Pureflow
OZONE DIV.

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ADVANCED OXIDATION PROCESSES

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THE TREATMENT OF 1,4 DIOXANE WITH OZONE AND HYDROGEN PEROXIDE

ADVANCED OXIDATION PROCESS (AOP)

Advanced Oxidation Process (AOP) technology has been in use to address water quality challenges since the 1970s. AOP involves the generation of hydroxyl (•OH) ions as a strong oxidant to address problematic water quality issues in potable, wastewater and industrial applications.

This process creates powerful oxidizing agents in the form of a hydroxide (OH-), but more specifically, its neutral variant the hydroxyl radical (•OH). Its oxidation potential is twice that of chlorine (Cl2), a commonly used oxidant/disinfectant. Hydroxyl radicals are the driving forces behind many advanced oxidation processes.

Advanced Oxidation Processes usually involve the combination of two oxidative compounds to create and/or increase generation of hydroxyl radicals (·OH) to provide enhanced treatment results. Ozone (O3), when coupled with hydrogen peroxide (H2O2) is often used to produce •OH in sufficient quantities to degrade organic (and some inorganic) pollutants.

The following data indicates the higher oxidation potential of the OH radical when compared to some of the more commonly used oxidation chemicals in the industry:

Oxidant	Oxidation Potential (V)	Oxidation Potential Relative to chlorine (Cl2) (V)
Hydroxyl Radical	2.80	2.05
Ozone	2.07	1.52
Hydrogen Peroxide	1.78	1.31
Potassium Permanganate	1.70	1.25
Sodium Hypochlorite	1.49	1.10
Chlorine	1.36	1.00
Chlorine Dioxide	1.27	0.93
Oxygen	1.23	0.90

The hydroxyl radical has a higher oxidation potential and reacts immediately with nearly all organic compounds. Therefore, this enhanced reaction leads to enhanced treatment results, advanced degradation of organics/inorganics and faster kinetics.

The theoretical oxidation potential of AOP may look encouraging, but practical applications/ sizing should be based on bench scale studies and/or field pilot trials to determine if there is any advantage in using an AOP. In practice, a high amount of so-called scavengers, e.g., carbonates, might quench hydroxyl radicals, resulting in the generated radicals not being available for the treatment process itself. For example, in wastewater treatment further possible pathways exist for radicals to react without significantly improving the treatment result.

The following factors are important when considering an AOP:

- The potential yield of hydroxyl radicals
- The presence and amount of radical scavengers
- The required energy input to create the hydroxyl radical
- Water / wastewater treatment plant design
- Initial investment and operational cost
- The presence of iron/manganese in the raw water that will stain the UV lamps and reduce UV transmittance

SUMMARY

The Advanced Oxidation concept has been around for many years. Recently, Industrial and Municipal engineers have been actively pursuing the use of AOP for special water treatment applications, such as the removal of 1,4-dioxane. The following are contaminants that can be treated with AOP:

- Endocrine Disrupting Chemicals (EDC’s)
- Taste and Odor (specifically Geosmin & Methylisoborneal (MIB))
- Algal Toxins / Microcystin
- 1,4-Dioxane
- Fuel and Fuel Additives (such as MTBE, hydrazine, and BTEX)
- Chlorinated hydrocarbons (e.g., TCE, Tetra-CE, DCE, DCEA, etc.)
- Pesticides and Herbicides
- Volatile Organic Compounds (such as PCE, TCE and Vinyl Chloride)
- Active Pharmaceutical Ingredients (API) and Personal Care Products (PCPs)
- Color reduction (potable water supplies)
- Hydrogen sulfide (H2S)
- Textile Dye Waste Water (color reduction)

1,4-DIOXANE

1,4-Dioxane is a manmade compound primarily used as an industrial solvent or solvent stabilizer, such as trichloroethane and trichloroethylene, that prevents the breakdown of chlorinated solvents during manufacturing processes.

Industrial solvents are used in degreasing, electronics, metal finishing, fabric cleaning, pharmaceuticals, herbicides and pesticides, antifreeze, paper manufacturing and many other applications.

1,4-Dioxane is a clear liquid with a faint pleasant odor. It mixes easily with water.

1,4-Dioxane is also present in ordinary household products such as:

- Shampoos: 50,000-300,000 ppb
- Liquid/dishwashing soap: 2,000-65,000 ppb
- Baby lotion: 11,000 ppb
- Hair lotions: 47,000-108,000 ppb)
- Bath foam: 22,000-41,000 ppb
- Other cosmetic products: 6,000-160,000 ppb

One source indicates that 1,4-dioxane is found in manufactured food additives (at 10,000 ppb level) and in shrimp, chicken, tomatoes, coffee and some condiments.

Little scientific data is available on the long-term effects of 1,4-dioxane on human health, although the U.S. Environmental Protection Agency (EPA) has listed 1,4-dioxane as a probable human carcinogen. The EPA has not yet established a federal drinking water standard or maximum contaminant level (MCL) for 1,4-dioxane.

California has also not set an MCL but has set an advisory Action Level (AL) of 3 ppb. An AL reflects calculations for acceptable risks based on best available data. Since there is no federal standard, the states of Michigan, Maine and Massachusetts have set safety levels at 85 ppb, 70 ppb and 50 ppb, respectively.

New York State has adopted a first-in-the-nation drinking water standard for the emerging contaminant, setting the MCL of only 1 ppb for 1,4-Dioxane. Due to limited health science data, there is a lack of agreement on the acceptable risk levels of 1,4-dioxane in water.

The greatest human threat from 1,4-dioxane has come from worker inhalation exposure at industrial sites. 1,4-Dioxane in water is a chronic or long-term threat to human health.

HEALTH EFFECTS OF 1,4-DIOXANE

When a substance is released either from a large area, such as an industrial plant, or from a container, such as a drum or bottle, it enters the environment. Such a release does not always lead to exposure. You can be exposed to a substance by breathing, eating, or drinking the substance, or by skin contact. If you are exposed to 1,4-dioxane, many factors will determine whether you will be harmed. These factors include how much (the dose), how long (the duration), and how you are exposed to the substance. You must also consider any other chemicals you are exposed to and your age, sex, diet, family traits, lifestyle, and state of health.

When you breathe air containing 1,4-dioxane, almost all of it will rapidly enter your body through your lungs. Most of the 1,4-dioxane in drinking water will rapidly enter your body through the digestive tract. Studies have found that some 1,4-dioxane can pass through skin when applied with certain preparations such as lotions, but much of it will evaporate before it can be absorbed. Once in your body, 1,4-dioxane is broken down into other chemicals. These other chemicals rapidly leave your body in urine.

As noted above, the effects of 1,4-dioxane on human health depends on how much 1,4-dioxane you are exposed to and the length of exposure. The limited environmental monitoring data available suggest that the levels of 1,4-dioxane to which the general public might be exposed through contact or use of consumer products (including food), or that are normally found in environmental media, are generally significantly lower than those used in studies with experimental animals. Eye and nose irritation have been reported by people exposed to low levels of 1,4-dioxane for short periods of time.

Exposure to very high levels may cause severe kidney and liver effects and possibly death. Studies in animals have shown that breathing vapors of 1,4-dioxane affects mainly the nasal cavity and the liver and kidneys. Swallowing liquid 1,4-dioxane or contaminated drinking water or having skin contact with liquid 1,4-dioxane also affects the liver and kidneys.

Laboratory rats that breathed vapors of 1,4-dioxane during most of their lives developed cancer inside the nose and in the abdominal cavity; they also developed benign tumors in the liver. Laboratory rats and mice that drank water containing 1,4-dioxane during most of their lives developed liver cancer; the rats also developed cancer inside the nose. Some scientists believe that 1,4-dioxane may cause cancer by a nongenotoxic mechanism.

Scientists are debating the degree to which the findings in rats and mice apply to exposure situations commonly encountered by people. The International Agency for Research on Cancer (IARC) has determined that 1,4-dioxane is possibly carcinogenic to humans. The U.S. Department of Health and Human Services (HHS) considers 1,4-dioxane as reasonably anticipated to be a human carcinogen.

The EPA has established that 1,4-dioxane is likely to be carcinogenic to humans.

REGULATIONS OF 1,4-DIOXANE

The Environmental Protection Agency (EPA) recommends that the levels of 1,4-dioxane in drinking water shall not exceed 4 milligrams per liter (mg/L) or 0.4 mg/L, if the contaminated drinking water is consumed for a period of 10 consecutive days. However, EPA has not established a federal drinking water standard maximum contaminant level.

In 2013, the EPA classified 1,4-dioxane as a likely human carcinogen and defined a concentration of 0.35 parts per billion in tap water as the amount expected to cause no more than one additional case of cancer in 1 million people who drink it for a lifetime.

But because there are no federal regulations limiting 1,4-dioxane in tap water, the following eight states have set their own criteria, with New York having the most stringent standards:

- In 2020, New York State adopted a first-in-the-nation drinking water standard for the emerging contaminant 1,4-Dioxane, setting the MCL of only 1.0 ppb for 1,4-Dioxane in drinking water
- California has set an Advisory Limit (AL) where water utilities must notify state regulators if 1,4-dioxane is detected above 1.0 ppb
- Colorado’s standard for 1,4-dioxane in groundwater is 0.35 ppb
- Maine’s drinking water guideline for 1,4-dioxane is 4 ppb
- Massachusetts’ non-enforceable drinking water guideline for 1,4-dioxane is 0.3 ppb.
- New Hampshire water utilities must report 1,4-dioxane at levels of 0.25 ppb and above
- New Jersey’s groundwater quality standard is 0.4 ppb for 1,4-dioxane
- North Carolina’s groundwater quality and surface water supply standards for 1,4-dioxane are 3.0 ppb and 0.35 ppb, respectively

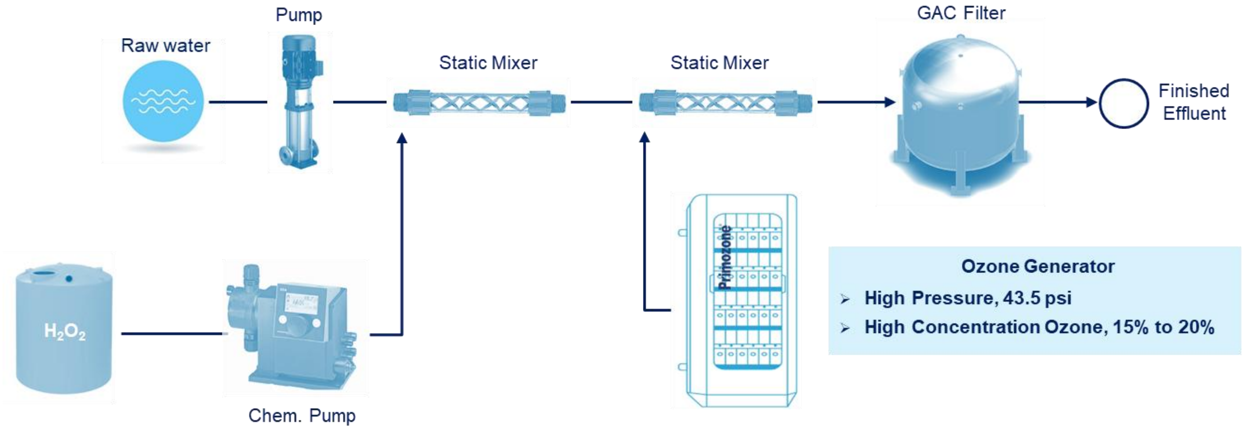
OZONE / HYDROGEN PEROXIDE AOP DESIGN FOR THE REMOVAL OF 1,4-DIOXANE

Each AOP project has its own requirements and environmental conditions that will influence the process design and the decision of which AOP system will provide the best treatment of the raw water contaminants. Unfortunately, there is no specific formula one can use to size an AOP system.

Although there is published data on “typical” dosages required for certain constituents, it can be difficult to accurately predict the reaction kinetics of the hydroxyl radical given the fact that each site will have different raw water quality. Although the concentration of the constituent in question may be known, the other water quality parameters may have a significant impact on the reaction kinetics and therefore on the actual required ozone, and/or hydrogen peroxide dose.

Due to these factors, it is always recommended that a site-specific pilot, or at a minimum a bench-scale test, be conducted to try and quantify the ozone/peroxide dose required for that specific water quality.

The **Primozone/Pureflow ozone/peroxide AOP process** provides many advantages over other ozone/peroxide systems because of the patented Primozone anodized aluminum reactor that offers high ozone concentration (up to 20% by weight), high operating pressure (up to 43 psi), reduced oxygen consumption, up to 50% less energy consumption, low O&M costs, modular design and small footprint. Low oxygen consumption and high ozone concentration result in the following benefits: high operating efficiency, improved mass transfer (20% ozone concentration is 4 x's more soluble than oxygen in water), smaller ozone contactor size, efficient optional direct inline injection of ozone, and smaller pumps/reduced motor horsepower.



Typical Ozone / Peroxide AOP Process Flow Diagram

BROMATE FORMATION AND MITIGATION

Ozone by-product formation (such as bromate) can be mitigated. The dose of hydrogen peroxide depends on the required contact time (higher peroxide doses will decrease the necessary contact time due to accelerated kinetics) and the necessity to mitigate bromate formation due to potential elevated bromide concentrations in the raw water (> 50 µg/L).

As a general rule the following ozone/ peroxide ratios are recommended for bench and/or pilot studies:

- 2:1 for normal retention times (20 minutes) and very low bromate mitigation capacity
- 1:1 for optimized retention times (5-10 minutes) and low bromate mitigation
- 1:2 for accelerated reaction, medium bromate mitigation capacity and short retention times (< 5 minutes)
- 1:5 for very short retention times (< 1 minute) and high bromate mitigation capacity

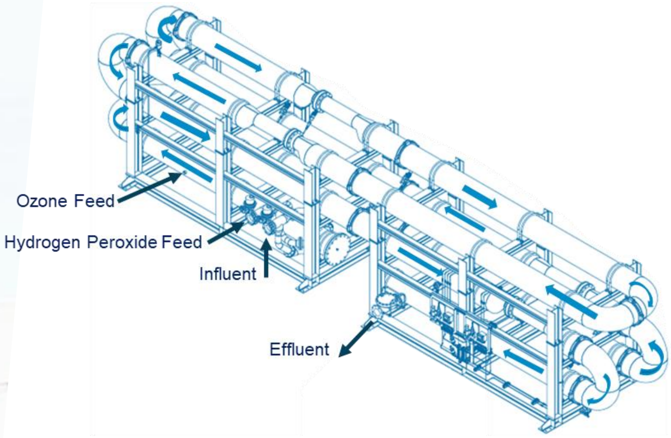
Note: The above suggested ratios are only guidelines, bench testing/field pilot studies will determine the optimum ratios of ozone/peroxide.

SERPENTINE OZONE / PEROXIDE REACTOR

Serpentine ozone reactors are an effective method of utilizing space to achieve contact time with flow rates from 100 gpm to 2,000 gpm, and a required contact time from 1 to 5 minutes. Process flows above 2,000 gpm dictate the use of concrete basins for a more practical design. When bromide is present in the raw water, flow rates do not exceed 2,000 gpm and the required contact time does not exceed 5 minutes, a stainless-steel serpentine reactor with multiple ozone/peroxide injection points and mixing elements can be used to mitigate the formation of bromate.

Peroxide is fed first to reduce the potential of bromate formation, then ozone is fed (each is followed by an inline wafer style static mixer). Multiple injection, inline static mixers and sample ports are provided to test, mix and trim the ozone/peroxide oxidant feed / dosage rates.

Note: The serpentine reactor can be used for other applications that require contact time.



Serpentine Ozone/Peroxide Reactor

Designed for Bromate Mitigation

POWER CONSUMPTION OF ALTERNATE AOP PROCESS

When considering alternate AOP technologies it is important to determine the power consumption required to generate the hydroxyl radical. The AOP technology selected must provide a process that operates efficiently and delivers a treated water quality that reduces all raw water contaminants/parameters to well below EPA and State standards.

UV / PEROXIDE TECHNOLOGY

For example, if we consider a 1 – log reduction of 1,4 dioxane for a 1,200 gpm well and assume that the required U.V. dosage rate is 1,500 mj /cm3 and the H2O2 dosage rate is 10 to 14 mg/L, the UV/peroxide system will require an estimated power consumption of 60 kilowatts.

OZONE / PEROXIDE TECHNOLOGY

Treating the same well (1,200 gpm), the required ozone dosage rate would be 8 mg/L and the H2O2 dosage rate would be 8 -10 mg/L. The ozone feed rate for this application would be 115 PPD at 14%, resulting in a power consumption of approximately 30 kilowatts. For this example, the energy consumption of the ozone/peroxide AOP is one half of the energy required by the UV/ peroxide AOP.

By using Primozone's "cutting edge" modular technology with higher ozone concentrations, reduced oxygen consumption, small footprint, built-in redundancy and efficient mass transfer customers will realize a significant reduction in the cost of operating their AOP.

It is also important to note that the ozone/peroxide system will require a lower peroxide dosage than a UV based AOP technology. This is due to the poor absorption rate of UV light caused by the hydrogen peroxide that is required to start the formation of hydroxyl radicals. Therefore, the chemical costs with the UV based AOP technology will be higher than the ozone based AOP technology.

QUENCHING OF PEROXIDE

After the formation of the hydroxyl radical, excess residual peroxide from either the UV, or ozone based AOP technology must be removed from the water by quenching.

Note: Excess peroxide is quenched from the treated water because hydrogen peroxide is not an approved disinfectant and will quench free chlorine residual.

The excess peroxide quenching process is typically performed by GAC filtration. Due to the higher dosage of peroxide with the UV based AOP technology larger GAC filters may be required, resulting in additional costs and/or shorter life cycle of the GAC.

EXECUTIVE SUMMARY

When using ozone with hydrogen peroxide for the removal of target contaminants such as 1,4-dioxane, the combination of these oxidants can have additional benefits including; color reduction, improved micro flocculation for downstream media filtration, disinfection and the oxidation of arsenic, iron, and manganese.

The combination of ozone with hydrogen peroxide will generate the hydroxyl radical which is necessary for the removal of 1,4-dioxane. The presence of ozone, hydrogen peroxide and the hydroxyl radicals will also have significant benefits for the treatment of other contaminants of emerging concern, or scavengers, found in the raw water source. This combination of oxidants that are dissolved in the water is the reason why ozone plays an important role in the generation of the hydroxyl radical and is more effective when compared to other AOP technologies, such as UV and peroxide. The removal of target contaminants is dependent on their sensitivity to ozone or the hydroxyl radical, and the levels of ozone or hydroxyl radicals depends on the water matrix. For these reasons we strongly recommend field pilot studies to select and optimize the AOP treatment process best suited for the application.

In addition to the contaminant treatment benefits provided by a Primozone / Pureflow ozone / peroxide AOP process, O&M costs such as a 50% reduction (approximate) in power and reduced oxygen consumption are significant and must be considered when comparing alternate AOP technologies.

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