**Using UV Technology to Generate Oxygen Radicals for Paper Mill Systems**

**Lance Card**

Abstract:

Ultra Violet (UV) light has been used for many years in municipal water systems to disinfect and treat drinking water. UV technology is one way to do an Advanced Oxidative Process (AOP). Advanced oxidation processes, in a broad sense, are a set of chemical treatment procedures designed to remove organic (and sometimes inorganic) materials in water and waste water by oxidation through reactions with hydroxyl radicals (·OH). AOP’s generated hydroxyl and oxygen radicals have higher oxidation potential than chlorine and ozone and a faster reaction time for attacking organic contaminants. AOP’s are recognized as safe and “green” as they do not have any harmful byproducts. Historic barriers to AOP generation have been complexity and cost. We have found a way to use UV technology to generate hydroxyl radicals from ambient air and apply them in paper mill systems to control microorganisms, anaerobes, and positive metal ions like calcium.

The system is designed to take a set amount of ambient air, at a set temperature range, and pull it across UV lamps for a set amount of time to convert the maximum amount of oxygen to oxygen radicals. Then, take the gas generated and apply it to a water, or air source to treat and clean. This technology has been proven highly effective against bacteria, anaerobes, algae, viruses & parasites. It has also been shown to remove and prevent scale build up. It can also remove and control H2S and other odors in a system. This technology can be contained in a cabinet that plugs into a standard outlet to produce just over 3 CFM of gas. One unit can treat up to 1MM GPD of water depending on contamination levels and goals.

Introduction:

AOP has long been used as method for controlling bacteria, viruses, odors, and other microbial pests. AOP’s have been expensive to generate though their effectiveness is unmatched in oxidative potential. Recent discoveries have led to methods that can generate AOP’s from ambient air to utilize and apply in systems to control the problems associated. These methods have been proven to generate enough AOP radicals without the high cost and wet chemical demands of typical AOP generators. These new AOP generating systems have low power demands and only use the air around them as a raw material.

**What is an AOP?**

Advanced oxidation processes (AOPs) were first proposed for potable water treatment in the 1980s [[1](https://link.springer.com/article/10.1007/s40726-015-0015-z#CR1), [2](https://link.springer.com/article/10.1007/s40726-015-0015-z#CR2)], which are defined as the oxidation processes involving the generation of hydroxyl radicals (OH·) in sufficient quantity to effect water purification. Later, the AOP concept has been extended to the oxidative processes with sulfate radicals (SO4 ·−). Different from common oxidants such as chlorine and ozone that have a dual role of decontamination and disinfection, AOPs are applied primarily for destruction of organic or inorganic contaminants in water and wastewater. Although AOP inactivation of pathogens and pathogenic indicators have been studied [[3](https://link.springer.com/article/10.1007/s40726-015-0015-z#CR3), [4](https://link.springer.com/article/10.1007/s40726-015-0015-z#CR4)], they are rarely employed for disinfection because these radicals have too short half-life (on the order of microseconds), so that the required detention times for disinfection are prohibitive due to extremely low radical concentrations [[5](https://link.springer.com/article/10.1007/s40726-015-0015-z#CR5)]. When AOPs are applied for wastewater treatment, these radicals, as a powerful oxidizing agent, are expected to sufficiently destruct wastewater pollutants, and transform them to less and even non-toxic products, thereby providing an ultimate solution for wastewater treatment [[6](https://link.springer.com/article/10.1007/s40726-015-0015-z#CR6)].

Hydroxyl Radical-Based AOPs

Hydroxyl radical is the most reactive oxidizing agent in water treatment, with an oxidation potential between 2.8 V (pH 0) and 1.95 V (pH 14) vs. SCE (saturated calomel electrode, the most commonly used reference electrode) [[5](https://link.springer.com/article/10.1007/s40726-015-0015-z#CR5)]. OH· is very nonselective in its behavior and rapidly reacts with numerous species with the rate constants on the order of 108–1010 M−1 s−1. Hydroxyl radicals attack organic pollutants through four basic pathways: radical addition, hydrogen abstraction, electron transfer, and radical combination [[7](https://link.springer.com/article/10.1007/s40726-015-0015-z#CR7)]. Their reactions with organic compounds produce carbon-centered radicals (R· or R·–OH). With O2, these carbon-center radicals may be transformed to organic peroxyl radicals (ROO·). All of the radicals further react accompanied with the formation of more reactive species such as H2O2 and super oxide (O2 •−), leading to chemical degradation and even mineralization of these organic compounds. Because hydroxyl radicals have a very short lifetime, they are only in situ produced during application through different methods, including a combination of oxidizing agents (such as H2O2 and O3), irradiation (such as ultraviolet light or ultrasound), and catalysts (such as Fe2+) [[6](https://link.springer.com/article/10.1007/s40726-015-0015-z#CR6)]. Hydroxyl radical generation mechanisms of the major AOPs for wastewater treatment are briefly summarized below.

Ozone-Based AOPs

Ozone (O3) is a strong oxidant itself with an oxidation potential of 2.07 V vs. SCE. However, direct O3 oxidation is a selective reaction, with typical reaction rate constants of 1.0 × 100–103 M−1 s−1 8, in which O3 preferentially reacts with the ionized and dissociated form of organic compounds, rather than the neutral form. Under certain conditions, OH· is produced from O3 to initiate the indiscriminate oxidation (indirect mechanisms). Different detailed mechanisms have been proposed to explain the complex OH· generation, and the overall reaction involving OH· generation is expressed as below [[8](https://link.springer.com/article/10.1007/s40726-015-0015-z#CR8)].

3O 3 +H 2 O→2OH⋅+4O 2  3O3+H2O→2OH⋅+4O2 (1)

In the presence of other oxidants or irradiation, the OH· yield can be significantly improved. For example, in the so-called peroxone (O3/H2O2) system, the O3 decomposition and OH· production are enhanced by hydroperoxide (HO2 −) produced from H2O2 decomposition.

H 2 O 2 →HO 2  − +H +  H2O2→HO2−+H+ (2)

HO 2  − +O 3 →OH⋅+O 2  − +O 2  HO2−+O3→OH⋅+O2−+O2 (3)

In the O3/ultraviolet (UV) irradiation, H2O2 is generated as an additional oxidant primarily through O3 photolysis (Eq. [4](https://link.springer.com/article/10.1007/s40726-015-0015-z#Equ4))

O 3 +H 2 O+*hv*→H 2 O 2 +O 2  O3+H2O+hv→H2O2+O2 (4)

As a consequence, OH· can be generated, at a minimum, through three pathways: (1) ozonation (Eq. [1](https://link.springer.com/article/10.1007/s40726-015-0015-z#Equ1)); (2) O3/H2O2 (Eqs. [2](https://link.springer.com/article/10.1007/s40726-015-0015-z#Equ2) and [3](https://link.springer.com/article/10.1007/s40726-015-0015-z#Equ3)); and (3) photolysis of H2O2, as shown in Eq. [5](https://link.springer.com/article/10.1007/s40726-015-0015-z#Equ5).

H 2 O 2 +*hv*→2OH⋅ H2O2+hv→2OH⋅ (5)

UV-Based AOPs

Hydroxyl radicals can be initiated by photons in the presence of catalysts or oxidants. The most common catalyst is titanium dioxide (TiO2), a RO-type semiconductor. TiO2 particles are excited to produce positive holes in the valence band (*hv* + vb) with an oxidative capacity, and negative electrons at the conduction band (*e* − cb) with a reductive capacity, as follows:

TiO 2 +*hv*→*e* −  cb +*hv* +  vb  TiO2+hv→e−cb+hv+vb (6)

With the reactions of OH−, H2O, and O2 ·− at the surface of TiO2, these holes and electrons can further form hydroxyl radicals [[9](https://link.springer.com/article/10.1007/s40726-015-0015-z#CR9)].

*hv* +  vb +OH −  (surface) →OH⋅ hv+vb+OH−(surface)→OH⋅ (7)

*hv* +  vb +H 2 O (absorbed) →OH⋅+H +  hv+vb+H2O(absorbed)→OH⋅+H+ (8)

*e* −  cb +O 2 (absorbed) →O 2  ⋅−  e−cb+O2 (absorbed)→O2⋅− (9)

In the presence of oxidants such as H2O2 or O3, additional OH· may be yielded under the UV irradiation. For example, a H2O2 molecule is cleaved by UV irradiation to generate two OH·.

H 2 O 2 +*hv*→2OH⋅ H2O2+hv→2OH⋅ (10)

In addition, at a wavelength less than 242 nm, OH· can also be produced possibly through photolysis of H2O.

H 2 O+*hv*→OH⋅+H⋅ H2O+hv→OH⋅+H⋅ (11)

Fenton-Related AOPs

Among these metals that are able to activate H2O2 and produce hydroxyl radicals in water, iron is the most frequently used. In the so-called Fenton process, H2O2 reacts with Fe2+ to generate strong reactive species. The reactive species produced are traditionally recognized as hydroxyl radicals, though other substances such as ferryl ions are proposed. The Fenton-related chemistry for water and wastewater treatment has been discussed in detail elsewhere [[10](https://link.springer.com/article/10.1007/s40726-015-0015-z#CR10)]. The classical Fenton radical mechanisms primarily involve the following reactions:

Fe 2+ +H 2 O 2 →Fe 3+ +OH⋅+OH −  Fe2++H2O2→Fe3++OH⋅+OH− (12)

Fe 3+ +H 2 O 2 →Fe 2+ +HO ⋅  2 +H +  Fe3++H2O2→Fe2++HO⋅2+H+ (13)

OH⋅+H 2 O 2 →HO ⋅  2 +H 2 O OH⋅+H2O2→HO⋅2+H2O (14)

OH⋅+Fe 2+ →Fe 3+ +OH −  OH⋅+Fe2+→Fe3++OH− (15)

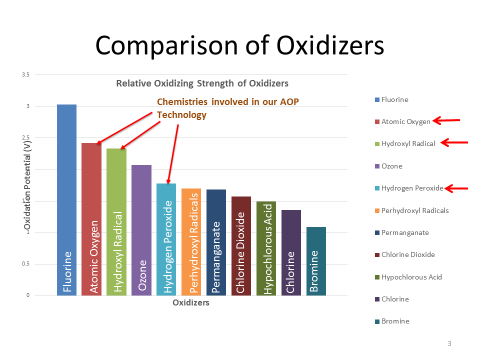
Fe 3+ +HO ⋅  2 →Fe 2+ +O 2 H +  Fe3++HO⋅2→Fe2++O2H+ (16)

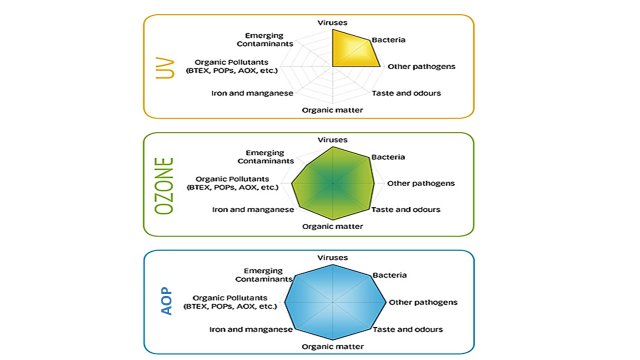
Fe 2+ +HO ⋅  2 +H + →Fe 3+ +H 2 O 2  Fe2++HO⋅2+H+→Fe3++H2O2 (17)

2HO ⋅  2 →H 2 O 2 +O 2  2HO⋅2→H2O2+O2 (18)

OH· is generated from Eq. [12](https://link.springer.com/article/10.1007/s40726-015-0015-z#Equ12) through electron transfer. However, OH· produced can be scavenged by either of Fenton reagents as shown in Eqs. [13](https://link.springer.com/article/10.1007/s40726-015-0015-z#Equ13) and [14](https://link.springer.com/article/10.1007/s40726-015-0015-z#Equ14). Therefore, the optimal molar ratio of iron ion to hydrogen peroxide needs to be experimentally determined for minimization of the unwanted scavenging. Although Eq. [13](https://link.springer.com/article/10.1007/s40726-015-0015-z#Equ13) indicates that the produced Fe3+ from Eq. [12](https://link.springer.com/article/10.1007/s40726-015-0015-z#Equ12) can be reduced to Fe2+, the iron cannot be a catalyst in the Fenton system because the rate constant in Eq. [13](https://link.springer.com/article/10.1007/s40726-015-0015-z#Equ13) is several orders of magnitude less than that in Eq. [12](https://link.springer.com/article/10.1007/s40726-015-0015-z#Equ12). Consequently, Fe3+ forms iron sludge at typical water and wastewater treatment conditions. The sludge needs to be separately disposed of, thus increasing the treatment complexity and operational costs. Of note, the generation of hydroxyl radicals during the Fenton reaction is the most effective only at an acidic pH condition. As a result, the application of Fenton reaction for wastewater treatment is restricted in practice.

Based on the classical Fenton treatment scheme, three modified Fenton processes are proposed, including the Fenton-like system, photo-Fenton system, and electro-Fenton system. In the Fenton-like reaction, Fe2+ is replaced by ferric ion (Fe3+), namely, the series of reactions in the Fenton system are initiated from Eq. [13](https://link.springer.com/article/10.1007/s40726-015-0015-z#Equ13) in the Fenton-like system, rather than from Eq. [12](https://link.springer.com/article/10.1007/s40726-015-0015-z#Equ12) in the traditional Fenton treatment. In the photo-Fenton reaction, UV irradiation is applied with the traditional Fenton system with a major purpose of enhancing the UV-induced reduction of dissolved Fe3+ to Fe2+. In the electro-Fenton reaction, either or both of the Fenton reagents may be generated through electrochemical methods.





**How do we generate our UV AOP?**

As is illustrated above the generation of AOP’s with an emphasis on hydroxyl radicals can seem to be a complicated process that requires a great deal of technology and equipment. However, when brought to the practical world and only concerning yourself with basic generation of radicals and not necessarily the form or amount things can be made quite simple. By using UV light of the two basic wavelength generations at various power outputs, a gas can be created and applied that has enough hydroxyl radicals and byproducts to manage the entire web of AOP capabilities.

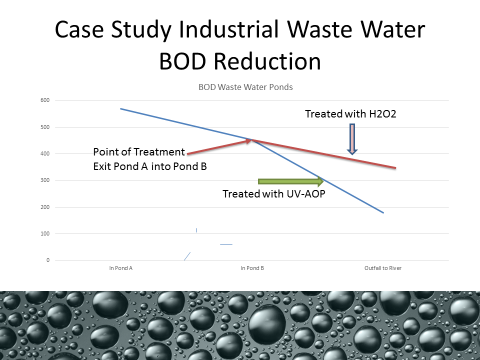
We do this by designing a system that pulls filtered ambient air through a compressor. By the nature of compressor the air is heated and must then be cooled before heading to a UV conversion chamber. The air passes through a high efficiency heat exchanger before being split for distribution through the UV chamber. The UV chamber is designed to send the air past a UV bulb at a set flow rate. The air is also forced periodically to a very close proximity to the UV bulb to further enhance O2 conversion. The converted air then exits the chamber and is applied to the treatment location. The AOP gas reacts quickly with the materials in the water or air being treated to cleans, disinfect, or deodorize.

The systems we use utilize a cabinet technology that houses all the needed components and monitoring devices to generate an AOP gas at a highly efficient rate for up to 18 months. The systems only need 110-120 volt plugs and pull 8-12 amps depending on type of cabinet and UV bulb power. Simple monitoring of the compressors is done to ensure that they are operating properly and staying lubricated. UV bulb chambers are easily replaced and bulbs should be replaced at 18 month intervals. We monitor UV bulb output and efficiency via bulb amperage readings which are recorded. In a water system we can also monitor ORP and microorganism ATP to verify how well the system is working on any given day or condition. We can also monitor H2S and other pollutants we can control via air monitoring systems.

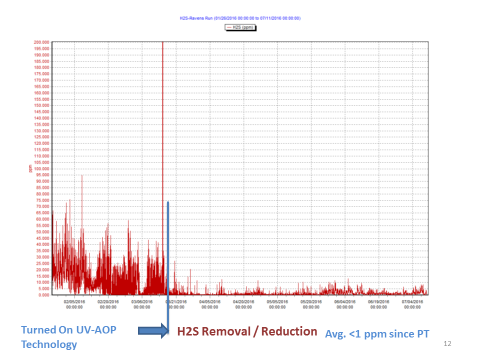
**How has our UV AOP been used in Paper Mill Systems**

The most highly effective area that our UV generated AOP radicals have treated in the paper mill are the eradication of anaerobic bacteria. Anaerobes have long been a problem in paper mill systems causing issues in iron laden fresh water used for showers, white water systems, and waste water systems. Anaerobes are difficult to kill with conventional chemicals and they produce acids as well as a very sticky residue that can plug downstream systems. The ORP in heavily anaerobic bacteria systems can be very negative. When evaluating a trim squirt water system that was having issues with plugging we found the warm fresh water tank supplying the system had an ORP of (-40). We started treating the system with a UV generated AOP introduced via an eductor recirculating back to the tank. Within 24 hours the tank’s ORP moved to 0 and within 48 hours the system ORP was 320 and has maintained ORP numbers 255-533 while being treated. Trim squirt pressure which would drop over an 8 hour period indicating that the filters needed cleaning started to maintain its pressure. Today the trim squirt filters only need cleaned every 4 weeks during a machine outage. Breaks due to poor trim squirt pressure and wet end edge defects went from 2-4 a day to 0.

For white water and waste water systems with heavy anaerobic populations, the issues are slightly different. The acids produced by the anaerobes can cause issues with equipment and in waste water systems effect beneficial bug populations needed for water treatment. We have seen the use of a UV generated AOP be beneficial in helping reduce BOD in waste water systems. The reasons for this are not completely clear as some of the systems where we have seen the greatest effects where not aerated systems which made them oxygen starved. Many of these systems used H2O2 to provide control of the anaerobes as well as supply oxygen into the water. By use of a UV generated AOP we were able to better kill and control the anaerobic population as well as supply a better source of oxygen that benefited the beneficial bug population. In all examples where regular aeration was not present the UV generated AOP out-performed the wet chemistry of H2O2.



Another use and benefit of using our UV generated AOP is the ability to remove smells and H2S in every system it is applied. The technology has been proven in municipal sewers where we applied the gas at a forced main where they were measuring H2S ppm at the end of the pipe. Certain conditions during the day can cause the H2S to fluctuate and move drastically up causing noxious odors in the effected neighborhoods. Our application provided constant treatment to the substrate in the pipe removing H2S and keeping H2S from forming. This made the neighborhoods not have any noticeable H2S smell and eliminated complaints about the smell.



We have also seen benefits of odor elimination in landfill leachate. Many landfills have obnoxious odors that cause issues in the community. These odors are almost always due to the leachate being collected from the landfill. The UV generated AOP system easily removes these odors making the landfill and surrounding area much fresher.

We have also removed odors from multiple sludge systems including paper mill sludge allowing it to be put into regular landfill systems.

Another benefit that we have seen but needs more investigation is the use of UV-AOP to remove NOX from stack emissions and removal of smell and other pollutants from stack emissions.

The use of the technology has just started, and by finding a way to generate a true AOP by use of UV light and ambient air has made it affordable and portable to be used almost anywhere. This technology is also easy to apply and has a very low energy demand, so is open to be tried at very low risk and cost into almost any application to control all bacteria, boost ORP, remove odors, and reduce pollutants.

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