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Demonstration of the HiPOx Advanced Oxidation Technology for the Treatment of MTBE-Contaminated Groundwater

Final Report

By

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Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

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E. Timothy Oppelt, Director
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Abstract

The HiPOx technology is an advanced oxidation process that incorporates high-precision delivery of ozone and hydrogen peroxide to chemically destroy organic contaminants with the promise of minimizing bromate formation. A MTBE-contaminated groundwater from the Ventura County Naval Base in Port Hueneme, CA was used to evaluate this technology. Due to extremely high concentrations of bromide in the feed water (1.3 mg/L) and the desire to limit bromate formation, an experimental system was operated with 630 ozone injector ports in series. In all trials, the HiPOx system reduced MTBE from 748 $\mu\text{g/L}$ to below its regulatory limit of 5 $\mu\text{g/L}$; however, bromate was not maintained below its regulatory limit of 10 $\mu\text{g/L}$. The oxidative intermediate tert-butyl alcohol (TBA) was below its regulatory effluent limit of 12 $\mu\text{g/L}$ in two of the three trials. Both MTBE and bromate were under their regulatory limits at intermediate sampling ports that corresponded to 330, 470, and 540 injector ports for the three runs. However, TBA was above its regulatory limit at these locations for all three runs. To control TBA, more injection ports were required. However, as shown above, additional injection ports increased the bromate concentration above its regulatory limit. Therefore, the experimental HiPOx system was not fully successful with this atypical water at the chosen oxidant doses.

A model calculation is presented that uses many simplifying assumptions to show that this HiPOx system may have been fully successful at this location under the chosen oxidant doses if the influent bromide concentration was 0.56 mg/L, or less. Since a bromide concentration of 0.56 mg/L is still extremely high for a drinking water source, the HiPOx system appears to hold promise for destroying MTBE and its oxidative byproduct TBA while controlling bromate formation, even in waters that have high bromide concentrations. However, before application to other sites, pilot testing will be needed due to the uncertainty in performance resulting from source-water quality differences.

Appendix A contain the manufacturer's supporting data from other sites and data collected by the manufacturer during the demonstration runs described herein.

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Due to lack of funds at the time of this technology's scheduled testing, a CRADA agreement between the USEPA and APT was created where APT supplied the USEPA with the funding necessary to cover the analytical costs of this project (approximately \$7K). The USEPA used the funds through its contractor (TetraTech) who ran the study, collected the samples, shipped the samples, paid for the analyses, and summarized the results. At no time did APT influence the results or the subsequent discussion. Please see Appendix A for APT's data and comments regarding this project.

1 Background

The U.S. Environmental Protection Agency (EPA), National Risk Management Research Laboratory (NRMRL) and the U.S. Navy entered into a memorandum of understanding to conduct a multi-year program involving demonstration and evaluation of innovative technologies for treatment of methyl *tert*-butyl ether (MTBE) in groundwater. Technology vendors were identified through an open solicitation that requested proposals for processes to treat MTBE. Vendors participating in the program were selected based on internal and external peer reviews.

One of the vendors selected for the demonstration program was Applied Process Technology, Inc. (APT), the developer of an advanced chemical oxidation technology called HiPOx. The site selected for the demonstration was the Ventura County Naval Base in Port Hueneme, CA, where a plume of MTBE-contaminated groundwater was present. The HiPOx technology was demonstrated as an *ex situ* application at a location known as the Wellhead Protection Zone, which is toward the toe of the MTBE plume. At this location, MTBE concentrations in the groundwater were attenuated to less than 1000 micrograms per liter ($\mu\text{g/L}$), and other gasoline components were not present. The purpose of the demonstration at this location was to show the capabilities of the technology for remediating MTBE-contaminated groundwater for potential reuse as a drinking water supply.

Besides MTBE, the primary contaminants of interest for the demonstration included *tert*-butyl alcohol (TBA), acetone, and bromate. TBA and acetone are intermediates in the oxidative degradation of MTBE, while bromate results from the oxidation of bromide during ozone treatment. Treatment goals for the demonstration were established for these parameters based on Maximum Contaminant Levels (MCL) and other regulatory standards for drinking water in the State of California. California currently regulates MTBE at 5 $\mu\text{g/L}$ (Enforceable Secondary MCL), TBA at 12 $\mu\text{g/L}$ (Action Level), and bromate at 10 $\mu\text{g/L}$ (EPA Stage 2 Disinfection By-product Rule). There were no drinking water standards for acetone at the time of testing, and thus no treatment goal was set for this parameter.

1.1 Technology description

The HiPOx technology developed by APT is similar to other advanced oxidation technologies that use ozone (O_3) and hydrogen peroxide (H_2O_2) to destroy organic compounds in contaminated waters. However, the vendor claims that the high-precision delivery of the oxidants and the use of multiple oxidant injection ports enhances process efficiency. In “traditional” applications of advanced oxidation technology, 2 to 3 percent ozone by weight is injected at a single point through a diffuser and is allowed to bubble up at atmospheric pressure through the contactor. Volatile organic compounds (VOCs) and other contaminants are destroyed over contact times as long as 20 minutes. The HiPOx technology enhances the mass transfer of ozone into the water by using higher ozone injection concentrations (8 to 10 percent by weight), higher operating pressures, and in-line mixers to promote efficient mixing. The vendor claims that the multiple reaction zones utilized in the HiPOx technology further enhances the process efficiency by keeping the localized ozone concentration low which in theory minimizes bromate formation.

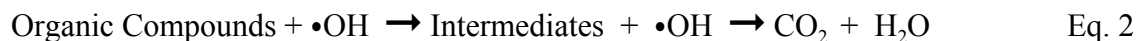
A general process flow diagram for the HiPOx process is shown in Figure 1-1. In the HiPOx process, liquid hydrogen peroxide is injected into the influent stream. Ozone, which is generated from liquid oxygen on site, is injected through multiple ports along a serpentine reactor. The reactor is maintained at a pressure of about 35 to 45 pounds per square inch gauge (psig) to provide efficient mass transfer of ozone into solution. Following each ozone injection port, the dosed fluid immediately flows through an in-line mixer to ensure that the ozone is mixed into solution, and then through a brief reaction zone. Thus, the reactor consists of a series of injection/mixing/reaction modules in series, the purpose of which is to maintain low instantaneous O₃:H₂O₂ mole ratios, as stated earlier.

1.2 Process chemistry

In aqueous solution, ozone dissociates and reacts with hydrogen peroxide to produce hydroxyl radicals (•OH). Hydroxyl radicals are powerful oxidizing agents and work alone or in concert with its precursors to oxidize organic contaminants. Given enough time, complete mineralization to carbon dioxide and water can be achieved. The following equation presents the overall balanced equation for hydroxyl radical formation from ozone and hydrogen peroxide:



The following equation represents the oxidation of organic compounds:



The oxidative degradation of MTBE involves a series of chemical reactions. The initial oxidation product is *tert*-butyl formate (TBF), a short-lived intermediate that is converted to a longer-lived intermediate, TBA. TBA is subsequently converted to acetone prior to conversion to carbon dioxide and water. Thus, the overall reaction sequence can be summarized as follows:



In addition to TBA and acetone, bromate may be formed by the oxidation of bromide by ozone and hydroxyl radicals. This is a drawback for ozone-based advanced oxidation processes. Therefore, a key question for the use of ozonation systems in drinking water applications is whether bromate formation can be controlled. The HiPOx vendor claims that formation of bromate is minimized by the HiPOx system's use of multiple ozone injection ports and in-line mixers that keep local ozone concentrations low. Appendix A contains information from APT on this technology, APT's data from this study, and supporting data from other studies/locations.

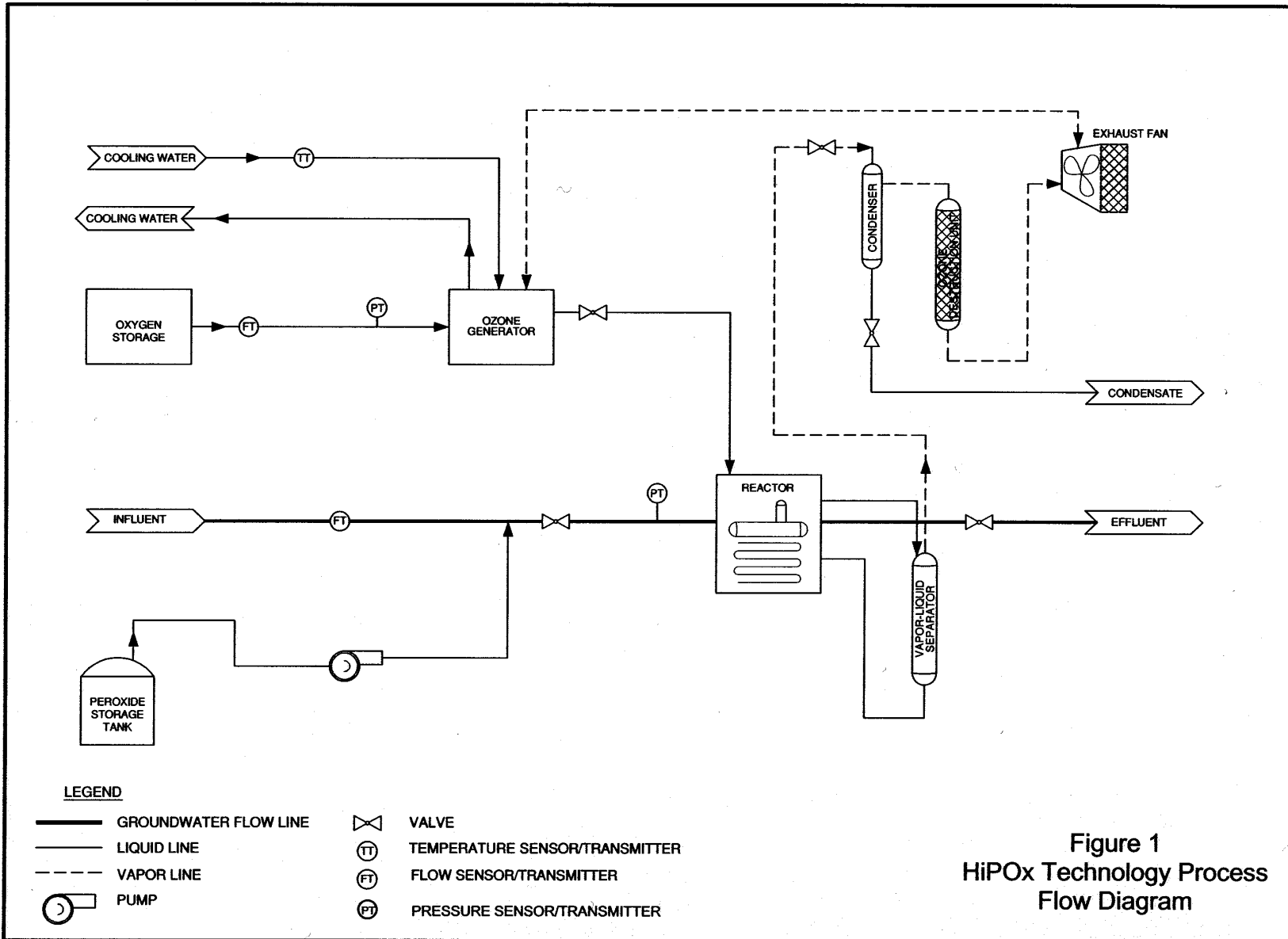


Figure 1
HiPOx Technology Process
Flow Diagram

2 Methods and Materials

The APT HiPOx Pilot Test Unit (PTU) was used in this demonstration. The PTU was housed in a mobile, box van approximately 14 feet in length. The PTU was designed as a simplified version of the HiPOx process for use in pilot studies. The PTU was configured with 18 reactor modules, which are sufficient to destroy most contaminants. For this demonstration, however, a larger number of modules was desired to demonstrate the ability of the technology to completely destroy MTBE and other oxidative intermediates while not producing bromate in this high bromide water. To address this need, the PTU was operated in a recirculating mode, in which a batch of contaminated groundwater was recycled through the PTU multiple times to simulate a reactor with a larger number of reactor modules. As stated above, a reactor module consists of an ozone injection port followed by a static mixing zone.

The PTU was set up at the Wellhead Protection Zone early in November 2001. The influent process water was drawn from a manifold that connected nine wells installed in the MTBE plume at the Wellhead Protection Zone. The optimal ozone and peroxide doses were determined from numerous trial studies conducted by the manufacturer. These data are not presented in this document. In preparation for the demonstration, a 1900-liter storage tank was filled to near capacity to facilitate the introduction of process water into the PTU. Approximately 300 liters were drawn into an intermediate 380-liter storage tank for initial hydrogen peroxide dosing.

The process demonstration occurred on November 15, 2001 and consisted of three runs at the same operating conditions. To initiate a run, the process water in the 380-liter intermediate storage tank was dosed with 60.8 mg/L of hydrogen peroxide, and the PTU reactor was filled with 70 liters of process water (the volume of the reactor plus the 7.6 liter recirculating tank). The system pump was then initiated and the process water was pumped continuously around the PTU reactor, with the reactor effluent being recycled back to the recirculating tank at a flow rate of 13 liters/min. The 7.6 liter recirculating tank was located at the beginning of the system. The 380-liter tank was not in the recycle loop. Since each run consisted of 35 cycles through the PTU, and the PTU incorporated 18 reactor modules, each run simulated a HiPOx treatment system with 630 reactor modules. Each process run took approximately 3 hours to complete all 35 cycles.

The ozone to hydrogen peroxide mole ratio was monitored and controlled using adjustments to the ozone's mass flow indicator and the hydrogen peroxide's metering pump. Ozone was dosed into the injection port of each reactor module continuously during each run (3.4 mg O₃ / L per cycle). The initial hydrogen peroxide dose was supplemented with a low dose (1.72 mg H₂O₂ /L per cycle) that was injected continuously into the effluent end of the PTU reactor. The total hydrogen peroxide and ozone doses for each run are listed in Table 1-1.

Table 1-1. Total Ozone and Peroxide Doses for the Three Runs.

	Run 1	Run 2	Run 3	Average
H₂O₂ dose (mg/L)	121	121	121	121
Ozone Dose (mg/L)	119	119	119	119

Samples of the process water were collected at five separate times/locations during each run. Initial (influent) samples were collected from the 380-liter intermediate storage tank before any chemical oxidants were added; treated process water samples were collected after 12, 24, 30, and 35 cycles (at the final effluent sample port). Prior to sample collection, the sampling port was purged to ensure that any stagnant water was flushed from the port. Separate samples were collected for analysis of VOCs, bromate, and general chemical parameters. Sample containers, preservatives, and other sampling procedures were in accordance with standard reference methods.

Ozone analysis of treated water samples was performed in the field with a Hach® ozone field kit to monitor ozone concentrations for process monitoring and control purposes. All other samples were shipped to a certified laboratory for chemical analysis. Samples were analyzed for VOCs in accordance with EPA Method 5030 (purge and trap) and EPA Method 8260 (capillary column gas chromatography/mass spectrometry). These EPA methods were modified to include MTBE and TBA as target analytes after method evaluation studies confirmed that these analytes were satisfactorily recovered and that quantitation limits below the treatment goals could be routinely achieved. Samples were also analyzed for bromate by ion chromatography in accordance with EPA Method 317. Metals and other general chemical parameters were analyzed in accordance with the appropriate EPA reference methods for water samples.

Off-gases from the reactor were passed through a condenser to separate water, and then through an ozone destruction unit, which contained a chemical reducing agent to destroy any residual ozone prior to venting to the atmosphere. Gases vented from the enclosure surrounding the ozone generation unit were also passed through this unit to ensure that fugitive emissions of ozone were not allowed into the process/control room. The treatment system was equipped with influent and effluent sampling ports, as well as flow measurement and process monitoring/control equipment, to assure that process operations were effectively monitored and controlled.

3 Results and Discussion

This section presents the analytical results for the process water samples collected from the PTU, and compares these results to the demonstration treatment objectives. As stated above, the primary objective for the demonstration was the reduction of MTBE to below 5 $\mu\text{g/L}$ in the final effluent. The second objective for the demonstration was the reduction of TBA, acetone, and bromate to below their respective regulatory limits.

To ensure that this study would produce valid data that were suitable for their intended use, a data quality review was conducted using results of both field quality control (QC) samples and laboratory QC samples. For the VOC analyses, results for matrix spike/matrix spike duplicate samples indicated that recoveries of detected VOCs were consistently within the acceptance range of 75 percent to 125 percent, and that the relative percent differences were less than the acceptance criterion of 25 percent. Trip blanks did not reveal contamination with any of the detected VOCs, although method blanks revealed occasional MTBE contamination below the laboratory quantitation limit. QC sample results for other analytical parameters were in compliance with method acceptance criteria. Thus, the only significant qualification of the data was the estimated nature of some MTBE results that were below the laboratory quantitation limit, which was set at the lowest standard concentration (1 µg/L), or that were above the calibration range of the instrument, as noted in the data tables below.

3.1 General water quality

The groundwater used in this study was relatively hard with high alkalinity as shown in Table 3-1. Most importantly, the bromide levels were very high (1.3 mg/L). This allowed for an evaluation of this technology under very challenging conditions for bromate formation. Turbidity levels were high, likely due to inadequate well development and/or iron precipitation. Sodium levels were also elevated as compared to a typical drinking water. The influent dissolved organic carbon (DOC) and total organic carbon (TOC) results were confusing in that the DOC values were greater than the TOC values in all cases. Also, the influent DOC concentrations went down from Run 1 through Run 3, whereas the influent TOC concentrations and influent UV absorbances did not. The synthetic organics: benzene, ethylbenzene, toluene, or total xylene were all below their detection limits of 10, 10, 10, and 30 µg/L, respectively. The water did contain *cis* 1,2 dichloroethene at concentrations estimated between 4 and 6 µg/L. This suggests that either *cis* 1,2 dichloroethene was following the MTBE plume closely or that the wells were contaminated from another source.

The effluent results for metals and general chemistry parameters are also listed in Table 3-1. Iron and manganese appear to be reduced in the effluent, likely due to precipitation and settling induced by the oxidative environment. Alkalinity and possibly calcium dropped slightly, but the other inorganics were not affected by treatment. This includes bromide, which is known to be the precursor to bromate; however, the small amount of conversion of bromide to bromate would not have impacted the quantitation of the high levels of bromide. Ozone was not found in the effluent samples due to excess hydrogen peroxide.

Both DOC and TOC were somewhat reduced in the effluent as compared to the influent indicating that some organic carbon was destroyed by the advanced oxidation treatment. However, consistently higher levels of DOC than TOC in both the influent and effluent could not be explained, nor could the drop in DOC influent values from Run 1 through Run 3 without a parallel drop in either effluent DOC, influent UV absorbance, influent TOC, or effluent TOC.

Table 3-1. Summary of Analytical Results for Metals and General Chemistry Parameters.

Run	Analytical Parameter	Influent Concentration (mg/L)*	Final Effluent Concentration (mg/L)*
1	Calcium	340	320
	Iron	7.4	5.2
	Magnesium	130	130
	Manganese	2	1.5
	Potassium	8.1	8.1
	Sodium	270	270
	Alkalinity	446	406
	Bromide	1.3	1.3
	DOC	8.3	3.1
	Ozone	0.0	0.1
	pH	7.10	7.52
	TOC	3	2.5
	Turbidity (NTU)	46.2	37.4
	UV @ 254nm (1/cm)	0.061	0.027
2	Calcium	360	320
	Iron	7.7	5.3
	Magnesium	140	130
	Manganese	2.1	1.4
	Potassium	8.4	7.9
	Sodium	280	270
	Alkalinity	458	406
	Bromide	1.2	1.3
	DOC	5	2.7
	Ozone	0.0	0.0
	pH	7.09	7.97
	TOC	3	2.2
	Turbidity (NTU)	48.6	23.0
	UV @ 254nm (1/cm)	0.059	0.011
3	Calcium	340	330
	Iron	7.5	5.7
	Magnesium	130	130
	Manganese	2	1.5
	Potassium	8	7.9
	Sodium	270	270
	Alkalinity	452	408
	Bromide	1.3	1.3
	DOC	3.6	3.7
	Ozone	0.0	0.0
	pH	7.17	8.04
	TOC	3	2.2
	Turbidity (NTU)	24.0	42.6
	UV @ 254nm (1/cm)	0.061	0.011

* unless noted otherwise

As part of this study, the influent and effluent waters were chlorinated at Uniform Formation Conditions (Summers et al., 1994). A chlorine dose of 2.7 mg/L was delivered to each of the waters. The reported final chlorine residual ranged between 0.90 and 1.25 mg/L implying that the organic constituents in the water reacted with the chlorine. However, the amounts of trihalomethane, haloacetic acid, and total organic halide formed were extremely low. The field notes indicate that the influent sample was mistakenly taken after hydrogen peroxide addition. The effluent sample also contained hydrogen peroxide, as expected, albeit at concentrations higher than first envisioned. Unfortunately, the high levels of hydrogen peroxide quickly reacted with the spiked chlorine (Connick, 1947; Held et al., 1978) preventing the reaction between chlorine and the natural organic material. The hydrogen peroxide also likely interfered with the DPD method used to measure chlorine (Sengupta et al., 1978; Bader et al., 1988). Therefore, the reported chlorine residual after 24 hours of between 0.90 and 1.25 mg/L was likely a false positive resulting from the presence of large amounts of hydrogen peroxide. In conclusion, the UFC results tell us nothing about the effect of HiPOx treatment on subsequent disinfection byproduct formation. In any event, it is unclear as to the worth of such information for such an atypically high-bromide water as that used in this study.

3.2 MTBE and byproducts

Table 3-2 shows the influent and final effluent (35 cycles) concentrations of MTBE during each of the three replicate runs. The percent removal of MTBE for each run is also listed. As shown in this table, the HiPOx system was able to reduce MTBE from an average of 748 µg/L in the influent to less than 1 µg/L, which was the laboratory quantitation limit. The average MTBE removal efficiency was greater than 99.87 percent, which reflects the near total destruction of MTBE by the HiPOx system. The treatment goal of 5 µg/L MTBE in the final effluent was easily achieved for all three runs.

Table 3-2: MTBE Removal Efficiency.

	Run 1 Start / End	Run 2 Start / End	Run 3 Start / End	Average
MTBE (µg/L)	744 / 0.3*	751 / <1	749 / <1	748 / <1
Removal Efficiency	99.96 %	>99.87 %	>99.87 %	>99.87 %

* Estimated value below laboratory quantitation limit.

Table 3-3 shows the concentrations of intermediates and by-products generated by the HiPOx treatment. The TBA concentration in the final effluent was below the regulatory goal of 12 µg/L in Runs 2 and 3, but not in Run 1. One possible explanation may be that the higher DOC levels in Run 1 may have scavenged the hydroxyl radicals, preventing them from destroying the TBA. However, as stated above, the DOC and TOC results are somewhat questionable. The concentration of acetone was high in the effluent (average = 135 µg/L) for all three runs. However, due to the lack of a drinking water regulation for acetone, no conclusion could be made as to the acceptability of these levels. Bromate was clearly generated as a by-product of the chemical oxidation treatment with effluent concentrations above the regulatory goal of 10 µg/L in all three runs.

Table 3-3: Oxidation Intermediates and By-products.

	Run 1 Start / End	Run 2 Start / End	Run 3 Start / End	Average
TBA (µg/L)	<40 / 29	<40 / 8.1	<40 / 5.9	<40 / 14.3
Acetone (µg/L)	<40 / 154	<40 / 135	<40 / 117	<40 / 135
Bromate (µg/L)	<1 / 12.1	<2 / 19.9	<2 / 27.0*	<2 / 19.7

* Estimated value above instrument calibration range.

Table 3-4 shows all the sample results for MTBE, TBA, acetone, and bromate for the three runs. The results are also shown in Figures 3-1, 3-2, and 3-3 for Runs 1, 2, and 3, respectively. Data that were estimated, as noted in Table 3-4, are presented in Figures 3-1 through 3-3. However, if a data point was reported as less than a certain value in Table 3-4, it was not plotted in the figures. The figures show that most of the MTBE was destroyed in the first 24 reactor cycles (432 injectors). TBA, acetone, and bromate exhibit different relationships with the number of reactor cycles, depending on the chemistry involved in their formation. TBA, which is an intermediate in the degradation of MTBE, initially increased in concentration (at 12 cycles), but then decreased over the remaining reactor cycles. Acetone concentrations increased rapidly through 24 cycles, in conjunction with MTBE destruction, but then appeared to stabilize. These trends are consistent with the reaction sequence for MTBE degradation suggested previously, wherein TBA is an initial intermediate, and acetone is the next-to-final product of MTBE degradation. Bromate concentrations increased steadily with the number of reactor cycles since its formation is related to oxidant dose, bromide concentration, and time, and is independent of MTBE degradation.

Table 3-4. Summary of Analytical Results for Organic Parameters.

Analytical Parameter	Run	Influent Concentration (µg/L)	After 12 Cycles (µg/L)	After 24 Cycles (µg/L)	After 30 Cycles (µg/L)	After 35 Cycles (µg/L)
MTBE	1	756 & 731	31	1.7	0.6*	0.3*
	2	766 & 736	15	0.3*	<1	<1
	3	758 & 740	10	3.9*	3.8*	<1
	Average	748	19	2.0*	<1.8*	NA
	Std Dev.	14.0	11	1.8*	1.7*	NA
TBA	1	11* & <40	126	67	48	29
	2	<40 & <40	96	33	20	8.1
	3	<40 & <40	99	21	<40	5.9
	Average.	NA	107	40.3	<36	14
	Std Dev.	NA	16	23.9	14	13
Acetone	1	<40 & <40	101	156	164	154
	2	<40 & <40	117	150	151	135
	3	<40 & <40	79	103	81	117
	Average	NA	99	136	132	135
	Std Dev.	NA	19	29	45	18
Bromate	1	<1 & <2	4.3	8.0	10.1	12.1
	2	<2 & 2.6	1.9	6.9	16.7	19.9
	3	<2 & <2	6.7	14	18.4	27.0*
	Average	NA	4.3	9.6	15.1	19.7*
	Std Dev.	NA	2.4	3.8	4.4	7.5*

* Estimated concentration (outside calibration range or below quantitation limit)

NA = Not applicable

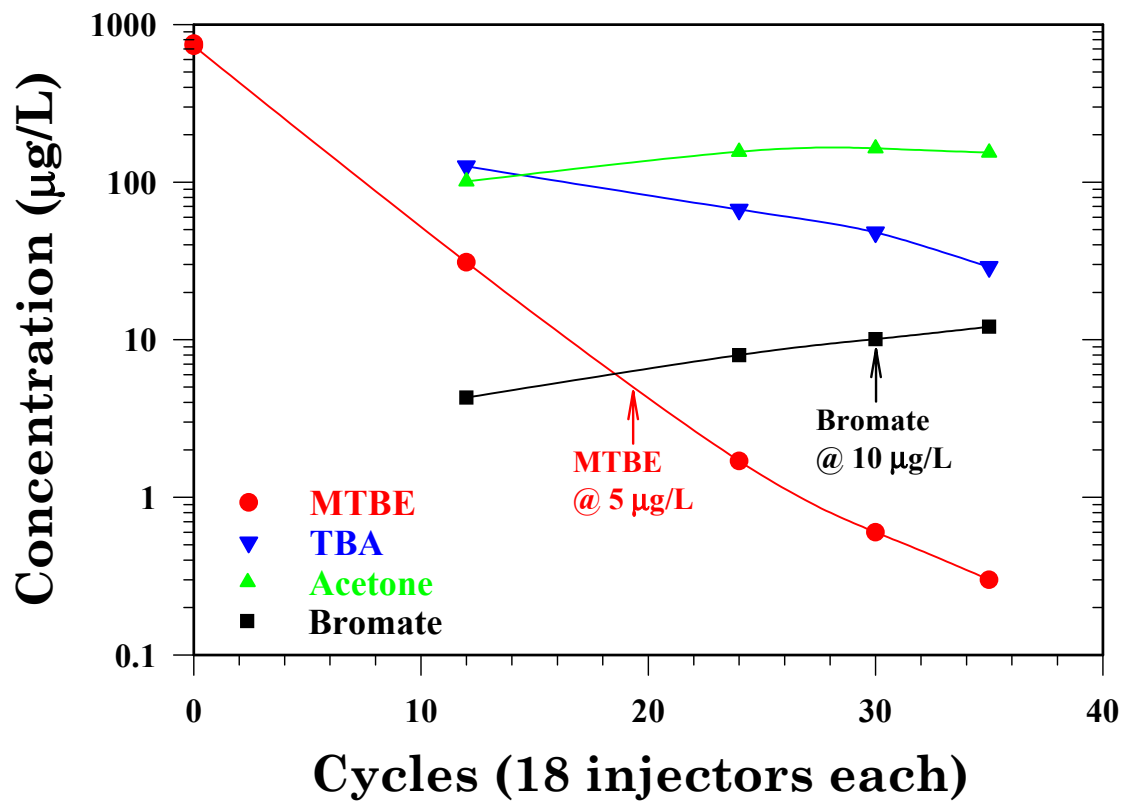


Figure 3-1. Destruction / Formation Curves for HiPOx Study at Port Hueneme (Test 1).

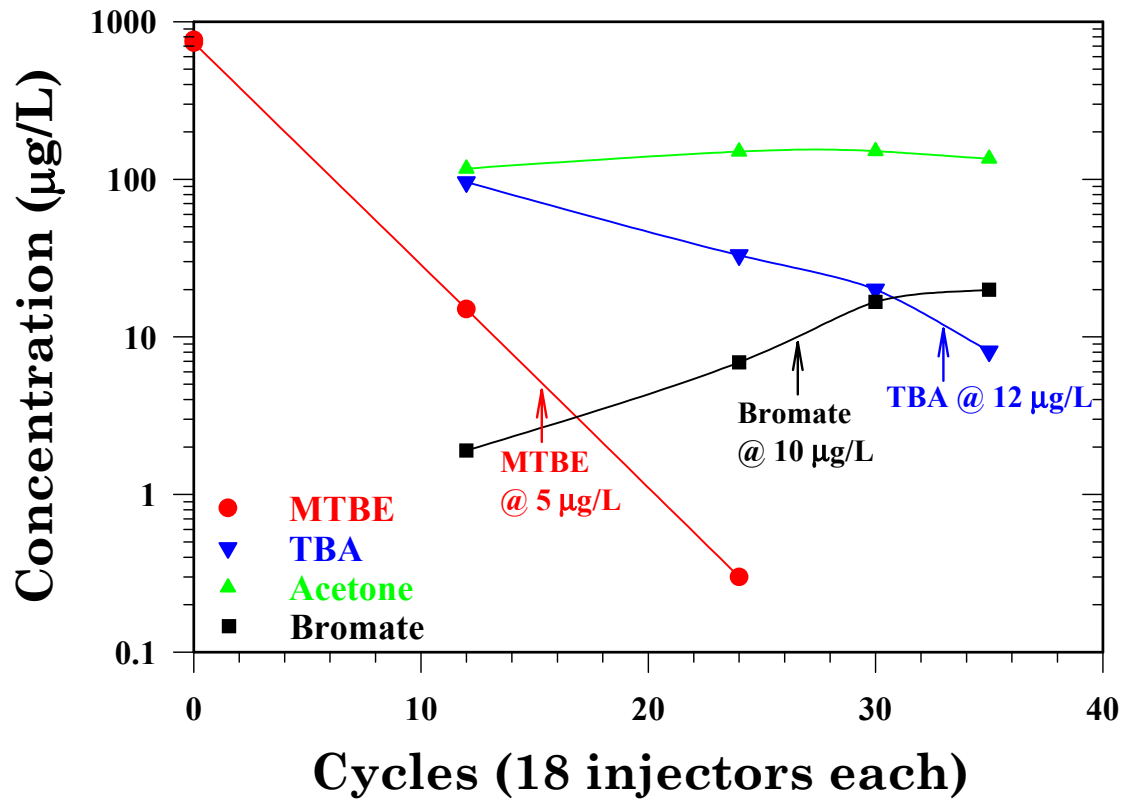


Figure 3-2. Destruction / Formation Curves for HiPOx Study at Port Hueneme (Test 2).

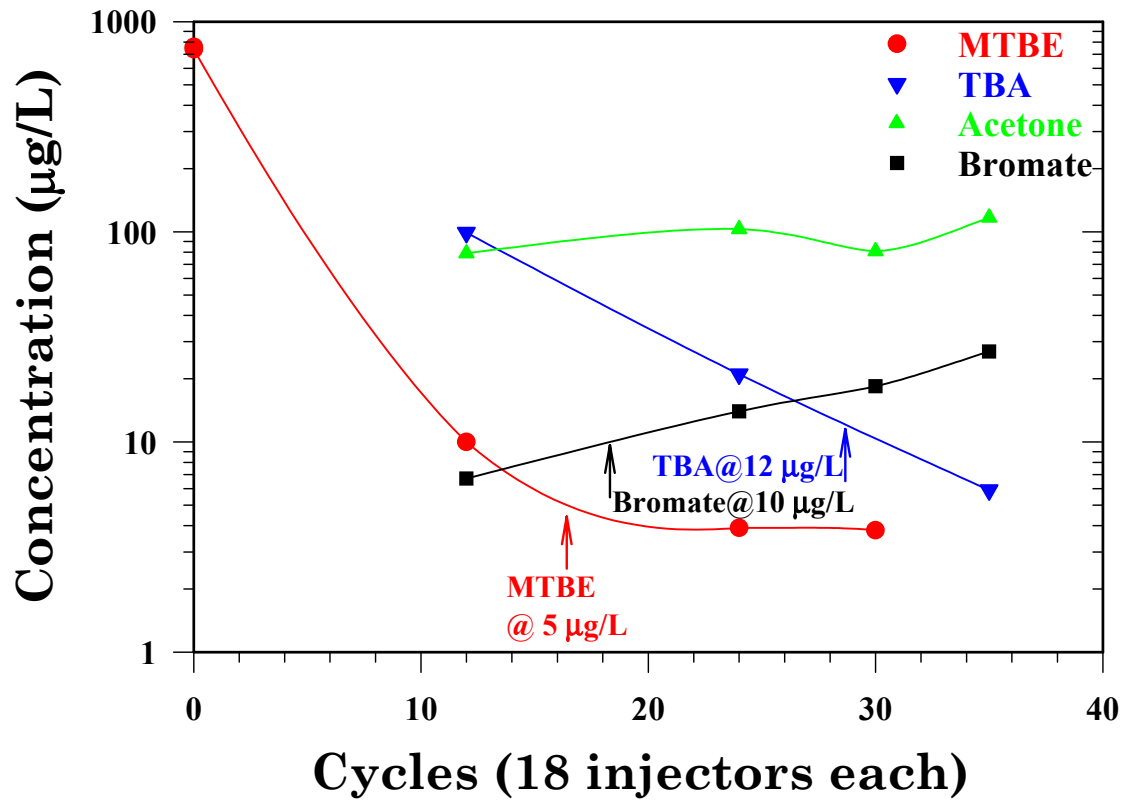


Figure 3-3. Destruction / Formation Curves for HiPOx Study at Port Hueneme (Test 3).

For the first run where the effluent TBA was above the regulatory limit, one of the two influent samples had a estimated TBA concentration of 11 µg/L. Also, for the second run, one of the two influent samples had a bromate concentration of 2.6 µg/L. These data raise questions as to whether all of the TBA or bromate in the system were formed from the oxidation process, or whether they were present in the influent water. TBA could have come from the natural breakdown of MTBE in the subsurface; however, it is more difficult to explain why bromate was present in the anoxic groundwater.

The location (number of cycles) where bromate reached 10 µg/L was estimated to be 30, 26, and 18 cycles (Figures 3-1, 3-2, and 3-3, respectively), with an average of 25 cycles (450 injectors). At these points, MTBE was below its regulatory limit of 5 µg/L, but TBA was above its regulatory limit of 12 µg/L for all three runs, and acetone was present at concentrations above 100 µg/L. Therefore, at no point was the system fully successful in treating this atypical water that represented a challenging scenario for bromate formation.

Figure 3-4 shows the three runs averaged together with the standard deviations plotted as error bars. The results show the same pattern as that discussed above. The MTBE was removed quickly, reaching the regulatory limit of 5 µg/L after 18 cycles (450 injectors). The average TBA concentration remained above its regulatory limit of 12 µg/L throughout the reactor, although the error bars on the final effluent samples are large, reaching below 12 µg/L. The bromate concentration reached its regulatory limit of 10 µg/L after 25 cycles (450 injectors). Also, the acetone concentrations remained relatively high.

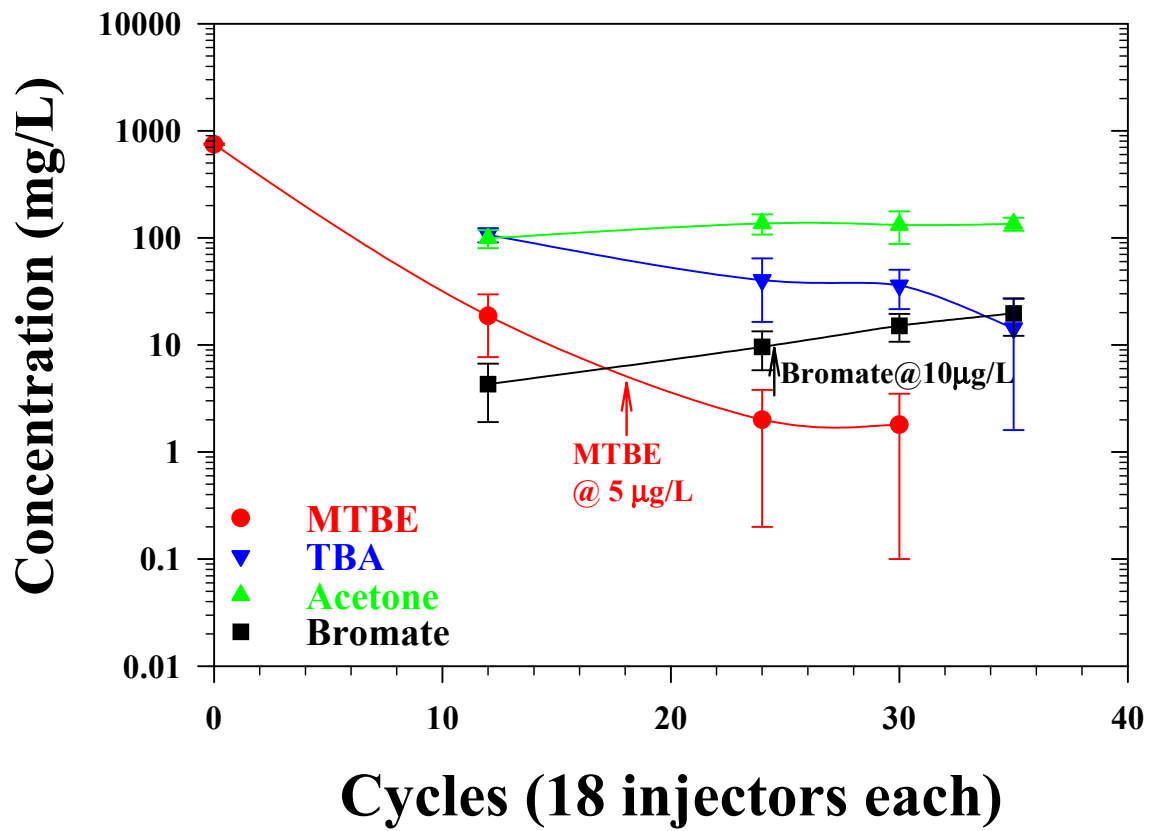


Figure 3-4. Combined Destruction/Formation Curves with Standard Deviations for HiPOx Study at Port Hueneme (Tests 1-3).

3.3 Bromide/bromate modeling

Although bromate was not successfully controlled in this water, it is possible to calculate the bromate formation for this water at hypothetically lower influent bromide levels. That is, assuming that all other water parameters and operational parameters remain the same, a calculation can be made to determine the influent bromide concentration that would result in an effluent bromate concentration of 10 µg/L. The formation of bromate is, in its simplest form, a reaction of bromide and hydroxyl radical.



It can be further assumed that in this oxidative system there is no reverse reaction. Therefore, the formation of bromate can be expressed as

$$d[\text{BrO}_3^-]/dt = k [\text{Br}^-] [\bullet\text{OH}] \quad \text{Eq. 5}$$

Because this system continually replenished ozone by using 630 injector ports, it is safe to say that if the system was operated in a similar dosing situation (Table 1-1), the concentration of hydroxyl radicals would be relatively stable over the reactor, and would be very similar to other hypothetical Port Hueneme groundwaters (where only the bromide concentration would change), regardless of the chosen influent bromide concentration. Therefore, bromide would be the only parameter that impacts the formation of bromate from one hypothetical Port Hueneme water to another under these operating conditions. By also assuming that the amount of bromate formed is insignificant when compared to the concentration of bromide, the bromide concentration remains constant over the reactor. Therefore, the rate of bromate formation is constant, and the integration results in a linear relationship. This linear relationship (shown below) can be utilized to calculate the influent bromide concentration that would result in an effluent bromate concentration of 10 µg/L in this water. This is done in Table 3-5 for each run. An implied assumption is that the hypothetical influent bromide concentration is still high enough not to be influenced by losses to the formation of bromate, as assumed in the original development. Since the hypothetical influent bromide concentrations range from 0.48 mg/L to 1.07 mg/L, and the final bromate concentration is set at 10 µg/L, this appears to be a safe assumption.

$$\text{Hypothetical influent bromide (mg/L)} = \frac{(1.3 \text{ mg/L bromide}) \cdot (10 \text{ µg/L bromate in effluent})}{(\text{Experimental effluent bromate conc., µg/L})} \quad \text{Eq. 6}$$

Table 3-5. Hypothetical Influent Bromide Concentration That Would Result in 10 mg/L of Bromate in the Effluent Water for 35 cycles.

Run / Test Number	Effluent Bromate Concentration from Experiment (µg/L)*	Hypothetical Influent Bromide Concentration that would Result in 10 µg/L of Bromate in the Effluent (mg/L)
1	12.1	1.07 [#]
2	19.9	0.63
3	27.0 ^E	0.48
Average of Runs 2 & 3	23.4	0.56

* Influent bromide concentration = 1.3 mg/L for all runs.

However, effluent contained TBA above its regulatory limit.

E = Estimated, outside of calibration range.

To determine an influent bromide concentration that will result in the achievement of all regulatory goals, it is not appropriate to use the data from the first run because the effluent TBA concentration was above its regulatory limit. Apparently, the system in Run 1 needed higher hydroxyl radical doses to further destroy the TBA. However, this would also have resulted in higher ozone concentrations, and hence, higher bromate formation. Because of this, the following discussion will only concern Runs 2 and 3.

The calculations for Runs 2 and 3 show that to achieve a bromate concentration of 10 µg/L, the influent bromide concentration would have to be 0.63 and 0.48 mg/L, respectively. The average of these two is 0.56 mg/L. Therefore, if all the operational and water quality parameters other than influent bromide remained the same, this HiPOx system could have treated this water if it contained less than 0.56 mg/L of bromide in the influent, without violating any of the water quality regulations, including bromate. Because 0.56 mg/L of bromide is extremely high for a typical source water, these calculations suggest that the HiPOx system, as operated here, is able to control bromate formation in the presence of high bromide concentrations, as theorized. It should be noted that this modeling effort made a number of simplifying assumptions that may not be entirely correct for other waters or operating conditions. Any future application of this technology would have to be piloted with the source water in question.

4 Conclusions

The results of this study were a function of the uniqueness of the feed water which represented a very challenging scenario for bromate formation/control. The high influent bromide concentrations (1.3 mg/L) necessitated operating under unusual conditions where ozone was injected at 630 separate ozone injector ports in series. The HiPOx process achieved greater than a 99.87 percent reduction in MTBE concentration and easily met the treatment goal of reducing the concentration of MTBE to below 5 µg/L. However, significant concentrations of MTBE degradation intermediates and oxidation by-products were present in the final effluent. TBA was produced early during the chemical oxidation process. Its concentration was diminished by further oxidation, reaching below its regulatory limit of 12 µg/L in two of the three runs. Acetone was generated and a sizable percentage was left unoxidized in the final effluent (>100 µg/L). Bromate concentrations increased with the number of reactor cycles, and the final effluent concentrations exceeded the drinking water standard of 10 µg/L for all three runs. Bromate formation was controlled up to 330 injection ports in all three runs. At this point, MTBE was reduced to below its target concentration of 5 µg/L, but TBA was above its regulatory target of 12 µg/L. Therefore, the HiPOx technology, as operated, effectively destroyed MTBE, but the effluent water quality did not conform to drinking water standards due to by-product formation.

Using a number of simplifying assumptions, it was calculated that if all the operational and water quality parameters other than influent bromide remained the same, this HiPOx system would have been able to meet all regulatory limits, including bromate, if the influent water at this site contained less than 0.56 mg/L of bromide. Because 0.56 mg/L of bromide is extremely high for a typical source water, these calculations suggest that the HiPOx system is able to control bromate formation in the presence of high bromide concentrations, as theorized. It is quite possible that the results of this study will allow for modifications to the HiPOx experimental unit that would improve performance to the point of controlling MTBE, its oxidation byproducts, and bromate at this location. More research is warranted. Because of the importance of water quality on final effluent quality, any future application of this technology would have to be piloted with the source water in question.

5 References

Bader, H, Sturzenegger, V, and Hoigné, J (1988) “Photometric Method for the Determination of Low Concentrations of Hydrogen Peroxide by the Peroxidase Catalyzed Oxidation of N,N-Diethyl-p-phenylenediamine (DPD),” *Water Research*, 22:9:1109-1115.

Connick, RE (1947) “The Interaction of Hydrogen Peroxide and Hypochlorous Acid in Acidic Solutions Containing Chloride Ion,” *Journal ACS*, 69:6:1509-1514.

Held, AM, Halko, DJ, and Hurst, JK (1978) “Mechanisms of Chlorine Oxidation of Hydrogen Peroxide,” *Journal ACS*, 100:18:5732-5740.

Sengupta, C, Helz, GR, Getz, JW, Higgins, P, Peterson, JC, Sigleo, AC, Sugam, R (1978) “Survey of Chlorine Analytical Methods Suitable for the Power Industry,” Electric Power Research Institute, EPRI-EA-929.

Summers, RS, Hooper, SM, Shukairy HM, Solarik, G, and Owen, DM (1994) “Assessing DBP Yield under Uniform Conditions,” *Journal AWWA*, 88:6:80.

6 Appendix A:

HiPOx Advanced Oxidation Treatment at Port Hueneme and Other Sites

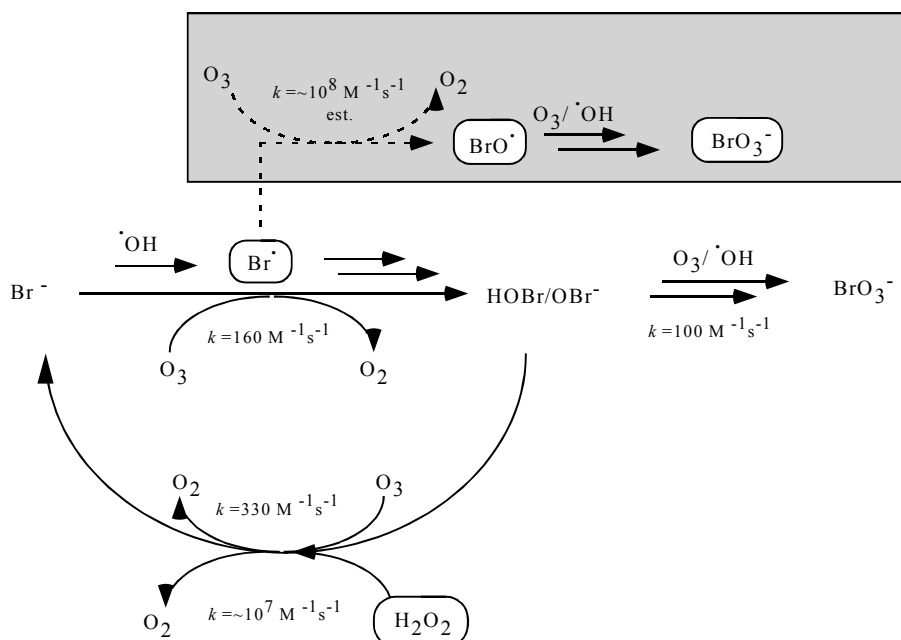
(As Supplied by: Applied Process Technology, Inc.)

This Appendix explains how the HiPOx technology controls the formation of bromate in bromide-containing waters, comments on the results obtained during the EPA demonstration at Port Hueneme, and provides additional examples of sites where HiPOx has destroyed VOC's and controlled the formation of bromate to below the regulatory limits for drinking water. This Appendix also provides examples of real-world applications in which HiPOx has destroyed TBA to below detectable levels and provides data pertaining to the reduction of acetone, an oxidation by-product that forms during the destruction of MTBE and TBA.

How HiPOx Controls Bromate Formation

The bromate control process employed in the HiPOx technology is based on the chemistry reported by Urs von Gunten¹ (see Figure 6-1). HiPOx is designed to minimize the amount of molecular ozone in solution by increasing the number of ozone injectors the system utilizes this has been patented by APT. By minimizing the amount of ozone in solution, less ozone is available to oxidize hypobromite (HOBr/OBr⁻) before hydrogen peroxide reduces hypobromite back to bromide. The reduction of hypobromite by hydrogen peroxide ($k = 1 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$) is orders of magnitude faster than the oxidation of hypobromite to bromate by ozone ($k = 100 \text{ M}^{-1} \text{ sec}^{-1}$).

Figure 6-1. Bromate Control Chemistry



¹ U. von Gunten and Y. Oliveras, *Envir. Sci. and Tech.*, 32, 63 (1998); U. von Gunten, Y. Oliveras, *Wat. Res.*, 31, 900 (1997); W.R. Haag, and J. Hoigne, *Envir. Sci. and Tech.*, 17, 261(1983); U. von Gunten, J. Hoigne and A. Bruchet, *Water Supply*, 13, 45 (1995)

Bromate Control at Port Hueneme, CA

During screening tests conducted at Port Hueneme, the HiPOx system utilized 216, 432 and finally 504 ozone injectors to treat the site's water. Analytical data from these test runs indicated that effluent bromate concentrations were 9.7, 7.0 and 5.2 µg/L, respectively. Therefore, in order to control bromate to less than 5 µg/L during the actual demonstration, it was determined that 632 ozone injectors would be required. During the screening tests conducted by APT, all bromate analyses were performed by Clinical Laboratory of San Bernardino (Clinical Lab) and VOC analyses were performed by Alpha Analytical, Inc.

During the actual demonstration, VOC destruction and bromate formation were measured by laboratories selected by the EPA. However during Run #3, a split sample was analyzed by both EPA-selected and APT-selected laboratories for comparison. Analytical data from all three runs, including the split taken during Run #3, are shown in Table 6-1 below.

Table 6-1. Comparison of Results on Run #3

	Concentrations (µg/L)							
	EPA Labs						APT Lab	
	Run #1		Run #2		Run #3		Run #3 ^{1,2}	
Component	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
MTBE	744	0.3	751	<1	740	<1	750	0.57
TBA	11	29	<40	8.1	<40	5.9	11	7.6
Acetone	<40	154	<40	135	<40	117	<20	140
Bromide	1,300	1,300	1,200	1,300	1,300	1,300	1,400	1,390
Bromate	<1	12.1	<2	19.9	<2	27	<5	<5

¹ VOC's Analysis conducted by Alpha Analytical, Inc., 255 Glendale Ave., Suite 21, Sparks, Nevada. On Run #3, sample splits submitted by Applied Process Technology.

² Bromides and Bromates Analysis conducted by Clinical Laboratory of San Bernardino Inc., 21881 Barton Rd., Grand Terrace, CA 92313. On Run #3 sample splits submitted by Applied Process Technology.

As shown in Table 6-1, VOC data reported for Run #3 by the EPA laboratories were very similar to those reported by Alpha Analytical. The bromide concentrations reported by both the EPA labs and Clinical Lab were also in very good agreement. However, the effluent bromate values reported by the EPA labs and Clinical Lab differed. The EPA labs reported influent and effluent bromide concentrations of 1,300 µg/L and an effluent bromate concentration of 27.0 µg/L. Clinical Lab reported an effluent bromate concentration below the detection limit of 5 µg/L, which would indicate the HiPOx system successfully controlled the formation of bromate. If the bromate values reported by the EPA labs are correct, then the HiPOx system would require additional injectors in order to control the formation of bromate.

Bromate Control at other Sites

Bromate control is a characteristic unique to the HiPOx technology. APT has conducted several trials demonstrating control of bromate formation and has placed a commercial HiPOx unit that treats contaminated ground water to produce drinking water. The locations of these sites, the contaminant destruction achieved, and the bromate results are listed in Table 6-2.

The site trials in Table 6-2 were conducted between 1998 and 2002 using a variety of source water. The system that operated at the LADWP Headworks site ran continuously for four weeks at 1,000 gallons per minute. Samples were taken every 6 hours to demonstrate reproducibility and scalability of the HiPOx technology.

The South Lake Tahoe Commercial HiPOx system is operating continuously, producing drink water for the South Lake Tahoe Public Utility District at 800 gallons per minute.

TBA Destruction and Acetone Reduction

Drinking water applications sometimes require complete destruction of TBA and acetone depending on the state regulations. Complete destruction of these constituents was not required during the Port Hueneme demonstration but has been achieved at other HiPOx installations.

The HiPOx technology has destroyed TBA concentrations to below detectable levels at a number of sites. Data from two of these sites are provided in Table 6-3. Both sites are commercial installations.

Acetone forms during destruction of MTBE and TBA by the HiPOx system, but it can be destroyed as oxidation continues. At sites where acetone formation during destruction of other contaminants is significant, then it becomes more cost effective to reduce acetone using a bioreactor on the effluent of the HiPOx system. This method, HiPOx followed by a bioreactor, has been used to control acetone at several sites treated by HiPOx including the two sites detailed in Table 6-3. Acetone formation and biodegradation data from these sites, both post-HiPOx and post-bioreactor, are also provided in Table 6-3.

Table 6-2. Bromate Control at other Locations with HiPOx Technology

Location (Month/Year)	Number Injectors	Sample Location	MTBE	Contaminant Concentration (ppb)					
				TBA	Acetone	PCE	TCE	Bromide	Bromate
Southern California (8/98)	18	Influent	54	<100	<10	NA	NA	321	<5
Southern California (8/98)	18	Effluent	0.86	<100	<10	NA	NA	318	5.4
Southern California (11/98)	162	Influent	980 ¹	<100	<10	NA	NA	1033 ²	<5
Southern California (11/98)	162	Effluent	0.58	40	120	NA	NA	1025	7.0
Headworks (4/99)	18	Influent	NA	NA	NA	50	100	211	<5
Headworks (4/99)	18	Effluent	NA	NA	NA	2.6 ³	<0.5	210	<5
South Lake Tahoe (4/00)	12	Influent	11	<10	<10	NA	NA	34	<1
South Lake Tahoe (4/00)	12	Effluent	<0.2	<10	<10	NA	NA	35	<3
New York (1/01)	18	Influent	6.6	<20	<5	10	2.6	120	<5
New York (1/01)	18	Effluent	<0.5	<20	<5	<0.5	<0.5	NA	<5
New York (1/01)	18	Influent	28 ⁴	<20	<5	11	2.5	100	NA
New York (1/01)	18	Effluent	<0.5	<20	<5	<0.5	<0.5	NA	<5
New York (1/01)	18	Influent	90 ⁵	<20	<5	11	2.6	100	NA
New York (1/01)	18	Effluent	<0.5	<20	7.8	<0.5	<0.5	NA	<5
South Lake Tahoe (7/02) ⁶	16	Influent	0.2	<10	<10	NA	NA	10	<1
South Lake Tahoe (7/02) ⁶	16	Effluent	<0.2	<10	<10	NA	NA	9	<3

¹ The concentration of 980 ppb MTBE was achieved by spiking the Raw Southern California Water which contained 54 ppb MTBE.

² The concentration of 1033 ppb bromide was achieved by spiking the Raw Southern California Water which contained 321 ppb bromide with additional sodium bromide.

³ The requirement was to achieve an effluent concentration of <3.0 ppb.

⁴ The concentration of 28 ppb MTBE was achieved by spiking the New York Raw Water which contained 6.6 ppb MTBE with additional MTBE.

⁵ The concentration of 90 ppb MTBE was achieved by spiking the New York Raw Water which contained 6.6 ppb MTBE with additional MTBE.

⁶ Operating at 800 gpm.

Table 6-3. TBA Destruction and Acetone Reduction at other Locations with HiPOx Technology (and Bioreactor Technology).

Location (Month/Year)	Contaminant Concentration (ppb)			
	Sample Location	MTBE	TBA	Acetone
Tustin, CA (March 2002)	Influent	17,000	200	110
Tustin, CA (March 2002)	HiPOx Effluent	<2	<4	680
Tustin, CA (March 2002)	Bioreactor Effluent	<2	<4	8.2*
Turlock, CA (May 2002)	Influent	3,400	220	<200
Turlock, CA (May 2002)	HiPOx Effluent	<0.5	<5	110
Turlock, CA (May 2002)	Bioreactor Effluent	<0.5	<5	<10

*Trip blank acetone: 5.7ppb.