7. PEROXONE (OZONE/HYDROGEN PEROXIDE)

Advanced oxidation processes generate highly reactive hydroxyl free radicals to oxidize various compounds in the water. As discussed in Chapter 3, hydroxyl radicals are produced during the spontaneous decomposition of ozone. By accelerating the ozone decomposition rate, the hydroxyl radical concentration is elevated, which increases the oxidation rate. This procedure increases the contribution of indirect oxidation over direct ozone oxidation as discussed in Chapter 3.

Several methods have been used to increase ozone decomposition and produce high concentrations of hydroxyl radicals. One of the most common of these processes involves adding hydrogen peroxide to ozonated water, a process commonly referred to as peroxone.

The Metropolitan Water District of Southern California (MWDSC) conducted extensive research into the use of peroxone to control organics and oxidize taste and odor compounds (e.g., geosmin and 2-methylisoborneol [MIB]) while providing sufficient levels of molecular ozone to guarantee CT values and primary disinfection. While this chapter focuses on peroxone as a disinfectant, similar results are expected from other advanced oxidation processes such as ozone plus UV, ozone at high pH, hydrogen peroxide plus UV, and other combinations.

A key issue with the use of peroxone as a disinfection process is that the process does not provide a measurable disinfectant residual. It is therefore not possible to calculate CT similar to the use of other disinfectants. While no credit can be given for hydroxyl free radicals because it cannot be measured directly, some credit may be considered for any detected ozone in peroxone systems. Peroxone does provide pathogen inactivation, as discussed in this chapter, but equivalent CT values or methods of calculating equipment CT credits have not been established at the date of publication of this guidance document.

7.1 Peroxone Chemistry

The ozone decomposition cycle is similar to that discussed in Chapter 3. However, the added hydrogen peroxide or ultraviolet radiation accelerates the decomposition of ozone and increases the hydroxyl radical concentration. By adding hydrogen peroxide, the net production of hydroxyl free radicals is 1.0 mole hydroxyl radical per mole ozone.

Similar to the discussion of ozone in Chapter 3, oxidation in the peroxone occurs due to two reactions (Hoigné and Bader, 1978):

- Direct oxidation of compounds by aqueous ozone ($O_{3(aq)}$); and
- Oxidation of compounds by hydroxyl radicals produced by the decomposition of ozone.

The two oxidation reactions compete for substrate (i.e., compounds to oxidize). The ratio of direct oxidation with molecular ozone is relatively slow (10^{-5}-$10^{7}M^{-1}sec^{-1}$) compared to hydroxyl radical oxidation (10^{12}-$10^{14}M^{-1}sec^{-1}$), but the concentration of ozone is relatively high. On the other hand, the hydroxyl radical reactions are very fast, but the concentration of hydroxyl radicals under normal ozonation conditions is relatively small.

A key difference between the ozone and peroxone processes is that the ozone process relies heavily on the direct oxidation of aqueous ozone while peroxone relies primarily on oxidation with hydroxyl radical. In the peroxone process, the ozone residual is short lived because the added peroxide greatly accelerates the ozone decomposition. However, the increased oxidation achieved by the hydroxyl radical greatly outweighs the reduction in direct ozone oxidation because the hydroxyl radical is much more reactive. The net result is that oxidation is more reactive and much faster in the peroxone process compared to the ozone molecular process. However, because an ozone residual is required for determining disinfection CT credit, peroxone may not be appropriate as a pre-disinfectant.

The peroxone process utilizes oxidation by hydroxyl radicals. The oxidation potential of the hydroxyl radical and ozone are as follows:

$$OH + e^- \rightarrow OH^- \qquad E^0 = +2.8V$$

$$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O \qquad E^0 = +2.07V$$

$$O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^- \qquad E^0 = +1.24V$$

In addition to having an oxidation potential of hydroxyl radical higher than ozone, the hydroxyl radical is also much more reactive approaching the diffusion control rates for solutes such as aromatic hydrocarbons, unsaturated compounds, aliphatic alcohols, and formic acid (Hoigné and Bader, 1976).

7.1.1 Oxidation Reactions

Because the radical oxidation is much more effective than direct oxidation with ozone, it has been used extensively to treat difficult to oxidize organics such as taste and odor compounds and chlorinated organics (e.g., geosmin, MIB, phenolic compounds, trichloroethylene [TCE], and perchloroethylene [PCE]).

Neither ozone nor peroxone significantly destroys TOC. Peroxone will oxidize the saturated organics and produce byproducts similar to those found in ozonation; namely, aldehydes, ketones, peroxides, bromate ion, and biodegradable organics (MWDSC and JMM, 1992). However, with peroxone, the

biodegradibility of the water (not the organic compounds) increases, rendering "a portion of the TOC" amenable to removal in biologically active filters.

Peroxone has found a niche in oxidizing difficult-to-treat organics, such as taste and odor compounds including geosmin and MIB (Pereira et al., 1996; Ferguson et al., 1990). In addition, peroxone and other advanced oxidation processes have been shown to be effective in oxidizing halogenated compounds such as 1,1-dichloropropene, trichloroethylene, 1-chloropentane, and 1,2-dichloroethane (Masten and Hoigné, 1992; Aieta et al., 1988; Glaze and Kang, 1988). Hydroxyl radicals will react with all these compounds plus refractory aliphatics such as alcohols and short-chain acids (Chutny and Kucera, 1974).

The optimum peroxide:ozone dose ratio to maximize hydroxyl radicals' reaction rate can be determined for a specific oxidation application. For instance, the optimum peroxide:ozone dose ratio for TCE and PCE oxidation in a ground water was determined to be 0.5 by weight (Glaze and Kang, 1988). Tests showed that TCE required lower ozone dosages for the same percentage removal compared to PCE.

LADWP conducted pilot studies and operated a 2,000 gpm full scale AOP demonstration plant in 1995. The peroxide:ozone dose ratio used was 0.5 to 0.6. Ground water containing up to 447 mg/L TCE and 163 mg/L PCE was treated to below the respective MCLs. However, bromate ion was formed in excess of the 0.010 mg/L MCL (Karimi et al., 1997).

7.1.2 Reactions with Other Water Quality Parameters

As with ozone alone, pH and bicarbonate alkalinity play a major role in peroxone effectiveness (Glaze and Kang, 1988). This role is primarily related to bicarbonate and carbonate competition for hydroxyl radical at high alkalinity and carbonate competition for hydroxyl radical at high pH levels. Also, excessive peroxide can also limit the formation of the hydroxyl radical and reduce the effectiveness of peroxone.

Turbidity alone does not appear to play a role in peroxone effectiveness nor does peroxone appear to remove turbidity. Tobiason et al. (1992) studied the impact of pre-oxidation on filtration and concluded that the pre-oxidation did not improve effluent turbidities, but did appear to increase filter run times because of lower head loss or delayed turbidity breakthrough. Filter effluent turbidities were similar for no-oxidant and pre-oxidant trains.

7.1.3 Comparison between Ozone and Peroxone

The key difference between ozone and peroxone is in the primary oxidation mode; that is, direct oxidation or hydroxyl radical oxidation. The reactivities of these compounds create a different effect in the reactions with water constituents and, thus, disinfection effectiveness. Table 7-1 summarizes the

key differences between ozone and peroxone as they relate to their application in drinking water treatment.

Table 7-1. Comparison between Ozone and Peroxone Oxidation

Process	Ozone	Peroxone
Ozone decomposition rate	"Normal" decomposition producing hydroxyl radical as an intermediate product	Accelerated ozone decomposition increases the hydroxyl radical concentration above that of ozone alone.
Ozone residual	5-10 minutes	Very short lived due to rapid reaction.
Oxidation path	Usually direct aqueous molecular ozone oxidation	Primarily hydroxyl radical oxidation.
Ability to oxidize iron and manganese	Excellent	Less effective.
Ability to oxidize taste and odor compounds	Variable	Good, hydroxyl radical more reactive than ozone.
Ability to oxidize chlorinated organics	Poor	Good, hydroxyl radical more reactive than ozone.
Disinfection ability	Excellent	Good, but systems can only receive CT credit if they have a measurable ozone residual.
Ability to detect residual for disinfection monitoring	Good	Poor. Cannot calculate CT value for disinfection credit.

7.2 Generation

The peroxone process requires an ozone generation system as described in Chapter 3 and a hydrogen peroxide feed system. The process involves two essential steps: ozone dissolution and hydrogen peroxide addition. Hydrogen peroxide can be added after ozone (thus allowing ozone oxidation and disinfection to occur first) or before ozone (i.e., using peroxide as a pre-oxidant, followed by hydroxyl radical reactions) or simultaneously. Addition of hydrogen peroxide following ozone is the best way to operate, however a system cannot obtain a CT credit unless the ozone residual is sufficiently high.

There are two major effects from the coupling of ozone with hydrogen peroxide (Duguet et al., 1985):

- Oxidation efficiency is increased by conversion of ozone molecules to hydroxyl radicals; and
- Ozone transfer from the gas phase to the liquid is improved due to an increase in ozone reaction rates.

The most efficient operation is to add ozone first to obtain CT disinfection credit, followed by peroxide for hydroxyl radical oxidation.

Ozonation can be described as occurring in two stages. In the first stage, ozone rapidly destroys the initial oxidant demand present, thereby enhancing the ozone transfer rate into solution from the gas phase. Addition of hydroxyl free radicals to the first stage should be minimized since the hydrogen peroxide competes with ozone-reactive molecules (i.e., initial demand) for the ozone present. In the second stage, organic matter is oxidized, taking place much slower than in the first stage. Adding hydrogen peroxide during the second stage makes it possible to raise the overall oxidation efficiency, since the reaction of hydrogen peroxide with ozone produces hydroxyl radicals enhancing chemical reaction rates. In practice, the addition of hydrogen peroxide to the second stage of ozonation can be achieved by injecting the hydrogen peroxide into the second chamber of an ozone contactor (Duguet et al., 1985). The most efficient operation is to use ozone first to obtain CT credit and peroxone second for micropollutant destruction.

Energy consumption of the peroxone process includes that for ozone generation and application, plus for metering pumps to feed peroxide. The peroxide addition step does not require any more training from an operator than any other liquid chemical feed system. Systems should be checked daily for proper operation and for leaks. Storage volumes should also be checked daily to ensure sufficient peroxide is on hand, and to monitor usage.

7.3 Primary Uses and Points of Application

Peroxone is used for oxidation of taste and odor compounds, and oxidation of synthetic organic compounds. Peroxone is also used for the destruction of herbicides (e.g., atrazine), pesticides, and VOCs. Peroxone is applied at points similar to ozone for oxidation. Addition of ozone first and hydrogen peroxide second is the better way to operate. Alternatively, hydrogen peroxide can be added upstream of ozone.

7.3.1 Primary Uses

7.3.1.1 Taste and Odor Compound Oxidation

Peroxone is used to remove taste and odor causing compounds because many of these compounds are very resistant to oxidation, even ozone-oxidation. More recently, significant attention has been given to tastes and odors from specific compounds such as geosmin, 2-methyliosborneol (MIB), and chlorinated compounds. Studies at MWDSC demonstrated the effectiveness of peroxone to remove geosmin and MIB during water treatment (Ferguson et al., 1990; Ferguson et al., 1991; Huck et al., 1995).

7.3.1.2 Synthetic Organic Compound Oxidation

Peroxone and other advanced oxidation processes have been shown to be effective in oxidizing halogenated compounds such as 1,1-dichloropropene (DCPE), TCE, 1-chloropentane (CPA), and 1,2-

dichloroethane (DCA) (Masten and Hoigné, 1992; Aieta et al., 1988; Glaze and Kang, 1988). The hydroxyl radicals formed react with all these compounds plus refractory aliphatics, such as alcohols and short-chain acids (Chutny and Kucera, 1974).

7.3.2 Points of Application

The peroxone process is applied at points similar to ozone for oxidation as discussed in Chapter 3. Importantly, peroxone addition should be after settling and prior to biological filtration. It is important to add hydrogen peroxide after the initial ozone demand is consumed to avoid hydroxyl free radical competition with the initial ozone demanding constituents.

7.3.2.1 Impact on Other Treatment Processes

Peroxide addition impacts other processes at the water treatment facility. These impacts include:

- The use of hydroxyl free radicals generates BDOC, which can cause biological growth in distribution systems if not reduced during biologically active filtration. When peroxide addition is placed before filters, it impacts the filters by increasing biological growths and increasing backwash frequency (depending on the level on BDOC produced).
- Hydroxyl free radicals are strong oxidants that interfere with addition of other oxidants, such as chlorine, until the ozone residual is quenched.
- The oxidation of iron and manganese by hydroxyl free radicals generates insoluble oxides that should be removed by sedimentation or filtration. This also may impact the filters by increasing the load on the filters and increasing backwash frequency.

The reader is referred to the *Microbial and Disinfection Byproduct Simultaneous Compliance Guidance Document* (currently in production) for additional information regarding the interaction between oxidants and other treatment processes.

7.4 Pathogen Inactivation

Both peroxone and other advanced oxidation processes have been proven to be equal or more effective than ozone for pathogen inactivation. Disinfection credits are typically described in terms of CT requirements. Because peroxone leaves no measurable, sustainable residual, calculation of an equivalent CT for disinfection credit is not possible unless there is measurable ozone residual.

7.4.1 Inactivation Mechanism

Experiments have indicated that long contact times and high concentrations of hydrogen peroxide are required for bacteria and virus inactivation (Lund, 1963; Yoshe-Purer and Eylan, 1968; Mentel and Schmidt, 1973). Achieving a 99 percent inactivation of poliovirus required either a hydrogen peroxide dose of 3,000 mg/L for 360 minutes or 15,000 mg/L for 24 minutes. Based on these results, when the combination of ozone and hydrogen peroxide is used, the primary cause for pathogen inactivation is

attributed to ozone, specifically the mechanisms associated with the oxidation of pathogens by direct ozone reaction and hydroxyl radicals.

As described in Chapter 3, the mode of action of ozone on microorganisms is poorly understood. Some studies on bacteria suggest that ozone alters proteins and unsaturated bonds of fatty acids in the cell membrane, leading to cell lysis (Scott and Lesher, 1963; Pryor et al., 1983), while other studies suggest that ozone may affect deoxyribonucleic acid (DNA) in the cell (Hamelin and Chung, 1974; Ohlrogge and Kernan, 1983; Ishizaki et al., 1987). Virus inactivation was reported to be related to the attack of the protein capsid by ozone (Riesser et al., 1977). Little information was found discussing the mode of action of ozone on protozoan oocysts. However, a few researchers have suggested that ozone causes the oocyst density to decrease and alters the oocyst structure (Wickramanayake, 1984; Wallis et al., 1990).

The debate continues regarding the primary mode of action for hydroxyl free radicals. Some researchers believe that ozone disinfection is a result of direct ozone reaction (Hoigné and Bader, 1975; Hoigné and Bader, 1978), while others believe that the hydroxyl radical mechanism for disinfection is the most important mechanism (Dahi, 1976; Bancroft et al., 1984). Studies using ozone-hydrogen peroxide have shown that disinfection of *E. coli* is less effective as the peroxide to ozone ratio increases to above approximately 0.2 mg/mg (Wolfe et al., 1989a; Wolfe et al., 1989b). The decrease in disinfection was believed to be cause by lower ozone residuals associated with higher peroxide to ozone ratios, which indicates that direct ozone reaction is an important mechanism for pathogen inactivation.

7.4.2 Environmental Effects

Although the chemistry of the peroxone process is still not completely understood, optimal production of the hydroxyl radical appears to depend on the pH, ozone concentration, ratio of hydrogen peroxide to ozone, contact time, and water composition (Glaze et al., 1987).

7.4.2.1 Competing Chemical Reactions

One disadvantage of the peroxone process is that it involves radical intermediates that are subject to interference from substances that react with hydroxyl radical, decreasing the effectiveness of the process. Alkalinity, bicarbonate, and pH play a major role in the effectiveness of hydroxyl free radicals. This effect is primarily related to bicarbonate competition for hydroxyl radical at high alkalinity and carbonate competition for hydroxyl radical at pH levels higher than 10.3 (see Chapter 3). Lowering the alkalinity prior to the application of the peroxone process may be necessary for water that has a high bicarbonate level. In addition to carbonate and bicarbonate, organic constituents of humic substances have also been found to react with the hydroxide radical (Glaze, 1986).

7.4.2.2 Ratio of Hydrogen Peroxide and Ozone

A study conducted at MWDSC indicated that the performance of peroxone is greatly dependent upon the peroxide:ozone ratio (Wolfe et al., 1989b). Results from previous studies at MWDSC suggested that the optimal ratio for disinfection was less than or equal to 0.3. One of the primary objectives of the 1989 study was to optimize further the process for disinfection by altering peroxide:ozone ratios and contact times. Results from the study indicated that peroxone at a 0.2 ratio of peroxide:ozone was comparable to ozone for disinfection of indicator organisms and *Giardia muris* cysts, and that at higher ratios, disinfection decreased because ozone decreased.

7.4.3 Disinfection Efficacy and Pathogen Inactivation

Recent studies have indicated that the disinfection effectiveness of peroxone and ozone are comparable (Wolfe et al., 1989b; Ferguson et al., 1990; Scott et al., 1992). A study conducted by Ferguson et al. (1990) compared the pathogen inactivation capability of peroxone and ozone using MS-2 and f2 coliphages as well as *E. coli.* and heterotrophic plate count (HPC) bacteria. The f2 and MS-2 coliphages were comparable in their resistance to ozone and peroxone. No differences in the amounts of MS-2 or f2 inactivation were apparent when the peroxide:ozone ratio was varied from 0 to 0.3. Results of the *E. coli.* and HPC studies showed that peroxone and ozone also had comparable results in regards to bacteria inactivation.

Table 7-2 lists CT values derived for inactivation of *Giardia muris* cysts by ozone and peroxone from another study conducted by MWDSC. The contact times used for calculating the CT values were based on 10% and 50% breakthrough of tracer compounds in the contactor. Ozone concentrations used for CT were based on the ozone residual and half of the residual and dose. The results of this study suggest that peroxone is slightly more potent than ozone based on the fact that CT values for ozone were greater than for peroxone. However, because ozone decomposes more rapidly in the presence of hydrogen peroxide, higher ozone dosages may be necessary with peroxone to achieve comparable residuals. Moreover, the use of ozone residuals to calculate CT products for peroxone may not take into account other oxidizing species that may have disinfectant capabilities.

Table 7-2. Calculated CT Values (mg•min/L) for the Inactivation of *Giardia muris*

Inactivation	Ozone C_1T_1[a]	Ozone C_2T_2[a]	Peroxone[b] C_1T_1[a]	Peroxone C_2T_2[a]
90%	1.6	2.8	1.2	2.6
99%	3.4	5.4	2.6	5.2

Data obtained from Wolfe et al., 1989b. Results at 14°C.

[a] C_1, ozone residual; C_2 (ozone dose + ozone residual)/2; T_1 and T_2 time (in minutes) to reach 10 percent and 50 percent breakthrough, respectively

[b] The H_2O_2/O_3 ratio for all results was 0.2.

7.5 Disinfection Byproducts

The principal byproducts associated with peroxone are expected to be similar to those for ozonation and are listed in Table 3-9. Additional DBPs could form from reactions with hydroxyl radicals. Peroxone does not form halogenated DBPs when participating in oxidation/reduction reactions with NOM. However, if bromide ion is present in raw water halogenated DBPs may be formed. Similar to ozone, the principal benefit of using peroxone for controlling THM formation appears to be that it eliminates the need for pre-chlorination and allows lower doses of free chlorine or chloramines to be applied later in the process train after precursors have been removed by coagulation, sedimentation, and/or filtration and at lower doses. But peroxone does not reduce the DBPFP.

Based upon studies and findings involving peroxone, there is no beneficial lowering of THMs as long as free chlorine is utilized as a secondary disinfectant, unless the application of peroxone allows chlorine to be applied later in the process train to water containing reduced precursor concentrations. The MWDSC study found that the use of peroxone/chlorine resulted in THM concentrations 10 to 38 percent greater than the use of ozone/chorine. However, the THM concentrations of waters disinfected with peroxone/chloramines and ozone/chloramines were similar (Ferguson et al., 1990).

The use of peroxone as a primary disinfectant and chloramines as a secondary disinfectant can successfully control halogenated DBP formation if bromide ion is not present and adequate CT credit can be established. As with ozone, bromate ion formation is a potential concern with source waters containing bromide ions. The oxidation reaction of bromide ion (Br^-) to hypobromite ion (BrO^-) and bromite ion (BrO_2^-) and subsequently to bromate ion (BrO_3^-) occurs due to direct reaction with ozone, intermediate reactions can also occur through hydroxide radical mediated mechanisms if bromide is not present and adequate CT credit can be established (Pereira et al., 1996).

In general, peroxone produces more bromate ion than ozone when similar ozone residuals (CT credits) are achieved (Krasner et al., 1993). On the other hand, when the ozone dosage is kept constant, peroxone has tended to produce comparable amounts of bromate ion as ozone. Although peroxone produces hydroxyl radicals that can increase bromate ion formation, hydrogen peroxide may also reduce the hypobromite ion (produced initially during the ozonation of bromide) back to bromide ion.

A study by MWDSC evaluated the effectiveness of peroxone to control taste and odor, DBPs, and microorganisms (Ferguson et al., 1990). In attempting to optimize the hydrogen peroxide to ozone ratio (H_2O_2:O_3) and the contact time for the source water, the study found pre-oxidation of source waters followed by secondary disinfection with chloramines was an effective strategy for controlling concentrations of THMs and other DBPs. The study found that the two source waters disinfected with peroxone, with free chlorine as the secondary disinfectant, resulted in THM concentrations ranging from 67 to 160 µg/L. Conversely, using chloramines as a secondary disinfectant resulted in THM concentrations consistently below 3.5 µg/L (Ferguson et al., 1990).

However, if a short free chlorine contact time is applied after biological filtration and before ammonia addition to inactivate heterotrophic plate count bacteria in the effluent of the biologically active filter—THMs and other DBPs will be formed at higher concentrations than from post chloramination alone. Depending on the TOC and bromide ion concentration of the water, as well as the pH of chlorination, temperature, and reaction time, between 2 and 28 µg/L of TTHMs have been formed in experiments conducted at MWDSC (personal communication, 1998).

Bromate formation in conventional ozonation, and advanced oxidation processes combining ozone and hydrogen peroxide, were recently investigated at five water treatment plants in France. The source water bromide ion concentrations ranged from 35 to 130 µg/L. Bromate ion formation during the ozonation step varied from less than 2 to 42 µg/L. In general, advanced oxidation results in greater bromate ion concentrations when compared with conventional ozonation, provided the same ozone residual is maintained for both processes. However, lower concentrations of bromate ion result if the ozone dosage is kept constant between the two processes and the hydrogen peroxide dosage is increased (von Gunten et al., 1996). To reduce bromate ion formation potential, the proposed ozone contactor at Stone Canyon Filtration Plant includes three ozone application points instead of two (Stolarik and Christie, 1997). Thus, when peroxone is used for obtaining CT credit, more bromate ion may form than during ozonation. However, if peroxone is only used for micropollutant destruction, less bromate ion may form than when ozone is used.

7.6 Status of Analytical Methods

Hydrogen peroxide in solution reacts with ozone to ultimately form water and oxygen. Consequently, the simultaneous presence of both oxidants is accepted as being only transient (Masschelein et al., 1977). Chapter 3 summarizes ozone analytical methods that can be used for ozone/hydrogen peroxide disinfectant residual monitoring. This section will present the status of analytical methods for hydrogen peroxide only.

7.6.1 Monitoring of Hydrogen Peroxide

Standard Methods (1995) does not list procedures for measuring hydrogen peroxide. Gordon et al. (1992) list several methods for hydrogen peroxide analysis including:

- Titration methods;
- Colorimetric methods; and
- Horseradish peroxidase methods.

Table 7-3 shows the working range, expected accuracy and precision, operator skill level required, interferences and current status for hydrogen peroxide analysis.

7.6.1.1 Titration Methods

Two titration methods are available for the analysis of hydrogen peroxide; namely, iodometric and permanganate. Precautions for the iodometric titration include the volatility of iodine, interferences by metals such as iron, copper, nickel, and chromium, and fading titration end points (Gordon et al., 1992). Organic and inorganic substances that react with permanganate will interfere with the permanganate titration.

Titration of hydrogen peroxide with permanganate or iodide ion is not sufficiently sensitive for determining residual concentrations (Masschelein et al., 1977).

7.6.1.2 Colorimetric Methods

The most widespread method for the colorimetric determination of hydrogen peroxide is that based on the oxidation of a Titanium (IV) salt (Masschelein et al., 1977). A yellow complex is formed and measured by absorption at 410 nm. On a qualitative basis, ozone and persulfates do not produce the same colored complex.

The oxidation of the leuco base of phenolphthalein is used as a qualitative test for hydrogen peroxide (Dukes and Hydier, 1964). Sensitivity and precision of the method is sufficient in the range between 5 and 100 μg/L. This low working analytical range makes this method impractical for measuring hydrogen peroxide residual levels. Also, the instability of the color obtained makes the method less suitable for manual use. No interference data are available, but it is expected that other oxidants would interfere (Gordon et al., 1992).

The oxidation of cobalt (II) and bicarbonate in the presence of hydrogen peroxide produces a carbonato-cobaltate (III) complex (Masschelein et al., 1977). This complex has absorption bands at 260, 440, and 635 nm. The 260 nm band has been used for the measurement of hydrogen peroxide. A detection limit of 0.01 mg/L has been reported (Masschelein et al., 1977). Optical interferences are caused by 100 mg/L nitrate and 1 mg/L chlorite ions. Other oxidizing agents do interfere with this method as will any compound with an absorption at 260 nm (Gordon et al., 1992).

Table 7-3. Characteristics and Comparisons of Hydrogen Peroxide Analytical Methods

Type of Test	Working Range (mg/L)	Expected Accuracy (± percent)	Expected Precision (± percent)	Skill Level[a]	Interferences	pH Range	Field Test	Automated Test	Current Status
Iodometric Titration	> 10	5	5	2	Oxidizing Species	Acidic	Yes	No	Currently Used
Permanganate Titration	0.1 - 100	5	5	2	Oxidizing Species	Acidic	Yes	No	Currently Used
Colorimetry, Titanium IV	0.1 - 5	NR	NR	2	Ozone	Acidic	Yes	No	Not Recommended
Colorimetry, Leuco Base of Phenolphthalein	0.005 - 0.1	NR	NR	2	Ozone	Neutral	Yes	Yes	Not Recommended
Colorimetry, Cobalt III/HCO_3^-	0.01 - 1	NR	NR	2	Ozone	Neutral	Yes	Yes	Not Recommended
HRP[b]	10^{-8} - 10^{-5}	NR	NR	2	Other Peroxides, Ozone	4.5 - 5.5	No	Yes	Currently Used

Notes:

[a] Operator Skill Levels: 1 = minimal, 2 = good technician, 3 = experienced chemist

NR = Not reported in literature cited by referenced source.

Adapted from Gordon et al., 1992

[b] This method can not be used in real peroxone-treated waters where the hydrogen peroxide concentration is significantly higher.

7.6.1.3 Horseradish Peroxidase Methods

Several methods incorporate the chemical reactions between peroxidase and hydrogen peroxide. Horseradish derived peroxidase (HRP) is used most often. The scopoletin procedure is one of the more widely accepted fluorescent methods of low levels of hydrogen peroxide utilizing HRP (Gordon et al., 1992). Again, no information is available on potential interference.

7.6.1.4 Summary

In general, the analytical procedures for hydrogen peroxide in drinking water are impacted by other oxidizing species such as ozone. Three of the methods are currently used, but not recommended for disinfectant residual measurement (Table 7-3). The scopoletin HRP method is the most promising, although additional study of potential interferences is required (Gordon et al., 1992).

7.7 Operational Considerations

Peroxide is a strong oxidant and contact with personnel should be avoided. Secondary containment should be provided for storage tanks to contain any spills. Dual containment piping should be considered to minimize the risk of exposure to plant personnel. Storage containers may explode in the presence of extreme heat or fire.

7.7.1 Process Considerations

The impacts of the peroxone process are similar to those described for ozone in Chapter 3. Because an additional oxidant is added to the water, the tendency to transform organic carbon compounds to a more biodegradable form may be increased with the addition of peroxide.

7.7.2 Space Requirements

The metering pumps used to add peroxide should be housed with adequate space around each pump for maintenance access. These pumps are generally not very large, so space requirements are not significant.

The storage area can range from small where peroxide is obtained in drums, to large tank farms if plant flow is great. As mentioned previously, secondary containment should be provided. Peroxide has a lower freezing point than water. Housing or heat tracing should be provided for storage tanks and exterior piping if extended periods with temperatures below freezing are anticipated.

7.7.3 Materials

Peroxide can be stored in polyethylene drums or tanks. The specific gravity is 1.39 for 50 percent peroxide, which should be considered in the design of the tank walls. Acceptable pipe materials for peroxide include 316 stainless steel, polyethylene, CPVC, and Teflon. Gaskets should be Teflon

because natural rubber, Hypalon and EPDM are not resistant to hydrogen peroxide. Metering pumps heads should be constructed of peroxide resistant materials.

Hydrogen peroxide is purchased from chemical suppliers and is commercially available in 35, 50, and 75 percent strengths. Peroxide is supplied in drums or in bulk by tankcar. Price depends on strength and quantity.

Peroxide can be stored onsite, but deteriorates gradually over time even when stored correctly. Peroxide deteriorates rapidly if contaminated and with heat or exposure to certain materials. Peroxide is added to the water with metering pumps to accurately control dose. Pumps should be designed to prevent potential air binding of peroxide off-gas. Multiple pumps should be provided for redundancy. As with any chemical added to water, adequate mixing should be provided.

7.8 Summary

7.8.1 Advantages and Disadvantages of Peroxone Use (Ozone/Hydrogen Peroxide)

The following list highlights selected advantages and disadvantages of using peroxone as a disinfection method for drinking water. Because of the wide variation of system size, water quality, and dosages applied, some of these advantages and disadvantages may not apply to a particular system.

Advantages

- Oxidation is more reactive and much faster in the peroxone process compared to the ozone molecular process.
- Peroxone is effective in oxidizing difficult-to-treat organics, such as taste and odor compounds.
- Peroxone processes have been shown to be effective in oxidizing halogenated compounds.
- The tendency to transform organic carbon compounds to a more biodegradable form may be increased with the addition of peroxide.
- Pumps used to house peroxide are not very large; so space requirements are not significant.

Disadvantages

- Peroxide is a strong oxidant and contact with personnel is extremely dangerous.
- Peroxide can be stored onsite, but deteriorates gradually even when stored correctly.

- Peroxone as a disinfection process does not provide a measurable disinfectant residual. It is therefore not possible to calculate CT similar to the use of other disinfectants.

- Peroxone's ability to oxidize iron and manganese is less effective than that of ozone.

7.8.2 Summary Table

Table 7-4 summarizes the considerations relative to peroxone disinfection considerations.

Table 7-4. Summary of Peroxone Disinfection Consideration

Consideration	Description
Generation	Because of its instability, ozone must be generated at the point-of-use. Hydrogen peroxide is purchased from chemical suppliers. Hydrogen peroxide can be stored onsite, but is subject to deterioration.
Primary uses	Primary use includes chemical oxidation. As an oxidizing agent, peroxone can be used to remove SOC pollutants and increase the biodegradability of organic compounds. Peroxone is an effective disinfectant but its CT credit has not been established. It is highly reactive and does not maintain an appreciable residual for CT credit calculations. Peroxone may be difficult to use for disinfection because it is highly reactive and does not maintain an appreciable ozone residual level.
Inactivation efficiency	Peroxone is one of the most potent and effective germicides used in water treatment. It is slightly more effective than ozone against bacteria, viruses, and protozoan cysts.
Byproduct formation	Peroxone itself does not form halogenated DBPs; however, if bromide is present in the raw water or if chlorine is added as a secondary disinfectant, halogenated DBPs including bromate may be formed. Other byproducts include organic acids and aldehydes.
Limitations	Ideally, ozone should be used as a primary disinfectant prior to peroxone treatment.
Point of application	For disinfection, peroxone addition should be after ozonation. Ozone contact should precede addition of hydrogen peroxide. For oxidation, peroxone can be added prior to coagulation/sedimentation or filtration depending on the constituents to be oxidized.
Special considerations	Ozone generation is a relatively complex process. Storage of LOX for ozone generation is subject to building and fire codes. Ozone is a highly toxic gas and the ozone production and application facilities must be monitored for ambient ozone. Hydrogen peroxide is a hazardous material requiring secondary containment for storage facilities.

7.9 References

1. Aieta, E.M., K.M. Reagan, J.S. Lang, L. McReynolds, J-W Kang, and W.H. Glaze. 1988. "Advanced Oxidation Processes for Treating Groundwater Contaminated with TCE and PCE: Pilot-Scale Evaluations." *J. AWWA.* 88(5): 64-72.

2. Bancroft, K.P., et al. 1984. "Ozonation and Oxidation Competition Values." *Water Res.* 18:473.

3. Chutny, B. and J. Kucera. 1974. "High Energy Radiation-induced Synthesis of Organic Compounds. I. Introduction Isomerization and Carbon-Skeleton Changes, Radiation Synthesis in Aqueous Solutions." *Rad. Res. Rev.* 5:1-54.

4. Dahi, E. 1976. "Physicochemical Aspects of Disinfection of Water by Means of Ultrasound and Ozone." *Water Res.* 10:677.

5. Duguet, J., E. Brodard, B. Dussert, and J. Malevialle. 1985. "Improvement in the Effectiveness of Ozonation of Drinking Water Through the Use of Hydrogen Peroxide."*Ozone Sci. Engrg.* 7(3):241-258.

6. Dukes, E.K., and M.L. Hydier. 1964. "Determination Of Peroxide By Automated Chemistry." *Anal. Chem.* 36:1689-1690.

7. Ferguson, D.W., J.T. Gramith, and M.J. McGuire. 1991. "Applying Ozone for Organics Control and Disinfection: A Utility Perspective." *J. AWWA.* 83(5):32-39.

8. Ferguson, D.W., M.J. McGuire, B. Koch, R.L. Wolfe, and E.M. Aieta. 1990. "Comparing Peroxone an Ozone for Controlling Taste and Odor Compounds, Disinfection Byproducts, and Microorganisms." *J. AWWA.* 82(4):181.

9. Glaze, W. H., et al. 1987. "The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide, and Ultraviolet Radiation." *Ozone: Sci. Engrg.* 9(4):335.

10. Glaze, W.H. 1986. "Reaction Products of Ozone: A Review." *Environ. Health Perspectives*, 69:151-157.

11. Glaze, W.H., and J-W Kang. 1988. "Advanced Oxidation Processes for Treating Groundwater Contaminated With TCE and PCE: Laboratory Studies." *J. AWWA.* 88(5): 57-63.

12. Gordon, G., Cooper, W.J., Rice, R.G., and Pacey, G.E. 1992. *Disinfectant Residual Measurement Methods.* Second Edition. AWWARF and AWWA, Denver, CO.

13. Hamelin, C. and Y.S. Chung. 1974. "Optimal Conditions for Mutagenesis by Ozone in *Escherichia coli* K12." *Mutation Res.* 24:271.

14. Hoigné, J. and H. Bader. 1975. "Ozonation of Water: Role of Hydroxyl Radicals as Oxidizing Intermediates." *Science*. 190(4216):782.

15. Hoigné J. and H. Bader. 1978. "Ozone Initiated Oxidations of Solutes in Wastewater: A Reaction Kinetic Approach." *Progress Water Technol.* 10(516):657.

16. Hoigné J. and Bader. 1976. "The Role of Hydroxyl Radical Reacting in Ozonation Processes in Aqueous Solutions." *Water Resources.* 10:377.

17. Huck, P..M., Anderson, W.B. Lang, C.L. Anderson, W.A. Fraser, J.C. Jasim, S.Y. Andrews, S.A. and Pereira, G. 1995. Ozone vs. Peroxone for Geosmin and 2-Methylisoborneol Control: Laboratory, Pilot and Modeling Studies. Conference proceedings, AWWA Annual Conference, Anaheim, CA.

18. Ishizaki, K. et al. 1987. "Effect of Ozone on Plasmid DNA of *Escherichia coli* In Situ." *Water Res.* 21(7):823.

19. Karimi, A.A., J.A. Redman, W.H. Glaze, and G.F. Stolarik. 1997. "Evaluation an AOP for TCE and PCE Removal." *J. AWWA.* 89(8):41-53.

20. Krasner, S.W., W.H. Glaze, H.S. Weinberg, P.A. Daniel, and I.N. Najm. 1993. "Formation and Control of Bromate During Ozonation of Waters Containing Bromide." *J. AWWA.* 85(1):73-81.

21. Lund, E. 1963. "Significance of Oxidation in Chemical Inactivation of Poliovirus." *Arch. Gesamite Virusforsch*. 12:648.

22. Masschelein, W., M. Denis, and R. Ledent. 1977. "Spectrophotometric Determination Of Residual Hydrogen Peroxide." *Water Sewage Works*. 69-72.

23. Masten, S.J. and J. Hoigné. 1992. "Comparison of Ozone and Hydroxyl Radical-Induced Oxidation of Chlorinated Hydrocarbons in Water." *Ozone Sci. Engrg.* 14(3):197-214.

24. Mentel, R. and J. Schmidt. 1973. "Investigations of Rhinoviruse Inactivation by Hydrogen Peroxide." *Acta Virol.*17:351.

25. MWDSC and JMM (Metropolitan Water District of Southern California and James M. Montgomery Consulting Engineers). 1992. "Pilot Scale Evaluation of Ozone and Peroxone." AWWARF and AWWA, Denver, CO.

26. Ohlrogge, J.B. and T.P. Kernan. 1983. "Toxicity of Activated Oxygen: Lack of Dependence on Membrane Fatty Acid Composition." *Biochemical and Biophysical Research Communications*. 113(1):301.

27. Pereira, G., P.M. Huck, and W.A. Anderson. 1996. "A Simplified Kinetic Model for Predicting Peroxone Performance for Geosmin Removal in Full-Scale Processes." Conference proceedings, AWWA Water Quality Technology Conference; Part I. New Orleans, LA.

28. Pryor, W.A. M.M. Dooley, and D.F. Church. 1983. "Mechanisms for the Reaction of Ozone with Biological Molecules: The Source of the Toxic Effects of Ozone." *Advances in Modern Environmental Toxicology*. M.G. Mustafa and M.A. Mehlman (editors). Ann Arbor Science Publishers, Ann Arbor, MI.

29. Riesser, V. N., et al. 1977. "Possible Mechanisms for Poliovirus Inactivation by Ozone." *Forum on Ozone Disinfection*. E.G. Fochtman, et al. (editors). International Ozone Institute Cleveland, OH.

30. Scott, D.B.N. and E.C. Lesher. 1963. "Effect of Ozone on Survival and Permeability of *Escherichia coli*." *J. Bacteriology*. 85:567.

31. Scott, K.N., et al. 1992. "Pilot-Plant-Scale Ozone and Peroxone Disinfection of *Giardia muris* Seeded Into Surface Water Supplies." *Ozone Sci. Engrg.* 14(1):71.

32. Standard Methods. 1995. *Standard Methods for the Examination of Water and Wastewater,* nineteenth edition, Franson, M.H., Eaton, A.D., Clesceri, L.S., and Greenberg, A.E., (editors). American Public Health Association, AWWA, and Water Environment Federation, Washington D.C.

33. Stolarik, G., and J.D. Christie. 1997. "A Decade of Ozonation in Los Angeles." Conference proceedings, IOA Pan American Group Annual Conference, Lake Tahoe, NV.

34. Tobiason, J.E., J.K. Edzwald, O.D. Schneider, M.B. Fox, and H.J. Dunn. 1992. "Pilot Study of the Effects of Ozone and Peroxone on In-Line Direct Filtration." *J. AWWA.* 84(12):72-84.

35. Von Gunten, U., A. Bruchet, and E. Costentin. 1996. "Bromate Formation in Advanced Oxidation Processes." *J. AWWA.* 88(6):53.

36. Wallis, P.M. et al. 1990. "Inactivation of Giardia Cysts in Pilot Plant Using Chlorine Dioxide and Ozone." Conference proceedings, AWWA Water Quality Technology Conference, Philadelphia, PA.

37. Wickramanayake, G.B. 1984. *Kinetics and Mechanism of Ozone Inactivation of Protozoan Cysts.* Ph.D dissertation, Ohio State University.

38. Wolfe, R.L. et al. 1989a. "Disinfection of Model Indicator Organisms in a Drinking Water Pilot Plant by Using Peroxone." *Appl. Environ. Microbiol.* 55:2230.

39. Wolfe, R.L., et al. 1989b. "Inactivation of *Giardia muris* and Indicator Organisms Seeded in Surface Water Supplies by Peroxone and Ozone." *Environ. Sci. Technol.* 23(6):774.

40. Yoshe-Purer, Y. and E. Eylan. 1968. "Disinfection of Water by Hydrogen Peroxide." *Health Lab Sci. 5.*

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