Author: Tim Baron

Water Treatment - Oxidation

Sources:

Water Treatment: Principles & Design (Crittenden)
Water Quality Control handbook (Alley)
Water Quality Engineering: Physical/Chemical Treatment Processes (Benjamin)
Water Quality Treatment: A Handbook On Drinking Water (Edzwald)
Principles of Water Treatment (Howe)
Chemistry (Burdge)
EPA Website (www.epa.gov)
USP Technologies website (http://www.h2o2.com)

What Is Oxidation?

Oxidation and reduction, also called "redox" reactions, are chemical reactions that can be used in wastewater treatment processes for the treatment of specific organic and inorganic species found in water. All chemical and biological wastewater treatments use redox reactions. Compounds that contain oxygen, nitrogen, sulfur, carbon, and metals with more than one oxidation state (for example: manganese, iron, and chromium) go through processes that change the oxidation state. This change significantly alters the chemical properties of these compounds and is the basis for the chemical removal of sulfur, nitrogen, organics, and metals from wastewater.

Conventional oxidation with ozone, oxygen, hydrogen peroxide, permanganate, potassium ferrate, chlorine, and chlorine dioxide is used in biological water treatment. Microorganisms catalyze these redox reactions. There are also advanced oxidation processes that use ozone in combination with hydrogen peroxide or ultraviolet radiation that produce hydroxyl radicals. Hydroxyl radicals are very powerful oxidants.

Redox reactions convert organic compounds into harmless non-objectionable forms. They often oxidize toxic organic compounds into carbon dioxide and mineral acids (such as HCl). Taste and odor compounds are oxidized into non-odorous compounds. An inorganic compound, like the odorous gas hydrogen sulfide, is oxidized into non-odorous sulfate.

Chemical equations are needed to understand redox reactions in wastewater treatment. Redox reactions consist of two parts: an oxidation reaction and a

reduction reaction. A balanced equation, representing a system in equilibrium with both products and reactants, is necessary. Oxidation occurs when a substance loses (or donates) electrons. This can also be thought of as the combination of a compound with oxygen (also known as an increase in oxidation state). Reduction occurs when a substance gains (or accepts) electrons (also known as a decrease in oxidation state).

Types of Reactions

Oxidation reactions can be categorized as reactions involving the transfer of electrons or the transfer of atoms and groups of atoms. These reactions can also be categorized as reactions involving species with paired electrons (ionic) and unpaired electrons (radical).

Several reactions involve free-radical species that occur upon adding oxidants to water. Free radicals are atoms, molecules, or ions that are highly reactive. This is due to their unpaired electrons. In water treatment these reactions are often encountered with ozone, chlorine dioxide, and most notably advanced oxidation processes. The addition of ozone always leads to some ozone decomposition, which results in the formation of hydroxyl radicals ($HO\bullet$). Hydroxyl radicals engage in reactions that generally lead to the formation of new free radical-species. The most common of these reactions are addition reactions, single-electron transfers, and hydrogen abstractions.

Catalysis

Many oxidation reactions are strongly affected by catalysts. Catalysts are constituents that alter reaction rates but are not formed or consumed in the reaction. Generally, catalysts participate in a key rate-limiting step and are regenerated during a later step. They usually provide an alternative pathway with lower activation energy, thus the reaction proceeds faster.

The most important catalytic processes in water treatment involve acids and bases. Specific acid base catalysis involves H^+ and specific base catalysis involves OH^-. In general, acid and base catalysis involves an electron acceptor and an electron donor. An example of this is the haloform reaction.

Reactions that involve the catalytic initiation of a free radical chain are also an important type of catalysis in oxidation processes. These include reactions such as decomposition of ozone by hydroxide and decomposition of chlorine by iron. In either case, the original oxidant will not react sufficiently with recalcitrant compounds (such as oxalate). With the presence of an appropriate catalyst decomposition will initiate, which leads to a series of chain propagation reactions in which oxalate will readily be converted to carbon dioxide.

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Oxidation reactions can also be catalyzed by the presence of solid phases in the system, which are able to adsorb one or more of the reacting species.

Reaction Pathways

Oxidation reactions in water treatment are often complex. The reaction may begin with one mechanism, but that mechanism can be followed by various non-oxidation processes such as elimination reactions, radical chain reactions, rearrangement reactions, and hydrolysis reactions.

For example, a reaction resulting in the formation of trihalomethanes may occur through many reaction pathways. A commonly studied reaction is the haloform reaction. This involves the stepwise chlorine substitution of the enolate form of methyl ketone. The rate-limiting step is the loss of a proton. This leads to the formation of enol. The reaction begins with base-catalyzed halogenations, which ultimately leads to a carboxylic acid and chloroform. It's base-catalyzed because the enol form of the methyl ketone is the species that reacts with hypochlorous acid. Any strong base catalyzes the reaction. The base that's consumed in the first step is regenerated in the second step. The enol forms a mono-halogenated intermediate when it undergoes electrophilic substitution. The halogens present on this carbon speed up subsequent enolization. This leads to complete halogenation of the α-carbon. This results in an intermediate that is a trihalogenated acetyl compound. It is subject to base-catalyzed hydrolysis, which results in a trihalomethane and a carboxylic acid. If the only halogenating species is hypochlorous acid, chloroform is the result.

Thermodynamics and Oxidation

Thermodynamics establishes the constraints of oxidation reactions. Chemical kinetics can be used to describe the mechanisms by which reactions occur and the rate of these reactions. Thermodynamic properties such as free energies, entropies, and enthalpies are a good starting point for characterizing and understanding oxidation reactions.

Oxidation Processes

There are many different oxidation processes and they are used in various applications. These can be broken down into three categories:

- **Conventional Oxidation Processes** – These use oxidants such as potassium permanganate, chlorine, and chlorine dioxide. They do not produce highly reactive species like the other two processes. Reactions are more specific in

regards to the type of organic molecules that can be oxidized. Reaction rates are slower than they are in the other processes. This process does not produce the hydroxyl radical ($HO\bullet$), which is a highly reactive species with an unpaired electron in the outer orbital. $HO\bullet$ radicals are highly reactive electrophiles and react with most organic compounds.

- **Oxidation Processes at Elevated Temperatures and/or Pressures** – These processes require elevated temperatures and/or pressures. They involve free-radical reactions with hydroxyl radicals ($HO\bullet$). They oxidize organic matter using processes such as: catalytic oxidation, gas-phase combustion, wet oxidation, and supercritical oxidation.

- **Advanced Oxidation Processes** – These processes generate hydroxyl radicals ($HO\bullet$) at room temperature and atmospheric pressure. These processes can remove toxic synthetic organic compounds (SOCs). They can remove fuels, solvents, pharmaceuticals, pesticides, and herbicides. Conventional oxidation processes cannot completely oxidize these substances. Advanced oxidation can completely convert organic compounds into carbon dioxide, mineral acids, and water.

Important Terms

- **Anode** – The electrode where oxidation occurs.

- **Cathode** – The electrode where reduction occurs.

- **Chromophores** – Functional groups on chemical compounds that are responsible for absorbing light.

- **Electron Acceptor** – An oxidant (reactant that gains electrons in redox reactions).

- **Electron Donor** – A reductant (reactant that loses electrons in redox reactions).

- **Oxidant** - A reactant that causes the oxidation of a reduced species during a redox reaction. Oxidants accept electrons.

- **Oxidation Reaction** – A chemical half-reaction where a reactant loses electrons.

- **Reductant** – A reactant that causes the reduction of an oxidized species during a redox reaction. Reductants donate electrons.

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- **Redox Reaction** – An oxidation-reduction reaction in which electrons are transferred from one reactant to another.

- **Reduction Reaction** – A chemical half-reaction in which a reactant gains electrons.

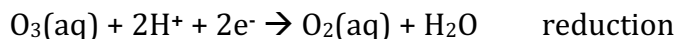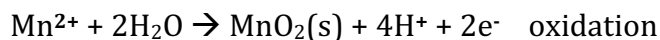# Chemical Oxidation/Reduction Fundamentals

Oxidation and reduction reactions, known as redox reactions, are processes involving the exchange of electrons between constituents. The force for the change of electrons is a decrease in electrical potential. This is similar to the action of electrons when a live electrical wire is grounded; all of the electrons flow to the ground.

Half Reactions

If a redox reaction takes place when an oxidant is added to water, electrons are transferred from the reductant to the oxidant. The chemical constituent that gains electrons (is reduced) is called the oxidant. The chemical constituent that loses electrons (is oxidized) is called the reductant. For example:

$$Mn^{2+} + O_3(aq) + H_2O \rightarrow MnO_2(s) + O_2(aq) + 2H^+$$

In this case the manganese (Mn^{2+}) ion is oxidized using ozone (O_3) and produces manganese oxide precipitate. Ozone is reduced to aqueous oxygen. Manganese loses two electrons, while ozone gains two electrons. Because of the exchange of electrons, this redox reaction can be separated into half reactions as such:

$$Mn^{2+} + 2H_2O \rightarrow MnO_2(s) + 4H^+ + 2e^- \quad \text{oxidation}$$

$$O_3(aq) + 2H^+ + 2e^- \rightarrow O_2(aq) + H_2O \quad \text{reduction}$$

In this case manganese is oxidized by ozone (loses two electrons), thus ozone is an oxidant. Since ozone is reduced by manganese (gains two electrons), manganese is a reductant. The first equation is the oxidation half-reaction and the second equation is the reduction half-reaction.

Redox Reactions – Balancing Half Reactions

Redox reactions can be balanced using the half-reaction method. Steps for balancing redox reactions using the half-reaction method are as follows:

1) Write down the principal reactants and products for one of the half reactions. Do not write down hydrogen and oxygen atoms.

2) Balance all of the atoms (except hydrogen and oxygen atoms) using probable forms that can be found in solution.

3) Balance oxygen atoms with the oxygen in water (H_2O).

4) Balance hydrogen atoms with H^+.

5) Balance the charge using electrons. If the reactants generate electrons the half-reaction is an oxidation reaction. If the reactants consume electrons the half-reaction is a reduction reaction.

6) Write down the principal reactants and products for the other half reaction. Do not write down hydrogen and oxygen atoms.

7) Balance all of the atoms (except hydrogen and oxygen atoms) using probable forms that can be found in solution.

8) Balance oxygen atoms with the oxygen in water (H_2O).

9) Balance hydrogen atoms with H^+.

10) Balance the charge using electrons. If the reactants generate electrons the half-reaction is an oxidation reaction. If the reactants consume electrons the half-reaction is a reduction reaction.

11) Obtain a balanced reaction by adding the half reactions together, which will eliminate electrons from the equation.

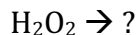# Example - Balancing Half Reactions (Crittenden et al.)

1)

Balance a redox reaction for hydrogen peroxide (H_2O_2) oxidation of 1,1-dichloroethene ($C_2H_2Cl_2$).

Write the unbalanced reaction:

$$C_2H_2Cl_2 + H_2O_2 \rightarrow HCl + CO_2$$

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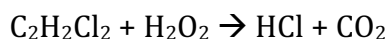
2)

Balance the reaction starting with the half reaction for hydrogen peroxide:

$$H_2O_2 \rightarrow ?$$

The expected reactants and products (other than oxygen and hydrogen) should be balanced. In this case, there are no atoms other than hydrogen and oxygen. Then balance the oxygen on the left side of the expression with the oxygen in the water on the right side:

$$H_2O_2 \rightarrow 2H_2O$$

Balance the hydrogen by placing $2H^+$ on the left-hand side of the expression:

$$H_2O_2 + 2H^+ \rightarrow 2H_2O$$
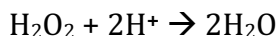
Balance the charge by placing two electrons on the left side of the expression:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$
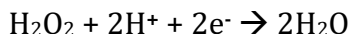
This reaction represents the reduction half reaction because the reactant gains electrons. Hydrogen peroxide is the oxidant because it accepts electrons from the oxidation half reaction.
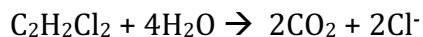
3)

Evaluate the oxidation half reaction in which the reactant loses electrons.

Balance the expected reactants and products (other than hydrogen and oxygen):

$$C_2H_2Cl_2 \rightarrow ?$$

$$C_2H_2Cl_2 \rightarrow CO_2 + 2Cl^-$$

$$C_2H_2Cl_2 \rightarrow 2CO_2 + 2Cl^-$$
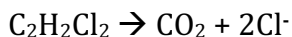
Balance the reaction for oxygen using the oxygen in water:

$$C_2H_2Cl_2 + 4H_2O \rightarrow 2CO_2 + 2Cl^-$$

Balance the reaction for hydrogen with H^+:

$$C_2H_2Cl_2 + 4H_2O \rightarrow 2CO_2 + 2Cl^- + 10H^+$$

Balance with electrons:

$$C_2H_2Cl_2 + 4H_2O \rightarrow 2CO_2 + 2Cl^- + 10H^+ + 8e^-$$
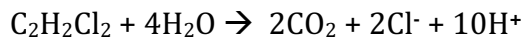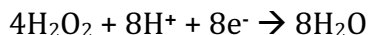
This expression represents the oxidation half reaction. The reactant loses electrons. Dichloroethene is the reductant because it causes the reduction of the oxidant (donates electrons).
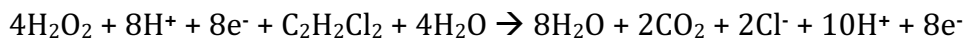
4)

Add the half reactions together and eliminate electrons from the reaction. Multiply the reduction half reaction by 4 so that when it is added to the oxidation half reaction electrons will be eliminated from the reaction:
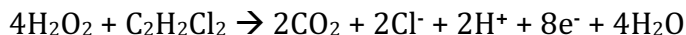
$$4H_2O_2 + 8H^+ + 8e^- \rightarrow 8H_2O$$

+

$$C_2H_2Cl_2 + 4H_2O \rightarrow 2CO_2 + 2Cl^- + 10H^+ + 8e^-$$

Adding the half reactions gives:

$$4H_2O_2 + 8H^+ + 8e^- + C_2H_2Cl_2 + 4H_2O \rightarrow 8H_2O + 2CO_2 + 2Cl^- + 10H^+ + 8e^-$$

5)

Manipulate molecules that have stoichiometric coefficients on both sides to obtain the final expression:

$$4H_2O_2 + C_2H_2Cl_2 \rightarrow 2CO_2 + 2Cl^- + 2H^+ + 8e^- + 4H_2O$$

As can be seen, hydrogen peroxide can oxidize dichloroethene. In practice, the reaction is impractical in large-scale treatment systems because the reaction rate is too slow. Dichloroethene requires advanced oxidation.

Standard Electrode Potentials

Electron exchange in redox reactions can be characterized from the standard electrode potentials for oxidation and reduction half reactions. Every reaction can be characterized by the EMF (or electrical potential). This potential is called the standard electrode potential and the unit of measurement is volts. (A table of standard electrode potentials is available online from various chemistry sources).

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To obtain the potential using the International Union of Pure and Applied Chemists (IUPAC) convention:

- Half reactions are written as reduction reactions.

- To obtain the oxidation reaction, reverse the direction of the reduction reaction and multiply the reduction potential by (-1).

- The calculated standard electrode potential values are given with respect to a reference standard hydrogen electrode (SHE) or normal hydrogen electrode (NHE).

Example – Redox Potential Using Oxygen

The value corresponds to these two half reactions:

$$O_2(aq) + 4H^+ + 4e^- \rightleftharpoons 2H_2O \qquad \text{(reduction)} \qquad E^0_{red} = 1.27 \text{ V}$$

$$H_2 \rightleftharpoons 2H^+ + 2e^- \qquad \text{(oxidation)} \qquad E^0_{OX} = 0 \text{ V}$$

Multiply the second equation by two, add the equations, and manipulate electrons and H^+ algebraically.

$$O_2 + 2H_2 \rightleftharpoons 2H_2O$$

$$\text{Now find } E^0_{RXN}$$
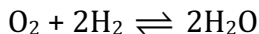
To find E^0_{RXN} add the reduction and oxidation potentials together (note sign convention). The numbers of electrons transferred are identical for reduction and oxidation reactions.

$$E^0_{RXN} = E^0_{red} + E^0_{OX}$$

$$= 1.27 + 0 = 1.27 \text{ V}$$

A positive value generally indicates that the reaction will proceed as written. Note that the electrical potential and free energy must be evaluated at the expected concentrations of the solution.

Conventional Oxidation Processes in Water Treatment

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Oxidation involves losing one or more electrons and reduction involves gaining one or more electrons. These redox reactions can be used for water treatment. Oxidation or reduction can be used in water treatment. However, oxidation is more commonly used. Oxidation destroys reduced state chemical constituents such as odorous compounds, toxic organic compounds, and inorganic compounds (such as: hydrogen sulfide, manganese, and iron).

Commonly Used Conventional Oxidants

Conventional oxidants for water treatment are used for taste and odor control, hydrogen sulfide removal, color removal, iron and manganese removal, and disinfection. The most commonly used oxidants are: hydrogen peroxide, permanganate, chlorine dioxide, ozone, and chlorine.

Hydrogen peroxide, permanganate, chlorine dioxide, and chlorine are used to convert soluble metals to insoluble forms. They also oxidize odorous sulfide and destroy metal organic complexes.

Ozone destroys taste and odorous compounds. It can also destroy toxin organics, eliminate color, reduce organic matter, and disinfect by-product precursors.

Oxidants are usually added at the beginning or the end of the wastewater treatment process. However, under some circumstances they may need to be added at various points during the treatment for best effect.

Additional information about common oxidants:

Chlorine

This is the most widely used oxidant in water treatment. It is available in gaseous [Cl_2], concentrated aqueous solution [bleach = sodium hypochlorite, NaOCl], and solid [calcium hypochlorite, $Ca(OCl)_2$] form. Chlorine can also be electrolytically generated on-site at the water treatment plant.

Gaseous chlorine is usually provided for water treatment in pressurized tanks. In this case, chlorine exists as a liquid under pressure. Chlorine is added to the water by reducing the pressure in the tank and releasing the chlorine as a gas. Handling chlorine gas is very dangerous, and extreme care must be taken when working with chlorine feeding equipment.

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$

Liquid sodium hypochlorite is generally added directly into the main plant flow from a concentrated NaOCl bulk solution with a liquid metering pump.

$$NaOCl \rightarrow Na^+ + OCl^-$$

$$OCl^- + H_2O = HOCl + OH^-$$
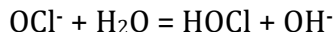
Solid granules of calcium hypochlorite can be added directly to wastewater, or a concentrated solution can be made from which the hypochlorite is metered into the main flow. Calcium hypochlorite is seldom used at municipal water treatment plants.

$$Ca(OCl)_2 \rightarrow Ca^{2+} + 2OCl^-$$

For many years, gaseous chlorine in pressured tanks has been the most common method of application in municipal water treatment. However, more recently, due to concerns about the transport and handling of hazardous materials, the use of liquid sodium hypochlorite is more widely used despite its higher cost. However, a potential concern when using sodium hypochlorite is stability. Hypochlorite degrades over time, especially when it is stored at high temperatures or when exposed to sunlight. A degradation product of sodium hypochlorite, chlorate (ClO_3^-), is a health concern. General practice is to limit on-site storage of sodium hypochlorite feedstock to 90 days. Another sodium hypochlorite inorganic disinfection by-product, bromate, is also a concern. When sodium hypochlorite is fed at the typical doses used in practice, bromate may be produced at levels that exceed regulatory limits. Practices need to be strictly followed to minimize the presence of bromate.

Free chlorine can be generated electrolytically on-site with brine solutions (salt water). Molecular chlorine generated at the anode can be dissolved in sodium hydroxide (NaOH), a by-product of the electrolysis reaction.

$$Cl_2 + NaOH \rightarrow NaOCl + H^+ + Cl^-$$

This produces a concentrated sodium hypochlorite solution. Producing chlorine gas on-site costs more than purchasing chlorine gas in pressurized tanks, but it eliminates the transport and handling hazards of working with pressurized chlorine containers. Even though it is more expensive than purchasing bulk sodium hypochlorite, it can be paced to the specific chlorine needs during treatment. This eliminates the need for storage and minimizes losses associated with degradation over time.
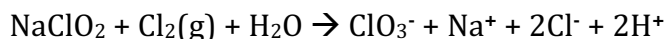
Chlorine Dioxide

Chlorine dioxide is never shipped in bulk because it is unstable in high concentrations and can explode from exposure to heat, light, electrical sparks, or shocks. Therefore, it is generated on-site. Aqueous solutions can be prepared from

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the gaseous chlorine generated on-site since it is very water-soluble. It does not hydrolyze in water like chlorine and therefore remains in its molecular form (ClO_2). It must be carefully handled at all times because it is volatile and can be easily stripped from aqueous solution. Generating chlorine dioxide is usually accomplished by reacting sodium chlorite ($NaClO_2$) with hypochlorous acid ($HOCl$) or gaseous chlorine (Cl_2) under acidic conditions.

$$2NaClO_2 + Cl_2(g) \rightarrow 2ClO_2(g) + 2Na^+ + 2Cl^-$$

$$2NaClO_2 + HOCl \rightarrow 2ClO_2(g) + 2Na^+ + Cl^- + OH^-$$

To drive the reaction to completion and to keep unreacted chlorite (ClO_2^-) out of the product stream, generators sometimes use excess chlorine. However, several generators are designed to allow for the sodium chlorite to be completely converted to chlorine dioxide without using excess chlorine. To overcome the basicity of sodium chlorite and hydroxide produced, acid can be added with hypochlorous acid. This is used to maintain the optimal pH for chlorine dioxide generation. The preferred pH is between 3.5-5.5 as more acidic pH values lead to chlorate (ClO_3^-) formation.

$$NaClO_2 + Cl_2(g) + H_2O \rightarrow ClO_3^- + Na^+ + 2Cl^- + 2H^+$$

Chlorine dioxide can also be produced by the acidification of a sodium chlorite solution.

$$5NaClO_2 + 4H^+ \rightarrow 4ClO_2(g) + 5Na^+ + Cl^- + 2H_2O$$
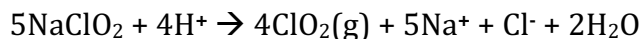
After it's been generated, chlorine dioxide can be dissolved in water. It is then stable provided there's no light or elevated temperatures. Chlorine dioxide disproportionates to form chlorite and chlorate (neither desirable in drinking water) if it is allowed to reach a high pH level or if it's exposed to light or elevated temperatures.

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$$

Chlorine dioxide has generally been used to treat water for taste and odor issues, but it is also effective as a disinfectant or an oxidant for reduced iron or manganese. An important advantage of chlorine dioxide is that it doesn't react with ammonia. Because of this, significantly lower does of chlorine dioxide are needed for most oxidative applications in comparison to chlorine dosage requirements. It also does not enter into substitution reactions with natural organic matter to the same degree that chlorine does, thus does not form trihalomethanes, haloacetic acids, or significant amounts of most of the other common halogenated disinfection by-products that result from chlorination. The disinfection/oxidation by-products of chlorine dioxide treatment such as aldehydes, carboxylic acids, and some halogenated compounds are only present in extremely low concentrations. Chlorine

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dioxide has garnered renewed interest due to the lack of formation of significant amounts of halogenated disinfection by-products. It also reacts very slowly with bromide. This eliminates concern for organic and inorganic brominated by-products when using a chlorine dioxide treatment.

Chlorine dioxide reacts with most reducing agents via a one-electron transfer. Because of this, chlorite is considered to be the principal oxidation by-product of chlorine dioxide usage. About 50% to 70% (by mass) of the chlorine dioxide applied during drinking water treatment ends up as chlorite.

$$ClO_2 + e^- \rightarrow ClO_2^-$$
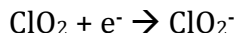
Chlorite has a number of potentially negative health effects based on laboratory studies. The Stage 1 and Stage 2 Disinfectants/Disinfection By-Products rules (USEPA, 1998, 2006) list a maximum contaminant level (MCL) of 1.0 mg/L for chlorite in a distribution system and a maximum residual disinfectant level (MRDL) of 0.8 mg/L for chlorine dioxide when it enters the distribution system. Currently, there are no regulations for chlorate. Since chlorine dioxide is quickly consumed during water treatment and about 70% of the applied chlorine dioxide is reduced to chlorite, the maximum upper limit for chlorine dioxide doses is approximately 1.4-1.5 mg/L (unless chlorite is removed).

Residual chlorite presents a second concern. It reacts with free chlorine and thus produces low levels of chlorine dioxide and/or chlorate.

$$HOCl + 2ClO_2^- \rightarrow 2ClO_2 + Cl^- + OH^-$$

$$HOCl + ClO_2^- \rightarrow ClO_3^- + Cl^- + H^+$$
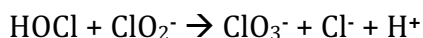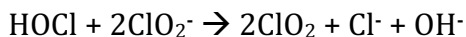
If chlorine dioxide is present in tap water, it can be released into a home or office environment when taps are opened. This can lead to chlorinous odors or react with the organic compounds released from new carpeting to produce other undesirable odors.

Chlorite, whether from incomplete oxidation of sodium chlorite in a chlorine dioxide generator or from chemical reduction of the chlorine dioxide during water treatment, can be removed from water using ferrous iron salts or reduced sulfur compounds.

$$4Fe^{2+} + ClO^-_2 + 10H_2O \rightarrow 4Fe(OH)_3(s) + Cl^- + 8H^+$$

$$2HSO^-_{3-} + ClO^-_2 \rightarrow 2SO_4^{2-} + Cl^- + 2H^+$$
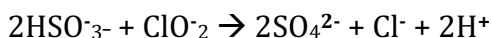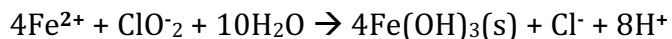
There's no cost effective way to remove chlorate, therefore it's necessary to minimize its formation during chlorine dioxide generation.

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Hydrogen Peroxide

Generally hydrogen peroxide (H_2O_2) is not used as a stand-alone treatment for disinfecting drinking water and is not approved as such. Hydrogen peroxide is a weak microbiocide compared to ozone, chlorine, and other commonly used disinfectants. However, hydrogen peroxide is part of some water treatment processes. The advanced oxidation process uses H_2O_2 with ozone (O_3) and/or UV light to produce hydroxyl radicals ($HO\bullet$). These are extremely effective in removing taste and odor compounds in organic and inorganic micropollutants. In addition, H_2O_2 can be catalyzed with iron to produce hydroxyl radicals by Fenton's reaction. Adding H_2O_2 together with UV light and/or ozone to produce hydroxyl radicals makes the treatment more effective than ozone or UV alone.

Hydrogen peroxide has been used for many years to reduce the biochemical oxygen demand and chemical oxygen demand of industrial wastewater. The cost in some cases is higher than using other physical and biological methods, however the use of H_2O_2 is warranted in some circumstances. Its use is notably warranted in pre-digestion of wastewaters containing moderate to high levels of compounds that are toxic and water that is recalcitrant to biological treatment, or inhibitory.

Ozone

Ozone (O3) is an unstable gas and must be generated on-site. A basic chemical representation of the formation of ozone is demonstrated by the following equations:

$$O_2 + \text{Energy} \rightarrow O + O$$

$$O + O_2 \rightarrow O_3$$
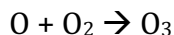
The energy required to produce elemental oxygen (O) from molecular oxygen (O_2) is supplied by an electric discharge with a peak voltage from 8-20 kV. An ozone generator passes dry, refrigerated, particle-free air, oxygen, or oxygen-enriched air through a narrow gap between two electrodes. A high-energy discharge is generated across the gap between the two electrodes. This corona (or cold plasma) is induced by an alternating current. The current creates a voltage cycle between the electrodes. Ozone yield depends on the voltage, frequency, and design of the ozone generator as well as the type and feed of the gas that's used. Ozone streams having 14% ozone by volume can be produced. Generators are available in low frequency (50-60 Hz), medium frequency (400-1,000 Hz), and high-frequency (2,000-3,000 Hz) configurations.
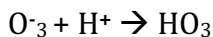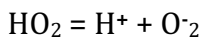
Ozone enriched air or oxygen gas is transferred into solution by passage through a gas absorption device. This is done using either a countercurrent

multistage bubble contactor using gaseous diffusers or an in-line gas injection system using Venturi-type injectors.

Ozone is unstable in aqueous solution. Ozone is highly reactive with many constituents found in drinking water. It undergoes a spontaneous decomposition process called auto-decomposition. This is a complex chain reaction process that involves several free-radical species. Decomposition can be initiated by some of the constituents found in water including hydroxide ions, natural organic matter, or ferrous iron. It can be initiated by adding hydrogen peroxide or irradiation using ultraviolet light (UV).

An example of auto-decomposition initiated by the hydroxide ion:

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

$$HO_2 = H^+ + O_2^-$$

$$O_2^- + O_3 \rightarrow O_2 + O_3^-$$

$$O_3^- + H^+ \rightarrow HO_3$$

$$HO_3 \rightarrow O_2 + OH$$

$$OH + O_3 \rightarrow HO_2 + O_2$$

Ozone is an autocatalytic reaction since the OH radical reacts rapidly with molecular ozone.

The reactions above are considered chain mechanisms because the hydroperoxyl radical (HO_2) generates additional superoxide (O_2^-). And this further contributes to the decomposition of ozone. In pure water, hundreds of ozone molecules may be decomposed by a single initiation step. The lifetime of ozone in water depends on pH, temperature, total organic carbon concentration, bicarbonate concentration, and carbonate concentration.

The hydroxyl radical ($HO\bullet$), produced as an intermediate during decomposition, is one of the strongest chemical oxidants known. It reacts with many organic and inorganic impurities in water. Ozone reacts by two types of pathways. There is a direct pathway involving molecular ozone (O_3) and an indirect pathway that originates with ozone decomposition and produces the hydroxyl radical ($HO\bullet$)

Mixed Oxidants

The electrolysis of brine has been used to produce chlorine since the nineteenth century. Recently, this process has been modified and adapted to

produce a mixture of free chlorine and other oxidants and disinfectants for use in water treatment. Devices are available that can generate liquid or gas phase oxidants. This process has been particularly applicable for small, rural water supplies.

The device is based on fundamental electrochemical theory. Chloride is oxidized to chlorine at the anode of the electrochemical cell, which afterwards hydrolyzes to hypochlorous acid.

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

$$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+$$
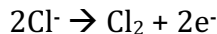
The pH of the anodic stream is generally between 3 and 5. Water is reduced to hydrogen gas at the cathode. This produces a strong alkaline solution with a pH between 10 and 11.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
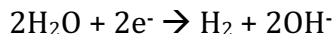
A semipermeable barrier is used to separate the cathodic and anodic streams. Although free chlorine is the primary oxidant produced in mixed oxidant generators, other reactions occur at the anode, usually resulting in the formation of ozone, chlorine dioxide, hydrogen peroxide, and other short-lived oxidants. In addition, a number of inorganic by-products are formed including chlorite, chlorate, and bromate. Additional research is necessary to fully characterize these product streams before these devices see widespread use.

Potassium Ferrate

Potassium ferrate (K_2FeO_4) is fairly new to the field of water treatment. Ferrate contains iron in the +VI oxidation state and has a standard half-cell potential of 2.07 V. These qualities make it a strong oxidant. When the Fe(VI) is reduced it produces Fe(III), which serves a coagulation function or an adsorptive function with respect to arsenic removal.

$$FeO_4{}^{2-} + 5H^+ + 3e^- \rightarrow Fe(OH)_3(s) + H_2O$$
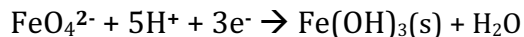
Ferrate is unstable in acidic conditions but stable in alkaline solutions. Ferrate can be produced in the lab through oxidization of Fe(III) solution with concentrated hypochlorite under alkaline conditions. It can also be produced electrochemically from metallic iron under strong alkaline conditions. Research indicates that ferrate rapidly oxidizes many of the trace organic contaminants in water such as endocrine disruptors and pharmaceutical compounds. Ferrate is also very effective at disinfection.

Potassium Permanganate

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Potassium permanganate ($KMnO_4$) is commercially available in crystalline form. It's either prepared as a concentrated solution on-site and the desired dose is metered into the water or it is directly fed into solution with a dry chemical feeder. Permanganate has manganese in the +VII oxidation state. Generally, treatment with permanganate oxidation involves a three-electron transfer where the permanganate (MnO^-_4) is reduced to insoluble manganese dioxide ($MnO_2(s)$).

$$MnO^-_4 + 4H^+ + 3e^- \rightarrow MnO_2(s) + 2H_2O$$
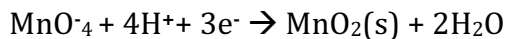
The manganese dioxide produced is a black precipitate that must be removed by a solid-liquid separation process. If it's not properly removed, it will create black particulate deposits in the distribution system and in household plumbing. It's usually removed by conventional clarification or filtration processes. Permanganate is generally added at the head of the treatment plant (as close to the intake as possible) because wastewater plant operators are fearful of seeing pink water (unreacted permanganate) going through their filters. When added at intake, permanganate will perform its oxidative function and be reduced completely, prior to reaching the filters.

Oxidation reaction kinetics involving permanganate are more rapid with increasing pH values. Therefore, in some cases, addition of a base prior to filtration may be necessary to speed up the reduction of permanganate.

Manganese dioxide, which forms as a result of permanganate reduction, has some useful attributes. It's a good adsorbent for ferrous iron (Fe^{2+}), manganous manganese (Mn^{2+}), radium (Ra^{2+}), and other trace inorganic cationic species. Additional removal of Fe^{2+} and Mn^{2+} occurs during permanganate treatment beyond that achieved by oxidation. The adsorptive behavior of $MnO_2(s)$ underlies the historic manganese greensand process where the filter media is coated with manganese dioxide and serves as an adsorbent for Fe^{2+}, Mn^{2+}, and Ra^{2+} in the filter influent. Permanganate is added to filter backwash water or to the filter influent to oxidize adsorbed Fe^{2+} and Mn^{2+} to create additional adsorption sites.

Solid manganese dioxide also adsorbs natural organic matter that serves as disinfection by-product precursors. This benefit is noticeably pronounced in hard waters, likely because of the bridging action of calcium and magnesium. This facilitates adsorption of natural organic matter to the negatively charged MnO_2 surface.

Taste and Odor Treatment

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A wide variety of treatment processes are used for taste and odor treatment because there are numerous combinations of organic and inorganic compounds that can cause tastes and odors in wastewater. Most taste and odor compounds in wastewater are found in a reduced form, thus oxidation is effective in treating them. Unfortunately, no simple treatment process is cost effective for all taste and odor wastewater issues. Each case must be analyzed individually.

Taste and Odor in Surface Water

Organic and inorganic compounds can cause taste and odor problems in water. Naturally occurring organic compounds from algal blooms and bacteria are responsible for most taste and odor problems in surface water. Outbreaks usually occur in June and October. It is thought that actinomycetes and cyanobacteria produce and release the three main organoleptic compounds: geosmin, 2-methylisoborneol (MIB), and cyclocitral. Concentrations of Geosmin and MIB above 7 and 12ng/L (respectively) have resulted in consumer complaints. The odor concentration thresholds for geosmin and MIB are 4 and 9ng/L (respectively). The goal is to get these compounds into a low ng/L concentration. Only ozone and ozone/hydrogen peroxide do an exceptional job at removing these types of odorous compounds.

Taste and Odor in Groundwater

Naturally occurring inorganic compounds and organic sulfides (mercaptans) are the most significant source of taste and odor problems in groundwater. This is caused by the reducing environment in groundwater. Iron, manganese, and hydrogen sulfide are the most significant contributors to taste and odor issues.

Oxidants for Controlling Taste and Odor

Chlorine dioxide, permanganate, ozone, hydrogen peroxide, and chlorine are the most commonly used oxidants for eliminating chemicals that cause unwanted tastes and odors.

Advanced oxidation processes can be used to eliminate geosmin and MIB in surface waters, but are generally unnecessary since ozone alone is effective in these cases. Ozone is also preferred because it is the only oxidant that does not increase total dissolved solids and water providers can receive disinfection credit when it's used.

Chlorine can increase odor issues when used to destroy odors that are industrial or algal in origin. It also forms volatile products, lyses of algae cells, and odorant release. If low dosages of chlorine are added to water containing phenols, chlorophenol compounds form and give the water an unpleasant medicinal taste.

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The intensity of this taste increases as the chlorine dose increases, eventually reaching a maximum intensity. Adding more doses of chlorine after the maximum intensity is reached will ultimately destroy the chlorophenolic taste. However, adding a large amount of chlorine to wastewater is not ideal because of the formation of chlorination by-products, therefore measures should be taken to remove phenol before chlorination.

Removing Hydrogen Sulfide

Groundwater sometimes contains hydrogen sulfide (H_2S). Hydrogen sulfide has a very unpleasant and recognizable "rotten egg" odor. This odor must be removed to make the water more pleasant to drink. Hydrogen sulfide can also increase the level of corrosiveness to metal and concrete of some waters. Sulfides also promote the growth of filamentous sulfur bacteria, which leads to an overall loss of water quality. Ozone, potassium permanganate, chlorine, and hydrogen peroxide have all been proven as effective oxidants for removing hydrogen sulfide.

Using oxidation to remove hydrogen sulfide causes two problems: the formation of polysulfides (normally S_8) and turbidity. There's no way to avoid the formation of polysulfides if the hydrogen sulfide concentration is greater than 1 mg/L. Oxidant dosages greater than the stoichiometric requirement and pH values greater than 8 are necessary for conversion to sulfate. Polysulfides do not form at pH values greater than 9. This may explain why alkaline groundwater that contains sulfides and has been lime softened does not exhibit threshold odors after chlorination.

Polysulfides bring some significant problems to the table.

- They have unique taste and odor problems.

- They are difficult to remove

- They can complex with metals in distribution systems. This leads to the formation of black water.

Studies must be performed to find the ideal treatment method(s) to avoid polysulfide formation and to determine the separation methods necessary to remove polysulfides once formed.

Color Removal

The color of water is due to the degradation of natural organic matter (dead plant matter). Characteristically, the color is yellow and is associated with double bonds in polyaromatic hydrocarbons. Soluble organic carbon such as humic acids

and other substances, which are generally referred to as humic substances, are formed from the degradation of natural organic matter. Color can be expressed in light absorption at a specified wavelength or in platinum-cobalt units. Double bonds that absorb UV light also absorb visible light. Light absorption of color and UV light at 254nm correlate with one another. Disinfectant by-product (DBP) formation and UV light absorption are also related. Thus, UV light absorption at 254nm, color, and disinfection by-product formation all relate to each other. The reason this parameter relationship exists is because there is a correspondence between the reaction centers and the chromofores on natural organic matter.

Chlorine can be used to remove color, but since the chlorine reacts with natural organic matter and forms chlorinated by-products it is no longer used. Chlorine dioxide can remove color, but it produces the by-product chlorite that must then be dealt with. Ozone can also be used to remove color, but this depends on the ozone-to-dissolve organic carbon dosage ratio. Ozone also produces biodegradable compounds like aldehydes and ketones; these may stimulate biofilm growth in a distribution system. When using ozone, the production of biodegradable organic matter must be considered and it may be necessary to perform biological treatment downstream of the coagulation process. Also, biologically active filtration is effective in the removal of biodegradable organic matter.

Oxidation As A Coagulation Aid

Oxidants can aid in coagulation, which is the removal of dirt and other particles suspended in water. They can also aid in flocculation, which is a process of contact and adhesion whereby the particles of a dispersion form larger-sized clusters.

Oxidants aid these processes in numerous ways. First off, particles adsorb negatively charged natural organic matter. This imparts a negative charge on the particles, which creates particle repulsion and stability. Adding oxidants also appears to react with negatively charged adsorbed natural organic matter and make it more polar. This causes some of the natural organic matter to desorb, which leads to particles with a lower net negative surface charge. The oxidant may also react with the adsorbed organics and make them readily bind with Al(III) and Fe(III). In these cases, the particles are destabilized more easily using metal salts or they lose some negative charge and thus flocculate more easily. Oxidants can also react with natural organic matter in the bulk solution. This will produce carboxylic acid groups that bind calcium ions. The binding of calcium ions can cause direct precipitation of natural organic matter.

In some cases, chemical oxidants may also destroy functional groups responsible for metal complexation. The amount of metal coagulant necessary for particle destabilization will be reduced by either reduction in natural organic matter complexation sites or natural organic matter precipitation.

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Removal of Iron and Manganese

These oxidants have been shown to oxidize and precipitate iron and manganese: potassium permanganate, hydrogen peroxide, ozone, chlorine dioxide, oxygen, and chlorine. However, oxygen, potassium permanganate, chlorine dioxide, and chlorine cannot oxidize iron in many waters. This is due to the fact that iron forms a strong complex with natural organic matter. Therefore, the effectiveness of using chemical oxidation for removing iron must be evaluated on a case-by-case basis using pilot or batch testing. In some cases chemical oxidation may need to be combined with other processes such as coagulation and adsorption, which can effectively remove natural organic matter.

Removal of Organic Micro-pollutants

Chemical oxidation is also important in the elimination of micro-pollutants found in water supplies. Micro-pollutants are substances such as synthetic organic chemicals, fuel additives, chlorinated solvents, pharmaceutical compounds, personal care products, endocrine disruptors, and algal toxins. In these cases, the reaction depends on the nature of the organic compound present, other compounds and constituents in the water that interfere or compete with the targeted contaminant, temperature, and pH. Some organic compounds are easy to oxidize and others are not so easy to oxidize. For any given oxidant, the products of the reaction will vary depending on the ratio of the oxidant to contaminant, the oxidant itself, the pathway by which the reaction occurs, and general characteristics of the water. It is rare that a contaminant is completely mineralized to carbon dioxide and water. It's possible for the oxidation products to be more dangerous to human health than the parent compound.

For example, when phenol is oxidized by low doses of chlorine, this leads to the formation of mono-, di-, and trichlorophenols. The aromatic ring is cleaved to generate halogen-containing products at high doses. When phenol is oxidized by low ozone doses, this results in the formation of catechol and benzoquinone before the aromatic ring is cleaved at higher doses and produces a variety of low-molecular-weight carboxylic acids such as cis, cis-muconic, glyoxylic, and maleic acid. When phenol is oxidized by chlorine dioxide, this produces quinones, hydroxophenols, and several chloroquinones and chlorophenols as low oxidant doses. Further ring cleavage with higher doses of chlorine dioxide results in the formation of carboxylic acids as with ozone. Chlorination of natural organic matter leads to the formation of halogenated disinfection by-products.

Molecular ozone has selectivity for various types of contaminants. As an example, the rate constants when oxidizing pesticides span more than five orders of

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magnitude. Naphthalene and phenol are quickly oxidized by molecular ozone but atrazine, alachlor, methyl tertiary butyl ether, benzene, trichloroethene, and tetrachloroethene are slowly oxidized by molecular ozone. However, all of these are quickly oxidized by the hydroxyl radical ($HO\bullet$), which results from the decomposition of ozone. Therefore, processes that result in the formation of hydroxyl radicals are ideal for destroying these harmful contaminants. Such processes include ozonation at elevated pH values, usage of ozone with UV irradiation, or ozone with the addition of hydrogen peroxide (advanced oxidation processes). Processes that decrease the level of hydroxyl radicals decrease the effectiveness of advanced oxidation processes. This is particularly true for water supplies with high alkalinity, as they contain high concentrations of bicarbonate and carbonate which both scavenge hydroxyl radicals. Since micro-pollutants are generally present in low concentrations compared to the presence of natural organic matter, advanced oxidation processes are generally less effective in water with high levels of natural organic matter. It should be noted that in some cases, the presence of natural organic matter could accelerate oxidation.

Chlorine dioxide is also very selective as an oxidant. Research suggests that olefins, aromatic hydrocarbons, primary and secondary amines, ketones, aldehydes, and carbohydrates have low reactivity with chloride dioxide when used in water treatment. However, thiols, tertiary amines, and deprotonated phenols generally have high reaction rate constants. Before a noticeable elimination of micro-pollutants is achieved the oxidant demand of natural organic matter present must be overcome.

Endocrine disruptors, cyanotoxins, and pharmaceutically active compounds can also be oxidized by strong oxidants as follows:

Removal of Cyanotoxins

Research done by Rositano et al. (2001) indicates that 100% of the cyanotoxins microcystin-LR and microcystin-LA of were eliminated by ozonation of four treated waters with significantly different water qualities. The degree of elimination was related to the residual ozone concentration present after five minutes, which was also related to water quality. The research concluded that direct reaction with molecular ozone could be responsible for cyanotoxin elimination.

Further research by Rodriguez et al. (2007) looked at the oxidation of three cyanotoxins: cylindrospermopsin, anatoxin-a, and microcystin-LR. They oxidized these with ozone, chlorine, chlorine dioxide, and permanganate. Chlorine was able to oxidize cylindrospermopsin and microcystin-LR. Permanganate was able to oxidize anatoxin-a and microcystin-LR. Chlorine dioxide was not able to eliminate any of the cyanotoxins. Ozone was able to oxidize all three toxins at a higher rate than any of the other oxidants. Onstad et al. (2007) determined that hydroxyl radicals ($HO\bullet$) had a significant contribution in oxidizing these toxins with ozone in

natural waters. The order of reactivity corresponds with the relative magnitudes of the second order rate constants as such: anatoxin-a > cylindrospermopsin > microcystin-LR. The research concludes that since ozone primarily attacks the structural moieties responsible for toxic effects of these algal toxins, ozone selectively removes toxins from these compounds.

Removal of Pharmaceuticals, Endocrine Disruptors, and Personal Care Products

Research by Huber et al. (2003) calculated second-order rate constants for the reaction of certain pharmaceuticals with ozone and hydroxyl radicals. Five pharmaceuticals (carbamazepine, diclofenac, 17α-ethinylestradiol, sulfamethoxazole, and roxithromycin) had rate constants greater than $5 \times 10^4 \, M^{-1}S^{-1}$ with ozone at pH 7. This indicates that these compounds are completely transformed during the ozonation process. Ibuprofen, Diazepam, and iopromide had reactions that were orders of magnitude slower with values for the rate constants with hydroxyl radicals ranging from 3.3×10^9 to $9.8 \times 10^9 \, M^{-1}s^{-1}$. In comparison to other micro-pollutants such as methyl tertiary butyl ether and atrazine, the chosen pharmaceuticals reacted 2 to 3 times faster with hydroxyl radicals. The research concluded that ozonation and advanced oxidation processes were promising methods for the removal of pharmaceuticals in drinking water.

Research by Westerhoff et al. (2005) studied sixty-two different endocrine disrupting compounds, pharmaceutically active compounds, and personal care products. Their research indicates that chlorine and ozone decreased the concentrations of these contaminants by 10% - 90%. Ozone was more efficient at oxidizing steroids with phenolic moieties (estrone, ethinylestradiol, and estradiol) than it was at oxidizing those without aromatic or phenolic moieties (androstenedione, progesterone, and testosterone). Six compounds studied were oxidized by greater than 20% by chlorine or ozone (tri[2-chloroethyl] phosphate, BHC, chlordane, dieldrin, heptachlor epoxide, and musk ketone). Ozone was more effective than chlorine at removing twenty-four of the compounds. The other compounds were readily oxidized by chlorine or ozone.

Research by Broseus et al. (2009) looked at the oxidation number of pharmaceuticals, endocrine-disrupting compounds, and pesticides such as: caffeine, trimethoprim, carbamazepine, naproxen, gemfibrozil, estrone, estriol, estradiol, 17α-ethinylestradiol, progesterone, cyanazine, and diethylatrazine. They concluded that ozonation using ozone at standard doses applied to drinking water removed 80% of caffeine, pharmaceuticals, and endocrine disruptors. The pesticides examined were the most difficult and resistant compounds to oxidize.

Ikehata et al. (2008) found that ozonation and advanced oxidation processes were effective at eliminating a wide variety of pharmaceuticals, personal care products, endocrine-disrupting compounds, pesticides, and surfactants.

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Carbamazepine, 17-estradiol, diclofenac, and pentachlorophenol were found to be very reactive toward hydroxyl radicals and ozone. Halogenated pesticides, x-ray contrast agents, and surfactants were found to be resistant to oxidation by molecular ozone. However, UV-assisted advanced oxidation was more effective in degrading halogenated organics compared to ozonation because of enhanced generation of hydroxyl radicals and photon-initiated cleavage of carbon-halogen bonds.

Research by Huber et al. (2005) indicates that chlorine dioxide rapidly oxidized sulfonamide, macrolide antibiotics, pyrazolone derivatives, and estrogens. However, many other pharmaceutically active compounds were resistant to chlorine dioxide. Ozone reacted more quickly and with more compounds than chlorine dioxide, but chlorine dioxide reacted faster than chlorine.

Removal of Methyl Tertiary Butyl Ether

Methyl tertiary butyl ether (MBTE) is a common fuel additive found as a contaminant in groundwater. It can be quickly oxidized by ozone and peroxide. The products of this reaction are t-butyl formulate, t-butyl alcohol, acetone, and several aldehydes (many are biodegradable). Research by Acero et al. (2001) indicates that methyl tertiary butyl ether reacts slowly with molecular ozone but quickly with the hydroxyl radical. Also, they found that the oxidation products reacted slowly with molecular ozone. The concentration of several organic micro-pollutants is reduced by chemical oxidation, but in many cases the compounds are not completely mineralized. Oxidation reactions generate what are called "daughter products" which can themselves be public health concerns. It is always important to keep in mind these "daughter products" before significant implementation of any process to control micro-pollutants.

Biological Growths in Treatment Plants

It's important to control biological growths in treatment plants. Chlorine, in particular, is very effective at controlling unwanted aquatic growths in water treatment facilities. It can control growths in flocculation and sedimentation basins on filters. Keeping a free chlorine residual throughout the treatment plant keeps the growth of microorganisms to a minimum, particularly in open basins that are exposed to sunlight. Permanganate, ozone, and chlorine dioxide are also effective at minimizing these growths, but because of the necessary doses and chemical instability of these oxidants over time, it is difficult to maintain a residual across sedimentation basins. Also, since ozone, advanced oxidation processes, chlorine dioxide, and permanganate oxidize natural organic matter and produce low-molecular-weight biodegradable organic compounds, oxidative treatment will increase the possibility of microbial growth in pretreatment basins and on filter media in the absence of disinfectant residual. These growths must be maintained to

minimize this. This is often dealt with through the use of free or combined chlorine following their application, periodic shock treatments of the basins or filters with chlorine, or engineering and operating filters in a biological mode. Although chlorine often produces biodegradable organic compounds, the presence of a chlorine residual controls these biological growths.

Advanced Oxidation Processes in Water Treatment

Water supplies may contain toxic synthetic organic compounds (SOCs). To protect public health these compounds must be destroyed or removed. Some of the compounds found in water supplies that may be harmful to humans include: human and veterinary drugs, solvents, fuels, agricultural herbicides, agricultural pesticides, and other potential endocrine disruptors. Any oxidation process used to remove these compounds must oxidize the synthetic organic compounds completely into carbon dioxide, water, and mineral acids because of the uncertainty of the toxicity of by-products potentially produced by oxidation.

A conventional oxidant, such as chlorine, is selective as to which compounds it can remove. Advanced oxidation processes (AOPs) can completely convert organic compounds into carbon dioxide, water, and mineral acids.

Advanced oxidation processes have several advantages over conventional processes:

- Contaminants that are not adsorbable or volatile can be destroyed.

- Contaminants can be destroyed completely.

- Mass transfer processes such as adsorbing or stripping only transfer the contaminant to another phase. This means the water may require additional treatment.

Advanced oxidation processes are ideal for full-scale use in the destruction of organic compounds because they generate hydroxyl radicals ($HO\bullet$) at room temperature and atmospheric pressure. Alternative processes that generate hydroxyl radicals such as wet oxidation, supercritical oxidation, gas-phase combustion, and catalytic oxidation processes need elevated pressures and/or temperatures and are also mediated by free-radical chain reactions involving hydroxyl radicals. The dot in the formula for the hydroxyl radical indicates that there is an unpaired electron in the outer orbital. This is an abbreviated Lewis structure notation. Lewis structure notation is used to indicate whether all eight electrons in the outer orbitals of nitrogen, oxygen, and carbon are filled. Here for the

hydroxyl radical ($HO\bullet$), there are three sets of paired electrons that are not shown, but the single unpaired electron is indicated by the dot after O.

Hydroxyl radicals are very effective at destroying organic chemicals. This is because they are reactive electrophiles (they are electron preferring) and react rapidly and non-selectively with most electron-rich compounds. In addition, the second-order rate constants for the hydroxyl radical for most organic pollutants in water are between $10^8 – 10^9$ L/mol$\cdot$sec. Acid-base reactions are generally the fastest aqueous–phase chemical reactions. This is because there is only the transfer of a hydrated proton. In comparison to other oxidants, these second order rate constants are three to four orders of magnitude greater.

Important Terms

- **Advanced Oxidation Process** – An oxidation process that produces hydroxyl radicals at room temperature and atmospheric pressure.

- **Electrical Efficiency Per Log Order Reduction (EE/O)** – The required electrical energy in kWh/m^3 to reduce the concentration of a pollutant by one order of magnitude.

- **Extinction Coefficient** – A measurement of how strongly a substance absorbs light at a given wavelength per mass unit.

- **Hydroxyl Radical ($HO\bullet$)** – Chemical species that contain oxygen and hydrogen. They are differentiated from hydroxide ion (OH$^-$) because they have an unpaired electron in the outer shell. This unpaired electron makes it a powerful, unselective electrophile able to oxidize a wide range of organic compounds.

- **Photocatalysis** – The acceleration of photolysis due to a catalyst.

- **Photolysis** – A process in which compounds absorb photons. They release energy that is able to initiate advanced oxidation.

- **Photon** – A small packet of energy. Photons carry electromagnetic radiation.

- **Sonolysis** – Using ultrasound to break apart chemical bonds. The breakage forms radicals, which cause oxidation.

- **Ultraviolet Light (UV)** – Electromagnetic radiation with wavelengths between 100-400 nm.

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Advanced Oxidation Processes and Associated Characteristics

The following processes are advanced oxidation processes that produce hydroxyl radicals:

Hydrogen Peroxide & UV Light

The H_2O_2/UV light process involves using a hydrogen peroxide injection and mixing followed by the use of a reactor equipped with UV lights. Generally, the UV reactor is a stainless steel column containing UV lights in a crisscross pattern. This process cannot be used for potable water treatment because it has high effluent hydrogen peroxide concentrations. These concentrations cannot be avoided because high doses of hydrogen peroxide are needed in order to efficiently use the UV light to produce hydroxyl radicals. The high effluent hydrogen peroxide concentrations pose a health issue. In addition, residual hydrogen peroxide consumes chlorine and interferes with disinfection. Hence, this treatment needs more research before it can be used for drinking water.

This process has the following characteristics:

- Hydrogen peroxide is stable and can be stored for long periods of time.

- Hydrogen peroxide is a poor UV absorber. If the water absorbs a significant amount of light energy, most of the light input going into the reaction will be wasted.

- Reactors designed specifically for UV illumination are required.

- There will be residual hydrogen peroxide, which must be taken care of.

Hydrogen Peroxide & Ozone

The O_3/H_2O_2 process, also known as the peroxone process, is used for treating contaminated water. Hydrogen peroxide initiates the decomposition of ozone with the hydroperoxide ion (HO_2^-) ultimately yielding the overall equation as shown:

$$H_2O_2 + 2O_3 \rightarrow 2\,HO\cdot\ + 3O_2$$
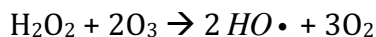
Two $HO\bullet$ are formed for each mole of H_2O_2. If H_2O_2 is introduced in quantities that significantly exceed the stoichiometry it will scavenge $HO\bullet$ and reduce the overall effectiveness of the process.

Alkalinity is important in this process. If alkalinity is high, influent pH adjustment may be necessary for irradiated matrices. This is to shift the carbonate-bicarbonate equilibrium from carbonate (which is a scavenger) to carbonic acid (which is not a scavenger).

Processes that use only ozone or only hydrogen peroxide to produce hydroxyl radicals have been studied, however the combination of the two is quite effective.

This process has the following characteristics:

- Waters that have poor UV light transmission can be treated.

- Reactors designed specifically for UV illumination are required.

- Volatile organics are stripped from the ozone contactor.

- Production of O_3 is often expensive and inefficient.

- Gaseous ozone in the off-gas of the ozone contactor must be removed.

- It can be difficult to determine and maintain the correct dosage of ozone and hydrogen peroxide.

- Low pH negatively affects the process.

Titanium Dioxide & UV

This process takes advantage of the fact that when a photon with sufficient light energy is absorbed by titanium dioxide, an electron in the outer orbital moves up to the conduction band from the valance band. The difference in potential between these bands is called the band gap. The band gap for titanium dioxide is 3.2 eV. This electron movement produces a hole in the valance band and an electron can move freely in the conduction band. A hydroxyl radical is formed when the hole in the valance band reacts with water. The addition of hydrogen peroxide can increase the reaction rate. The primary reaction for oxidation of organic pollutants that are electron-rich starts with an attack of the pollutant by hydroxyl radicals. Further organic radical chain reactions with oxygen and other species will eventually mineralize the parent compound.

- Greater light transmission is achievable due to activation with near-UV light.

- Catalyst may foul.

- TiO_2 must be recovered if used as slurry.

Ozone & UV

This process starts with the formation of hydrogen peroxide by photolysis of ozone. Reactions between hydrogen peroxide and ozone then produce the hydroxyl radical. However, using ozone to produce hydrogen peroxide, which then reacts with ozone to produce hydroxyl radicals is very inefficient because it takes a significant amount of energy to form ozone on site. Since significant amounts of energy are necessary to produce ozone and UV light, this process is most appropriate in situations where direct photolysis of the contaminants is significant, such as PCE and some aromatic halides. This is because the radical chain reactions are initiated from reactions between ozone and photolytic by-products.

This process has the following characteristics:

- It is not necessary to maintain precise dosages of ozone and hydrogen peroxide.

- Residual oxidant degrades quickly (half-life of ozone is about 7 minutes).

- Ozone absorbs more light than hydrogen peroxide (at equivalent doses).

- This process uses ozone and UV light to produce hydrogen peroxide, which is the primary means of producing hydroxyl radicals. Using ozone to produce hydrogen peroxide is very inefficient compared to just adding hydrogen peroxide.

- Reactors designed specifically for UV illumination are required.

- Removal of ozone in the off-gas is necessary.

- The process will strip volatile compounds.

Ozone, UV, & Hydrogen Peroxide

This process combines the ozone, UV, and hydrogen peroxide processes.

This process has the following characteristics:

- This process and technology are commercially available.

- Hydrogen peroxide promotes ozone mass transfer.

- Reactors designed specifically for UV illumination are required.

- Removal of ozone in the off-gas is necessary.

- The process will strip volatile compounds.

Ozone at Elevated pH (8-10)

This process involves using ozone at elevated pH.

This process has the following characteristics:

- Process does not require adding UV light or hydrogen peroxide.

- Removal of ozone in the off-gas is necessary.

- pH adjustment is impractical

- There aren't any commercial applications.

- This process is inefficient for removing synthetic organic compounds

Fenton's Reactions (Fe & Hydrogen Peroxide, Photo-Fenton's, or Fe & Ozone)

The Fenton process can be used on contaminated water and soil. This process uses reductive metal ions, which can catalyze the hydrolysis of hydrogen peroxide to form hydroxyl radicals. Fenton's reagent, which is a mixture of ferrous iron and hydrogen peroxide, produces a powerful oxidant to treat organic contaminants. The Fenton process can also be combined with ultrasonic irradiation, ozone, and photocatalysis.

- Groundwater may contain enough Fe to drive Fenton's reaction.

- Commercial processes use this technology and are available.

- This process requires a low pH.

Sonolysis (Ultrasonic Irradiation)

Author: Tim Baron

This process uses ultrasonic irradiation to destroy many environmentally important and refractory contaminants. It affects chlorinated hydrocarbons, pesticides, atrazine, fuel additives, aromatic compounds, parathion, and humic acids. Sonolysis uses ultrasound to eliminate organics by generating small bubbles by cavitation. This occurs during the low-pressure portion of a wave cycle. High temperatures and high pressures occur throughout bubble collapse. The high temperatures and pressures cause pyrolysis of organics and produce highly reactive chemical radicals. The approximate transient temperature is in the neighborhood of 4,000 – 10,000 K and the pressure is estimated to be in the range of 300 – 975 bar. The localized high temperature and pressure provide enough energy for the pyrolysis of most, or all, contaminants (including water) to form radicals. Two mechanisms are responsible for the elimination of contaminants during the ultrasonic irradiation process: radical reactions by $HO\bullet$ and $H\bullet$ formed through the ultrasonic irradiation process and pyrolysis reactions at the cavitation bubble. The pyrolysis of contaminants can also produce radicals and initiate chain reactions. This process has shown itself to be effective on a small scale. The electrical efficiency per log order reduction (EE/O) for the ultrasonic irradiation of organic compounds is in the neighborhood of 2600 kWh/m^3 per order of destruction. Combining ultrasonic irradiation with other advanced oxidation processes, such as ozone and elemental iron can further improve the elimination of contaminants and process intermediates. This enhancement is due to the improvement of $HO\bullet$ and/or $H\bullet$ radical production.

This process has the following characteristics:

- This process can be used in waters that have low light penetration.

- This process is not commercially available and requires significant energy input.

Ozone & Sonolysis

This process combines the ozone and ultrasonic irradiation processes.

This process has the following characteristics:

- This process is generally faster than sonolysis alone.

- There aren't any commercial applications.

- Requires a significant amount of energy and a specialized reactor.

Supercritical Water Oxidation (SCWO)

Author: Tim Baron

This treatment is a proven treatment for contaminated water. This process consists of oxidation of organic material in water at temperatures and pressures that are above the critical point of water (374 ^{o}C & 22MPa). In addition an oxidant such as O_2 or H_2O_2 is present. The process is generally performed at 400-650 ^{o}C and 25MPa. If below the critical point, the liquid and gas phases can coexist in equilibrium. Above the critical point, water exists in one phase, which is supercritical water. Supercritical water has significantly different chemical and physical properties than water under normal conditions. Density, viscosity, diffusivity, ion mobility, and dielectric constant are altered by the phase change. Diffusivity and ion mobility are higher when water is supercritical. The density of water decreases, and as the density decreases, hydrogen bonding and the solvent polarity of water decrease. The dielectric constant (a measure of hydrogen bonding and polarizability of molecules decreases from 78.5 (at standard conditions) to about 5 (at supercritical conditions). Supercritical water has properties similar to a nonpolar organic solvent. Thus, nonpolar organic compounds and oxidants become highly soluble in or miscible with supercritical water. Thus, the supercritical water oxidation process is not mass-transfer limited and has high reaction rates.

Supercritical water oxidation ensues through a free-radical reaction mechanism. Pyrolysis can occur because of the high temperatures that are present under supercritical conditions. Pyrolysis is not a major pathway for contaminant elimination because its reaction rates are significantly lower than those of oxidation. The two most common oxidants used are O_2 and H_2O_2.

Alkalinity is an important parameter in oxidation processes that involve hydroxyl radicals. If alkalinity is high, influent pH adjustment may be necessary in supercritical water oxidation to shift the carbonate-bicarbonate equilibrium. This is a shift from carbonate (which is a scavenger) to carbonic acid (which is not a scavenger). When the impact of hydroxyl radical scavengers is assessed and the influent characteristics are adjusted to minimize scavenger impact, the effect of supercritical conditions on all applicable chemical reactions must be analyzed.

Research indicates that the use of catalysts improves oxidation of complex organic compounds at lower supercritical water oxidation temperatures (380 – 450 ^{o}C) and produces short reactor residence times (less than 30 seconds).

This process has the following characteristics:

- This process can obtain complete mineralization for complex hazardous materials.

- This process requires a specialized reactor that operates at high energy and consumes a large amount of energy.

- Significant corrosion can occur if high concentrations of chlorine are present.

- This process is expensive and generally designed for small flows of less than 50 L/min.

Ozone and Titanium Dioxide

This process combines ozone and titanium dioxide processes.

This process has the following characteristics:

- Process can have faster destruction rates compared to titanium dioxide alone.

- There aren't any commercial applications.

Ozone, Titanium Dioxide, and Hydrogen Peroxide

This process combines the ozone, titanium dioxide, and hydrogen peroxide processes.

This process has the following characteristics:

- Process can have faster destruction rates compared to titanium dioxide alone.

- There aren't any commercial applications.

Pulsed Corona Discharges & Non-thermal Plasma Catalytic Oxidation

These processes have been used to treat contaminated air. A non-thermal plasma is one in which the mean electron kinetic energy is much higher than that of the molecules in the bulk gas. Generally non-thermal plasmas are produced by a gas discharge. The gas discharge is under the application of a strong electric field. Electrons and ions are accelerated to high energies under such conditions. Electrons are accelerated to higher energies than the ions. The high-energy electrons react with wet air to form hydroxyl radicals. Non-thermal plasmas can be produced by electron beam irradiation or electrical discharge.

A pulsed corona reactor is one in which at least one of the electrodes is a thin wire, needle, or sharp edge. The other electrode is a plate or a cylinder. Short electrical high voltage pulses are sent between the electrodes to produce electrical discharges called coronas.

Author: Tim Baron

This process has the following characteristics:

- Elevated temperatures are not required.

- When used in gas-phase applications, this process does not require temperatures that are as high as thermal incineration.

- When used in aqueous-phase applications, this process does not require temperatures that are as high as supercritical water oxidation.

- Only certain compounds may be degraded in the aqueous phase.

- The production of dioxins and furans must be avoided in gas-phase applications.

Electron Beam Irradiation

This process uses a beam of high-energy electrons produced by an electron generator to irradiate water or air. An electron beam current is passed through a tungsten filament in a vacuum to generate a stream of electrons. The electron stream is accelerated through the application of an electric field at a specified voltage. It is focused into a beam by collimating devices. The applied voltage determines the speed of the accelerated electrons. The speed (energy) determines the depth to which the electron beam can penetrate in the medium being irradiated. The beam current is proportional to the number of electrons emitted per unit time. The electron beam power is the product of the accelerating voltage and the beam current. The electron beam generated is injected into a reaction chamber through a thin foil titanium window. The window serves as the vacuum seal necessary for high-energy electron conversion. An electron accelerator can impart electron energies in the range of 0.1 – 10 MeV. High-energy electron beams at approximately 2 MeV are used for irradiating water. Medium-energy beams at approximately 0.2 MeV are used for irradiating air. Electron beam penetration in water is considerably less than the depths reached by gamma rays and x-rays. A 1 MeV electron delivers its energy in water within a depth of 4 mm. Because of this, electron beams are generally used to treat contaminated water at shallow depths. The mechanism of hydroxyl radical formation is determined by the medium being irradiated. Electron beams used to irradiate water cause the formation of three reactive species: hydroxyl radicals, $e^-(aq)$, and $H \cdot$. These species are responsible for organic compound elimination.

Alkalinity is an important parameter in the electron beam oxidation process. If alkalinity is high, influent pH adjustment may be necessary for irradiated water to shift the carbonate-bicarbonate equilibrium. This is a shift from carbonate (which is a scavenger) to carbonic acid (which is not a scavenger).

This process has the following characteristics:

- Elevated temperatures are not required.

- There aren't any commercial applications.

- Requires a significant amount of energy and a specialized reactor.

Ozone and Electron Beam Irradiation

This process combines the ozone and beam irradiation processes.

This process has the following characteristics:

- Elevated temperatures are not required.

- May have faster destruction rates than electron beam irradiation alone.

- There aren't any commercial applications.

- Requires a significant amount of energy and a specialized reactor.

Gamma Radiation

The gamma ray process has been used to treat both contaminated water and contaminated soil. Gamma rays are high-energy photons that atomic nuclei emit when in transition to a state of lower excitation. The radioactive decay of cobalt 60 is the most common source of gamma rays. Cobalt 60 emits gamma rays at energies of 1.17 – 1.33 million electron volts (MeV) as it decays to nickel 60. Its half-life is 5.27 years. Upon collision with irradiated water, high-energy electrons are generated along the trajectory of the gamma rays through three processes: photoelectric, electron-positron pair production, and Compton scattering. Several thousand reactions are initiated by the high-energy electrons generated from gamma rays as they dissipate energy in irradiated water. These reactions cause the formation of three reactive species: hydroxyl radicals, e^-(aq), and $H \cdot$. These species are responsible for organic compound elimination. Multiple mechanisms for organic compound elimination are provided by irradiation because strong oxidizing species (hydroxyl radicals) and strong reducing species (e^-(aq), $H \cdot$) are formed in approximately equal concentrations.

Alkalinity is important in the gamma-ray process. If alkalinity is high, pH adjustment may be necessary for the irradiated water. This is to shift the carbonate-bicarbonate equilibrium from carbonate (which is a scavenger) to carbonic acid (which is not a scavenger).

Author: Tim Baron

Gamma rays have high penetration depth in water. Research indicates that a water depth of approximately 76 cm is required to absorb 90% of a gamma-ray energy level of 1.25 MeV. Thus, gamma radiation can be used to treat both standing liquid waste and flowing waste streams.

This process has the following characteristics:

- Elevated temperatures are not required.

- There aren't any commercial applications.

- Requires a significant amount of energy and a specialized reactor.

Electrohydraulic Cavitation

Electrohydraulic cavitation involves injecting energy into a liquid matrix via a plasma channel. Plasma is a highly ionized gas that consists of a nearly equal number of positive and negative free charges. These charges are positive ions and electrons. Sending short pulses of a high-voltage, high current electrical discharge between two underwater electrodes creates a plasma channel. The plasma channel produces a high-pressure shockwave as it expands. Cavitation occurs when the shockwave is reflected back from a material in the reaction vessel with a different acoustic impedance. The temperature in the plasma channel can reach temperatures in excess of 13,000 ^{o}C. Formation of the plasma channel results in additional reaction mechanisms. These reactions destroy organic compounds directly by pyrolysis within the channel. The plasma channel occupies only a small volume, thus pyrolysis is not a primary reaction pathway. The high temperatures in the plasma channel cause it to function as a black body radiation source having maximum emittance in the vacuum UV region of the light spectrum. Because of this, soft x-rays and high-energy UV radiation from the plasma channel into the liquid creates hydroxyl radicals. Additionally, steam bubbles form and transfer thermal energy to the bulk liquid. The extreme temperature and pressure exhibited by these bubbles serve as an additional location for supercritical water oxidation (SCWO) to occur.

This process has the following characteristics:

- Elevated temperatures are not required.

- There aren't any commercial applications.

- Requires a significant amount of energy and a specialized reactor.