results in their violent collapse (Mason et al., 1988; Kang and Hoffman, 1998). Pulse plasma cavitation utilizes a high voltage discharge through water to create microbubbles. In hydrodynamic cavitation, microbubbles are generated using high velocity or pressure gradients (Pisani and Beale, 1997; Pisani, 1999a,b).
The production of •OH through cavitation processes can be enhanced with the use of ozone (Table 3-3). Gas-phase ozone thermally decomposes in the microbubbles, yielding oxygen atoms and molecular oxygen. This results in a number of reactions that subsequently yield hydroxyl radicals (Kang and Hoffmann, 1998):

\[
\begin{align*}
O_3 + H_2O & \rightarrow O_2 + 2 \cdot OH \\
O_3 + \cdot OH & \rightarrow HO_2^- + O_2 \\
O_3 + HO_2^- & \rightarrow OH + O_2^- + O_2
\end{align*}
\]

**System Description/Design Parameters**

As discussed above, there are three known methods of producing hydroxyl radicals using cavitation – namely, ultrasonic, hydrodynamic, and pulse plasma cavitation. A noble gas (e.g., krypton or argon) is sometimes used to achieve the optimal bubble production and size. MTBE removal occurs by both thermal decomposition at the bubble-water interface and by reaction with the radicals. The following sections will discuss the two most frequently studied and applied forms of cavitation: sonication and hydrodynamic cavitation.

**Ultrasonic Cavitation/Sonication**

When a liquid is irradiated with ultrasound, the ultrasound waves pass through the medium in a series of alternate compression and expansion cycles. When the acoustic amplitude is large enough to stretch the molecules during its negative pressure (rarefaction) cycle to a distance that is greater than the critical molecular distance to hold the liquid intact, microbubbles are created that then collapse in the subsequent compression cycle, giving rise to extremes of temperature and pressure. Estimates have suggested that temperatures greater than 5,000°C and pressures greater than 1000 atm can be produced locally during the collapse of these vapor bubbles (Pandit and Moholkar, 1996).

The main factors that affect ultrasonic cavitation include: 1) the intensity of the ultrasound field (i.e., the frequency and amplitude of radiation); 2) the physical properties of the water (e.g., viscosity, surface tension, and vapor pressure); 3) the temperature; and 4) the presence of dissolved gas (Martin and Ward, 1993). There are several different kinds of sonication reactors that are currently available for commercial use, namely (Martin and Ward, 1993):

*Ultrasonic Cleaning Bath:* Contaminated water is sonicated in a reactor with either external transducers (hooked to the container walls) or submersible transducer. This reactor is recommended for low-intensity irradiation applications.

*Probe System Reactors:* In these reactors, the small magnitude oscillations of a piezoelectric crystal are amplified by placing it in a metal probe that is, in turn, immersed in the water. These reactors are available in both batch and flow through designs.
**Tube Reactors:** In these reactors, the water flows through pipes that are surrounded by transducers. These reactors are typically employed for large flowrate applications.

The optimization of ultrasonic cavitation can be achieved by adjusting the ultrasonic frequency and saturating gas during sonication (Hua and Hoffman, 1997). Hua and Hoffman (1997) studied the production of hydroxyl radicals at ultrasonic frequencies of 20, 40, 80 and 500 kHz, respectively, in the presence of four different saturating gases (Kr, Ar, He and O₂). The highest rate of •OH production (0.391 uM/min) was observed during the sonication of Kr-saturated solutions at 500 kHz. Sonication of He-saturated solutions at 20 kHz resulted in the lowest rate of •OH production (0.0310 uM/min) (Hua and Hoffmann, 1997).

There are several mechanisms suggested to explain the higher hydroxyl radical production at higher frequencies. First, due to the shorter time allowed for bubble collapse at higher frequencies, there is less time for the hydroxyl radicals to recombine within the bubble and, thus, a higher hydroxyl radical production rate is observed (Petrier et al., 1992). Next, as the frequency increases, the bubbles may not completely collapse, but will rapidly oscillate and, in doing so, create a higher flux of hydroxyl radicals through the surface of the bubble (Hua and Hoffman, 1997). Finally, as an explanation for the apparent hydroxyl radical production rate dependence on inert gas, Hart and Henglein (1986) suggest that higher temperatures can be achieved within the bubbles for higher molecular weight gases. The nature of these arguments demonstrate that there are still many unknowns regarding the specific mechanism(s) for hydroxyl radical generation during sonication.

**Hydrodynamic Cavitation**

Hydrodynamic cavitation can be achieved when pressure at the orifice or any other mechanical constriction falls below the vapor pressure of the liquid, causing the formation of micro-bubbles. Once generated, microbubbles rapidly collapse downstream with a recovery of pressure giving rise to high temperature and pressure pulses. For water flowing through an orifice, a reduction in the cross-section of the flowing stream increases the velocity head at the expense of pressure head. During the re-expansion of flow, the fluid stream separates at the lower end of the orifice and generates eddies. At a particular velocity, the pressure during re-expansion falls below the vapor pressure of the water, causing the generation of micro-bubbles. If there is dissolved gas in the water, then cavitation is observed at pressures significantly above the vapor pressure because of the degassing that occurs at low pressures.

The hydrodynamic cavitation reactor is simple and easy to operate. By changing the ratio of the orifice to the pipe diameter, the discharge pressure, and the pressure recovery rate, one can manipulate the outcome of hydrodynamic cavitation to suit the conditions of individual reactions or physical processes (Chivate and Pandit, 1993). Due to the longer life of the bubble and the higher velocity from which they are swept away from their point of generation, the actual volume of the bulk fluid exposed to cavitation effects is higher for hydrodynamic cavitation. Because bubbles under hydrodynamic cavitation show oscillatory behavior, a large number of smaller magnitude pulses are observed (Pandit and Moholkar, 1996).
The configuration of a hydrodynamic cavitation process is comprised of a centrifugal feed pump and a cavitation reactor that is connected to the effluent pipeline (Pisani and Beale, 1997). Oxidation Systems Incorporated has a proprietary hydrodynamic cavitation reactor called Hydrox™ process. This process facilitates multiple-pass cavitation, using either a recycle line downstream of the cavitation reactor or several cavitation reactors placed in series. When necessary, the cavitation reactor designs can be expanded to include UV treatment modules as well as the addition of hydrogen peroxide by placing these systems either upstream or downstream in line with the cavitation reactor.

A schematic of a cavitation system is shown in Figure 3-3. The major components of a cavitation system include:

- Hydrodynamic/ultrasonic/pulse plasma cavitation generator
- Reactor chamber
- Chemical feed tanks and pumps
- Power source
- Temperature controller
- Supply and discharge pumps and piping
- Monitoring and control systems

![Figure 3-3. A schematic of a cavitation system (HYDROX) with supplemental chemical oxidants (e.g., H₂O₂) (drawing provided by Komex H2O Science, 1998).](image)
Advantages and Disadvantages

See Table 3-2 for a brief summary of the advantages and disadvantages of cavitation AOP processes. The advantages of the cavitation process include:

- The energy usage for cavitation systems is comparable to AOPs using UV lamps (Pisani and Beale, 1997). The only energy costs result from the use of pumps to create pressures of 50 to 100 psi.

- Cavitation systems use no moving parts, besides a feed pump and, thus, require minimal maintenance costs.

The disadvantages of cavitation processes are:

- Supplemental oxidants such as O₃ and H₂O₂ may be required to significantly increase (by a factor of 1.5 to 4) the rate of MTBE removal (Kang and Hoffmann, 1998). The use of these oxidants will raise O&M costs.

- Currently, no full-scale applications exist for this emerging technology.

- Hydrodynamic cavitation is currently a “black box” technology due to the reluctance of the primary vendor to share information regarding the specific operation of the cavitation device. Consequently, this technology is unlikely to be accepted for drinking water applications until all information concerning operation is generally publicized.

Bench-scale Studies

Ultrasonic cavitation assisted by ozone or peroxide addition has been studied for the destruction of a variety of compounds including NOM (Olson and Barbier, 1994), carbon tetrachloride (Hua and Hoffman, 1996), chlorophenols (Serpone et al., 1994), hydrogen sulfide (Kotronarou et al., 1992), and MTBE (Kang and Hoffmann, 1998). Kang and Hoffmann (1998) investigated the kinetics and mechanism of the degradation of MTBE in the presence of ozone at an ultrasonic frequency of 205 kHz and power of 200 Watts/L. The observed first-order degradation rate constant for MTBE increased from 4.1 x 10⁻⁴ s⁻¹ to 8.5 x 10⁻⁴ s⁻¹ as the initial concentration of MTBE decreased from 89 mg/L to 0.8 mg/L. The presence of O₃ at 12 mg/L was found to accelerate the rate of MTBE destruction by a factor of 1.5 to 3.9 depending on the initial concentration of MTBE. Ozone had a larger effect for low initial MTBE concentrations, suggesting that at higher contaminant concentrations, oxidation is limited by mass transfer of the hydroxyl radicals to the contaminant (Kang and Hoffman, 1998). TBF, TBA, methyl acetate, and acetone were found to be the primary by-products and intermediates of MTBE degradation, but were shown to disappear after 60 minutes of reaction.
Pilot/Field Studies and Vendor Information

Ultrasonic cavitation has been well studied at the bench-scale level, but there are no full-scale installations. Pulse plasma cavitation is energy intensive and, hence, has not progressed commercially for organic oxidation applications. However, hydrodynamically induced cavitation has been in full-scale application at approximately 30 installations for removal of polycyclic aromatic hydrocarbons, phenol, glycol, and polyhalogenated hydrocarbons. Oxidation Systems Incorporated (OSI), located in Arcadia, California, commercially supplies hydrodynamically induced (HYDROX) cavitation reactors (Pisani, 1999a,b). OSI has deployed several of their cavitation reactors for groundwater remediation applications. OSI’s full-scale applications have flow rates ranging from 1 to 2,000 gpm (Pisani, 1999b), with the largest single unit capable of handling 2,000 gpm. Larger (>500 gpm) scale HYDROX units were found to perform more efficiently than the smaller (<100 gpm) units (Pisani, 1999b). OSI has just completed Phase-1 field studies for MTBE removal at March Air Force Base, Riverside, California (Pisani, 1999a). This study was conducted for the U.S. Army Corps of Engineers. The flow rates varied from 10 to 30 gpm, with an average influent MTBE concentration of 500 µg/L. At these trials, verified by third parties, greater than 80 percent reduction in MTBE was accomplished (Pisani, 1999a). Tables 3-4 and 3-5 summarize the case study and vendor information, respectively, for the hydrodynamic cavitation process.

Summary

Hydrodynamically induced cavitation appears to be a promising AOP option for organic contaminant removal, including MTBE. However, all applications identified to date for MTBE have required the use of an additional oxidant to achieve MTBE concentrations that meet drinking water standards. Thus, more pilot and field studies will facilitate a better understanding of this AOP’s ability to meet drinking water standards for a reasonable cost. In addition, the largest vendor of hydrodynamic cavitation systems, OSI (Arcadia, CA), currently claims that the reactor chamber is proprietary information (i.e., a “black box” technology). Even if cavitation proves to be technically feasible for removal of MTBE to drinking water limits, it is unlikely that it will be adopted for widespread use in the drinking water industry until the OSI operational system is made generally available. In conclusion, while continued observation of this technology is warranted, further pilot- and field-scale remediation and drinking water applications are needed to prove its economic and technical feasibility.

3.5.3 TiO₂-Catalyzed UV Oxidation (TiO₂/UV)

Process Description

When TiO₂, a solid metal catalyst, is illuminated by UV light (380 nm), valence band electrons are excited to the conduction band and electron vacancies, or holes, are created (Kormann et al., 1991; Crittenden et al., 1996). This combination of excited-state electrons is capable of initiating a wide range of chemical reactions; however, hydroxyl radical
oxidation is the primary mechanism for organic contaminant destruction (Kormann et al., 1991; Crittenden et al., 1996). The production of hydroxyl radicals can occur via several pathways but, as with many of the other AOPs analyzed, is readily formed from hydrogen peroxide.

The production of hydrogen peroxide primarily occurs through the following three reaction mechanisms (Kormann et al., 1988). In the first mechanism, peroxide is created by the reduction of oxygen with two conduction band (CB) electrons. As the concentration of electron acceptors (e.g., oxygen) is increased in solution, the yield of these CB electrons is increased, thereby increasing the yield of hydrogen peroxide (Kormann et al., 1988). The presence of electron acceptors decreases the combination of excited electrons with holes and, thus, increases the formation of hydrogen peroxide or other radicals (Crittenden et al., 1996).

\[ O_2 + 2H^+ + 2e^-_{CB} \rightarrow H_2O_2 \]

Hydrogen peroxide is produced via the second mechanism through the oxidation of water by holes in the valence band (h\textsubscript{VB}). This mechanism is thought to occur only in the absence of electron acceptors and the presence of electron donors (e.g., H\textsubscript{2}O, OH\textsuperscript{-}, and HCO\textsubscript{3}\textsuperscript{-}) (Kormann et al., 1988; Hong et al., 1987; Turchi and Ollis, 1990).

\[ 2H_2O + 2h_{VB}^+ \rightarrow H_2O_2 + 2H^+ \]

Finally, hydrogen peroxide can be produced by secondary reactions between oxidized organic matter. These reactions are thought to be important at high TOC concentrations or after long illumination periods (Kormann et al., 1988).

Once hydrogen peroxide is formed, it can dissociate in the presence of UV radiation to form hydroxyl radicals (see H\textsubscript{2}O\textsubscript{2}/UV discussion) or react with other radicals (e.g., hydroperoxyl or superoxide radical) to form hydroxyl radicals. The hydroperoxyl radical is formed when oxygen is reduced by a CB electron (Prairie et al., 1993; Sjogren, 1995):

\[ O_2 + H^+ + e^-_{CB} \rightarrow HO_2\cdot \]

Deprotonation of the hydroperoxyl radical at neutral pH results in the formation of a superoxide radical (\cdotO\textsubscript{2}\textsuperscript{-}) which, in turn, reacts with hydrogen peroxide (Halliwell and Gutteridge, 1989):

\[ HO_2\cdot \rightarrow H^+ + \cdotO_2\textsuperscript{-} \]

\[ H_2O_2 + \cdotO_2\textsuperscript{-} \rightarrow OH^- + O_2 + \cdotOH \]

Finally, hydroxyl radicals can be formed from the direct reduction of TiO\textsubscript{2}-absorbed H\textsubscript{2}O\textsubscript{2} by a CB electron (Al-Ekabi et al., 1989):
\[ \text{H}_2\text{O}_2 + e_{CB}^- \rightarrow \text{OH}^- + \cdot\text{OH} \]

In addition, hydroxyl radicals can be produced by the reaction of a hole with a hydroxide ion (Hong et al., 1987; Turchi and Ollis, 1990; Sjogren, 1995):

\[ \text{OH}^- + h^+_{VB} \rightarrow \cdot\text{OH} \]

The above reactions are summarized in Table 3-3. Also summarized in this table are the reaction by-products, interfering compounds, and hierarchy of oxidants.

**System Description/Design Parameters**

TiO\(_2\)/UV systems experience interference due to the same radical scavengers that affect the other AOPs; however, TiO\(_2\)/UV systems are also fouled by the presence of anions (e.g., chloride, phosphate, and bicarbonate), cations, and neutral molecules, which compete with the contaminant for reactive sites on the surface of the TiO\(_2\) particles. The effect of cations and anions is strongly pH dependent. The pH of zero charge for TiO\(_2\) is approximately pH 6 (Kormann et al., 1988). Kormann et al. (1991) note that at low pH (pH 3 to 4), reaction rates were significantly retarded due to anion adsorption onto the positively charged TiO\(_2\) surface. At higher pH (pH >7), the TiO\(_2\) particles are negatively charged and there was negligible anion adsorption; however, the presence of cations (e.g., cobalt [II], aluminum [III], and zinc [II]) was shown to decrease the reaction rate (Kormann et al., 1991). As a result of this decreased activity, TiO\(_2\) systems may require ion-exchange pre-treatment to remove both anions and cations (Crittenden et al., 1996).

In a TiO\(_2\)/UV reaction system, catalysts can be either injected or dispersed (i.e., slurry design) into the system or attached to a support medium. For slurry design, rigorous bench- and pilot-scale testing is required for each source water to determine the optimum TiO\(_2\) dose. A low TiO\(_2\) dose can result in a surface site limiting reaction and insufficient radical generation whereas a high TiO\(_2\) dose can reduce the transmittance of the UV light. Kormann et al. (1988) found that a suspension of 500 mg/L TiO\(_2\) allowed the absorption of greater than 95 percent of the UV light at 330 nm. TiO\(_2\) particles can vary in size and shape; however, those particles used by Kormann et al. (1988) are spherical in shape with an average diameter of approximately 30 nm. As the above reactions suggest, bubbling air through the system results in higher dissolved oxygen (DO) concentrations, which yield faster reaction rates (Kormann et al., 1988; Venkatadri and Peters, 1993; Barreto et al., 1995). Significant change (from 6.8 to 4.2) in pH was observed under TiO\(_2\)-catalyzed UV treatment (Barreto et al., 1994).

When TiO\(_2\) is attached to a support substrate (e.g., silica-based material, cobalt [II]-based material, or synthetic resins sorbents [see Chapter 5 for further discussion]), it eliminates the need for a post-treatment separation system, which is required for slurry designs (Hong et al., 1987; Crittenden et al., 1996). In one fixed TiO\(_2\) design, TiO\(_2\) was mixed into a silica gel,
which was subsequently hardened. The silica gel had 9-nm pore sizes with a total surface area of 480 m²/g (Crittenden et al., 1996). The UV light penetrates this porous silica gel to activate the catalyst, which in-turn oxidizes contaminants in the source water as it is run through the TiO₂ impregnated silica gel. The catalytic activity of imbedded TiO₂ is improved by the addition of metals such as silver or platinum to the TiO₂ surface (Venkatadri and Peters, 1993; Crittenden et al., 1996).

Research has shown that destruction of BTEX compounds (2 mg/L) was slow when DO levels were below 3 mg/L and very rapid as DO levels increased to above 15 mg/L (Crittenden et al., 1996).

The major components of a TiO₂/UV system include:

• TiO₂ slurry injection and extraction system (Option 1)
• TiO₂ impregnated resin fluidized bed reactor (Option 2)
• UV lamps, lamp sleeves, and lamp cleaning system
• Static mixing device
• Supply and discharge pumps and piping
• Monitoring and control systems

A schematic of a fluidized bed TiO₂/UV system (Option 1) is shown in Figure 3-4.

Advantages and Disadvantages

The advantages and disadvantages of the UV/TiO₂ system are briefly summarized in Table 3-2. The advantages are:

• TiO₂ assisted photocatalysis can be performed at higher (300 to 380 nm) wavelengths than the other UV oxidation processes (Prairie et al., 1993; Sjogren and Sierka, 1994; Sjogren, 1995).

• The TiO₂ oxidation process has been studied for many organic compounds, including MTBE, under a variety of water qualities.

The disadvantages of the TiO₂ system are:

• Currently, no full-scale applications exist for this emerging technology.

• In attached TiO₂ systems, pre-treatment is required to avoid fouling of the active TiO₂ sites and destructive inhibition of the TiO₂ catalyst (Dewaal, 1999). Significant fouling was observed due to deposition of NOM, inorganic particulates, photoreduced metal cations
and, to a lesser extent, prolonged exposure to UV radiation (Crittenden et al., 1996). Inhibition was observed to occur due to the presence of increased alkalinity and other anionic species (e.g., sulfates [>100 mg/L] and chlorides) (Crittenden et al., 1996).

• If TiO$_2$ is added to the system as a slurry, then a separation step is required to remove the solid TiO$_2$ from the treated water (Barreto, 1995; Sjogren, 1995).

• There is a potential for rapid loss of TiO$_2$ photocatalytic activity, resulting in the need for a large volume of replacement catalyst on-site or a catalytic regeneration process (Crittenden et al., 1996).

• If DO concentrations in the source water are low (e.g., as in some groundwaters) oxygen sparging may be required to increase the rate of contaminant destruction.
• The reaction efficiency is highly dependent on the pH of the system, resulting in the need for close monitoring and control.

**Bench/Pilot/Field Studies and Vendor Information**

Several researchers have studied TiO$_2$ assisted UV oxidation processes for the following applications:

• To destroy a number of organic contaminants at a variety of concentrations (Mathews, 1988; Al-Ekabi et al., 1989; Kormann et al., 1991; Crittenden et al., 1996).

• To remove toxic inorganic species (e.g., cyanide) and heavy metal ions (Peral and Domenech, 1992; Sabate et al., 1992; Prairie et al., 1993).

• To inactivate bacteria (Ireland et al., 1993) and viruses (Sjogren and Sierka, 1994; Sjogren 1995).

Barreto et al. (1995) performed bench-scale studies on MTBE removal in TiO$_2$ slurry systems. At an optimum TiO$_2$ dose of 125 mg/L and 2 hours of oxygen sparging, Barreto et al. (1995) found that 76 percent of the initial MTBE (88 mg/L or 1 mM) was removed in the first 20 minutes (first order rate constant of $1.2 \times 10^{-3}$ s$^{-1}$). After 20 minutes, the rate slowed, requiring nearly 4 hours to remove MTBE below detection levels (pseudo first order reaction rate of $1.3 \times 10^{-4}$ s$^{-1}$) and 8 hours to achieve 95 percent oxidation of by-products such as TBA and TBF (Barreto et al., 1995). In these experiments, there was no measured direct photolysis of MTBE, TBA, or TBF (Barreto et al., 1995).

There are currently no full-scale applications of the UV/TiO$_2$ process for MTBE treatment. Hydroxyl Systems Incorporated (Sidney, British Columbia, Canada), has developed a fluidized bed TiO$_2$ system for commercial use (Harp, 1999). Trojan Technologies (London, Ontario, Canada) also has a UV/TiO$_2$ reactor for full-scale applications. In the Trojan Technologies (London, Ontario) process, the TiO$_2$ is attached to a substrate (Dewaal, 1999). Table 3-5 lists information for vendors of TiO$_2$/UV systems.

**Summary**

TiO$_2$ catalyzed UV oxidation is a process recommended for use in ultra-pure water applications (e.g., semi-conductor industry) and for treating waters with low contaminant concentrations. Although this technology shows promise, it is still in the developmental stages, and additional studies are needed prior to its use in large-scale remediation or drinking water treatment applications. Consequently, this technology will no longer be evaluated in the remainder of this chapter.
3.5.4 Fenton’s Reaction

Process Description

Hydrogen peroxide reacts with iron (II) to form Fenton’s reagent (an unstable iron-oxide complex) that subsequently reacts to form hydroxyl radicals (Fenton, 1894). The net reaction is shown below:

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH}
\]

\[
k = 76 \text{ M}^{-1}\text{s}^{-1} \quad \text{(Walling, 1975)}
\]

This reaction can occur either in homogeneous systems with dissolved ferrous iron or in heterogeneous systems in the presence of complexed iron such as goethite (FeOOH). The by-product, ferric iron, in turn reacts with peroxide or superoxide (O$_2^-$) radical to reproduce ferrous iron as shown below:

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \cdot\text{O}_2^- + 2\text{H}^+
\]

\[
\cdot\text{O}_2^- + \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{O}_2
\]

The above three reactions cycle iron between the ferrous and ferric oxidation states until the H$_2$O$_2$ is fully consumed, producing •OH in the process. As in other AOPs, the destruction of organics (including MTBE) is primarily due to oxidation reactions initiated by the hydroxyl radical. Fenton’s reactions are summarized in Table 3-3. Similar reactions can occur with copper (II) in place of iron (II).

System Description/Design Parameters

The use of Fenton’s chemistry to destroy MTBE in drinking water requires the addition of iron and H$_2$O$_2$ to the source water. The dosages of Fe(II) and H$_2$O$_2$ are determined based on the organic contaminant removals required. The reactor must be configured to provide adequate mixing of Fe(II) and H$_2$O$_2$ in order to optimize hydroxyl radical formation and destruction of MTBE. To keep iron in solution, a very low pH (~2.5) is required. For drinking water applications, an iron removal system is required prior to delivery to the distribution system. A diagram of a system utilizing Fenton’s reaction is shown in Figure 3-5.

The major components include:

• Fe(II) and hydrogen peroxide storage and injection systems
• Completely stirred tank reactor
• pH controllers
• Iron removal system
• Supply and discharge pumps and piping
• Monitoring and control systems

Advantages and Disadvantages

A summary of advantages and disadvantages for Fenton’s Reaction is shown in Table 3-2. The advantages of Fenton’s Reaction are:

• This process requires very little energy compared to other oxidation technologies that utilize O3 or UV.
• This process produces no vapor emissions and, therefore, requires no off-gas treatment or air permits.

The disadvantages are:

• No full-scale applications exist for this emerging technology.
• An iron extraction system is needed to remove residual iron from the treated water, which may increase the costs for the system.

Figure 3-5. A schematic of a system utilizing Fenton’s Reaction (drawing provided by Komex H2O Science, 1998).
A very low pH (<2.5) environment is necessary to keep the iron in solution (Potter and Roth, 1993; Mohanty and Wei, 1993; Huling, 1996). Therefore, pH adjustment before and after treatment will be required. The requisite acid and base injections will increase the O&M costs.

Pilot/Field Studies and Vendor Information

AOPs based on Fenton’s Reaction and its associated reactions have been widely studied. Fenton’s process has been employed to treat contaminants in drinking water and wastewater (Potter and Roth, 1993; Mohanty and Wei, 1993; Venkatadri and Peters, 1993) and to serve as a pretreatment for biologically recalcitrant contaminants (Koyama et al., 1994; Yeh and Novak, 1995; Huling, 1996).

Yeh and Novak (1995) performed some bench-scale studies on MTBE degradation in soil systems. In these studies, the chemical oxidation of MTBE was found to be related to H$_2$O$_2$ concentration, pH, and the presence of ferrous iron, but was found to be independent of the iron concentration (most likely because iron was not limiting). These findings were later confirmed by Chen et al., (1998). The application of Fenton’s reaction for MTBE removal has been well studied in bench-scale systems, but has not yet been implemented in pilot or field studies. Calgon Carbon, Inc. (Markham, Ontario, Canada) has a patented AOP system that employs Fenton’s chemistry. In this process, the contaminant is adsorbed to a proprietary carbon sorbent, which is regenerated by Fenton’s reaction (Huling et al., 1999). In addition, other vendors currently market Fenton’s chemistry for remediation of gasoline components. Refer to Table 3-5 for more information on Calgon Carbon, Inc. (Markham, Ontario, Canada).

Summary

Since Fenton’s reaction is an emerging process, it is highly unlikely that it will be used in full-scale drinking water applications in the near future. For Fenton’s reaction to be applicable for drinking water treatment, the catalyst (iron or copper) must be attached to a solid matrix. Otherwise, costly iron or copper removal must be performed. Catalyst attachment has not yet been done in a commercial application, other than for the use of Fenton’s reaction as a carbon regeneration tool. In addition, pH adjustments and the potential for increased iron concentrations in the finished water suggest that this technology is currently not viable for drinking water treatment. In conclusion, while continued observation of this technology is warranted in a remediation context, it is not recommended for drinking water treatment.
3.6 Comparative Discussions of AOPS

3.6.1 Permitting

As with all drinking water treatment systems, the installation and operation of an AOP system will require multiple state and local construction permits; water, wastewater, and air discharge permits; and/or operational permits. A detailed discussion of all necessary permits is beyond the scope of this document; however, the key permitting issue that differentiates AOPs from other drinking water treatment technologies is the formation of oxidation by-products. Several of the oxidation by-products of MTBE are potential human carcinogens (e.g., formaldehyde and acetaldehyde). In addition, as mentioned previously, the combination of AOPs with pre- or post-chlorination may increase the formation of THMs or HAA₉s, which are regulated under the Stage 1 D/DBP Rule. Consequently, whether the regulated compounds are THMs, HAA₉s, or an oxidation breakdown product of MTBE, strict monitoring requirements will likely be enforced by the governing regulatory agency to ensure that treated water quality does not contain any of these organic secondary contaminants above drinking water standards. To mitigate these concerns, a GAC filter will likely be required to polish the effluent from AOPs. However, complicating this mitigation measure, it is likely that most polishing filters will sustain biological growth (due to the biodegradability of oxidation by-products). Biological processes for drinking water treatment are only now becoming accepted and, thus, the use of a biologically activated filter as a polishing step for an AOP will be under close regulatory scrutiny. In summary, control of AOP by-products will require further technical and regulatory study.

Other relevant permitting considerations for AOPs include meeting the following standards:

- A 1-hour ozone effluent gas concentration of less than 0.12 ppmv according to the Clean Air Act (Code of Federal Regulations Title 40, Part 50) and less than 0.09 ppmv according to the California Code of Regulations Title 17, Section 70200 (H₂O₂/O₃, O₃/UV).

- H₂O₂ concentrations below 1 mg/L (1.4 mg/m³) according to an OSHA permissible exposure limit (PEL) (NIOSH, 1997).

- Iron concentrations below 0.3 mg/L according to the SDWA Secondary MCL (Fenton’s reaction).

- pH level between 6.6 and 8.5 according to SDWA Secondary MCL (all AOPs).

- THMs below 80 µg/L according to Stage 1 D/DBP Rule (all AOPs).

- HAA₉ below 60 µg/L according to Stage 1 D/DBP Rule (all AOPs).

- Bromate below 10 µg/L according to Stage 1 D/DBP Rule (H₂O₂/O₃, O₃/UV).
3.6.2 Flow Rate

Most of the AOP reactors that are discussed in the earlier sections are available from the manufacturers for treating waters at some pre-design flows (e.g., 100 gpm or 1,000 gpm). Typical ranges of AOP reactor capacities are shown in Table 3-7. Smaller or larger AOP reactors can be custom built. Most AOPs are modular processes; hence, more than one reactor can be employed in series (to obtain higher retention times) or parallel (to process larger volumes) mode to achieve the desired effluent goals for a given flow rate.

Table 3-7
Range of AOP Reactor Capacities and MTBE Removal Efficiencies

<table>
<thead>
<tr>
<th>Technology</th>
<th>Range of Reactor Capacities</th>
<th>Reported MTBE Removal Efficiencies</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$_2$/O$_3$</td>
<td>• 1 to 100 gpm, small portable site remediation HiPOx systems (Waters, 1999)</td>
<td>• up to 80% (Liang et al., 1999a)</td>
</tr>
<tr>
<td></td>
<td>• 500 to 3000 gpm, potable and large remediation HiPOx systems (Waters, 1999)</td>
<td>• &gt;99% (Table 3-5, APT and Hydroxyl Systems Case Studies)</td>
</tr>
<tr>
<td></td>
<td>• Parallel HiPOx modules (&gt; 3000 gpm)</td>
<td></td>
</tr>
<tr>
<td>O$_3$/UV</td>
<td>• 5 to 1200 gpm, Ultrox System (Himebaugh, 1999)</td>
<td>• No published removal efficiencies for drinking water systems.</td>
</tr>
<tr>
<td></td>
<td>• Rayox-O Process – custom-built for desired capacity (Cater, 1999)</td>
<td></td>
</tr>
<tr>
<td>H$_2$O$_2$/UV</td>
<td>• Single UV Lamp Reactor: 50-700 gpm (Crawford, 1999)</td>
<td>• 80 – 95% (Wagler and Malley, 1994)</td>
</tr>
<tr>
<td></td>
<td>• Up to 3000 gpm, Rayox Tower System (Crawford, 1999)</td>
<td>• &gt; 99% (Table 3-5, Charnock Well Field Case Study)</td>
</tr>
<tr>
<td></td>
<td>• 5 to 1200 gpm, Ultrox System (Himebaugh, 1999)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Riptide™ Pulsed UV Reactors: 8-350 gpm (Bender, 1999)</td>
<td></td>
</tr>
<tr>
<td>E-beam</td>
<td>• 40 to 100 gpm, mobile unit (Tornatore, 1999)</td>
<td>• &gt;80% (Cooper, 1998)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• 60 – 99% (Cooper et al., 1999)</td>
</tr>
<tr>
<td>Hydrodynamic Cavitation</td>
<td>• 100 to 2000 gpm, Hydrox System (Pisani, 1999)</td>
<td>• &gt;80% (Pisani, 1999)</td>
</tr>
<tr>
<td>TiO$_2$-Catalyzed UV Oxidation</td>
<td>• Custom-built units</td>
<td>• 76 – 95% (Barreto et al., 1995)</td>
</tr>
<tr>
<td>Fenton's Reaction</td>
<td>• Custom-built units</td>
<td>No published removal efficiencies for drinking water systems.</td>
</tr>
</tbody>
</table>
3.6.3 Removal Efficiency

Table 3-7 summarizes the reported MTBE removal efficiencies from field and pilot studies. Clearly, removal efficiencies will be a function of operating parameters (e.g., reactor residence time) and water quality parameters (e.g., alkalinity, NOM content). Table 3-7 presents some comparative removal efficiencies reported in the literature for the various processes. In general, higher MTBE removal can be obtained under longer retention times and greater chemical dosages. Refer to sections 3.4 and 3.5 for a more detailed discussion of removal efficiencies that have been observed.

3.6.4 Other Factors

A comparative discussion of each of the AOP technologies relative to their applicability and effectiveness is presented below. Specifically, the AOP technologies are compared with respect to their reliability, flexibility, adaptability, potential for modifications and other related relevant factors.

Reliability

Reliability of AOP technologies can be addressed under two broad categories — namely, process reliability and mechanical reliability. Technologies with fewer moving or replaceable parts are considered to be more mechanically reliable because they will likely require less frequent maintenance. Consequently, the H₂O₂/O₃ process receives the highest rating for mechanically reliability. In the H₂O₂/O₃ process, periodic checking and cleaning of the ozone generator and ozone gas diffusers is required (Cater, 1999). Fouling of spargers from precipitation of carbonates has been observed at potable water ozonation (disinfection) facilities (Cater, 1999). Sparger fouling can lead to inefficient ozone transfer. Hydrodynamic cavitation contains no moving parts, besides a pump. However, this technology is still a “black box” and, thus, requires vendor support if problems arise, resulting in a medium rating for mechanical reliability. The UV-based AOP technologies such as O₃/UV and H₂O₂/UV receive a medium rating for mechanical reliability since they require periodic replacement and inspection of UV lamps and quartz sleeves to prevent leakage and scaling. Similarly, E-beam has a large number of specialty parts and equipment requiring experts for maintenance and possible replacement and, thus, receives a low score for mechanical reliability. TiO₂/UV and Fenton’s process also receive a low rating for mechanical reliability due to the required addition of TiO₂ or iron to the reactor. These technologies require significant operational and maintenance oversight in addition to continuous attention to mixing and pH controls.

Process reliability for the various AOP technologies, defined as the ability of a given technology to consistently meet effluent goals, varies widely. Established technologies, including H₂O₂/O₃, O₃/UV, and H₂O₂/UV, have been proven to consistently meet low effluent goals and are, thus, considered highly reliable. Currently, the lack of large-scale potable water treatment
applications for E-beam credits it with a medium rating; however, an optimized E-beam system should be able to consistently remove MTBE to below effluent goals. Other emerging technologies, such as cavitation, Fenton’s reaction, and UV-catalyzed TiO₂, receive the lowest rating for process reliability due to their untested nature in drinking water applications and the secondary chemicals used for treatment that subsequently require removal (e.g., precipitated iron, TiO₂ slurry). For all AOP technologies, including those with high reliability ratings, monitoring and controls are recommended to optimize the treatment process.

**Flexibility**

Flexibility is defined as the ability of a technology to handle wide fluctuations in the influent water flow rate following design and installation. Occasionally, during the operation of a treatment process, the influent stream flows increase or decrease significantly compared to the design flow. A flexible technology should be able to handle these fluctuations with no major impact on the treatment process outcome. When designed with sufficient safety factors, established AOPs (H₂O₂/O₃, O₃/UV, and H₂O₂/UV) can handle a large turndown ratio (i.e., ratio of maximum to minimum allowable flow rates). In addition, chemical additions or UV dose can be changed to respond to changing flow rates. These technologies receive a high rating. Hydrodynamic cavitation is known to perform better at higher (2000 gpm) flow rates compared to smaller (100 gpm) flow rates, and, thus, performance is expected to decrease if flow rates fall, suggesting a low rating. E-beam may require significant changes to its stream distribution or spreading system when the water flow rates increase, again suggesting a low rating. Finally, UV/TiO₂ and Fenton’s reactions are likely performed in semi-batch reactors that can handle changes in flow rates, suggesting a medium rating; however, there is still significant uncertainty related to the design of these reactor systems. Flexible technologies, when necessary, can also be scaled up with little or no difficulty. The capacities of the modular AOP technologies, such as O₃/H₂O₂, O₃/UV, H₂O₂/UV, UV/TiO₂, Fenton’s reaction, and hydrodynamic cavitation, can be expanded by adding additional reactors either in series (to extend the reaction time) or in parallel (to increase flow rates).

**Adaptability**

In this report, adaptability of a technology is defined as its ability to handle fluctuations in water quality conditions, such as influent contaminant concentrations, hardness, alkalinity, and turbidity. All the AOP technologies discussed previously can achieve MTBE removal efficiencies that are independent of the influent MTBE concentration, but that vary widely with water quality conditions. If influent MTBE concentrations increase while effluent goals remain unchanged, it will be necessary to increase the contact time or oxidant doses in the reaction chamber to meet effluent goals. Since oxidation via hydroxyl radicals is the predominant mechanism for MTBE removal for each of the AOPs discussed above, the presence of radical scavengers will affect treatment
performance, independent of the selected AOP. However, those technologies that generate a larger number of hydroxyl radicals more rapidly will be less affected by the presence of radical scavengers. Thus, hydrodynamic cavitation, TiO$_2$/UV, and E-beam, which rapidly generate a large number of hydroxyl radicals due to the multiple oxidizing and reducing species introduced, receive a high rating. Alternatively, the removal efficiency of UV-based technologies, such as O$_3$/UV, H$_2$O$_2$/UV, and TiO$_2$/UV, is hindered by water quality parameters other than radical scavengers (e.g., excess turbidity [which masks the penetration of the UV light], the presence of nitrate [which absorbs effective UV radiation], and iron and other fouling agents [which scale the quartz sleeves]). Thus, O$_3$/UV and H$_2$O$_2$/UV receive a low rating and TiO$_2$/UV is reduced to medium rating. Finally, the effectiveness of H$_2$O$_2$/O$_3$ and O$_3$/UV can be reduced by the presence of excess particulate matter or scaling parameters that foul the ozone gas diffusers — these technologies, in addition to Fenton’s reaction, receive a medium rating. The removal efficiency of each AOP technology is strongly dependent on the characteristics of the influent water quality. Hence, in the design of AOP systems, due consideration must be given to the concentrations (and expected fluctuations) of radical scavengers and other interfering compounds.

### Potential for Modifications

The potential for modifications is defined as the ability to alter the installed system — including the addition of any necessary pre- and post-treatments processes — to accommodate changes in the design criteria and conditions (e.g., lowered target concentrations of MTBE, removal of high alkalinities or iron, by-products polishing). For example, most AOPs that treat source waters with medium to high (>100 mg/L) alkalinities may require pretreatment for alkalinities removal, which may include a pH adjustment step followed by CO$_2$ stripping. Most modular processes (e.g., H$_2$O$_2$/O$_3$, O$_3$/UV, H$_2$O$_2$/UV, hydrodynamic cavitation, TiO$_2$/UV, and Fenton’s reaction) are more easily amenable to changes compared to non-modular processes (e.g., E-beam). Also, in modular processes, several modular units in parallel or series can supply additional contact time.

When necessary, all of the AOP technologies evaluated can be supplemented with pre- and post-treatment systems. However, for some AOPs, these pre- or post-treatment systems are mandatory prior to drinking water distribution and, thus, these AOPs will receive a lower rating. For example, Fenton’s reaction and TiO$_2$/UV require post-treatment for removal of iron and TiO$_2$ from drinking water, resulting in a low rating. TiO$_2$/UV systems also require pretreatment for removal of metal ions and addition of DO. For waters with high bromide concentrations (>100 µg/L), control of bromate formation will be necessary in ozone-based AOP systems (e.g., H$_2$O$_2$/O$_3$ and O$_3$/UV), although this effect can be mitigated without pretreating, as mentioned previously. In addition, ozone-based processes require ozone off-gas treatment, resulting in a low rating. H$_2$O$_2$/UV processes may require a post-treatment temperature adjustment for small systems or pre-treatment to remove turbidity, nitrates, or scaling agents; however, these pre- and post-treatments are not always necessary, suggesting a medium rating. Similarly, hydrodynamic cavitation will likely require the use of additional
oxidants, such as ozone or hydrogen peroxide, to effect MTBE removal, suggesting a medium rating. E-beam requires no pre- or post-treatment processes, resulting in a high rating.

Other Design and Implementation Factors

In addition to reliability, flexibility, adaptability, and potential for modifications, there are other factors that could favor a specific AOP technology. Table 3-8 presents a comparison of AOP technologies with respect to other essential decision driving factors, including bromate formation potential, energy usage, costs, public acceptability, and ease of implementation.

**Bromate Regulatory Compliance.** Bromate is classified by the International Agency for Research on Cancer (IARC) as a possible human carcinogen and is strictly regulated under the Stage 1 D/DBP Rule with a maximum contaminant level of 10 µg/L. This MCL may become more stringent in future rulemaking. Thus, AOPs that generate bromate (O$_3$-based processes) receive a lower rating than alternatives; however, as discussed previously, bromate formation can be mitigated by varying chemical doses for the H$_2$O$_2$/O$_3$ process.

**Energy Efficiency.** Energy usage is rated low for systems that use a combination of O$_3$ and UV light and is rated medium for AOPs that are based on either O$_3$ or UV alone or in combination with other oxidants. Fenton’s reaction does not require electrical energy beyond the feed pumps, resulting in a high energy efficiency rating. The energy requirements for cavitation processes are stated to be comparable to those of the UV systems, suggesting a medium rating. E-beam requires significant energy for operation, resulting in a low rating.

**Public Acceptability.** Systems that are widely used in remediation and drinking water treatment applications are rated as highly acceptable to the public whereas emerging AOPs with little or no field applications are classed as medium acceptability. E-beam is given a low rating for public acceptability due to its reliance on a radiation source for contaminant removal, which has received significant public criticism for use in the food industry. Fenton’s reaction and TiO$_2$/UV are also rated low due to the required addition of inorganic materials (i.e., iron and TiO$_2$) to the water. Finally, cavitation is given a low rating due to the industry’s reluctance to install “black box” technologies for drinking water applications.

**Ease of Implementation.** The number of field installations was used as a surrogate to determine the ease of implementation. Accordingly, the AOPs that use some combination of O$_3$, UV, and H$_2$O$_2$ were rated high for ease of implementation whereas emerging AOPs such as Fenton’s reaction and TiO$_2$/UV with no field applications were given a low grade. E-beam and cavitation were given a medium rating due to the presence of a limited number of field- and pilot-scale treatment systems.
## Table 3-8
Comparative Analysis of Various AOPs

<table>
<thead>
<tr>
<th>AOP TECH.</th>
<th>H$_2$O$_2$/O$_3$</th>
<th>O$_3$/UV</th>
<th>H$_2$O$_2$/UV</th>
<th>E-beam</th>
<th>Hydrodynamic Cavitation</th>
<th>TiO$_2$ - Catalyzed UV</th>
<th>Oxidation</th>
<th>Fenton’s Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reliability</td>
<td>High</td>
<td>Medium</td>
<td>Medium</td>
<td>Low</td>
<td>Low</td>
<td>Medium</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Flexibility</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Adaptability</td>
<td>High</td>
<td>Medium</td>
<td>Medium</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Potential for Modifications</td>
<td>Low</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
<td>High</td>
<td>Medium</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Energy Efficiency</td>
<td>Medium</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Bromate Regulatory Compliances</td>
<td>Low</td>
<td>Low</td>
<td>Medium</td>
<td>Low</td>
<td>Low</td>
<td>Medium</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Public Acceptance</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Ease of Implementation</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>Medium</td>
<td>Medium</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
</tr>
</tbody>
</table>
3.7 Cost Evaluation

Cost estimates were developed to allow direct comparison among the various AOPs and for comparison with the costs developed for air stripping (Chapter 2), GAC (Chapter 4), and synthetic resin sorbents (Chapter 5). The costs for AOPs are highly dependent on the quality of the source water to be treated and effluent treatment goals. The cost comparison developed in this report should be used as a guideline. An understanding of actual costs will require pilot testing to determine site specific costs. As discussed in the previous section, cost is only one factor in the selection of an AOP, and other considerations may result in selection of an AOP that is not the most cost effective. In addition to those factors listed in Section 3.6, one should consider treatment plant location, duration of treatment required, environmental concerns, community impacts, and other considerations identified through the preparation of an initial study in compliance with the National Environmental Permitting Act (NEPA) or the California Environmental Quality Act (CEQA).

3.7.1 Overall Costs of AOP Systems

In order to compare the costs of the various AOPs, AOP equipment vendors were provided with a number of treatment scenarios and asked to provide costs for equipment, chemical dosages, electricity, and replacement parts. Four vendors provided detailed information to assist in this cost evaluation.

1. Calgon Carbon Corporation (Calgon) \( \text{H}_2\text{O}_2/\text{MP-UV system} \)
2. Applied Process Technology, Inc. (APT) \( \text{H}_2\text{O}_2/\text{O}_3 \) system
3. Oxidation Systems, Inc. (OSI) Hydrodynamic cavitation with \( \text{H}_2\text{O}_2 \)
4. Hydroxyl Systems, Inc. (HSI) \( \text{TiO}_2\text{-catalyzed/H}_2\text{O}_2 \)

Other vendors, including Magnum Water Technologies (\( \text{H}_2\text{O}_2/\text{MP-UV} \)) and Calgon Carbon Corporation (Fenton’s Reaction), also participated; however, these costs could not be verified with sufficiently detailed information or field data. Consequently, these costs are not included in this evaluation. In addition, Haley and Aldrich (E-beam system) provided cost estimates that suggest that E-beam may be cost-competitive with other AOPs. These costs were not included due their high degree of uncertainty resulting from the emerging nature of this technology for drinking water applications.

The cost evaluation consisted of several treatment scenarios to evaluate a typical range of drinking water well production rates, MTBE influent concentrations, and effluent treatment goals.

- Influent flows of 60, 600, and 6,000 gpm.
- Influent MTBE concentrations of 20, 200, and 2,000 µg/L.
- Effluent MTBE discharge requirements of 20, 5, and 0.5 µg/L.
The vendors were provided with the following influent water characteristics:

- Hardness: 200 mg/L as CaCO₃
- Alkalinity: 250 mg/L as CaCO₃
- Bromide: ND
- Iron: <1 mg/L
- pH: 7.0
- Temperature: 65°F
- TDS: 500 mg/L
- Nitrate: 25 mg/L as NO₃ or 5 mg/L as N

One important issue in comparing AOPs is the formation and control of oxidation by-products. Most of the vendors did not adequately identify or estimate the formation of by-products, such as acetone, methyl acetate, formaldehyde, acetic acid, formic acid, pyruvic acid, oxalic acid, H₂O₂, TBA, and TBF. Therefore, to facilitate the comparison of these AOPs with other drinking water treatment technologies, supplemental costs for biologically activated carbon polishing were developed for each AOP for removal of oxidation by-products. Capital costs for this system are based on a Calgon GAC system using Filtrasorb 600 carbon. Operational costs were estimated to be similar to those identified in Chapter 4. Carbon replacement costs were estimated, but are difficult to predict due to the biological nature of this polishing process. Water quality may dictate some carbon changeouts, based on adsorption of contaminants onto the carbon. Relevant assumptions and costs for these polishing systems are included in Table 3-9.

Table 3-10 provides a sample calculation of total capital costs, summary of annual costs, total annual costs, and unit treatment costs. As this table indicates, the capital costs provided by the vendors were used as the bases for estimating the complete installed system costs. Piping, valves, and electrical work was estimated at 30 percent of the system equipment costs. Site work was estimated at 10 percent of equipment costs, engineering was estimated at 15 percent of equipment costs, and contractor O&P was estimated at 15 percent of equipment costs. A contingency of 20 percent of the total costs was then added.

Table 3-11 presents a summary of the capital costs for the four AOP technologies evaluated under the scenarios identified. The capital costs include the complete treatment system and installation.

Table 3-12 presents a summary of the annual O&M costs for the four AOP technologies evaluated under the same scenarios described above. The O&M costs consist of replacement parts, labor costs, analytical costs, chemical costs, and electrical costs. The replacement part costs are based on vendor estimates and include replacement parts, such as UV lamps, and spare parts. Some of the vendors have estimated the replacement costs based on a percentage
of the capital cost of the equipment. The labor costs include labor for sampling of water, system operation and general maintenance for the specific type of AOP. The maintenance and sampling labor rate used was $80/hr. Analytical costs are based on weekly sampling of the influent and the effluent from each reactor and are estimated at $200 per sample. Chemical costs include H$_2$O$_2$, O$_3$, and TiO$_2$ as they apply to the technology and were provided by the vendor (both dosage and costs). The electrical costs were based on power consumption and was estimated by the vendors based on $0.08/kWh.

Details of the O&M costs are included in tables in Appendix 3A. Replacement part costs are presented in Table 3A-1, labor costs in Table 3A-2, analytical costs in Table 3A-3, chemical costs in Table 3A-4, and electrical costs in Table 3A-5. Labor costs are further broken down by technology and are presented in Tables 3A-6 to Tables 3A-9 in Appendix 3. Note that these costs do not include the polishing treatment required for removal of oxidation by-products.

Amortized annual capital costs and annual O&M costs were combined to determine the total amortized operating costs for each system per 1,000 gallons of treated water as presented in Table 3-13. The equipment was amortized at a discount rate of seven percent over a 30-year period.
### Table 3-9
Cost of Hydrogen Peroxide Removal and Oxidation By-product Removal

#### H₂O₂ Treatment Systems (Centaur Carbon)

<table>
<thead>
<tr>
<th>Flow Rate Gallons Per Minute</th>
<th>Capital Costs $</th>
<th>Annual O&amp; M Costs $</th>
<th>Total Amortized Operating Costs $/1,000 Gallons</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>18,000</td>
<td>39,000</td>
<td>1.27</td>
</tr>
<tr>
<td>600</td>
<td>89,000</td>
<td>44,000</td>
<td>0.60</td>
</tr>
<tr>
<td>6,000</td>
<td>667,000</td>
<td>194,000</td>
<td>0.10</td>
</tr>
</tbody>
</table>

**Notes:**
- 60 gpm system consists of one 500 pound GAC vessel.
- 600 gpm system consists of one 5,000 pound GAC vessel.
- 6,000 gpm system consists of ten 5,000 pound GAC vessels.

**O & M Costs Include:**
- Carbon replacement
- Analytical sampling
- Oversight during changeouts
- General system O & M

**Capital Costs include:**
- Equipment (Costs provided by vendor)
- Piping, valves, electrical (30%)
- Site work (10%)
- Contractor O & P (15%)
- Engineering (15%)
- Contingency (20%)

#### Treatment for TBA, TBF, Acetone, & other By-products (Bio-GAC)

<table>
<thead>
<tr>
<th>Flow Rate Gallons Per Minute</th>
<th>Capital Costs $</th>
<th>Annual O&amp; M Costs $</th>
<th>Total Amortized Operating Costs $/1,000 Gallons</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>16,700</td>
<td>42,200</td>
<td>1.38</td>
</tr>
<tr>
<td>600</td>
<td>67,800</td>
<td>42,700</td>
<td>0.15</td>
</tr>
<tr>
<td>6,000</td>
<td>667,000</td>
<td>204,800</td>
<td>0.08</td>
</tr>
</tbody>
</table>

**Notes:**
- 60 gpm system consists of one 1,000 pound GAC vessel.
- 600 gpm system consists of one 10,000 pound GAC vessel.
- 6,000 gpm system consists of five 20,000 pound GAC vessels.

**O & M Costs Include:**
- Carbon replacement
- Analytical sampling
- Oversight during changeouts
- General system O & M

**Capital Costs include:**
- Equipment (Costs provided by vendor)
- Piping, valves, electrical (30%)
- Site work (10%)
- Contractor O & P (15%)
- Engineering (15%)
- Contingency (20%)
Table 3-10
Costs of H\textsubscript{2}O\textsubscript{2}/O\textsubscript{3} System for MTBE Removal (Applied Process Technology, Inc.)

<table>
<thead>
<tr>
<th>ITEM</th>
<th>COST</th>
</tr>
</thead>
<tbody>
<tr>
<td>Advanced Oxidation Unit (^1)</td>
<td>$750,000</td>
</tr>
<tr>
<td>Piping, Valves, Electrical (30%)</td>
<td>$225,000</td>
</tr>
<tr>
<td>Site Work (10%)</td>
<td>$75,000</td>
</tr>
<tr>
<td>SUBTOTAL</td>
<td>$1,050,000</td>
</tr>
<tr>
<td>Contractor O&amp;P (15%)</td>
<td>$157,500</td>
</tr>
<tr>
<td>SUBTOTAL</td>
<td>$1,207,500</td>
</tr>
<tr>
<td>Engineering (15%)</td>
<td>$181,125</td>
</tr>
<tr>
<td>SUBTOTAL</td>
<td>$1,388,625</td>
</tr>
<tr>
<td>Contingency (20%)</td>
<td>$277,725</td>
</tr>
<tr>
<td>TOTAL CAPITAL</td>
<td>$1,666,400</td>
</tr>
</tbody>
</table>

AMORTIZED CAPITAL\(^{1A}\) $134,290

ANNUAL O&M $129,692

TOTAL ANNUAL COST $263,981

TOTAL COST PER 1,000 GALLONS TREATED $0.84

Summary of Annual O&M Costs

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>Quantity</th>
<th>Unit Cost</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Replacement Parts (^2)</td>
<td>Lump sum</td>
<td>1</td>
<td>$11,250</td>
<td>$11,250</td>
</tr>
<tr>
<td>Labor (^3)</td>
<td>Hour</td>
<td>724</td>
<td>$80</td>
<td>$57,920</td>
</tr>
<tr>
<td>Analytical costs (^4)</td>
<td>Sample</td>
<td>208</td>
<td>$200</td>
<td>$41,600</td>
</tr>
<tr>
<td>Chemical costs (^5)</td>
<td>$/1000 gal</td>
<td>315360</td>
<td>$0.03</td>
<td>$9,461</td>
</tr>
<tr>
<td>Power ($0.08/kWh) (^6)</td>
<td>kWh</td>
<td>118263</td>
<td>$0.08</td>
<td>$9,461</td>
</tr>
</tbody>
</table>

ANNUAL O&M $129,692

System Parameters: 600 gpm
200 µg/L influent MTBE concentration
20 µg/L effluent MTBE concentration

\(^1\) Cost of oxidation unit from vendor.
\(^{1A}\) Amortization based on 30 year period at 7% discount rate.
\(^2\) Replacement is based on vendor’s estimate of 1.5% capital cost.
\(^3\) Breakdowns of labor costs are given in Tables 3A-6 to 3A-9 in Appendix 3, based on a rate of $80/hr.
\(^4\) Sampling conducted weekly at 4 locations.
\(^5\) Chemical costs based on dosages and prices estimated by vendor.
\(^6\) Power is based on consumption estimates provided by vendor, priced at $0.08/kWh.
<table>
<thead>
<tr>
<th>Flow (gpm)</th>
<th>Influent (mg/L)</th>
<th>Effluent (mg/L)</th>
<th>Removal Efficiency (%)</th>
<th>Capital Costs of AOPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>20</td>
<td>0.5</td>
<td>97.50</td>
<td>$444,400</td>
</tr>
<tr>
<td>60</td>
<td>20</td>
<td>5</td>
<td>97.50</td>
<td>$444,400</td>
</tr>
<tr>
<td>60</td>
<td>20</td>
<td>0.5</td>
<td>97.50</td>
<td>$444,400</td>
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<td>60</td>
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<td>0.5</td>
<td>97.50</td>
<td>$444,400</td>
</tr>
<tr>
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<td>20</td>
<td>0.5</td>
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<td>$444,400</td>
</tr>
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<td>20</td>
<td>0.5</td>
<td>97.50</td>
<td>$444,400</td>
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<td>20</td>
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<td>20</td>
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<tr>
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<td>97.50</td>
<td>$444,400</td>
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<td>5</td>
<td>97.50</td>
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<td>60</td>
<td>20</td>
<td>5</td>
<td>97.50</td>
<td>$444,400</td>
</tr>
</tbody>
</table>

Capital Costs include:
- Equipment Costs (provided by vendor)
- Piping, valves, electrical (30%)
- Site work (10%)
- Contractor O&P (15%)
- Engineering (15%)
- Contingency (20%)

Costs exclude polishing treatment. Refer to Table 3-9 for additional treatment costs.
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>20</td>
<td>20</td>
<td>75.00%</td>
<td>$47,162</td>
<td>$48,800</td>
<td>$42,900</td>
<td>$63,700</td>
</tr>
<tr>
<td>2000</td>
<td>20</td>
<td>20</td>
<td>97.50%</td>
<td>$47,162</td>
<td>$48,800</td>
<td>$42,900</td>
<td>$63,700</td>
</tr>
<tr>
<td>6000</td>
<td>20</td>
<td>20</td>
<td>97.50%</td>
<td>$47,162</td>
<td>$48,800</td>
<td>$42,900</td>
<td>$63,700</td>
</tr>
</tbody>
</table>

**Table 3-12**

**Annual O&M Costs of AOPs**

O&M Costs include:
- Replacement Parts (Based on vendor's estimate).
- Labor costs at $80/hr.
- Analytical costs for sampling conducted weekly at $200 per sample.
- Chemical costs based on dose and price estimated by vendor.
- Power based on consumption estimates provided by vendor, priced at $0.08/kWh.

Costs exclude polishing treatment. Refer to Table 3-9 for additional treatment costs.
<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>20</td>
<td>5</td>
<td>75.00%</td>
<td>$ 2.18</td>
<td>$ 2.63</td>
<td>$ 2.25</td>
<td>$ 3.08</td>
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<td>60</td>
<td>20</td>
<td>0.5</td>
<td>97.50%</td>
<td>$ 2.50</td>
<td>$ 2.68</td>
<td>$ 2.61</td>
<td>$ 3.58</td>
</tr>
<tr>
<td>60</td>
<td>200</td>
<td>20</td>
<td>90.00%</td>
<td>$ 2.32</td>
<td>$ 2.65</td>
<td>$ 2.32</td>
<td>$ 3.60</td>
</tr>
<tr>
<td>60</td>
<td>200</td>
<td>5</td>
<td>97.50%</td>
<td>$ 2.50</td>
<td>$ 2.68</td>
<td>$ 2.61</td>
<td>$ 3.67</td>
</tr>
<tr>
<td>60</td>
<td>200</td>
<td>0.5</td>
<td>99.75%</td>
<td>$ 2.72</td>
<td>$ 2.98</td>
<td>$ 2.77</td>
<td>$ 4.36</td>
</tr>
<tr>
<td>60</td>
<td>2000</td>
<td>20</td>
<td>99.00%</td>
<td>$ 3.07</td>
<td>$ 3.29</td>
<td>$ 2.94</td>
<td>$ 4.67</td>
</tr>
<tr>
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<td>2000</td>
<td>5</td>
<td>99.75%</td>
<td>$ 3.47</td>
<td>$ 3.31</td>
<td>$ 3.03</td>
<td>$ 4.36</td>
</tr>
<tr>
<td>60</td>
<td>2000</td>
<td>0.5</td>
<td>99.98%</td>
<td>$ 4.11</td>
<td>$ 3.62</td>
<td>$ 3.05</td>
<td>$ 5.17</td>
</tr>
<tr>
<td>600</td>
<td>20</td>
<td>5</td>
<td>75.00%</td>
<td>$ 0.57</td>
<td>$ 0.82</td>
<td>$ 0.62</td>
<td>$ 1.13</td>
</tr>
<tr>
<td>600</td>
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<td>0.5</td>
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<td>$ 0.91</td>
<td>$ 0.90</td>
<td>$ 0.67</td>
<td>$ 1.22</td>
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<td>90.00%</td>
<td>$ 0.71</td>
<td>$ 0.84</td>
<td>$ 0.62</td>
<td>$ 1.23</td>
</tr>
<tr>
<td>600</td>
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<td>97.50%</td>
<td>$ 0.96</td>
<td>$ 0.90</td>
<td>$ 0.67</td>
<td>$ 1.49</td>
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<tr>
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<td>2000</td>
<td>20</td>
<td>99.00%</td>
<td>$ 1.27</td>
<td>$ 0.95</td>
<td>$ 0.86</td>
<td>$ 1.63</td>
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<tr>
<td>600</td>
<td>2000</td>
<td>5</td>
<td>99.75%</td>
<td>$ 1.52</td>
<td>$ 1.07</td>
<td>$ 0.77</td>
<td>$ 1.70</td>
</tr>
<tr>
<td>600</td>
<td>2000</td>
<td>0.5</td>
<td>99.98%</td>
<td>$ 1.75</td>
<td>$ 1.13</td>
<td>$ 0.86</td>
<td>$ 2.11</td>
</tr>
<tr>
<td>600</td>
<td>2000</td>
<td>0.5</td>
<td>99.98%</td>
<td>$ 2.08</td>
<td>$ 1.19</td>
<td>$ 0.88</td>
<td>$ 2.32</td>
</tr>
</tbody>
</table>

Note: Amortized at 7% over 30 years. Costs exclude polishing treatment. Refer to Table 3-9 for additional treatment costs.

Total Amortized Operating Costs (per 1,000 Gallons Treated) for AOPs
3.7.2 Evaluation of Cost Estimates for Specific AOP Technologies

For nearly all of the cost estimates provided by vendors, the primary factors affecting system costs were flow rate and removal efficiency, independent of influent concentration. For example, the cost to reduce MTBE from 20 µg/L to 0.5 µg/L (97.5-percent reduction) at 6,000 gpm was nearly identical to the cost to reduce MTBE from 200 µg/L to 5 µg/L (97.5-percent reduction). However, as expected, the O&M costs increased substantially as the removal efficiency exceeded 99.9 percent.

Capital costs for both Calgon and OSI were lower than APT and HSI for all of the flow rates. However, for high influent concentrations (2,000 µg/L) and high removal efficiencies (99.98 percent) capital costs increased substantially for Calgon. O&M costs were lowest for APT with Calgon and OSI O&M costs approximately 50 percent higher for the 60 and 600 gpm systems. HSI O&M costs were significantly higher under all but one flow rate and OSI O&M costs were significantly higher at 6,000 gpm. Combining capital and O&M, annual operating costs were the lowest for APT, Calgon, and OSI, ranging from approximately $2.18/1,000 gallons at 60 gpm to $0.32/1,000 gallons at 6,000 gpm. Again, it should be noted that these costs are intended for estimating purposes only and should not be used in place of site-specific engineering cost estimates. Many assumptions were made to facilitate an equal comparison; however, these assumptions may not necessarily be accurate for each technology. For example, the application of standard multipliers for piping, valves, electrical, site work, engineering, and contractor O&P may not accurately reflect the actual costs of the system, but allowed for a more uniform comparison.

The following is a detailed discussion of each of the cost estimates provided by vendors/manufacturers:

**Applied Process Technology, Inc. (H₂O₂/O₃)**

Cost estimates provided by APT were for their H₂O₂/O₃ system. The costs per 1,000 gallons of water treated ranged between $0.35 (6,000 gpm, 20 µg/L) and $3.62 (60 gpm, 2,000 µg/L). These cost figures represent some of the lowest costs collected from any of the four vendors for this analysis. Although the capital costs (Table 3-11) for this system are significantly higher than those for Calgon and OSI, the lower operations and maintenance costs (Table 3-12), particularly with regard to chemical (Table 3A-4) and electrical (Table 3A-5) costs, make this system cost-competitive in terms of total amortized unit costs. Furthermore, under many circumstances, APT capital costs are expected to be lower since they provide a packaged treatment system that comes complete with piping, valves, electrical, and engineering. Thus, actual cost multipliers would be expected to be lower than the standard numbers applied in this report, making the APT system even more cost-effective than shown in the tables.
The cost estimates prepared by APT were based on effluent water with by-product formation, specifically TBA, TBF, and acetone, estimated at approximately 10 percent of the MTBE influent concentration for effluent MTBE treatment goals of 20 µg/L, and 5 µg/L (Applebury, 1999). When the effluent goal of MTBE is 0.5 µg/L, the applied ozone and peroxide doses were high enough to eliminate nearly all formation of TBA or TBF; however, acetone is still expected to be produced in the effluent water at about 10 percent of the MTBE influent concentrations (Applebury, 1999). APT has performed numerous pilot tests that confirm these results. APT estimates minimal peroxide residual due to the unique dosing mechanism (see Figure 3-1b) and, thus, the biologically activated polishing filter required for removal of oxidation by-products (see Table 3-9) is expected to be capable of reducing peroxide concentrations to non-detect levels.

**Calgon Carbon Corporation (H₂O₂/MP-UV)**

The cost estimates provided by Calgon Carbon Corporation were for their H₂O₂/MP-UV system. The cost per 1,000 gallons of treated water ranged from $0.32 (6,000 gpm, 20 µg/L) and $4.11 (60 gpm, 2,000 µg/L). Calgon had among the lowest capital costs, but O&M costs were higher than for APT or OSI for the 6,000 gpm system. The costs prepared by Calgon were based on meeting the specified effluent concentration of MTBE. However, by-products produced as a result of the oxidation process would require further treatment to meet drinking water standards. Calgon provided the most complete analyses on by-product formations and quantified by-product formation based on the data extrapolated from an actual study and provided estimates for the 600 gpm scenario (see Table 3-14). In addition, Calgon calculated the hydrogen peroxide residual remaining in the treated water. Because these concentrations are high (>10 mg/L), an additional treatment step will be required for H₂O₂ removal. Calgon recommended using Centaur carbon for removal of the excess H₂O₂ and a biologically activated carbon system for removal of the TBF, TBA, acetone, formaldehyde, and other acids prior to distribution of the treated drinking water. Costs for these two polishing systems were presented in Table 3-9.
<table>
<thead>
<tr>
<th>System Size, kW</th>
<th>UV Dose, kWh/1,000 Gallons</th>
<th>% Removal</th>
<th>Initial MTBE Concentration</th>
<th>Final MTBE Concentration</th>
<th>By-product Formation/Residuals, mg/L in the effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>270</td>
<td>6.6</td>
<td>99.00%</td>
<td>2000</td>
<td>20</td>
<td>TBF: 174, Acetone: 95, Acetic Acid: 5, Formic Acid: 5</td>
</tr>
<tr>
<td>360</td>
<td>9.1</td>
<td>99.75%</td>
<td>2000</td>
<td>0.5</td>
<td>TBA: 87, Formaldehyde: 60, Oxalic Acid: 190, Methanol: 12</td>
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<tr>
<td>540</td>
<td>10.6</td>
<td>99.98%</td>
<td>2000</td>
<td>0.5</td>
<td>TBF: 50, Acetone: 30, Acetic Acid: 30, Formic Acid: 30</td>
</tr>
<tr>
<td>90</td>
<td>2.3</td>
<td>90.00%</td>
<td>1800</td>
<td>20</td>
<td>TBF: 38, Acetone: 19, Acetic Acid: 12, Formic Acid: 12</td>
</tr>
<tr>
<td>180</td>
<td>4</td>
<td>97.50%</td>
<td>2000</td>
<td>5</td>
<td>TBF: 24, Acetone: 10, Acetic Acid: 5, Formic Acid: 5</td>
</tr>
<tr>
<td>270</td>
<td>6.6</td>
<td>99.00%</td>
<td>2000</td>
<td>0.5</td>
<td>TBF: 10, Acetone: 5, Acetic Acid: 5, Formic Acid: 5</td>
</tr>
<tr>
<td>360</td>
<td>9.1</td>
<td>99.75%</td>
<td>2000</td>
<td>0</td>
<td>TBF: 2, Acetone: 0.5, Acetic Acid: 0.5, Formic Acid: 0.5</td>
</tr>
<tr>
<td>540</td>
<td>10.6</td>
<td>99.98%</td>
<td>2000</td>
<td>0.5</td>
<td>TBF: 0.2, Acetone: 0.2, Acetic Acid: 0.2, Formic Acid: 0.2</td>
</tr>
<tr>
<td>180</td>
<td>4</td>
<td>90.00%</td>
<td>1800</td>
<td>20</td>
<td>TBF: 0.03, Acetone: 0.03, Acetic Acid: 0.03, Formic Acid: 0.03</td>
</tr>
<tr>
<td>360</td>
<td>9.1</td>
<td>99.75%</td>
<td>2000</td>
<td>5</td>
<td>TBF: 0.06, Acetone: 0.06, Acetic Acid: 0.06, Formic Acid: 0.06</td>
</tr>
<tr>
<td>540</td>
<td>10.6</td>
<td>99.98%</td>
<td>2000</td>
<td>5</td>
<td>TBF: 0.1, Acetone: 0.1, Acetic Acid: 0.1, Formic Acid: 0.1</td>
</tr>
</tbody>
</table>

Table 3-14: Estimated By-product Formations and Residual Oxidant Concentrations for H$_2$O$_2$/MP-UV (Calgon Carbon Corporation)
Oxidation Systems, Inc. (Hydrodynamic Cavitation with H₂O₂)

Oxidation Systems Inc. (OSI) provided cost estimates for hydrodynamic cavitation combined with H₂O₂. Based on their cost figures, this AOP is comparable to the systems offered by Calgon or APT. Costs per 1,000 gallons of treated water range between $0.39 (6,000 gpm at 20 µg/L) and $3.05 (60 gpm at 2,000 µg/L). At high flows (600 gpm and 6,000 gpm) and high influent MTBE concentration (2,000 µg/L), this system had the lowest capital cost. This technology is expected to produce oxidation by-products as a result of incomplete oxidation. However, there is limited field information available to adequately estimate by-product formations and to confirm estimates by OSI. Phase II field-testing by OSI is expected to begin in 2000 and should address oxidation by-product formation and control. Regardless, this technology is expected to require a polishing system such as a biologically activated carbon system for removal of AOP by-products (see Table 3-9 for costs).

Hydroxyl Systems, Inc. (TiO₂-catalyzed UV)

Hydroxyl Systems Inc. (HSI) provided cost estimates for TiO₂-catalyzed UV. Based on these estimates, this process is less economical than the other AOPs evaluated. Costs per 1,000 gallons of treated water range between $1.01 (6,000 gpm at 20 µg/L) and $5.17 (60 gpm at 2,000 µg/L). Relative to the other AOPs, capital costs were the highest, particularly at the higher flow rates and influent MTBE concentrations. O&M costs were also high, although not significantly higher than for Calgon. There is limited information about by-product formation and, thus, vendor claims regarding by-product control currently cannot be verified. This technology is expected to require a polishing system such as a biologically activated carbon system for removal of AOP by-products (see Table 3-9 for costs).

3.7.3 Sensitivity Analysis

The presence of other chemical constituents in the source water will affect the performance and economics of AOPs. The constituents of concern are common gasoline aromatics, BTEX, and dissolved NOM expressed as TOC. A sensitivity analysis was performed to evaluate the impacts of BTEX and TOC on AOP drinking water treatment costs. In addition, the costs presented above are based on a treatment plant life of 30 years, as is standard for community drinking water treatment plants. However, some of the smaller treatment applications may be installed for a much shorter period and, thus, a sensitivity analysis was completed to evaluate the effect of facility lifetime on AOP drinking water treatment costs. All sensitivity analyses performed were based on information supplied by vendors and engineering judgement. Actual costs will vary depending on site-specific circumstances.

The concentration of TOC in groundwater varies; therefore, TOC concentrations of 0.8 mg/L, 2 mg/L, and 8 mg/L were evaluated. Although BTEX is not expected to be detected in large community drinking water supplies due to the reliance of these supplies on deep aquifers, BTEX compounds are likely to be present in shallow aquifers contaminated with gasoline.
Thus, BTEX sensitivity analyses based on concentrations of 800 µg/L and 80 µg/L were completed to evaluate the impacts of BTEX on AOP treatment costs. Finally, cost estimates for 2-, 10-, and 30-year treatment facility lifetimes were also completed.

The sensitivity analyses of AOPs were evaluated for the following base case:

- Flow rate of 600 gpm
- Influent MTBE of 200 µg/L
- Effluent MTBE of 5 µg/L

Results of the sensitivity analyses are as follows:

**TOC Sensitivity**

The capital, operating, and total cost per 1,000 gallons of treated water are summarized in Table 3-15. For three of the AOPs (H₂O₂/O₃ system [APT], H₂O₂/MP-UV system [Calgon], and hydrodynamic cavitation [OSI]), the vendors claimed that the levels of TOC included in the evaluation would not affect the capital cost (i.e., the size of the reactor would not be affected). In the fourth case, TiO₂/UV, the vendor said that capital cost would significantly increase, as the TOC is expected to foul the catalyst and absorb some of the UV light; hence, requiring more lamps, a larger reactor, and more catalyst.

Under high TOC concentrations, O&M costs are expected to increase for all systems with few exceptions. For the H₂O₂/O₃ (APT) and H₂O₂/MP-UV (Calgon) systems, TOC levels of 0.8 and 2 mg/L are not expected to increase O&M costs. The vendors claim that these levels of TOC do not significantly interfere with UV light or scavenge hydroxyl radicals in their design, and they have several field tests that support their claims. In the case of hydrodynamic cavitation, elevated levels of TOC will require greater operator maintenance and energy due to increased recycling. Elevated TOC levels are expected to have the greatest impact on the TiO₂/UV system and make this technology cost prohibitive. Elevated TOC levels in these systems will necessitate more catalyst change-outs, more frequent reactor and lamp cleanings, and increased H₂O₂ consumption.

**BTEX Sensitivity**

The capital, operating, and total cost per 1,000 gallons of treated water are summarized in Table 3-16 for this sensitivity analysis. In the case of H₂O₂/O₃ (APT), these levels of BTEX are expected to have no impact on cost at 80 µg/L, and only a slight impact (increase of $0.04/1,000 gallons treated) at 800 µg/L. Field data is available from APT to support their claim. In the case of H₂O₂/MP-UV (Calgon), BTEX at 80 µg/L is not expected to increase costs; however, BTEX at 800 µg/L is expected to increase costs by approximately 17 percent. In the case of hydrodynamic cavitation, elevated BTEX is not expected to increase capital cost but will increase O&M costs. For this AOP, 80 µg/L BTEX are expected to increase
O&M cost 10 percent while 800 µg/L BTEX are expected to increase O&M costs 25 percent. The vendor has demonstrated pilot units successfully for MTBE removal with complete BTEX removal at these concentrations. Finally, in the case of TiO₂/UV, elevated BTEX is expected to increase capital and O&M costs. The increase in cost per 1,000 gallons treated is expected to be approximately 7 percent for 80 µg/L BTEX and 30 percent for 800 µg/L BTEX. However, there is currently no field data to support these assumptions.

**Design Life Sensitivity**

The results of the sensitivity analyses on the design life of the treatment system is presented in Table 3-17. As can be expected, shortening the design life of these systems is expected to result in higher amortized capital costs. Reducing the design life from 30 years to 2 years, while maintaining a seven percent discount rate, results in an approximate doubling of the unit costs for the Calgon system ($0.96 to $1.69/1,000 gallons) and for the OSI system ($0.67 to $1.36/1,000 gallons). For APT and HSI, the costs increased even more significantly by reducing the life from 30 years to 2 years. The greater difference is attributed to the higher system capital costs. APT costs increased approximately fourfold ($0.90 to $3.56/1,000 gallons) while the HSI costs increased by almost threefold ($1.49 to $4.08/1,000 gallons).

**Table 3-15**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Capital Cost</strong></td>
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<td></td>
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</tr>
<tr>
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<td>$1,777,400</td>
<td>$461,200</td>
<td>$1,730,800</td>
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<tr>
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<td>$461,200</td>
<td>$1,730,800</td>
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<tr>
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<td>$488,800</td>
<td>$1,777,400</td>
<td>$461,200</td>
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</tr>
<tr>
<td><strong>Annual Operation and Maintenance Costs</strong></td>
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<td>$136,800</td>
<td>$185,500</td>
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<td>$542,200</td>
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<td><strong>Total Amortized Operating Cost (Per 1,000 gallons Treated)</strong></td>
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<tr>
<td>0.8</td>
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<td>$0.71</td>
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<td>$1.13</td>
<td>$0.93</td>
<td>$0.85</td>
<td>$3.08</td>
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Base case is a 600 gpm system treating an influent of 200 µg/L MTBE with an effluent of 5 µg/L.
### Table 3-16
Effects of Additional BTEX Contamination on AOP Treatment Costs

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<tbody>
<tr>
<td></td>
<td>Capital Cost</td>
<td>Annual Operation and Maintenance Costs</td>
<td>Total Amortized Operating Cost (per 1,000 gallons Treated)</td>
<td></td>
</tr>
<tr>
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<td>$1,777,400</td>
<td>$1,903,900</td>
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<tr>
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</table>

Base case is a 600 gpm system treating an influent of 200 µg/L MTBE with an effluent of 5 µg/L.

### Table 3-17
Effects of Design Life on AOP Treatment Costs

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</thead>
<tbody>
<tr>
<td></td>
<td>Capital costs</td>
<td>Annual Operation and Maintenance Cost</td>
<td>Total Amortized Operating Cost (Per 1,000 gallons Treated)</td>
<td></td>
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<tr>
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<td>$1,730,800</td>
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<tr>
<td>30</td>
<td>$0.96</td>
<td>$0.90</td>
<td>$0.67</td>
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</tr>
</tbody>
</table>

Base case is a 600 gpm system treating an influent of 200 µg/L MTBE with an effluent of 5 µg/L.


3.8 Conclusions and Recommendations for Future Research

3.8.1 Recommended Technologies

When compared to other drinking water treatment alternatives, such as air stripping and activated carbon, AOPs are an emerging technology. Currently, there are only a few cases where organic contaminants (e.g., PCE and NDMA) are being removed from drinking water using an AOP. Furthermore, there were no identified cases where MTBE is being removed from drinking water prior to distribution. Thus, thorough pilot- and field-scale testing of the selected AOP is required to demonstrate the capabilities and possible limitations of AOPs to produce drinking water from contaminated source water.

Based on this evaluation, the two most promising AOP technologies appear to be \( \text{H}_2\text{O}_2/\text{O}_3 \) and \( \text{H}_2\text{O}_2/\text{MP-UV} \). Both of these processes are well-understood and have been demonstrated at several bench- and field-scale sites to successfully remove MTBE from water to meet drinking water standards. Besides being the most technically feasible, these two technologies — in addition to cavitation — appear to be the most economically feasible. However, these costs are strongly dependent on source water quality and are difficult to verify due to the untested nature of these technologies in large-scale applications. Cavitation costs involve the most uncertainty because there are no pilot-, field-, or full-scale drinking water treatment applications for MTBE removal. Consequently, while there is significant uncertainty for all the cost estimates, \( \text{H}_2\text{O}_2/\text{O}_3 \) and \( \text{H}_2\text{O}_2/\text{MP-UV} \) technologies are essentially equivalent in cost and less expensive than the other AOPs evaluated.

In addition to these two relatively established AOPs, E-beam and cavitation are two emerging AOPs that warrant future consideration due to their technical feasibility for removing MTBE from drinking water to meet standards. These technologies are still in their infant stages for removal of organic contaminants in drinking water applications; however, they have been widely demonstrated for disinfection and remediation applications.

3.8.2 Recommendation for Future Research

As stated previously, there remains a significant amount of uncertainty regarding the technical and economic effectiveness of AOPs for removing MTBE from drinking water under a variety of water quality scenarios. More pilot- and field-scale studies need to be conducted to determine the removal efficiencies that can be achieved under different water quality conditions and operational parameters. In addition, the following specific topics warrant further research:

1) \textit{Water quality impacts on AOP effectiveness}. The effectiveness of AOPs is directly related to water quality parameters such as pH, alkalinity, NOM, TOC, turbidity, and concentrations of other interfering compounds (e.g., nitrate and bromide). Future studies on AOP treatment of MTBE must independently evaluate the impact of each of the above-listed water quality parameters. The evaluation criteria must include MTBE removal efficiency,
oxidation by-product formation, DBP formation potential, and costs. For ozone-based AOPs, the effect of influent bromide concentration on bromate formation must also be evaluated. Similarly, a detailed analysis of the effect of influent water turbidity and nitrate concentrations on the effectiveness of AOPs relying on UV-light (LP, MP, pulsed) is warranted.

2) **By-product formation and control.** One of the most significant areas of future research is the issue of by-product formation and control. The oxidation of MTBE to carbon dioxide and water involves many steps and the formation of many oxidation by-products (e.g., TBA, TBF, acetone). If these by-products are not completely mineralized, they will be present in treated water, resulting in elevated concentrations of potentially toxic by-products in the treated water. A better understanding of by-product formation mechanisms and subsequent mitigation strategies will be necessary prior to the acceptance of AOPs by the regulatory community for drinking water applications. This includes research to determine the most cost-effective treatment option, such as biologically activated carbon, for by-product removal in drinking water applications.

3) **Cost evaluation as a function of water quality and contamination scenario.** Finally, future research should evaluate engineering costs for MTBE oxidation by AOPs. Capital and O&M costs for each AOP process should be developed as a function of water quality, flow rate, influent MTBE concentration, and required removal efficiency. These cost evaluations must be performed under uniform design criteria (e.g., required removal efficiency) and operational assumptions (e.g., power rate). A unified costing approach will enable a direct comparison of the various AOPs for specific water qualities.


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