Technical Brief:
Advanced Oxidation Processes

Spontaneous decomposition of ozone results in the production of highly reactive hydroxyl radicals that can easily oxidize various compounds. However, this process is slow to occur. Development of advanced oxidation processes and techniques have accelerated the ozone decomposition rate, allowing for an elevated concentration of hydroxyl radicals in solution.

Advanced oxidation processes (AOP) are useful because they take precedence over less reactive molecular ozone reactions.

Several established combination of commonly used technology for advanced oxidation processes include **ozone in elevated pH (>8.5) solution**, **ozone and hydrogen peroxide (O3/H2O2)**, and **ozone and ultraviolet irradiation (O3/UV)**.

AOP: Ozone at elevated pH

Past remediation studies have consistently demonstrated the positive effects of elevated pH (>8.5) on the decomposition rate of ozone in aqueous solutions. At a pH of 10, the half-life of ozone in water is very shortóless than 1 minute.[3] As a result, ozone remediation at basic pH levels is also an accepted form of advanced oxidation.

Accelerated decomposition of ozone occurs at high pH levels because the basicity of the aqueous solution has a much higher concentration of hydroxyl ions. Similar to the peroxone oxidation process, the reaction between hydroxyl ions and ozone produces superoxide anion radical O2- and hydroperoxyl radical HO2- products.[3]

A final reaction between existing ozone in solution and the intermediate superoxide anion yield the ozonide anion (O3-), which then decomposes to form the reactive hydroxyl radical.[3] However, caution must be taken when proceeding with elevated pH ozone oxidation in aqueous environments.

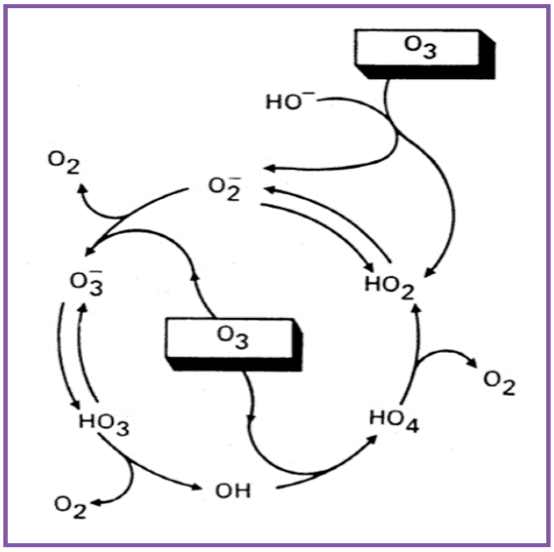

Figure 3

Basic pH values also elevate concentrations of bicarbonate and carbonate ions in solution. These compounds act as OH radical scavengers and can suppress the ozone degradation chain reaction if present in high concentrations.[5] Tert-butyl alcohol and radical/radical coupling processes are also capable of halting the decomposition process.[5]

(Continued from page 1)

Advanced Oxidation Processes play an important role in ozone remediation of soil and groundwater contaminants. Their ability to produce high concentrations of hydroxyl radicals at rapid rates allows these processes to better treat contaminants that are not easily broken down by ozone alone.

AOP: Ozone and H2O2

Combined use of ozone and hydrogen peroxide is one of the more common processes used for advanced oxidation. This process has been thoroughly investigated and a kinetic model and mechanism have been developed in order to explain the method in which the hydroxyl radical is produced. Kuo, et al. conducted an in depth investigation into the mechanism of hydroxyl radical formation via this process.

Formation of the hydroperoxide ion HO2- occurs from the reaction between ozone and the hydroxyl ion, OH- in solution.[1] However, addition of hydrogen peroxide - a weak acid - in aqueous solution produces additional hydroperoxide ions, which react with ozone to form the reactive hydroxyl radical that is key in advanced oxidation processes.

The addition of hydrogen peroxide yields 1.0 mole of hydroxyl radical per mole of ozone consumed.[2] Following the formation of hydroxyl radicals, a series of chain reactions involving the formation of hydroxyl radical, superoxide, and ozonide (figure 1) may also occur.[1]

$$O_3 + OH^- \longrightarrow HO_2^- + O_2$$

Reaction of ozone with hydroxyl ion in solution

$$H_2O_2 \longleftrightarrow HO_2^- + H^+$$

Dissociation of hydrogen peroxide to hydroperoxide and hydrogen ions

$$O_3 + HO_2^- \longrightarrow HO^\cdot + O_2^{-\cdot} + O_2$$

Reaction of ozone and hydroperoxide ion to produce hydroxyl radical

$$O_3 + HO^\cdot \longrightarrow HO_2^\cdot + O_2$$
$$H_2O_2 + HO^\cdot \longrightarrow HO_2^\cdot + H_2O$$
$$HO_2^- + HO \longrightarrow HO_2^\cdot + OH^-$$
$$HO_2^\cdot \longleftrightarrow O_2^{-\cdot} + H^+$$
$$OH^- + HO \longrightarrow H_2O + O^-$$
$$O_3 + O_2^- \longrightarrow O_3^- + O_2$$
$$O_3^- + H^+ \longrightarrow HO^\cdot + O_2$$
$$O^- + H_2O \longrightarrow HO^\cdot + OH^-$$

Chain reactions involving hydroxyl radical, superoxide and ozonide ions

Figure 1.

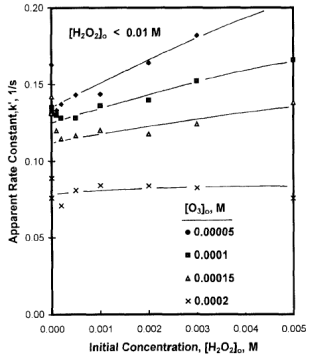

Figure 4 — Effect of hydrogen peroxide at low concentrations.

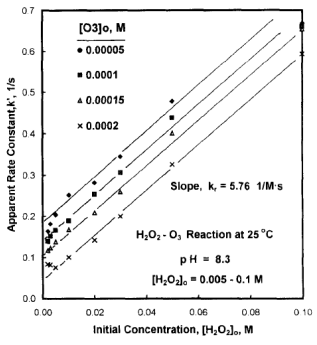

Figure 5 — Effect of hydrogen peroxide at high concentrations.

AOP: Ozone and UltraViolet Irradiation (O3+UV)

Ozone/UV is another established Advanced Oxidation Process that is commonly used in aqueous environments. This combined process has higher removal efficiency when compared with the effectiveness of ozone or UV when used separately.

Exposure of ozone in aqueous solution to low pressure ultraviolet rays at a wavelength of 254 nm produces a hydrogen peroxide intermediate, which decomposes to hydroxyl radicals upon interaction with ozone.[3] Similar to peroxone oxidation, this method destroys contaminants using a combination of oxidants including hydroxyl radicals, direct molecular ozone, and UV photolysis.[3,4]

UV photolysis can also be used with hydrogen peroxide; however, multiple studies have proven that ozone absorption of UV rays is much stronger than that of H2O2, resulting in a greater yield of hydroxyl radicals.[4] Approximately 2 moles of hydroxyl radical are produced from every 1 mole of hydrogen peroxide intermediate.

Case studies and remediation projects demonstrate that ozone/UV advanced oxidation treatments have been effective in destroying TCE, PCE, PCP, VOCs, and explosives such as 2,4,6-trinitrotoluene (TNT), and RDX.[4]

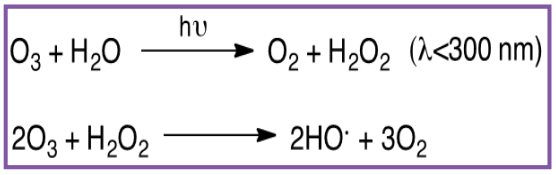

Figure 2

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.

Table 5. Theoretical amount of oxidants and UV required for the formation of ˙OH radicals in O_3/H_2O_2/UV systems [1]

System	Moles of O_3/mole ˙OH	Moles of UV photons, einsteins/mole ˙OH	Moles of H_2O_2/mole ˙OH
O_3/OH^-	1.5	0	0
O_3/UV	1.5	0.5	0.5 (H_2O_2 *in situ*)
O_3/H_2O_2	1.0	0	0.5
H_2O_2/UV	0	0.5	0.5

Table 1. Relative oxidation power of some oxidizing species [2, 3]

Oxidizing species	Relative oxidation power
Chlorine	1.00
Hypochlorous acid	1.10
Permanganate	1.24
Hydrogen peroxide	1.31
Ozone	1.52
Atomic oxygen	1.78
Hydroxyl radical	2.05
Positively charged hole on titanium dioxide, TiO_2^+	2.35

Table 2. Reaction rate constants (k, M^{-1} s^{-1}) of ozone vs. hydroxyl radical [4]

Compound	O_3	˙OH
Chlorinated alkenes	10^3–10^4	10^9–10^{11}
Phenols	10^3	10^9–10^{10}
N-containing organics	10–10^2	10^8–10^{10}
Aromatics	1–10^2	10^8–10^{10}
Ketones	1	10^9–10^{10}
Alcohols	10^{-2}–1	10^8–10^9

Table 4. Comparative operating costs of some AOPs [2]

Process	Cost of oxidant	Cost of UV
O_3/UV	High	Medium
O_3/H_2O_2	High	0
H_2O_2/UV	Medium	High
Photocatalytic oxidation	Very low	Medium to high

Experience

At Piper, we have extensive experience with both ozone and Advanced Oxidation Processes, and can custom build a remediation system that will best fit the needs of the customer and contaminants at hand.

Several of our case studies are listed below:

- **2008-2009:** Montgomery County landfill leachate remediation project in Montgomery County, TN. A 56 ppd (pound per day) ex-situ ozone system was used to successfully treat chlorinated compounds, total organic carbon (TOC), dichloroacetate (DCA), odor issues, and surfactants. An ozone/hydrogen peroxide AOP was injected into the leachate discharge in order to ensure total remediation. The project was successful with significant chlorinated compound reductions observed in groundwater both on and off-site.
- **2013:** Remediation project for Matrix Environmental Technologies in Cross River, NY. An ozone/UV ex-situ Advanced Oxidation Process was applied to treat MTBE and TBA compounds found on site. The project was successful with 100% MTBE decomposition and approximately 80-100% TBA degradation.
- **2013:** Piper completed design build ex-situ ozone/hydrogen peroxide AOP building system for an Ohio project. Please see corresponding case study. This structure replaced the temporary system currently in place at the facility and aid in remediation of 1,4-dioxane and numerous other contaminants on site.

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TABLE I. THEORETICAL AMOUNTS OF OXIDANTS AND UV REQUIRED FOR FORMATION OF HYDROXYL RADICAL IN OZONE - PEROXIDE - UV SYSTEMS

System	Moles of Oxidant Consumed per Mole of OH Formed		
	O_3	UV[a]	H_2O_2
Ozone - Hydroxide Ion[b]	1.5	---	---
Ozone - UV	1.5	0.5	(0.5)[c]
Ozone - Hydrogen Peroxide[b]	1.0	---	0.5
Hydrogen Peroxide - UV	---	0.5	0.5

[a] Moles of photons (Einsteins) required for each mole of OH formed.

[b] Assumes that superoxide formed in the primary step yields one OH radical per O_2^-, which may not be the case in certain waters.

[c] Hydrogen peroxide formed in situ (13,42).

References

[1] Kuo, C.-H., Zappi, M. E., & Hong, A. P. (1999). Kinetics and Mechanism of the Reaction Between Ozone and Hydrogen Peroxide in Aqueous Solutions. *The Canadian Journal of Chemical Engineering*, *77*, 473-482.

[2] US Environmental Protection Agency Alternative Disinfectants and Oxidants. (1999, April). *PEROXONE (OZONE/ HYDROGEN PEROXIDE)* (US EPA, Comp.).

[3] Munter, R. (2001). Advanced oxidation processes- current status and prospects. *Proc. Estonian Acad. Sci. Chem.*, (50), 59-80.

[4] Kommineni, S., Zoeckler, J., Stocking, A., Liang, S., Flores, A., & Kavanaugh, M. (n.d.). *3.0 Advanced Oxidation Processes*.

[5] Glaze, W. H., Kang, J.-W., & Chapin, D. H. (1987). The chemistry of water treatment processes involving ozone, hydrogen peroxide, and ultraviolet radiation. *Ozone Science and Engineering*, *9*, 335-352.

Company Profile

Piper Environmental Group, Inc. offers ozone technology, equipment, and services for a wide-range of environmental applications. The company designs, manufactures, and integrates ozone systems and related equipment for short and long-term projects, offering equipment for rent or purchase. Services include project design assistance, oxidation pilot studies, contract service, equipment repair, consulting. Our area of expertise is large remediation projects.

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